

Preparation and testing of organic dye molecules as single photon sources on a chip

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Abstract

The physical realisation of a photonic quantum computer requires a reliable, fast, on-demand source of single indistinguishable photons. A promising candidate for one of these sources is a single dye molecule in a solid state matrix placed within the evanescent field of a photonic waveguide.

This thesis explores the possibility of coupling of single dibenzoterrylene (DBT) molecules in an anthracene matrix to a silicon nitride waveguide at room temperature. I first discuss the theory by which photons from a DBT molecule can be evanescently coupled to a ridge waveguide. I present a novel growth method to form DBT-doped anthracene crystals which is very promising for applications to photonic devices.

I discuss the methodology and the theory of such growth. I describe the confocal microscope I developed and used to image and characterise the emission of the single DBT molecules embedded in these crystals. My measurements show that the molecules are extremely stable single quantum emitters with a well-defined polarization relative to the crystal axes. Measurements of the saturation intensity at room temperature allow me to estimate that a single DBT molecule could deliver at least 10^{12} photons before bleaching.

This method of growth was used to deposit DBT molecules on top of a silicon nitride ridge waveguide. The results of the coupling experiment are shown. These include confocal images, saturation and lifetime measurements. The coupling efficiency is calculated and compared to what was simulated. The challenges of such structures are then presented. To tackle these challenges I deposited the molecules on top of lithium niobate and in silicon nitride slots.

I conclude with a proposal for constructing the best photonic structure which would guarantee an easy deposition of the molecules and high coupling efficiencies.

Declaration

I declare that the work, both experimental and theoretical, presented in this thesis is only my own and what is not has been appropriately referenced

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Chapter 1

Introduction

The aim of this thesis is to investigate how organic dye molecules can be used to deliver single photons to a photonic waveguide. But why is this on-chip generation of single photons important? What are its applications? What properties of dye molecules make them so attractive for this task? This introduction will try to answer these questions and offer a motivation and a theoretical framework for the experimental work presented later.

1.1 The importance of single photons

1.1.1 What is a single photon?

Let us first try to answer a very fundamental question: what is a single photon? Single photons are quantised excitations of the electromagnetic field well defined both in space and in time. A photon of angular frequency ω has energy $\hbar\omega$, with $\hbar$ being the Planck's constant divided by 2π . To demonstrate that a source of light generates single photons one can send them through a beam-splitter. Each photon can go to either of the two outputs (with equal probability in case of a 50:50 beam-splitter). Measuring a photon at a detector on one output implies that no photon is present in the other. Monitoring the detectors at each output of the beamsplitter, the probability of simultaneously detecting a photon by each detector is therefore zero. When this probability is less than 0.5, the source displays non-classical antibunching behaviour. A better single photon source has probability closer to zero. Generally, the difference between the measured probability and zero is defined as the impurity of the source.

1.1.2 Quantum information with single photons

Over the past decades many groups started exploiting quantum phenomena to create a quantum computer capable of performing operations in a much faster and secure way than in any classical computer. The five conditions proposed by Di Vincenzo [1, 2, 3] that any universal quantum computer must meet are the following:

1. A scalable physical system with well characterised qubits (units of quantum information).
2. The ability to initialise the state of the qubits to a simple fiducial state.
3. Long relevant decoherence times.
4. A universal set of quantum gates.
5. A qubit-specific measurement capability.

In 2001, Knill, Laflamme and Milburn showed that these conditions could be met in an optical system using photons. The proposed optical quantum computer could be built using a high-fidelity single photon source, beam splitters, phase shifters and photo-detectors [4]. Information can be encoded in the various degrees of freedom of a single photon, such as polarization, time bin or their presence in optical systems (cavities, resonators etc.) [5]. Standard optical elements can be used to switch between encodings as well as to perform quantum algorithms. When information is encoded in the polarization degree of freedom for example, unitary gates on one qubit can be carried out by wave-plates. In this case the simplest Hadamard gate, which is the transformation $|0\rangle \rightarrow \frac{|0\rangle+|1\rangle}{\sqrt{2}}$, can be achieved with a half-wave-plate. More complex operations, such as a controlled-NOT (C-NOT) gate, which switches the state of a qubit conditional on the control being on, can be performed using wave-plates and beam-splitters, exploiting antibunching described above, as demonstrated by O’ Brien *et al.* [6, 7, 8]. The scheme proposed by Knill, Laflamme and Milburn is a highly resource-intensive protocol [9] and for a practical realization of an optical quantum computer one might have to rely on for example cluster states [10].

Photons are appealing as carriers of quantum information because they are easily transported with low loss and couple only weakly to the environment, but despite much effort no photonic universal computer has yet been built over ~ 10 qubits. Advances

in the field of single photon detectors have been significant over the past few years with the development of ever more efficient silicon avalanche photodiodes (Si-APDs) and the invention of the superconducting nanowire photodetectors to efficiently detect infrared photon [11, 12]. Nowadays, one of the missing pieces of an all-optical quantum computer is an on-demand and bright source of indistinguishable single photons and that is the subject of this thesis.

1.2 Single photon sources

1.2.1 Desiderable properties of an ideal source

Before mentioning examples of common systems used to produce single photons, it is important to create a checklist of the desirable properties an ideal source must have. First, an ideal source needs to deliver single photons with a high fidelity. This is typically measured by looking at the purity of antibunching. In order to interfere with each other, the photons generated must also be indistinguishable. They must be the same in the spatial and temporal modes and must also have the same spectrum and the same well-defined polarization. The degree of indistinguishability between two photons is typically measured with a Hong-Ou-Mandel interference experiment [13]. To be a practical source, the photons need to be generated on-demand, which means that they are delivered at specific times when triggered. It would be advantageous if the source could also be easily integrated into a photonic structure, in order to deliver the photons to a chip capable of performing quantum computation without additional losses [14, 15]. Because some complex quantum operations require many photons simultaneously, it is desirable to be able to reproduce many identical copies of the same source across a device. It may be useful for such source to deliver photons with a wavelength between 1530-1650 nm [16]. This is the most popular wavelength in the telecom industry and the wavelength used in integrated silicon photonics, which is a very mature technology whose fabrication is capable of a high degree of precision.

1.2.2 Attenuated laser

One single photon source is a highly-attenuated laser pulse. Lasers are sources of light that output a coherent state, $|\alpha\rangle$. In the basis of Fock states, $|n\rangle$, $|\alpha\rangle$ can be written as:

$$|\alpha\rangle = e^{-|\alpha|^2/2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |n\rangle, \quad (1.1)$$

where α is the eigenvalue associated with the state $|\alpha\rangle$, whose square denotes the mean energy, and n is the number of photons. This means that an attenuator with $\alpha = \sqrt{0.1}$ leads to the state $|\alpha\rangle \simeq \sqrt{0.9}|0\rangle + \sqrt{0.09}|1\rangle + \sqrt{0.0045}|2\rangle + \dots$. Most of the time the output is no photon. The probability of one photon is smaller by a factor α^2 , while the probability of two photon is smaller again, by a further factor $\frac{\alpha^2}{2}$. The purity is compromised by the possibility of two or more photons, but by lowering α , one can increase purity. It is obvious though from Eq. 1.1 that increasing the purity by means of attenuation also increases the probability of no photon being generated. Hence the source would not be bright. Attenuation results in a Poissonian distribution of the arrival times of photons. This means that the output is not a train of single photons generated after well-defined time intervals.

1.2.3 Photon pair sources

Another method for the generation of single photons is spontaneous parametric down-conversion (S-PDC). Ever since its discovery in 1970 it has been widely used across the research field of quantum optics for generating photon pairs [17, 18]. This method involves sending a photon with a known frequency ω_0 to a nonlinear $\chi^{(2)}$ crystal. In the first experiment, Burnham and Weinberg used ammonium dihydrogen phosphate (ADP). Since then other crystals, such as potassium dihydrogen phosphate (KDP) or barium borate (BBO), have proved to be brighter and more reliable sources [19]. As the photon passes through the crystal it is annihilated and a photon pair is created. The two photons generated are called the signal and the idler. Because of conservation of energy, the photon pair has frequency $\omega_1 + \omega_2 = \omega_0$. Momentum must also be conserved, which means $\vec{k}_1 + \vec{k}_2 = \vec{k}_0$. It follows that the photons are generated around a cone at a specific angle with respect to the pump beam. By detecting the presence of the idler photon, one

can infer the existence of signal photon at a well-defined point in time and space [20]. S-PDC has been used extensively in experiments proving the non-classical nature of light [21] and the possibility of realising gate operations [6]. However the arrival times still follow a Poissonian distribution because the production of photon pairs relies on random generation by the nonlinear $\chi^{(2)}$ crystal. Moreover, S-PDC also generates multiple photon pairs a portion of the time limiting the purity of the single photons.

