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Dispersion and Incorporation of Metal-Organic Frameworks into Mixed Matrix Membranes for Organic Solvent Nanofiltration

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Declaration of Originality

I declare that this thesis and all of its contents are my own and that all contributions are appropriately acknowledged through references or acknowledgements.

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Abstract

The principle objectives of this work were fourfold: first, to quantify and control the suspension properties of a metal-organic framework (MOF), MIL-101; second, to use this knowledge to understand the formation of thin film nanocomposite (TFN) membranes made via interfacial polymerisation (IP); third, to identify other secondary filler effects; and fourth, to relate IP reaction conditions to filler incorporation.

Preliminary studies revealed that trimesoyl chloride (TMC) adsorption onto MIL-101 in *n*-hexane significantly affected membrane performance. More importantly, aggregation led to non-selective defects for TFN membranes synthesised with *n*-hexane. To control aggregation, the Hamaker constant of a MOF was determined for the first time and Derjaguin, Landau, Verwey, Overbeek (DLVO) theory was related to quantifiable dispersion measurements, showing that hydrophobic solvents like those used to make TFN membranes provide poor dispersion. Surface-selective modification of a MOF increased the concentration of well-dispersed MOF by over an order of magnitude, while the use of nitrobenzene increase it by over two orders.

Thus, nitrobenzene was used to fabricate TFN membranes via IP. These membranes demonstrated pure solvent permeance increases relative to the thin film composite membrane control of up to factors of 1.9 for methanol and 2.7 for water, while maintaining a dye rejection of ~90 % (MW $\approx$ 314 g·mol⁻¹). Further exploration revealed that aggregates introduce non-selective defects in certain circumstances and semi-selective defects in others, the latter of which can enhance solvent permeance without major reductions in rejection. Additionally, MIL-101 adsorbed less than half of the TMC in nitrobenzene compared to that adsorbed in *n*-hexane, mitigating this secondary effect. Finally, membrane surface roughness was controlled and correlated with whether or not MIL-101 addition to the organic phase impacted membrane performance, with smoother membranes showing no performance differences and rougher membranes showing differences similar to those observed by previous researchers [1].

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Acronyms and Abbreviations

Act - Acetone

AFM – Atomic Force Microscopy

ATPS – Amine Terminated Polystyrene

FTIR – Fourier-Transform Infrared Spectroscopy

BA – Benzoic Acid

BET – Brunauer-Emmett-Teller

BuOH – *n*-butanol

CD – (2-Hydroxypropyl)- γ -cyclodextrin

CI – Confidence Interval

CP – Concentration Polarisation

CUS – Coordinatively Unsaturated Sites

DCM - Dichloromethane

DeOH – *n*-decanol

DI – Deionised

DLVO – Derjaguin, Landau, Verwey, Overbeek

DMF – *N,N*-Dimethylformamide

DOL – 1,3-Dioxolane

DR – *N*-Ethyl-*N*-(2-hydroxyethyl)-4-(4-nitrophenylazo)aniline, Disperse Red 1

DVS – Dynamic Vapour Sorption

EA – Ethyl Acetate

EDS – Energy Dispersive X-Ray Spectroscopy

EEP – Environmental Ellipsometric Porosimetry

ELSD – Evaporative Light Scattering Detector

EtOH – Ethanol

exDLVO – Extended Darjaguin, Landau, Verwey, Overbeek

FWHM – Full-Width-Half-Maximum

HPLC – High Pressure Liquid Chromatography

HX/Hex – *n*-hexane

IP – Interfacial Polymerisation

IPA – Isopropyl Alcohol, 2-propanol

IPG – IsoPar G

IR - Infrared

IS – Interfacial Synthesis

ISA – Integrally Skinned Asymmetric

ISG – *in situ* Growth

MeOH – Methanol
MMM – Mixed Matrix Membrane
MOF – Metal-Organic Framework
MPD – m-Phenylenediamine
MW – Molecular Weight
NB – Nitrobenzene
NF – Nanofiltration
OA – 1-Octylamine
OSRO – Organic Solvent Reverse Osmosis
OSN – Organic Solvent Nanofiltration
PAN – Polyacrylonitrile
PI/P84 – Polyimide
PIP – Piperazine
PS – Polystyrene
RMS – Root Mean Square
RO – Reverse Osmosis
SE – Spectroscopic Ellipsometry
SEM – Scanning Electron Microscopy
STP – Standard Temperature and Pressure
TEM – Transmission Electron Microscopy
TFC – Thin Film Composite
TFN – Thin Film Nanocomposite
TGA – Thermogravimetric Analysis
TMC – Trimesoyl Chloride
TPA – Terephthalic Acid
UF – Ultrafiltration
UV - Ultraviolet
UV-Vis – Ultraviolet-Visible
XPS – X-Ray Photoelectron Spectroscopy
XRD – X-Ray Diffraction

Symbols

- (a, b, c, d) empirical parameters
- (A) Hamaker constant
- (A) area of membrane or surface
- ($A_{MS/S}$) non-retarded Hamaker constant of the solvent-filled MOF body in a select solvent
- (A/C) specific absorbance
- (B) parameter related to oscillator strength in the microwave region
- (Cr) the number of chromium atoms measured by XPS
- (C_{IR}) absorption strength in the IR range
- (C_{UV}) absorption strength in the UV range
- ($\overline{C_{A,i}}$) average concentration of solute (i) in the membrane's pore
- ($C_{F,i}$) concentration of solute (i) in the feed
- ($C_{M,i}$) concentration of solute (i) at the membrane's surface
- ($C_{P,i}$) concentration of solute (i) in the permeate
- (D) the degree of modification
- (D_i) diffusivity of solute (i)
- (d) distance between two particles
- (d_H) hydraulic diameter
- (e) elementary charge
- (g) gravity
- (h) Planck's constant
- [$h(x, y)$] height as a function of x and y on a Cartesian coordinate plane
- (I) ionic strength
- ($J_{E,i/l}$) the effective membrane flux of solute i or solvent l
- (K_c) uncharged hindrance factor for convection
- (K_d) uncharged hindrance factor for diffusion
- (k_B) the Boltzmann constant
- (k_i) mass transfer coefficient of species i
- (k_s) is a pseudo-second order adsorption constant
- (L) length
- (M_W) is the molecular weight of compound W
- (M_{vol}) molar volume
- (m) pre-exponential constant that is a function of particle size and relative refractive index
- (N) number of nitrogen atoms measured by XPS
- (N_A) Avagadro's number

(n) refractive index if associated with optical equations
 (n) number of samples or iterations used in statistics or summations e.g. (95 % CI, $n = 4$)
 (O) the number of oxygen atoms measured by XPS
 $(P_{l,i/l})$ the measured intrinsic permeance of solute i or solvent l
 $(P_{E,i/l}^C)$ the calculated intrinsic permeance of solute i or solvent l
 $(P_{D,l}^*)$ osmotic defect permeance of solvent l
 (p) number of unconstrained parameters
 (Pe') modified Peclet number
 (q) radius in the polar coordinate system
 (q_e) mass of TMC adsorbed per mass of MIL-101 at equilibrium
 (q_t) mass of TMC adsorbed per mass of MIL-101 at time t
 (R_q) root mean square roughness
 (R) universal gas constant
 (R_x) residual of the unmodified (U) and modified (M) MIL-101
 (r_i) hydrodynamic radius of solute i
 (r_p) pore radius
 (r_l) hydrodynamic radius of solvent l
 (r) particle radius
 $(R_{o,i})$ observed rejection of solute (i)
 $(R_{l,i})$ intrinsic rejection of solute (i)
 (Re) Reynolds number
 (Sc) Schmidt number
 (Sh) Sherwood number
 (T) temperature
 (t) time
 (V_l) volume of permeate
 (v) particle settling velocity
 (w) whole number integers
 (X) degree of crosslinking
 (Y) dimensionless grouping
 (z) wavelength exponent

Greek Symbols

$(\alpha_{l/i})$ permselectivity of solvent l and species i
 (Γ) coating surface coverage

(Δ) fitting parameter
 $(\Delta_{MS/S})$ difference in dielectric response
 $(\Delta\pi)$ transmembrane osmotic pressure
 (ΔP) transmembrane hydraulic pressure
 (δ) coating thickness
 (ε) porosity
 (ε_M) porosity of MIL-101
 (ε_F) porosity of film
 (ε_0) permittivity of free space
 (ε_h) relative permittivity of the host solvent
 $[\varepsilon_M(0)]$ static permittivity of MIL-101
 $[\varepsilon_W(0)]$ static permittivity of water
 $[\varepsilon_{E,Calc}(0)]$ calculated effective static permittivity of the medium
 $[\varepsilon_{E,Exp}(0)]$ measured effective static permittivity of the medium
 $[\varepsilon_{MS}(i\xi_n)]$ complex dielectric response functions of the MOF filled with solvent
 $[\varepsilon_M(i\xi_n)]$ complex dielectric response functions of the MOF skeletal structure
 $[\varepsilon_S(i\xi_n)]$ complex dielectric response functions of the pure solvent
 $[\varepsilon(i\xi_n)]$ is the complex dielectric function
 $(i\xi_n)$ the discrete, imaginary frequencies at which the function is evaluated
 (ζ) zeta potential
 (η_l) kinematic viscosity of solvent l
 (θ) angle in the polar coordinate system
 (θ_l) volume fraction of membrane component (l), including: polymer (P), filler (F), defects
 (D) and defect-free region (DF)
 (θ_c) percolation volume fraction
 (θ_M) volume fraction of MIL-101
 (κ) Debye length
 (λ) wavelength
 (μ) dynamic viscosity
 (μ_p) is the dynamic viscosity in the pore
 (μ_0) dynamic viscosity in the bulk solution
 (ρ_l) fluid density
 (ρ_M) MIL-101 density
 (ρ_{PA}) polyamide density
 (ρ_P) polymer density

- (σ) reflection coefficient
- (τ) tortuosity
- (τ_{MW}) dampening term related to absorption in the microwave region
- (v) empirical value related to particle morphology
- (Φ) is the steric partition coefficient
- (χ) Flory-Huggins parameter
- (ψ) the volumetric ratio of MIL-101 to polymer in the membrane
- (ω) wave frequency
- (ω_{IR}) characteristic absorption frequency in the IR range
- (ω_{UV}) characteristic absorption frequency in the UV range

1 Introduction and Literature Review

1.1 The Need for Low-Energy, Cost-Effective Separations

To support the increase in population and industrialisation of emerging economies, energy demand is projected to increase by 30% from 2017 to 2040 [2]. Energy is becoming an increasingly valuable resource because of this increase in demand and concerns around climate change. Currently, 28% of all energy usage comes from industry and the Intergovernmental Panel on Climate Change reports that industry could reduce its energy intensity by up to 25%, which will be important in reducing greenhouse gas emissions [3]. Scholl and Lively recently calculated that 10-15 % of US's total energy consumption is from separations and that developing alternatives could make 80% of those separations ten times as efficient [4]. Moreover, in these industries, separations usually account for 40 – 70% of the total capital and operational costs [5], leaving room for significant savings. Membrane-based separations can substantially reduce energy consumption compared with traditional, thermally-based alternatives. Furthermore, they may be able to simplify more complex separations such as chromatography and crystallisation, thus saving on cost [6]. This is already the case in desalination, where water production costs for reverse osmosis are 0.66 USD·m³, whereas multi-stage flash evaporation, multi-effect distillation and freeze desalination all have higher water costs: 1.16, 0.86 and 0.93 USD·m³, respectively [7]. While membranes have been very successful in the field of desalination, they have yet to achieve such success in the separation of organic solvents.

1.2 Organic Solvent Nanofiltration

Organic solvent nanofiltration (OSN) is a pressure-driven membrane separation process that targets molecules less than 2 nm in size [8]. It lies between ultrafiltration (UF), the separation of 2 to 200 nm sized molecules, and organic solvent reverse osmosis (OSRO), which only allows pure solvent to pass. Although that is the technical definition, these separation techniques are often seen to overlap [9]. The three main types of OSN processes, as defined by Marchetti et al., are: concentration, diafiltration and purification [6]. These processes are presented in **Figure 1**. In concentration, solutes are concentrated by retaining them with the membrane and allowing solvent to pass. In diafiltration, solvent is allowed to pass and additional solvent is added to the retentate, which is defined as the solution retained by the membrane. Finally, in purification, solvent and solutes are permeated, thus isolating other solutes in the retentate. These processes can be used for the concentration of products, solvent recovery, solvent exchange, catalyst recovery, impurity removal, crystallisation or separation of reaction products/by-products/reactants. The aforementioned separations are integral to manufacturers in the pharmaceutical, base, consumer and specialty chemical

industries [6]. Marchetti et al. provide a review detailing the development of this field since the 1960s.

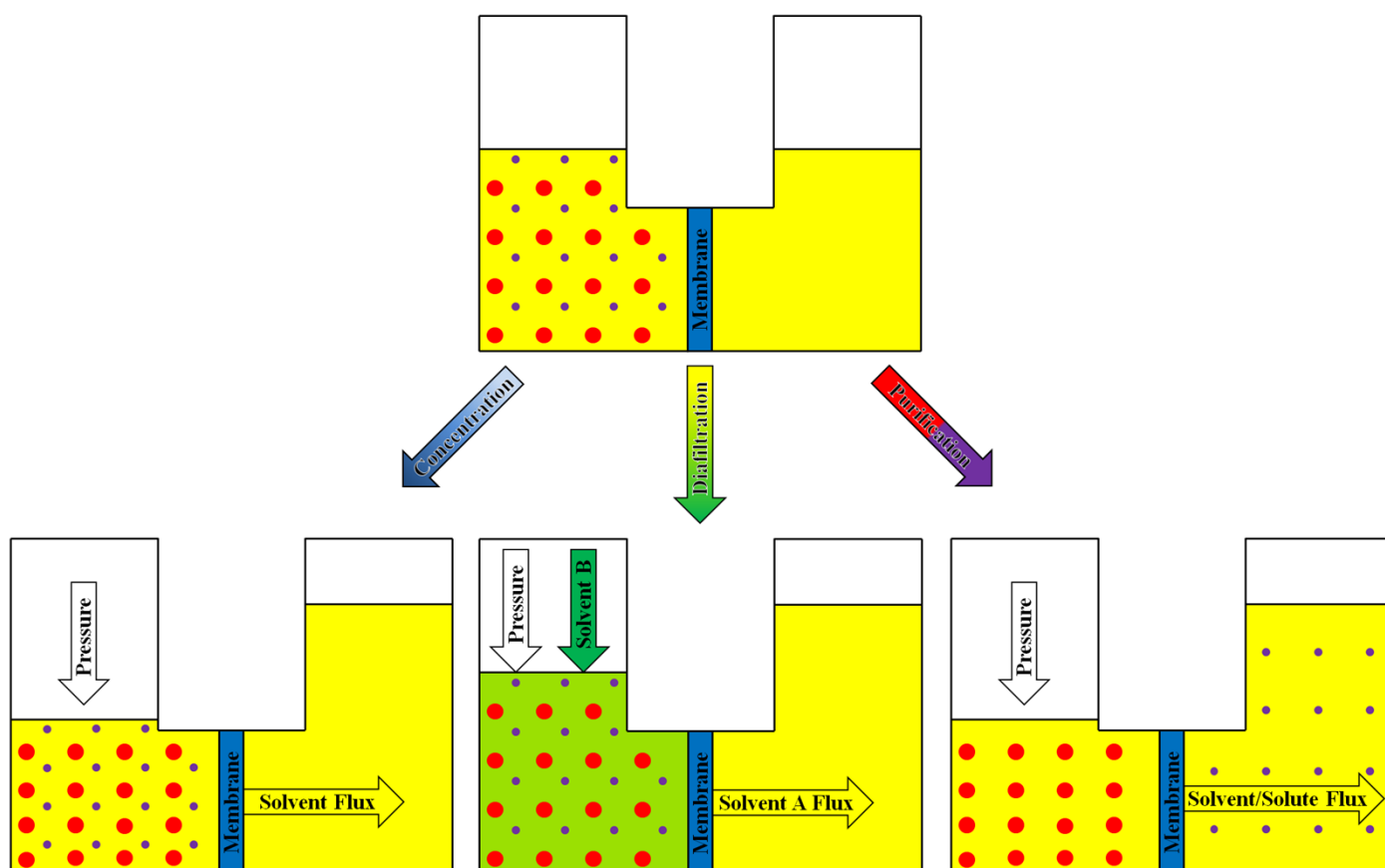


Figure 1. Illustration of typical organic solvent nanofiltration (OSN) processes, including: concentration, diafiltration and purification [10].

The need for higher selectivity membranes for OSN is clear. Obtaining the necessary purity and yield is still not possible in many applications without the additional use of membrane cascades [6,11]. In some circumstances, it is not possible to obtain satisfactory purity and yield even with the use of such cascades because of practical limits on the number of membrane cascades one can effectively operate. It is difficult to say what the limits of selectivity might be in different systems, but it is interesting that even the separation of enantiomers [12] and alkanes may be possible [13]. Additional clear challenges include the deleterious effects of membrane aging (compaction) and fouling, which reduce permeance over time and can either increase or reduce selectivity, leading to different issues depending on the final application. In terms of stability, membranes have been demonstrated to withstand extreme heat, solvents and pH effects [6,9]. However, maintaining ideal performance throughout remains a challenge.

There is less clarity on whether increased permeance could increase membrane applicability. Indeed, it has been debated for some time whether or not greater efficiency could be achieved for desalination in the RO community already [14] and recently the same debate has begun for OSN [15]. Shi et al. demonstrated via modelling that it might not be useful to increase membrane performance past $20 \text{ L}\cdot\text{m}^{-2}\text{h}^{-1}\text{bar}^{-1}$ because of concentration polarisation (CP) and pressure drop. However, Shi et al. does not explore the wide range of possible applications that are available in OSN, OSRO, nanofiltration (NF) and RO, focusing rather on specific membrane module designs and a narrow range of operating conditions. The authors' point is well taken that improvements to module design could help the field of membrane science and, moreover, that the conditions examined are practical for many applications. However, the range explored is far from other definitively valuable applications. For example, the removal of trace contaminants from freshwater in low resource contexts is: unarguably valuable and mandates ultra-low energy consumption. The osmotic pressure for this application can be estimated with the van 't Hoff equation ($\pi = C_iRT$) using the maximum concentration of freshwater (500 ppm) and an average molecular weight for ions ($25 \text{ g}\cdot\text{L}^{-1}$). The resulting osmotic pressure is less than one tenth than that examined by Shi et al.

The impact of lower concentration and operating pressure on ultimate membrane performance can be estimated using the equations for osmotic transport detailed in Section 1.3.3.1, assuming 100 % rejection ($\sigma = 1$). In one calculation, the lowest concentration examined by Shi et al. was used. In the other, the maximum concentration of freshwater was used. To be consistent with Shi et al.'s work, 30 bar was used for their calculations while only 1 bar was used for filtration of freshwater. Both calculations were performed at 30°C and used a mass transfer coefficient of $5 \times 10^{-5} \text{ m}\cdot\text{s}^{-1}$. Finally, the ultimate flux was defined as that achieved at a permeance of $10^9 \text{ L}\cdot\text{m}^{-2}\text{h}^{-1}\text{bar}^{-1}$.

The results are presented in **Figure 2**, which demonstrate that 90% of the ultimate flux for the concentration Shi et al. used is achieved at $60 \text{ L}\cdot\text{m}^{-2}\text{h}^{-1}\text{bar}^{-1}$, not dissimilar from their published values. In the scenario of trace contaminant removal, however, 90% of the ultimate flux would not be achieved until membranes have a permeance of $\sim 1,700 \text{ L}\cdot\text{m}^{-2}\text{h}^{-1}\text{bar}^{-1}$. This demonstrates that some applications not considered by Shi et al. could benefit from continued increases in membrane permeance. Of course, these calculations do not consider module design and related pressure drop. It should be noted, however, that low pressure operation reduces this pressure drop since there are relatively lower fluxes. Regardless, though this application was chosen for its easily agreeable premises, there are comparable applications in OSN. Trace catalyst recovery or recycling, for instance, could have similar requirements.

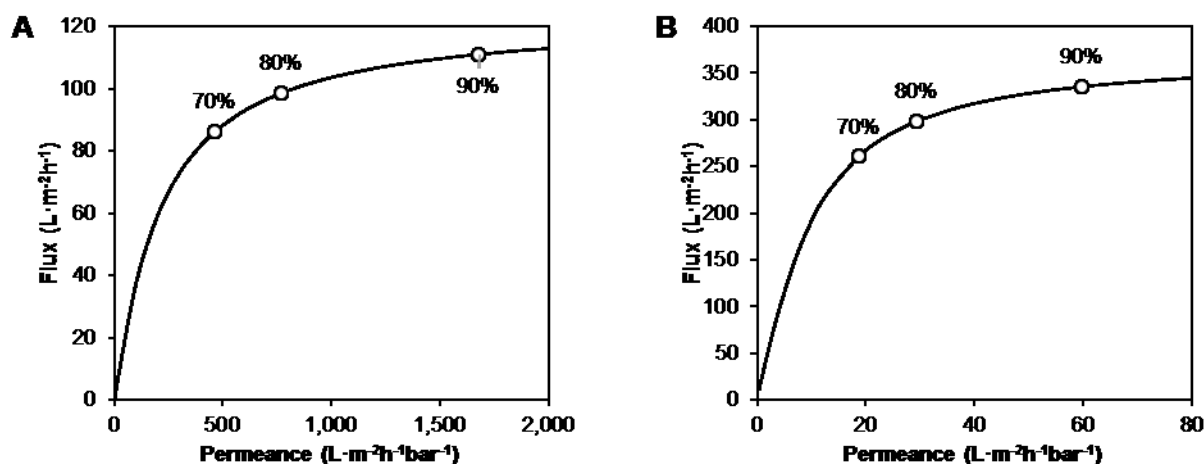


Figure 2. Modelled membrane flux versus permeance, accounting for concentration polarisation (CP) by using a mass transfer coefficient of $5 \times 10^{-5} \text{ m} \cdot \text{s}^{-1}$ and temperature of 30°C . Plot (A) uses the maximum concentration of fresh water at 1 bar transmembrane pressure while (B) uses the minimum concentration examined previously at 30 bar [15].

1.3 Membranes for Organic Solvent Nanofiltration

1.3.1 Definitions and Overview

There are a variety of high-quality text books giving a broad overview of different types of membranes [16–20]. Major landmarks in the development of membranes for liquid separations include Loeb and Sourirajan's cellulose acetate-based integrally skinned asymmetric (ISA) membrane formed via phase inversion, made in the 1960s [21], and Cadotte's polyamide thin film composite (TFC) membranes formed via interfacial polymerisation (IP) made in the 1980s [22,23]. The former tends to have a graded porosity, with a thin selective skin layer and a thicker, more porous support, shown in **Figure 3A**. TFC membranes, on the other hand, have an open porous support and a thin selective layer comprised of a different material, shown in **Figure 3B**. This enables more optimal performance because it is possible to target different material properties that are best for the support and separating layer independently [24]. The thin, highly selective layer of these membranes is what enables high-performance reverse osmosis (RO) separation because it solved the key challenge of simultaneously achieving high levels of sodium chloride removal and high water flux [18].

TFC and ISA membranes can be inorganic or polymeric, each having their own unique advantages and disadvantages. Polymeric membranes are easy to manufacture and handle in large areas, enabling the production of defect-free membrane modules with large surface area to volume ratios [18]. However, their chemical, thermal and mechanical stabilities are surpassed by inorganic membranes [17]. Inorganic materials with well-defined porous structures can out-perform polymeric materials [25], as illustrated by the upper bound

proposed by Robeson et al. [26,27] in 1991. One field that seeks to hybridise the manufacturability of polymeric materials with the performance of inorganic materials is that of mixed matrix membranes (MMM), where an inorganic filler is included within the polymeric structure of a membrane. These membranes can be either of the ISA type morphology, shown in **Figure 3C**, or the TFC morphology, shown in **Figure 3D**. Fillers can be included in both the support and selective layer of TFC membranes to impart greater stability and performance, respectively. This type of membrane is often referred to as a thin film nanocomposite (TFN) membrane, a term proposed by Jeong et al. in 2007 [1] during his seminal work forming these types of membrane via IP. It is notable that Lee et al. used this same concept with non-porous particles to mitigate biofouling and was published within days of Jeong et al., even though Lee et al. submitted their article sooner to their respective journal [28]. These membranes have been increasingly popular to explore because simple modifications to an existing manufacturing process were shown to substantially improve membrane performance [29]. However, TFN membranes seem to have only achieved a small fraction of their potential. This is described in greater detail later.

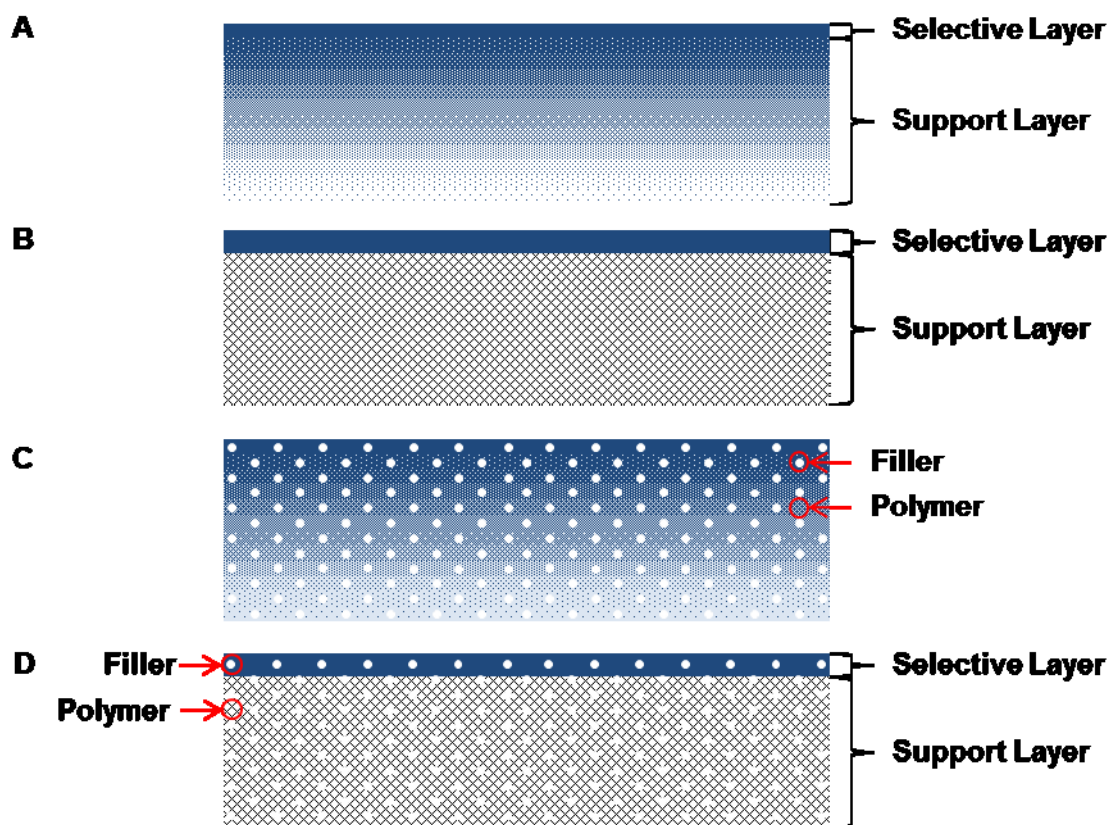


Figure 3. Simplified depictions of (A) integrally skinned asymmetric (ISA), (B) thin film composite (TFC), (C) mixed matrix membrane (MMM), (D) thin film nanocomposite (TFN) membranes. Not to scale [10].

1.3.2 Membrane Fabrication

1.3.2.1 Polymeric Ultrafiltration Membrane Supports

Polypropylene, polyether ether ketone, polysulfone, polyether sulfone, polyimide (P84) and polyacrylonitrile (PAN) have all been used as supports for TFC or TFN membranes. Most of these support membranes were formed by some type of phase inversion, predominantly non-solvent-induced. In this form of phase inversion, a polymer is solubilised in a solvent and spread with a casting knife over a nonwoven support. The nonwoven is typically a wet-laid or melt-blown polypropylene, polyethylene or polyethylene terephthalate. Finally, the coated nonwoven is immersed into a non-solvent bath. Factors such as solvent choice, room humidity, casting thickness, additives, temperature, machine tension and casting rate can affect the final membrane [6,18–20]. Some of the early TFN membrane work used zeolites as additives to reduce the compaction of the membrane support [30], but recent work suggests that this may not work as well at higher pressures more typical of RO processes [31]. For this work, P84 and PAN supports were fabricated based on existing recipes [32–35].

After casting, membranes can be subjected to heat treatments, solvent exchange, crosslinking, conditioning and/or drying [32–35]. While some supports require treatment with a pore preserving agent to avoid pore collapse [33], others can be dried while still maintaining fairly large pores [34,35]. Pore preserving agents can interfere with membrane coating processes. Since IP is very sensitive to contamination [36,37], supports that required pore preservation, like P84, were simply stored in solvent instead of dried. This is not an industrially viable approach but works at the bench scale. P84 is often crosslinked using 1,6-hexanediamine, though other amines have been tried as well. This creates a membrane support stable to polar aprotic solvents [32,33]. PAN retains its porosity only upon annealing after phase inversion [38]. After annealing, it can be dried to create a high-performance membrane support [34,35]. While PAN supports are often hydrolysed or crosslinked [39–41] to achieve higher performance or stability in select applications, it is not necessary to do so for good TFC performance [42].

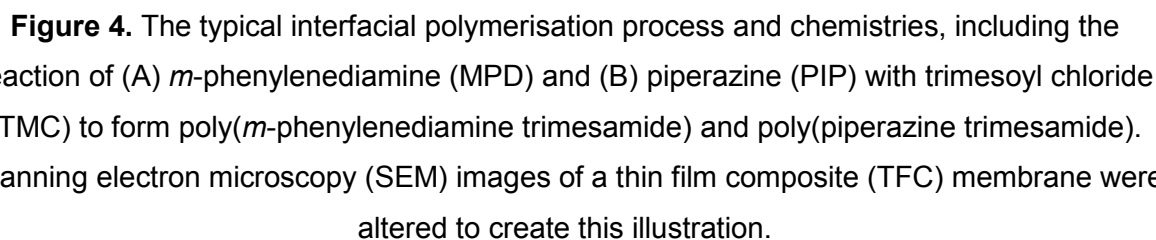
The selection of support can be important to final membrane performance. Researchers have theoretically and experimentally attributed changes in membrane performance and fouling propensity to the hydrophilicity, porosity and pore size of the support membrane [43–47]. Some of these effects have been explained by changes to the IP process itself such as the role hydrophilicity plays in generating greater surface roughness [43,47]. Recent research has been focused on the impact of pore geometry, pore size and membrane porosity, which can affect the flow path of water [44,46]. These studies show that these geometric considerations can have a substantial influence on membrane performance.

1.3.2.2 *Thin Film Composite and Thin Film Nanocomposite Membrane Formation via Interfacial Polymerisation*

Many of the industrially dominant commercial RO membranes are made via IP. In a typical laboratory-scale membrane fabrication process, illustrated by **Figure 4**, a membrane support is soaked in aqueous diamine, such as piperazine (PIP) or *m*-phenylenediamine (MPD), for a set period of time. For high levels of reproducibility, this time is set according to when the concentration of diamine within the pores of the support are at an equilibrium [48]. The excess diamine solution is typically removed via air knife [49] or rubber roller [48]. If excess solution is left on the membrane surface, it can lead to pinhole formation. Once excess aqueous amine is removed, the support's surface is covered with an immiscible organic liquid containing an acyl chloride, often trimesoyl chloride (TMC). Generally, it is thought that the diamine will diffuse into the organic phase and react with the acyl chloride at the interface of the aqueous and organic phases [36,37,50]. As the polyamide film is rapidly formed, that film limits further diffusion of reactants, thus slowing the polymerisation process. This enables the formation of rough films with an apparent thickness, a thickness that includes the dimensions of the peak and valley structures on the surface, of less than 300 nm [51,52]. Some report that these films have a smaller real thickness, asserting that the apparent thickness is made of a crumpled, sub-10 nm film [45,46,53,54]. The formation of this structure is still a matter of debate with different authors pointing to surface phenomena, convection, polymerisation dynamics and even boiling as possible causes [45,50,55]. Ideally, the polyamide film forms on the surface of the membrane, but it has been shown that polyamide can form within the pores of the membrane under certain reaction conditions and with certain supports [47,53,56]. After the polymer film is formed, the reaction is quenched by rinsing off excess acyl chloride with organic solvent and submerging it into DI water.

While most researchers focus on using PIP and MPD in the aqueous phase and TMC or isophthaloyl chloride in the organic (often alkane or alkene) phase, others have used a variety of solvent systems and reactive monomers to make polyester, polyurea, polyurethane, polyimides, polyanilines, polysiloxanes, polyamines, other polyamides and more [57,58]. Moreover, though most researchers at least allow the organic phase to dry off afterward, post treatment methods are common and include: grafting, curing, plasma treatment, UV exposure, chemical treatment and solvent activation [6,9]. Using a solvent-stable membrane support, like crosslinked P84, solvent activation using aggressive polar aprotic solvents like *N,N*-dimethylformamide (DMF) is possible [33]. DMF activation can substantially improve solvent permeance of poly(*m*-phenylenediamine trimesamide) membranes, but does little to alter the performance of poly(piperazine trimesamide) membranes [33,59]. There is still debate in the literature as to the precise mechanism of this activation, with some authors showing evidence

Many researchers will incorporate additives in the organic or aqueous phase during the IP process. Common additives include: surfactants, solvents, sulfur-containing compounds, water soluble polymers, polyhydric alcohols, phosphate-containing compounds, [58] and filler materials [29]. The latter is the primary additive that will be the focus of this work. To date, zeolites [1,30,62–65], silicas [66], silver [28], titanium oxides [67], carbon nanotubes [68], graphene [69], boron nitride [70], covalent organic frameworks [71], cyclodextrins [72], polyoctahedral oligomeric silsesquioxanes [73,74] and metal-organic frameworks (MOFs)



[75,76,85–87,77–84] have been successfully used to make TFN membranes via IP. Most authors report an increase in permeance with no major impact to rejection, or even a slight increase [29], unless significant aggregation occurs. The majority of researchers incorporate the filler material into the organic phase, as was the case with the earliest works [1,28]. However, many have tried to incorporate fillers into the IP process in less conventional ways, including vacuum filtration [69], evaporation [80,81,88] and Langmuir-Schaefer deposition [77]. While performance improvements are observed, the preponderance of these data seem to suggest that secondary filler effects, detailed later in this review, are predominantly responsible for these performance improvements when materials are deposited onto the membrane's surface prior to IP. One study showed that filler degradation could be the dominant mechanism through which MOFs changed membrane performance [80]. Another found that polyamide formed on top of the deposited MOFs [77], which would largely exclude them from contributing to the ultimate separation. The performance improvements observed in that study may be from effectively changing the porosity and properties of the support membrane's interface [43,47], similar to previous authors' work on deposited nanostrands [45]. This explanation also corresponds to what is known about IP, which is that it dominantly occurs in the organic phase [36,37]. Therefore, any deposited materials that are in the aqueous phase during IP should be covered by polyamide. Some authors have included fillers directly in the aqueous phase [69,70,83,87,89–94], but there is no evidence suggesting that these materials are not also covered by polyamide.

Regardless, these filler materials add a new dimension of tailorability to TFC membranes, which enables: fouling reduction, surface charge modification, surface roughness changes, surface energy shifts, permeance enhancement, selectivity increases, greater thermal stability and better mechanical strength. Furthermore, while not all formation techniques enable rapid commercialisation, certain techniques have already been commercialised with success, as demonstrated by LG Chem's acquisition of NanoH2O. This was achievable because fillers were simply incorporated into the organic phase, which only requires slight modification of decades-old TFC membrane manufacturing technology.

1.3.3 Membrane Characterisation

1.3.3.1 Membrane Performance

OSN membrane performance can be grouped into three key areas: permeability, selectivity and mechanical/chemical/thermal stability. The specific requirements of these considerations are highly dependent on the intended application and can be evaluated via multiple techniques.

Every membrane is tested for permeability and selectivity, though analogue values like permeance and flux are often used for the former, while selectivity is often expressed in terms of rejection. Permeability ($P_{E,l/i}$) is an intrinsic material property that describes the amount of solvent (l) or solute (i) that flows through the membrane per some driving force. Permeance ($P_{E,l}$) is the permeability divided by the membrane's selective layer's thickness. The volumetric flux ($J_{E,l}$) of a membrane, or flow per unit area of membrane, can be derived from irreversible thermodynamics and written as follows [19,95]:

$$J_{E,l} = P_{E,l}(\Delta P - \sigma \Delta \pi) \quad (1)$$

where ΔP is the transmembrane hydraulic pressure, σ is the reflection coefficient, $\Delta \pi$ is the transmembrane osmotic pressure [19,95,96]. To measure pure solvent permeance, pure solvent or extremely dilute solvent flux can be measured after compaction. When using dilute solvents, note that the hydraulic pressure must greatly exceed the osmotic pressure ($\Delta P \gg \sigma \Delta \pi$) and fouling must be negligible. Pragmatically, flux data are taken by measuring the volume of permeate (V_l) over a period of time (t) given a certain hydraulic pressure and membrane area (A). Thus, the following equation is commonly used to calculate membrane permeance:

$$P_{E,l} = \frac{J_{E,l}}{\Delta P} = \frac{V_l}{At \Delta P} \quad (2)$$

In liquid filtration, observed rejection ($R_{O,i}$) of solute (i) is most commonly used to describe selectivity. Rejection is defined as:

$$R_{O,i} = \left(1 - \frac{C_{P,i}}{C_{F,i}} \right) \quad (3)$$

which only requires the measurement of the solute concentrations in the permeate ($C_{P,i}$) and feed ($C_{F,i}$).

Rejection and permeance are measured in dead end or crossflow modes, as depicted in **Figure 5**. In dead end operation, the flow is perpendicular to the membrane surface. This is an easy method to use in the laboratory to assess membrane filtration; however, there tends to be high levels of CP. CP is the accumulation of solute at the membrane interface caused by the quick removal of solvent and relatively slow back diffusion of rejected solute. Since CP reduces membrane permeance by increasing the osmotic pressure at the membrane interface and reduces rejection by creating a higher actual concentration of solute at the interface than that measured in the bulk, most industrial NF processes use crossflow filtration. Crossflow filtration reduces CP by introducing turbulent flow at the interface by circulating the feed solution in a direction that is parallel to the membrane's surface. The effects of CP in certain

crossflow apparatuses are well documented [18,19,96,97]; therefore, it is preferred to run steady state experiments in crossflow, as the resulting data is more reliable.

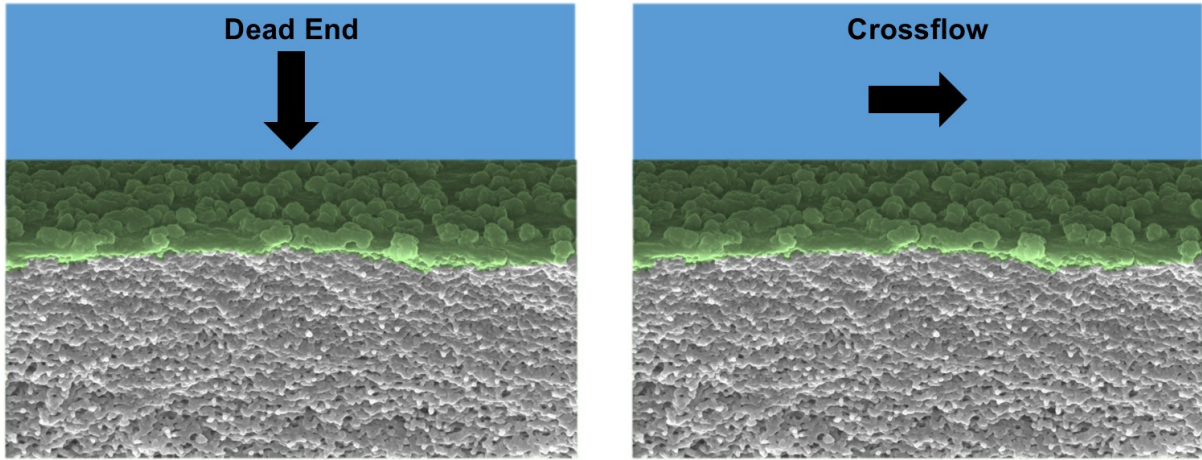


Figure 5. Schematic representation of dead end and crossflow filtration.

Using a crossflow system, the mass transfer coefficient of solute i (k_i) for certain systems can be calculated using an equation that takes the form of:

$$Sh = \frac{k_i d_H}{D_i} = a Re^b Sc^c \left(\frac{d_H}{L} \right)^d \quad (4)$$

where Sh , Re and Sc are the dimensionless Sherwood, Reynolds and Schmidt numbers; d_H and L are geometric parameters; D_i is the diffusivity of solute i ; and $a - d$ are empirical parameters available in the literature [19,96]. With these data, it is possible to calculate the concentration of solute at the membrane's interface ($C_{M,i}$) using the following equation [19,96]:

$$C_{M,i} = (C_{F,i} - C_{P,i}) e^{(J_{E,i}/k_i)} + C_{P,i} \quad (5)$$

This is helpful in calculating intrinsic rejection ($R_{I,i}$), defined as [19]:

$$R_{I,i} = \left(1 - \frac{C_{P,i}}{C_{M,i}} \right) \quad (6)$$

For OSN, there is still no standard solute that serves as a common benchmark. Dyes are common due to their relative ease of testing, only requiring a UV-visible spectrophotometer. Homologous series and polymers such as alkanes, polyisobutylene, polyethylene glycol, sugars, lipids and polystyrene have been used as well. These tend to require a chromatographic measurement technique such as high pressure liquid chromatography with a UV-visible, evaporative light scattering or refractive index detector or gas chromatography with a flame ionisation or thermal conductivity detector [6,98]. Considerations for solute selection include intended application, solubility, hydration, polarity, charge and purity. Of these techniques, polystyrene oligomers are inert, pure, nonpolar and soluble in a fairly large

range of solvents [98]. This technique can be more expensive and time consuming, however, so select dyes can also be useful for screening.

Mechanical, thermal and chemical stability can be tested in a variety of ways. These can be roughly categorised into *in situ* and *ex situ* testing. Common *ex situ* tests include: immersing a membrane into a solvent to see if it dissolves [32]; thermogravimetric analysis (TGA) or differential scanning calorimetry to assess thermal properties; and mechanical tests such as tensile strength [99]. For *in situ* testing, rejection and permeance are typically measured during various solvent and/or thermal cycles over time [99]. A decrease in permeance and increase in rejection is usually associated with membrane compaction, while visa versa is indicative of degradation.

1.3.3.2 Morphological and Physicochemical

A large range of testing techniques have been employed to explore membrane morphology and physicochemical properties. When it comes to morphology, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) are the most common techniques. SEM is used for qualitative observation of surface morphology and approximate apparent thickness [20]. Real thickness is typically measured by TEM, AFM or some combination. This usually requires dissolution of the membrane support or synthesising films without a support and then mounting the polyamide membrane in a resin or on a smooth surface [45,46,52,100]. AFM is also commonly used to assess surface roughness [20], though for membranes with larger pores it can also be used to approximate surface porosity and pore diameter [101]. Roughness data can be combined with contact angle data to obtain a normalised contact angle [86,102]. The contact angle can be used to determine a wide variety of physicochemical properties such as surface charge, zeta potential, wettability and hydrophilicity [103]. This can be supplemented with streaming potential measurements to determine the isoelectric point and surface charge of the membrane [20]. Chemical analysis can be performed using Raman spectroscopy, Fourier-transform infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDS), elemental microanalysis and X-ray photoelectron spectroscopy (XPS) [19,20]. Each spectroscopic technique has its own depth of penetration and should be used accordingly.

1.3.4 Thin Film Nanocomposite Membrane Formation via Interfacial Polymerisation

1.3.4.1 Morphological Considerations

Certainly there have been a number of preliminary morphological investigations indicating that filler is present in the polyamide structure [1,28,29,62,65,68,75,86,104,105]; however, these images fall short of being conclusive. There could be a variety of morphologies, as presented in **Figure 6**. The filler could sit on top, rest underneath or bisect the polyamide layer, as shown

in cases 1 through 3 respectively. Alternatively, the membrane morphology could be some combination of these cases, as shown in case 4. Finally, it is also possible that there is some aggregation, as shown in case 5. All these cases would suggest markedly different performances. In cases 1 and 2, one would expect minimal filler effect on membrane performance, as the filler would resist permeation in series with the film. Case 3 demonstrates the maximum filler effect, where permeation occurs in parallel. Case 4 is indicative of some combination of these and would have mixed effects. Finally, if the aggregates shown in case 5 introduce non-selective interparticle voids, then the membrane would have reduced selectivity. However, these aggregates could be positioned similarly to the particles illustrated in cases 1 through 4.

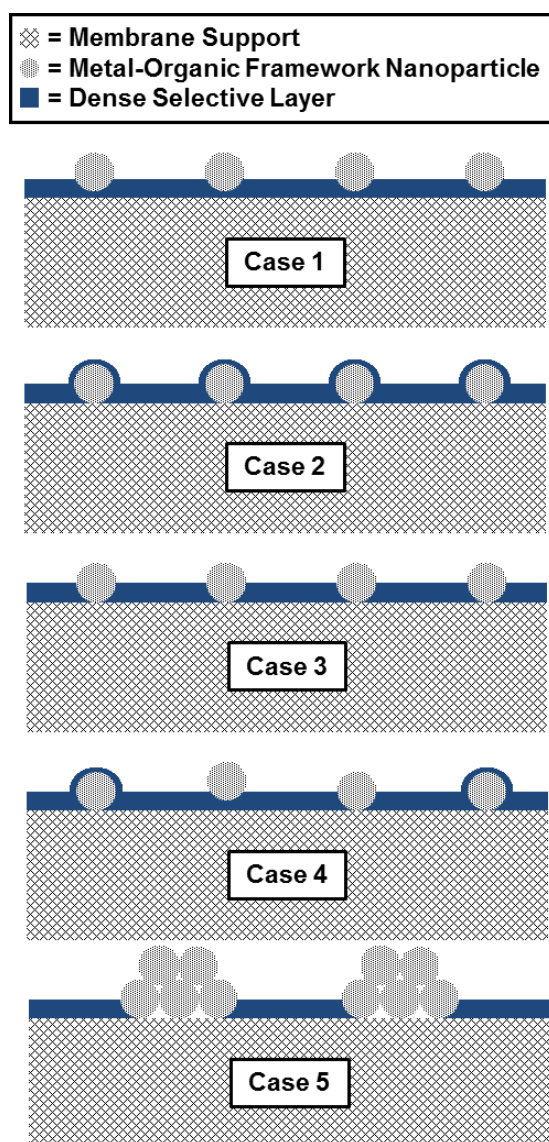


Figure 6. Illustration of possible TFN membrane morphologies [10].