Another method used to generate pairs of single photons is spontaneous four-wave mixing (S-FWM). Similarly to S-PDC, S-FWM also relies on nonlinear effects. In this case though, $\chi^{(3)}$ nonlinearities are used to generate a photon pair from two input photons. Similarly to S-PDC, by detecting the idler one can infer the existence of the signal photon. The photon pairs generated inside micro-structured fibres with holes in the cladding proved that this method can be easily integrated into a photonic quantum computing device [22]. Indeed, Clark *et al.* demonstrated a high-fidelity CNOT gate using two heralded photonic crystal fibers to generate photon pairs [23]. Still, together with the methods discussed so far, S-FWM is intrinsically a random process. There have been numerous efforts to improve this source to promptly deliver single photons on-demand, using spatial [24, 25] and temporal [26, 27] multiplexing.

1.2.4 Atoms and ions as single quantum emitters

In order to create a single photon at a well-defined moment in time one could use a two-level system where a single photon is generated upon electrical or optical excitation of an allowed transition. The simplest of these systems is a single atom. Laser-driven atomic transitions are very narrow and have been thoroughly understood theoretically and precisely measured experimentally. Almost 40 years ago, Kimble *et al.* proved the generation of single photons after optically pumping the $3^2S_{1/2}$, $F = 2 \rightarrow 3^2P_{3/2}$, $F = 3$ transition of a beam of sodium atoms [28]. Similarly, antibunching was also measured at different excitation intensities for a single ion of magnesium held in a radio-frequency (or Paul) trap [29]. Although the linewidths of the atomic transitions are extremely narrow, and one can generate single indistinguishable photons with a high fidelity, scalability for these systems is an issue. The experimental setups involved in atomic physics or ion-trapping experiments are very bulky and complex. Moreover, the generation of single photons cannot be immediate at the push of a button because of the long reloading times

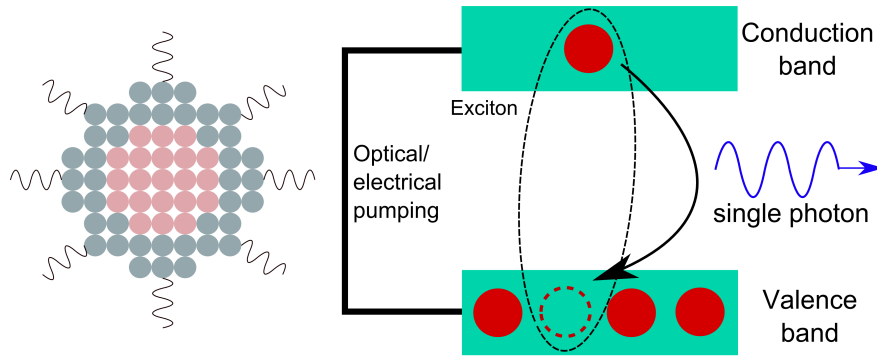


Figure 1.1: A schematic representation of a single colloidal quantum dot. The dot is in the region of low bandgap (pink) surrounded by a shell of high bandgap material (grey). The functionalisation on the surface prevents coagulation. The alternating colours highlight the low bandgap material embedded in the higher bandgap material. Generation of a single photon from a quantum dot is achieved when an electron-hole pair (or exciton) recombines.

of these systems, sometimes of the order of minutes.

1.2.5 Solid state two-level systems

To fulfil the scalability requirement and constantly deliver bright streams of single photons there has been an increased interest in solid-state atom-like systems. Quantum dots are a promising example [30]. They are artificial semiconductor structures that can be synthesised or grown by epitaxy. A common type of synthesised dot, a colloidal dot, is shown schematically in Fig. 1.1. In the centre of the shell a low bandgap material is present, surrounded by a high bandgap material and functionalisation groups that ensure solubility. As in every semiconductor material, upon excitation, an electron from the valence band is promoted to the conduction band. This leaves a hole in a valence band. The electron-hole pair formed in this process is known as an exciton. The size of the dot, generally a few nm [31], is smaller than the exciton Bohr radius and this leads to a confinement of the exciton and to the quantisation of the energy levels [32]. As shown in Fig. 1.1, when the electron-hole pair recombines, a photon is emitted. This process does not occur however with unity probability. Structural imperfections tend to create energy gaps where the electron or hole could fall and not recombine. This causes intermittent fluorescence (blinking), which reduces the dot's quantum yield. Low bandgap materials can be embedded in a very large bandgap materials, leading to quantum yields larger than

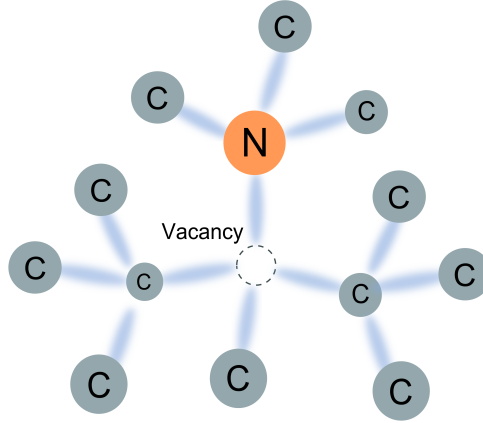


Figure 1.2: Schematic representation of a nitrogen-vacancy centre in bulk diamond. Two adjacent carbon atoms are substituted in the lattice structure. One is replaced with a nitrogen atom while the space of the other is left vacant. This creates a two-level system which can be excited at 546 nm and whose emission peaks at 689 nm [41].

0.90 [33]. It was shown that quantum dots could deliver single photons in 2000, when Michler *et al.* proved antibunching for a single InAs quantum dot in a microdisk structure excited optically [34]. Two years later, Yuan *et al.* confirmed that the generation of single photons could also occur upon electrical generation of the electron-hole pair [35]. Quantum dots can generate single photons very rapidly because the lifetime of the electron-hole recombination is only a few hundred ps. However these photons are strongly dephased by lattice phonons because the dots are bonded to their surroundings. This dephasing depends on the material and the size of the dot together with its environment and even at cryogenic temperatures cannot sometimes be fully suppressed. In 2002 Santori *et al.* measured a level of indistinguishability, based on Hong-Ou-Mandel interference between two successively emitted photons, of 0.81 [36]. More recently, values up to 0.98 have been measured [37, 38]. Quantum dots are attractive because of the ability to build photonic structures such as microdisks, micropillar cavities and photonic waveguides, around them. In 2012, Laucht *et al.* showed a quantum dot emitting around 900 nm coupling single photons to a photonic crystal waveguide [39]. By incorporating the emitter in the photonic structure the group was able to achieve coupling efficiencies up to 85%. Two years later, this coupling efficiency approached unity when the emission of an InAs quantum dot was enhanced inside a GaAs photonic crystal waveguide [40].

The other most popular solid-state system for generating single photons are colour-

centres in diamond. Of these, the most thoroughly studied is the Nitrogen-Vacancy (N-V) centre [41]. As shown in Fig. 1.2, it consists of a nitrogen atom substituting for a carbon atom in the diamond structure together with an adjacent vacancy. The creation of N-V centres relies on ion implantation and annealing at temperatures between 800-1000°C. N-V centres can be optically excited to generate single photons at a wavelength in the green part of the visible spectrum and show red-detuned fluorescence emission [42, 43]. N-V centres can emit indistinguishable photons at temperatures of 1.8 K, when a 13 MHz-wide emission peak can be measured around 637 nm for a negatively charged N-V centre [44]. In contrast to quantum dots though, only 2.4-3% of the photons emitted are generated by the same well-defined optical transition [45, 46]. Only a very small number of photons generated can therefore be used for quantum information processing. Nanocrystals of diamond have been used in photonic structures [47]. They can be easily moved around a structure with the tip of an atomic-force microscope because of their hardness and large size. Using this method, in 2014 Liebermeister *et al.* [48] placed a nanodiamond in the vicinity of a tapered optical nanofibre and successfully coupled 10% of single photons from a single N-V centre to the fibre mode. This experiment was carried out at room temperature and more recently there has been a report of such coupling at cryogenic temperatures of 9 K [49].

Another promising colour-centre is the Silicon-Vacancy (Si-V), which emits at a wavelength around 738 nm [50]. Recent progress has been made to produce single photons with a 200 MHz line and a high yield (88%) [51]. Hong-Ou-Mandel interference experiments have proven that they can be promising sources of indistinguishable single photons [52]. The coupling of Si-V centres to photonic structures is achieved by fabricating the structure, such as a photonic crystal cavity, around the desired vacancy in a nanocrystal [53, 54].

Very recently, there have been other reports of novel single photon emitters found in bulk crystalline structures, for example 4H-silicon carbide [55] or Pr^{3+} ion in yttrium aluminium garnet [56]. It is however premature to discuss the viability of these systems as sources of single photons.

1.3 Single molecules as single photon sources

The focus of the rest of this chapter will be on the generation of single photons from organic dye molecules and why their properties make them so attractive for applications to photonic devices.

1.3.1 The family of organic dye molecules and their optical properties

The organic dye molecules used for single photon production are polycyclic aromatic hydrocarbons (PAHs). These are organic compounds composed of multiple benzene rings with delocalised electrons. They generally contain only hydrogen and carbon atoms but they can be functionalised with the addition of other chemical groups. Many experiments in single molecule spectroscopy, especially the ones at cryogenic temperatures, have been done with the polycyclic aromatic hydrocarbon as a guest dispersed or dissolved in an organic matrix (host) [57]. There have been many reports of guest-host combinations that have produced stable and narrow fluorescence emission [57]. This process follows the promotion of an electron to the first excited state by means of optical pumping and allows the generation of single photons close to unity yield [58]. The generation of these photons occurs when an electron from the first excited state decays to the ground state. The molecule therefore behaves as a two-level system whose properties match the ideal source requirements mentioned before [59]. Below ~ 4 K a number of different molecules can emit a high yield of single indistinguishable photons with very narrow linewidths of few tens of MHz [60]. Because most molecules act as dipole sources, the photons have not only the same frequency but also the same well-defined polarization. There has been a report of single photon emission from a molecule driven by electrodes at room temperature [61]. More commonly, molecules are optically pumped to emit single photons. This means one can switch them on and off on-demand. Scalable devices can also be made with single molecules since they are very small (~ 2 nm) and one can therefore deposit many molecules across the same region. Researchers have also tried to move matrices around micro-structures using an atomic-force-microscope with some degree of success [62]. The physical apparatus for experiments in single molecule spectroscopy is also relatively simple and does not require vacuum, strong magnetic fields or high-power lasers.

1.3.2 History of single molecule spectroscopy

Single dye molecules are ideally suited to be used as bright and stable sources for single photon production. Addressing single molecules however has not been an easy task. It has in fact been such a great achievement that it granted Moerner, along with Betzig and Hell, the 2014 Nobel Prize for chemistry. Moerner is known for the imaging and switching of the green fluorescent protein at room temperature [63]. Another contribution to the field is the first spectral isolation of a single molecule in a solid state matrix [64]. In 1989 Moerner and Kador reported the measurement of a single pentacene molecule in a p-terphenyl crystal in a helium bath at 1.6 K [65]. The two scientists managed to address the same optical transition of a single molecule measuring a lifetime-limited absorption profile of 65 MHz. A year later, Orrit and Bernard confirmed the ability of measuring lifetime-limited linewidths by looking at the fluorescence excitation spectrum of the same molecule-host system placed at the end of a cleaved optical fibre [66]. These two proof-of-concept experiments paved the way to many more measurements of a single molecule at cryogenic temperatures. Ambrose *et al.* [67] investigated for the first time spectral diffusion, blinking, saturation and spectral broadening. They also showed how the linewidth of a single molecule broadens exponentially above 4 K because of dephasing. For this reason, when using single molecules to generate indistinguishable photons one requires liquid helium temperatures. Within the same host matrix, each individual molecule is surrounded by a different nanoenvironment. Hence, each molecule has a different energy gap between the ground state and the first excited state causing the detected fluorescence frequencies from different molecules to differ by a GHz or more. The spread of these frequencies is known as the inhomogeneous linewidth [68]. This is the reason why many efforts were made in the 1980s to isolate single molecules by spectral hole burning [69], a process by which a narrowband laser induces some molecules within the inhomogeneous linewidth to undergo a photo-physical or chemical change. These molecules are then driven to another region of the spectrum (hence leaving a hole) [70]. It was only in 1987 that Moerner and Carter developed frequency-modulation spectroscopy techniques which made spectral hole burning redundant and allowed the milestone experiment of 1989 to take place [71].

After initial measurements on pentacene, terryelene was studied in a p-terphenyl matrix

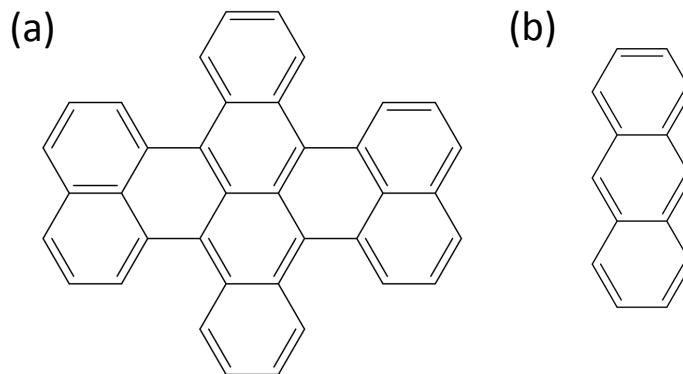


Figure 1.3: Structural formula images of the ten rings of benzene making the dibenzoterrylene ($C_{38}H_{20}$), (a), and anthracene molecules, (b).

[72]. Many more molecule-host combinations have since then been investigated. For example dibenzanthanthrene (DBATT) molecules were isolated in a naphthalene crystal [73]. In the Centre for Cold Matter in Imperial College London we focus our attention on single dibenzoterrylene (DBT) molecules in anthracene because it has been extensively studied and shows a convenient absorption peak at frequencies where laser diodes are readily available. Moreover, our work has been motivated by the overlap of the emission from DBT with the spectral transitions of the rubidium D_1 and D_2 lines, also noted by Siyushev *et al.*[74].

1.3.3 Our system of choice: DBT in anthracene

Dibenzoterrylene, abbreviated to DBT, is a large polycyclic aromatic hydrocarbon (PAH). It has chemical formula $C_{38}H_{20}$ and consists of ten rings of benzene arranged as illustrated in Fig.1.3 (a). It was first synthesised for optical experiments in 1996 and was embedded in naphthalene where it showed a lifetime-limited absorption line with a width of 27 MHz at 785 nm when in a bath cryostat at 2.0 K [75, 76]. Recently, there have been studies of DBT in 2,3-dimethylnaphthalene [77] and para-Dichlorobenzene [78]. However, we chose the well-known molecule of anthracene as a host. Anthracene is much smaller than DBT and consists of only three rings of benzene which all lie in the same plane, as shown in Fig. 1.3 (b). The first examination of this guest-host system by Hofmann *et al.* in 2005 showed a very stable molecule emitting at 785 nm at cryogenic temperatures [79]. The measured linewidth of 35 MHz was one of the narrowest reported to date and it was seen to be broadened when increasing the excitation power. The spectral properties of DBT in

anthracene were extensively studied by Nicolet *et al.* In the first of two papers, transitions as narrow as 30 MHz were reported [80]. The group also measured a very low inter-system crossing rate of 10^{-7} [80]. This low probability together with the excited state lifetime of a few ns, implies that a DBT molecule could deliver a bright stream of single photons continuously. The low probability of inter-system crossing also reduces the probability that the molecule will react with nearby oxygen and be photo-chemically damaged (a process known as photo-bleaching). In a second paper, Nicolet *et al.* also investigated in depth the principal insertion sites of DBT in anthracene [81]. The main emission at 785 nm was already mentioned. In this case the long axis of the terrylene moiety of the DBT aligns with the b-axis of the anthracene matrix. It could also align at 7° to the b-axis, in a secondary site named the red site because of its red-detuned fluorescence at 794 nm.

Trebbia *et al.* noticed the attractiveness of DBT in anthracene and used it to generate single indistinguishable photons. They measured antibunching both under pulsed and continuous-wave excitation [82]. As mentioned before, indistinguishability is measured with a two-photon Hong-Ou-Mandel interference experiment. The same group carried out this experiment using photons from an individual DBT molecule at 2 K [83]. To gather information on radiative decays other than the main peak, vibronic spectra for DBT molecules were also studied, together with density-functional-theory simulations showing the shape of the DBT molecule when it is held inside an anthracene matrix [84]. Toninelli *et al.* coupled a single molecule to a Fabry-Perot microcavity at room temperature [85, 86]. In this regime though coherent studies are affected by strong dephasing. Wang *et al.* very recently managed to investigate the coupling of a single DBT molecule to a microcavity at 3-3.6 K [87]. They showed that the molecule extinguishes more than a third of the light entering the cavity demonstrating the potential of this system for nonlinear quantum effects.

1.4 On-chip generation of single photons from dye molecules

Our group has recently reported the study of quantum dynamics of a single DBT molecule in various nano-environments [88]. This was part of our focus over the past 5 years which, has been the experimental realisation of the proposal by Hwang and Hinds [89] to efficiently couple of single indistinguishable photons from DBT molecules to a nearby

waveguide [89, 90]. As mentioned previously, the coupling of single indistinguishable photons, promptly delivered on demand to a waveguide on chip, would allow one to perform quantum computation with a high fidelity, and to scale the complexity of the quantum operations.