1.3.4.2 Comparing Permeation Models to Experimental Findings

Since the seminal articles on TFN membranes made via IP [1,28], there has been a host of research on various filler materials and methods of filler incorporation [29], but none to date have produced radically different changes in membrane performance. It is worth asking the question then: have we reached the potential limit of this technology? No MMM models have been applied to real data to date, so it is of interest to consider what models might reveal. Given these theories of possible morphologies, the optimal film would be a monolayer of optimally packed filler material, bridged with some small amount of polyamide. The support would have to be ideal, providing no additional resistance. Such a film could be modeled using a resistance model [19], where the effective permeance ($P_{E,i/l}$) of solute (i) or solvent (l) can be written as:

$$P_{E,i/l} = \sum \theta_I P_{I,i/l} = \theta_P P_{P,i/l} + \theta_F P_{F,i/l} \quad (7)$$

where θ_I are the volume fractions of the membrane components I , which consist of polymer (P) and filler (F). The corresponding solute flux term to the solvent flux term used earlier for the equations is [19,95,96]:

$$J_{E,i} = P_{E,i} \Delta C + (1 - \sigma) \overline{C}_{A,i} J_{E,l} \quad (8)$$

where $\overline{C}_{A,i}$ is the average solute concentration in the membrane pore. If the reflection coefficient is close to unity, the second term can be ignored, which enables the calculation of solute permeance from practical measurements as follows:

$$P_{E,i} = \frac{J_{E,i}}{\Delta C} = \frac{J_{E,l} C_{P,i}}{\Delta C} = \frac{J_{E,l} C_{F,i} (1 - R_{O,i})}{\Delta C} \quad (9)$$

Finally, under these assumptions, an observed rejection can be calculated [96]:

$$R_{O,i} = \frac{J_{E,l}}{J_{E,l} + P_{E,i}} \quad (10)$$

These equations require values for the permeances and surface areas of the filler and polymer as well as the rejection of the polymer. The areal fraction of perfectly packed circles is ~0.9 [106]. Permeance and rejection values of the polyamide film with some model filler can be taken from previous work [75]. The filler of greatest interest from the cited study is MIL-101, a type of MOF. This filler is also the focus of this work and was chosen for reasons detailed in Section 1.4.3. Since it is experimentally difficult to determine the true permeance of a MOF, an approximation needs to be used. Because of the relatively large pores of MIL-101, it is fair to assume that a constricted pore flow model is applicable [107]. Thus, one can assume that the Hagen-Poiseuille equation is applicable, which suggests that:

$$P_{E,l} = \frac{\varepsilon r_p^2}{8\mu_p \tau L} \quad (11)$$

$$\mu_p = \mu_0 \left(1 + 36 \left(\frac{r_l}{r_p} \right) - 18 \left(\frac{r_l}{r_p} \right)^2 \right) \quad (12)$$

where r_p is the pore radius, r_l is the solvent radius, μ_p is the dynamic viscosity in the pore, μ_0 is the dynamic viscosity in the bulk solution, τ is tortuosity, ε is porosity and L is the length of the pore. It is most conservative to use the pore windows of MIL-101 as the radius of the pore. The pore window radius, 0.6 and 0.8 nm, can be found in the literature along with the porosity [108]. The same study reports that MIL-101's pores are found in a ratio of 2:1 inside MIL-101, so a number weighted average can be used. Instead of a perfect sphere, it is conservative to assume that MIL-101 is essentially a cylinder with a length of 47 nm, based on particle size diameter measurements from literature [75]. Using these data, the calculated permeance would be $\sim 75 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$. For rejection, the Bowen and Welfoot model can be used [20,107]:

$$R_{l,i} = 1 - \frac{(K_c - Y)\Phi}{1 - [1 - (K_c - Y)\Phi] \exp[-Pe']} \quad (13)$$

$$Pe' = \frac{(K_c - Y)r_p^2}{8K_d\mu_0 D_i} \Delta P \quad (14)$$

$$Y = \frac{8M_{vol}K_d\mu_0 D_i}{RT r_p^2} \quad (15)$$

$$K_c = (2 - \Phi) \left(1.0 + 0.054 \left(\frac{r_i}{r_p} \right) - 0.988 \left(\frac{r_i}{r_p} \right)^2 + 0.441 \left(\frac{r_i}{r_p} \right)^3 \right) \quad (16)$$

$$K_d = (2 - \Phi) \left(1.0 + 2.30 \left(\frac{r_i}{r_p} \right) - 1.154 \left(\frac{r_i}{r_p} \right)^2 + 0.244 \left(\frac{r_i}{r_p} \right)^3 \right) \quad (17)$$

$$\Phi = \left(1 - \frac{r_i}{r_p} \right)^2 \quad (18)$$

where r_i is the solute radius, Φ is the steric partition coefficient, K_c and K_d are the uncharged hindrance factors for convection and diffusion, Y is a dimensionless grouping, M_{vol} is the molar volume of the solvent, R is the universal gas constant, T is the temperature, D_i is the solute diffusivity and Pe' is the modified Peclet number. Finally, the diffusivity can be approximated for molecular species using their Stokes' radii:

$$D_i = \frac{k_B T}{6\pi\mu r_i} \quad (19)$$

where k_B is the Boltzmann constant. The solute radius in this instance was approximated based on the van der Waals volume of polystyrene dimer to be $\sim 0.4 \text{ nm}$ [109], resulting in a diffusivity of $\sim 1 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$. This approximated rejection enables the calculation of an effective solute permeance of each pore. The number weighted average of these values was

taken as the effective solute permeance of the MOF, which in turn can be used to calculate an ultimate rejection of ~49 % for MIL-101. With these values, an idealised film permeance of ~68 L·m⁻²h⁻¹bar⁻¹ and ~49 % rejection can be calculated, corresponding to an increase in permeance by a factor of 40 and a reduction in rejection of 51 %. Sorribas et al. was only able to achieve a 2.6 times increase in methanol permeance and a decrease in rejection of only 2-3 % for the polystyrene dimer in methanol. One explanation for this gap is the relatively small amount of MIL-101 present in the film as measured by Sorribas et al.: 12 ± 1 % (w/w) or ~23 % (v/v). The differential from this loading and ideal loading leaves significant room for potential improvement. According to the aforementioned model, however, the corresponding increase in methanol permeance observed in that study would suggest a MIL-101 content of only 3 % (v/v). This suggests that there must be some other explanation for the observed performance. To explore whether this is purely morphological, another common model to describe MMMs can be used, that is Maxwell's equation [110]:

$$P_{E,i/l} = P_{P,i/l} \left[\frac{P_{F,i/l} + 2P_{P,i/l} - 2\theta_F(P_{P,i/l} - P_{F,i/l})}{P_{F,i/l} + 2P_{P,i/l} - \theta_F(P_{P,i/l} - P_{F,i/l})} \right] \quad (20)$$

This equation models the composite material as a continuous polymer phase with spherical, uniformly dispersed fillers within the phase. Maxwell's equation calculates that Sorribas et al. would need a filler fraction of 33 % (v/v), higher than that measured. At this loading, there would also be a negligible impact on rejection. Indeed, the data of Sorribas et al. would need to be fit to some empirical model to make sense, of which there are many available [110,111]. While the calculations are not shown here, similar conclusions were found when applying these models to a variety of TFN membrane data. To be clear, the empirical models do not enable any fit though. These data are within the theoretical maximum and minimum boundaries [110]. Since many of these fillers should be approximately spherical, there are four conclusions that may be possible. The first is that the approximation for MIL-101 permeance is wrong. Assuredly it is off to a degree. However, as shown in the Section 9.3.8, this simple method closely approximates more advanced molecular modelling techniques for other MOFs and the theory is fairly well established. The second option is that the membranes do have a random morphology, similar to that depicted in **Figure 6**, case 3, having some undetermined fraction that bisects the polyamide layer. This would suggest that improvements to TFN membrane performance could be made if better morphological control was possible. The third is that there may be some secondary effect of the filler on membrane performance, such as those described in the next section. These are effects not attributable to the porosity of the filler material, such as the inclusion of aggregates. To enhance membrane performance through secondary effects would require understanding and optimising these effects. The final possibility is, of course, some combination of these causes, which would require the

investigation of all of the aforementioned factors. Note that this is a slightly different conclusion than that arrived at by van Goethem et al. They only considered Maxwell's equation [80] and attributed any discrepancy to secondary filler effects. The analysis here shows that this argument is over simplified, since it does not account for membrane morphology or realistic permeance data. In the case of their specific fabrication technique and filler material, the secondary effect of filler degradation does seem to contribute to ultimate membrane performance. Furthermore, there is strong evidence of other secondary filler effects in the literature, as detailed in the next section.

1.3.4.3 Secondary Filler Effects

In the first paper on TFN membranes made via IP [1], Jeong et al. measured the permeance of a pore-filled and regular zeolite. The regular zeolite showed the highest percent increase in permeance relative to the TFC membrane control of ~ 30 %. The pore filler zeolite also increased the membrane's permeance by ~ 20 %. These data suggest that something on the order of ~ 60 % of a TFN membrane's increase in performance is attributable to something other than the filler's porosity. These contributions to membrane performance beyond that of the porosity of the filler can be called secondary effects of filler inclusion. Secondary effects have been hypothesised to include catalytic effects, TMC hydrolysis, proton quenching, filler degradation, monomer transport effects, filler hydration, filler-polymer interactions and filler aggregation [62,63,65,81,112]. Few TFN membrane publications focus exclusively on these effects and rather focus on the ultimate membrane performance changes caused by novel filler addition to the IP process. The author is aware of one work published during the year of writing this thesis that was exclusively dedicated to exploring secondary filler effects [80]. While most of these proposed effects have little or no evidence published on them to date, filler degradation, filler hydration, filler-polymer interactions and aggregation have at least some literature discussing these concepts.

Table 1 and **Figure 7** provide a brief illustrative summary of filler-polymer interactions based on previous descriptions [112]. The first two cases describe whether there is intimate filler contact. Ideally, as in case 1, the filler contacts the polymer intimately. In case 2, there is void space between the filler and polymer, causing the introduction of non-selective regions into the membrane. This is often caused by low filler-polymer interaction and glassy polymers are exceptionally prone to the issue. Membrane fabrication processes which cause the polymer to expand or contract, such as heat or solvent treatments, can also exacerbate the issue. Finally, in cases where there is good filler-polymer contact, there can be rigidified polymer at the interface or polymer plugging the pores of the nanoparticle, shown as case 3 and case 4.

The former explains why non-porous particles can increase membrane selectivity. The latter, on the other hand, causes the porous fillers to be largely excluded from any separation.

Table 1. Description of filler-polymer contact for mixed matrix membranes (MMM) [10].

Case Number	Filler-Polymer Contact	Filler-Polymer Interaction
1	Intimate Contact	None
2	Interfacial Voids	None
3	Intimate Contact	Rigidification of Polymer at Interfacial Space
4	Intimate Contact	Pore Blockage of Filler at Interfacial Space

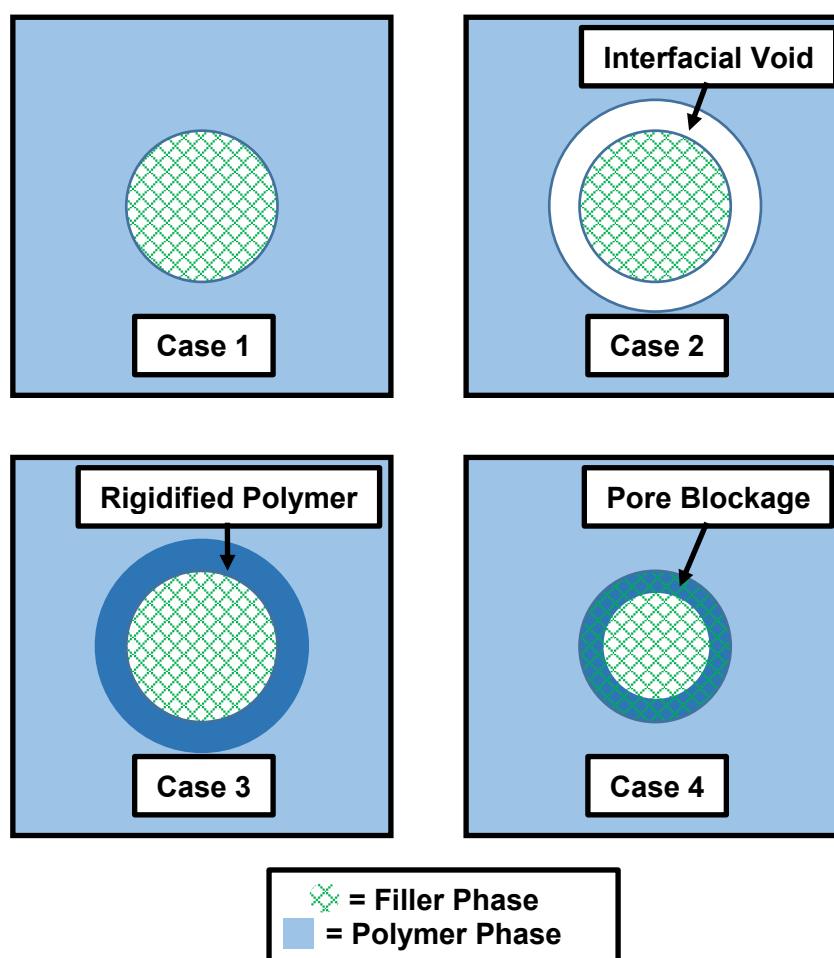


Figure 7. Illustration of filler-polymer contact for mixed matrix membranes adapted from the literature [10].

Early studies showed the impact of increasing the temperature of the IP reaction on the final membrane performance, showing an overall increase in permeance with increasing temperature [49]. Recently, researchers have hypothesised that heat effects during IP are responsible for roughness in poly(*m*-phenylenediamine trimesamide) membranes [45]. Just as this is being written, the first report investigating the temperature of IP reactions at the

interface via *in situ* measurements was published showing reaction temperatures as high as 80 to 90 °C for certain IP systems [113]; however, the experiment was performed in a microfluidic device under convective flow, which should affect both the reaction rate (heat generation) and heat transfer (heat dissipation). Thus, it is not trivial to work out whether the static IP that occurs in most laboratory conditions would achieve higher or lower temperatures. Ukrainsky and Ramon do show that doubling the flow rate can increase the temperature by something on the order of 20 °C at the interface at typical reaction times, suggesting that the increase in reaction kinetics seem to outpace that of heat transfer. Regardless, it seems that this and other research have shown that the heat of reaction and enthalpy of formation have some correlation with morphology [55]. Lind et al. hypothesised that the hydration energy of zeolite could cause local temperature difference during reaction since it has hydration energies between 0.4 and 0.6 kJ·g⁻¹ [65]. MOFs can have even higher hydration energies, with MIL-101 demonstrating one as high as 2.6 kJ·g⁻¹ [114]. It is difficult to say given the current evidence whether or not the kinetics of hydration and location of filler are sufficient to impact the local temperature of reaction.

A recent work also identified filler degradation as a significant secondary effect [80]. In that study, ZIF-8 was deposited onto the membrane support prior to IP. Van Goethem et al. found no signs of ZIF-8 in the final polyamide structure after chemical and crystallographic analysis. Moreover, it was demonstrated that zinc nitrate could increase permeance and decrease the rejection of membranes. Finally, some ZIF-8 could be detected in the polyamide film if an acid quenching reagent was used. Since ZIF-8 was known to be sensitive to acid, it was determined that performance improvements of membranes synthesised in this way with ZIF-8 could be at least partially attributed to filler degradation. It would be of interest to see if these data hold true for other fillers and membrane fabrication processes.

Aggregation was recognised by early TFN membrane researchers as a possible source of performance change [62,63], even in TFN membranes with high rejection. It has since remained a consistently cited phenomenon to describe membrane performance behaviour [29]. Usually researchers identify and attribute aggregation on the basis of SEM imaging or performance data. SEM imaging, however, is qualitative and can often be misleading. Some authors claim superior dispersion when it is difficult to assess given the images provided. Most authors simply use performance data. The benefit of this method is that it is quantitative and produced for nearly every membrane paper, since selective permeation is the point of a membrane. A reduction in rejection and increase in solvent permeance would be observed if aggregates introduce non-selective defects. However, it is not obviously true that aggregates do introduce non-selective defects. No quantitative method of assessing aggregation in TFN membranes has been employed to date. Regardless, most TFN membrane researchers stop

increasing filler content in the organic phase because of a precipitous decrease in rejection [29]. So not only is aggregation not quantified, but it also seems to prevent higher filler loading in the organic phase. Perhaps this is a factor limiting filler loading in the final membrane, preventing the formation of more ideal, highly-loaded TFN membrane structures such as that presented in the previous section.

1.4 Metal-Organic Frameworks

1.4.1 Overview

MOFs are crystalline materials in which secondary building units consisting of metal clusters are connected with organic linkers using reticular synthesis. There are a series of valuable reviews in the field [115–117], the most recent of which came out in a series in Chemical Reviews in 2017 that details various areas of MOF research [118]. These materials are unusually porous, achieving densities as low as $0.126 \text{ g}\cdot\text{cm}^{-3}$, pore sizes of 9.8 nm and BET surface areas as large as $7,140 \text{ m}^2\cdot\text{g}^{-1}$, notably higher than alternative porous materials [115]. These properties are attributable to MOF's readily accessible bulk volume and well-defined pore structure [116]. There are also multiple methods of tailoring MOFs to suite specific applications, including: post-synthetic modification, using alternative ligand functionalities, using alternative metal clusters, encapsulating materials, surface-specific functionalisation, introducing hierarchical porosity and more. It is no wonder the applications of MOF materials are rapidly expanding, with research already having been conducted on: drug delivery, optics, conductors, chemical sensors, catalysis, separation, adsorption and gas storage [115–118]. Of course, these reasons make MOFs highly attractive for membrane separations. It is supposed that MOFs have higher filler-polymer compatibility than alternative fillers because of their organic ligands, which could help prevent non-selective void formation [119]. Indeed, even glassy polymers seem to be compatible with MOFs without the need for additional coatings. There are several reviews on MMMs based on MOFs that demonstrate successes in a variety of separations [119,120]. Most MOFs are synthesised via conventional heating of ligands and metals in a strong solvent. Different MOF morphologies and crystallinities are possible via a variety of alternative synthesis methods including: electrochemical, mechanochemical, sonochemical, interfacial, microemulsion and microwave-assisted syntheses [121,122]. Importantly, size can be controlled down to the nanoscale, enabling application to TFN membranes.

1.4.2 Characterisation of Metal-Organic Frameworks

A number of characterisation techniques that are used for membranes have strong overlap with those used to characterise MOFs, such as SEM, TEM, AFM, XPS, EDS and FTIR. SEM,

TEM and AFM are generally used for morphological investigation. EDS can give chemical analysis in conjunction with SEM and diffraction patterns can be investigated with TEM. ImageJ can be used to analyse images and determine particle size distribution as well as a number of other parameters. XPS and FTIR are used for analysis of chemical modification, overall composition and the identification of functional groups. Other techniques used to characterise MOFs can also be used on membranes; however, these techniques are discussed here as they are more common to the field of MOFs. Adsorption isotherms of gases and vapours are one of the most widely used characterisation techniques. Nitrogen adsorption for BET surface area [123] and t-plot micropore volume [124] are typical measurements, though many other analyses, gases or vapours could be used. X-ray diffraction (XRD) is perhaps the most common technique, as the crystal structure of the MOF defines the material [116]. Sample spectra can be referenced using a database, such as the Cambridge Structural Database [125], to determine whether or not it is already discovered or to confirm a material's identity. Alternatively, one could calculate new predicted structures. Finally, crystallite size can be investigated through the use of Scherrer's equation [126] or modified forms [127]. TGA can be used to determine MOF loading, modification, quality of activation and thermal decomposition. A newer technique for the assessment of porosity is environmental ellipsometric porosimetry (EEP). This technique can be used to assess the porosity as well as mechanical, optical and dielectric properties of thin MOF films [128], but has only been applied in a small number of studies mostly focused on adsorption and sensing applications [129–133]. Dynamic light scattering is also common for assessing particle size distributions of MOF nanoparticles in suspensions. It can be combined with an electrode to take electrophoretic measurements, enabling the determination of the zeta potential. The zeta potential is an important measurement to quantify MOF colloidal interactions.

1.4.3 Consideration for Membrane Performance

Between 2003 and 2013, over 20,000 new MOFs were reported and the doubling time for new MOF reports was less than 10 years [115]. This mandates that some type of rational selection criteria must guide MOF selection. The issue with developing such criteria for TFN membrane formation is that the precise mechanism of performance improvement is not well established. Regardless, it is preliminarily helpful to propose the question: if fillers are incorporated into the polymeric matrix, then what are their ideal properties? Possible characteristics to consider would be pore diameter, porosity, tortuosity, stability, particle size and filler-polymer compatibility. It appears that MIL-101 may be uniquely suited to TFN membrane formation, as detailed below.

1.) *Porosity, tortuosity and pore diameter.* For NF, a MOF should have a pore window

diameter between ~ 0.3 and 2.0 nm. Having pore diameters much smaller than ~ 0.3 nm does not make sense for common liquid applications as, even if the pore is fully wetted, one of the smallest solvent molecules, water, would be too large to pass. The upper limit, although somewhat arbitrary, is simply that prescribed by the definition of NF according to the International Union of Pure and Applied Chemistry (IUPAC) [8]. The higher the porosity and tortuosity, the higher the permeance should be according to hydrodynamic theory.

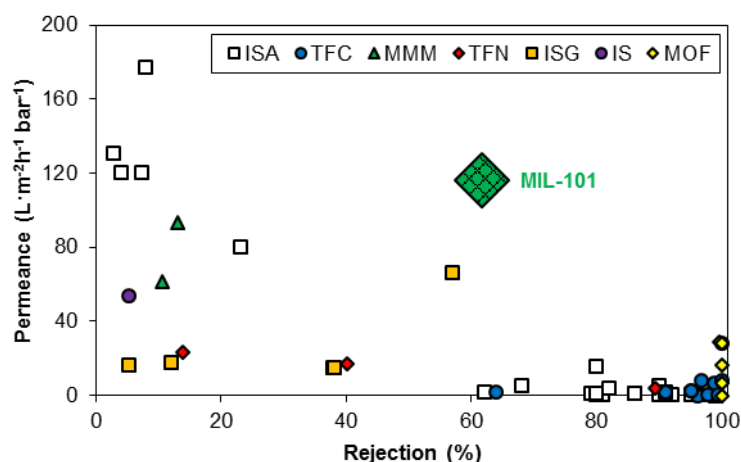


Figure 8. Measured acetone permeance and polystyrene dimer rejection from the literature [6] for integrally skinned asymmetric (ISA) membranes [134,135], thin film composite (TFC) membranes [33,45,136], mixed matrix membranes (MMM), thin film nanocomposite (TFN) membranes [10], *in situ* growth (ISG) [137], membranes and interfacial synthesis (IS) membranes [138,139]. Performance of select metal-organic frameworks (MOFs) included, modelled using hydrodynamic theory [107].

By using the Hagen-Poiseuille equation and Bowen and Welfoot model described in Section 1.3.4.2, it is possible to predict MOF performance based on their pore size, porosity and tortuosity. If compared to membrane performance data, it helps to predict what MOFs might fill important gaps in membrane performance. **Figure 8** presents the approximated performance of some common MOFs, including MIL-53, MIL-101, UiO-66, UiO-67 and ZIF-8 [108,140–142]. **Figure 8** also shows membrane performance data summarised from the literature. Researchers have already accomplished remarkably high permeance and high rejections with conventional TFC membranes. Surprisingly, many MOFs seem incapable of surpassing these performances according to hydrodynamic theory. Moreover, it is possible to have membranes that achieve high permeance and no polystyrene dimer rejection, which usually requires pore sizes well outside the range in which many MOFs are stable. However, it appears that there is a dearth of materials available for high-performance membranes at rejections of ~ 50 %. A MOF-based membrane using HKUST-1 was able to achieve the best

performance in this range to date, despite HKUST-1's lack of hydrolytic stability. It appears that MIL-101 is an ideal candidate for achieving performances within this range of separation. This is attributable to MIL-101's large pore volumes, diameters and windows of 12.7 nm³, 2.9 nm and 1.2 nm as well as 20.6 nm³, 3.4 nm and 1.6 nm [108]. Indeed, MIL-101 is one of the most porous MOFs, with a porosity of 0.83 and Langmuir surface area of 5,900 m²g⁻¹. Of course, a note of caution is that directly relating the porous properties of a material and expected TFN membrane performance may be problematic because the role of secondary effects has not been quantified in most TFN membrane formation systems.

2.) *Stability.* Many of the popular early MOFs were not hydrolytically stable, but now there are many water-stable MOFs [143]. MOF thermal, chemical, mechanical, pH and solvent stability are a must for industrial application [116]. Depending on the application, there can be certain ranges or tolerances that are acceptable; however, water stability should not be compromised for most NF/OSN applications. Beyond application, the MOF must be stable during the membrane fabrication process. Recent research has specifically identified MOF degradation as an issue during the membrane formation process [80]. Specific to TFN membrane formation, it is helpful to have an acid-stable MOF that does not degrade in the presence of amines, acyl chlorides or other IP additives. Moreover, MOFs prone to sonomechanical degradation should be avoided, as sonication is typically used to suspend MOFs prior to IP. Another aspect of stability is pore opening or breathing effects [144]. Changes in MOFs pore structures have been shown to be either advantageous or deleterious in certain applications. Application and synthetic stabilities are less obvious criteria if secondary effects play a dominant role. If the MOF does not bisect the polyamide film, then application stability could be meaningless. Moreover, a controlled MOF degradation could improve or worsen the IP process by releasing additives over time. MIL-101 is stable in acidic conditions [145], aqueous conditions [146] and high temperatures [75]. Moreover, the author is aware of no reports on poor sonomechanical stability, degradation during IP or breathing effects.

3.) *Particle Size.* Larger changes in membrane performance are observed with smaller particles [62]. It is unclear whether this is caused by increased filler incorporation or secondary filler effects, though the latter seems more likely. As discussed in the proceeding section, smaller particles are more prone to aggregation. Additionally, past MMM research shows increased filler-polymer interactions with decreased particle size [112]. Regardless, TFN membrane researchers have successfully made membranes using particles less than 300 nm in diameter [62,75]. This is on the same order of magnitude as the apparent thickness of many TFC membranes [52]. It is sometimes assumed that the filler must be smaller than the

apparent thickness, but this has yet to be proven.

4.) *Filler-Polymer Compatibility.* This is necessary to prevent non-selective void formation in MMMs, as discussed earlier. However, if the MOF does not bisect the selective layer and secondary effects dominate the impacts on membrane performance, it is less clear the role that filler-polymer compatibility would play, if any. Regardless, MIL-101 has been successfully incorporated into a variety of MMM and TFN membranes, making it a suitable material for further exploration [75,78,119].

1.4.4 The Colloid Science of Metal-Organic Frameworks

Recently, there has been an emerging interest in the colloid science of MOFs. This interest is not an uncommon development to most materials, which eventually reach a stage of maturity where routes to commercial application are necessary. The importance of colloid science is intrinsic to certain fields. In drug delivery and biomedical imaging, the precise size, state of aggregation and surface properties of colloidal particles can prove critical in determining pharmacokinetics, delivery targets and detection [147,148]. Interfacial phenomenon can also determine the adsorption and corresponding catalysis of materials [149,150]. A variety of applications including separation, optics, gas storage require the creation of MOF monoliths or composites for practical application [151,152]. One example is the focus of this work: TFN membranes. As detailed earlier, the quality of dispersions and interfacial phenomena can affect defect formation and membrane performance significantly.

Within the last 10 years, there have been some works dedicated entirely to the colloidal properties, surface modification and self-assembly of MOF structures [132,133,161–165,153–160]. To achieve suspension in hydrophobic solvents, these authors resorted to modification of the MOF's surface in most cases. In aqueous environments, authors were able to more easily disperse MOFs. The linker was shown to play a role in dispersion and, as is discussed later in this section, pH was found to be important. To date, most MOF application articles achieve suspension by trial and error. The author could not find any more fundamental articles that relate material parameters to the colloidal behaviours observed.

Derjaguin, Landau, Verwey, Overbeek (DLVO) theory has been successfully applied to a wide variety of colloidal systems. Indeed, with the surge in publications on nanoparticles in recent years, it has only become more popular. DLVO theory states that particle interactions in a continuous fluid medium are a function of van der Waals attractive forces and electric double layer repulsive forces, which can be modelled as follows [166]:

$$E(d) = \frac{2\pi\epsilon_0\epsilon_h r \zeta^2}{k_B T} e^{-\kappa d} - \frac{Ar}{12k_B T d} \quad (21)$$

where ε_0 is the permittivity of free space ($\text{F}\cdot\text{m}^{-1}$), ε_h is the relative permittivity of the host solvent, r is the particle's radius (m), ζ is the zeta potential (V), k_B is the Boltzmann constant, T is the temperature (K), d is the distance between two particles (m), A is the Hamaker constant (J) [167], N_A is Avogadro's number (mol^{-1}) and κ is the Debye length, which is defined as:

$$\kappa^{-1} = \sqrt{\frac{\varepsilon_0 \varepsilon_h k_B T}{2 N_A e^2 I}} \quad (22)$$

where e is the elementary charge (C) and I is the ionic strength of the solvent ($\text{mol}\cdot\text{m}^{-3}$).

The first term of the DLVO equation corresponds to the electric double layer forces. As illustrated in **Figure 9**, charged particles in electrolyte solutions will develop a double layer consisting of the Stern layer and Gouy-Chapman diffuse layer. The Stern layer consists of ions adsorbed to the particle's surface. The Gouy-Chapman layer is a diffuse layer of ions, the thickness of which is equivalent to the Debye length. The energy associated with the electric double layer repulsive term in the DLVO equation increases with fluid dielectric constant, particle size, and particle zeta potential. The electric double layer force decreases with ionic strength and interparticle distance. The zeta potential, also illustrated in **Figure 9**, can be sensitive to pH, dielectric constant, electrolyte type/concentration and particle concentration. These variables can alter the surface charge in both magnitude and sign by replacing ions at the surface, associating or disassociating surface functional moieties and/or compressing or expanding the electric double layer.

The second term in the DLVO equation, the van der Waals attractive term, increases with particle radius and Hamaker constant and decreases over interparticle distance. The balance of these two terms over the distance of two particles will create an energy barrier, as shown by the green line in **Figure 10**. The larger this energy barrier, the less likely particles are to aggregate. However, if the van der Waals attractive forces dominate, there will be no energy barrier and particles will aggregate as shown in **Figure 10**. Since both the van der Waals attractive forces and electric double layer repulsive forces are proportional to particle radius, the radius will increase or decrease the magnitude of energy, but not affect the overall sign. This is one reason why nanoparticles are harder to prevent from aggregating.

The author is unaware of any researcher having rigorously applied DLVO theory to MOFs. The main reason is likely the determination of the Hamaker constant, which can be difficult for porous particles because most measurement techniques require the material to be a monolith of some type [168]. There could be an opportunity to see how well this theory describes MOFs'

observed colloidal behaviour. If successful, this could enable better control of membrane formation systems based on theoretical predictions.

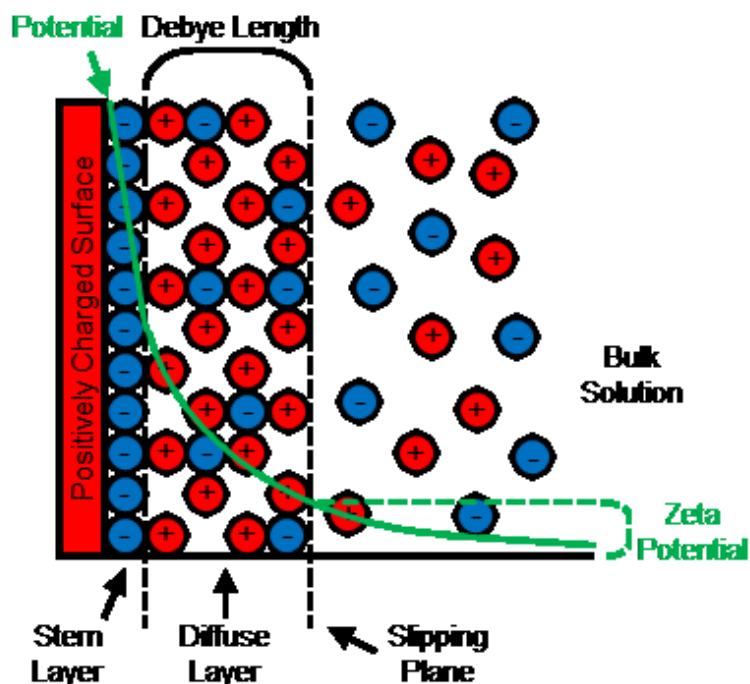


Figure 9. Schematic of positive charges (red), negative charges (blue) and potential (green) of a surface submerged in an electrolyte solution, based on literature [166].

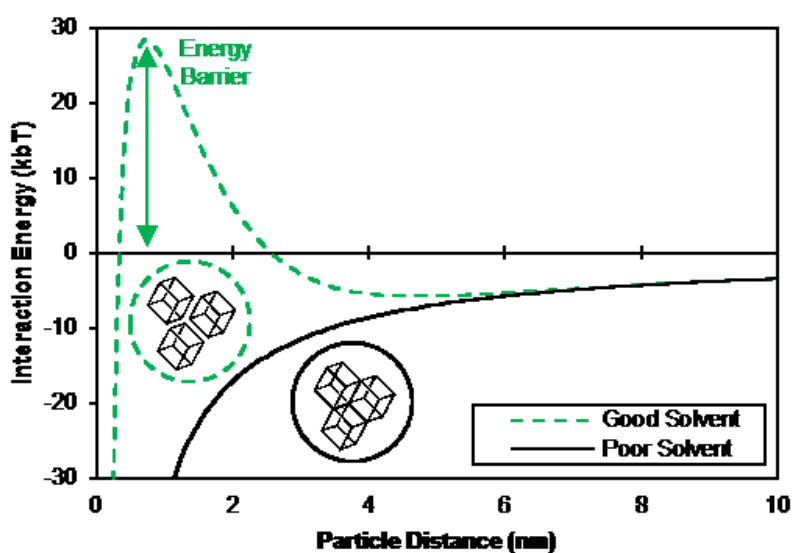


Figure 10. Example DLVO calculations and resulting colloidal behaviour of particle [166].

1.5 Challenges and Literature Gaps

The main challenges and literature gaps can be summarised into three key sections: one, the role of secondary effects in TFN membrane formation; two, the dispersion of MOFs; and three,

TFN membrane formation and performance. Within each of these sections, key gaps that are the focus of this work are italicised and elaborated upon.

1.5.1 Secondary Effects in Thin Film Nanocomposite Membrane Formation

With only one paper dedicated to the role of secondary filler effects during TFN membrane formation via IP [80], it is one of the least explored avenues in TFN membrane fabrication. Yet speculation and discussions around these aspects go back to some of the earliest published studies in the field [1,62]. Some authors have shown that filler degradation is a concern for certain materials and conditions, while others suspect that filler-polymer interactions, aggregation and a host of parameters that could affect the IP process itself could be important. The impacts of reactive monomer adsorption and aggregation are two reasonable areas for further investigation.

I: Reactive Monomer Adsorption

Surprisingly, no one has discussed or investigated whether or not reactive monomers adsorb to the filler materials, even though it is well documented that changes to the reactive monomer concentrations can have significant effects on membrane performance [45,48,61]. Early research may have assumed this is not a significant phenomenon because the pores of the filler were smaller than that of the TMC. However, filler materials with pores large enough to accommodate TMC have been used without thought to this potentially critical phenomenon [75,169]. Since membrane performance often peaks at a certain TMC concentration, this may be an important phenomenon to control in order to achieve optimal performance.

II: Filler Aggregation

Even though it is widely accepted that aggregation plays a significant role in other MMM formats, no researchers to date have sought to quantify the state of aggregation of the filler material and relate it to membrane performance for TFN membranes. Rather, researchers rely on a combination of qualitative imaging and indirect measurements like rejection. Both of these measurements are standard to the field of membrane science, but SEM imaging is only qualitative and indirect measurements can be misleading. Indeed, prior to any serious exploration of TFN membrane morphology, one must isolate and exclude the impacts of filler aggregation and its role on membrane performance. Otherwise, it is impossible to separate the impact of the filler's properties on membrane performance from that of the aggregate's properties. Filler aggregation seems like a particularly important target as well, because one would expect that increasing the concentration of well-dispersed filler in the organic phase prior to IP should result in higher membrane loadings and, therefore, better membrane performance.

1.5.2 The Dispersion of Metal-Organic Frameworks

III: DLVO Theory and Dispersion

While many researchers have made devices from colloidal suspensions of MOFs or implemented MOFs in applications that are sensitive to their colloidal properties, none have sought to quantify MOFs' colloidal properties via a theoretical framework and relate these properties to a MOF's dispersion. This has not been explored systematically because most researchers achieve their goals via trial and error. Furthermore, measuring fundamental colloidal properties beyond zeta potential and particle size can prove challenging for nanoparticles. Regardless, if the fundamental colloidal parameters of a MOF are quantified, then one should be able to predict dispersion in a range of scenarios, thus reducing the amount of trial and error required to achieve a stable suspension. This could expedite the application of MOFs to a range of fields, including that of membrane science.

IV: Dispersion in Hydrophobic Solvents

Certainly, quantifying the classic DLVO parameters and relating those to dispersion will be useful, but it does not mean that an adequate system for IP will be obvious. DLVO theory predicts that dispersion in low dielectric constant solvents should be challenging and typical solvents used for IP have low dielectric constants. The selection of these types of solvents are no mistake, as they are preferable for IP due to their low water miscibility. Therefore, dispersion of the selected MOF, MIL-101, in hydrophobic solvents is important. While there are some reports in the literature on methods to achieve colloidal suspensions of MOFs in hydrophobic solvents via post-synthetic functionalisation, the author is aware of none that quantify the degree of dispersion of those techniques, making it difficult to assess whether they would be valuable for TFN membrane fabrication. Although it is difficult to say why authors did not explore the effects of particle or solute concentration on the suspension state, these considerations are important in many fields, including TFN membrane fabrication. Beginning to understand the potential and limits of suspending MOFs via post-synthetic functionalisation could help researchers more quickly determine the optimal formulation conditions for their application, including membrane fabrication.

1.5.3 Thin Film Nanocomposite Membrane Formation and Performance

V: Reactive Conditions

To date, few researchers have explored the relationship between the formation of the polyamide thin film and how it might play a role in the successful creation of a TFN membrane with good performance characteristics. Most TFN membranes employ poly(*m*-phenylenediamine trimesamide) as a polymer and place the filler in the organic phase [29]. There is significantly less research on poly(piperazine trimesamide) TFN membranes. Even

though researchers report that membranes made with filler content in the aqueous phase have small effect sizes or are simply covered by the polyamide film [77,88], many researchers making poly(piperazine trimesamide) TFN membranes include their filler in the aqueous phase [69,70,83,87,89–94]. Those who have reported filler incorporation in the organic phase had either low effect sizes [170] or required special filler modification [171,172]. There is not a clear explanation in the research published to date for this seemingly unusual approach. It seems as if there may be some fundamental difference between how fillers contribute to TFN membrane formation in poly(piperazine trimesamide) versus poly(*m*-phenylenediamine trimesamide). Identifying this difference could lead to higher quality poly(piperazine trimesamide) TFN membranes and provide insights into the mechanisms of TFN membrane formation.

2 Thesis Motivation, Objectives and Structure

2.1.1 Motivation

The demanding nature of OSN applications still leave opportunity for improvement in permeance, selectivity, stability, fouling and, importantly, all of the aforementioned factors in a single membrane, particularly in the higher NF pore size range. TFN membranes made via IP could enhance existing TFC membranes, which already prove promising for achieving high permeability, selectivity and stability. However, TFN membranes have only achieved a small fraction of their potential when compared to their hypothetical ideal form, with reports to date demonstrating less than a third of the ideal filler volume fraction, less than a tenth of the ideal permeance and less than ideal selectivity. TFN membrane formation via IP is a complex and relatively new field with many gaps of understanding. Indeed, this thesis only covers a fraction of what could be investigated, but by beginning to understand the mechanisms behind membrane formation and how they relate to membrane performance, perhaps the potential of this membrane formation technique could be actualised.

2.1.2 Objectives

The primary aim of this work is to explore TFN membrane fabrication for general application to OSN to improve their separation performance. To do so, unknown or less-explored impacts of TFN membrane formation on the ultimate membrane performance were studied. There is a particular focus on how colloid science informs the membrane formation process. Below is a list of the objectives:

Objective 1: Explore the impact of reactive monomer adsorption on membrane performance

(Chapters 3 and 6)

Objective 2: Control filler aggregation to determine its effect on membrane performance

(Chapters 3 and 6)

Objective 3: Validate the relationship between a MOF's dispersion and DLVO theory

(Chapter 4)

Objective 4: Control and quantify a MOF's dispersion in hydrophobic solvents

(Chapter 5)

Objective 5: Understand why different IP conditions change TFN membrane performance

(Chapter 6)

2.1.3 Structure

Chapter 1 – Introduction and Literature Review

This chapter provides research motivation as well as a brief overview of membrane and MOF technologies. Finally, it highlights gaps in the literature.

Chapter 2 – Thesis Objectives and Structure

This chapter provides the overall structure of the thesis as well as the objectives for each section.

Chapter 3 – Secondary Filler Effects on Thin Film Nanocomposite Membranes

After establishing a reliable TFC control and filler material, this chapter evaluates secondary effects including filler aggregation and reactive monomer adsorption (Objectives 1 and 2). Poly(*m*-phenylenediamine trimesamide) TFN membranes were created using MIL-101 and characterised for membrane performance and morphology to relate filler aggregation to membrane performance. Additionally, TMC adsorption studies were performed on MIL-101. After demonstrating control over the equilibrium TMC concentration, TFN membranes were fabricated and their ultimate membrane performance was studied.

Chapter 4 – The Dispersion and DLVO Theory of a Metal-Organic Framework

The objective of this chapter was to quantify the colloidal properties of a MOF, MIL-101, and relate its dispersion to DLVO theory (Objective 3). After optimising a dip coating process, MIL-101 particles were deposited on a silicon wafer to create optical-quality, sub-micron, and uniform films. The first Hamaker constant of any MOF was measured via a unique combination of techniques, EEP and SE. This was combined with colloidal characterisation techniques like zeta potential measurements and UV-Visible spectrometry to calculate energy barriers using DLVO theory and relate those energy barriers to dispersion for nine different solvents.

Chapter 5 – Surface-Selective Modification of a Metal-Organic Framework

The objective of this chapter was to suspend MIL-101 in hydrophobic solvents suitable for IP (Objective 4). MIL-101 was treated with a variety of chemicals and polymers with the hope of grafting them to the coordinatively unsaturated sites (CUSs) of the MOF. Two molecules were selected after an initial screening and the resulting modified materials were characterised with XRD, FTIR, TGA, XPS and nitrogen sorption to assess their properties.

Chapter 6 – A Novel Thin Film Nanocomposite Formation System

The objectives of this chapter were twofold: first, was to confirm the mitigation or elimination of secondary effects such as aggregation, reactive monomer adsorption and filler degradation (Objectives 1 and 2); and second, to relate MIL-101 incorporation to IP reaction conditions (Objective 5). High-quality poly(piperazine trimesamide) TFN membranes were fabricated by

using filler in the organic phase without filler modification. Nitrobenzene (NB) was compared with *n*-hexane (HX) to explore their relative effects on filler aggregation, reactive monomer adsorption and filler degradation. These secondary effects were related to membrane performance. TFC membranes were made using NB under a series of reaction conditions. Select conditions were used to synthesise TFN membranes and determine the impact of reaction condition on filler incorporation.

Chapter 7 – Conclusions and Future Work

This chapter summarises key findings and potential areas for future research.

3 Secondary Filler Effects on Thin Film Nanocomposite Membranes

3.1 Abstract

The goal of this work was to first establish consistent thin film composite (TFC) membrane and MIL-101 samples. With these samples, it is possible to evaluate the impacts of filler aggregation and reactive monomer adsorption on the performance of thin film nanocomposite (TFN) membranes made via interfacial polymerisation (IP). Poly(*m*-phenylenediamine trimesamide) TFC membranes were fabricated and their performance was characterised using acetone (Act) and methanol (MeOH) as solvents and polystyrene (PS) and disperse red (DR) as solutes. The poly(*m*-phenylenediamine trimesamide) TFC membranes were treated with *N,N*-dimethylformamide (DMF) via filtration and soaking, showing differences in performance between membrane sets as high as 62.6 % and 2.2 % for MeOH permeance and DR rejection. However, avoiding DMF activation resulted in consistent membranes. Highly crystalline, well-activated MIL-101 with a particle size of ~100 nm and Brunauer-Emmet-Teller (BET) surface area of 2,900 m²·g⁻¹ was synthesised and used to make poly(*m*-phenylenediamine trimesamide) TFN membranes. Clear aggregation was observed during TFN membrane synthesis and aggregates were identified on the membrane's surface using scanning electron microscopy (SEM). Though the membrane permeance increased by a factor of 73 relative to the TFC membrane control, the aggregation led to a reduction in rejection of the PS trimer from 99.8 to 13.7 %. These data suggest that aggregates led to non-selective void formation. Adsorption kinetics and equilibrium loadings were determined for trimesoyl chloride (TMC) on MIL-101 in *n*-hexane (HX). Equilibrium adsorption occurs at ~2 hours, with a maximum loading of 0.4 g TMC·g⁻¹ MIL-101. TMC concentrations were controlled in the organic phase during the synthesis of TFN membranes. The MeOH permeance increased by a factor of 2.4 when the equilibrium TMC concentration was held at 0.10 % (w/v), while it increased further to 2.8 when TMC equilibrium concentrations were treated as usual. This implies that part of the performance improvement of TFN membranes fabricated in this way is attributable to reactive monomer adsorption.

3.2 Introduction and Background

To adequately measure the effect size of filler addition to TFN membranes, it is necessary to establish a well-defined TFC membrane control. One of the most commonly studied types of TFC membrane is made of poly(*m*-phenylenediamine trimesamide). This is created from the reaction of *m*-phenylenediamine (MPD) with TMC [18,19,22,23]. This membrane format became more popular in the field of OSN after the use of crosslinked polyimide supports that were stable in polar aprotic solvents [6,32,33]. This advance enabled their treatment with DMF. The DMF activation of poly(*m*-phenylenediamine trimesamide) TFC membranes has certainly been shown to increase membrane permeance [33,43,59,60]. This has been attributed to the dissolution of polyamide fragments high in carboxylate content and polymer swelling, similar to previous authors that studied activation with ethanol or isopropyl alcohol (IPA) [33,173]. Indeed, fragments between 1,700 and 11,700 g·mol⁻¹ in size were found in the DMF activating solvent. Activation is also associated with a decreased isoelectric point [60] and decreased areal density of carboxylic acid [174]. Recent researchers, however, observe no significant chemical changes to the membrane upon DMF activation and attribute the performance changes to an increase in polymer free volume [45,61]. There are conflicting reports on whether or not DMF activation increases [60], decreases [59] or does not change [33,43] solute rejection. Interestingly, almost all neutral solutes measured seem to have the same rejection before and after activation [33,43]. The behaviour of charged solutes seems more complicated, however, with Gorgojo et al. demonstrating a significant improvement in sodium chloride rejection [60] and Xia et al. demonstrating a large and consistent decrease in methyl orange rejection [59]. Regardless, it is difficult to ascertain the controllability of processes that rely on either etching or swelling a polymer. Therefore, for the purposes of this work, it would be of interest to ensure reproducibility and assess performance differences in the solvent-solute systems of choice.

In the seminal work creating TFN membranes based on metal-organic frameworks (MOFs), tremendous promise for this approach was demonstrated. A 2.3 factor increase in permeance was achieved with the addition of MIL-101, while maintaining high rejections [75]. Since then, authors have attempted to replicate this work. At MIL-101 loadings greater than 0.2 % (w/v) in the HX phase, researchers have found reductions in rejection by more than 50 % for NaCl in water, 10% for Na₂SO₄ in water [175], 10 % for sunset yellow in MeOH [76] and 3 % for PS dimer in MeOH [75]. Indeed, some authors observe a decrease in rejection at loadings less than 0.10 % (w/v) in the HX phase as well [175], but this is not the case for several other authors [75,78]. Whether or not there is a decrease in rejection is important. If the decrease in rejection is accompanied by the presence of aggregates, perhaps the increase in

permeance could be attributed to the aggregates, rather than the porosity of the MOF. Early TFN membrane reports identified this as a possibility for their membranes [62].

Aggregation is one of the so-called secondary effects of filler inclusion, effects beyond that of the porosity of incorporated filler materials. An indication of these were found in the seminal work, where a pore-filled zeolite still demonstrated an impact on membrane performance [1]. Secondary effects could also include effects that would alter the IP reaction, including: catalysis, hydrolysis, proton quenching, heat release and monomer transport dynamics [62,63,65,80]. Another completely unexplored possibility is that MIL-101 may adsorb TMC. It has been widely reported that membrane rejection, selectivity and permeance can be altered by more than 110, 80 and 70 % difference due to changes in TMC concentration [42,48,176], easily on the same order of magnitude as the effect of filler incorporation. Many filler materials used for TFN membranes have pore window sizes less than 0.5 nm and, therefore, the adsorption of TMC inside the particles' pore networks is unlikely since it has a van der Waals diameter of 0.7 nm [109]. However, for materials with pore window sizes equivalent to or greater than the size of TMC, adsorption could be a significant secondary effect that has not been explored to date in the literature. Certainly, with MIL-101's large pore window sizes of 1.2 and 1.6 nm [108], this must be considered.

3.3 Methods

3.3.1 Materials Synthesis

3.3.1.1 MIL-101 Synthesis

MIL-101 was synthesised at 180 °C for 30 minutes using a 10 minute temperature ramp in a microwave oven (MARS 5 Microwave Digestion Oven, CEM Corporation), similar to the method proposed by Khan et al. and built on by Sorribas et al. [75,177]. 1.35 g of chromium(III) chloride hexahydrate ($\text{CrCl}_3 \cdot \text{H}_2\text{O}$, purum p.a., >98 % (RT), Aldrich® Chemistry) was weighed and placed into a high-pressure microwave vessel (XP 1500 Plus, CEM Corporation). Then, the chromium was stirred in with 50 mL of DI water (Centra® R200, Elga) and, finally, 0.865 g of terephthalic acid (TPA, 98 %, Sigma-Aldrich) was added. After the reaction, the vessels were cooled to room temperature and activated.

The activation procedure involved three solvent washes using DI water, DMF (AnalaR Normapur®, VWR) and MeOH (AnalaR Normapur®, VWR). First, the contents of the reaction vessels were centrifuged (Centrifuge 5810R, Eppendorf) at 15,000 rcf for 30 minutes. After decanting the supernatant, the centrifuge tubes were filled with DI water, shaken vigorously and re-centrifuged. After three such water washes, an additional three DMF washes were conducted and the solids were combined into a round bottom flask with 300 mL of DMF. This was stirred overnight at 120 °C and the contents were centrifuged again. Three additional

MeOH washes were conducted prior to combining the solids with 300 mL of MeOH and stirring the suspension overnight under reflux conditions. After a final centrifugation, the purified MIL-101 was dried in air at 60 °C (Heratherm™ Oven, Fisher Scientific) for several hours before transfer to a vacuum oven set to 120 °C overnight (Vacutherm™ vacuum oven, ThermoFisher Scientific™). Finally, the dried product was stored in a desiccator.