DBT molecules in anthracene are ideally suited for this task. Before getting lost in the experimental details, it is important to present the theoretical framework that motivated this work. I will now briefly review the derivation of coupling a single emitter to a waveguide from first principles, following Hwang and Hinds [89], to find which features must be optimised to make this process efficient. The full derivation of what follows is in Appendix A of this thesis.

Let us consider a dipole, such as a radiating DBT molecule, emitting light when inside a homogenous dielectric medium, such as anthracene, on top of a waveguide. The expression for the spontaneous emission rate of a molecule with transition dipole matrix element $\vec{d}$ into the transverse electric field mode i based on first order perturbation theory (Fermi's golden rule) is [91, 92]

$$\Gamma = \frac{2\pi}{\hbar^2} \sum_i [dE_i(r_0) \cos(\theta)]^2 D_i(\omega). \quad (1.2)$$

In this equation, d is the magnitude of the dipole transition matrix element $\vec{d}$, $E_i(r_0)$ is the magnitude of the resonant vacuum electric field in mode i at the position of the molecule r_0 , and θ is the angle between the two. In Eq.1.2, $D_i(\omega)$ is the number of modes per unit frequency at the resonant frequency of the molecule having transverse mode i . Eq. 1.2 can be simplified by expressing it in terms of the coupling g_i :

$$g_i = \frac{1}{\hbar} |dE_i(r_0) \cos(\theta)|. \quad (1.3)$$

Hence Fermi's golden rule reads

$$\Gamma = 2\pi \sum_i g_i^2 D_i. \quad (1.4)$$

When a DBT molecule in anthracene is placed within the evanescent field of a single-mode waveguide, part of the radiation is coupled to the only transverse mode supported by the

waveguide at the transition frequency. The photonic density of states can be calculated by considering the periodic boundary conditions over a length L of waves travelling in one direction.

$$D(\omega) = \frac{dN}{d\omega} = \frac{L}{2\pi v_g}. \quad (1.5)$$

Here v_g is the group velocity and the index i was dropped because only one mode is supported. Because anthracene is an homogeneous dielectric, the permittivity can be expressed in terms of the refractive index n as $\epsilon = n^2$. Assuming the guided mode is polarised along the x direction, only the transition matrix element d_x of the molecule would couple to it. One can therefore express the coupling as

$$|g|^2 = \frac{d_x^2 \omega}{2\hbar n^2 \epsilon_0 L A_{eff}}. \quad (1.6)$$

Here, A_{eff} is the effective mode cross section. Combining all of the above, the spontaneous emission rate to the guided mode of a waveguide is

$$\Gamma_{\mathbf{wg}} = \frac{d_x^2 \omega}{2\hbar n^2 \epsilon_0 A_{eff} v_g}. \quad (1.7)$$

As pointed out by many authors in the literature, one has to correct Eq. 1.7 taking into account an extra factor due to local field effects [93]. Here I consider the correction factor generally used for impurities, such as molecules, in non-absorbing dielectric media [94, 95]. Such Lorentz local-field approach leads to a correction factor equal to [94, 95, 96, 97]:

$$f(n) = \left(\frac{n^2 + 2}{3} \right)^2 \quad (1.8)$$

Hence

$$\Gamma_{\mathbf{wg}} = \frac{d_x^2 \omega}{2\hbar n^2 \epsilon_0 A_{eff} v_g} \left(\frac{n^2 + 2}{3} \right)^2. \quad (1.9)$$

Let us now compare this rate to the rate of emission of a molecule inside an homogenous dielectric. This can be expressed as $\Gamma_{\mathbf{rad}} = n\Gamma_0 f(n)$, where Γ_0 is the spontaneous emission rate in free space. Mathematically $\Gamma_{\mathbf{rad}}$ can be written following [91]

$$\Gamma_{\mathbf{rad}} = n \frac{d^2 \omega^3}{3\pi \hbar \epsilon_0 c^3} \left(\frac{n^2 + 2}{3} \right)^2. \quad (1.10)$$

We can now define the coupling of the molecules to the waveguide as the ratio between the rate of radiation of a molecule to the waveguide and the rate of radiation to its surrounding dielectric medium,

$$\beta = \frac{\Gamma_{\text{wg}}}{\Gamma_{\text{rad}}} = \frac{1}{4} \frac{\left(\frac{3\lambda^2}{2\pi n^2}\right) \frac{c}{n}}{A_{\text{eff}} v_g}. \quad (1.11)$$

In the last step I assumed that the molecule only aligns with one axis of the dielectric material such that $d^2 = d_x^2 + d_y^2 + d_z^2 \sim d_x^2$. The terms $\frac{3\lambda^2}{2\pi n^2}$ were grouped because that is the optical cross section of the DBT molecule inside a crystal of refractive index n . From Eq. 1.11 one can see that the greatest coupling is achieved for very small effective mode areas, high wavelength of radiation and low group velocity v_g . The design of the waveguides used in the Centre for Cold Matter were such to have small mode areas while the choice of DBT in anthracene fixed the wavelength of radiation. The wavelength of radiation also constrained the waveguide materials the group could use. This is the reason why the waveguides were etched in silicon nitride and not for example silicon. With this design, Hwang and Hinds predicted that coupling efficiencies up to 28% could be achieved.

Hwang and Hinds proposed this in 2011. To date, numerous groups worked to realise their vision. Faez *et al.* [98] coupled a DBT molecule in naphthalene to a glass capillary nanoguide with a diameter of 600 nm. They reported a coupling of 18% of indistinguishable single photons from a single molecule held in a bath cryostat. Skoff *et al.* coupled single terrylene in pterphenyl to the evanescent guided mode of an optical nanofibre [99]. This showed that evanescent photon coupling from dye molecules to a nanoguide is possible. Still, one would like to achieve such a coupling on an integrated-photonics based systems so that indistinguishable photons could be directly interfered allowing quantum operations to be performed. Earlier this year, Lombardi *et al.* showed a single DBT molecule at room temperature delivering a large fraction of the emitted photons into a silicon nitride ridge waveguide [100]. The collection of the fluorescence coupled to the photonic structure was via grating far-field couplers at each end. A similar approach was taken by Türschmann *et al.*, who created titanium dioxide waveguides with grating couplers at each end [101]. By using capillary forces, similarly to Faez *et al.* [98], they filled the waveguide's surroundings with DBT-doped anthracene crystals. They proved a coupling $\beta \sim 7\%$ at cryogenic temperatures where they could carry out coherent linear and non-linear spectroscopy.

1.5 Thesis guide

The rest of this thesis will present the experimental work carried out to couple photons from DBT molecules in anthracene to a waveguide on a chip at room temperature [89]. In chapter 2, I review the chemical structures of DBT and anthracene and I present a new method I developed for the growth of anthracene crystals suitable for applications to photonic devices. I provide theoretical interpretation of the experimental observations and I measure the vapour pressure of anthracene at room temperature. In chapter 3, I discuss the optical setup I built to characterise the fluorescence emission from DBT molecules in crystals grown with the new method. The results of this are the subject of chapter 4. In chapter 5, I discuss the design and the material chosen for the fabrication of waveguides intended to maximise the collection of DBT fluorescence. I present experimental data showing DBT molecules delivering photons transmitted over 10 mm of waveguide. To improve the coupling of photons to photonic structures I discuss and show in chapter 6 how lithium niobate could align the dipoles of the DBT molecules. In chapter 7 I then show how positioning a molecule in a slot can dramatically increase the coupling efficiency even further. There I show images of DBT molecules in nanoslots. To conclude the thesis in chapter 8, I will propose an optimised photonic structure to collect single photons from DBT molecules in anthracene.

Chapter 2

Novel method for thin film growth of dibenzoterrylene-doped anthracene crystals

2.1 Introduction

This chapter describes a novel method I developed for growing very thin ($\sim$ tens of nm) anthracene crystals with single DBT molecules inside. I first review the properties of DBT molecules and how they are embedded in anthracene. I then present previously-known methods to grow DBT-doped anthracene crystals for photonic applications. I discuss the need for thin crystals and show the experimental apparatus I built to achieve it. I show pictures of anthracene crystals acquired with an atomic-force microscope. I then use these results to comment on the thermodynamics of crystal growth and present a measurement of the vapour pressure of anthracene at room temperature.

2.2 DBT molecules in anthracene crystals

2.2.1 Chemical structure of DBT

DBT appears green because of its strong absorption at blue and red wavelengths. Its chemical formula is $C_{38}H_{20}$ and its structural formula is shown in Fig. 2.1 (a). As one can see, it consists of eight rings of benzene and four single bonds. In the centre it has

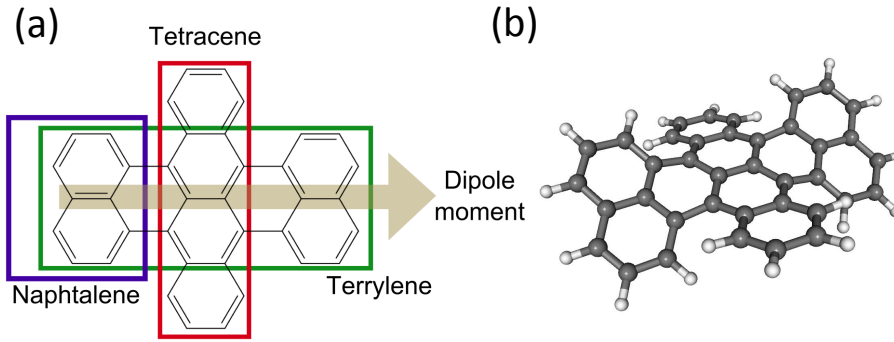


Figure 2.1: (a) Structural formula images of the ten rings of benzene making the dibenzoterrylene (DBT) molecule. The central four rings form the tetracene moiety, highlighted in red. This is attached to two naphthalene moieties on either side, one of them highlighted in blue. The transition dipole moment, measured by Nicolet *et al.* [81], arising when the molecule is excited from the ground state to the upper state is shown in light brown. This lies along the long axis of the terrylene moiety (green). (b) Carbon (grey) and hydrogen (white) atoms in the stick and ball model of the DBT molecule.

a tetracene moiety (red) with two naphthalene moieties (blue) attached by single bonds on either side. The three naphthalene moieties in a row in the central part also form the terrylene moiety, highlighted in green. The eight rings of benzene are individually planar, however in the most stable configuration in the gas phase [81, 77] the tetracene unit is tilted out of the plane of the two naphthalenes by a dihedral angle θ . Moreover, the two benzene rings at each end of the tetracene are bent out of the plane of the central rings, at an angle ψ . These angles were also calculated by Major [102] making a density functional theory simulation of a single DBT in free space. They are $\theta \sim 28^\circ$ and $\psi \sim 16^\circ$ [81, 77, 102] and lead to the conformation in the stick and balls model presented in Fig 2.1 (b).

2.3 Optical transitions of DBT molecules in anthracene

A photon with the right frequency incident on a DBT molecule can promote an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). There is an associated transition dipole moment that Nicolet *et al.* measured to be oriented along the terrylene moiety [81]. The molecule has a singlet excited state when the spins of the hole in the HOMO and the electron in the LUMO are anti-parallel and a triplet state when they are parallel. The triplet state has lower energy, as one would expect from Hund's rule [103]. The transition from the ground state to the

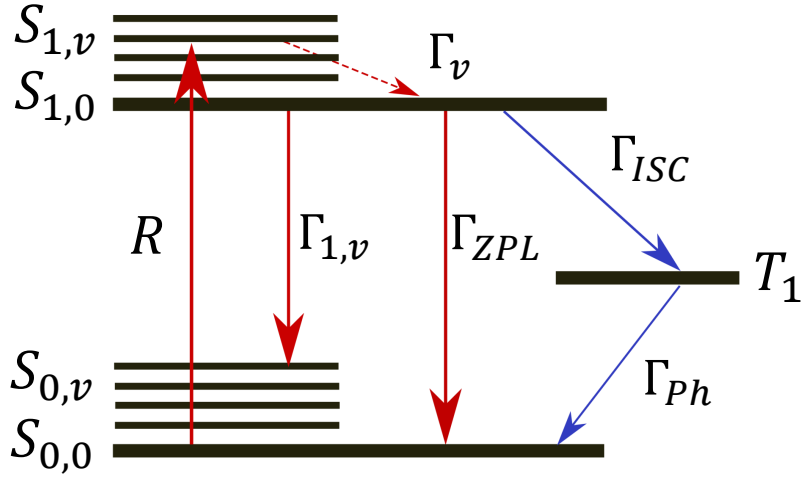


Figure 2.2: The energy level diagram for a DBT molecule in a solid-state matrix. The levels are denoted $S_{n,m}$, where n corresponds to an electronic level and m to a vibronic level. The rates of decay are also indicated. $\Gamma_{1,v}$ is the radiative rate from the state $S_{1,0}$ to $S_{0,v}$, Γ_{ZPL} the rate of the zero-phonon line decay from $S_{1,0}$ to $S_{0,0}$. Γ_{ISC} the inter-system crossing rate and Γ_{Ph} the phosphorescence decay rate.

triplet state is spin-forbidden. Because the DBT molecule sits in a well-defined position in an anthracene crystal, it does not have a rotational degree of freedom. It has however many vibrational degrees of freedom and therefore each of the electronic excited states has a manifold of vibrational states which affect its optical properties.

A simplified energy-level diagram, also known as a Jablonski diagram, of a DBT molecule is shown in Fig. 2.2. The ground state of the molecule is the singlet $S_{0,0}$, where the first index denotes the electronic level and the second the vibrational level. The rotational degrees of freedom are not considered because the solid host, i.e. the anthracene crystal, prevents the molecule from undergoing such motion. The higher excited states can be singlets, $S_{i,v}$, and triplets, $T_{i,v}$. The main transition we exploit for the on-demand production of single photons is the singlet-singlet, or $S_{1,0} \rightarrow S_{0,0}$ transition. When the DBT is embedded in anthracene it has a lifetime of ~ 4 ns [104, 82, 80] and given that it occurs from a zeroth vibrational level to another zeroth vibrational level is generally denoted as the zero phonon line (ZPL). Our group has measured this transition to be at 783.73 nm [88]. At temperatures below 4 K, this transition can be lifetime-limited with a linewidth as narrow as 30 MHz [82, 80]. As the temperature increases, the linewidth of the ZPL is homogeneously broadened by coupling to phonons in the lattice [105, 106]. This thermal broadening increases the linewidth to tens of THz at room temperature. In order

to populate the $S_{1,0}$ level, we use a laser of wavelength ~ 780 nm to excite the transition $S_{0,0} \rightarrow S_{1,v}$. In Fig. 2.2 this excitation rate is denoted as R . From $S_{1,v}$, the molecule relaxes to $S_{1,0}$, at a rate Γ_v . This transition is non radiative and generally takes only a few ps [103, 107]. After relaxing rapidly to the state $S_{1,0}$, the molecule decays radiatively to the ground state with a lifetime of ~ 4 ns. The ratio between the decay rate to the ground state $S_{0,0}$ and the total decay rate into all the vibrational sublevels $S_{0,v}$ is the branching ratio, α . For DBT molecules in anthracene the branching ratio is $\alpha \sim 0.33$ [80] and it was recently reported to be even higher (0.44) in para-Dichlorobenzene [78]. Each molecule in the crystal is embedded in a slightly different nanoenvironment, which shifts the ZPL and causes an inhomogeneous width of ~ 400 GHz [88].

Finally, as mentioned before, the $S_{1,0} \rightarrow T_1$ transition, commonly referred to as inter-system crossing, is spin-forbidden and therefore weak. For DBT in anthracene this decay occurs with a probability as little as 10^{-7} [80]. The lifetime of the triplet state was determined in [80] to be between $40 \mu\text{s}$ and $200 \mu\text{s}$. Because of the very low branching ratio, fluorescence from the inter-system branch is exceedingly weak, and consequently the energy of the $S_{1,0} \rightarrow T_1$ transition has not yet been measured. The triplet state plays an important role in determining the photostability of the DBT molecules in anthracene, as will be discussed in section 4.8.

2.3.1 Anthracene as a transparent host

Similarly to DBT, anthracene is also a polycyclic aromatic hydrocarbon (PAH), with chemical formula $\text{C}_{14}\text{H}_{10}$, and was first discovered almost two hundred years ago by Dumas and Laurent [108]. Nowadays it is mainly used in the production of dyes such as the red dye alizarin and in the semiconductor industry because of its wide band-gap. It appears colourless because its main absorption peaks are in the ultraviolet with fluorescence emission in the blue of the visible between 380 and 500 nm ($S_{1,0} \rightarrow S_{0,v}$ in Fig. 2.3 [109]). The transition from the ground state to the triplet state ($T_1 \rightarrow S_{0,v}$) has a wavelength of ~ 690 nm [110, 111] and as shown schematically in Fig. 2.3 it lies energetically above the singlet excited state of DBT. Because of all the transitions being far from the infrared, anthracene acts as a transparent host.