3.3.1.2 *Crosslinked Polyimide Support Membranes*

Polyimide (P84, HP Polymer GmbH) was dissolved in DMF in an 11:39 mass ratio using a conventional stir plate at room temperature. After stirring for 8 hours, the solution was left still overnight to degas. The resulting dope had a viscosity of 2,400 cP. Membranes were cast on a continuous casting machine using a polypropylene nonwoven support (Novatex 2471, Freudenberg), 11 % tension, 15 rpm, 200 µm blade height and a 25 °C DI water bath temperature. The room's relative humidity was ~40 %.

After casting, the membranes were soaked in DI water three times for one hour each. The membranes were then transferred to three separate IPA baths (IPA, 2-Propanol, GPR Rectapur®, VWR), each being at least two hours long. Finally, the membranes were crosslinked at room temperature by soaking them in 120 g·L⁻¹ 1,6-hexanediamine (>99.5 %, Acros Organics) for 16 hours, per previous protocols [32]. These membranes were washed with IPA three times again. The final supports were stored in IPA.

3.3.1.3 *Thin Film Composite and Thin Film Nanocomposite Membrane Synthesis*

To form the TFC membrane, the membrane support was soaked in DI water overnight prior to the day of the experiment. The support was then submerged into an aqueous 2 % (w/v) MPD solution (Flakes, 99 %, Sigma-Aldrich®) for 15 minutes. MPD was purified via sublimation at $\sim 1 \times 10^{-2}$ mbar and 75 °C prior to solution preparation since IP is significantly affected by impurities [36,37]. An ice-chilled water trap was used each time. The membrane was placed on a custom frame and gasket rig, similar to that reported previously [48]. Excess MPD solution was removed using a rubber plate roller (VWR). After closing the frame's gasket, a HX (AnalaR NormaPur®, VWR) solution with 0.10 % (w/v) TMC (ReagentPlus®, 99 %, Sigma-Aldrich) was poured onto the membrane's surface and left to sit still for 60 seconds. Note that different concentrations of TMC were used for the reactive monomer adsorption study and are labelled appropriately in the Results and Discussion. After the reaction, the solution was promptly poured off and rinsed with HX to quench the reaction. The membrane was air dried for 30 seconds prior to submersion in DI water, where it remained until performance characterisation.

TFN membranes were made similarly to TFC membranes with the exception that the organic phase was prepared to have 0.05 – 0.25 % of MIL-101. The MIL-101 was dried in a vacuum

oven at 120 °C overnight. Dry nitrogen was used to return the vacuum oven to ambient pressure. The MIL-101 was allowed to cool under dry, flowing nitrogen for about 30 minutes. Then, it was weighed and submerged in a pre-measured volume of solvent. Weighing MIL-101 dry in this way insures accurate measurements because it can have significantly different water uptake at different humidities. It also provides greater reproducibility because any water in the organic phase could lead to TMC hydrolysis. The suspension was sonicated at 37 hz, 100 % power and 20 – 30 °C for 60 minutes under pulse mode (Elmasonic P, Elma). The samples were left to stir overnight. In the morning, the samples were sonicated under the same conditions for a second time and allowed to cool for 2 hours under stirring before adding the TMC. The samples were finally allowed to rest an additional 2 hours under stirring prior to membrane synthesis, allowing the ultimate TMC concentration to come into equilibrium prior to IP.

Membranes were activated with DMF using two techniques. The first was to soak the membranes in DMF for 65 minutes, rinsing with MeOH and then characterising their performance. The second was to filter DMF at 30 bar, 30 °C and 50 L·h⁻¹ crossflow in the crossflow rig. Residual DMF was carefully removed from the rig by washing three times with MeOH prior to measurements being taken.

3.3.2 MIL-101 Characterisation

3.3.2.1 Physicochemical Characterisation

Powder X-Ray Diffraction (XRD) was performed using Cu- α radiation and a Ni filter at 40 kV and 40 mA (X'Pert Pro XRD, PANalytical). Prior to nitrogen sorption, MIL-101 was first degassed for 4 hours at 120 °C in the vacuum oven and then degassed overnight at 120 °C under vacuum (VacPrep 061 Sample Degas System, Micromeritics). An additional five hour *in situ* degas was performed as well, at 120 °C under vacuum. Nitrogen gas adsorption measurements were conducted at 77.4 K (3Flex Surface Characterisation System, Micromeritics®) and BET analysis was used to characterise sample surface area [123]. Similarly, MIL-101 samples were degassed prior to thermogravimetric analysis (TGA) by placing them in a vacuum oven at 120 °C overnight. The vacuum oven was flushed with dry nitrogen so that the samples could be transported under dry nitrogen to the instrument for analysis. Measurable inconsistencies in the TGA residuals were observed if this step was not undertaken. TGA was performed by heating MIL-101 from 25 to 900 °C at 10 °C·m⁻¹ (TG209F1 Libra®, Netzsch), using air and nitrogen flow rates of 96 and 33 cm³ (STP)·m⁻¹, respectively. Finally, for SEM imaging, MIL-101 powder was dip coated from dilute MeOH suspensions onto a glass slide and mounted to sample stubs using carbon tape. Samples were coated with 15 nm of chromium at 120 mA (Q150T S Plus, Quorum Technologies) and imaged at 10 kV (LEO 1525, Karl Zeiss).

3.3.2.2 Trimesoyl Chloride Adsorption Study

MIL-101 was suspended at 0.10 % (w/v) in the same manner as that used for membrane synthesis in a 50 mL solution of HX. These solutions were allowed to cool to room temperature prior to the addition of TMC by micropipette (VWR Signature™ Pipette, VWR). These solutions were stirred gently throughout the adsorption process. Samples were taken at various time intervals using a syringe (Luer-Lok™ 1 mL Syringe, BD), reusable filter housing (Swinnex Filter Holder, 25 mm, SX0002500, Millipore) and 0.45 µm Teflon filter (Omnipore Membrane Filter, 0.45 µm, 25 mm, JHWP02500, Millipore). After volumetric dilution, quartz cuvettes (Quartz SUPRASIL® High Precision Cell, 10 mm light path, Hellma Analytics) were used to measure the concentration of TMC in HX using UV-visible spectrophotometry (UV-1800 UV Spectrophotometer, Shimadzu).

3.3.3 Membrane Characterisation

SEM images of membrane samples were taken to assess their morphology. Samples were attached to sample stubs using carbon tape. The same coating technique and imaging parameters as those used for MIL-101 were used on membrane samples as well.

Membrane performance was evaluated in a crossflow membrane testing rig detailed in previous work [96,97]. All experiments were performed in quadruplicate at 30 °C, 30 bar and 50 L·h⁻¹ crossflow. Reported data is taken at steady state, which is defined as 48 ± 1 hours. At this time, all membranes experienced a change in permeance of less than one standard deviation over the course of 24 hours.

Solvent flux measurements were taken with Act (Technical Grade, VWR) and MeOH containing either dye or polystyrene. *N*-Ethyl-*N*-(2-hydroxyethyl)-4-(4-nitrophenylazo)aniline (DR, Disperse Red 1, 95 %, Aldrich) was added to the rig in concentrations of 20 mg·mL⁻¹ for the assessment of rejection in MeOH. DR concentration was measured using a UV-visible spectrophotometer with PS cuvettes (PS Semi-Micro Disposable Cuvettes, BRAND GMBH + CO KG). The highest point of absorption was 482 nm and a simple one-point calibration was used to calculate concentrations as the dye's absorbance adheres to the Beer-Lambert law. PS rejection was measured similarly to that presented in previous work [98]. 0.5 g·L⁻¹ of each 580 and 1000 g·mol⁻¹ of PS (PS580 and PS1000, Agilent Technologies) as well as 0.01 g·L⁻¹ of α -methylstyrene dimer (2,4-diphenyl-4-methyl-1-pentene, 97 %, Sigma-Aldrich®) were added to Act or MeOH for crossflow filtration experiments. The rejection of these PS polymers was determined via high pressure liquid chromatography (HPLC, Agilent Series 1200, Agilent Technologies) using a UV-Visible detector set to 264 nm and a C18 column (ACE 5 C18-300, Hichrom Limited). Isocratic elution was used with a volumetric ratio of 20:80 MeOH:tetrahydrofuran (HiPerSolv Chromanorm®, VWR). Both solvents had 0.1 % (v/v)

trifluoroacetic acid (99 %, ReagentPlus®, Sigma-Aldrich). All permeate samples were concentrated by a factor of 10 prior to analysis by collecting 10 mL of permeate in a vial, evaporating it overnight in ambient conditions and re-suspending the PS in 1 mL of Act. Note that rejection calculations were accomplished by assuming a linear response between the UV signal and PS concentration. In this way, the rejection calculation can simply be made by replacing theoretical concentrations with the measured area corresponding to each PS oligomer.

3.4 Results and Discussion

3.4.1 Stochastic Performance of Activated Thin Film Composite Membranes

Establishing a consistent and quality control is critical to assessing whether or not a statistically significant change in performance can be attributed to some intervention. For the purposes of this work, a TFC membrane control is necessary to compare performance changes attributable to the introduction of MIL-101 into the IP process. Over 100 membranes were tested to examine different membrane fabrication and characterisation conditions to see whether they had a significant impact on batch to batch performance. While all these data and methods are not presented here, the most significant source of variation is: DMF activation.

DMF activation was conducted via filtration and immersion and the data is presented in **Table 2**. With either DMF activation method, the permeance increases by at least a factor of 5, while the rejection changes by a statistically insignificant amount. This fits well with previous data showing no change in rejection for neutral solutes [33,43]. However, this author is hesitant to generalise the finding with regards to rejection to all poly(*m*-phenylenediamine trimesamide) membranes. Indeed, it is possible that the polymeric supports used for this work are tighter and more prone to compaction than those used by researchers reporting rejection decreases [59]. It has been demonstrated that even low levels of resistance to solute permeability over defects can substantially enhance overall membrane selectivity [17]. Therefore, there is reason to believe that the right support membrane can mitigate solute passage. To be clear, with the current data available this is only speculation and there are a variety of other possibilities behind these discrepancies that could arise from differences in membrane fabrication or performance measurements.

While the overall trends of rejection and permeance seem explicable, it is difficult to determine precisely what causes the unpredictable magnitudes of change. Whether activated via filtration or immersion, TFC membranes had a range of permeances and rejections from 1.79

± 0.38 to $4.80 \pm 0.21 \text{ L}\cdot\text{m}^{-2}\text{h}^{-1}\text{bar}^{-1}$ and from 98.2 ± 0.4 to $94.1 \pm 0.3 \%$ (95 % CI, $n = 4$).¹ Each activation technique carried out on two separate days demonstrated up to 62.6 % difference on permeance and 2.3 % difference on rejection. Comparably, pristine TFC membranes demonstrated a less than 8.7 % difference in permeance and 1.3 % difference in rejection between 4 separate batches ($n = 16$). This proves that the methods used for this work are consistent, except for DMF activation. Unfortunately, many studies on DMF activation have not represented statistical error. Works that have measured variance show a 95% confidence interval of ~60 % of the mean for MeOH permeance [59] ($n = 3$ assumed) and a percent difference in water permeance of up to 91% [60]. The difference in solute rejection varied up to 32 % between membrane sets for some studies [60]. One can only speculate as to the reasons. It is possible that synthesising the membranes on different days led to different humidity conditions, which could ultimately affect the quantity and distribution of carboxylate-rich polyamide fragments. Alternatively, it is possible that the activation process is extremely sensitive to small changes in the membrane support. Moreover, if polymer swelling is a significant aspect of the phenomenon, it may be expected to have a large variation. While further investigation of this phenomenon is out of the scope of this work, it could be interesting to rigorously explore as the performance enhancements can be significant.

Table 2. Observed methanol (MeOH) permeance and disperse red (DR) rejection of thin film composite (TFC) membranes with and without *N,N*-dimethylformamide (DMF) activation.

Statements of error are based on 95 % confidence intervals ($n = 4$).¹

DMF Activation Procedure	Trial	MeOH Permeance ($\text{L}\cdot\text{m}^{-2}\text{h}^{-1}\text{bar}^{-1}$)	Observed DR Rejection (%)	MeOH Permeance Difference (%)	DR Rejection Difference (%)
30 Minute Filtration	1	2.51 ± 0.57	96.2 ± 0.5	62.6	2.2
	2	4.80 ± 0.21	94.1 ± 0.3		
65 Minute Bath	1	1.79 ± 0.38	98.2 ± 0.4	48.6	2.3
	2	2.94 ± 0.27	96.0 ± 0.2		
None	1	0.34 ± 0.02	96.8 ± 5.1	< 8.7	< 1.3
	2	0.36 ± 0.02	97.4 ± 3.1		
	3	0.33 ± 0.02	97.4 ± 4.2		
	4	0.35 ± 0.03	96.2 ± 3.3		

For the purposes of this work, these data demonstrated that using DMF activation would obfuscate the effects of TFN membrane made via IP. This is significant, as there are a number of TFN membrane studies that use DMF activation [75,76]. It is difficult to determine whether their claims of enhanced membrane performance are from filler inclusion or the stochastic

¹ Note that '95 % CI' stands for 95 % confidence interval and 'n' is the number of samples used to produce the average and confidence interval reported herein.

nature of DMF activation. Regardless, this process was avoided for the duration of this work so that the data reported could be more reliable.

3.4.2 MIL-101 Characterisation

MIL-101 was synthesised in water using a microwave-assisted method capable of reducing its particle size [177]. MIL-101 was first characterised with XRD to ensure it has the typical crystalline structure. These data are shown in red in **Figure 11A**, with a simulated XRD pattern in black. The samples synthesised for this work clearly demonstrate all of the typical peaks expected of MIL-101. The synthesised product also had a typical BET surface area of $2,900 \text{ m}^2\text{-g}^{-1}$ and the typical two-heel micropore adsorption [75,177], as shown in **Figure 11B**. The BET surface area is somewhat less than those achieved by traditional solvothermal syntheses [108], likely because of defects that occur during synthesis on such short timescales. **Figure 11C** shows that the batch demonstrated the common thermal decomposition of $\sim 350^\circ\text{C}$ in air, leaving a residual of 28.5 % by mass. Overall these data demonstrate that MIL-101 is highly porous and well activated. Finally, as shown in the SEM image in **Figure 11D**, the particle size is $\sim 100 \text{ nm}$, on the right order of magnitude for TFN membrane fabrication.

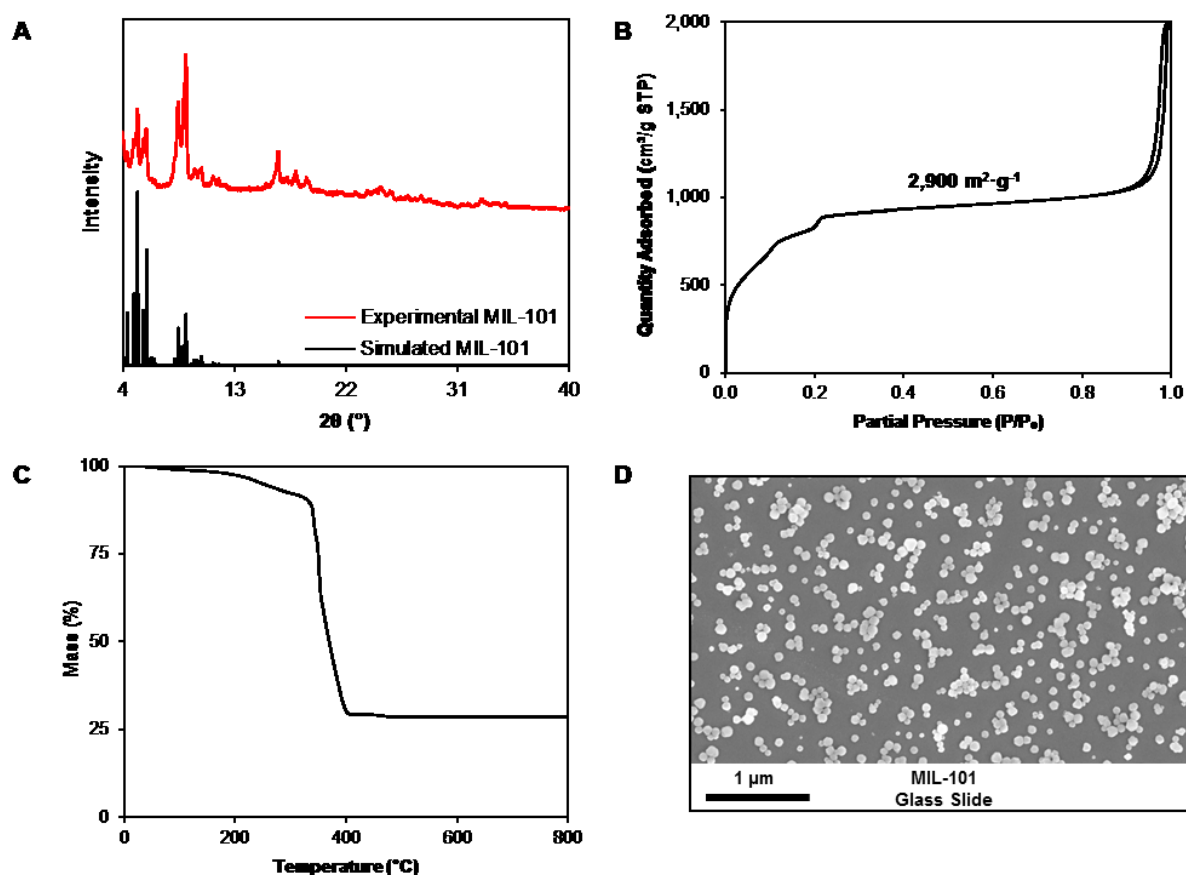


Figure 11. (A) X-Ray diffraction (XRD), (B) nitrogen adsorption, (C) thermogravimetric analysis (TGA) and (D) scanning electron microscopy (SEM) image of MIL-101.

3.4.3 Aggregation and Defect Formation in Thin Film Nanocomposite Membranes

TFN membranes were made via IP similarly to previous authors [75,76,78,175] by adding 0.10 – 0.40 % (w/v) of MIL-101 to the HX phase prior to IP. It was previously reported that defect-free membranes were made this way; however, these results could not be reproduced consistently herein. Indeed, many membranes looked as if their performance were affected by defects, as shown in **Figure 12**.

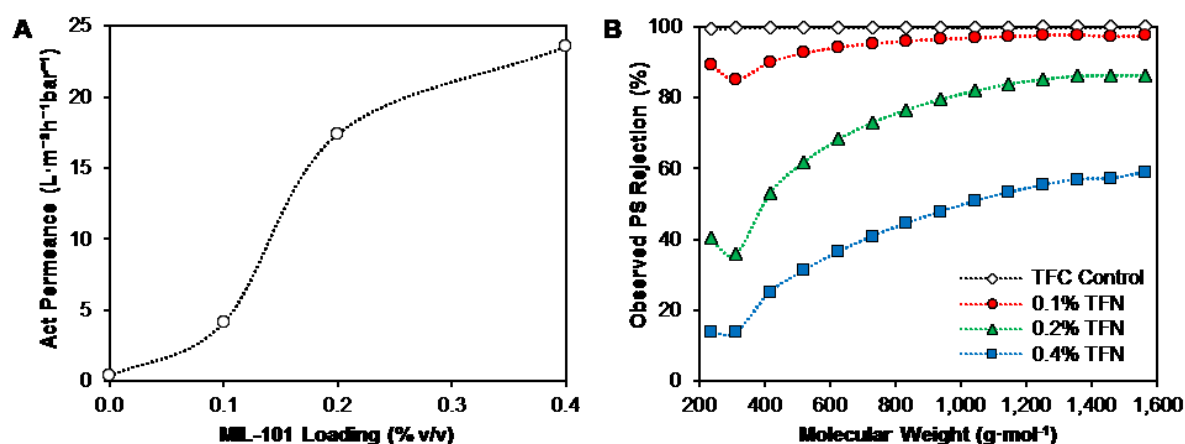


Figure 12. (A) Acetone (Act) permeance and (B) polystyrene (PS) rejection curves of thin film composite (TFC) membranes at various MIL-101 loadings, tested in duplicate.

The permeance increase shown in **Figure 12A** is clearly similar to that described by previous authors [75,76,78,175]; however, **Figure 12B** shows a significant decrease in rejection for all concentrations of MIL-101 studied. While the TFC membrane control demonstrates a greater than 99 % rejection for all PS oligomers, this high rejection is not observed even at molecular weights greater than 1,000 g·mol⁻¹ for any TFN membrane. Not achieving 100 % rejection at these molecular weights suggests the presence of significant membrane defects. The fact that increasing concentrations of MIL-101 in the HX phase correlates strongly with decreasing rejections implies that the aggregation of MIL-101 in the HX phase prior to IP leads to defects in the TFN membrane.

The presence of these aggregates in the film are clearly seen in SEM images, shown in **Figure 13**. Aggregates up to 10 μm in diameter are visible on the membranes' surfaces and are consistently present for all TFN membranes. When preparing the suspensions, MIL-101 actually deposits onto the glass vial if left undisturbed and settles rapidly, suggesting that the suspension is unstable. Thus, this is not entirely unexpected given the qualitative observations prior to IP. Interestingly, these SEM images show the typical leaf-like structure reported for poly(*m*-phenylenediamine trimesamide) TFC membranes [52,178], but show a much smoother polymer layer for TFN membranes. This was also observed by Sorribas et al. [75].

It has been observed that smoother membranes are formed at lower TMC concentrations for this IP system within these reactant ranges [45]. These observations inspired the exploration of the impact of reactive monomer adsorption on membrane performance detailed in the proceeding section.

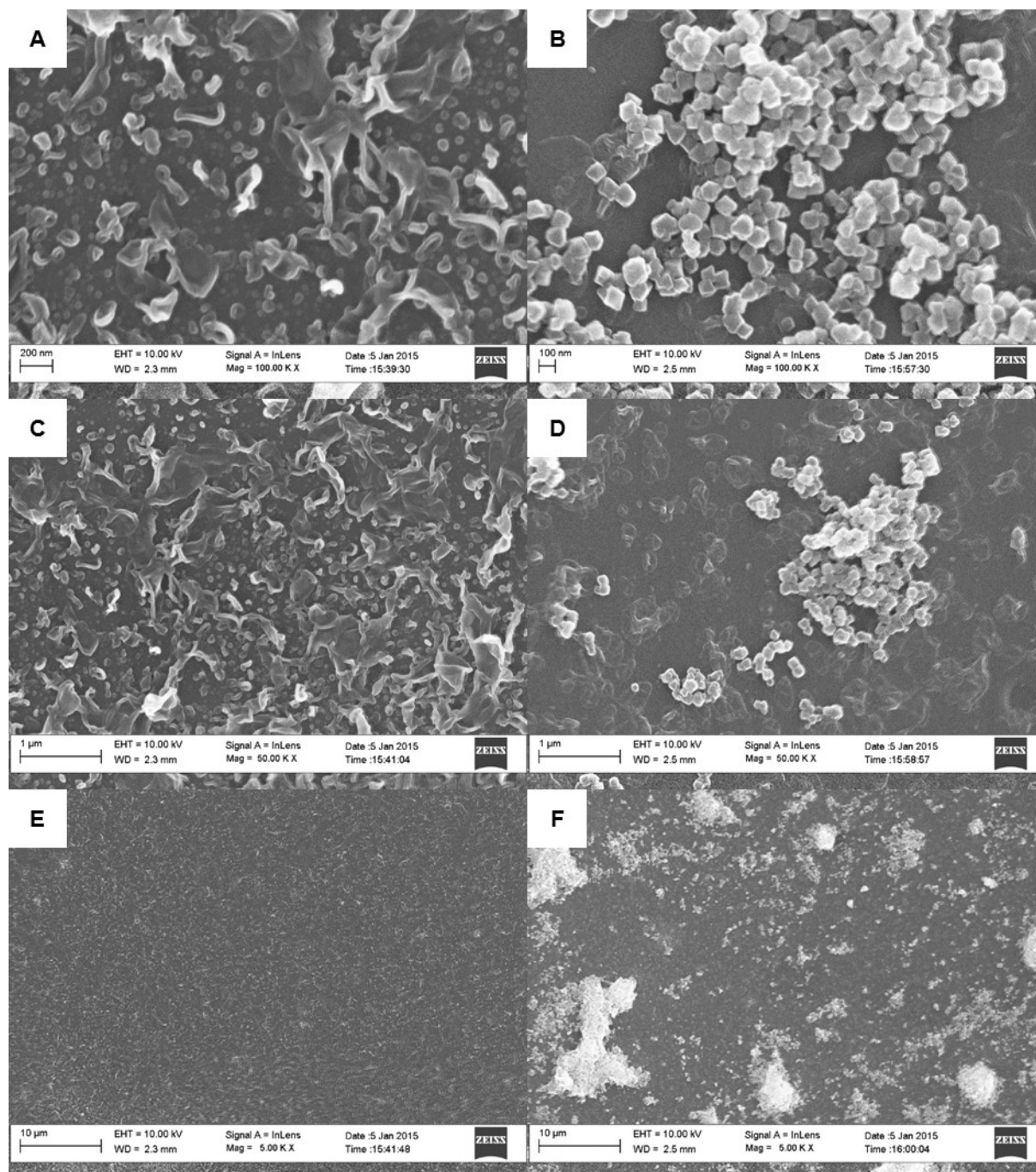


Figure 13. Scanning electron microscopy (SEM) images of (A, C and E) thin film composite (TFC) and (B, D and F) thin film nanocomposite (TFN) membranes, the latter of which was synthesised using 0.10 % (w/v) MIL-101 in the *n*-hexane (HX) phase.

It is difficult to reconcile the seemingly contradictory claims in the literature reviewed in the introduction. While one can only speculate, this could be explained by either subtle differences in membrane fabrication or experimental measurements. Regardless, one reasonable critique is that many works show error bars for one standard deviation of up to 5 [75], 8 [76] and 7 [175] %. These magnitudes of error make a difference between a rejection of 99.9 % and 95 % statistically meaningless, even though the consequences in real applications would be significant. Indeed, some authors only use two or three samples, suggesting that mean differences would have to exceed well beyond 10 % to provide statistically meaningful differences. In other words, real reductions in rejection may simply be unobservable due to the lack of consistency, sensitivity and/or repetition of measured rejection results.

To be critical of this work, the reduction in rejection is dramatic compared to some of the literature. In the author's MSc thesis, better and worse membranes were made this way [10], suggesting that the results of previous work may be possible, but also that this method of membrane formation is stochastic. Taking a broad look at the data presented as a part of this work and the data from literature, one could also conclude that MIL-101 aggregates in HX can introduce defects into membranes and that these defects could lead to a reduction in rejection. This suggests that controlling MIL-101 aggregation could enhance the consistency of TFN membrane formation and prevent non-selective defect formation.

3.4.4 Reactive Monomer Adsorption in Thin Film Nanocomposite Membranes

The purpose of this work was to investigate the quantity of TMC that MIL-101 is capable of adsorbing, the associated kinetics and the impact on TFN membrane performance. First, the kinetics must be established to determine approximate timing of equilibrium sampling. This was accomplished by suspending 0.10 % (w/v) MIL-101 in a 0.10 % TMC (w/v) HX solution and sampling over time. As shown in **Figure 14A**, the TMC adsorption approximately followed pseudo-second order kinetics [179], as described by the equation:

$$q_t = \frac{k_s q_e^2 t}{1 + k_s q_e t} \quad (23)$$

where q_t and q_e are the quantities of TMC adsorbed per quantity of MIL-101 at time t and equilibrium, respectively and k_s is a constant. The equilibrium concentration, as calculated by performing a linear regression on $\frac{q_t}{t}$ versus t ($R^2 > 0.999$), was found to be 0.41 g TMC·g⁻¹ MIL-101. This concentration was achieved at 120 minutes.

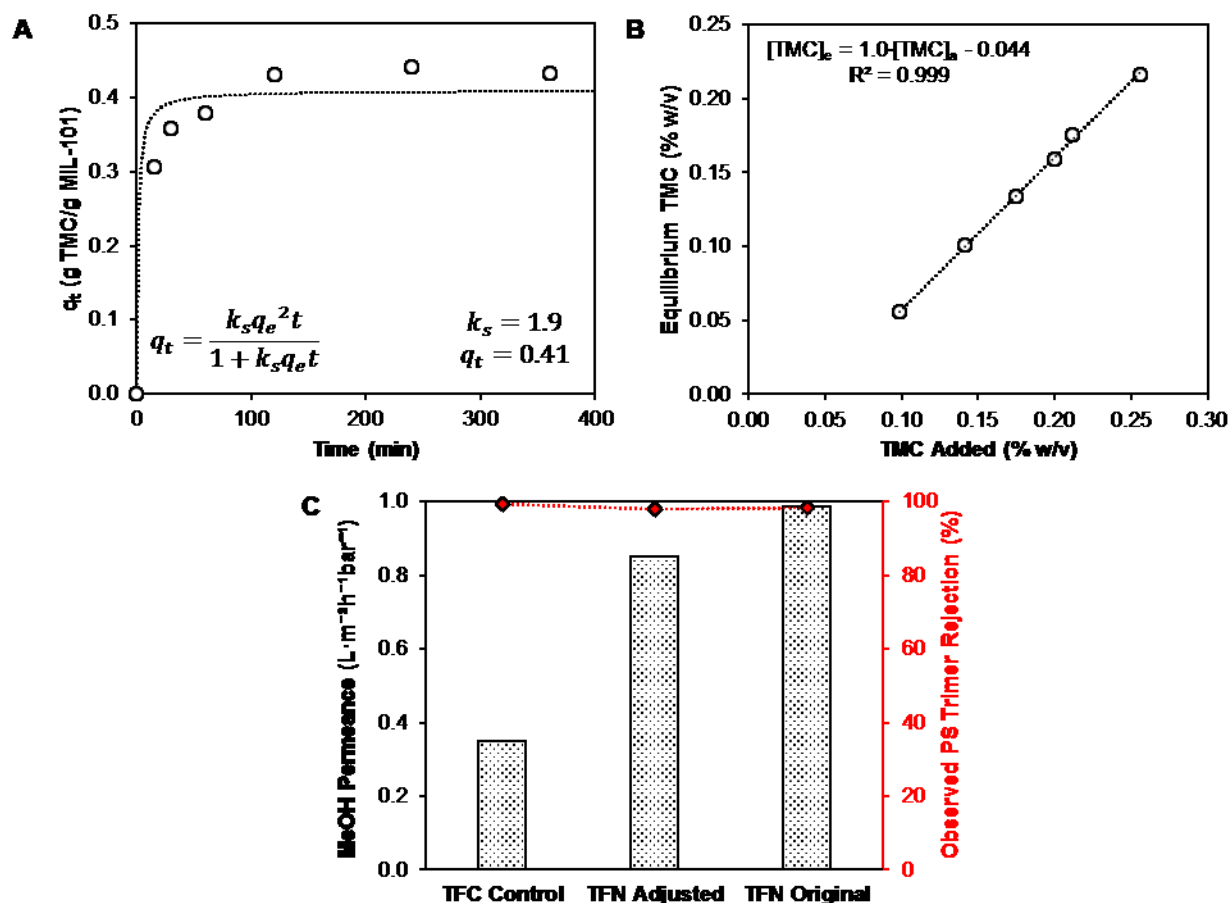


Figure 14. (A) Adsorption kinetics of 0.10 % (w/v) trimesoyl chloride (TMC) and MIL-101 in *n*-hexane (HX). (B) Equilibrium TMC concentrations of HX solutions containing 0.10 % (w/v) MIL-101. (C) Observed methanol (MeOH) permeance and polystyrene (PS) trimer rejection of thin film composite (TFC) and thin film nanocomposite (TFN) membranes. TFN membranes were synthesised with 0.10 % (w/v) of MIL-101 in the HX phase. The adjusted TFN membrane had an equilibrium TMC concentration of 0.10 % (w/v). The original TFN membrane had an initial TMC concentration of 0.10 % (w/v).

After equilibrium kinetics were established, solutions of 0.10 % (w/v) MIL-101 in HX with various TMC concentrations were sampled after 240 minutes of stirring. The resulting data, presented in **Figure 14B**, shows a linear increase of equilibrium TMC concentration with increasing quantity of TMC added at the beginning. This means that MIL-101's adsorption sites were saturated with TMC across the entire range measured. Hence, the slope of the line is unity and the x-intercept is 0.04 g TMC, implying that MIL-101 adsorbs ~ 0.4 g TMC $\cdot$ g $^{-1}$ MIL-101. If each of these data points are taken to create an average equilibrium adsorption, that value would be 0.40 ± 0.02 (95 % CI, $n = 7$). This suggests that the equilibrium adsorption calculated from fitting the pseudo-second order model to the kinetic data in **Figure 14A** is within experimental error. This adsorption capacity is also equivalent to 1.5 mmol $\cdot$ g $^{-1}$ MIL-101,

or 51 % of MIL-101's total coordinatively unsaturated sites (CUS). Considering that pseudo-second order adsorption kinetics are applicable to coordination between metals and ligands [179], the mechanism of adsorption for TMC on MIL-101 may be the coordination of the oxygen on the carbonyl group of TMC with the CUSs on MIL-101. However, this is highly speculative and would require spectroscopic analysis for confirmation, which is out of the scope of this study. Moreover, reactive adsorption cannot be ruled out from these data. There may be dangling carboxylate groups in certain areas of MIL-101, which could react with TMC.

With the adsorption kinetics and equilibria established, it is possible to actually measure the effect of TMC adsorption on membrane performance. Typically, the adsorption of TMC onto the filler is ignored. Therefore, one can create a 'TFN Original' membrane where 0.10 % (w/v) TMC is added in the HX solution with 0.10 % (w/v) MIL-101. The equilibrium TMC concentration of this sample should be 0.06 % (w/v) TMC. Then, a 'TFN Adjusted' membrane can be made where 0.14 % (w/v) of TMC is added into the HX solution with 0.10 % (w/v) MIL-101. The ultimate TMC concentration at equilibrium should be 0.10 % (w/v), which is the same as the 'TFC Control' membrane. The performance data of these membranes are presented in **Figure 14C**.

TMC adsorption does seem to have a significant effect on the ultimate membrane performance. Instead of making it worse for this system, the TMC adsorption seems to actually enhance membrane permeance. The 'TFN Original' membrane had a 180 % increase in permeance, while the 'TFN Adjusted' membrane only had a 140 % increase. That means about one fifth of the membrane performance improvement can be attributed to a reduction in TMC that leads to more optimal IP conditions. This could be more important for certain TFN membrane fabrication systems, particularly those using as much as 0.40 % (w/v) of MIL-101 [75]. Indeed, this is a worthwhile check for any TFN membrane fabrication system that has the potential to adsorb significant quantities of TMC as it is possible to separate out the effects of filler inclusion and reactive monomer adsorption. Additionally, depending on the degree of TMC adsorption, controlling for this effect could help maintain optimal TMC concentrations.

A comparison of these membrane performance data and the TFN membrane set formed in the previous section is useful. In **Figure 14C**, the PS trimer rejection does slightly decrease, by ~1 %, for both of the TFN membranes relative to the TFC membrane control. This is less than the observed 15 % decrease in Act under similar conditions in **Figure 12B**. The TFC membrane controls for each data set show similar PS trimer rejection, both greater than 99 %. The similarity in TFC membrane performance and discrepancy in TFN membrane performance reflects the inconsistency associated with this method of TFN membrane

fabrication, discussed in the previous section. It is not possible to rule out possible contributions from differences in the solvent used, however.

3.5 Conclusions and Future Work

This work identified issues with analysing the performance of TFN membranes made via IP. One concern is that of the TFC membrane control. DMF activation was shown to be a key source of error and was avoided for the fabrication of TFN membranes. Even though it was relatively easy to synthesise nano-sized MIL-101 reliably with comparable properties to samples in literature, its use in TFN membrane fabrication proved more difficult. Filler aggregation was an unequivocal issue, causing inconsistent performance and large decreases in rejection due to non-selective defect formation. Adsorption studies of MIL-101 indicated that a significant quantity of TMC was adsorbed in HX solutions. This TMC adsorption could be adequately controlled during membrane fabrication. The resulting characterisation of these membranes revealed that TMC adsorption had a significant effect on the ultimate membrane performance. This work made it apparent that any further investigation into TFN membrane formation, whether focused on the primary or secondary effects of fillers, was contingent on properly controlling filler dispersibility since aggregation resulted in the largest changes in membrane performance. The following two chapters, therefore, closely investigate strategies for achieving high-quality dispersions of MIL-101.

4 The Dispersion and DLVO Theory of a Metal-Organic Framework

4.1 Abstract

Metal-organic frameworks (MOFs) have enormous potential in applications such as drug delivery, catalysis and separation [115], but to actualise this potential, researchers must be able to control particle suspensions either during application or device fabrication. Thin film nanocomposite (TFN) membranes, the focus of this work, is but one example, where the state of dispersion and particle settling can significantly affect key membrane performance metrics [29]. Successes have been achieved via trial and error, but a more fundamental approach could accelerate the growth of this field. To those ends, uniform, sub-micrometre films of MIL-101 nanoparticles were produced via dip coating, achieving hierarchical porosity and a void fraction as high as 90 %. These films were characterised with environmental ellipsometric porosimetry (EEP) and spectroscopic ellipsometry (SE) to determine the Hamaker constant of a MOF for the first time. These data were combined with other colloidal characterisation data to relate Derjaguin, Landau, Verwey and Overbeek (DLVO) theory to the suspension properties of MIL-101 in nine solvents. Solvents' dielectric constants strongly determined the suspension properties of MIL-101, though it also seems that DLVO theory cannot entirely describe the suspension of MIL-101 in certain solvents. These data support the observed aggregation phenomena in the previous chapter. Additionally, this approach enables the prediction of the colloidal properties of MIL-101 suspensions based on readily available spectral data of solvents. The implication for TFN membrane fabrication is that there could be a contradiction between the optimal solvent properties for colloidal suspension, namely a high dielectric constant, versus the optimal solvent properties for interfacial polymerisation (IP), namely a high octanol-water partition coefficient.

4.2 Introduction

The desire to create MOFs with record-breaking material properties such as porosity, surface area and ion conductivity has led scientists to master the molecular behaviour of metal clusters and organic ligands, enabling the formation of multidimensional, well-defined structures [115,180]. Now, to fully leverage the potential of MOFs in major applications, scientists must master their colloidal behaviour and surface properties so as to direct their liquid-phase behaviour, which is critical to the fabrication of functional devices.

In the case of liquid-phase adsorption, catalysis and/or drug delivery this is integral to the application itself. For instance, in drug delivery applications, surface properties and dispersion play a critical role in affecting where particles travel to in the body [181]. The efficacy of catalysis and adsorption devices also depends heavily on interfacial phenomenon of constituent MOF particles [149,150].

Most possible MOF applications require the formation of some type of monolith or composite material. Some examples of applications which require a monolith include depositing thin films of MOF particles for optical devices, conductors, or chemical sensors. Alternatively, monoliths and composite materials are also used for catalysis, gas storage and separation. An interesting example of this is in membrane science, where mixed matrix membranes based on MOFs often demonstrate non-selective defects formed by MOF aggregation. Moreover, even where this issue can be overcome, MOF-polymer interactions must be considered to achieve optimal separation performance [119,120]. Hence, the colloidal phenomena of MOF particles during membrane formation can wholly determine the ultimate device performance.

While there is an abundance of articles exploring applications of colloidal MOFs, there have been relatively few articles dedicated to the colloidal properties of MOFs. The majority of these works have been dedicated to modifying the surfaces of MOF particles with phosphates [153–155,182], polymers [156–160] and silica [161]. These compounds are either covalently attached to coordinatively unsaturated sites (CUSs) or attached by van der Waals forces in order to direct colloidal behaviour in select environments. Some researchers investigating MOF modification have even been able to implement their findings to demonstrate self-assembly, while others have done so without modification [132,133,162,163]. Finally, the effect of pH [164] or linkers [165] on the colloidal properties of select MOFs has also been explored, finding that both can play a significant role in aggregation and disaggregation.

While the importance of interparticle forces on the observed colloidal behaviour is recognised by the community, the author is unaware of any work to date which explores and quantifies the fundamental surface property parameters of MOF particles. This has led many researchers to rely on a trial and error approach to formulate colloidal suspensions and create monoliths

for various applications. While impressive successes have been achieved, a faster, more effective approach based on the fundamentals of colloid and interface science would be of great utility to this now large body of research.

In this work the author addresses this knowledge gap by applying DLVO theory to a MOF for the first time. The widely reported MIL-101 was chosen for initial study as an analogue for carboxylate MOFs, because similar MOFs demonstrate high porosity and hydrolytic stability [108] and it is the target of study for this thesis. According to DLVO theory, MIL-101 should suspend well in high dielectric constant solvents and poorly in low dielectric constant solvents.

To apply DLVO theory, the complex dielectric function of MIL-101 must be determined. A combination of EEP and SE could be a unique solution to measuring the dielectric properties of highly porous nanoparticles. SE is typically used for measuring optical properties in the UV-visible light range [168] and EEP has been used to evaluate the porosity of MOF films [129–133]. Since these measurements can be taken on the same instrument, it is possible that the film's porosity and complex dielectric function can be taken simultaneously, enabling the isolation of the dielectric properties of the nanoparticle through an effective medium model.

4.3 Background

This work focuses on the application of DLVO theory, which was described in Section 1.4.4. To summarise, this theory states that there is a balance of electric double layer repulsive forces and van der Waals attractive forces that create an energy barrier that prevents particles in a colloidal solution from aggregating. The larger this energy barrier, the greater the solution stability. As van der Waals attractive forces dominate, or in situations where there are smaller electric double layer repulsive forces, the energy barrier decreases in magnitude or is even eliminated entirely. The result is unstable colloidal suspensions whose particles rapidly aggregate [166]. To quantify the electric double layer repulsive forces, one must know the solvent's dielectric constant, ionic strength and temperature as well as the particle's radius and zeta potential. The rest of the terms are fundamental constants. Temperature and ionic strength are controlled variables; the solvent's dielectric constant can be found in the literature; and the particle radius and zeta potential must be measured. To quantify the van der Waals attractive forces, one must determine the Hamaker constant. This requires further theory to quantify.

There are a number of articles and review papers detailing the calculation of various forms of the Hamaker constant using different data sources and models [168,183]. For the purposes of this study, a simple form of the Nijmegen-Parsegian representation was chosen because it has given good estimations for inorganic materials when there is access to limited data sets.

In that representation, an imaginary dielectric response function with no physical significance is used for mathematical convenience:

$$\varepsilon(i\xi_n) = 1 + \frac{C_{UV}}{1 + (\xi/\omega_{UV})^2} + \frac{C_{IR}}{1 + (\xi/\omega_{IR})^2} \quad (24)$$

where $\varepsilon(i\xi_n)$ is the complex dielectric function, C_{UV} and C_{IR} are the absorption strengths in the ultraviolet (UV) and infrared (IR) range, ω_{UV} and ω_{IR} are the characteristic absorption frequencies ($\text{rad}\cdot\text{s}^{-1}$) in the ultraviolet (UV) and infrared (IR) range and $i\xi_n$ are the discrete, imaginary frequencies at which the function is evaluated, as defined by:

$$\xi_n = w \left(\frac{2\pi k_B T}{h} \right) \quad (25)$$

where h is the Planck constant ($\text{J}\cdot\text{s}$), k_B is the Boltzmann constant ($\text{J}\cdot\text{K}^{-1}$), T is temperature (K) and m are integers greater than or equal to zero. This relatively simplistic spectral representation has been demonstrated to work effectively for a variety of inorganic materials, with the main qualification being that there are low absorption strengths in the UV and IR ranges [168]. Since MOFs have large void fractions, one would predict that the imaginary dielectric response function is strongly hybridised with that of the solvent, thus muting any effects the MOF spectral data would have on the final Hamaker constant calculation. This could be quantified through the Clausius-Mosotti representation, which is equivalent to the Ninham-Parsegian representation [183] and can be used to show that:

$$\frac{\varepsilon_{MS}(i\xi_n) - 1}{\varepsilon_{MS}(i\xi_n) + 2} = \varepsilon_M \left(\frac{\varepsilon_M(i\xi_n) - 1}{\varepsilon_M(i\xi_n) + 2} \right) + (1 - \varepsilon_M) \left(\frac{\varepsilon_S(i\xi_n) - 1}{\varepsilon_S(i\xi_n) + 2} \right) \quad (26)$$

where ε_M is the void fraction within the MOF that would be filled with solvent and $\varepsilon_{MS}(i\xi_n)$, $\varepsilon_M(i\xi_n)$, $\varepsilon_S(i\xi_n)$ are the complex dielectric response functions of the MOF filled with solvent, MOF skeletal structure and pure solvent, respectively. One can calculate the non-retarded Hamaker constant of the solvent-filled MOF body in a variety of solvents ($A_{MS/S}$) using the expression derived by Lifshitz:

$$A_{MS/S} = \frac{3k_B T}{2} \sum_{n=0}^{\infty} \sum_{s=1}^{\infty} \frac{\Delta_{MS/S}^{2s}}{s^3} \quad (27)$$

where $\Delta_{MS/S}$ is the difference in dielectric response, as defined by:

$$\Delta_{MS/S} = \frac{\varepsilon_{MS}(i\xi_n) - \varepsilon_S(i\xi_n)}{\varepsilon_{MS}(i\xi_n) + \varepsilon_S(i\xi_n)} \quad (28)$$

Note that it has been shown that accurate non-retarded Hamaker constants can be calculated by using the summation of s from 1 to 4 and of n from 0 to 4000, giving the 0th term half weight [168]. In most situations, adding extra terms changes only non-significant figures.

The only data needed to complete this representation are the spectral parameters of solvents and of the MOFs of choice. Most of the solvent data can be readily found in the literature. Exceptionally, the following representation was used for water [168,184,185]:

$$\varepsilon(i\xi_n) = 1 + \frac{B}{1 + \xi\tau_{MW}} + \sum_{j=1}^N \frac{C_j}{1 + (\xi/\omega_j)^2 + g_j\xi/\omega_j^2} \quad (29)$$

where $B = 76.8$ and $\frac{1}{\tau_{MW}} = 1.08 \times 10^{11} \text{ rad}\cdot\text{s}^{-1}$ and the duration of the parameters are defined in **Table 3**.

Table 3. Parameters for the complex dielectric function of water [168,184,185].

C_{UV}	ω_{UV} (rad/s)	g_{UV} (rad/s)	C_{IR}	ω_{IR} (rad/s)	g_{IR} (rad/s)
0.0484	$1.25 \cdot 10^{16}$	$9.57 \cdot 10^{14}$	1.46	$3.14 \cdot 10^{13}$	$2.29 \cdot 10^{13}$
0.0387	$1.52 \cdot 10^{16}$	$1.28 \cdot 10^{15}$	0.737	$1.05 \cdot 10^{14}$	$5.78 \cdot 10^{13}$
0.0923	$1.73 \cdot 10^{16}$	$3.11 \cdot 10^{15}$	0.152	$1.40 \cdot 10^{14}$	$4.22 \cdot 10^{13}$
0.3440	$2.07 \cdot 10^{16}$	$5.92 \cdot 10^{15}$	0.0136	$3.06 \cdot 10^{14}$	$3.81 \cdot 10^{13}$
0.3600	$2.70 \cdot 10^{16}$	$1.11 \cdot 10^{16}$	0.0751	$6.46 \cdot 10^{14}$	$8.54 \cdot 10^{13}$
0.0383	$3.83 \cdot 10^{16}$	$8.11 \cdot 10^{15}$	-	-	-

Finally, one must measure and model the complex dielectric function of the MOF to determine its spectral parameters, conduct these calculations and quantify the Hamaker constant. If the MOF has a relatively low dielectric constant and, therefore, relatively low absorption in the IR region then it is possible to do so by obtaining the complex dielectric function using SE. The details for this experiment are in the proceeding Methods section.

4.4 Methods

4.4.1 MIL-101 Powder

MIL-101 was synthesised in the same manor used in Chapter 3. Nitrogen sorption, X-ray diffraction (XRD) and thermogravimetric analysis (TGA) were performed to confirm that the textural properties, crystallinity and thermal decomposition were suitable and consistent with the previous sample. These samples were also characterised via dynamic vapour sorption (DVS) at 25 °C (DVS Vacuum, Surface Measurement Systems). Prior to this measurement, the samples were degassed overnight at 120 °C in a vacuum oven and cooled under flowing dry nitrogen. These samples were then degassed *in situ* for 2 hours at 120 °C under vacuum.

4.4.2 MIL-101 Colloidal Suspensions

4.4.2.1 Preparation

MIL-101 was first dried at 120 °C in a vacuum oven, cooled under dry flowing nitrogen and weighed. Then, the appropriate amount of solvent was added. The solvents used for these

experiments were DI water, methanol (MeOH, AnalaR Normapur®, VWR), *N,N*-dimethylformamide (DMF, AnalaR Normapur®, VWR), *n*-butanol (BuOH, AnalaR Normapur®, VWR), *n*-decanol (DeOH, 99%, Aldrich Chemicals), *n*-hexane (Hex, AnalaR Normapur®, VWR), dichloromethane (DCM, GPR Rectapur®, VWR), ethyl acetate (EA, GPR Rectapur®, VWR) and acetone (Act, GPR Rectapur®, VWR). To achieve suspension, the solutions were sonicated in pulse mode for 60 minutes at 37 kHz, 100% power at 20 – 30 °C (Elmasonic P, Elma) and left to stir overnight. After ~16 hours, the samples were freshly sonicated under the same conditions and left to stir for one hour before analysis. All suspensions were created in this manner to determine the zeta potential, critical point of aggregation and static permittivity of MIL-101, as detailed in the colloidal characterisation section below.