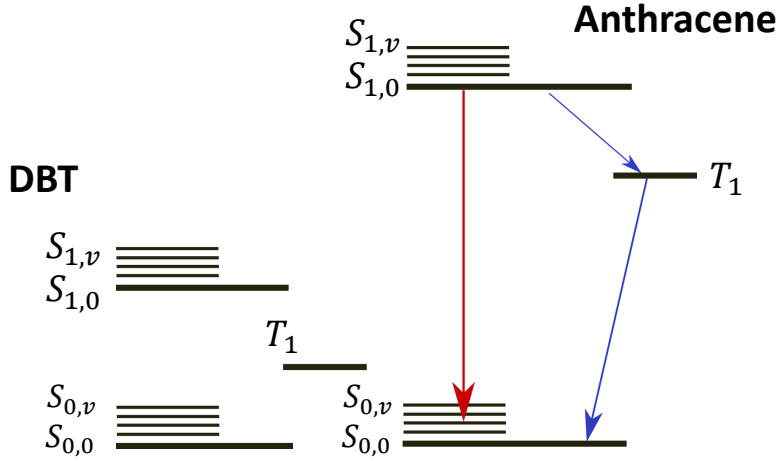


Figure 2.3: The energy level diagram for a DBT molecule next to the one of anthracene. The levels are denoted $S_{n,m}$, where n corresponds to an electronic level and m to a vibronic level. The main rates of decay of the anthracene molecule are also indicated. Both the singlet excited state and the triplet state lie above the singlet excited state of the DBT molecule. Because of this, anthracene acts as a transparent host.

2.3.2 Chemical structure of anthracene

Anthracene molecules are held together by Van der Waals forces form a monoclinic crystal which has been studied since 1933 [113]. In the crystal form, the molecules are located both at the vertices of the unit cell and at the centre of each cell, oriented to form a ‘herringbone’ structure as illustrated in Fig. 2.4 (a) [102]. At 290 K the lattice constants of the anthracene are $a = 8.562 \text{ \AA}$, $b = 6.038 \text{ \AA}$, and $c = 11.184 \text{ \AA}$, [114, 115], where a , b and c refer to the crystal axes. Anthracene crystals are typically grown by sublimation. For such crystals, it is normally easy to find the b -axis because it is pointing towards the angle A of the crystal (see Fig. 2.4 (b)). This angle was measured to be 109.757° [112]. Similarly, the other angle B was measured as 125.122° . Because of the Van der Waals bonds between individual atoms, anthracene has a low melting point of $213\text{-}216^\circ$ [116, 117].

The refractive indices of anthracene have been measured at 546 nm by El-Sharkawi and Kao [118]. Referring to Fig. 2.4, the refractive indices along the three orthogonal polarization axes are $n_x = 1.82$, $n_y = 2.22$ and $n_z = 1.57$ [118]. Our group has confirmed these values at 635 nm by measuring the thickness of anthracene crystals grown via sublimation and melt methods [119, 120]. Throughout this thesis, I shall assume that in the

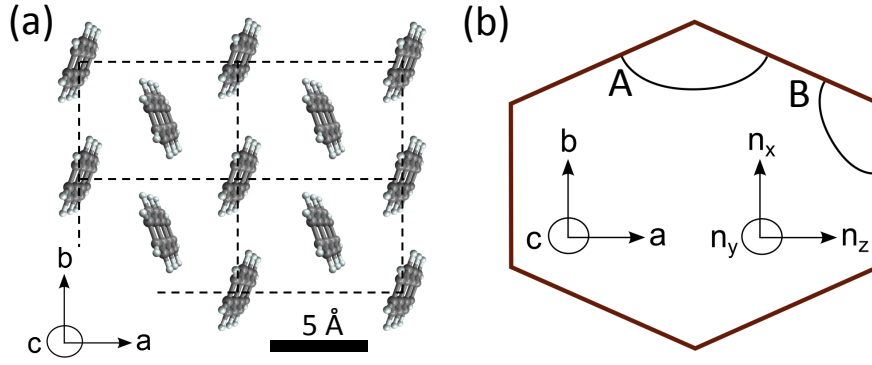


Figure 2.4: (a) Diagram to scale showing the view down the long axis (or c axis) of the anthracene looking at the ‘herringbone’ packing structure of the anthracene. (b) Top view of an anthracene crystal, showing the b -axis pointing along the angle $A = 109.757^\circ$ [112]. The angle B is 125.112° . For completeness both the orientation of the crystal axes a , b and c and the orthogonal polarization axes n_x , n_y and n_z are shown with arrows indicating the polarization direction.

near-infrared at ~ 780 nm the indices are the same. This assumption is motivated by the fact that the band edge of the anthracene is in the blue and 780 nm is far from any resonance excitation. The two measurements mentioned above suggest that it might be the case for anthracene as well.

2.3.3 Insertion of dibenzoterrylene in anthracene

Nicolet *et al.* investigated the substitution sites of a DBT molecule inside an anthracene unit cell both experimentally and theoretically [81]. They found that the DBT is inserted in two sites, namely the ‘main’ site and the ‘red’ site, whose transitions are shifted to the red side of the ‘main’ ones. The insertion sites in the ‘herringbone’ packing structure of the anthracene are shown in Fig. 2.5. When a DBT molecule occupies the ‘main’ site, it replaces three anthracene molecules removed along the b -axis of the crystal [81, 84]. In this site, the transition dipole moment of the DBT lies along the b -axis of the crystal. In the ‘red’ site, the DBT molecule also replaces three anthracene molecules, but it arranges itself in a more triangular structure. It replaces two anthracene molecules along the b -axis and one anthracene at the centre of the unit cell. In this case, the transition dipole moment also lies in the a - b plane of the anthracene but is rotated by 7° with respect to the b axis [80]. By looking at the bulk fluorescence spectrum at cryogenic temperatures, Nicolet *et al.* found that the number of molecules in the ‘main’ site is one hundred times

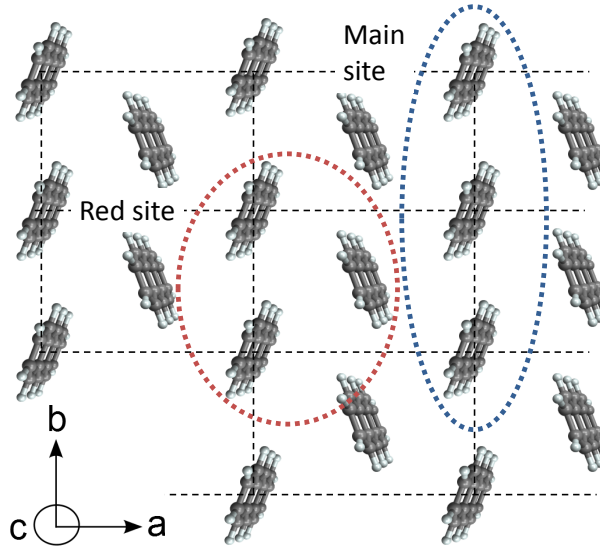


Figure 2.5: Insertion sites of a DBT molecule in the ‘herringbone’ packing structure of an anthracene crystal. The DBT can replace three anthracene molecules along the *b*-axis (main site) or two molecules along the *b*-axis and the molecule at the centre of the unit cell (red site).

larger than the number of molecules in the ‘red’ one. Within this work, I will assume that the DBT molecules occupy the ‘main’ insertion site.

2.4 The need for thin films of anthracene

As mentioned in the introduction, DBT molecules in an anthracene crystal deposited in the vicinity of a waveguide could deliver on-demand bright streams of single photons to the guided mode. The geometry of the photonic structure and the environment of the molecule increase or decrease the coupling. I studied this using Finite-Difference Time-Domain (FDTD) simulations. The material of the waveguide is chosen to be silicon nitride (Si_3N_4), whose refractive index at the DBT emission wavelength is $n = 2$. I fixed the waveguide to be 500 nm wide and 120 nm-thick [89]. I then investigated how the molecule’s environment affects the coupling. The molecule was simulated as an electric dipole emitting at a single frequency at 783.73 nm [88]. I immediately found that the closer a molecule is to the waveguide, the higher the coupling. I therefore fixed the molecule’s position 5 nm above the waveguide and varied the thickness of the 2 μm -square anthracene crystal embedding the DBT. The coupling was calculated using Lumerical FDTD Solutions (Version 8.16,

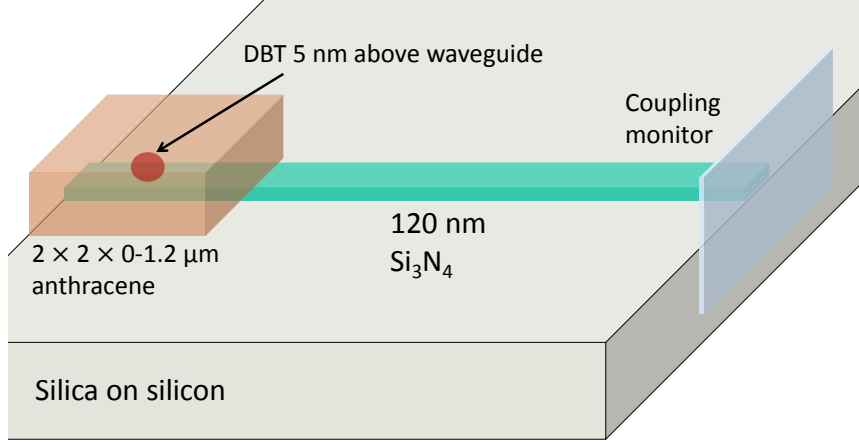


Figure 2.6: Sketch of the geometry used in Lumerical FDTD solution to estimate the coupling efficiency of the photons generated by a DBT molecule embedded in an anthracene crystal whose thickness was varied between 0 and 1.2 μm . The molecule was placed 5 nm above the centre of a silicon nitride waveguide 500 nm wide and 120 nm-thick on 1 μm of silica on silicon. The coupling efficiency was calculated by measuring the power transmitted through a $2 \times 2 \mu\text{m}$ box placed 10 μm from the molecule as fraction of the total emitted power.