4.4.2.2 Critical Point of Aggregation

The critical point of aggregation was assessed using UV-visible spectrophotometry (UV-1800 UV Spectrophotometer, Shimadzu). Suspensions between 10 and 3000 ppmv of MIL-101 were prepared and the absorbance was measured as a function of wavelength (375 – 525 nm) in quartz cuvettes (Quartz SUPRASIL® High Precision Cell, 10 mm light path, Hellma Analytics). The method of analysis is based on that developed by Heller et al. [186–190]. They found that specific absorbances (A/C) of dilute colloidal solutions are a function of wavelength (λ):

$$\frac{A}{C} = m\lambda^{-z} \quad (30)$$

where m is a constant that is a function of particle size and relative refractive index and z is the wavelength exponent. The wavelength exponent of a suspension can be estimated as the slope of a log-log plot of specific absorbance versus wavelength, since the above equation can be manipulated to show:

$$z = -\left(\frac{d\log(A/C)}{d\log(\lambda)}\right) + \left(\frac{d\log(m)}{d\log(\lambda)}\right) \quad (31)$$

Note that m is constant over small wavelength ranges, like those used in this work, so the second term is effectively equivalent to zero. While this technique has become less common, it is still a sensitive technique for assessing particle aggregation. As shown in **Figure 15**, the wavelength exponent should remain constant for well-dispersed particles and decrease with increasing aggregate size. The point of interception between the constant wavelength exponent region and decreasing wavelength exponent region is considered the critical point of aggregation.

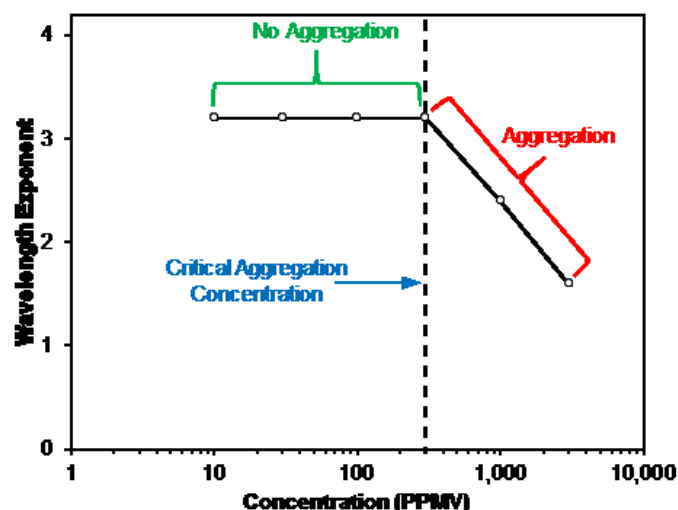


Figure 15. Illustration of how to determine the critical point of aggregation based on the wavelength exponent.

4.4.2.3 Zeta Potential and pH

Zeta potential measurements were carried out on 300 ppmv suspensions of MIL-101 in select solvents at 25 °C using the Smoluchowski model [191] for analysis (PALS Zeta Potential Analyser, BI-SERL Electrode Assembly, BI-SCGO Glass Cuvettes, Brookhaven Instruments Corporation). The pH of select 300 ppmv MIL-101 suspensions were determined (inoLab pH 7310, SenTix™ 81, WTW) after a fresh, three point calibration using factory standards. The suspension was stirred throughout and the measurement was recorded after at least 5 minutes of observing a stable pH value. Of course, zeta potential measurements require knowledge of certain solvent properties. These are listed in **Table 4** along with some other properties important to this study.

Table 4. Solvent properties [192,193] and spectral parameters [194] used for this work.

Solvent	Dielectric Constant	Specific Gravity	Refractive Index	Viscosity (cP)	C_{UV}	ω_{UV} (rad·s ⁻¹)	C_{IR}	ω_{IR} (rad·s ⁻¹)
Act	20.56	0.784	1.355	0.3029	0.8199	$1.82 \cdot 10^{16}$	-	$3.23 \cdot 10^{14}$
BuOH	17.8	0.806	1.397	3.006	0.9306	$1.88 \cdot 10^{16}$	-	$5.58 \cdot 10^{14}$
DCM	9.1	1.326	1.424	0.4043	0.9938	$1.81 \cdot 10^{16}$	-	$1.39 \cdot 10^{14}$
DeOH	8.1	0.8297	1.439	11.32	-	-	-	-
DMF	37.2	0.95	1.428	0.802	1.0029	$1.62 \cdot 10^{16}$	-	$3.16 \cdot 10^{14}$
EA	6.02	0.895	1.370	0.426	0.8592	$1.92 \cdot 10^{16}$	-	$3.28 \cdot 10^{14}$
Hex	1.88	0.655	1.375	0.294	0.8662	$1.88 \cdot 10^{16}$	0.0238	$5.57 \cdot 10^{14}$
MeOH	32.66	0.786	1.326	0.59	0.7448	$1.91 \cdot 10^{16}$	3.955	$3.52 \cdot 10^{14}$
Water	81	1	1.333	0.89	-	-	-	-

4.4.2.4 Dielectric Constant

Static permittivities of MIL-101 suspensions between 0 and 10% v/v were measured at 21.9 ± 0.2 °C (BI-870 Dielectric Constant Meter, Brookhaven Instruments Corporation). Between

each measurement, the MIL-101 particles were centrifuged, refluxed in DI water and re-suspended at various concentrations. This was done until the measurement was stable to ensure that no remaining soluble material affected the experiment. This measurement and purification process was completed a total of five times, the last three of which were used as the mean effective static permittivity values. The general effective medium model [111] was then used to fit to these data using the following set of equations:

$$-\Omega(\varepsilon_{E,Calc}(0)^{1/\nu})^2 + \varepsilon_{E,Calc}(0)^{1/\nu}[\varepsilon_W(0)^{1/\nu}(\Omega(1 - \theta_M) - \theta_M) + \varepsilon_M(0)^{1/\nu}(\Omega\theta_M - (1 - \theta_M))]$$

$$+ \varepsilon_W(0)^{1/\nu}\varepsilon_M(0)^{1/\nu} \quad (32)$$

$$\Omega = \frac{1 - \theta_c}{\theta_c} \quad (33)$$

$$\Delta = \left(\frac{\sum_n ((\varepsilon(0)_{E,Calc} - \varepsilon(0)_{E,Exp}) / \varepsilon(0)_{E,Calc})^2}{n - p} \right)^{1/2} \quad (34)$$

where: ν is an empirical value related to particle morphology, θ_c is the percolation volume fraction; θ_M is the volume fraction of MIL-101; $\varepsilon_M(0)$ is the static permittivity of MIL-101; $\varepsilon_W(0)$ is the static permittivity of water; $\varepsilon_{E,Calc}(0)$ is the calculated effective static permittivity of the medium; $\varepsilon_{E,Exp}(0)$ is the measured effective static permittivity of the medium; n is the number of data points; and p is the number of unconstrained parameters, which was 3 for this work. Note that, based on equation 32, $\varepsilon_{E,Calc}(0)$ is the one real root of the quadratic formula. Δ was minimised via an evolutionary method by changing ν , θ_c and $\varepsilon_M(0)$ using realistic physical constraints on the former two variables. This enables the calculation of an extrapolated value of $\varepsilon_M(0)$.

4.4.3 Optical-Quality Metal-Organic Framework Film

4.4.3.1 Fabrication

A silicon substrate (1 x 1 cm silicon wafer, Agar Scientific), chosen for its well-defined optical properties, was cleaned with 1 M aqueous sodium hydroxide (NaOH, >98% pellets {anhydrous}, Sigma-Aldrich) and ethanol (EtOH, absolute, GPR Rectapur®, VWR) by sonicating the wafers in each solution using pulse mode for 30 minutes at 37 hz and 100% power. The substrate was dried in an oven (Heratherm™ Oven, Fisher Scientific) in a glass petri dish at 120 °C. The substrate was finally dip coated at room temperature at withdrawal speeds of 0.5 to 50 mm·m⁻¹ (RDC15 Dip Coater, Bungard) using MIL-101 suspensions between 500 ppmv and 10.5% (v·v⁻¹) in MeOH and DMF.

4.4.3.2 Scanning Electron Microscopy

The films were qualitatively analysed with scanning electron microscopy (SEM) imaging as previously conducted in Chapter 3, except at 5 kV instead of 10 kV. SEM images were processed for particle size distribution and surface coverage (ImageJ, NIH). The films used for these images were created by dip coating silicon wafers in 100 ppmv MeOH at 5 mm·m⁻¹.

4.4.3.3 Atomic Force Microscopy

Atomic force microscopy (AFM) was conducted (Dimension Icon, Bruker) using a silicon probe with a <12 nm tip radius, 70 kHz response frequency and 0.4 N·m⁻¹ spring constant (ScanAsyst®, Bruker). A resolution of 256 point per line on less than 3 x 3 µm areas was used with a 0.4 Hz scan rate. The images were flattened and cleaned with data visualisation software and root-mean-square roughness (R_q) was calculated (Gwyddion 2.44 SPM).

4.4.3.4 Spectroscopic Ellipsometry and Environmental Ellipsometric Porosimetry: Determining the UV-Visible Spectral Parameters

SE and EEP measurements were performed using a spectroscopic ellipsometer (SE2000 Modular Optical Platform, Semilab) and analysed with the software of the manufacturer (SEA) [195]. All measurements were carried out at an incident angle of 73 °, corresponding to the approximate Brewster angle of the silicon substrate. Measurements were conducted at ambient temperatures after drying the samples on a hot plate for 5 minutes at 120 °C. SE measurements were taken prior to EEP measurements. Data fitting was performed using a standard Cauchy dispersion law in the non-absorbing regions of the spectra. During EEP measurements, the refractive index was obtained at each humidity point to generate an adsorption-desorption isotherm. The isotherm enabled the determination of the relative adsorbed solvent volume and corresponding absolute porosity as well as a pore radius distribution via a Lorentz-Lorentz effective medium approximation and a modified Kelvin formula, respectively [128].

4.5 Results and Discussion

4.5.1 The Formation of Sub-Micrometre Optical-Quality MIL-101 Films

To assess the Hamaker constant of MIL-101, optical-quality nanofilms must be created from the particles. After confirming favourable charge conditions (see Section 9.1.1), two solvents (MeOH and DMF) with various MIL-101 concentrations were used at different dip coating speeds. SEM imaging was used to analyse the samples and determine what range of parameters produce quality films. A broad range of parameters were tested, but just the key trends found in the data are described here. MeOH was the initial focus of these results, using 500 ppmv to ~10 % (v·v⁻¹) solutions at 1 to 16 mm·m⁻¹ withdrawal speeds. The critical point of aggregation of MIL-101 in MeOH, the data for which is presented later in this chapter, was

~1,000 ppmv. As exemplified by **Figure 16**, reasonable dispersion and low surface coverage were found at concentrations below the critical point of aggregation. At concentrations above the critical point of aggregation, poor dispersion and better surface coverage was found. Complete surface coverage, shown in **Figure 16D**, could be obtained at ~10 % ($v \cdot v^{-1}$); however, the dispersion issues led to visibly rough and disordered films. Indeed, any significant dispersion issues led to inconsistent films over large areas. As shown in **Figure 17**, when the surface coverage was increased by increasing the dip coating speed, what were initially small aggregates became larger and more disruptive to film continuity.

Since it appeared that most of the dip coating inconsistencies were attributable to dispersion issues, the best solvent for dispersion was chosen as an alternative: DMF. As shown in **Figure 18**, concentrations of MIL-101 ranging from 0.1 to 10.5 % ($v \cdot v^{-1}$) were tested. Concentrations of less than 2.6 % ($v \cdot v^{-1}$) led to poor surface coverage. The 5.3 % ($v \cdot v^{-1}$) suspension provided good coverage, but it was not as evenly covered as the film made from the 7.9 % ($v \cdot v^{-1}$) suspension. At 10.5 % ($v \cdot v^{-1}$), however, the film began to form cracks due to drying, likely due to the additional thickness leading to stress cracking. **Figure 19** reveals that these cracks were exacerbated at higher withdrawal speeds, which makes sense because thicker films are formed with increasing withdrawal speed in the draining regime [196]. Lower withdrawal speeds created smoother, more uniform films at high MIL-101 concentrations. Further experiments were performed at 7.9% ($v \cdot v^{-1}$) and withdrawal speeds of 0.5 to 4 $\text{mm} \cdot \text{m}^{-1}$, similar to the conditions used to produce the film in **Figure 18B**. The surface topology of these films all looked nearly equivalent, indicating that it is a stable region for forming high-quality optical films of MIL-101. Interestingly, high concentration suspensions at high withdrawal speeds led to the patterned crack formation observed in **Figure 18C** and **Figure 18D**. Dalstein et al. demonstrated control over cracking to create optical sensing devices [133], though much lower withdrawal speeds were required. The lower withdrawal speeds also led to a seemingly higher degree of order in the patterned cracking.

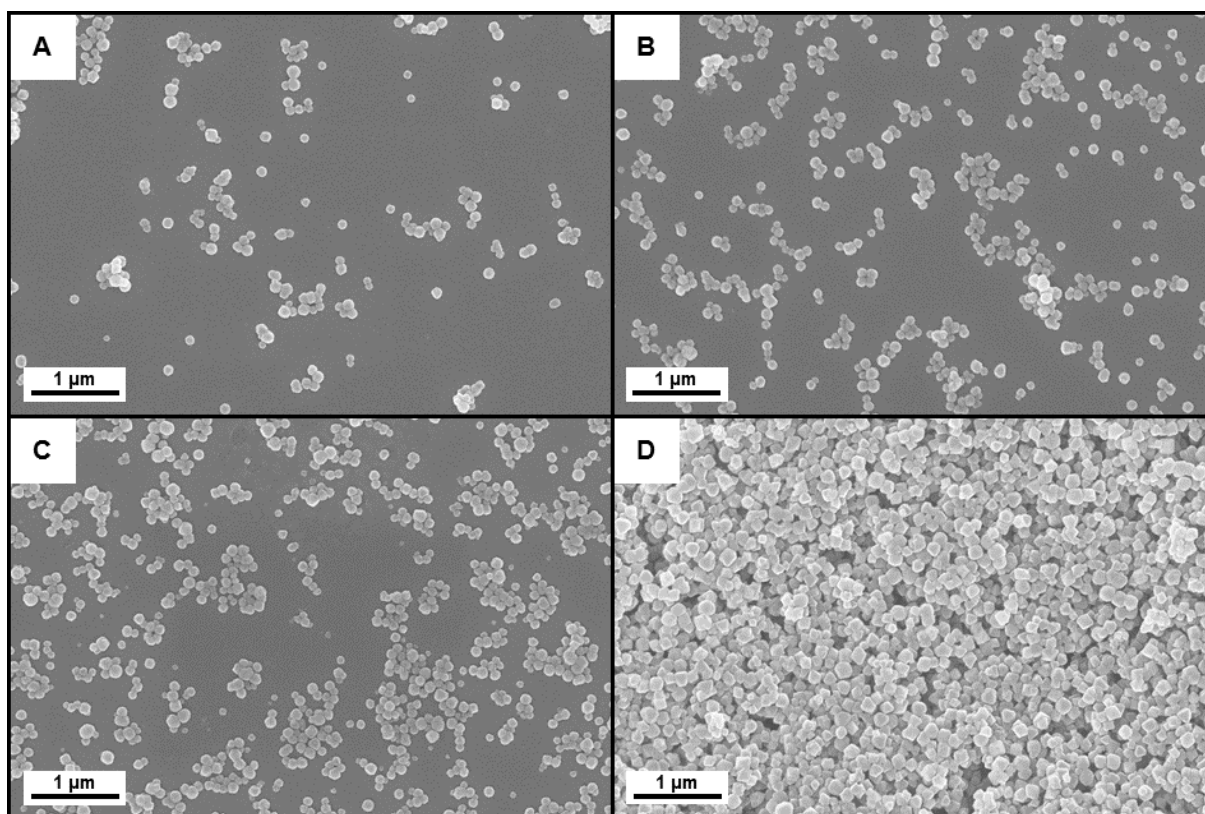


Figure 16. Scanning electron microscopy (SEM) images of 500 ppmv, 1000 ppmv, 5000 ppmv and $\sim 10\%$ ($\text{v}\cdot\text{v}^{-1}$) MIL-101 in methanol (MeOH) dip coated onto silicon wafers at $8\text{ mm}\cdot\text{m}^{-1}$ (A-D, respectively).

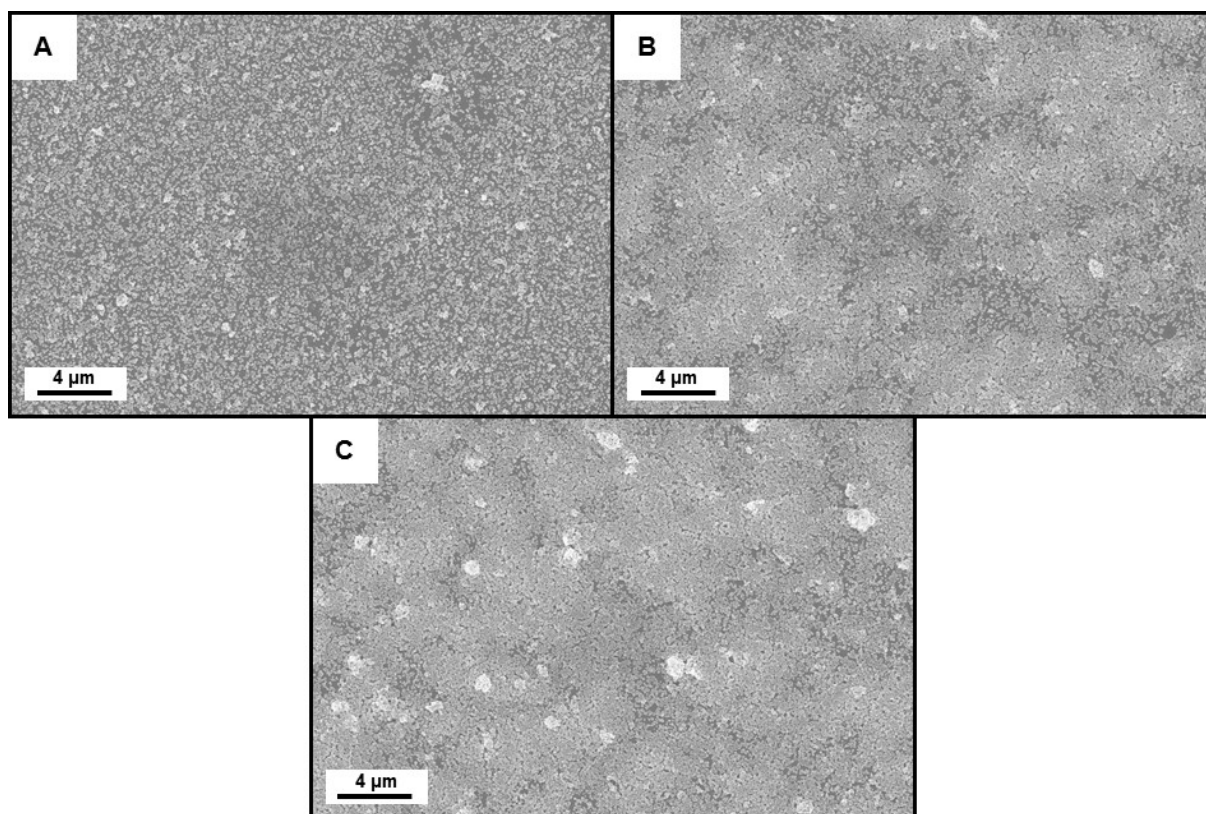


Figure 17. Scanning electron microscopy (SEM) images of 5000 ppmv MIL-101 in methanol (MeOH) dip coated onto silicon wafers at 1, 8 and 16 mm·m⁻¹ (A-C, respectively).

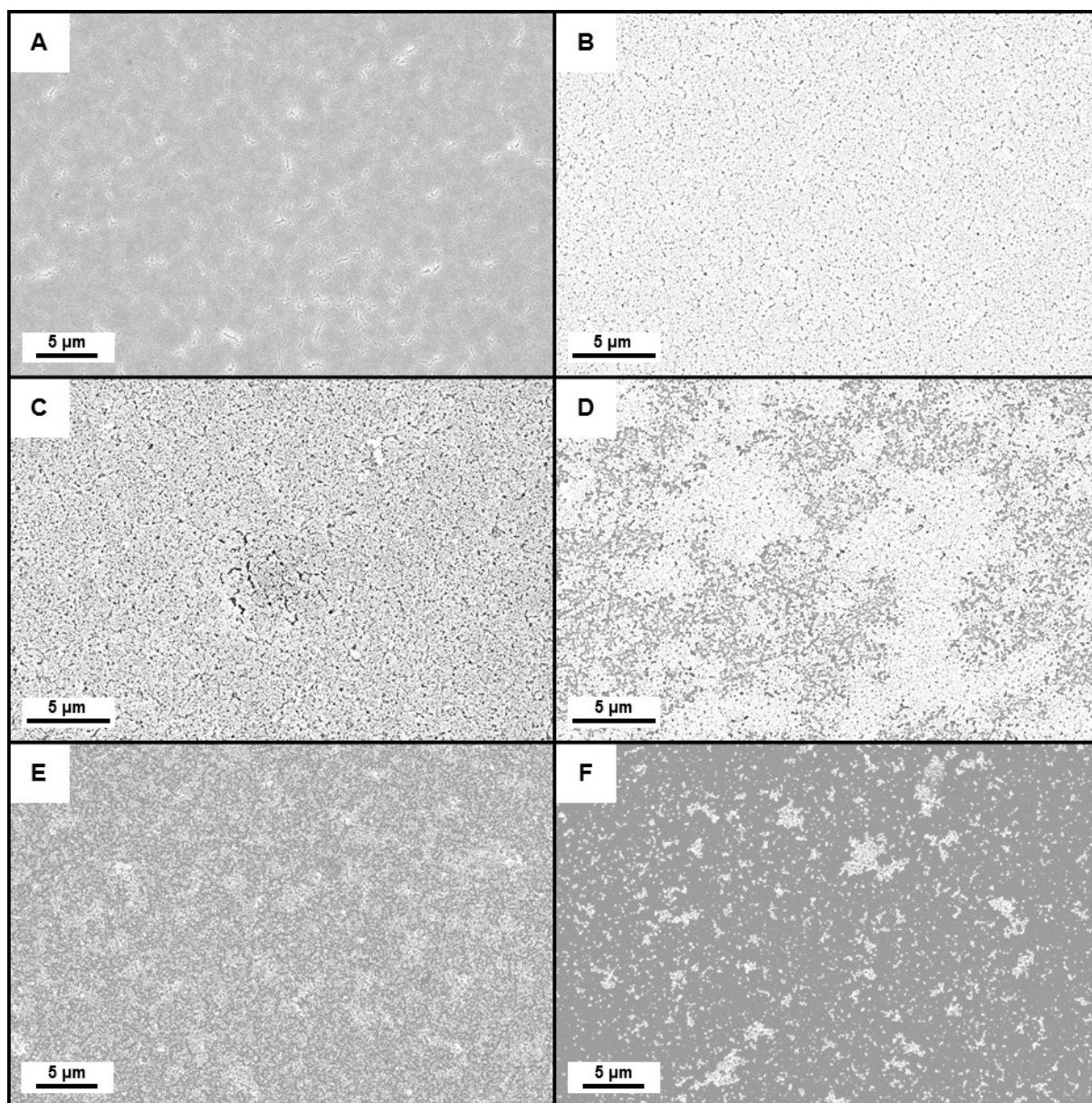


Figure 18. Scanning electron microscopy (SEM) images of 10.5, 7.9, 5.3, 2.6, 1.1, 0.1% ($v \cdot v^{-1}$) MIL-101 in *N,N*-dimethylformamide (DMF) dip coated onto silicon wafers at 0.5 $mm \cdot m^{-1}$ (A-F, respectively). Note that the disrupted film region in (C) is a measurement artefact.

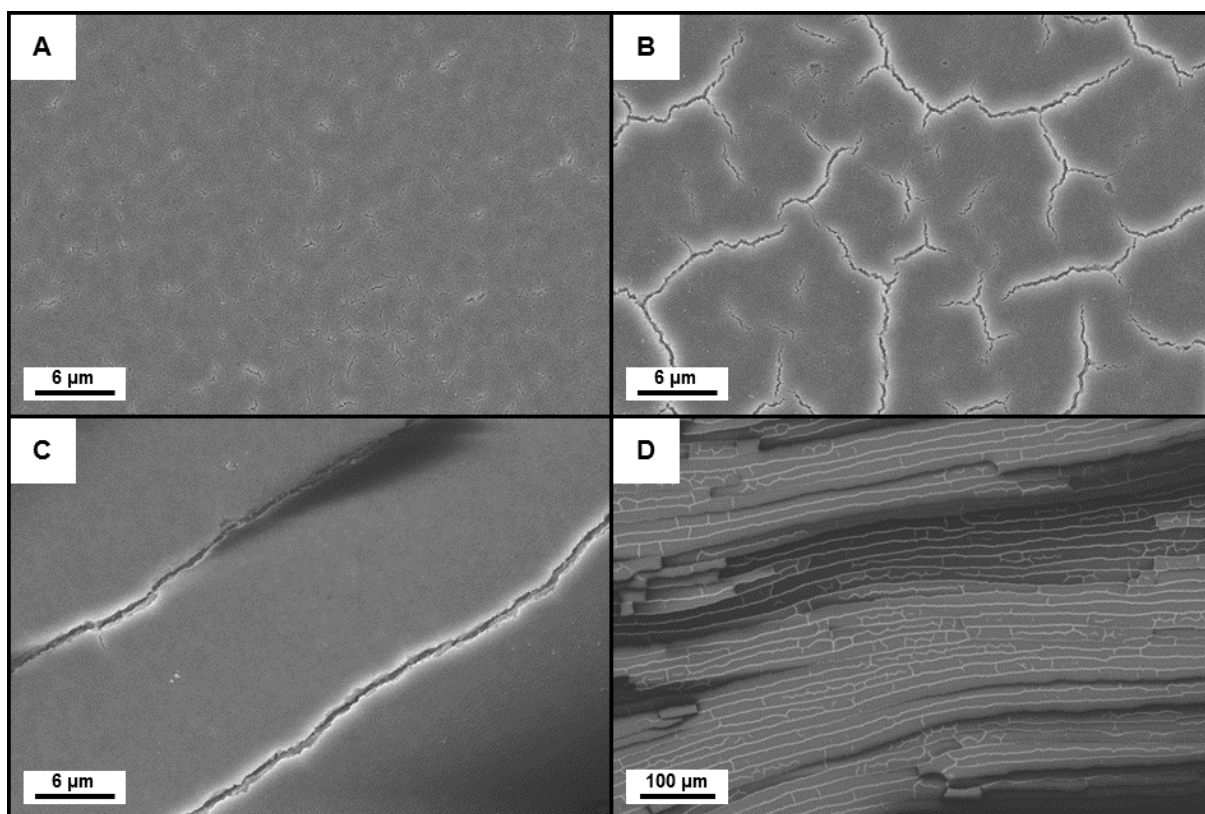


Figure 19. Scanning electron microscopy (SEM) images of 10.5 % (v·v⁻¹) MIL-101 in *N,N*-dimethylformamide (DMF) dip coated onto silicon wafers at 0.5, 5, 50 and 50 mm·m⁻¹ (A-D, respectively).

4.5.2 The Characterisation of Sub-Micrometre, Optical-Quality MIL-101 Films

Additional MIL-101 nanofilms were formed with suspensions of 7.9 % v·v⁻¹ MIL-101 in DMF at a withdrawal speed of 1.0 mm·min⁻¹. SEM and AFM were conducted to verify the quality of these films to be sure they were suitable for EEP and SE. Coloured SEM images shown in **Figure 20A** at different magnifications demonstrate consistent coverage over a large surface area and reasonably uniform particle packing. This is necessary for quality EEP and SE measurements. A cross-sectional image of the film was taken (**Figure 20C**), which confirmed that film thickness was on the order of ~1 μm or less, confirming that it was a suitable thickness for characterisation with EEP and SE.

Films coated with 100 ppmv of MIL-101 in MeOH at 5 mm·m⁻¹ were analysed with ImageJ to determine the particle size distribution presented in **Figure 20B**. This is important for assessing the overall magnitude of the energy barrier using the DLVO equation, as discussed earlier. 40 particles were selected from multiple SEM images similar to the one shown in **Figure 21**. Particle doublets or triplets were excluded. These could be an artefact of the drying process. Since the mean particle diameter was 113 nm with a standard deviation of 17 nm, these data imply a film thickness of ~9 particles.

Finally, **Figure 20D** shows the AFM imaging of the film, confirming a low root mean square surface roughness of 28 nm. This implies that surface roughness should not significantly interfere with the SE and EEP measurements as it is more than an order of magnitude smaller than the wavelength of light used for analysis. As a reality check, calculations were conducted to verify whether or not this roughness is reasonable for such a film (see Section 9.1.2). The root mean square roughness of a sphere of 113 nm in diameter was about 40 nm. However, there will obviously be void space around the sphere that will reduce the overall roughness. If the superficial void space is modelled as a flat plane with zero surface roughness, one can back-calculate an estimated superficial void fraction of 0.51, which is reasonable for irregularly packed spheres [197].

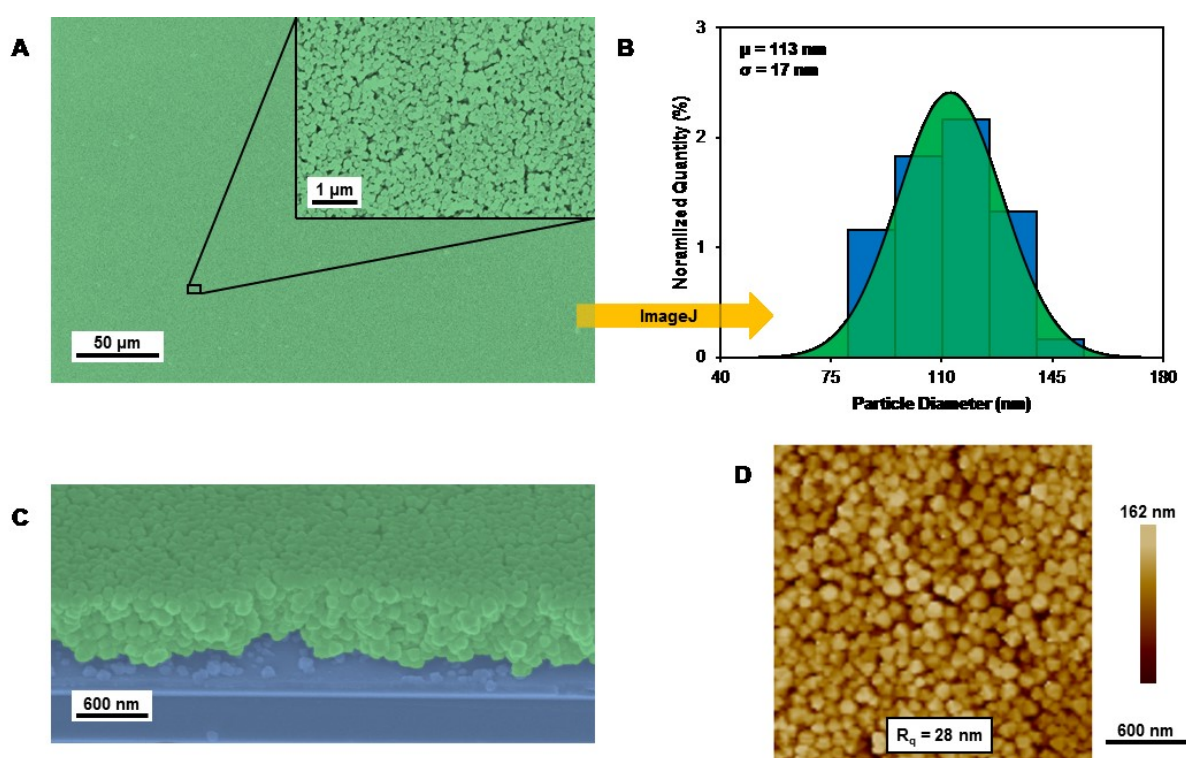


Figure 20. (A) Surface SEM images with coloured support (blue) and particles (green), (B) particle size distribution from ImageJ analysis, (C) 45° angled SEM cross-section image and (D) AFM image of MIL-101 films created by dip coating silicon substrates in 7.9 % $\text{v}\cdot\text{v}^{-1}$ MIL-101 in DMF and using a withdrawal speed of $1.0 \text{ mm}\cdot\text{min}^{-1}$.

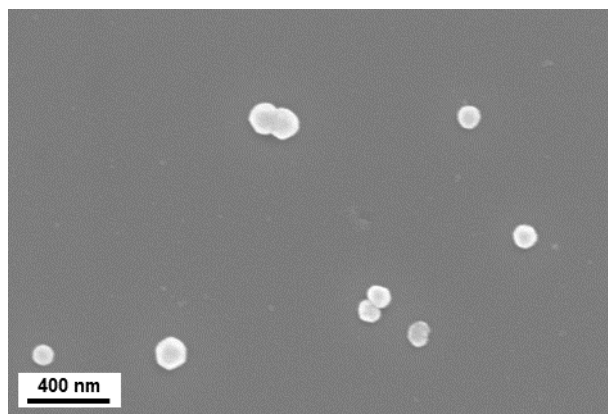


Figure 21. Exemplary scanning electron microscopy (SEM) image of disperse MIL-101 nanoparticles used to calculate particle size distribution.

4.5.3 Determining Fundamental Colloidal Parameters

After confirming nanoparticle film quality, SE measurements were conducted and a Cauchy dispersion model was applied to the data to obtain film thickness and refractive index values. Interestingly, the film thickness was comparable to that shown by the SEM image in **Figure 20C** at $\sim 1 \mu\text{m}$. These refractive index values are used later to determine the spectral parameters of the MIL-101 particle in isolation. To perform this calculation, interparticle voidage must be determined first, however. To do so, the water vapour isotherm measured via EEP was interrogated. **Figure 22A** shows that the film follows a type V isotherm at partial pressures below 0.95 with a H1 type of hysteresis, typical of capillary condensation inside pores [198]. Moreover, it remains relatively flat between partial pressures of ~ 0.5 until ~ 0.8 , after which it increases. This latter region can be attributed to the mesoporous regions of this hierarchically porous film, while the vapour sorption between ~ 0.3 and ~ 0.5 can be attributed to microporous MIL-101 particles [129]. Indeed, the remarkable fidelity of EEP can be used to confirm this. MIL-101 has reported pore radii of 1.4 and 1.7 nm [108]. As shown in **Figure 22B**, pore size distributions can be calculated using the Kelvin model for water sorption into pores [128]. The porosimetry data demonstrate two median radii of ~ 1.50 and ~ 1.75 nm - within 7 % error of the reported pore radii. While this fidelity is typically not seen in bulk measurements of MIL-101 [199], it has been observed for other such thin films. Proponents of EEP argue that these differences arise from diffusion limitations into bulk sample during bulk porosimetry [163].

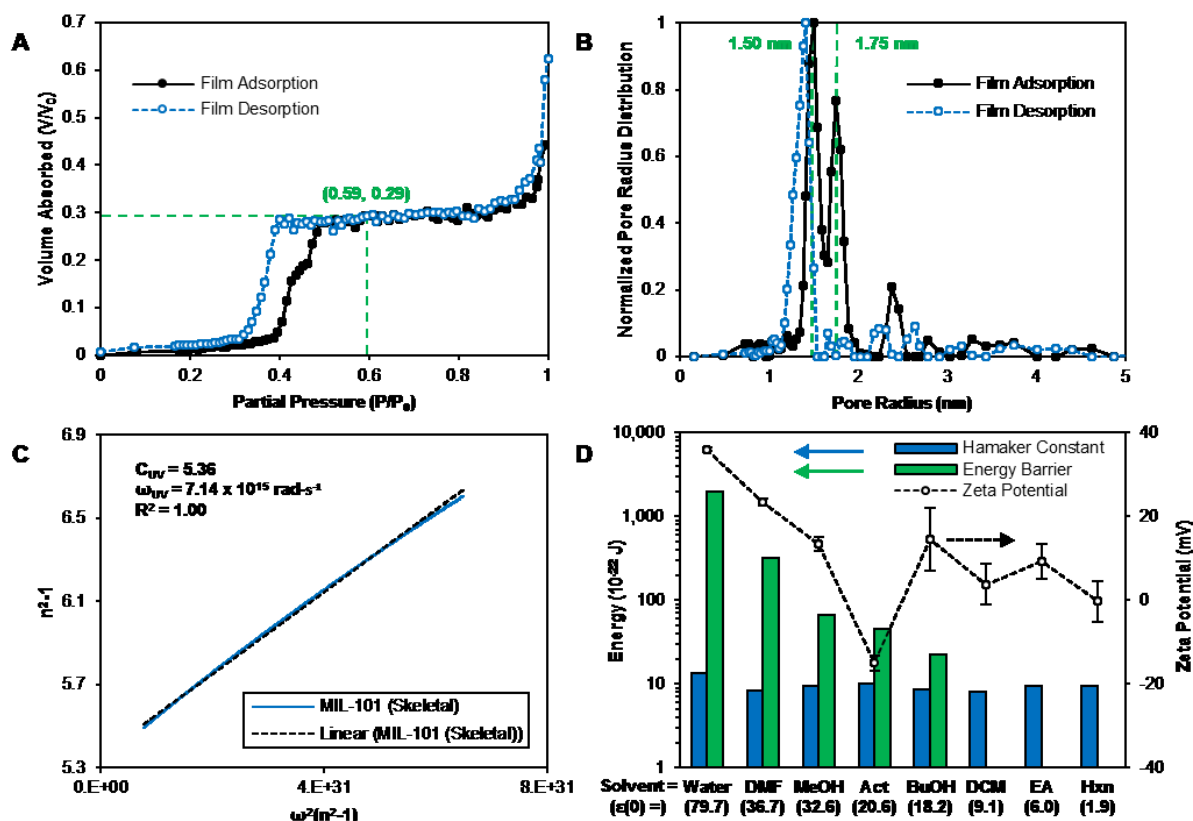


Figure 22. The determination of van der Waals attractive and electric repulsive forces and the resulting predictions. (A) Environmental ellipsometric porosimetry (EEP) water sorption measurements (V_0 = volume of MIL-101 film), (B) the resulting pore size distribution and (C) Cauchy plot of the skeletal MIL-101 spectral data. (D) Dielectric constants [192], zeta potential, Hamaker constants and energy barrier maxima. Dielectric constants are listed below each solvent name. Green lines mark the point at which water sorption in the microporous region is complete and the median pore sizes of MIL-101 in (A) and (B), respectively. All measurements were taken at 25 °C.

By comparing the relative water uptake of this film and bulk measurements of MIL-101 at a partial pressure of 0.59, one can calculate an interparticle void volume fraction. As the DVS data shown in **Figure 23** demonstrates, the bulk water sorption measurements follow the same trends observed in the EEP measurements. Both DVS and EEP curves follow a type V isotherm at partial pressures below 0.95, which is typical of capillary condensation inside pores. While the film remains relatively flat between partial pressures of ~ 0.5 and ~ 0.8 , the bulk measurement increases gradually. This increase could be attributed to differences in interparticle packing. Regardless, since this adsorption is outside the point at which the pores of MIL-101 should adsorb water, the comparison of water uptake between the bulk and film measurements were restricted to the region immediately after the point of capillary

condensation. At a partial pressure of 0.59, MIL-101 adsorbs up to ~83% ($\text{g}\cdot\text{g}^{-1}$) of water, while the film absorbs ~29% ($\text{v}\cdot\text{v}^{-1}$) of water at the same point.

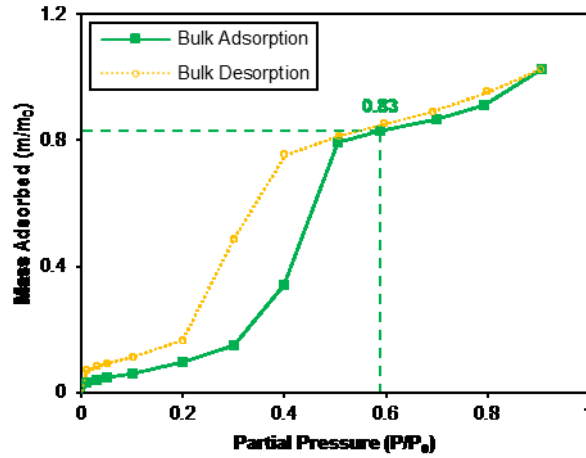


Figure 23. Bulk MIL-101 water adsorption isotherm measured with DVS at 25 °C.

With these data and those readily available in the literature [108], one can approximate the volume fraction of MIL-101 particles in the MIL-101 film (θ_M) as:

$$\theta_M = \frac{0.293 \text{ mL } H_2O \text{ in MIL} - 101}{1 \text{ mL Film}} \times \frac{0.997 \text{ g } H_2O \text{ in MIL} - 101}{1 \text{ mL } H_2O \text{ in MIL} - 101} \times \frac{1 \text{ g MIL} - 101}{0.832 \text{ g } H_2O \text{ in MIL} - 101} \\ \times \frac{1 \text{ mL MIL} - 101}{0.62 \text{ g MIL} - 101} = \frac{0.57 \text{ mL MIL} - 101}{1 \text{ mL Film}}$$

This yields an interparticle void volume fraction of 0.43, well within the plausible range for irregularly packed spheres [197]. Interestingly, this is also not too far off from the value approximated via AFM earlier. It makes sense that the surface interparticle voidage is a little higher than the bulk voidage measurement here as the surface should not terminate with a perfect monolayer when spheres are irregularly packed. The total void volume fraction in the MIL-101 film (ε_F) is the interparticle void volume fraction plus the porosity MIL-101 (ε_M). This can be written mathematically as:

$$\varepsilon_F = \varepsilon_M \theta_M + (1 - \theta_M) \quad (35)$$

The MOF void space has been previously reported as 0.83 [108]. Therefore, the overall void space of the MIL-101 film is ~0.90. This is a remarkable total voidage for a hierarchically porous film, which could have interesting applications in its own right. However, for our purposes, these data are used to fit the SE data to determine the refractive index of MIL-101 as a function of wavelength in the UV-visible range. These fits were accomplished using the Cauchy dispersion law and a Lorentz-Lorentz effective medium approximation. The refractive index ($n(\omega)$) data were transformed into a Cauchy plot, where the y-intercept and slope are

equivalent to C_{UV} and the reciprocal of ω_{UV} squared, as demonstrated by the equation below, and presented in **Figure 22C**.

$$n^2(\omega) - 1 = (n^2(\omega) - 1) \frac{\omega^2}{\omega_{UV}^2} + C_{UV} \quad (36)$$

A linear regression was performed to determine the spectral parameters: $C_{UV} = 5.36$ and $\omega_{UV} = 7.14 \cdot 10^{15} \text{ rad} \cdot \text{s}^{-1}$. These are reasonable values for comparable inorganic materials [168]. Note that these spectral parameters are intended to be used to define just the skeletal structure of MIL-101 for the purpose of calculating the Hamaker constant of MIL-101 filled with a variety of solvents and are not indicative of bulk MIL-101 properties in other environments.

Since the contribution of the IR region to the Hamaker constant can be ignored if the dielectric constant is small [168], the dielectric constant was approximated to determine whether or not spectral data from this region was necessary. After all, the dielectric constant of many MOFs measured in the literature has been relatively low to date [200,201]. To those ends, a rough approximation was made by extrapolating an effective medium model of MIL-101 in water presented in **Figure 24**. Note that the 95 % confidence intervals are not visible because they are smaller than the data points. These data indicate a relatively low percolation threshold, which makes sense given the critical point of aggregation of MIL-101 in water. The predicted dielectric constant of MIL-101 is ~ 2.2 , which is reasonable given past estimates of MOF dielectric constants. While extrapolating data is never ideal, these data indicate that the static permittivity of MIL-101 should be sufficiently low enough such that the contribution of the IR region on the Hamaker constant of MIL-101 in various solvents is negligible.

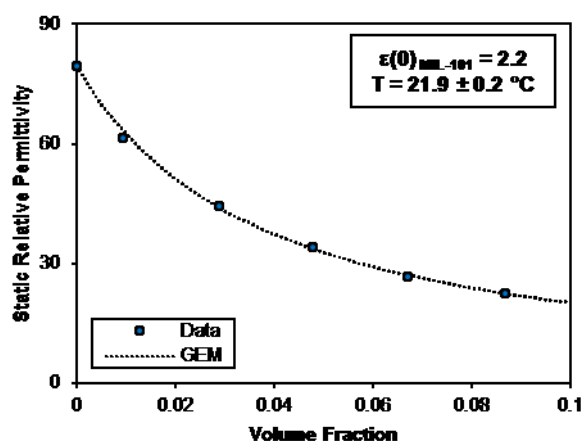


Figure 24. The static permittivity of MIL-101 suspensions at various concentrations in water. The general effective medium approximation was used to fit the data.

If the IR region is negligible and the UV-visible spectral parameters are determined, it is possible to calculate the Hamaker constant as outlined in the Section 4.3. In this way, a

Hamaker constant of $3.31 \cdot 10^{-21}$ J was found for MIL-101 in a vacuum. Moreover, MIL-101 spectral parameters were combined with the data in **Table 3** and **Table 4** to produce the Hamaker constant values in **Figure 22D**. These Hamaker constants range between 0.80 and $1.33 \cdot 10^{-21}$ J with DCM being the lowest and water being the highest. This is a narrow range that would be considered relatively low for a non-porous inorganic solid. However, this low Hamaker constant can be explained by the large voidage of MIL-101, which is filled with the solvent in which the particles are suspended. In this case, the macroscopic dielectric properties of MIL-101 largely resemble that of the solvent environment. Since it is the difference in these dielectric properties which leads to the van der Waals attractive force, it is entirely reasonable that a highly porous material would have a low Hamaker constant when compared to non-porous materials.

Figure 22D also contains MIL-101's zeta potential in each solvent as well as each solvent's dielectric constant. As would be expected, the absolute value of the zeta potential decreases with decreasing solvent dielectric constant. When all these quantities are entered in to the DLVO equation, the energy barrier (see **Figure 10**) can be quantified. If the electric double layer repulsive forces are strong enough, an energy barrier should maintain a reasonable MOF colloidal dispersion, shown by the green dashed line. However, if the electric repulsive forces are sufficiently low, the van der Waals attractive forces will dominate, leading to unstable colloidal suspensions, shown by the black solid line. Since the electric double layer repulsive forces are proportional to the dielectric constant and the square of zeta potential, the calculated energy barrier decreases rapidly as these quantities decrease. This establishes, for the first time, a quantified theoretical basis for the colloidal properties of a MOF. But how well does it describe real suspensions?

4.5.4 DLVO Predictions versus Experimental Measurements

While the method of measuring the wavelength exponent via UV-visible spectrometry outlined in Section 4.4.2.2 has been shown to be sensitive [186], previous studies lacked statistical support. Prior to these measurements, a method of statistical analysis was created and validated (see Section 9.1.3). With the method of analysis established, aggregation data in a variety of solvents was gathered and summarised in **Figure 25**. Overall, the theoretical predictions from DLVO theory appear to correlate well with the measured aggregation behaviour. When considering the series of alcohols in **Figure 25A**, decreasing the solvent dielectric constant by increasing the alcohol chain length leads to lower critical points of aggregation. The picture becomes somewhat more complex when looking at a variety of functional groups, however.

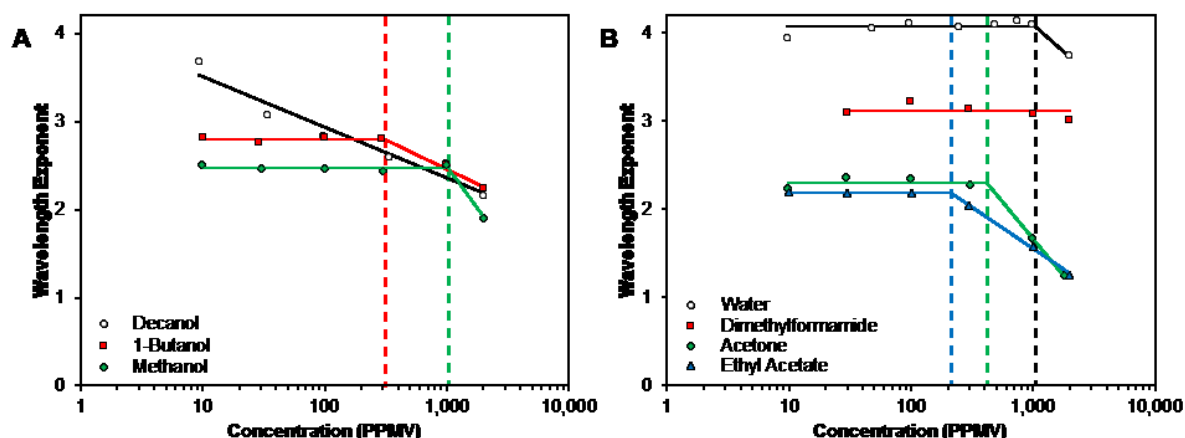


Figure 25. Wavelength exponent versus concentration plots are for MIL-101 in select solvents. Vertical lines mark the critical point of aggregation for corresponding solvents.

Overall, as shown in **Figure 25B**, the solvents that suspend MIL-101 nanoparticles better do indeed have higher dielectric constants: water, DMF, MeOH, Act, EtOH and BuOH. Moreover, aggregation is observed in most instances where the energy barrier ceases to exist, as is the case for DCM and Hex. The aggregation for these solvents were so significant, that accurate measurements could not be taken. This is discussed in greater depth in the next section. Interestingly, while EA shows no energy barrier, stable dilute suspensions do seem possible. Also, while the calculations suggest that water would be the best suspension solvent, DMF appears to have a higher critical point of aggregation. These two observations could be related to acid-base interactions. After all, MIL-101 is synthesised in excess terephthalic acid and clearly demonstrates a positive charge in most solvents. Furthermore, recent literature points towards acid-base interactions being a significant driver of colloidal behaviour of MOFs [164,202]. DMF is a stronger base than water and the same can be said for EA relative to DCM and Hex, as illustrated by their donicity [203]. Of course, while this explanation is coherent for this data set, further tests would need to be performed to confirm the role of acid-base interactions.

When it comes to formulation of products for monoliths based on MIL-101 and other similar MOFs, these data suggest that it would be best to find high dielectric constant solvents and perhaps those that can behave as bases as well. Additionally, since MIL-101 can achieve suspension in higher dielectric constant solvents, the data show why certain MOFs might readily be applied to aqueous environments such as in drug delivery. Regardless, it seems that stable suspensions of native MIL-101 are theoretically and observably unachievable in hydrophobic solvents such as DCM and Hex. While this should not be a problem for many MOF composite syntheses, it could lead to aggregates and defect formation for others.

Particularly, these theoretical and practical measurements support the aggregation of MIL-101 in Hex during TFN membrane synthesis.

4.5.5 Particle Settling versus Aggregation

Particle settling, aggregation and/or both can matter when formulating certain products. In the case of TFN membrane fabrication, both could play a role. Given the nature of the manufacturing process for TFN membranes, insignificant degrees of aggregation and settling is preferred. This implies that the solvent properties must enable good dispersion and have sufficient viscosity to prevent settling. To better understand the data above in relation to particle settling, a thought experiment was conducted. The most common expression for particle settling is Stoke's Law:

$$v = \frac{2(\rho_M - \rho_l)gr^2}{9\mu} \quad (37)$$

where v is the particle's terminal settling velocity ($\text{m}\cdot\text{s}^{-1}$), g is the acceleration of gravity ($\text{m}\cdot\text{s}^{-2}$), r is the particle's radius (m), μ is the dynamic viscosity ($\text{Pa}\cdot\text{s}$) and ρ_M and ρ_l are the densities of the MIL-101 and solvent ($\text{kg}\cdot\text{m}^{-3}$), respectively. The particle density was approximated by taking the volumetric average of the skeletal particle density and the solvent in which the particle was suspended. By assuming no aggregation occurs, a particle diameter of 113 nm can be used. The results of these calculations are presented in **Figure 26A** in terms of settling velocities that have been normalised to that of Hex.

Note that these data can be split into four regions, as summarised by **Figure 26A** and **Figure 26C**. In region 1, the predicted settling velocity is low and there is little to no aggregation. This means that very good measurements can be taken and the solution demonstrates remarkable stability. Since solvents in region 1 have higher dielectric constants than those in other regions, aggregation is also likely not an issue at certain concentrations and conditions. **Figure 26D** shows that MIL-101 suspensions remain stable in DMF even when left alone for over a week. This type of suspension is possible within region 1 and is certainly optimal for TFN membrane fabrication.

Region 2 has similar aggregation characteristics to region 1, except the settling velocity is higher. This means that even well-dispersed suspensions may not remain suspended if the particles have sufficient density. For the solvents measured in this work, the suspensions were certainly stable enough to obtain good measurements that indicated a lack of aggregation within certain ranges. However, these suspensions did settle over time. While settling velocity could play a role, there could also be slow aggregation kinetics at play.

In region 3, there is a lower dielectric constant, so most solvents measured in this region did prove to have aggregation. Despite there being measurable aggregation, the viscosity and density of the solvents are still sufficiently high to impede settling over the course of the measurement (~45 seconds). This is shown in **Figure 26D**, where IsoPar G (IPG) remains the same at 45 seconds, but settles out completely over the course of 10 minutes. DeOH is sufficiently viscous to enable a longer settling time than that seen for Act, even though clear aggregates are present in DeOH throughout the measured range. Since the settling velocity of any particle in DeOH is 38 times that of Act, this could make sense. It would mean that the mean aggregate sizes in DeOH are less than six particles in diameter at low concentrations – not unreasonable given the sensitivity of the UV-visible measurements.

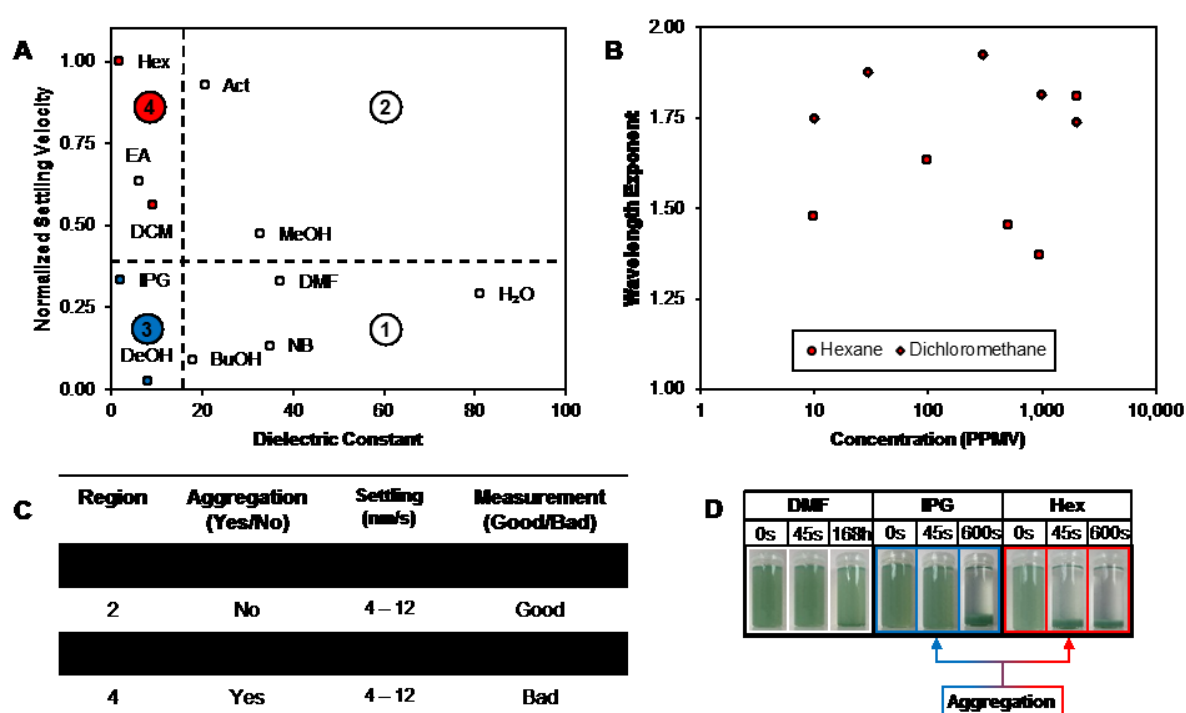


Figure 26. (A) Normalised settling velocities assuming no aggregation. (B) Wavelength exponent values for region 4 solvents. (C) Tabulated definitions for different regions. (D) Images of MIL-101 settling in select solvents.

Finally, in region 4, there is both aggregation and a high predicted settling velocity. The attempt at measuring the wavelength exponent in these solutions resulted in completely random data, as shown in **Figure 26B**. This random data is a result of particle settling during the measurement. As shown in **Figure 26D**, MIL-101 settles completely within 45 seconds when suspended in Hex. Moreover, the MIL-101 has a propensity to deposit itself onto the edge of the UV-Vis cuvettes in solvents such as DCM and Hex, suggesting that the hydroxyl groups on the surface of the quartz cuvettes are more attractive to MIL-101 than these hydrophobic solvents. Of course, this also complicates any UV-visible measurement.

This analysis supports that rapid aggregation of MIL-101 in Hex and DCM occurs because their viscosities and densities are similar to that of Act, but Act provides a stable suspension over certain time periods. Therefore, according to Stoke's Law, the large observable increase in settling velocity must be attributed to greater particle size, which could only be caused by aggregation. Similar reasoning suggests that EA must exhibit a lower degree of aggregation than DCM, even though DCM has a higher dielectric constant. As discussed earlier, this could arise from acid-base interactions.

4.6 Conclusions and Future Work

Optical-quality nanoparticle films of MIL-101 were fabricated via dip coating. These films were characterised with a unique combination of EEP and SE to determine the spectral properties intrinsic to nano-sized MIL-101. These films were $\sim 1\ \mu\text{m}$ thick and were found to have properties which could be useful in a variety of applications: long-range order, hierarchical porosity and a void fraction of $\sim 90\%$. The interparticle van der Waals attractive forces of MOF nanoparticles in nine solvent environments were determined for the first time and found to be relatively low. Thus, good suspensions were achieved in high dielectric constant solvents via electric double layer repulsive forces, as described by DLVO theory. However, the electric double layer repulsive forces diminished in low dielectric constant solvents, leading to unstable suspensions. With this approach, one can now reasonably predict the suspension of MIL-101 in any solvent using DLVO theory, thus decreasing the amount of trial and error required for MOF product formulation via colloidal suspensions. While imperfect, the calculations at least give a good prediction for seven out of nine solvents. In the future, these predictions could become more accurate with additional investigation of other colloidal interactions, including: acid-base interactions, hydrophobic forces, hydrogen bonding and hydration pressure [204].

The consequences of this study for mixed matrix membrane (MMM) fabrication are of interest to this overall thesis. Many MMM formulation systems that create integrally skinned asymmetric membranes use polar aprotic solvents, such as DMF, to suspend the polymer in prior to phase inversion. This appears to be a reasonable choice, with the caution that adding polymer can substantially alter the dielectric constant as well as other parameters affecting the colloidal stability. This is why many researchers prime the nanoparticles with polymer prior to inclusion in the final dope solution or use filler modification [25,110,112,119,120,205–207]. For the specific type of MMM that is the focus of this thesis, TFN membranes made via IP, this conclusion is challenging. This chapter shows that high dielectric constant solvents can achieve better dispersion at higher MIL-101 loadings and the previous chapter shows that severe aggregation in solvents such as Hex can lead to non-selective defects and inconsistent membrane performance. However, the organic solvent used in IP must be immiscible with water and inert towards acyl chlorides. This creates contradictory conditions for an ideal

solvent: one with a high octanol-water partition coefficient and low dielectric constant. Considering such solvents are not common, filler modification is an obvious route to explore.

5 Surface-Selective Modification of a Metal-Organic Framework

5.1 Abstract

In the previous chapter, it was empirically and theoretically demonstrated that a metal-organic framework (MOF), MIL-101, aggregated and made poor suspensions in low dielectric constant solvents. This is a problem for thin film nanocomposite (TFN) membranes made via interfacial polymerisation (IP) because the filler material is typically incorporated through its suspension in the organic phase [29] and the organic phase tends to have a low dielectric constant. To achieve suspension in solvents suitable for IP, 1-octylamine (OA) and amine terminated polystyrene (ATPS), were successfully coordinated to MIL-101's coordinatively unsaturated sites (CUSs) without harming MIL-101's crystalline structure. These materials were characterised with X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS) and nitrogen sorption. The results of these characterisations indicated that OA modified the internal structure and external envelope of MIL-101, while the ATPS selectively modified the external envelope. In this way, OA modification reduced MIL-101's porosity, while the ATPS modification did so to a significantly smaller degree. Both modifications enabled the suspension of ~300 ppmv of well-dispersed MIL-101 in IsoPar G, a typical solvent used for IP. Past this concentration, aggregates started to form even though the suspension was reasonably stable. This technology may be useful for some applications [115]; however, given the complexity of modification, this approach might not be ideal for TFN membrane fabrication. After all, 300 ppmv is a much smaller MIL-101 loading than is typically used to obtain a significant performance enhancement [75].

5.2 Introduction

Precise control of MOF suspensions is crucial for their implementation in a range of applications, including: drug delivery, optics, conductors, chemical sensors, catalysis, separation, adsorption and gas storage [120,150,208–212]. A MOF's colloidal properties can play an integral role in the application itself, such as drug delivery, or be important for the fabrication of MOF devices, such as membranes. In the previous chapter, theoretical calculations and empirical measurements were used to establish that electric double layer repulsive forces can be a significant contributor to the state of dispersion of a MOF, MIL-101. It was found that low dielectric constant solvents provide poorly dispersed, unstable suspensions. This explains why high-quality demonstrations of self-assembly of MOFs from colloidal solutions tend to use solvent environments with high dielectric constants [132,133,162,163]. The primary goal of this work is to suspend MIL-101 in a hydrophobic solvent in a way that could be suitable for TFN membrane fabrication.

Wang et al. monopolised on the unique chemistry of zirconium-based MOFs by coordinating 1,2-dioleoyl-sn-glycero-3-phosphate to their CUSs. This study showed self-assembly behaviour for particles cast from chloroform, minimal impacts on porosity for larger particles and stable nanoparticle suspensions in *N,N*-dimethylformamide (DMF) [154]. Phosphate modification proved to be generalisable to other MOFs, as shown by the attachment of phosphate-terminated oligonucleotides to nine different MOFs with four different types of metal clusters [155]. Yang et al. demonstrated the potential efficacy of this technology in drug delivery as well [182]. Zhu et al. showed the potential of a similar chemistry, using 1,2-dipalmitoyl-sn-glycero-3-galloyl to self-assemble larger nanoparticles at an air-water interface and create polymethyl methacrylate composite films [153]. This chemistry was shown to be acid-sensitive, however. This can be advantageous in that the modification can be reversed if desired. On the other hand, in the case of TFN membrane synthesis, it could cause issues to the final application stability. Some other modification techniques include those using polystyrene sulfonate, polymethyl methacrylate, 2-isopropenyl-2-oxazoline, polyethylene glycols, oligoaminos and polyvinylpyrrolidone. These molecules have been deposited, polymerised or coordinated onto MOF's surfaces [156–160]. Some of these techniques were shown to be potentially useful in drug delivery and other fields. MOF particles were also coated with silica for controlled release and sensing applications [161]. The modification techniques that seem to provide the greatest degree of hydrophobicity and control over MOF suspension in hydrophobic solvents are those which coordinate hydrophobic molecules to CUSs of MOFs. While some have shown self-assembly of well-defined structures [153,154], few have explored or quantified the impact of filler loading on dispersion in solvents typical to the IP systems used for TFN membrane fabrication. This work explored the modification of the CUSs

of MIL-101 with amine-based chemistries: OA and ATPS. The modification was quantifiably related to the suspension of MIL-101 nanoparticles in a model hydrophobic solvent. Finally, this behaviour was modelled by extended Derjaguin, Landau, Verwey, Overbeek (exDLVO) theory.

5.3 Background

In the Section 1.4.4, the DLVO equation is defined and discussed. It is also applied to the work in Chapter 4. For this study, an additional term was appended to the DLVO equation to account for steric repulsion. Some authors call this equation, and similar equations that attempt to include non-DLVO forces, an exDLVO equation [166].

$$E(d) = \frac{2\pi\epsilon_0\epsilon_h r \zeta^2}{k_B T} e^{-\kappa d} - \frac{Ar}{12k_B T d} + \frac{4\pi N_A \Gamma^2}{3\rho_P^2 M_{vol}} (0.5 - \chi) \left(1 - \frac{d}{2\delta}\right)^2 \left(3r + 2\delta + \frac{d}{2}\right) \quad (38)$$

The first two terms are defined in the Section 1.4.4 and the last term describes the steric repulsive force, which is written in terms of: Γ , the coating surface coverage ($\text{g}\cdot\text{m}^{-2}$); ρ_P , the polymer density ($\text{kg}\cdot\text{m}^{-3}$); M_{vol} , the molar volume ($\text{mol}\cdot\text{m}^3$); χ , the Flory-Huggins parameter; and δ , the coating thickness (m). This suggests that higher surface coverage, lower polymer density, lower Flory-Huggins parameter and lower molar volume increase the steric repulsive forces. The Flory-Huggins parameter decrease with increasing polymer solubility in the solvent used for suspension [213]. The right-hand side of the steric repulsive term describes the distance at which the steric repulsive forces dominate as a function of particle radius and coating thickness.

The layer thickness can be approximated by multiplying the root mean square of the radius of gyration by two to get an effective diameter of OA and ATPS in solvents similar to that which is used for tests in these experiments (1.4 and 5.7 nm, respectively) [214,215]. The molar volume (239 and $9,520 \text{ cm}^3\cdot\text{mol}^{-1}$) can be calculated from the densities (0.782 and $1.05 \text{ g}\cdot\text{cm}^{-3}$) and molecular weights (M_W , 188 and $10,000 \text{ g}\cdot\text{mol}^{-1}$) reported by the supplier. The absorbed weight (0.25 and $4.3 \text{ mg}\cdot\text{m}^{-2}$) can be calculated from the degree of modification (D , $\text{mmol}\cdot\text{g}^{-1}$) using following equation derived from spherical geometry:

$$\Gamma = \frac{D\rho_M M_W ((r + \delta)^3 - r^3)}{3r^2} \quad (39)$$

The degree of modification can be measured via thermogravimetric analysis (TGA) or X-ray photoelectron spectroscopy (XPS), the latter being preferable as it is a surface-sensitive technique. The Flory-Huggins parameter should be reasonably low for OA and ATPS in hydrocarbons since it is proportional to the relative difference in solubility parameters and that difference is small [213,216]. Taken as a whole, these calculations produce an energy barrier

similar to the orange line in **Figure 27**. This energy barrier increases dramatically at a distance that is twice the diameter of the grafted molecule.

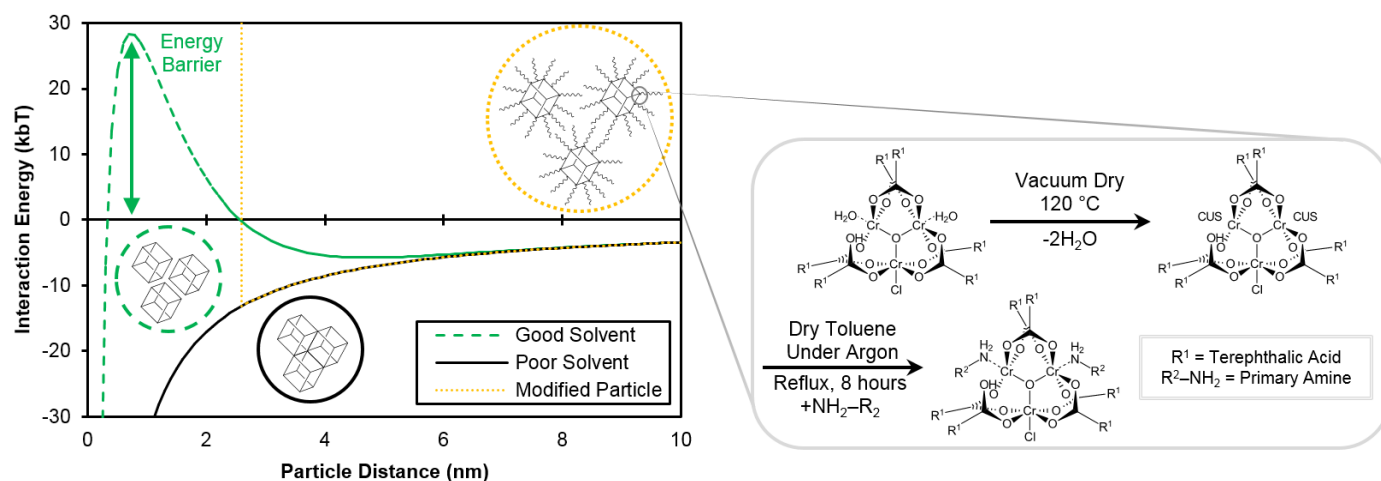


Figure 27. Colloidal science theory following the classic and extended DLVO models along with the chemistry of the MIL-101 modification.

5.4 Methods

5.4.1 Materials Synthesis

Several grams of MIL-101 were made according to the microwave synthesis and activation procedure outlined in Chapter 3. This bulk powder was split into three ~1 g portions. One portion was used as an unmodified control [MIL-101 (UM)]; another portion was post-synthetically modified with OA [MIL-101 (OA)]; and the final portion was modified with ATPS [MIL-101 (ATPS)]. **Figure 27** contains a reaction schematic summarising the modification process. To remove water from the CUSs of MIL-101, ~1 g was dried overnight in a vacuum oven (Vacutherm™ vacuum oven, ThermoFisher Scientific™) at 120 °C. The vacuum oven was back-flushed with dry nitrogen (Research Grade, BOC) and the MIL-101 was cooled under flowing dry nitrogen. The cooled MIL-101 was added to a dry flask and three vacuum-argon (Research Grade, BOC) flushes were conducted. 100 mL of toluene (AnalaR Normapur®, VWR) was dried with molecular sieves (4Å, VWR) and added to the flask to suspend the MIL-101. To coordinate the primary amine molecules to MIL-101's CUSs, 1.7 mL of OA (99%, Aldrich Chemicals) or 1 g of ATPS ($M_n = 10,000$, Sigma-Aldrich) was added to the suspension. The suspension was sonicated at 80 °C for 2 hours at 100% power and 37 hz in pulse mode (Elmasonic P, Elma). Then it was stirred at reflux for 5 hours. To isolate the product, the suspension was centrifuged (Centrifuge 5810R, Eppendorf) at 15,000 rcf for 30 minutes. The modified MIL-101 was then re-suspended in toluene and re-centrifuged three times for purification. The final product was dried in a vacuum oven at 120 °C overnight.

5.4.2 Materials Characterisation

XRD, TGA and nitrogen sorption were performed on modified and unmodified MIL-101 samples using the standard methods described in Chapters 3 and 4. Using the technique detailed in Chapter 4, the wavelength exponent was measured by UV-visible spectrophotometry in IsoPar G (IPG), a common industrial solvent used for IP consisting largely of alkanes. These data were used to determine the critical point of aggregation of the unmodified and modified MIL-101 samples. Fourier-transform infrared spectroscopy (FTIR) was performed at a 2 cm⁻¹ resolution using 1 cm⁻¹ sampling intervals for 16 trials per sample (Spectrum 100, PerkinElmer). The degree of modification was calculated by attributing the difference in residuals measured by TGA to the presence of OA or ATPS via the following equation:

$$D = \frac{R_{UM}/R_M - 1}{M_W} \quad (40)$$

where R_x is the residual of the unmodified (UM) and modified ($M = \text{OA or ATPS}$) MIL-101 (g·g⁻¹). This equation assumes that OA and ATPS have negligible residuals, which can be experimentally confirmed.

XPS was conducted (K-Alpha+™, Thermo Scientific™) using a K_α monochromated X-ray source (MXR3 Al, $h\nu = 1486.6$ eV). The power was set to 72 W using a 20 eV pass energy and 0.1 eV step size. Samples were mounted on carbon tape. Data was analysed (Thermo Advantage, Thermo Scientific™) after normalising the binding energies to the adventitious carbon peak at 284.8 eV. Sample counts were normalised to the chromium peak when comparing spectra. The percent modification was calculated by dividing the final value of the following equation by the ideal number of MIL-101's CUSs (3 mmol·g⁻¹):

$$\frac{N \text{ atoms } N}{Cr \text{ atoms } Cr} \times \frac{\frac{1 \text{ molecule OA/ATPS}}{1 \text{ atom } N}}{\frac{1 \text{ molecule MIL-101}}{3 \text{ atoms } Cr}} \times \frac{N_A \frac{\text{molecule MIL-101}}{\text{mol MIL-101}}}{N_A \frac{\text{molecule OA/ATPS}}{\text{mol OA/ATPS}}} \times \frac{\frac{1,000 \text{ mmol OA/ATPS}}{1 \text{ mol OA/ATPS}}}{\frac{1,006 \text{ g MIL-101}}{1 \text{ mol MIL-101}}}$$

where N divided by Cr is the ratio between the number of nitrogen and chromium atoms measured by XPS. Note that the ratio of chromium to MIL-101 and the molecular weight of MIL-101 are those reported in the literature [108], except that a chloride is used instead of a fluoride when calculating the molecular weight.

5.5 Results and Discussion

MIL-101 [MIL-101 (UM)] was post-synthetically modified by attaching OA [MIL-101 (OA)] and ATPS [MIL-101 (ATPS)] to its CUSs with the goal of enhancing its suspension in hydrophobic solvents conducive to IP. To insure MIL-101 retained its structure, XRD was performed. The

XRD data (**Figure 28A**) illustrate that the crystalline structures of the modified MIL-101s remained unaffected by the modification procedure.

As a preliminary confirmation of modification, FTIR was used to investigate the samples. First, pure samples of OA and ATPS were measured to identify the most intense peaks. These data are shown in **Figure 29**. The most significant peaks for OA were formed at 2956, 2922 and $\sim 2853\text{ cm}^{-1}$. These peaks are attributable to alkyl C-H stretching [217]. For the ATPS, similar C-H stretching peaks at 2922 and 3026 cm^{-1} were detected. Additionally, peaks at 695 and 748 cm^{-1} were identified. **Figure 28B** shows that these same peaks were detected in the FTIR spectra of the modified samples of MIL-101. The enlarged portion of the spectra highlights these peaks. While this is indicative of modification, more conclusive evidence was found with XPS.

The XPS spectra strongly confirm the presence of OA and ATPS on MIL-101. Experimental and theoretical compositions of MIL-101 (UM), MIL-101 (OA) and MIL-101 (ATPS) are presented in **Figure 30**. The MIL-101 (UM) sample revealed that there was close to no water coordinated in the sample beyond the two waters that are intrinsic to the structure. This is attributed to the rigorous degassing. Nitrogen was detected in MIL-101 (UM), the only source of which could be DMF from the activation (see Section 3.3.1.1). Therefore, the theoretical calculation of MIL-101 (UM) includes stoichiometric values of carbon and oxygen based on the quantity of nitrogen measured. A similar treatment was applied to the theoretical values of MIL-101 (OA) and MIL-101 (ATPS), except that some of the nitrogen peak was attributable to OA and ATPS. OA and ATPS have carbon to nitrogen ratios of 8:1 and 770:1, respectively. The details of the carbon peak fits can be found in the Section 9.2.1. The difference between theoretical values calculated in this way and experimental values was less than 4.5 % for each element. This demonstrates that the changes in composition between the unmodified and modified samples can be directly linked to the stoichiometric ratios of OA and ATPS, supporting that these molecules are clearly present. This compositional data can be used as described in Section 5.4.2 to estimate a degree of modification of 69.7% for the MIL-101 (OA). A much smaller degree of modification of only 3.7 % was estimated for the MIL-101 (ATPS).

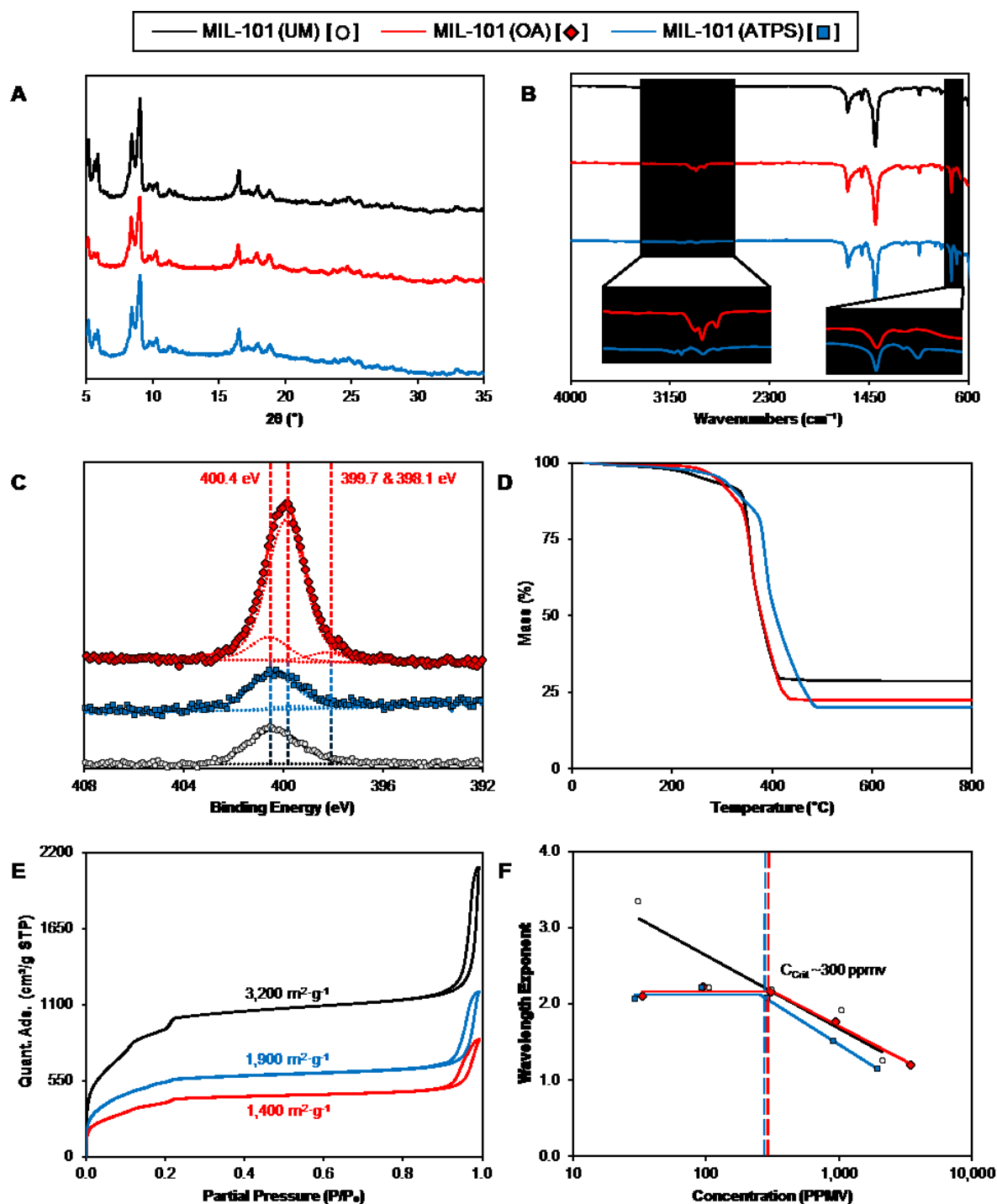


Figure 28. Characterisation of modified and unmodified MIL-101: (A) XRD, (B) FTIR, (C) XPS, (D) TGA, (E) nitrogen isotherm and (F) wavelength exponent in IsoPar G (IPG). Vertical lines highlight peak binding energies, peak transmission energies and the critical point of aggregation in (B), (C) and (F), respectively. BET surface areas are written on (E).

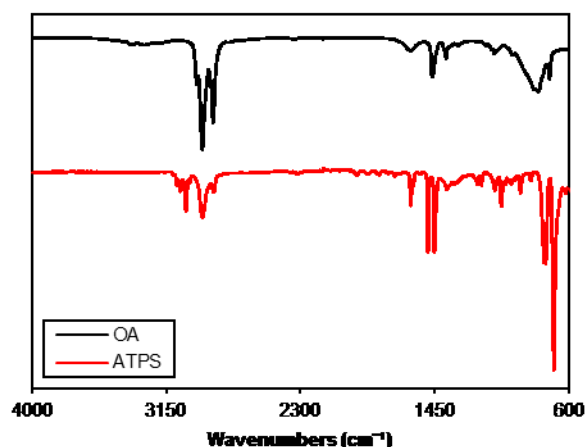


Figure 29. Fourier-transform infrared (FTIR) spectroscopy of 1-octylamine (OA) and amine terminated polystyrene (ATPS).

A closer investigation of the spectra in the N(1s) region (**Figure 28C**) confirms the coordination of OA and ATPS to the CUSs of MIL-101. The peak at 400.4 eV in the MIL-101 control is attributable to DMF [218]. This peak only accounts for a part of the total amine content in the modified samples, however. New peaks for MIL-101 (OA) and MIL-101 (ATPS) can be detected at 399.7 eV and 398.1 eV. Uncoordinated primary amines would have binding energies of at least 400.3 eV, whereas coordinated amines typically have binding energies between 399.7 – 400.0 eV. Thus, the peaks at 399.7 eV suggest that OA is coordinated to MIL-101. The smaller peak at 398.1 eV was a surprising necessity of the fit. This smaller peak at 398.1 eV could be deprotonated OA, which has been shown to be present during coordination of amines in previous studies [219].

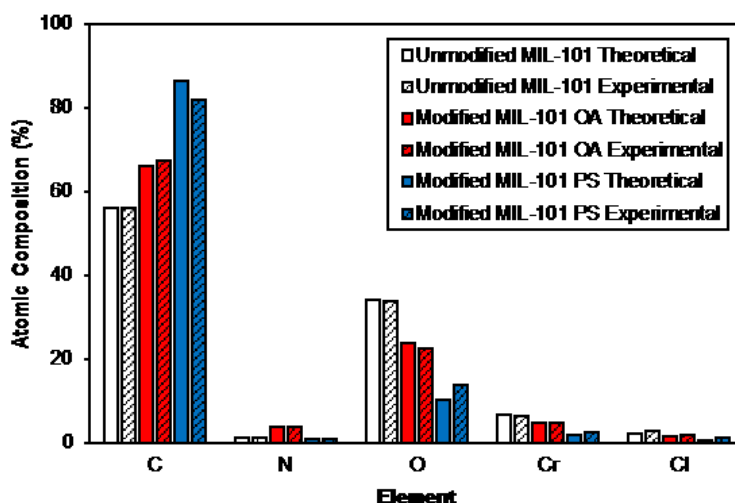


Figure 30. Theoretical and experimental elemental composition of MIL-101 (UM), MIL-101 (OA) and MIL-101 (ATPS) based on X-ray photoelectron spectroscopy (XPS) analysis.

The degree of modification can also be estimated by TGA. For easy comparison between samples, MIL-101 (UM), MIL-101 (OA) and MIL-101 (ATPS) are graphed in **Figure 28D**. Modified samples have a lower residual mass because OA and ATPS leave a negligible residual mass at 900 °C, as demonstrated by **Figure 31A**. Therefore, the difference in residual masses between the unmodified MIL-101 and modified MIL-101s corresponds to the quantity of ATPS or OA. Each sample was run between 4 and 5 times to perform a statistical analysis. **Figure 31B**, **Figure 31C** and **Figure 31D** show an average residual of 28.66 ± 0.19 , 22.43 ± 0.06 , and 20.11 ± 0.39 % for MIL-101 (UM), MIL-101 (OA) and MIL-101 (ATPS), respectively (95 % CI, n = 4 or 5). The upper bound of percent modification was calculated using the lower bound of residual mass of MIL-101 (UM) and upper bound of residual mass of the modified MIL-101. The lower bound of percent modification was calculated using the upper bound of residual mass of MIL-101 (UM) and lower bound of residual mass of the modified MIL-101.

The estimated degree of modification for MIL-101 (OA) measured via XPS was ~2 % different than that measured by TGA, $71.2 \pm 3.1\%$ (95 % CI, n = 4). These values are well within experimental error and consistent with other similar modifications [220]. Moreover, nitrogen sorption revealed a 58 % reduction in the BET surface area (**Figure 28E**). Even when the surface areas were mass-normalised to account for the OA, there was still a reduction in the BET surface area of 46 %. This decrease is attributed to the presence of OA inside the pores of MIL-101. Since XPS is a surface sensitive technique and TGA/BET analyses measure bulk properties, these data indicate that the modification occurred uniformly throughout the microporous structure of MIL-101.

In contrast to the MIL-101 (OA), the MIL-101 (ATPS) exhibited a surface-selective modification. The degree of modification measured via TGA was 1.4 ± 0.1 % (95 % CI, n = 4), 2.6 times smaller than that measured by XPS and well outside the range of experimental error. This suggests that there is a greater concentration of ATPS on the surface of the MIL-101 particle than in the bulk structure. Moreover, the mass-normalised BET surface area loss was only 17%, which is within the error of analysis for nitrogen sorption (**Figure 28E**). This is what one might expect from a molecule with a diameter of gyration as large as that of ATPS: 5.7 nm [214]. After all, it is much larger than the largest pore window diameter of MIL-101: 1.8 nm [108]. As a whole, these data demonstrate that it is possible to achieve surface-selective modification of a MOF through simple geometric considerations.

Figure 28F reveals that both modified compounds resulted in better-suspended MIL-101 in IPG, which has a dielectric constant of ~2. Instead of observing aggregation across the entire measured range, up to ~300 ppmv of MIL-101 could be suspended in IPG. Hence, these compounds look like the results presented in **Figure 27**, which predict a strong steric repulsive

force. However, it is notable that this theoretical approach predicts a larger energy barrier than many of the solvents presented in the last Chapter, even though the critical point of aggregation is not substantially larger. Therefore, even though this approach provides greater MIL-101 suspension in hydrophobic solvents, it is difficult to precisely predict that suspension *a priori*. Of course, even if the equation does work well, one must modify and characterise particles to determine the surface coverage. This requires significant experimental work anyway.

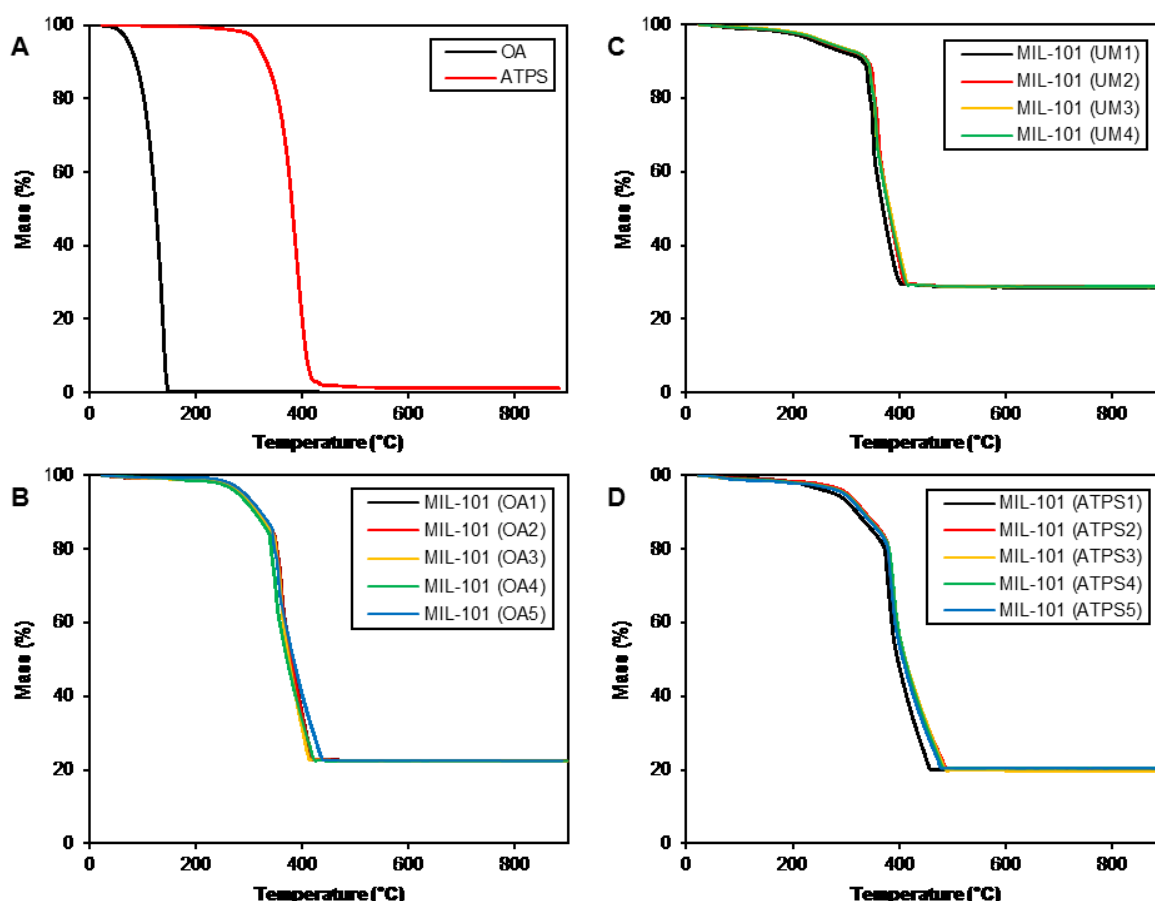


Figure 31. Thermogravimetric analysis (TGA) of (A) 1-octylamine (OA) and amine terminated polystyrene (ATPS), (B) MIL-101 (UM), (C) MIL-101 (OA) and (D) MIL-101 (ATPS).

Compared with a surfactant-driven suspension approach, this method of modification has several pragmatic advantages. The first advantage is that grafting mono-terminated amines to the CUSs of MIL-101 is not easily reversible, and is therefore more robust during processing and handling. Additionally, the product can be synthesised and modified at one facility and then readily shipped to another in a dry powder format for subsequent re-suspension. Finally, while not explored in this work, this modification approach could be valuable in a variety of applications [220]. While the MIL-101 (OA) is relatively hydrophobic throughout its pore structure, the MIL-101 (ATPS) has the interesting property of retaining MIL-101's natural

textural and chemical properties while generating a hydrophobic shell that actually allows the MIL-101 (ATPS) to float on water – an unusual phenomenon for a MOF so hydrophilic that it usually makes a crackling sound when added to water!

5.6 Conclusions and Future Work

In Chapter 4, the suspension of native MIL-101 in hydrophobic solvents was found to be impossible. To ameliorate this challenge, novel post-synthetic modifications were conducted on MIL-101 nanoparticles. Amine-terminated molecules were attached to MIL-101's CUSs. These molecules induced steric repulsion between MIL-101 particles in suspension, thus enabling uniform suspension of MIL-101 nanoparticles in a low dielectric constant solvent, IPG. Simple molecular geometry can be used to determine whether or not a molecule modifies the entirety of a MOF's pore structure or just targets the particle's envelope. This enables distinct and separate tuning of the MOF's surface envelope and pore properties via post-synthetic modification.

Although this technology could enable the successful application of MIL-101 to hydrophobic formulation systems requiring dilute quantities of MIL-101, it does not appear to be useful for the intended application of this thesis: TFN membrane formation. According to previous literature [75,76], 300 ppmv of MIL-101 in the organic phase should have a negligible impact on membrane performance, with most authors using twice that quantity. Given the complexity of producing such a product, a more significant loading in the organic phase would be required to justify its use. Thus, it was necessary to trial the use of alternative IP solvents, using the predictive capabilities generated in Chapter 4. The following chapter describes the successful use of a solvent with unique properties to resolve the aggregation dilemma.

6 A Novel Thin Film Nanocomposite Formation System

6.1 Abstract

Chapter 3 showed that reactive monomer adsorption and aggregation could significantly alter membrane performance. In particular, aggregation reduced membrane selectivity even at low MIL-101 loadings in the organic phase. In an attempt to mitigate these issues, nitrobenzene (NB) was used for the first time to make high-quality poly(piperazine trimesamide) thin film nanocomposite (TFN) membranes. For comparison, TFN membranes were also fabricated using *n*-hexane (HX). Similar to the poly(*m*-phenylenediamine trimesamide) TFN membranes presented in Chapter 3, poly(piperazine trimesamide) TFN membranes fabricated using HX demonstrated significant aggregation that reduced membrane selectivity. The membrane performance was even more stochastic than that observed in Chapter 3.

While MIL-101 aggregates on HX across the range measured, NB was found to create well-dispersed suspensions in concentrations as high as ~2,300 ppmv. Additionally, while MIL-101 adsorbed 95 % of the TMC in HX, it adsorbed only 19 % of the TMC in NB. NB made thin film composite (TFC) membranes with methanol (MeOH) permeances as high as $2.2 \pm 0.6 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ and disperse red (DR) rejections as high as $87.4 \pm 2.4 \%$ (95 % CI, $n = 4$). These preliminary data suggest that NB is a more optimal solvent for TFN membrane formation than HX as it mitigates reactive monomer adsorption and aggregation while simultaneously making high-quality TFC membranes.

TFN membranes were fabricated using NB under two reaction conditions, one leading to smoother membranes with a root mean square roughness of 8 nm and the other leading to rougher membranes with a root mean square roughness of 180 nm. When increasing the MIL-101 loading in the organic phase, the smoother membranes showed no changes in permeance or rejection, while the rougher membranes showed a 3.6-fold increase in permeance with negligible decrease in DR rejection. These data suggest that changing the interfacial polymerisation (IP) process to produce rougher membranes simultaneously enables filler materials to have a more significant impact on membrane performance. Finally, for rough TFN membranes, a lower rejection of a high molecular weight solute was observed when MIL-101 loadings exceeded the critical point of aggregation. Aggregates were also observed on the surface of these membranes using scanning electron microscopy (SEM). This establishes a clear relationship between aggregation and membrane performance.

6.2 Introduction and Background

The success of membrane technologies in aqueous applications is unequivocal. Large-scale reverse osmosis (RO) desalination plants provide clean water to large populations at a fraction of the energy expenditure it would take to use traditional thermal separations [58,221]. Additionally, nanofiltration has found a series of applications in water treatment, including contaminant removal from: wastewater, ground water, surface water and brackish water [20]. The equivalent technologies for organic solvents, including organic solvent reverse osmosis (OSRO) and organic solvent nanofiltration (OSN), have yet to find a dominant commercial application. However, their application is rapidly growing in the pharmaceutical, oil and gas, base chemical, consumer chemical and specialty chemical industries. Proposed application barriers to OSN and OSRO include the need for greater selectivity and permeance as well as better thermal, chemical and mechanical stability [6,9].

To those ends, there are many ongoing efforts aimed at enhancing membrane performance and stability. One promising effort is the emerging field of TFN membranes made via IP [1,29,30,62–65,75]. This concept was first introduced by Jeong et al. in 2007, who suspended zeolite in the organic phase prior to IP. Since then, researchers have successfully incorporated zeolite [1,30,62–65], silica [66], silver [28], titanium oxide [67], carbon nanotube [68], graphene [69], boron nitride [70], covalent organic framework [71], cyclodextrin [72], polyoctahedral oligomeric silsesquioxane [73,74] and MOF [75,76,85–87,77–84]. MIL-101 was the focus for this work as it has been shown to have the most significant OSN performance enhancement to date of any MOF [75].

While there are many promising results [29], the mechanism of membrane performance improvement is still poorly understood. Even in the seminal work, a permeance increase was observed with pore filled zeolite [1]. This indicates that there must be some secondary effects to filler incorporation, effects beyond that of the filler porosity. For example, secondary effects could arise from: alteration of the IP process, filler degradation [80], filler hydration, reactive monomer adsorption (see Chapter 3) and defect formation due to aggregation [62,63,65]. The latter two secondary effects are studied herein as they lead to a stochastic membrane formation process.

Alkanes, such as HX, are typically used during IP; nevertheless, this solvent induces aggregation that leads to defect formation and stochastic membrane performance (Chapter 3). Additionally, alkanes can enable the adsorption of a significant amount of TMC, affecting the ultimate membrane performance (Chapter 3). Higher dielectric constant solvents provide for better MIL-101 suspension (Chapter 4); however, many of these solvents have low octanol-water partition coefficients and/or functional groups that could react with acyl chlorides. The

former can lead to miscibility, TMC hydrolysis and unfavourable film formation conditions, while the latter would quench the reaction altogether. Solvents with nitro groups, while not without safety risks, are a unique solution to this problem. Particularly, NB is a promising solvent because it: has a dielectric constant of 35.7 [192]; is immiscible with water; has a high octanol-water partition coefficient [222]; and is non-reactive with acyl chlorides. NB may also have the additional benefit of reducing TMC adsorption because their chemical structures are so similar.

Poly(piperazine trimesamide) was chosen as the polymer of focus for this study because it is known to produce looser membranes that are more suitable to NF than the more widely studied poly(*m*-phenylenediamine trimesamide) [6].² The preponderance of poly(piperazine trimesamide) TFN membranes reported to date include their filler in the aqueous phase [69,70,83,87,89–94], which is a less conventional TFN membrane formation technique than including filler in the organic phase. Those who have reported using the conventional approach have either low effect sizes [170] or required special filler modification [171,172]. The majority of papers on poly(*m*-phenylenediamine trimesamide) TFN membranes made in the conventional manner show significant increase in permeance though [29]. One notable difference between poly(*m*-phenylenediamine trimesamide) and poly(piperazine trimesamide) TFC membranes is that the latter is known to have a much lower surface roughness than the former. This difference has been attributed to the relative reactivity of PIP and MPD [50] and local heat generation at the interface [45,113]. Perhaps these film formation factors play a role in the incorporation of filler particles during IP. To test this hypothesis, different reaction conditions can be used to form smooth and rough TFN membrane films. Then, changes in TFN membrane performance relative to the TFC membrane control can be compared.