Academic KX License, Lumerical Solutions Inc.) to solve Maxwell’s equations numerically. A sketch of the simulation geometry is shown in Fig. 2.6. The DBT molecule was oriented as in the ‘main’ site with the transition dipole moment aligned with the vacuum electric field of the propagating waveguide mode. The same geometry, viewed from the side is shown in Fig. 2.7 (a). Fig. 2.7 (b)-(d) show the magnitude of the field radiated by the molecule according to my simulations. One sees that for an anthracene thickness of 70 nm most of the radiation propagates in the waveguide. However, as this thickness increases the radiation goes into the anthracene layer and is lost. This is because the refractive index of the anthracene along the direction of the dipole moment, $n_x = 1.82$, is close to that of silicon nitride ($n = 2.00$). The coupling into the waveguide mode was calculated by measuring the power transmitted through a $2 \mu\text{m}$ -square box centered in the middle of the waveguide and placed 10 μm away from the molecule. This was compared with the total power emitted by the DBT. The coupling as function of the anthracene thickness is plotted in Fig. 2.8. One can see that a maximum coupling of more than 27% (total including both directions) is achieved for a crystal whose thickness is in the range 40-100 nm. This coupling falls to $\sim 12\%$ for crystals with a thickness of 700 nm. The oscillatory behaviour is due to the appearance of new propagating modes as the crystal becomes

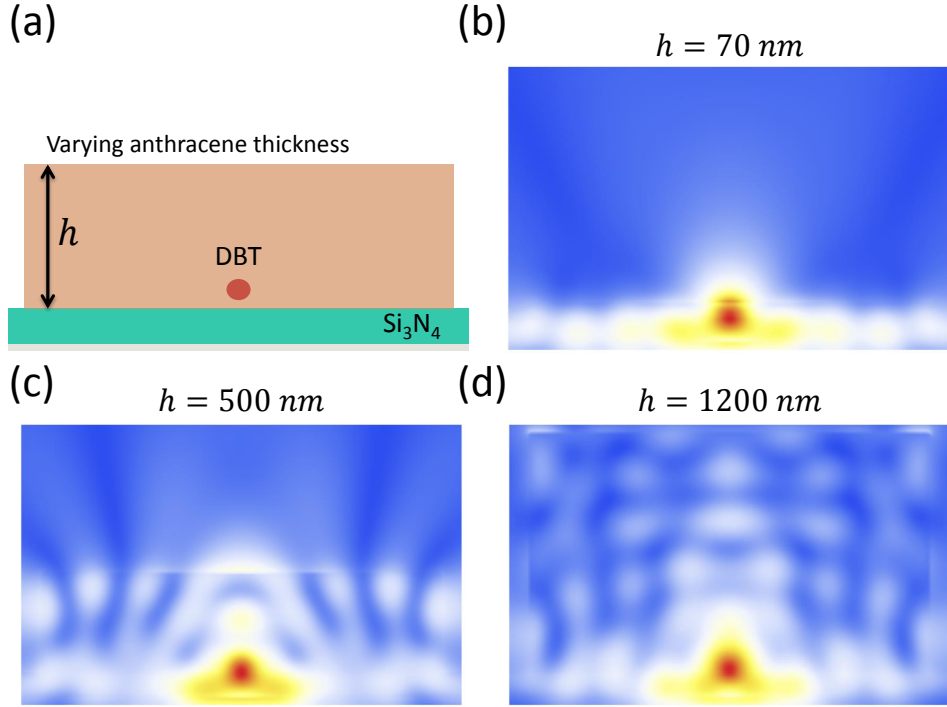


Figure 2.7: (a) Side view of the geometry: silica buffer with the silicon nitride and anthracene layer. (b) Radiation couples to the waveguide mode when the anthracene crystal is thin. (c)-(d) As the thickness of the anthracene increases radiation is lost into the anthracene layer.

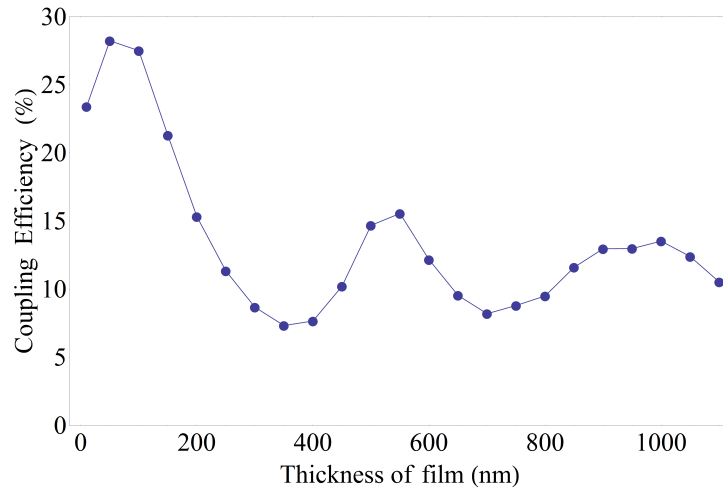


Figure 2.8: Graph showing the coupling efficiency (total in both directions) to the waveguide's mode as the thickness of the anthracene crystal is varied. It has a maximum of $\sim 28\%$ for a thickness of 80 nm.

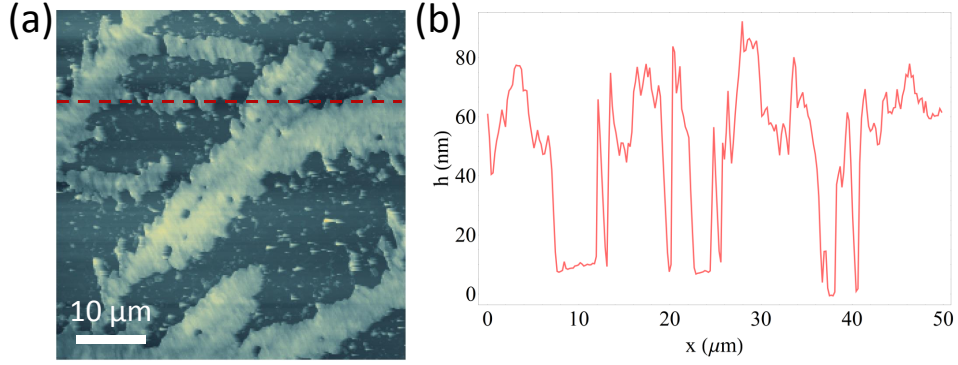


Figure 2.9: (a) Atomic-force microscope image of anthracene crystals I grew using the method developed by Toninelli *et al.* [85]. (b) Cut-through along the horizontal dashed red line of the image in (a). One can see the big variation of the film thickness, which makes this crystals not suitable for the coupling of the molecules to photonic structures.

thicker (see [90]).

To achieve efficient evanescent coupling one therefore needs to (i) place the DBT molecule as close as possible to the waveguide (to reach a higher value of the waveguide's guided field) (ii) within an anthracene crystal between 10-150 nm-thick. While the co-sublimation method is suitable for making doped crystals [81, 80, 82, 83], it produces crystals which are too thick for our purpose. According to Major *et al.* the smallest achievable thickness is ~ 700 nm [112]. Moreover the DBT molecules are randomly distributed within the crystal, so it is unlikely that one will be close to the waveguide. As mentioned in the introduction, Toninelli *et al.* coupled single DBT molecules to a Fabry-Perot cavity [85, 86]. In order to do so, they developed a new growth method which produced anthracene crystals ~ 20 nm thick, with a roughness reported as 1 nm [85]. This method relied on spin coating a solution of DBT, anthracene and benzene on the desired substrate. My attempts to replicate this, produced crystals such as those shown in Fig. 2.9, which are of the desired thickness, Fig. 2.9 (b). Photonic structures however are not amenable to spin coating because they have ridges and troughs. Therefore I developed another method for growing DBT-doped anthracene crystals. My technique involves spreading DBT on the surface by any suitable method - for example a dropper - then grow anthracene on top. When doing this, the molecules are taken up in the crystal but remain close to the surface.