6.3 Materials and Methods

6.3.1 Membrane Synthesis

6.3.1.1 Polyacrylonitrile (PAN) Support Membranes

Polyacrylonitrile (PAN) membranes were synthesised similar to previous work [34,35]. PAN (Copolymer [99.5 % AN/0.5 % MA], 50 μm powder, 230,000 $\text{g}\cdot\text{mol}^{-1}$, GoodFellow Cambridge Limited), dimethyl sulfoxide ($\geq 99.5\%$, AnalaR Normapur®, VWR) and 1,3-dioxolane (99.8 %, Anhydrous, Sigma-Aldrich) were weighed (PE 3600 DeltaRange®, Mettler) and combined in a 1:4:4 ratio using an overhead stirrer (Eurostar 20, IKA®) set to 400 rpm. After stirring for 24

² Poly(piperazine trimesamide) is not affected by *N,N*-dimethylformamide (DMF) activation [33], which was shown to produce stochastic results in Chapter 3. Additionally, non-activated poly(*m*-phenylenediamine trimesamide) membranes were shown to have ten times less methanol (MeOH) permeance than poly(piperazine trimesamide) membranes, with a statistically insignificant difference in rejection (see Section 9.3.1).

hours at 75 °C (MR Hei-Standard, Heidolph), the dope solution was filtered using a pressurised filtration cell (XX4004740, Merck) at no more than 20 bar of pressure under nitrogen (Research Grade, BOC) through a 41 µm (NY4104700, Merck) and then 11 µm (NY1104700, Merck) PET filter disk. The resulting dope has a viscosity of ~30,000 cP (Model 2020 Viscometer, Cannon Instrument Company®). Membranes were cast on a continuous casting machine (Continuous Casting Machine, SepraTek Membrane System) using a polyethylene terephthalate nonwoven support (RO Grade, Hirose) at a 4 rpm speed, 10 % nonwoven tension, 122 µm blade height, 14 °C water bath temperature, 19.8 ± 0.2 °C (95 % CI, n > 30) room temperature and 31.3 ± 0.1 % (95 % CI, n > 30) room relative humidity. The membrane was then submerged in DI water at 80 °C for 3 h [38], rinsed three times with room temperature DI water (Streamline® FilterPlus® Reverse Osmosis System, Varitech Systems) and dried at a 22.0 ± 0.1 °C (95 % CI, n > 30) room temperature and 36.4 ± 0.7 % (95 % CI, n > 30) room relative humidity.

6.3.1.2 Thin Film Composite and Thin Film Nanocomposite Membranes

TFC and TFN membranes were made similarly to those described in Chapter 4. Moreover, the MIL-101 synthesis method used was the same as that for all chapters. Exceptionally, NB was used as an organic phase for this study and TMC concentrations in the organic phase of 0.30 and 0.10 % (w/v) were used.

Membranes were labelled according to the following system:

AA-B.BB-CCC-D.DD

where ‘AA’ refers to the type of solvent used in the organic phase, ‘B.BB’ refers to the concentration of TMC used in the organic phase, ‘CCC’ refers to the type of membrane and ‘D.DD’ refers to the concentration of MIL-101 in the organic phase. **Table 5** lists all of the possible values. For example, a TFN membrane made using 0.10 % (w/v) of TMC and 0.15 % (w/v) MIL-101 in HX would be ‘HX-0.10-TFN-0.15’; and a TFC membrane made using 0.30 % (w/v) of TMC in NB would be ‘NB-0.30-TFC-0.00’.

Table 5. Membrane identification key.

AA	B.BB	CCC	D.DD
Organic Solvent	Trimesoyl Chloride (TMC) (% w/v)	Membrane Type	MIL-101 (% w/v)
Nitrobenzene (NB)	0.10	Thin Film Composite (TFC)	0.05
<i>n</i> -Hexane (HX)	0.30	Thin Film Nanocomposite (TFN)	0.10
			0.15
			0.20
			0.25

6.3.2 Membrane Fabrication Solution Characterisation

The critical point of aggregation was determined by measuring the wavelength exponent, as detailed in Chapter 4. Instead of the usual wavelength range, wavelengths between 800 and 1,100 nm were used for this work as this is a non-absorbing region for NB. TMC adsorption experiments were carried out in the same manner as those described in Chapter 3. While using UV-visible spectrophotometry to measure TMC in HX is possible, it is not for measuring TMC in NB because of the strong overlap in the lower UV-visible region.

Instead, reversed-phase high pressure liquid chromatography (HPLC, Agilent Series 1200, Agilent Technologies) was used. The HPLC was equipped with a UV detector and C18 column (ACE 5 C18-300, Hichrom Limited). The organic phase was made of a 20:80 ratio of tetrahydrofuran (HiPerSolv Chromanorm®, VWR) to isopropyl alcohol (IPA, HiPerSolv Chromanorm®, VWR), while the aqueous phase was pure water (HiPerSolve Chromanorm®, VWR). 0.10 % (v/v) trifluoroacetic acid (99 %, ReagentPlus®, Sigma-Aldrich) was added to both phases as a buffer. A 60 μL injection volume was used. An initial isocratic elution at 3:2 aqueous:organic ratio was used for 10 minutes, followed by a 20-minute-long gradient elution finalising at a 1:19 aqueous:organic ratio. The flow and temperature were set to 1 $\text{mL}\cdot\text{min}^{-1}$ and 30 $^{\circ}\text{C}$.

Prior to HPLC injection, TMC samples were reacted with 1-octylamine (OA, 99 %, Aldrich Chemicals) to make $\text{N}^1\text{-N}^3\text{-N}^5\text{-trioctylbenzene-1,3,5-tricarboxamide}$. This increased the molecule's size and hydrophobicity, thus enabling a clean separation of NB from the solute. 1 mL of sample was pipetted into a 10 mL vial and 9.34 μL of OA, a five-fold excess, was then added and stirred vigorously for 15 minutes. The solution became cloudy during this process. Then, the reacted sample was diluted tenfold with organic phase and stirred, during which time it became transparent.

6.3.3 Membrane Performance Characterisation

Membrane performance was evaluated in a crossflow membrane testing rig using the same conditions and testing methods as those detailed in Section 3.3. Pure solvent flux measurements were taken with acetone (Act, Technical Grade, VWR), MeOH (AnalaR Normapur®, VWR), ethanol (EtOH, absolute, GPR Rectapur®, VWR), IPA (2-Propanol, GPR Rectapur®, VWR) and DI water. The osmotic pressure was less than 0.2 % of the hydraulic pressure for all of the membranes measured here, even when accounting for the effects of concentration polarisation (CP). Details of the method of calculating CP can be found in the Section 9.3.5 and Section 1.3.3.1.

20 $\text{mg}\cdot\text{mL}^{-1}$ of *N*-ethyl-*N*-(2-hydroxyethyl)-4-(4-nitrophenylazo)aniline (DR, Disperse Red-1, 95 %, Aldrich) in MeOH was added to the rig. Concentrations were measured using a UV-visible

spectrophotometer with polystyrene cuvettes (PS Semi-Micro Disposable Cuvettes, BRAND GMBH + CO KG). (2-Hydroxypropyl)- γ -cyclodextrin (CD, ≥ 98.0 %, Wacker Chemie AG) was added to the rig at a separate time at 1.66 ± 0.07 g·L⁻¹ in MeOH. CD concentration was determined via HPLC with an evaporative light scattering detector (ELSD, Varian 385-LC, Agilent Technologies) and C18 column. An organic phase with a volumetric ratio of 4:1 acetonitrile (HiPerSolv Chromanorm®, VWR) to MeOH (HiPerSolv Chromanorm®, VWR) was used to isocratically elute the samples, using a 3:2 organic:aqueous ratio. A 30 μ L injection volume was used and the samples were run at 1 mL·min⁻¹ and 30 °C.

6.3.4 Physicochemical Membrane Characterisation

Prior to any physicochemical membrane characterisation, membranes were cleaned to insure all components analysed were integral to the membrane surface itself rather than an artefact. This was accomplished by rinsing in EtOH three times and then sonicating in EtOH at 37 hz, 20 – 50 °C, 100 % power for one hour in pulse mode. Finally, the membranes were rinsed three additional times in EtOH and left to dry in covered, ambient conditions. SEM, atomic force microscopy (AFM) and X-ray photoelectron microscopy (XPS) were used as described in Section 3.3. and Section 4.4., with the exception that 10 x 10 μ m areas were analysed using 512 point per line for AFM.

It is useful to calculate the volume fraction of MIL-101 present in the membrane. This requires normalising the chromium content to some other elemental quantity. If one attributes all of the oxygen peaks to the polyamide and MIL-101, it is possible to use the atomic ratio of chromium in the MIL-101 to oxygen in the polyamide to calculate the volume fraction of MIL-101 in the membrane (θ_M) as follows.

$$\psi = \frac{Cr \text{ atoms } Cr}{O - 5Cr \text{ atoms } O} \times \frac{\frac{1 \text{ molecule MIL-101}}{3 \text{ atoms } Cr}}{\frac{1 \text{ molecule PA}}{6.4 \text{ atom } O}} \times \frac{N_A}{N_A} \times \frac{M_M}{M_{PA}} \times \frac{\rho_{PA}}{\rho_M} \quad (41)$$

$$\theta_M = \frac{\psi}{1 + \psi} \quad (42)$$

where ψ is the volumetric ratio of MIL-101:PA in the membrane; Cr and O are the number of chromium and oxygen atoms measured by XPS, respectively; N_A is Avagadro's number (molecules·mol⁻¹); M_M and M_{PA} are the molecular weights (g·mol⁻¹) of MIL-101 and polyamide, respectively; and ρ_M and ρ_{PA} are the densities of MIL-101 and polyamide, respectively. Since the structure of MIL-101 is well-defined, the stoichiometric ratio of chromium to MIL-101 molecule (3:1), the molecular weight (1,006 g·mol⁻¹) and the density (0.62 g·mL⁻¹) are either calculable or already tabulated in the literature [108]. Note that 5 oxygens for each chromium are subtracted from the total oxygen content. This subtracts MIL-101's contribution to the

overall oxygen content, thus only leaving oxygen that is attributable to the polymer. The data in Section 9.2.1 validates the use of a 5:1 O:Cr ratio to normalise the quantity of oxygen.

The polyamide structure of the membrane is more poorly defined as various degrees of crosslinking are possible, as demonstrated in **Figure 4A**. Regardless, the density of poly(piperazine amide) was estimated based on the literature to be $\sim 1.2 \text{ g}\cdot\text{mL}^{-1}$ [45,223]. A number-weighted average could be used to estimate the molecular weight of a unit and the corresponding stoichiometric ratio of oxygen to PA. Assuming the most extreme form is a completely linear ($X = 0$) or completely crosslinked ($X = 1$) polymer, it is possible to estimate the degree of crosslinking from the O:N ratios. After normalising the oxygen content, the following equation can be applied:

$$X = \frac{2(2-O:N)}{1+O:N} \quad (43)$$

Note that this equation suggests that an O:N ratio of 1 would be 100 % crosslinking and an O:N ratio of 2 would be 0 % crosslinking. However, since these segments terminate with TMC, two of the acyl chloride groups are hydrolysed, generating an O:N ratio of 5:2. This explains why O:N ratios exceeding 2 are possible. It also highlights the underlying assumption of this equation: that the quantity of these terminal groups is negligible. This is only valid for highly crosslinked, high molecular weight polymers.

6.4 Results and Discussion

6.4.1 Thin Film Nanocomposite Membranes Formed with *n*-Hexane

For comparison with the NB system, TFN membranes were fabricated using the most common technique: by incorporating MIL-101 in an organic phase of HX. 0.10 % (w/v) TMC and 0.00 – 0.25 % (w/v) MIL-101. No discernible pattern could be ascertained from this membrane data set, as shown in **Figure 32A**. All HX-0.10-TFN membranes demonstrated large 95 % confidence intervals (95 % CI, $n = 4$) for permeance and rejection ($0.7 - 4.7 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and $10.4 - 33.0 \%$). This makes any possible mean differences in performance statistically insignificant. Regardless of statistical significance, it also appears that none of the membrane performance metrics correlate with MIL-101 loading in the HX or polyamide phase. The MIL-101 loading linearly increases up to $\sim 15 \%$ (v/v) in the membrane at 0.15 % (w/v) MIL-101 loading in the HX phase ($R^2 = 0.996$). Nevertheless, it suddenly drops to $\sim 10 \%$ (v/v) and then goes back up to $\sim 15 \%$ (v/v) for the HX-0.10-TFN-0.20 and HX-0.10-TFN-0.25 samples, respectively.

As a whole, the performance data could be the result of a stochastic membrane formation process driven by aggregate formation. This is evidenced by the drop in DR rejection relative to the TFC membrane control and SEM imaging. The TFC membrane control exhibited a

reasonable permeance and rejection of $4.9 \pm 0.2 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ and $95.7 \pm 4.8 \%$ (95 % CI, $n = 4$), respectively. However, the rejection dropped to mean values between 40.7 and 76.4 % for all TFN membranes. Moreover, aggregate formation was confirmed via the SEM imaging presented in **Figure 33**. The TFC membrane control presents a typical poly(piperazine trimesamide) film [45] with a low root means square roughness of 9 nm (see Section 9.3.2). On the other hand, the HX-0.10-TFN membranes all have aggregates that are greater than one micron in diameter.

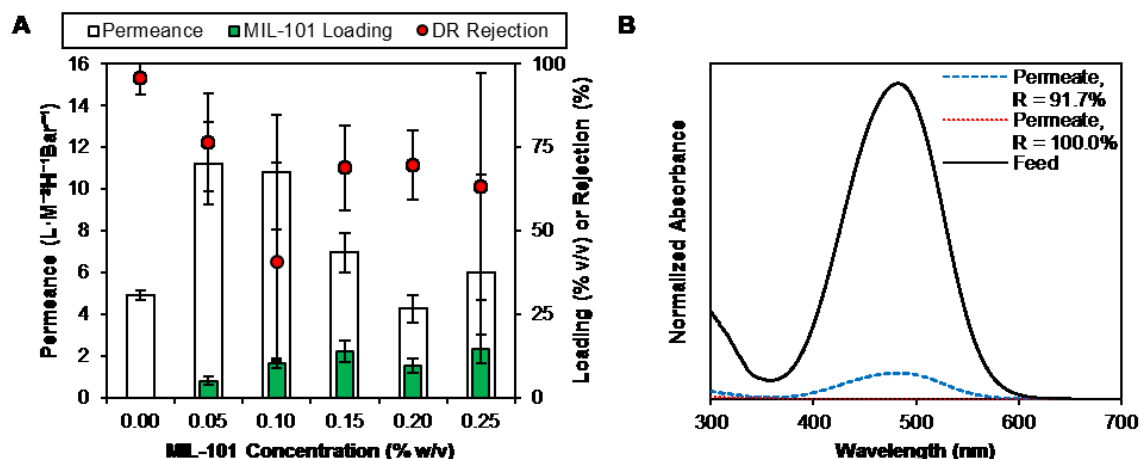


Figure 32. (A) Methanol (MeOH) permeance and disperse red (DR) rejection of thin film composite (TFC) and thin film nanocomposite (TFN) membranes synthesised using 0.10 % TMC and 0.00 – 0.25 % MIL-101 in an *n*-hexane (HX) organic phase. Error bars represent a 95 % confidence interval ($n = 4$). (B) UV-Visible spectra of DR in MeOH.

Most poly(piperazine trimesamide) membranes are reported to have O:N ratios between 1.1 and 1.3 [45,69,83,87,94] and use PIP:TMC mass ratios between 1.75 and 10. For ratios outside this range, O:N ratios exceeding 2.0 are found [171,224]. Diverging from a certain range of reactive monomer ratios encourages the formation of low molecular weight polymer segments [36,37], which explains these high O:N ratios. However, despite the relatively high ratio of PIP to TMC used in this study (20:1), an O:N ratio of 1.3 ± 0.0 (95 % CI, $n = 4$) was found. This value is towards the higher end of other high-quality membranes, which makes sense given the ratio of reactants used. The rest of the XPS data for the HX-0.10-TFN membrane set are included in **Table 6**, along with the data for the PAN support membrane. As described in previous studies for both zeolites [62,63] and ZIF-8 [86], the O:N ratio appears to go up with increasing filler concentration in the HX phase. Indeed these values seem highly correlated ($R^2 \sim 0.9$) and the change is statistically significant, increasing to values as high as 1.8 ± 0.2 (95 % CI, $n = 4$). This suggests that the HX-0.10-TFN-0.25 membrane is weakly crosslinked. Perhaps this is a result of aggregates disrupting the membrane formation process.

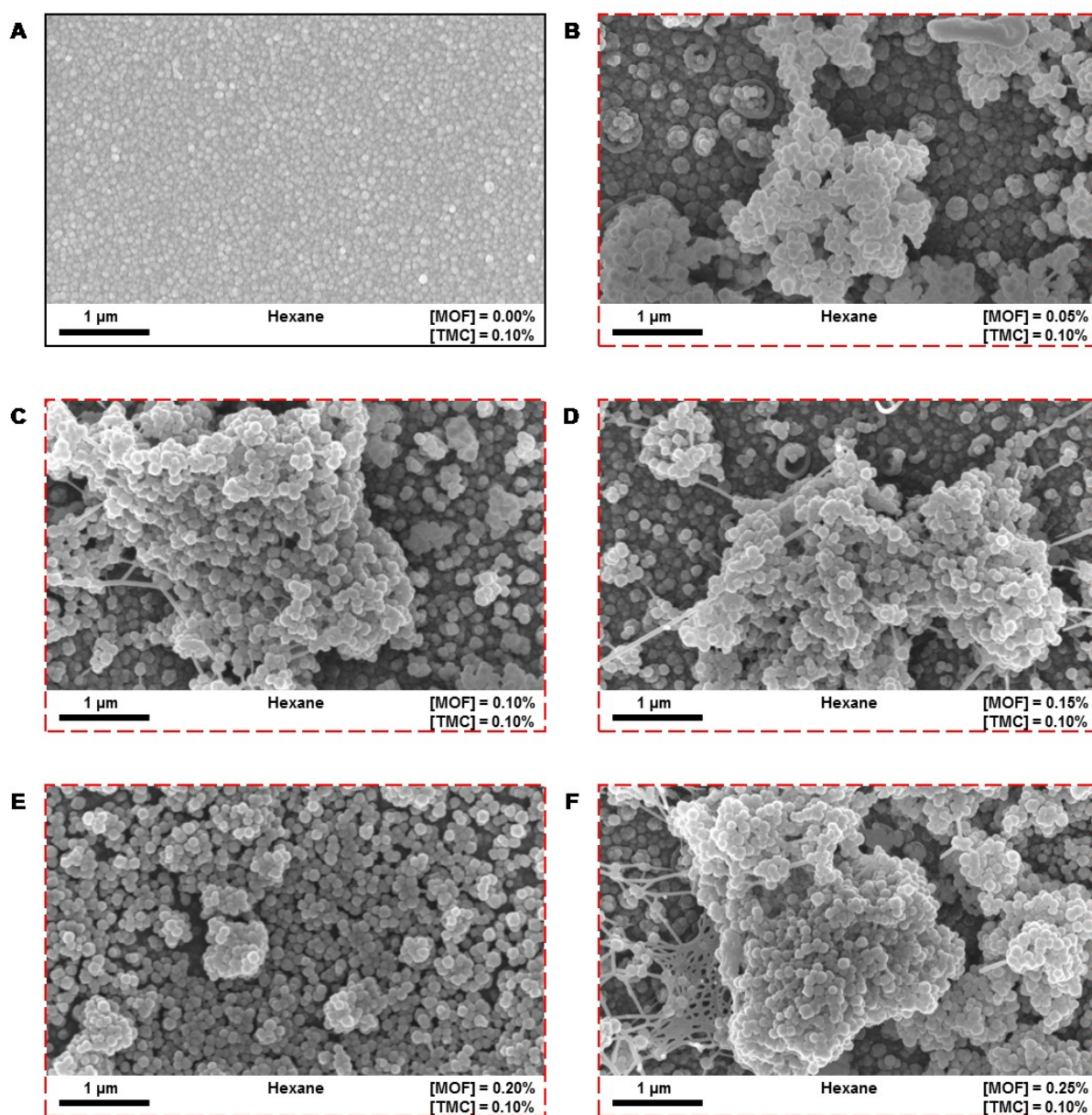


Figure 33. Scanning electron microscopy (SEM) imaging of thin film composite (TFC) and thin film nanocomposite (TFN) membranes synthesised using 0.10 % TMC and 0.0 – 0.25 % MIL-101 (A – F, respectively) in an *n*-hexane (HX) organic phase. Images outlined in red show aggregation.

Interestingly, the poly(*m*-phenylenediamine trimesamide) TFN membranes in Chapter 3 had decreasing rejection with increasing MIL-101 concentration in the HX phase. This was attributed to aggregate formation. Although the poly(piperazine trimesamide) TFN membrane set shares the issues of aggregates leading to defect formation, the lack of a clear trend seems specific to the chemistry. Perhaps this is why previous researchers resorted to less conventional techniques to incorporate fillers into poly(piperazine trimesamide) TFN

membranes [69,70,83,87,89–94]. Before determining the root cause of this behaviour, the aggregation issue must be resolved.

Table 6. Membrane composition data from X-Ray Photoelectron Spectroscopy (XPS) for the polyacrylonitrile (PAN) support membrane, HX-0.10-TFC-0.00 membrane and HX-0.10-TFN membrane set. O:N and O:Cr ratios are normalised to account for MIL-101 content. 95 % confidence intervals (n = 4) are shown.

Membrane	C	N	O	Cr	O:Cr	O:N
PAN Support	76.7 ± 1.3	20.6 ± 1.2	2.8 ± 0.4	0.0 ± 0.0	-	0.1 ± 0.0
HX-0.10-TFC-0.00	70.7 ± 0.7	12.8 ± 0.5	16.5 ± 0.3	0.0 ± 0.0	-	1.3 ± 0.0
HX-0.10-TFN-0.05	70.3 ± 0.3	12.1 ± 0.2	17.5 ± 0.3	0.1 ± 0.0	160 ± 42	1.4 ± 0.0
HX-0.10-TFN-0.10	70.6 ± 1.2	11.2 ± 0.3	18.0 ± 1.4	0.2 ± 0.0	78 ± 11	1.5 ± 0.1
HX-0.10-TFN-0.15	71.2 ± 1.1	10.8 ± 0.6	17.7 ± 0.6	0.3 ± 0.1	54 ± 13	1.5 ± 0.0
HX-0.10-TFN-0.20	70.6 ± 1.2	11.0 ± 0.1	18.2 ± 1.3	0.2 ± 0.0	84 ± 15	1.6 ± 0.1
HX-0.10-TFN-0.25	69.4 ± 0.6	10.3 ± 0.7	20.0 ± 1.0	0.3 ± 0.1	56 ± 18	1.8 ± 0.2

6.4.2 Eliminating Aggregation with Nitrobenzene

As opposed to evaluating aggregation via membrane performance, it is faster, less costly and more accurate to use a technique that directly evaluates the solution precursors used for membrane formation. To these ends, suspensions of MIL-101 in NB were made from ~100 to ~30,000 ppmv and compared with suspensions of MIL-101 in HX via UV-visible spectrometry, as presented in **Figure 34**.

The representative sloping curve produced by 3000 ppmv MIL-101 in NB presented in **Figure 34A** is very typical of this technique. Indeed, NB created similar curves across the entire range studied. From these data, the wavelength exponent was calculated and it was determined that the critical point of aggregation is ~0.14 (w/v) (~2300 ppmv) for MIL-101 in NB, as shown in **Figure 34B**.

No such plot could be produced to determine the critical point of aggregation for HX. Indeed, HX showed random data over the entire range of concentrations studied, as typified by the ~3000 ppmv of MIL-101 in HX data shown in **Figure 34A**. The random data produced by MIL-101 in HX occurs because of rapid settling (<30 seconds), as shown in the photographs in **Figure 34A**. As aggregates rapidly settle out during the measurement, the absorbance takes a downward turn, which causes a drop in measured concentration and, therefore, absorption. These data confirm that MIL-101 aggregates in HX over the entire range studied and that NB is a superior solvent for suspension.

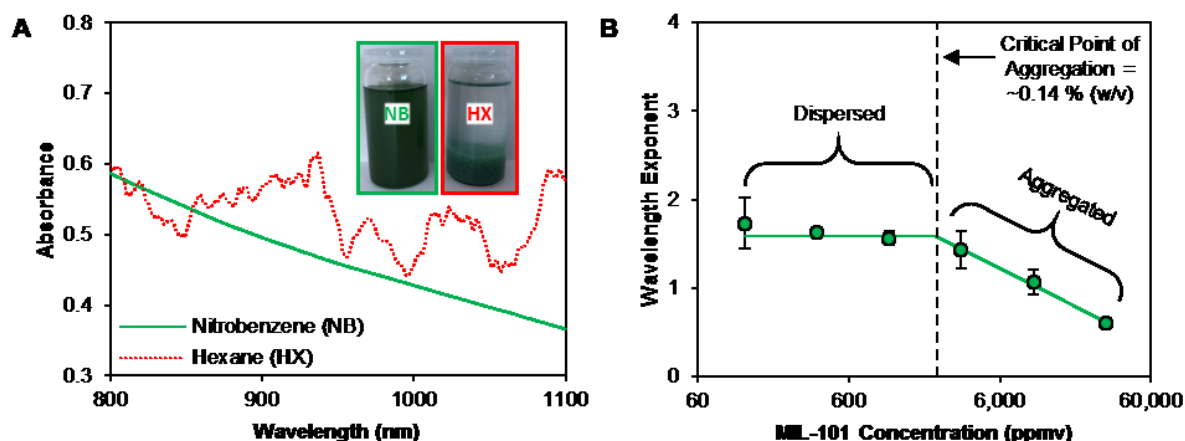


Figure 34. (A) Representative UV-visible spectra and corresponding photos taken after 30 s of MIL-101 suspension in *n*-hexane (HX) and nitrobenzene (NB). (B) Wavelength exponent plot of MIL-101 in NB with a vertical line at the critical point of aggregation.

6.4.3 Mitigating Reactive Monomer Adsorption with Nitrobenzene

Since it was established in Chapter 3 that reactive monomer adsorption could significantly affect TFN membrane formation, another interesting aspect of NB is that it mitigates TMC adsorption onto MIL-101. Though TMC concentration can be measured in HX using UV-visible spectrometry, as shown in **Figure 35C**, a more complex technique detailed in the methods was used to determine TMC concentration in NB. After the reaction detailed in **Figure 35A**, samples could be diluted and run on the HPLC. **Figure 35B** shows that the HPLC method proved effective at determining TMC concentration. The clean chromatogram and linear calibration curve ($R^2 = 0.99$) indicate that the TMC completely reacted to form $N^1-N^3-N^5$ -trioctylbenzene-1,3,5-tricarboxamide because there would likely be additional peaks or a non-linear calibration if a partial reaction occurred. The high yield of reaction is expected given the excess OA used, OA's nucleophilicity and the reactivity of TMC.

Figure 35D shows the TMC loading of MIL-101 in HX (calculated from **Figure 14B**) and NB (measured) at an equilibrium TMC concentration of 0.07 % (w/v) TMC. MIL-101 adsorbs 65 % less TMC in NB compared to HX. This difference becomes even more significant when considering that previous reports required 0.40 % (w/v) MIL-101 to get the same two-fold increase in permeance exhibited by the 0.15 % (w/v) MIL-101 TFN membrane sample in Section 6.4.5 [75]. This was explored by adding 0.40 % (w/v) MIL-101 to 0.10 % (w/v) TMC in HX. A greater than 90 % decrease in TMC was observed at equilibrium. Comparatively, adding 0.15 % (w/v) MIL-101 into 0.10 % (w/v) TMC in NB reduces the equilibrium TMC concentration by 20 %. This is close to the 15 % (w/v) reduction in TMC concentration at equilibrium observed when 0.40 % (w/v) Linde Type A Zeolite was added to 0.10 % (w/v) TMC in HX. This zeolite concentration was previously shown to increase permeance two-fold [1]. The pore

window diameter of the zeolite, ~ 0.4 nm [225], is significantly less than the van der Waals diameter of TMC, 0.7 nm [109]. Thus, adsorption throughout the zeolite's porous network is unlikely. The reduction in TMC could be due to adsorption of the TMC onto the zeolite particle's envelope or defects. In the case of MIL-101, TMC likely adsorbs throughout the pore network, as it has large pore window diameters (1.2 and 1.6 nm [108]).

In Chapter 3, a ~ 40 % decrease in TMC concentration led to a ~ 20 % difference in membrane permeance. Therefore, it is possible that a 15 - 20 % reduction in TMC does not cause a dramatic impact on membrane performance. However, it is unlikely that the greater than 90 % reduction in TMC seen for MIL-101 in HX has no effect. Since equilibrium occurs on a timescale of ~ 120 minutes (see Chapter 3), it is difficult to tell what TMC concentration is present in a sample during IP until equilibrium has been achieved. This is no trivial matter because random TMC concentrations in the organic phase should result in stochastic, sub-optimal membrane performance.

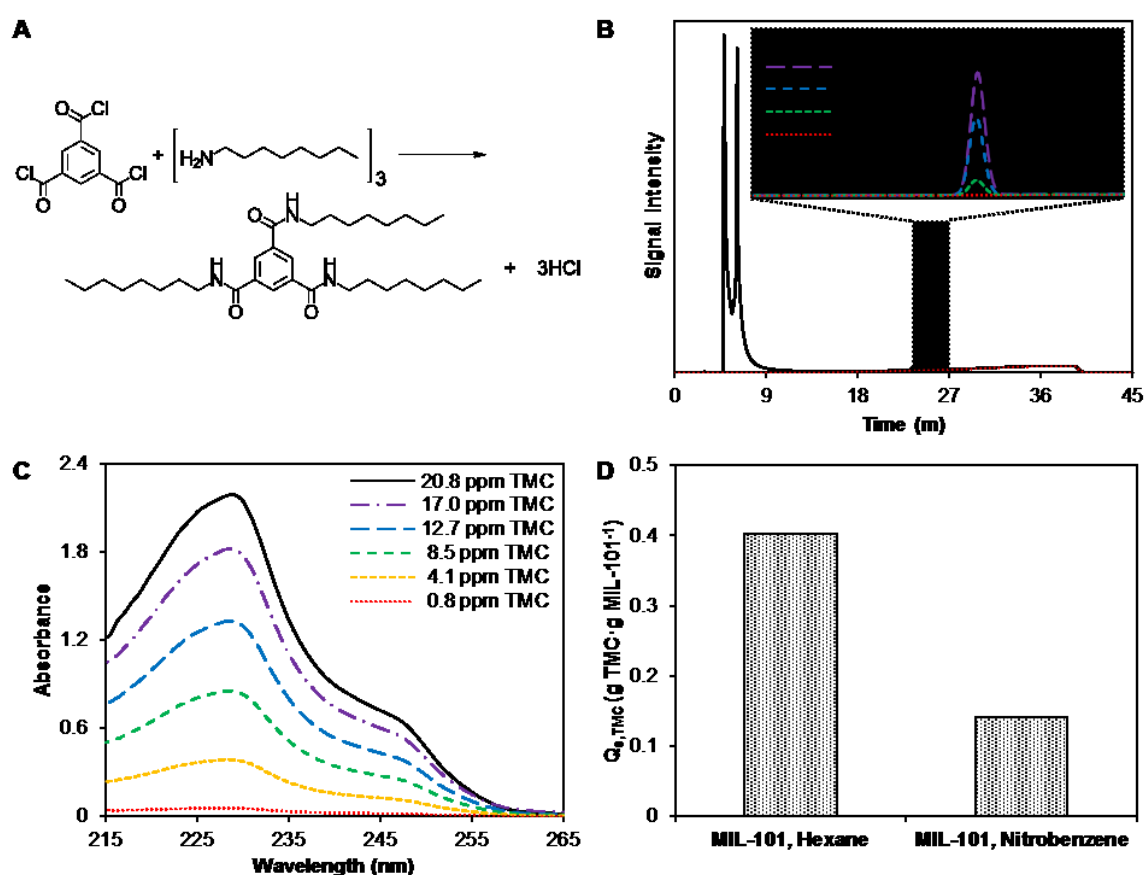


Figure 35. (A) Trimesoyl chloride (TMC) and 1-octylamine (OA) reacting to form N¹-N³-N⁵-trioctylbenzene-1,3,5-tricarboxamide. (B) Representative HPLC spectra of TMC in nitrobenzene (NB). (C) Representative UV-visible spectra of TMC in *n*-hexane (HX). (D) Quantity of TMC adsorbed at an equilibrium concentration of 0.07 % (w/v) TMC.

6.4.4 Smooth Thin Film Nanocomposite Membranes Formed with Nitrobenzene

After quantifying NB's impact on aggregation and reactive monomer adsorption with solution-phase measurements, membranes were fabricated to see how these factors affect the ultimate membrane performance. To those ends, NB was substituted for HX to make a new TFC membrane control. 0.30 % (w/v) TMC was used and all other variables were held constant. The membrane permeance and rejection, illustrated in **Figure 36**, was $1.3 \pm 0.1 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ and $95.6 \pm 1.4 \%$ (95 % CI, $n = 4$). While this is a statistically insignificant change in rejection relative to the HX-0.10-TFC-0.00 membrane, it is a lower permeance membrane. Solvent permeance reduced from 4.9 ± 0.2 to $1.3 \pm 0.1 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ (95 % CI, $n = 4$) and solute permeance reduced from 1.1 ± 1.3 to $0.4 \pm 0.2 \times 10^{-6} \text{ m} \cdot \text{s}^{-1}$ (95 % CI, $n = 4$). This does fit well with what is known about IP. PIP should have a partition coefficient between NB and water that is larger than that between HX and water [37,49]. Additionally, according to Stokes Law, piperazine should have a 6.1 times lower diffusivity in NB compared to HX because of the relatively higher viscosity of NB [192]. A lower diffusivity and higher partition coefficient for the reactive diamine has been correlated with lower solvent permeance [49]. This seems to hold true for this system. Crosslinking is likely playing a role in the performance differences observed here. The NB-0.30-TFC-0.00 has a $1.0 \pm 0.1 \text{ O:N}$ ratio (95 % CI, $n = 4$), as shown in **Table 7**. This suggests a significantly higher degree of crosslinking when compared to the HX-0.10-TFC-0.00.

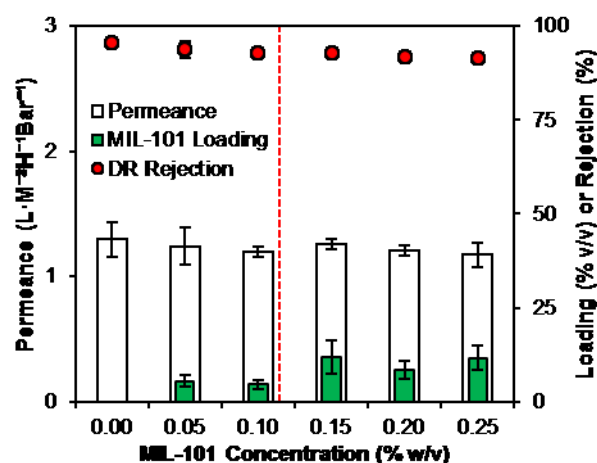


Figure 36. Methanol (MeOH) permeance and disperse red (DR) rejection of thin film composite (TFC) and thin film nanocomposite (TFN) membranes synthesised using 0.30 % TMC and 0.00 – 0.25 % MIL-101 in a nitrobenzene (NB) organic phase. The red, vertical line denotes the critical point of aggregation for MIL-101 in NB (0.14 % (w/v)). Error bars represent a 95 % confidence interval ($n = 4$).

Table 7. Membrane composition data from X-Ray Photoelectron Spectroscopy (XPS) for the NB-0.30-TFC-0.00 membrane and NB-0.30-TFN membrane set. O:N and O:Cr ratios are normalised to account for MIL-101 content. 95 % confidence intervals (n = 4) are shown.

Membrane	C	N	O	Cr	O:Cr	O:N
NB-0.30-TFC-0.00	73.1 ± 1.0	13.3 ± 1.1	13.7 ± 0.3	0.0 ± 0.0	-	1.0 ± 0.1
NB-0.30-TFN-0.05	72.1 ± 0.9	12.8 ± 0.6	14.8 ± 0.2	0.2 ± 0.1	124 ± 41	1.1 ± 0.1
NB-0.30-TFN-0.10	72.8 ± 0.4	13.0 ± 0.3	14.2 ± 0.4	0.1 ± 0.0	151 ± 43	1.1 ± 0.0
NB-0.30-TFN-0.15	71.8 ± 1.8	11.9 ± 0.5	15.9 ± 1.9	0.4 ± 0.1	58 ± 24	1.2 ± 0.1
NB-0.30-TFN-0.20	71.4 ± 0.6	12.7 ± 0.2	15.8 ± 0.4	0.2 ± 0.1	82 ± 27	1.2 ± 0.0
NB-0.30-TFN-0.25	73.9 ± 0.7	11.5 ± 0.7	14.3 ± 0.2	0.2 ± 0.1	58 ± 17	1.1 ± 0.0

The focus of this work is the resulting impacts of NB on TFN membrane formation. Performance data in **Figure 36** shows a slight rejection decrease is correlated with increased MIL-101 concentration in the NB phase ($R^2 \sim 0.9$). This decrease is close to the margin of error for the measurement, however. The first sample to have a statistically significant lower rejection than the NB-0.30-TFC-0.00 membrane control is the NB-0.30-TFN-0.10 membrane, which has a 2.6 % lower mean rejection. Note that 95 % confidence intervals are as high as ± 2.3 % for certain membranes. The rejection remains statistically insignificantly different with increased MIL-101 loadings from thereon. This conclusion remains unchanged when accounting for CP, showing a decrease of 96 ± 1 to 94 ± 1 % (95 % CI, n = 4) from the NB-0.30-TFC-0.00 to the NB-0.30-TFN-0.10 membrane. Again, 95 % confidence intervals were as high as ± 2 % for certain membranes.

The XPS data in **Table 7** gives little additional insight. The amount of MIL-101 remains 5 ± 0 % (95 % CI, n = 8) for the NB-0.30-TFN-0.05 and NB-0.30-TFN-0.10 membranes and then jumps to 11 ± 2 % (95 % CI, n = 12) for the rest of the NB-0.30-TFN membranes. The degree of crosslinking follows a similar trend, with O:N ratios being ~ 1.1 on average for the NB-0.30-TFN-0.05 and NB-0.30-TFN-0.10 membranes and ~ 1.2 on average for the rest of the NB-0.30-TFN membranes. While there is a mean increase in O:N ratios for the NB-0.30-TFN-0.05 and NB-0.30-TFN-0.10 membranes relative to the NB-0.30-TFC-0.00 membrane control, it is not statistically significant. For higher MIL-101 loadings, the increase is statistically significant, with mean sample set differences between 0.1 and 0.2 and 95 % confidence intervals as high as 0.1. However, the changes being measured between sample sets approach the variation within a sample set. Overall, it appears that there is some compositional difference between the two distinct regions separated by the critical point of aggregation, which is ~ 0.14 % (w/v). This could be related to aggregate incorporation.

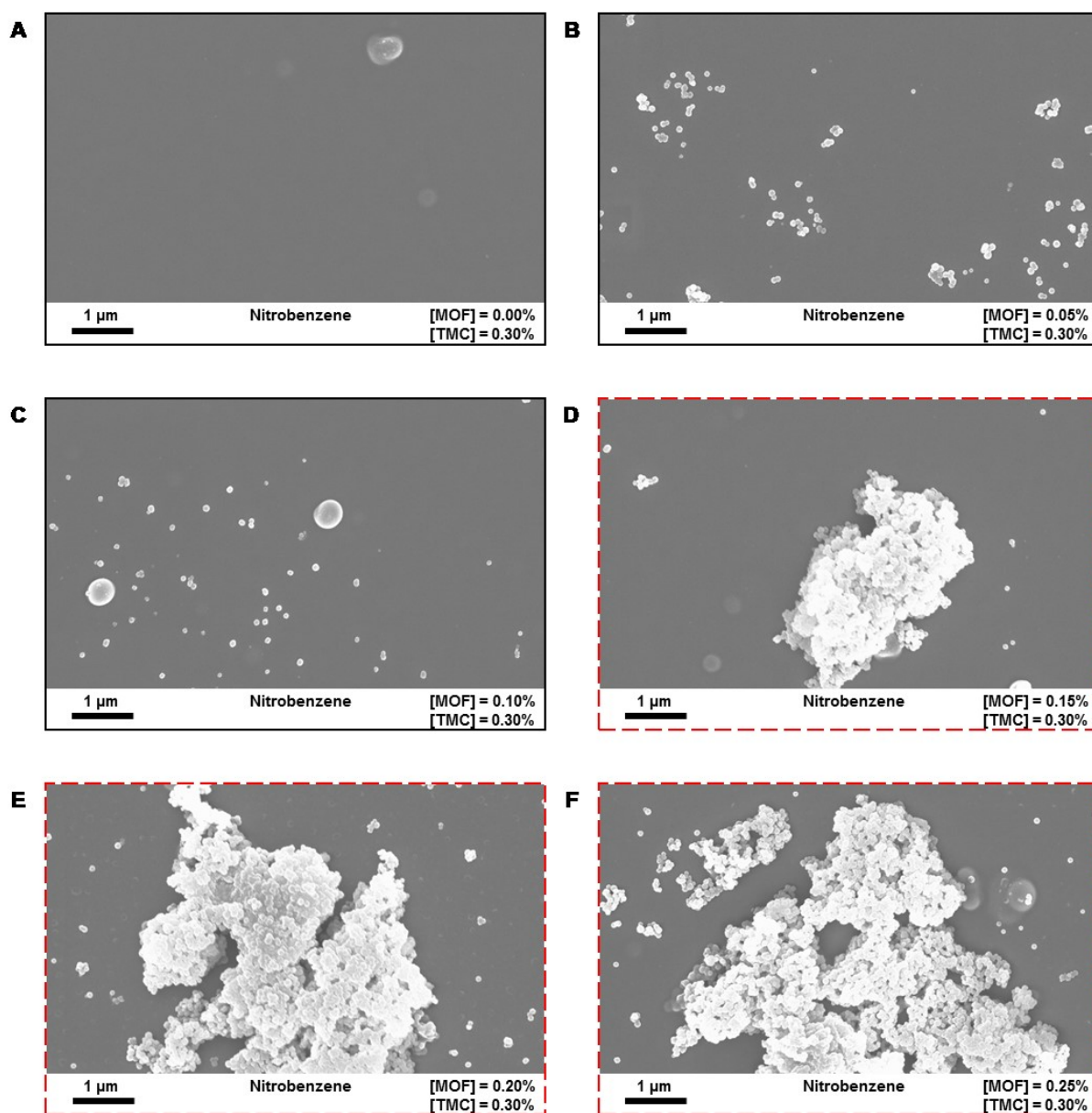


Figure 37. Scanning electron microscopy (SEM) imaging of thin film composite (TFC) and thin film nanocomposite (TFN) membranes synthesised using 0.30 % TMC and 0.0 – 0.25 % MIL-101 (A – F, respectively) in a nitrobenzene (NB) organic phase. Images outlined in red show aggregation.

The representative SEM images gathered and presented in **Figure 37** clearly show aggregates of MIL-101 on the membrane surface at MIL-101 concentrations exceeding the critical point of aggregation. The NB-0.30-TFN-0.15 sample, on the threshold of the critical point of aggregation, qualitatively had smaller aggregates on average than the NB-0.30-TFN-0.20 and NB-0.30-TFN-0.25 samples. At the lower concentrations of MIL-101 used for the NB-0.30-TFN-0.05 and NB-0.30-TFN-0.10 membranes, there are few MIL-101 particles on the membrane's surface and most appear to be well-dispersed. This seems to correlate well with

the aforementioned XPS results, where small amounts of MIL-101 were detected on the samples with lower MIL-101 loadings. These results also seem to corroborate the solution-phase measurements of MIL-101 aggregation.

These data seem to suggest that poly(piperazine trimesamide) TFN membranes made via incorporation of filler in the organic phase have two type of membrane archetypes, neither of which are particularly helpful for membrane performance. When the filler is well dispersed or aggregation is mitigated, few statistically significant changes to the membrane performance are observed with increased MIL-101 loadings. When aggregation is severe, as was the case with the HX-0.10-TFN membrane set, a reduction in rejection and stochastic performance is observed. While these data are inconsistent with reports on poly(*m*-phenylenediamine trimesamide) TFN membranes, they do explain why the majority of reported poly(piperazine trimesamide) TFN membranes are made via filler inclusion in the aqueous phase [69,70,83,87,89–94].

To successfully form poly(piperazine trimesamide) TFN membranes with good performance, understanding these phenomena are critical. To verify that the observed membrane performance behaviour to date was not somehow caused by MIL-101 degradation, samples were subjected to various stages of the IP process were examined. MIL-101 retained its crystalline structure throughout and no signs of degradation were observed (see Section 9.3.6). Since the only clear difference between poly(*m*-phenylenediamine trimesamide) and poly(piperazine trimesamide) TFN membranes is surface roughness, making rougher poly(piperazine trimesamide) membranes may be of interest to explore.

6.4.5 Rough Thin Film Nanocomposites Formed with Nitrobenzene

There is still debate on the cause of membrane surface roughness greater than 50 nm. However, for this work, it is more important that the surface roughness of TFC membranes made with NB can be controlled by changing the concentration of TMC used during IP. As detailed in the Section 9.3.3, membranes with a root mean square roughness of ~8 nm are fabricated at TMC concentrations greater than 0.30 % (w/v). A maximum root mean square roughness is achieved at 0.10 % (w/v), and this roughness decreases at lower TMC concentrations. Thus, TFN membranes with a root mean square roughness of ~180 nm (see Section 9.3.2) were fabricated using 0.10 % (w/v) NB and their performances were evaluated. The data is summarised in **Figure 38A**.

The TFC membrane control exhibited a solvent permeance, solute permeance and rejection of $2.2 \pm 0.6 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$, $2.1 \pm 0.6 \times 10^{-6} \text{ m} \cdot \text{s}^{-1}$ and $87.4 \pm 2.4 \%$ (95 % CI, $n = 4$), respectively. Compared with the TFC membrane control made from 0.30 % TMC, this is a statistically significantly higher permeance and lower rejection. The cause of this difference in

performance is not entirely clear. The O:N ratio of the NB-0.10-TFC-0.00 membrane is not significantly different to that of the NB-0.30-TFC-0.00 membrane, as shown in **Table 8**, with a mean normalised O:N ratio of 1.1 ± 0.0 (95 % CI, $n = 4$). Given what is known about IP dynamics, one might expect a thicker film given the reduction in TMC concentration [50]. However, a thicker film would reduce permeance. With other options ruled out, it seems that the increase in permeance is most probably related to surface roughness. After all, rougher films have higher permeance by generating higher real film area per area of observed membrane surface [45].

The membrane performance trends for the NB-0.10-TFN membranes with MIL-101 loadings of up to 0.15 % (w/v) typify those previously reported for poly(*m*-phenylenediamine trimesamide) TFN membranes made with HX [1,69,75]. At 0.10 % (w/v) MIL-101, the mean membrane permeance increased by a factor of 1.9 relative to the TFC membrane control, a statistically significant difference. While the permeance increased with diminishing returns up to 0.15 % (w/v), differences in DR rejection remained statistically insignificant. Membrane permeance linearly increases with increasing MIL-101 concentration in the NB phase up to 0.10 % (w/v) MIL-101 ($R^2 = 0.998$). For the first time, these data demonstrate that membrane formation conditions that cause rougher polyamide TFC membrane surfaces substantially enhance the impact of filler incorporation on the ultimate membrane formation. With the data available, one can only speculate about the root cause of this phenomenon. It is likely to be fundamentally related to the mechanism of film formation. There may also be an element simply of geometric consideration. Perhaps thin, smooth films cannot properly incorporate particles while rough, thick films can (see Section 9.3.4). For now, it is of interest to relate the MIL-101 loading to performance data to explore the relationship between aggregation, IP conditions and membrane performance.

As shown in **Figure 38A**, the MIL-101 concentration in the polyamide film increases linearly ($R^2 = 0.999$) up to 14 % (v/v) with the incorporation of MIL-101 of up to 0.10 % (w/v) in the NB phase. However, MIL-101 incorporation into the membrane is entirely independent ($R^2 = 0.025$) of MIL-101 loading in the NB phase between concentrations of 0.15 and 0.25 % (w/v). The first point of interest is that the MIL-101 loading in the membrane is substantially higher than that suspended on a volumetric basis, suggesting that MIL-101 partitions towards the NB-water interface. Because MIL-101 has a very low contact angle [226], it will likely strongly adsorb to the NB-water interface [227]. It is possible that there might be diminishing increases to MIL-101 concentration at the interface with increasing bulk MIL-101 concentrations [228,229], particularly between 0.10 and 0.25 % (w/v) MIL-101 loading in the NB phase. This could also be compounded by aggregation. While this would explain there being a statistically significant increase in MIL-101 loading in the membrane past a MIL-101 loading of 0.10 %

(w/v) in the NB phase, further measurements would need to be conducted to confirm this explanation.

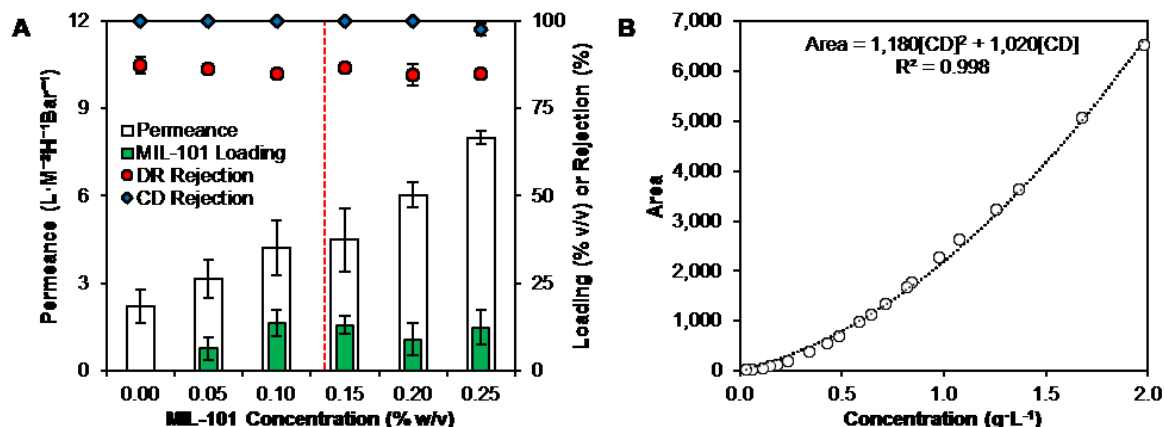


Figure 38. (A) Methanol (MeOH) permeance, disperse red 1 (DR) rejection and (2-Hydroxypropyl)- γ -cyclodextrin (CD) rejection of thin film composite (TFC) and thin film nanocomposite (TFN) membranes synthesised using 0.10 % TMC and 0.00 – 0.25 % MIL-101 in a nitrobenzene (NB) organic phase. The red, vertical line denotes the critical point of aggregation for MIL-101 in NB (0.14 % (w/v)). Error bars represent a 95 % confidence interval ($n = 4$). (B) CD calibration curve.

Table 8. Membrane composition data from X-Ray Photoelectron Spectroscopy (XPS) for the NB-0.10-TFC-0.00 membrane and NB-0.10-TFN membrane set. O:N and O:Cr ratios are normalised to account for MIL-101 content. 95 % confidence intervals ($n = 4$) are shown.

Membrane	C	N	O	Cr	O:Cr	O:N
NB-0.10-TFC-0.00	74.1 $\pm$ 2.4	12.5 $\pm$ 1.4	13.4 $\pm$ 1.0	0.0 $\pm$ 0.0	-	1.1 $\pm$ 0.0
NB-0.10-TFN-0.05	74.2 $\pm$ 2.7	12.5 $\pm$ 1.1	13.1 $\pm$ 1.7	0.1 $\pm$ 0.1	123 $\pm$ 69	1.0 $\pm$ 0.0
NB-0.10-TFN-0.10	73.2 $\pm$ 1.6	11.8 $\pm$ 0.5	14.8 $\pm$ 1.3	0.3 $\pm$ 0.1	49 $\pm$ 14	1.1 $\pm$ 0.1
NB-0.10-TFN-0.15	73.0 $\pm$ 0.6	11.7 $\pm$ 0.7	15.0 $\pm$ 0.3	0.3 $\pm$ 0.1	50 $\pm$ 12	1.2 $\pm$ 0.1
NB-0.10-TFN-0.20	73.7 $\pm$ 2.6	12.5 $\pm$ 1.4	13.6 $\pm$ 1.4	0.2 $\pm$ 0.1	84 $\pm$ 49	1.0 $\pm$ 0.1
NB-0.10-TFN-0.25	78.6 $\pm$ 3.6	9.3 $\pm$ 2.2	11.9 $\pm$ 1.8	0.2 $\pm$ 0.1	56 $\pm$ 26	1.2 $\pm$ 0.1

Even though MIL-101 membrane loading does not increase significantly after 0.10 % (w/v) MIL-101 loading in the NB phase, the permeance continues to increase. After the statistically insignificant permeance increase between the 0.10 and 0.15 % (w/v) samples, there is a statistically significant increase for the 0.20 and 0.25 % (w/v) samples, the latter of which increases up to 3.6 times relative to the TFC membrane control. Additionally, the DR rejection does not change in a statistically significant way except for the NB-0.10-TFN-0.25, which is slightly lower than the NB-0.10-TFC-0.00. However, if one accounts for CP, mean intrinsic DR rejection values increase with increasing MIL-101 loading from 90 % for the NB-0.10-TFN-

0.25 to 94 % for the NB-0.10-TFC-0.00 membrane. Again, all membranes fail a two-tail Welch's t-test ($p < 0.05$) except for the NB-0.10-TFN-0.25 and NB-0.10-TFC-0.00. Given that rejection increases or decreases depending on whether CP is accounted for implies that there is not a truly measurable change in rejection overall. Similar to the previous membrane set, the mean differences in performances are simply too similar in magnitude to that of experimental error. Usually, a second increase in permeance like this is also accompanied by a more significant decrease in observed rejection that is attributed to aggregation formation. This was the case for the poly(*m*-phenylenediamine trimesamide) membranes in Chapter 3.

For less equivocal performance data, rejection tests were performed using CD in MeOH. A calibration was performed to relate integrated signal areas to concentration ($R^2 = 0.998$, see **Figure 38B**), as ELSD typically does not have a linear response. Note that this CD is modified to have good solubility properties in hydrophilic solvents. Additionally, it has a well-defined, uniform molecular diameter of > 1.7 nm [230]. This makes it a geometric impossibility for the CD to pass through MIL-101. Furthermore, no CD was detected in the permeate of the NB-0.10-TFC-0.00 membrane. Therefore, the only way for CD to permeate through the membranes created for this work is if there are defects in the membrane. While CD was undetectable in the permeate of the NB-0.10-TFN-0.05 and NB-0.10-TFN-0.10 membranes, trace amounts were detected NB-0.10-TFN-0.15 and NB-0.10-TFN-0.20 membranes. The observed rejection of CD dropped to 99.9 ± 0.4 % (95 % CI, $n = 4$) for these samples and was as low as 97.6 ± 1.8 % (95 % CI, $n = 4$) for the NB-0.10-TFN-0.25 membrane sample. This latter decrease is statistically significant. Regardless, any reduction in rejection is telling given no measurable CD permeates the NB-0.10-TFC-0.00 membrane control. It demonstrates that aggregation leads to the permeation of large molecular weight species. The SEM images of these TFN membranes in **Figure 39** reveal that aggregation is an issue past the critical point of aggregation of MIL-101 in NB. No aggregates are observed at 0.05 and 0.10 % (w/v) MIL-101 loadings. On the threshold of the critical point of aggregation (0.15 % (w/v)), some aggregates do seem to form, though they are not as severe. Finally, at 0.20 and 0.25 % (w/v) MIL-101 loading, aggregates larger than 1 μm can readily be observed.

Taken as a whole, these data paint a coherent picture of how aggregation plays a role in TFN membrane performance. Permeance increases up to about 0.10 % of MIL-101 loading in the NB phase are likely attributed to defect-free MIL-101 incorporation into the polyamide film. Starting at 0.15 % onward, additional permeance increases can be attributed to defect formation due to agglomeration in the organic phase. This is supported by the following facts: one, the critical point of aggregation is 0.14 % (w/v); 2.) SEM imaging show aggregates starting at 0.15 % (w/v) in the NB phase; 3.) CD rejection decreases starting at 0.15 % (w/v); 4.) while no additional MIL-101 is found in the membrane after 0.15% (w/v) loading in the NB

phase, the permeance continues to increase. Coupled with the fact that DR rejection does not dramatically decrease, as would be predicted by modelling (see Section 9.3.5.3), these facts imply that the defects introduced by aggregates in this IP system have lower selectivity, but are not entirely non-selective. Note that these explanations assume that MIL-101 is incorporated into the membrane. Since performance is correlated with solution-phase aggregation measurements, this seems likely. Precise definition of membrane morphology would be needed to confirm this though.

These observations also correspond with XPS data on crosslinking. Similar to the NB-0.30-TFN membrane set, **Table 8** shows O:N ratios between 1.0 and 1.2 with 95 % confidence intervals on the order of ± 0.1 ($n = 4$). In other words, the effect size is on the same order of magnitude as the error and differences in crosslinking are either immeasurable via XPS or there is no change. This is contrary to TFN membrane formation systems that use HX as a solvent, as shown in this work and previous works [62,63,65,86]. These works observed a lower degree of crosslinking and attributed it to aggregation or heating effects from the adsorption of water. The data presented here seem to suggest that the culprit is more likely the former than the latter. However, these data cannot rule out heat-related effects.

Since defects introduced by aggregates are semi-selective, it may be possible that the interparticle voids are bridged by some amount of polyamide. Alternatively, aggregates could rest on top of the polyamide or underneath the polyamide. The latter seems implausible given the imaging in **Figure 33**, **Figure 37** and **Figure 39**, as aggregates are plainly visible on the surfaces of the membranes. It does seem plausible that reactive monomers could diffuse through the interparticle spaces or cover the membrane-facing side of the aggregates. The former would explain why strands of polymer can be seen bridging the tops of even large aggregates greater than 1 μm in diameter (**Figure 33**). If aggregates interfere with reactive monomer diffusion, it also makes sense that a lower degree of crosslinking is measured.

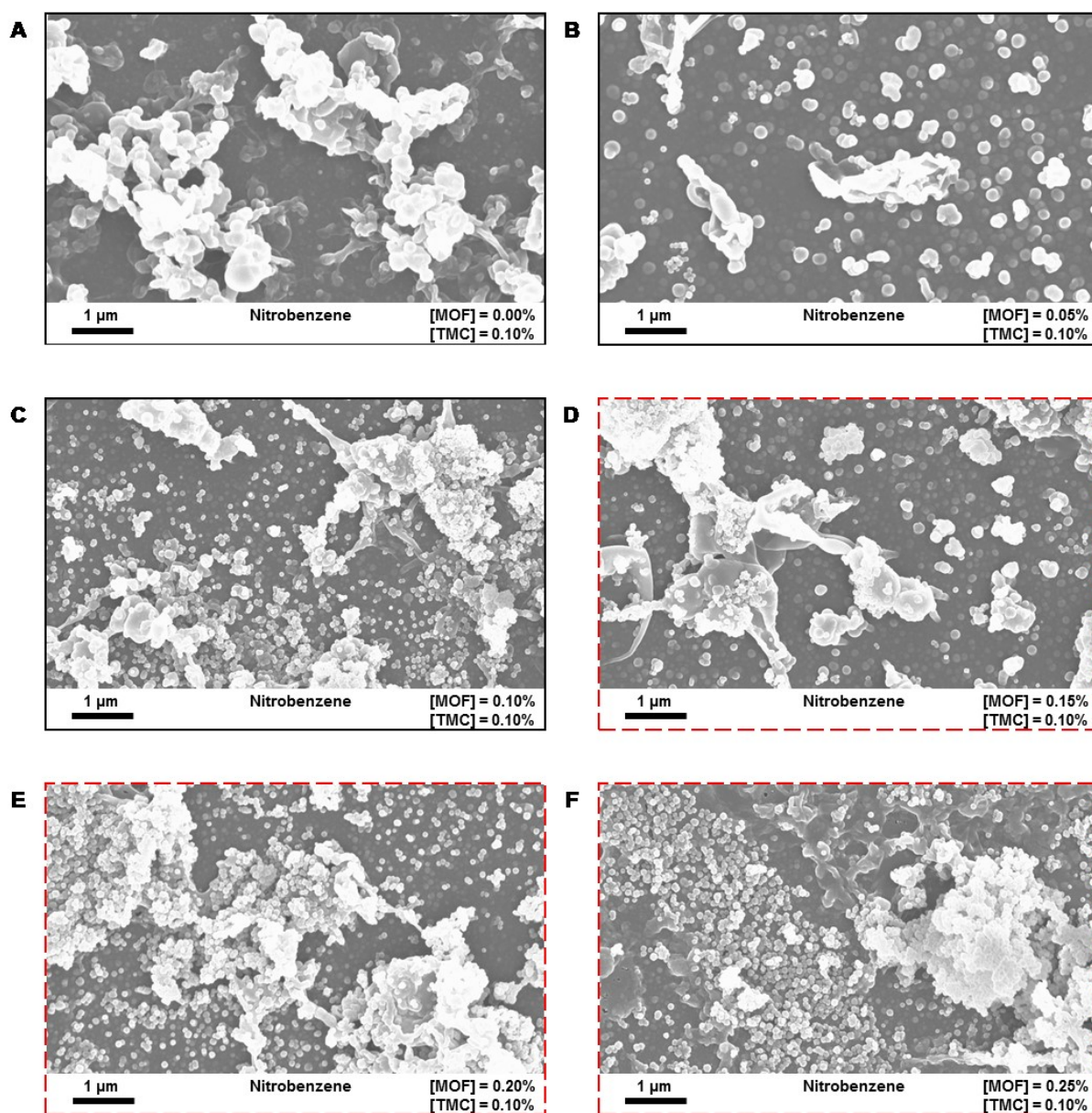


Figure 39. Scanning electron microscopy (SEM) imaging of thin film composite (TFC) and thin film nanocomposite (TFN) membranes synthesised using 0.10 % TMC and 0.0 – 0.25 % MIL-101 (A – F, respectively) in a nitrobenzene (NB) organic phase. Images outlined in red show aggregation.

6.5 Conclusions

This is the first report of the fabrication of a poly(piperazine trimesamide) TFN membrane via IP based on MIL-101. TFN membranes fabricated using HX demonstrated variable performance and lower rejection than the TFC membrane control. One of the principle causes of these performance issues was significant aggregation of MIL-101 in the HX phase. Another possible cause was the adsorption of TMC to MIL-101. Through the use of NB for the first time as an organic phase during the IP of a membrane, aggregate-free MIL-101 suspension in the

organic phase was increased by at least two orders of magnitude. Moreover, MIL-101 only adsorbed 19 % of the TMC in NB, whereas it adsorbed 95 % in HX. Then, by changing the concentration of TMC in the organic phase, the root mean square roughness of the TFC membrane control increased by a factor of ~ 20 . This was correlated with a significant increase in the effect of MIL-101 on membrane performance. For rough TFN membranes, MeOH permeance was increased by 1.9 times relative to the TFC membrane control, while maintaining undetectable levels of CD ($MW \approx 1,600 \text{ g}\cdot\text{mol}^{-1}$) in the permeate and ~ 90 % intrinsic DR rejection ($MW \approx 314 \text{ g}\cdot\text{mol}^{-1}$). However, smooth TFN membranes had statistically insignificant changes in permeance and rejection. Additionally, while it is often the case that aggregates in the organic phase of the IP will lead to non-selective defects, experimental results and theoretical modelling suggest that aggregates tend to introduce regions of lower selectivity for TFN membranes made with NB. While certainly this work shows some progress towards achieving higher performance membranes via the inclusion of fillers into the IP process, it is geometrically possible to include over five times more filler. This could exponentially increase membrane permeance while simultaneously enhancing selectivity [110], suggesting large untapped potential for this field. Regardless, the 1.9 fold increase in permeance shown here should increase the cost to manufacture membrane modules by less than 5 % of the final sales price (see Section 9.3.8). This suggests that this technology could be valuable in certain applications.

7 Conclusions and Future Work

7.1 Conclusions

The key conclusions of this work are summarised by each chapter. Overall, Chapter 3 establishes some key challenges to thin film nanocomposite (TFN) membrane formation, the primary two being reactive monomer adsorption and aggregation (Objectives 1 & 2). Chapters 4 and 5 review the theoretical underpinnings and pragmatic challenges associated with getting colloidal dispersions of MIL-101 (Objectives 3 & 4). In Chapter 6, this knowledge is implemented to design a new interfacial polymerisation (IP) system that mitigates reactive monomer adsorption and aggregation (Objectives 1 & 2). Additionally, IP conditions are correlated with the degree to which fillers enhance membrane performance (Objective 5).

Chapter 3 – Secondary Filler Effects on Thin Film Nanocomposite Membranes

The objectives of this chapter were to begin exploring the impacts of reactive monomer adsorption and filler aggregation on membrane performance. First, high-quality poly(*m*-phenylenediamine trimesamide) TFC membranes were established as controls to mitigate the variability that could have influenced previous findings. It was shown that trimesoyl chloride (TMC) could adsorb in quantities as high as $\sim 0.4 \text{ g TMC} \cdot \text{g}^{-1} \text{ MIL-101}$, resulting in significant changes to membrane performance. Additionally, significant aggregation of MIL-101 in the organic phase led to defect formation, resulting in poor rejection and inconsistent results. For these reasons, filler aggregation was deemed the most important issue to focus on. Aggregation was also hypothesised to be a key limit to achieving higher MIL-101 loadings and, therefore, better performance.

Chapter 4 – The Dispersion and DLVO Theory of a Metal-Organic Framework

This work sought to empirically and theoretically explore the colloidal suspension of a MOF: MIL-101. Optical-quality, sub-micron, and uniform films were produced via dip coating. These films exhibited hierarchical porosity and had a void fraction of ~ 0.90 . The spectral properties of MIL-101 were determined by characterising these films using a combination of environmental ellipsometric porosimetry (EEP) and spectroscopic ellipsometry (SE). These data were used to calculate the Hamaker constant. Combined with other colloidal characterisation of MIL-101, the energy barrier to particle aggregation was calculated using Derjaguin, Landau, Verwey, Overbeek (DLVO) theory. This was related with the measured dispersion of MIL-101 in a variety of solvents, showing that DLVO theory described the dispersion trends for seven out of nine solvents. In summary, the dielectric constant of the host medium was found to be the most important factor determining MOF dispersion, with increased dielectric constant leading to greater dispersion stability.

Chapter 5 – Surface-Selective Modification of a Metal-Organic Framework

In this chapter, the goal was to find a method of suspending MIL-101 in a low dielectric constant solvent. To those ends, MIL-101 was successfully modified with two molecules: 1-octylamine (OA) and amine-terminated polystyrene (ATPS). The modification quantity and location were confirmed using X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA). The modified compounds had the same crystalline structure as the original MIL-101, as determined by X-ray diffraction (XRD). However, the OA-modified compound had a significant reduction in its porosity. MIL-101 modified with ATPS had a small reduction in porosity and surface sensitive measurements detected far more ATPS than the bulk measurements, suggesting a surface-selective modification. Both modifications enabled dilute suspensions of MIL-101; however, these suspensions were likely not concentrated enough to achieve a significant increase in membrane performance if used to fabricate TFN membranes.

Chapter 6 – A Novel Thin Film Nanocomposite (TFN) Formation System

The primary goal of this chapter was to explore a potential solution that could mitigate reactive monomer adsorption and aggregation: the use of nitrobenzene (NB) as the organic phase. There was an additional goal to relate IP conditions to the efficacy of MIL-101 inclusion. The TMC concentration in NB only reduced by 19 %, while that in *n*-hexane (HX) reduced by 95 %. This demonstrated that NB mitigated reactive monomer adsorption. NB also achieved a high-quality MIL-101 dispersion at concentrations over two orders of magnitude higher than that achievable by HX. With aggregation quantified and controlled, it was possible to create membranes with and without defects. Interestingly, the TFN membranes made with NB with aggregates exhibited regions of lower selectivity rather than completely non-selective voids. This was not the case with TFN membranes made from HX, which showed significant decreases in rejection. Observations of aggregation and membrane performance are summarised in **Table 9**. Finally, smooth TFN membranes made from well-dispersed MIL-101 suspensions showed no statistically significant change in membrane performance. However, rough TFN membranes showed permeance increases of up to 1.9 with no reduction in rejection.

Table 9. Summary of performance [permeance, disperse red 1 (DR) rejection and (2-Hydroxypropyl)- γ -cyclodextrin (CD)], X-ray photoelectron spectroscopy [(XPS), membrane crosslinking] and scanning electron microscopy [(SEM), aggregate presence] observations for different states of aggregation.

	Severe Aggregation	Mild Aggregation	No Aggregation
Permeance	Stochastic	Higher	Higher
CD Rejection	Lower	Lower	Similar
Aggregate Presence	Observable	Observable	None Observable

7.2 Future Work

As described in the Literature Review, it seems that TFN membranes made via IP have only achieved a small portion of their potential. This remains true even after the contributions of this work. While NB enables high degrees of control over filler dispersion within ranges that have significant impacts on membrane performance, it only increases membrane performance on the same order as that achievable via cheaper additives, like solvents, surfactants and silicas [29,58]. Indeed, this work only explored a small number of secondary effects such as aggregation and acyl chloride adsorption. With the proposed method of aggregation control, perhaps it is possible to more thoroughly investigate other secondary effects. Regardless, the biggest gain to be made in this field probably has more to do with optimising the IP process. Rougher films seem to have more significant performance enhancements when including MOFs in the IP process, but it is still unclear why this occurs. Isolating these films and performing advance morphological characterisation could provide some clues. Finally, another potential avenue of exploration is to determine whether it is possible to control the filler's positioning such that it bisects the polyamide film. This would maximise the impact of filler inclusion. Exploring *in situ* interfacial measurements could reveal much more behind the mechanisms of film formation and filler incorporation.

There are certainly gains to be made, both inside and outside the field of membrane science, by furthering the colloid science behind MOFs. It would be of interest to assess the spectral properties of a variety of MOFs synthesised via different means using EEP and SE to explore relationships between metal clusters, ligand and defect quantity on these properties. Tabulating Hamaker constants could be useful for the MOF community. Perhaps even more importantly, quantifying other interparticle forces could be critical in truly understanding the behaviour of MOFs in a variety of environments, particularly acid-base interactions. Beyond these fundamental considerations, the ease through which uniform MOF nanofilms can be

made via dip coating is promising for a variety of applications. Additionally, the increasing degree of control over their self-assembly at interfaces is remarkable. These advances could certainly lead to innovations in membrane science, perhaps even achieving some MOF-polymer composite that approaches the technology's real potential one day.

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9 Appendix

9.1 Supporting Information for Chapter 4

9.1.1 MIL-101 Deposition and Charge Effects

Since charge can play an important role in deposition [231], it was investigated preliminarily through some measurements. The isoelectric point of the silicon substrate was confirmed by measuring the zeta potential (SurPASS™, Anton Paar Ltd.) from a pH of 6 to 2, using 50 mM hydrochloric acid (HCl, 37%, AnalaR Normapur®, VWR) to acidify the solution. Two 1 x 1 cm silicon wafers were taped to the square sample holder with water-proof tape and the Helmholtz-Smoluchowski equation was used for analysis [232].

The isoelectric point of the silicon substrate was established to be ~3, as shown in **Figure 40**. It develops a strong negative charge between -30.7 and -46.0 between the pH values of 4.5 and 5.5, respectively. Zeta potential data for MIL-101 in water, MeOH and DMF are plotted in the same figure. Over a similar range in pH, their zeta potentials range from 13.4 mV to 36.1 mV. These data suggest that the electric double layer force should be attractive between the particles and the substrate, which could play a helpful role in the deposition of MIL-101.

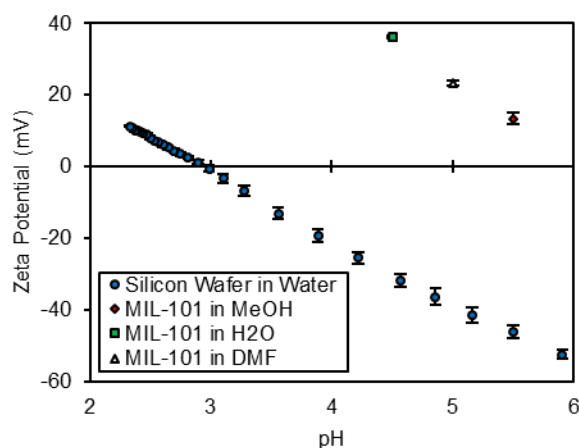


Figure 40. Zeta potential as a function of pH for a silicon wafer in water as well as 300 ppmv MIL-101 in MeOH, water and DMF. Error bars correspond to one standard deviation.

9.1.2 Modelling Root Mean Square Roughness

To evaluate the validity of the AFM data, the theoretical surface roughness was calculated according to the following derivation. By definition:

$$R_q = \sqrt{\frac{1}{A} \iint h(x,y)^2 dA} \quad (44)$$

where A is the area and $h(x, y)$ is the height as a function of x and y on a Cartesian coordinate plane. If one models a particle as a perfect hemisphere, then the $h(x, y)^2$ can be expressed as:

$$h(x, y)^2 = r^2 - x^2 - y^2 \quad (45)$$

where r is the radius of the sphere. By combining the equations above and expressing them in polar coordinates, one can easily solve for the root-mean-square surface roughness (R_q) of a sphere as a function of particle radius:

$$R_q = \sqrt{\frac{1}{A} \int_0^{2\pi} \int_0^r (r^2 - q^2) q \, dq \, d\theta} = \sqrt{\frac{\pi r^4}{2A}} = \frac{r}{\sqrt{2}} \quad (46)$$

Note that q is unusually used as the radius in the polar coordinate system.

9.1.3 Statistical Analysis of Wavelength Number Measurements

To determine what the variability of measurement might be for the UV-visible spectrophotometry, MIL-101 suspensions in MeOH were run in triplicate. As shown in **Figure 41**, the standard deviation varies from 0.06 to 0.20 for areas on the flat portion of the curve and yields a low R^2 value of less than 0.20. The standard deviation increases to 0.43 for values that lie beyond the critical point of aggregation. This increase is due to rapid settling during the measurement because of particle flocculation or aggregation.

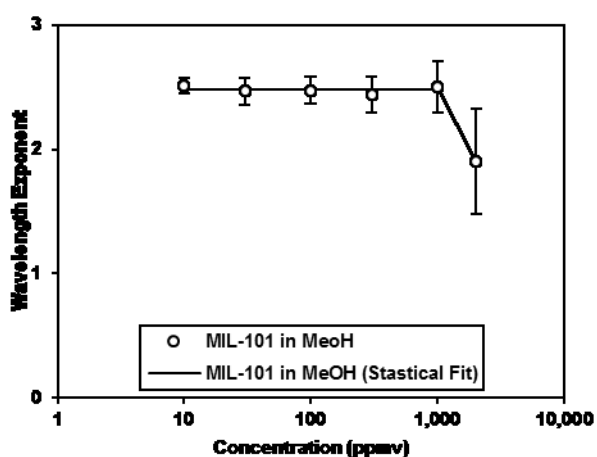


Figure 41. Wavelength exponent values for independently prepared MIL-101 suspensions in MeOH. Error bars represent one standard deviation ($n = 3$).

From these data, it is reasonable to conclude that constant wavelength exponent regions can be defined by the data set interval in which the R^2 value of a fitted line and the standard deviation of the data set were both less than 0.20. Moreover, where applicable, this region must directly connect with a decreasing wavelength exponent region, which would have

maximum R^2 across any given interval within the dataset. As examples, this process is detailed in **Table 10** and **Table 11**.

Table 10. Statistical data used to evaluate all possible fitted lines and their R^2 values as well as the averages and standard deviations for MIL-101 in IsoParG.

Log($C \cdot 10^6$) Upper Value	Log($C \cdot 10^6$) Lower Value	Slope	Y-Intercept	R^2	Average	Standard Deviation
<i>3.3</i>	<i>1.5</i>	<i>-0.95</i>	<i>4.54</i>	<i>0.87318</i>	<i>2.18</i>	<i>0.76</i>
3.0	1.5	-0.86	4.36	0.78239	2.41	0.63
2.5	1.5	-1.18	4.94	0.79681	2.58	0.66
2.0	1.5	-2.13	6.53	1.00000	2.78	0.80
3.5	2.0	-0.67	3.72	0.75496	1.89	0.45
3.3	2.5	-1.05	4.88	0.85487	1.78	0.48
3.3	3.0	-2.16	8.44	1.00000	1.58	0.47

Table 11. Statistical data used to evaluate all possible fitted lines and their R^2 values as well as the averages and standard deviations for MIL-101 (OA) in IsoParG.

Log($C \cdot 10^6$) Upper Value	Log($C \cdot 10^6$) Lower Value	Slope	Y-Intercept	R^2	Average	Standard Deviation
3.5	1.5	-0.46	3.03	0.74342	1.89	0.42
3.0	1.5	-0.23	2.57	0.48621	2.06	0.21
<i>2.5</i>	<i>1.5</i>	<i>0.05</i>	<i>2.06</i>	<i>0.13924</i>	<i>2.21</i>	<i>0.06</i>
2.0	1.5	0.27	1.68	1.00000	2.16	0.09
3.5	2.0	-0.67	3.68	0.92011	1.83	0.47
<i>3.5</i>	<i>2.5</i>	<i>-0.90</i>	<i>4.41</i>	<i>0.99622</i>	<i>1.70</i>	<i>0.48</i>
3.5	3.0	-0.99	4.71	1.00000	1.48	0.39

First note that for five data points, there are seven continuous segments that can be defined. In **Table 10**, the standard deviation and the R^2 value never falls below 0.20 for any continuous range. Moreover, the highest R^2 value is calculated based on the line passing through the entire data set, which has been italicised in red. Note that there are R^2 values equivalent to 1.0; however, these are for two-point lines and are therefore discarded from this analysis. As a whole, the data in **Table 10** indicate that aggregation occurs across the entire range of measured values. This is best described by a line with a slope of -0.95 and y-intercept of 4.54.

In **Table 11**, the data leads one to a different conclusion. A standard deviation and R^2 value each less than 0.20 are found in a range that has been italicised in red. In the other adjacent region, italicised in blue, the highest valid R^2 value can be found. These data indicate that the particles are well dispersed when Log($C \cdot 10^6$) is less than 2.5 but begin to aggregate thereafter. The well-dispersed region is described by a line where the slope is zero and the y-intercept is the average of the wavelength exponent values in that region: 2.21. The region in which aggregation occurs is described by a line whose slope is -0.90 and y-intercept is 4.41. The critical point of aggregation is simply calculated by determining the intercept of these lines, which is 314 ppmv.

9.1.4 Kinetics of Aggregation in a Stable Dispersion

To see if flocculation kinetics could play a substantial role in well-dispersed colloidal suspensions, the wavelength exponent value was measured as a function of time, as shown in **Figure 42**. For all wavelength exponent experiments, batches of solutions were prepared in parallel as described in Section 4.4.2.2 and then measured in series within 20 minutes. Within this window, there was a -0.2 % observed change in the wavelength exponent. Over the course of 8 hours, the wavelength exponent increased by 3.1 %. Since these changes are well within the experimental error illustrated by **Figure 41**, it is safe to conclude that aggregation kinetics have little impact on this measurement for solvents that achieve good dispersion.

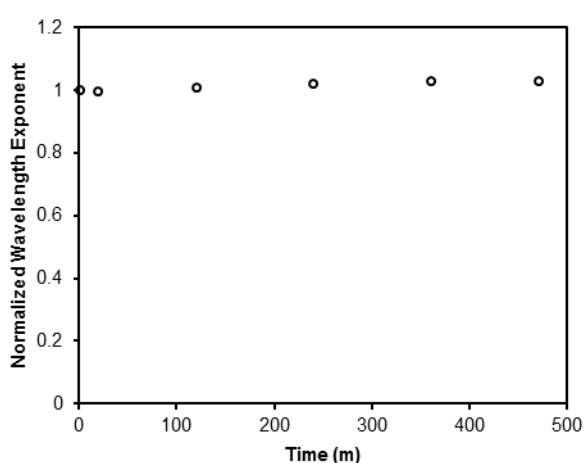


Figure 42. Normalised wavelength exponent of $1 \text{ g}\cdot\text{L}^{-1}$ of MIL-101 in water over time.

9.2 Supporting Information for Chapter 5

9.2.1 X-Ray Photoelectron Spectroscopy Analysis

As shown by the survey in **Figure 43A**, samples are relatively clean and show the typical peaks of the primary elements expected in MIL-101: carbon, nitrogen, oxygen, chromium and chloride. For the C(1s) region presented in **Figure 43B**, three major peaks were identified at binding energies at 284.0, 284.8 and 288.1 eV. These correspond with aromatic, alkyl/adventitious and carboxylate carbons. There was also a small peak at 290.7 eV, which is typical for the π - π^* satellite feature of terephthalate [233]. Note that the carboxylate peak was set to one third the height of the aromatic peak, since this ratio must be maintained by terephthalate. In reality, the alkyl/adventitious carbon peak assigned here likely accounts for a series of molecules adsorbed or coordinated to MIL-101 in trace quantities. Regardless, this simple analysis provided for highly reproducible curve fits with sensible atomic ratios. For instance, the average carboxylate to chromium ratio of MIL-101 and MIL-101 (OA) is 2.0:1.0, as is theoretically expected from the molecular formula.

Evidence for OA and ATPS modification is found in the carbon spectra, as the total carbon content increased from 55.7 for MIL-101 (UM) to 67.7 for MIL-101 (OA) and 81.8 % for MIL-101 (ATPS). These increases directly relate to the increase in carbon from the alkyl chain of the OA and polystyrene chain of the ATPS. Again, the ratio of these peaks to that of chromium is instructive. While MIL-101 (UM) has a chromium to adventitious/alkyl carbon ratio of 1.0:2.4, MIL-101 (OA) has a ratio of 1.0:8.0. Interestingly, this 1.0:5.6 increase is the calculated amount expected based on the composition of nitrogen attributable to OA. This is strong evidence for the presence of OA in MIL-101 (OA). Moreover, a similar calculation can be performed for the MIL-101 (ATPS), mirroring both an increase of ~1:20 in the chromium to aromatic carbon peak and ~1:6 increase in the alkyl carbon peak, close to the expected theoretical compositional increases.

As shown in **Figure 43C**, there are two primary oxygen peaks at 531.4 and 529.3 eV. The peak at 531.4 eV accounts for a variety of different types of oxygen present in species such as water, DMF and TPA. These species of organic oxygen can be difficult to differentiate, hence only one peak was chosen for simplicity. The peak at 529.3 eV corresponds to the oxygen in the chromium cluster and is in a typical position for that of metal oxides. This peak is differentiable due to the large chemical shift. Fitting yields a sensible mean chromium oxygen ratio of ~3:1. The overall oxygen to chromium ratios of MIL-101 (UM), MIL-101 (OA) and MIL-101 (ATPS) are 5.5:1.0, 4.9:1.0 and 5.6:1.0, respectively. According to the molecular formula, MIL-101 has a 5.0:1.0 ratio of oxygen to chromium, with the possibility of many more oxygens from coordinated water molecules. The low oxygen to chromium ratios of all samples imply that they are very dry because of the handling procedures. Since OA is coordinated throughout the porosity of MIL-101 (OA), it makes sense that it has a lower oxygen to chromium ratio than MIL-101 (UM) and MIL-101 (ATPS). These latter two samples still have significant quantities of CUSs that attract water.

While a more detailed fitting of the chromium spectra could be conducted [234], this study simply seeks to determine a total amount of chromium. So, as shown in **Figure 43D**, one peak was used for each the Cr(2p₃) and Cr(2p₁) orbitals at 576.7 and 586.1 eV, respectively. For quantification, just the Cr(2p₃) orbital was used to avoid counting the satellite peak in the Cr(2p₁) orbital. This fit yielded several reasonable stoichiometric ratios detailed earlier in this section. A similarly simple fit for quantification was also used for the Cl(2p₁) and Cl(2p₃) spectra, shown in **Figure 43E**. The peaks were fitted to 198.5 and 196.8 eV, respectively [234]. The overall quantity of chloride was higher than predicted. This suggests that some additional chloride ions remain in MIL-101 beyond those required for charge balance, even after rigorous washing.

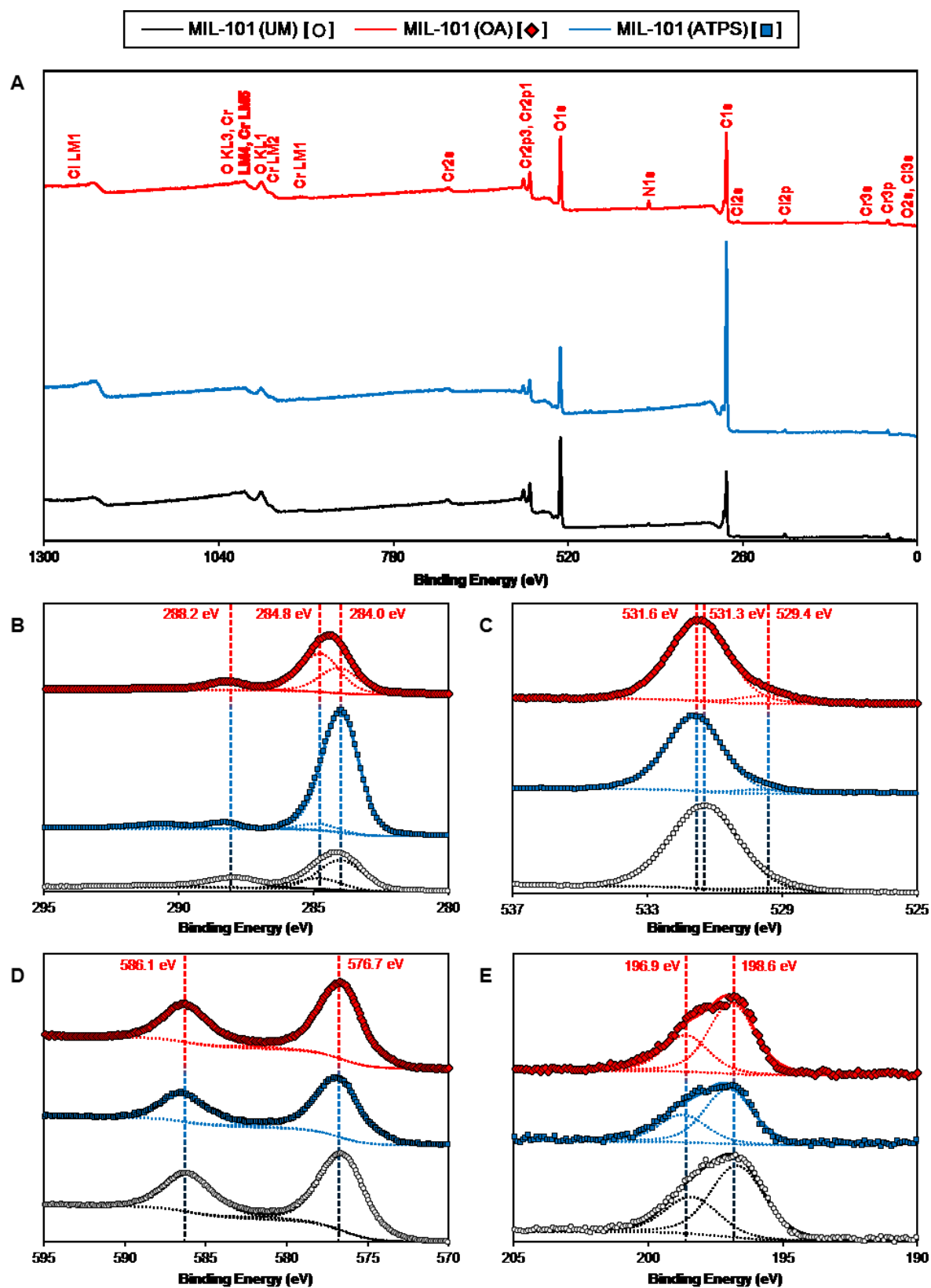


Figure 43. X-Ray photoelectron spectroscopy (XPS) spectra, Gaussian-Lorentzian curve fittings and their binding energies for the (A) survey, (B) C(1s), (C) O(1s), (D) Cr(2p) and (E) Cl(2p) core levels of MIL-101 (UM), MIL-101 (OA) and MIL-101 (ATPS).

9.3 Supporting Information for Chapter 6

9.3.1 Benchmarking Thin Film Composite Membranes

With the goal of creating a high-quality, consistent control, poly(piperazine trimesamide) TFC membranes were produced and compared with poly(*m*-phenylenediamine trimesamide) TFC membranes. These data are in **Figure 44**. The increase in permeance of the poly(piperazine trimesamide) TFC membrane is expected according to previous studies [59,235,236]. Regardless, the tenfold increase shown here is higher than usual. PIP is typically known to form a looser structure than MPD [22,23], which is likely the case here even though the DR rejection shows a statistically insignificant difference between the two membranes. The most likely explanation is that DR is slightly too large to show a discrepancy between the films. Regardless, given that the poly(piperazine trimesamide) TFC membrane has a 95 % confidence interval that is only 13 % of the total magnitude of the permeance, it seems that this membrane is far more reproducible than DMF-activated poly(*m*-phenylenediamine trimesamide) TFC membranes. Indeed, the DR rejection is the same for the poly(piperazine trimesamide) TFC membranes made on crosslinked P84, shown here, and on PAN, shown in **Figure 32**. The PAN support used in the main text because it enables higher permeance.

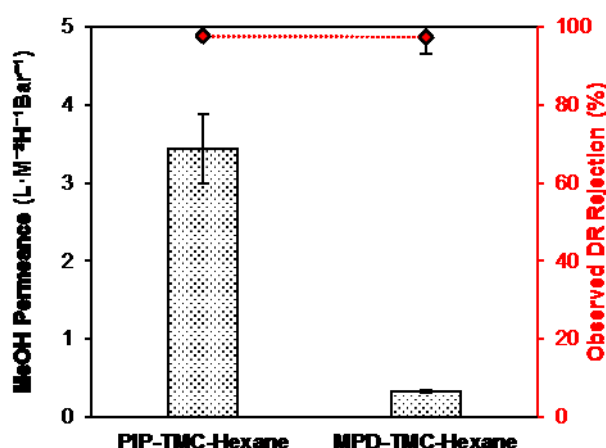


Figure 44. Observed methanol (MeOH) permeance and disperse red 1 (DR) rejection of poly(piperazine trimesamide) and poly(*m*-phenylenediamine trimesamide) thin film composite (TFC) membranes on crosslinked P84 supports without *N,N*-dimethylformamide (DMF) activation. Error bars are based on a 95 % confidence interval ($n = 4$).

9.3.2 Atomic Force Microscopy Measurements

AFM was measured to determine the root mean square roughness of the TFC membrane controls used for this study. These data are found in **Figure 45**. The PAN support, HX-0.10-TFC-0.00, NB-0.10-TFC-0.00 and NB-0.30-TFC-0.00 had root mean square roughnesses of 2, 9, 180 and 8 nm. Note that the TFN membrane data were not included here due to difficulties

in obtaining high-quality images. In general, these membranes were significantly rougher, as can be qualitatively ascertained by the SEM images in **Figure 37** and **Figure 39**.

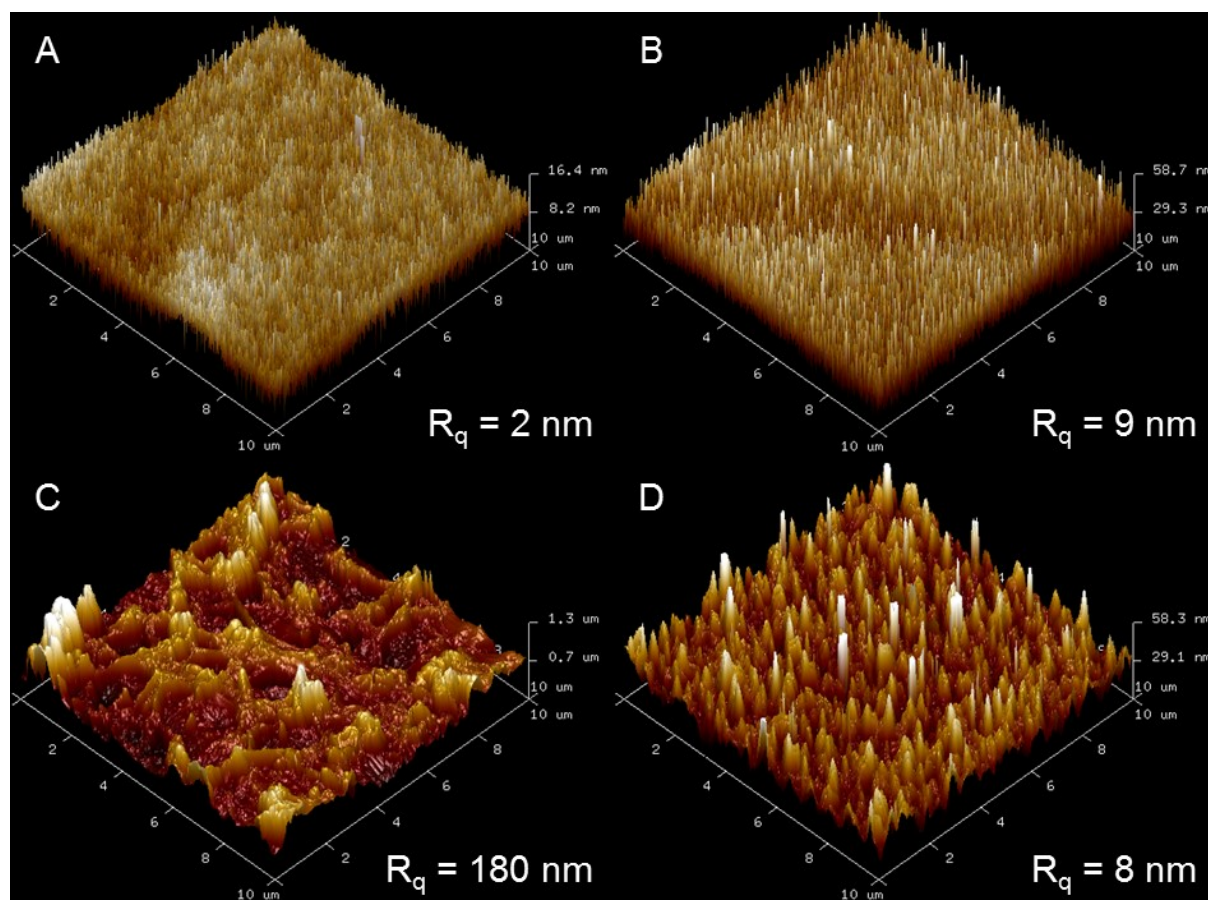


Figure 45. Atomic force microscopy (AFM) images and calculated root mean square roughnesses (R_q) of: (A) the polyacrylonitrile (PAN) support, (B) HX-0.10-TFC-0.00, (C) NB-0.10-TFC-0.00 and (D) NB-0.30-TFC-0.00.

9.3.3 Forming Rough Thin Film Composite Membrane Films

Smooth or rough TFC membranes can be fabricated by changing the TMC concentration in NB. A series of membranes were made and characterised via FTIR, AFM and SEM. Note that all other membrane fabrication parameters other than TMC concentration remained the same at those outlined in Section 6.3.1. However, the support membranes were cast in a different humidity and the NB used was from a different supplier. The results in the main chapter imply that the overall trend observed in these data is valid, but also that the absolute values may be misleading. Regardless, these results are presented in **Figure 46**.

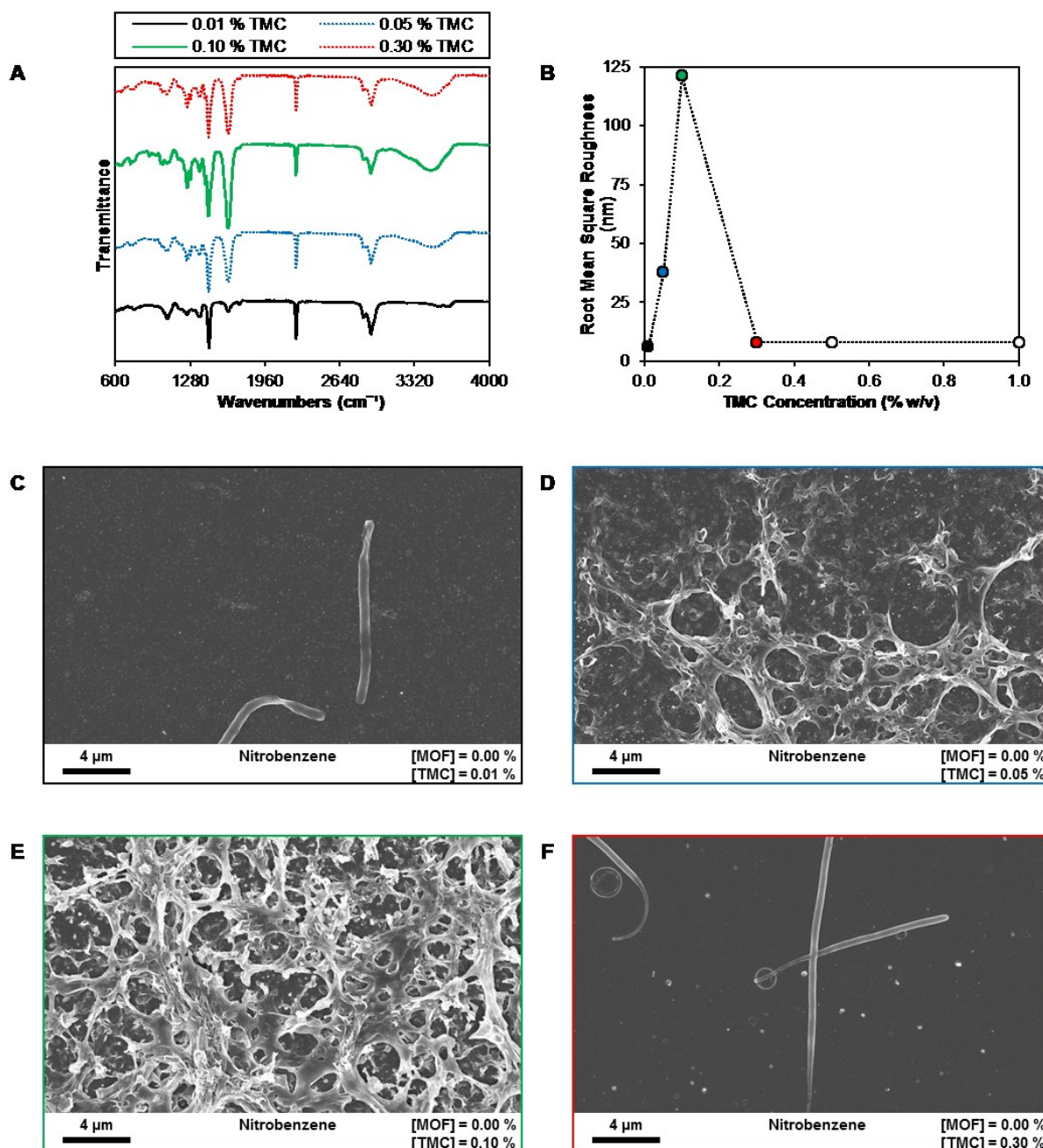


Figure 46. (A) FTIR-ATR, (B) root mean square roughness as measured by AFM and (C – F) SEM images of TFC membranes formed using various TMC concentrations in the nitrobenzene (NB) phase.

Signs of polyamide formation were found at 0.01 % TMC using FTIR. These include: carbonyl stretching at $\sim 1626 \text{ cm}^{-1}$ from the amide and carboxylate groups of polyamide; increased C-H stretching at $\sim 2924 \text{ cm}^{-1}$ from the hydrogens on the aromatic and alkyl rings of TMC and PIP, respectively; and a broad peak emerging in the 3,100 – 3,700 range which contains N-H and O-H stretching from the amide and carboxylate groups of the polyamide. The lower wavenumber regions contain many peaks from both the polyamide film and the PAN support.

The nitrile peak from the PAN support is also visible at $\sim 2243\text{ cm}^{-1}$. As the TMC concentration of the sample increases from 0.01 to 0.10 % (w/v), the peaks associated with polyamide peaks absorb more strongly, while the distinctive nitrile peak diminishes. The polyamide peaks appear to be strongest for the 0.10 % (w/v) TMC sample. Indeed, the ratio of transmission between the carbonyl and nitrile peak is close to 1.5, higher than that of any other samples. As the TMC concentration of the sample increases from 0.10 to 1.00 % (w/v), this ratio decreases to values between 1.0 and 1.3. The 0.50 and 1.00 % (w/v) samples have spectra similar to that of the 0.30 % (w/v) sample, as presented in **Figure 46A**.

The FTIR data correlate well with the root mean square roughness data in **Figure 46B**. A peak rough mean square roughness of 120 nm is found for the 0.10 % (w/v) TMC sample, with all other samples having a significantly lower roughnesses of 40 nm or less. It appears that the rougher sample had higher absorbance of peaks attributable to polyamide, which makes sense as the rougher films would have more polyamide on the surface of the membrane. The SEM images qualitatively confirm what was measured by AFM. Web-like protuberances are present only in the samples which were fabricated from 0.05 and 0.10 % (w/v) TMC. At higher TMC concentrations, typified by the 0.30 % (w/v) TMC sample in **Figure 46F**, the films appear to be smooth and dense with sporadic thread-like structures attached to the surface. Similar morphologies are found at lower TMC concentrations, typified by the 0.01 % (w/v) TMC sample in **Figure 46C**.

These data suggest that there is a very particular range of TMC concentrations under which rough polyamide films can be formed using the NB-based IP system, the optimum being at approximately 0.10 % TMC (w/v). This behaviour is not typical of films formed from HX [61]. The overall morphology of the rough films looks similar to films formed via the inclusion of co-solvent in the organic phase [237]. However, these data show that this only occurs within certain ranges of reaction for NB-based IP. While it is only possible to speculate, it might be that if the reaction kinetics are sufficiently slow, solvent mixing occurs at the interface. This could broaden the reaction zone and/or increase the heat of reaction [113], both of which have been hypothesised to generate greater surface roughness [45,50,51]. If the kinetics were very slow, allowing the NB and water to mix too much, the film may fail to form continuously altogether. This might explain the low quantities of polyamide formed at TMC concentrations less than 0.01 % (w/v).

9.3.4 On the Correlation between Roughness and Performance

9.3.4.1 Facts on the Correlation between Roughness and Performance

To be clear, the only logical deduction that can be truly made based on the data presented in this work is that there is a correlation between membrane surface roughness and the degree

to which MIL-101 affects the permeance of TFN membranes. The smooth TFN membrane set was fabricated in IP conditions that created a TFC membrane with a root mean square roughness of 8 nm. This TFN membrane set showed no statistically significant changes to performance with increasing MIL-101 loading in the organic phase. The rough TFN membrane set were fabricated in IP conditions that created a TFC membrane with a root mean square roughness of 180 nm. This TFN membrane set showed a statistically significant increase in permeance with increasing MIL-101 loading in the organic phase. Note that this was only investigated using NB as a solvent and roughness was controlled by changing the TMC concentration in the organic phase. While it might seem that this relationship exists more generally based on a close reading of the literature, further work would need to be accomplished to ensure generalizability.

9.3.4.2 Speculation on the Correlation between Roughness and Performance

Since it is known that secondary filler effects can play a significant role in membrane performance, it is difficult to make strong claims with regards to the mechanism behind this correlation. Herein, the author assumes that MIL-101 is genuinely incorporated into the polyamide film's structure. If true, than this morphological explanation can be verified by carefully analysing TEM cross-sections in future studies.

The difference in filler incorporation between rough and smooth films are roughly characterised by **Figure 47**. Indeed, in reality the film is not a solid mass as depicted, but rather an undulating surface with a complex network of porosity [45,51,52,55,178,238]. Regardless, the greater the size of these protuberances, the more filler material can make it into the core of the membrane's structure, as shown in **Figure 47C** and **Figure 47D**. If the polyamide film is smooth and thin, however, it is more likely that fillers simply rest towards the top of this surface, as shown in **Figure 47A** and **Figure 47B**. Additionally, some researchers observe a dense core layer of polyamide [51,52]. If true, the filler would need to bisect such a layer to have a significant impact on membrane performance. This is also illustrated in **Figure 47**. Of course, these morphological factors are driven by fundamental IP dynamics that are still debated in the literature.

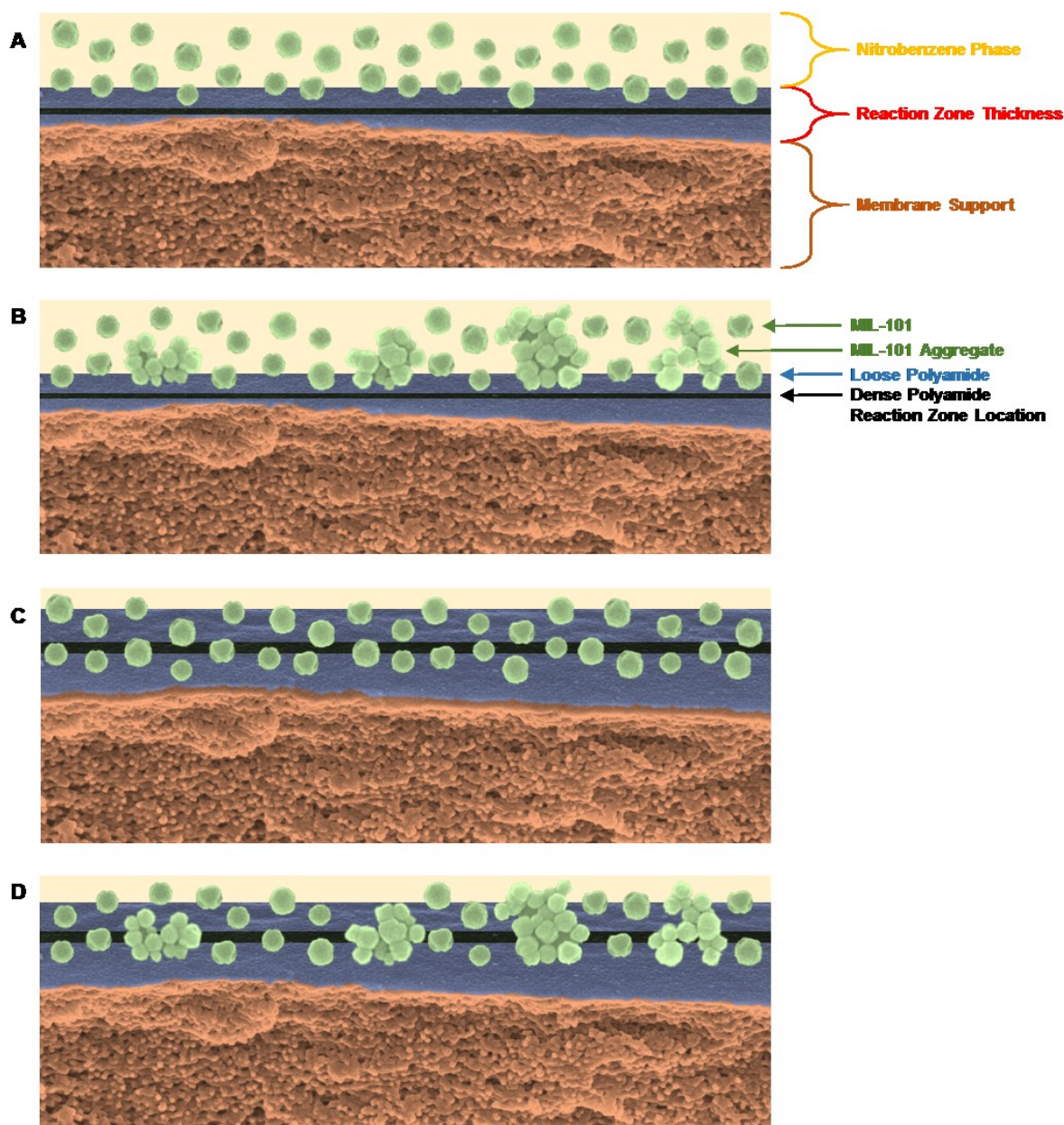


Figure 47. Cartoon (not to scale) of the hypothetical position of MIL-101 (green) and MIL-101 aggregates (green) within the dense (black) and loose (blue) polyamide layer on top of a membrane support (orange). (A) and (B) represent what might occur with smooth membranes such as those made with 0.30 % (w/v) TMC. (C) and (D) represent what might occur with rough membranes such as those made with 0.10 % (w/v) TMC.

9.3.5 Membrane Transport Modelling

9.3.5.1 Concentration Polarisation Calculations

The mass transfer of the crossflow membrane testing cells were characterised using benzoic acid (BA) in previous work [31,96,97]. Since the geometric parameters can be assumed to be constant and the duration of the parameters were previously defined for benzoic acid, the mass transfer coefficient of a given solute can be calculated with the following equation:

$$\frac{k_i}{k_{BA}} = \left(\frac{\eta_l}{\eta_{H_2O}} \right)^{c-b} \left(\frac{D_i}{D_{BA}} \right)^{1-c} \quad (47)$$

where η_l is the kinematic viscosity of solvent l . Values of 0.33 and 0.5774 were used for constants b and c [97]. The Stokes-Einstein equation was used to approximate the diffusivities of the solutes base on the approximate hydraulic radii. **Table 12** summarises the parameters used for CP calculations for this work.

Table 12. Parameters used to calculate mass transfer coefficients of select solutes.

	BA	DR	CD
r_i (nm)	-	4×10^{-10} [109]	7×10^{-10} [239,240]
D_i (m ² /s)	8×10^{-10} [241]	1×10^{-9}	6×10^{-10}
k_i (m/s)	7×10^{-5} [31]	8×10^{-5}	6×10^{-5}

With these data and equations, it is possible to calculate the concentration of solute at the membrane's interface using the equations described in Section 1.3.3.1. This can then be used in combination with the equations outlined in Section 1 to calculate an effective solute permeance:

$$P_{E,i} = \frac{J_{E,i}}{\Delta C_i} = \frac{J_{E,i} C_{P,i}}{C_{P,i}(C_{M,i} - C_{P,i})} \quad (48)$$

9.3.5.2 Effective Medium Model Calculations

While there are numerous models available in the literature to model the permeance of mixed matrix membranes and potential defects [110], the most simplistic model was chosen for this work because it fit the data remarkably well and required only a single fitted parameter. By assuming that MIL-101 bisects the polyamide layer, one can model the mixed matrix film as if the polymer and MIL-101 act as parallel permeation barriers. This is not unreasonable given that the particle size is equal to or larger than the polyamide film, so the percolation threshold should be achieved from the onset of filler inclusion [1,62,63]. One can derive an equation for the effective intrinsic permeance of solute i or solvent l ($P_{E,i/l}$) as follows:

$$P_{E,i/l} = \sum \theta_I P_{I,i/l} = \theta_P P_{P,i/l} + \theta_F P_{F,i/l} + \theta_D P_{D,i/l} \quad (49)$$

where $P_{I,i/l}$ is the intrinsic permeance of solute i or solvent l ; and θ_I are the volume fractions of the membrane components I , which consist of polymer (P), filler (F) and defects (D). For a defect-free membrane, $\theta_D = 0$, the polymer and filler volume fractions can be related by:

$$\theta_P = 1 - \theta_F \quad (50)$$

and the equation reduces to a linearised form that expresses the effective intrinsic permeance as a function of filler fraction:

$$P_{E,i/l} = (P_{F,i/l} - P_{P,i/l})\theta_{F,i} + P_{P,i/l} \quad (51)$$

The effective and polymer intrinsic permeances of various solvent and solute species can be experimentally measured for membranes as detailed in Section 6.3.3. After measuring the TFN membrane composition via XPS and calculating the volumetric filler loading as detailed previously, it is easy to solve for the only parameter that requires fitting: intrinsic filler permeance. This enables a calculated, defect-free membrane intrinsic permeance of solute i or solvent l , $P_{E,i/l}^C$, as a function of filler volumetric loading. For this work, this model is called the defect-free parallel permeation model.

It is most useful to establish an effective medium model in terms of experimental parameters. In this case those parameters are MIL-101 loading and membrane performance. If a defect-free performance is established for all membrane loadings according to the aforementioned procedure, then it could be possible to define a defective membrane in terms of its defect-free (θ_{DF}) and defective components. These components can then be related as follows:

$$\theta_{DF} = 1 - \theta_D \quad (52)$$

Some algebraic manipulation of the aforementioned equations would enable an expression of the effective permeance of a defective membrane as a function of an observed filler volume fraction and some defect volume fraction:

$$P_{E,i/l} = (1 - \theta_D)P_{E,i/l}^C + \theta_DP_{D,i/l} \quad (53)$$

The effective permeance is easily measured, whereas the defect volume fraction is difficult to experimentally obtain. So it is helpful to rearrange equation 54 to produce an approximate defect volume fraction:

$$\theta_D = \frac{P_{E,l} - P_{E,l}^C}{P_{D,l} - P_{E,l}^C} \quad (54)$$

The defect volume fraction can be calculated most accurately with pure solvent permeance measurements because solute permeance measurements will contain errors from: solvent permeance measurements, solute concentration measurements and CP estimates. For TFC membranes, the defect permeance can be taken to be that of the membrane support layer if the defect provides negligible resistance. After calculating a defect volume fraction, it is possible to calculate the volumetric solvent flux using the defective parallel permeation model:

$$J_{E,l} = [(1 - \theta_D)P_{E,l}^C + \theta_DP_{D,l}]\Delta P \quad (55)$$

The effect flux can be used to predict intrinsic solute rejection of said solute [96]:

$$R_{O,i} = \frac{J_{E,l}}{J_{E,l} + P_{E,i}} \quad (56)$$

To obtain the effective defect solute permeance, it is of interest to define it in terms of selectivity so that it can be compared with the defect-free portion of the membrane. Permselectivity is often defined as follows for membranes [242]:

$$\alpha_{l/i} = \frac{P_{E,l}^*}{P_{E,i}} \quad (57)$$

where $P_{E,l}^*$ is an effective osmotic permeance as defined by [242]:

$$P_{E,l}^* = \frac{P_{E,l}RT}{M_{vol}} \quad (58)$$

where R , T , and M_{vol} are the universal gas constant, temperature and molar volume of the solvent, respectively.

9.3.5.3 Solute and Solvent Transport Modelling Results

Data from **Figure 32** and fitted models are presented in **Figure 48A**. The model fit the data well ($R^2 = 1.000$) for both MeOH and DR permeance for MIL-101 loadings in the membrane between 0 and 14 % (v/v). The modelled permeances of MIL-101 for MeOH and DR were $17.1 \text{ L}\cdot\text{m}^{-2}\text{h}^{-1}\text{bar}^{-1}$ and $1.6 \times 10^{-5} \text{ m}\cdot\text{s}^{-1}$. It is likely that these values are artificially low due to the modelling approach. After all, the assumption that MIL-101 particles all perfectly bisect the polyamide layer is highly idealised. In reality, as shown in **Figure 47**, particles could be in various locations throughout the polyamide film. Note that secondary effects are also lumped into this term. While this linear model provides accurate predictions at low filler loadings, it would significantly under-predict any extrapolated values, the grossest error being associated with a filler fraction of unity. This is because many effective medium models predict that the effective permeance increases at a greater rate with increasing filler concentration, whereas this models predicts that the effective permeance increases at a constant rate. To validate the claim that this estimate of MIL-101 permeance is low, a rough calculation can be performed to see what an ideal permeance might be according to Hagen-Poiseuille flow, as detailed in the Section 1.3.4.2. This calculation yields a permeance of $\sim 30 \text{ L}\cdot\text{m}^{-2}\text{h}^{-1}\text{bar}^{-1}$. Indeed, this value is $\sim 80 \%$ higher than that proposed by the model in this work.

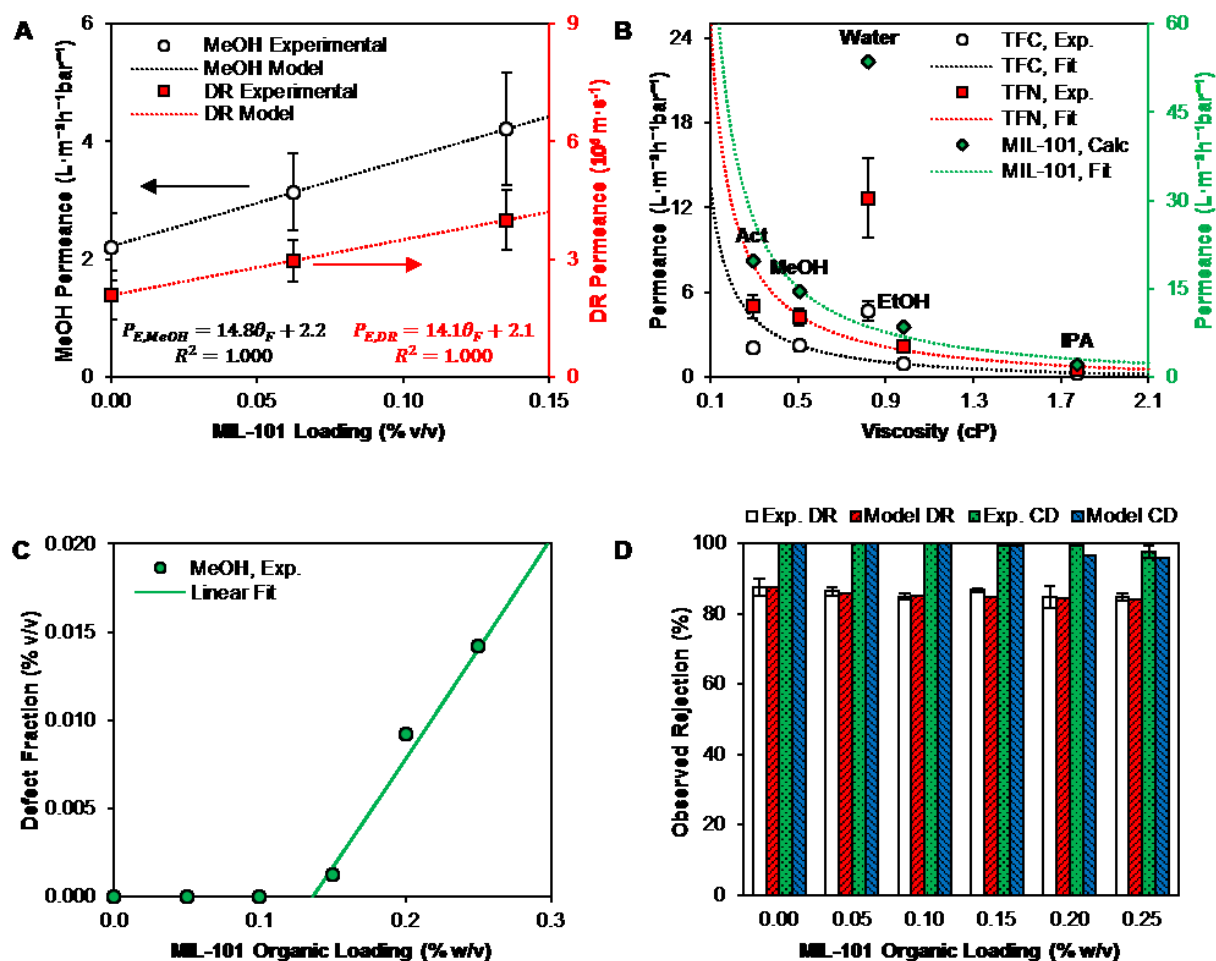


Figure 48. (A) Experimental data and fitted curves for methanol (MeOH) and disperse red (DR) permeance through defect-free thin film nanocomposite (TFN) and thin film composite (TFC) membranes: NB-0.10-TFC-0.00, NB-0.10-TFN-0.05 and NB-0.10-TFN-0.10. Error bars represent 95 % confidence intervals ($n = 4$). (B) Permeance of select solvents for the NB-0.10-TFN-0.10 and NB-0.10-TFC-0.00 membranes as well as the modelled MIL-101 permeance. Solvent permeance as a function of viscosity was derived from fitting an intrinsic permeance coefficient to the alcohol series. Error bars represent 95 % confidence intervals ($n = 3$). (C) Defect loading calculated from MeOH permeance. A linear regression was performed to fit a line to the latter three data points. (D) Experimental and calculated MeOH permeances, DR rejections and CD rejections for the NB-0.10-TFN membrane set adjusting for semi-selective defects. Error bars represent 95 % confidence intervals ($n = 4$)

The defect-free TFN membrane model was extended to Act, MeOH, water, EtOH and IPA to calculate the MIL-101 permeance. This was accomplished by experimentally measuring the pure solvent permeance of the NB-0.10-TFC-0.00 and NB-0.10-TFN-0.10 samples in triplicate. From these data, a two-point estimation was used for the model. These data are presented in **Figure 48B** and can be used to estimate solvent permeance of TFN membranes

at MIL-101 loadings less than 14 % (v/v). There are a variety of transport models used to describe the flow of different solvents through membranes with application to OSN [6,19,243]. Regardless, every model developed describes the permeance as being inversely related to the fluid viscosity. For the alcohol series used here and presented in **Figure 48B**, this relationship holds true. The intrinsic alcohol permeances for the TFC membrane, TFN membrane and MIL-101 are 3.8, 7.0 and 23 nm ($R^2 = 1.00, 0.98$ and 0.95), respectively. However, this relationship over-predicts Act permeance by 25 – 60 % difference and under-predicts water permeance by 120 – 145 % difference. The percent difference decreases for Act and increases for water with increasing MIL-101 content. This could be related to variety of membrane-solvent interactions [6]. Interestingly, the Hagen-Poiseuille model using constricted pore flow predicts higher MIL-101 permeances than those predicted in **Figure 48B** by factors between 1.6 and 4.0 for all solvents measured with the notable exception of water. When doing similar calculations for previous work on TFN membranes based on ZIF-8 used for aqueous separations [86], the same type of result was produced. One can only speculate as to the cause of this behaviour. Because of water's relatively small Stokes radius compared to most organic solvents, it is possible that it could access smaller free volume elements within the nanocomposite film. These elements could arise from primary and secondary filler effects [1,62,63,65,80], but further work would need to be conducted to elucidate the fundamental mechanism of solvent transport. For the readers' interest, a summary Hansen solubility parameters and solvent size parameters are tabulated in **Figure 49**.

To complete the defective membrane transport model, MeOH solvent permeance and DR rejection of the PAN support was measured at 48 hours in the crossflow rig at 30 °C, 30 bar and 50 L·h⁻¹ crossflow. The resulting permeance and rejection was 275 ± 33 L·m⁻²h⁻¹bar⁻¹ and 0.1 ± 0.2 %, respectively (95 % CI, $n = 4$). Given that the rejection data is clearly within error of zero, it was taken as zero. These data were used in the calculations for **Figure 48C**, which shows that the defect volume fraction increases nearly linearly, from 0.001 to 0.014, with increasing concentration of MIL-101 in the NB phase. Interestingly, the line has an x-intercept of 0.14 % (w/v), which is only a 3.5 % difference compared with the critical point of aggregation estimate obtained via UV-visible spectrometry, well within experimental error. This gives some experimental validation of this model and is another piece of evidence that ties the increase in TFN membrane permeance to the introduction of aggregates.

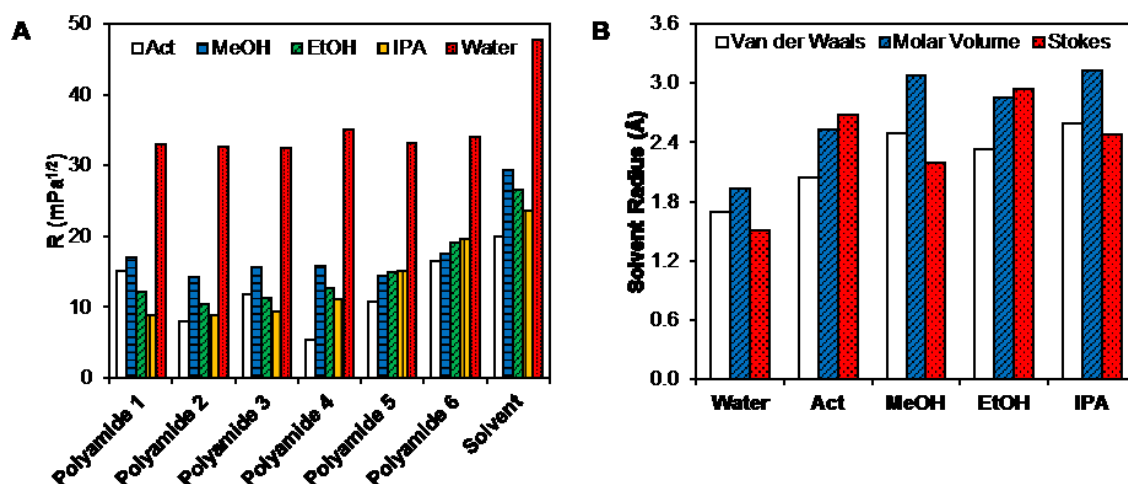


Figure 49. (A) Distance between Hansen parameters in space of select solvents for select polyamides, using estimations from commercial [216] and laboratory [244–246] polymers. (B) Van der Waals [109], molar volume [192] and Stokes [247,248] radii for select solvents.

It is possible to calculate a MeOH/DR selectivity of ~180 for the defect-free membranes. Of course, a similar selectivity calculation for MeOH/CD would approach that of infinity since no measurable CD permeates the control membrane. Initially, calculations were performed assuming non-selective void formation due to aggregate introduction and using the defect fraction estimates from **Figure 48C**. The resulting calculations predicted significantly lower rejection than that observed. However, by assuming selectivities of ~100 and ~240 for MeOH/DR and MeOH/CD, reasonable values were predicted. The resulting numbers are presented in **Figure 48E** alongside real observed rejections for comparison. All calculated values are less than 4 % different than the experimental values, within experimental error for most membranes. These calculations support that defects introduced by aggregates are semi-selective for the NB-based TFN membrane formation system.

9.3.6 Assessing MIL-101 Degradation under Interfacial Polymerisation Conditions

9.3.6.1 Method

Before using the MIL-101 for experiments, it was dried overnight at 120 °C in a vacuum oven, which was back flushed with dry nitrogen to re-pressurise. Samples were cooled under dry, flowing nitrogen for 30 minutes prior to weighing (Adventurer Pro Model: AV114CM, Ohaus®) out an amount and immediately adding a pre-measured volume of solvent. One batch of MIL-101 (MIL-101 HX and MIL-101 NB) was sonicated (Elmasonic P, Elma) at 37 hz, 100 % power and 20 – 30 °C for 60 minutes under pulse mode in HX or NB, left to stir overnight, sonicated again under the same conditions and then filtered onto a 0.20 µm polytetrafluoroethylene disk (Whatman® PTFE Membrane Filters, TE 35, 50 mm, 0.20 µm, GE Healthcare Life Sciences) using a vacuum funnel. Three aliquots of ~30 mL of Act (Technical, VWR) were washed over

each sample. Another batch of MIL-101 (MIL-101 HX-TMC and MIL-101 NB-TMC) was treated in the same way, except that they endured an additional 4 hours of stirring with 0.10 % (w/v) of TMC. A final batch of MIL-101 (MIL-101 HX-IP and MIL-101 NB-IP) was treated the same as the previous batch except that the sample was also vigorously shaken with an equivolumetric portion of 2 % (w/v) PIP in DI water for one minute. The latter batch could not be filtered and was instead centrifuged at 15,000 rcf for 30 minutes to isolate the polymer-MIL-101 composite. These samples were also washed with three aliquots of ~30 mL of Act, using the same centrifugation conditions to separate the product. Prior to XRD analysis, all samples were dried at room temperature and placed in the vacuum oven overnight at 120 °C. Note that this sample treatment mirrors the fabrication of TFN membranes detailed in Section 3.3.1.3.

9.3.6.2 *Results and Discussion*

Recently, van Goethem et al. demonstrated that ZIF-8 degrades during IP when using their evaporative deposition method. In this method, ZIF-8 is deposited on the surface of a membrane prior to IP [80]. To verify whether or not this secondary effect may impact the systems studied for this work, MIL-101 was subjected to a variety of stages of the IP process including: suspension into the organic phase, TMC addition to the organic phase and actual IP. This was done with bulk MIL-101 because it is very difficult to get convincing diffraction patterns from thin films, particularly when those films contain some small fraction (< 20 % (v/v)) of crystalline material. The result of the bulk measurements, presented in **Figure 50**, is that MIL-101 retained its crystalline structure throughout each membrane formation stages, regardless of the solvent. In other words, no evidence of degradation was found.

Van Goethem et al. cited the cause of ZIF-8 degradation as the acid generated during IP. ZIF-8 is likely more sensitive to acid degradation compared to MIL-101. Indeed, MIL-101 is synthesised in acidic conditions that are known to degrade ZIF-8 [249]. Additionally, MIL-101 has been shown to lose less than 2 % of its adsorption capacity upon exposure to hydrogen sulphide [250], whereas ZIF-8 loses more than 8 % [251]. Finally, MIL-101 is placed into the organic phase during IP. Deposition, as conducted by van Goethem et al., may cause the MOF to experience greater exposure to acid produced during IP. After all, the acid produced partitions into the aqueous phase and the MOF should be largely immersed in the aqueous phase. If the MOF is immersed in the organic phase, it could be shielded from the effects of acid. While these bulk measurements seem to support an explanation along those lines, they are not conclusive. It is possible that they may not be entirely representative of what occurs at the interface.

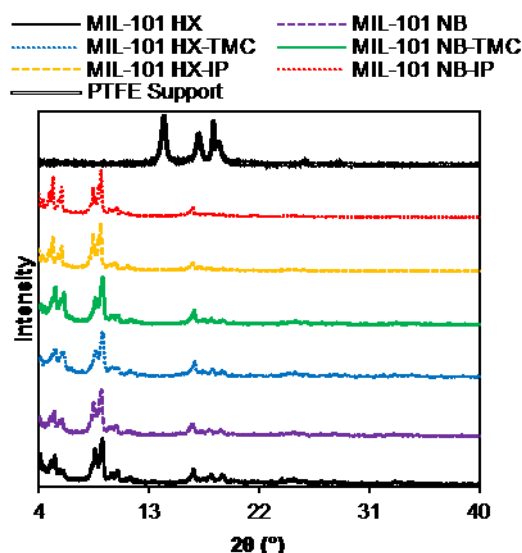


Figure 50. X-Ray Diffraction (XRD) spectra of MIL-101 subjected to a various stages of the interfacial polymerisation (IP) process including: organic phase suspension (MIL-101 NB and MIL-101 HX), trimesoyl chloride (TMC) addition (MIL-101 NB-TMC and MIL-101 HX-TMC) and interfacial polymerisation (MIL-101 NB-IP and MIL-101 HX-IP).

9.3.7 X-Ray Photoelectron Spectroscopy (XPS) Analysis

Even though the way in which the XPS data was used was simply for elemental composition, below is a brief outline rationalising the experimental fits and corrections. First is the issue of charge correction. Beamson and Briggs recommend correcting polymers to the unfunctionalised C(1s) peak of 285.0 eV. In the case where there is no such peak, as is the case with both samples measured here, different strategies were employed. For the case of purely aromatic polymers, the aromatic peaks can be fit to 284.7 eV. For polymers where all carbons atoms were shifted, a reference of contamination, degradation, additive or a heteroatom was used [252]. For the purposes of the polyamide films, aromatic and adventitious carbons were grouped into one peak and set to 285.0 eV, per previous studies [45,253]. Some of these studies normalised each core level to some value. It is noteworthy that others have used lower references, consistent with that of Beamson and Briggs [252,254–256], though few have distinguished between the aromatic and aliphatic peaks. The aforementioned researchers all included a carbon associated with the amide and/or carboxylate groups at ~288.3 eV, as was the case here. Some were able to distinguish between the amide and carboxylate, but the data here did not provide sufficient resolution for such a deconvolution. The C-N peak is often grouped with any C-O peaks, and is typically at ~286.4 eV. Finally, some authors have the convention of assigned a β -shift carbon at ~285.6 eV [45,253]. To achieve more a stable fit, this height was set to that of the carboxylate peak in this work.

The N(1s) core level was fit simply with a single peak. Previous researchers have suggested the fitting of protonated and deprotonated amines [45,253]. The latter is an impossibility in this instance and the former was found to be significantly small enough that it was difficult to ascertain whether or not it was a real peak on the basis of the resolution of the spectra. A similar issue occurred with the oxygen spectra, where the oxygens on the carboxylate peak could not be adequately distinguished as previous authors had [252,255]. That being said, the binding energies and FWHM for the N(1s) and O(1s) core levels are still reasonable given what is in the literature. Finally, just the Cr(2p_{3/2}) orbital of chromium was fit for quantification due to the known satellite feature common to the Cr(2p_{1/2}) orbital. With the low quantities of MIL-101, the chromium peak was not further deconvoluted due to the resolution. This is challenging even with pristine MIL-101, as shown in Section 9.2.

Table 13. Typical carbon (C [1s]), nitrogen (N[1s]), oxygen (O[1s]) and chromium (Cr[2p]) binding energies (± 0.1) and full-width-half-maxima (± 0.1) for poly(piperazine trimesamide) thin film nanocomposite (TFN) membranes.

Core Level	Binding Energy (eV ± 0.2)	State	Full-Width-Half- Maximum (eV ± 0.1)
C (1s)	285.0	C-H, C-C, C=C	1.3
	285.6	C-CNOH, C-COOH	
	286.4	C-N	
	288.3	N-C=O, O-C=O	
N (1s)	400.3	R ₂ -N-C=O	1.3
O (1s)	531.7	N-C=O	1.5
	533.1	O-C=O	
Cr (2p)	578 $\pm$ 2	Cr(2p _{3/2})	3.5

The PAN was fitted according to well-established procedures [252]. The height of all three C(1s) peaks attributable to the PAN were set to be equivalent in size and within their expected range of binding energies (~ 285.5 , ~ 286.4 and ~ 296.7 eV). An additional adventitious carbon peak had to be added at ~ 285.0 eV. All data for the PAN was normalised to the N(1s) nitrile peak at 399.6 eV. Though pure PAN has no oxygen content, this PAN showed an oxygen peak. The total elemental composition of oxygen was less than 3 %. The peaks at 532.0 and 533.5 eV are typical for carboxylate and amide groups. They are similar to the peaks in polyacrylic acid and polyacrylamide [252]. These peaks could come from the partial hydrolysis of PAN [40], though they could also arise from the co-polymer added by the manufacturer.

Finally, a note of caution on the use of the XPS data in the work. Contributions from the membrane support and film heterogeneity could affect the final XPS crosslinking and MIL-101

loading values used in the main text. While these values appear to be quite reasonable, they can only reliably be used to describe trends.

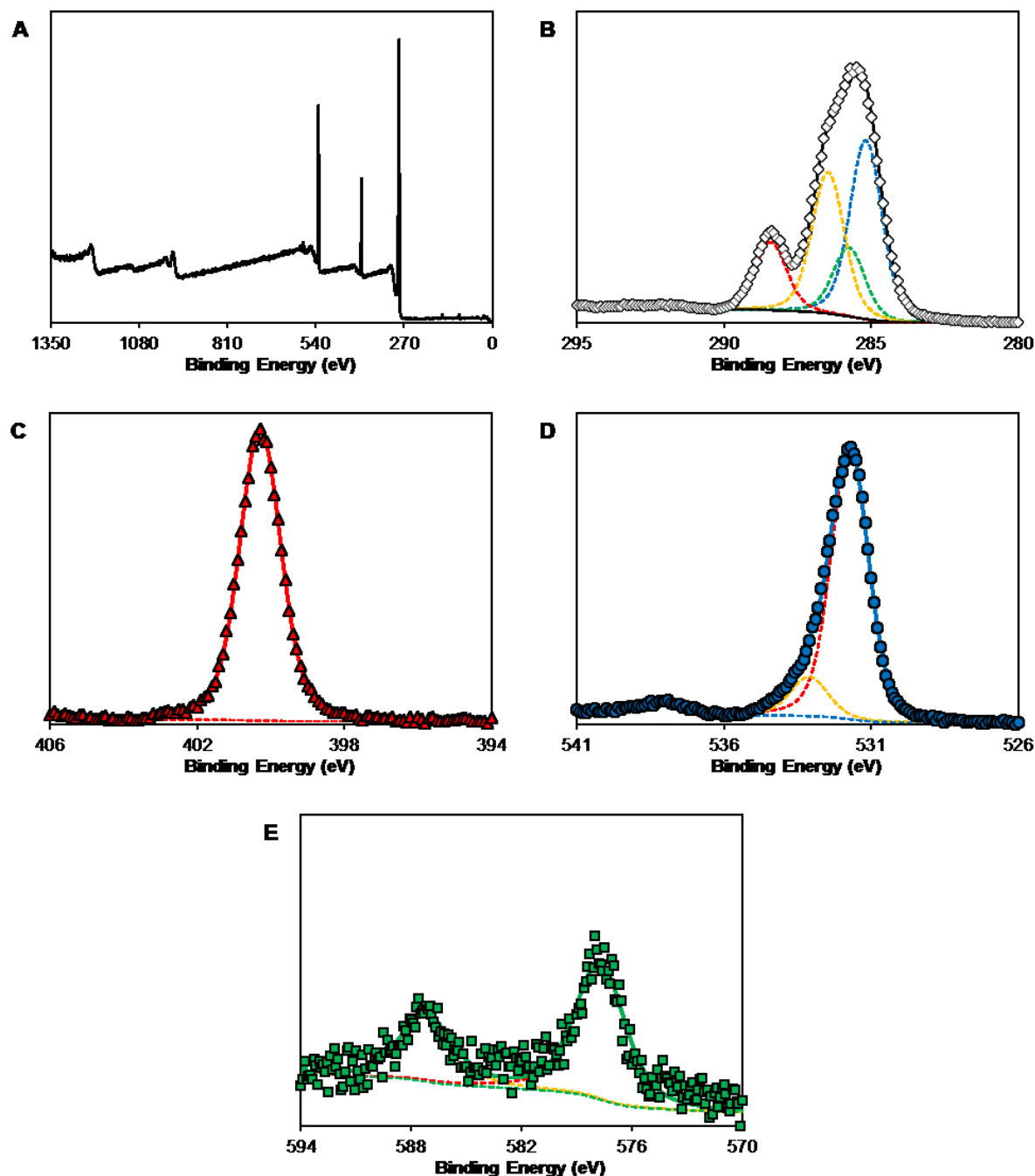


Figure 51. X-Ray Photoelectron Spectroscopy (XPS) data from a thin film nanocomposite (TFN) membrane synthesised using 0.10 % (w/v) trimesoyl chloride (TMC) and 0.10 % (w/v) MIL-101 in an organic phase composed of nitrobenzene (NB) (NB-0.10-TFN-0.10), including: (A) survey, (B) carbon (C [1s]), (C) nitrogen (N[1s]), (D) oxygen (O[1s]) and (E) chromium (Cr[2p]) spectra. All data were normalised to an adventitious carbon peak of 285.0 eV.

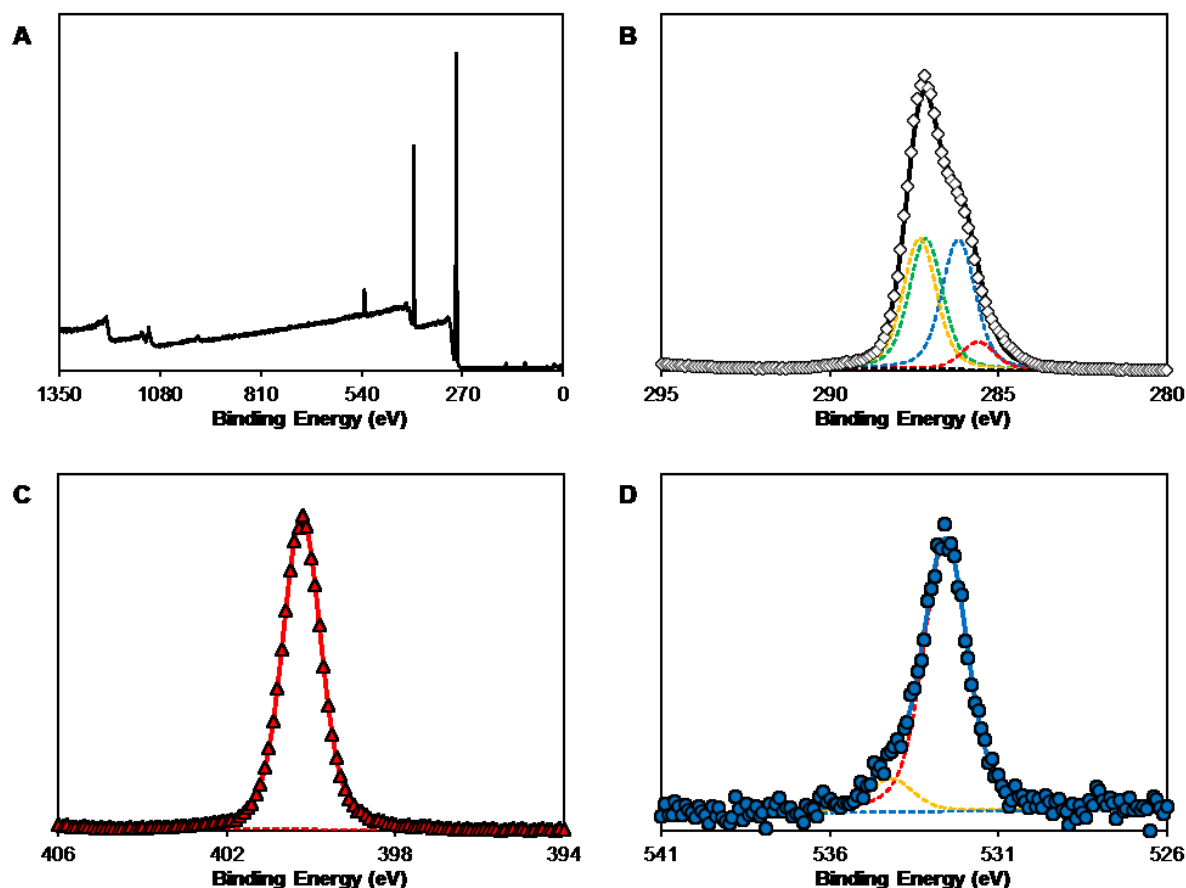


Figure 52. X-Ray Photoelectron Spectroscopy (XPS) data from a polyacrylonitrile (PAN) support membrane, including: (A) survey, (B) carbon (C [1s]), (C) nitrogen (N[1s]) and (D) oxygen (O[1s]) spectra. All data were normalised to an adventitious nitrogen peak of 399.6 eV [252].

Table 14. Typical carbon (C [1s]), nitrogen (N[1s]), oxygen (O[1s]) binding energies (± 0.1) and full-width-half-maxima (± 0.1) for polyacrylonitrile (PAN) support membranes.

Core Level	Binding Energy (± 0.2 eV)	State	Full-Width-Half- Maximum (± 0.1 eV)
C (1s)	285.0	Adventitious	1.2
	285.5	C-H ₂	
	286.4	C-H	
	286.7	C $\equiv$ N	
N (1s)	399.6	C $\equiv$ N	1.1
O (1s)	532.0	O-C=O*, N-C=O*	1.6
	533.5	*O-C=O	

9.3.8 Thin Film Nanocomposite Membrane Cost Calculations

For a typical RO membrane, one might use a commercially available ZIF-8, Basolite® Z1200, that costs ~ 12 USD $\cdot$ g⁻¹ [257], which has an envelope density of 0.95 g $\cdot$ mL⁻¹ [141]. A volume fraction of, at most, ~ 0.04 was calculated as detailed in Section 6.3.4. This calculation was

based on XPS data in the literature [86]. An apparent thickness ~100 nm was found in the same publication. Since membrane modules with ~40 m² of membrane are typically sold for ~600 USD or more as of the date of this thesis submission, a cost increase of less than 1 % can be calculated as follows:

$$\frac{12 \text{ USD}}{\text{g}} \times \frac{0.95 \times 10^{-6} \text{ g}}{\text{m}^3 \text{ MOF}} \times \frac{40 \text{ m}^2 \text{ membrane}}{\text{module}} \times 100 \times 10^{-9} \text{ m membrane} \times \frac{0.04 \text{ m}^3 \text{ MOF}}{\text{m}^3 \text{ membrane}} \\ \times \frac{\text{module}}{600 \text{ USD}} \times 100 \% < 1 \%$$

This calculation does not include any additional preparation steps to membrane synthesis such as stirring, sonication, added health/safety considerations or post-cleaning procedures, but it is doubtful that the total additional production costs would exceed 5 % per module. However, costs could be higher if unused MOFs are not recycled. The main reason for the low added cost is that these materials are incorporated only into a film that is usually less than 300 nm [51], so a low volume of material is needed. Additionally, MOFs have low densities and small loadings in the membrane seem to lead to significant performance enhancement. In the instance of the paper studied here, a 2.6-fold permeance increase was observed [86]. Certain membrane applications do not benefit greatly from higher permeance [14,15]. However, it seems likely that there could be some application for which this permeance increase is enough of a value-add for customers such that a comfortable margin could be made by a manufacturer.

A similar calculation can be performed for the system synthesised herein. The cost of MIL-101(Cr) was estimated on the basis of MIL-101 (Al), the latter of which is sold for ~11 USD·g⁻¹ [258] under the commercial name Basolite® A100. In 2017, aluminium was ~4.8 times less expensive than chromium, so under the conservative assumption that the entire cost of the MOF is due to the materials, the cost of MIL-101(Cr) could be assumed to be ~53 USD·g⁻¹. This large multiplier should conservatively account for a number of other possible pricing discrepancies. These calculations used an apparent thickness of 50 nm [51], an envelope density of 0.62 g·mL⁻¹ [108] and the maximum MIL-101 loading accomplished as a part of this work. The final cost of incorporating MIL-101 should be less than 2 % of the overall module cost. Despite the large material cost differential, this price still seems reasonable for the afforded 1.9- to 2.7-fold increase in permeance.

$$\frac{53 \text{ USD}}{\text{g}} \times \frac{0.62 \times 10^{-6} \text{ g}}{\text{m}^3 \text{ MOF}} \times \frac{40 \text{ m}^2 \text{ membrane}}{\text{module}} \times 50 \times 10^{-9} \text{ m membrane} \times \frac{0.14 \text{ m}^3 \text{ MOF}}{\text{m}^3 \text{ membrane}} \\ \times \frac{\text{module}}{600 \text{ USD}} \times 100 \% < 2 \%$$

9.4 Copyright Permission

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