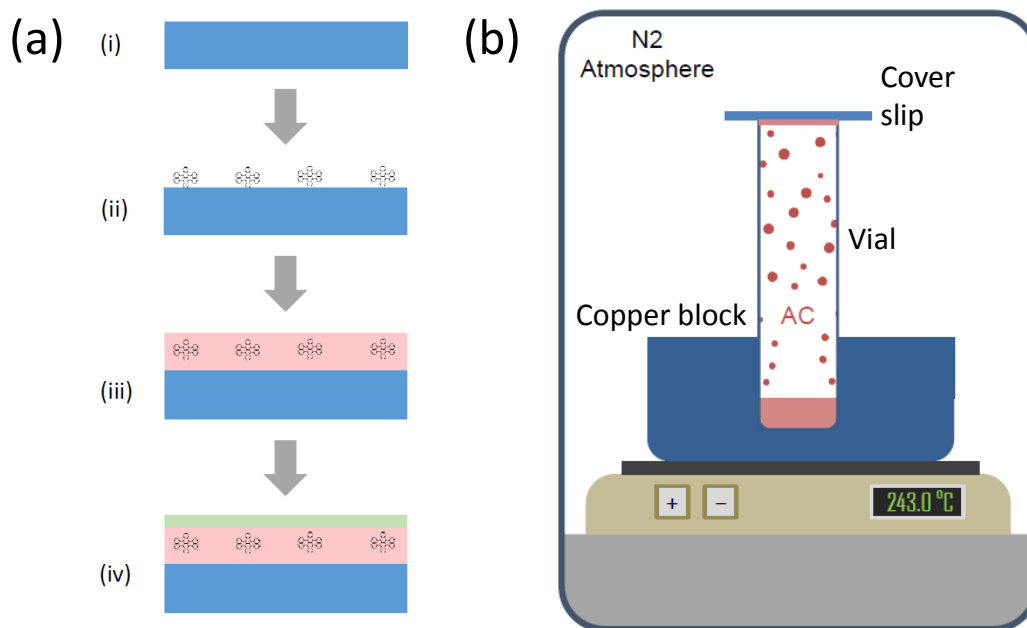


Figure 2.10: (a) Illustration of the method to grow thin crystals of DBT-doped anthracene. (i) Glass cover-slips are cleaned with oxygen plasma. (ii) A solution of DBT in toluene and diethyl ether is spin coated on top of the glass. (iii) Anthracene crystals are grown on top of the molecules which move a few nanometers inside the crystal. (iv) A solution of PVA is spin coated on top to prevent the crystals from evaporating. (b) The crystal growth apparatus. A glass vial containing anthracene is placed on top of a copper block which sits on a hotplate. The temperature of the hotplate is carefully adjusted within 1-2° by a PID controller. Normally the temperature is set to 243° C. Once the anthracene starts to evaporate, the cover glass is placed over the top and crystal growth occurs. Everything is in a nitrogen atmosphere inside a glove bag. Figure taken from [104]

2.5 Method

2.5.1 Depositing the DBT molecules

The novel method to grow thin DBT-doped anthracene crystals is illustrated in Fig. 2.10. Fig. 2.10 (a) lists the processing steps, while Fig. 2.10 (b) shows the apparatus used. In step (i), a 22 mm-square glass cover (631-0125 VWR) was cleaned with oxygen plasma at the London Centre for Nanotechnology. These cover slips were chosen to be 160 μm thick because the oil-objective lens of my confocal microscope is corrected for aberrations at that thickness. For step (ii) I prepared a 1 mMol solution of DBT molecules in toluene using 7,8,15,16-dibenzoterrylene supplied by Dr. Schmidt (Institut für PAH-Forschung, Greifenberg, Bavaria). This solution was then further diluted in diethyl ether, at a ratio

of 1:1000 (volume), and a volume of 20 μl was spin coated onto the glass cover slip. The speed of the spin coater was ramped up to 2000 rpm over 5 s, held there for 60 s, then brought to an immediate stop (SCS 6800, Specialty Coating Systems). With this recipe, a surface coverage of 0.4 DBT per square micron was obtained. For a higher concentration of DBT, the dilution in diethyl ether can be changed, keeping the spin coating process the same.

2.5.2 Crystal growth

Once the DBT solution was deposited on it, the glass cover slip was placed in a glove bag for step (iii), the growth of the anthracene crystals. I placed ~ 3 g of anthracene for synthesis (8.20109.0100 Merck Millipore) in a type III soda lime glass vial with a capacity of 28 ml (150999C, Wheaton UK). Before this, I grinded the anthracene with a mortar and a pestle. The vial was then placed inside the glove bag (AldrichRTM AtmosBag size L, Sigma Aldrich). In order to clear out the oxygen, the bag was pumped out and back-filled five times with clean, dry nitrogen. As illustrated in Fig. 2.10, there was a copper block inside the glove bag on top of the hotplate (120 V basic hotplate, Troemner). The temperature of the copper block was carefully controlled by a proportional-integral-derivative controller (PID330 controller, Tempatron), which turned on and off the hotplate to maintain the desired temperature. The glass vial containing the anthracene was placed inside the copper block which heated the anthracene at its bottom end. Once this temperature was stabilised and the anthracene evaporated, the DBT-coated cover slip was placed on top of the vial and kept there for up to 60 s to grow the crystals. During this time, the temperature of the cover slip was approximately 25° C.

I measured the shape of the anthracene crystals using an atomic-force microscope (Dimension 3100, Digital Instruments). In order to find the experimental parameters for which crystals grow wide and flat and could be used for applications to photonic devices, I grew crystals at successively higher values of the vial's bottom temperature (T_b). The results are shown in Fig. 2.11. I observed that at a temperature below the melting point of the anthracene, $T_b \leq 217$ °C, the crystals are thin and elongated in cross section, (a) to (c), and resemble the ones that stick up from the surface as 3-dimensional structures described by Major *et al.* [112]. As the temperature increases, $T_b \geq 243$ °C, the crystals change to flat and wide mesas, (e) and (f), due to the crystal growing in the a - b plane of

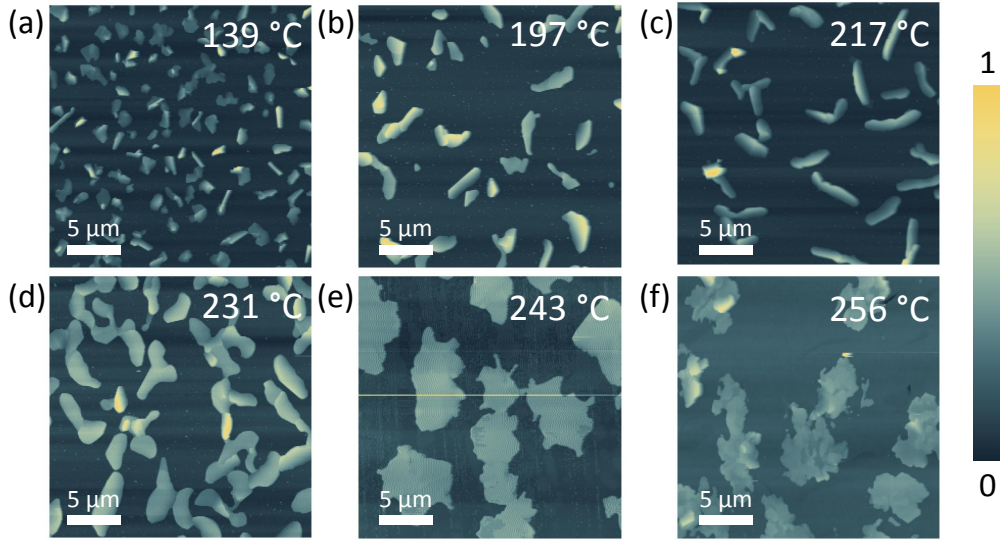


Figure 2.11: Atomic-force microscope images of crystals grown at various temperatures of the copper block holding the vial. (a) 139 °C, (b) 197 °C, (c) 217 °C, (d) 231 °C, (e) 243 °C, (f) 256 °C. Each image is normalised to its maximum. There is a clear transition at temperatures between 220 and 240 °C from long and tall crystals to wide and flat mesas.

the anthracene. The transition from crystals thin and elongated in cross section that stick up from the surface edge on and wide and flat mesas is presented in Fig. 2.12. Here a cut-through of Fig. 2.11 (a) on the left shows crystals very tall and thin compared to the cut-through Fig. 2.11 (f) on the right which shows much wider and flat mesas.

One of these mesas is shown in Fig. 2.13 (a). This crystal was selected from a sample grown for 50 s at a temperature $T_b = 243$ °C. Its shape does not resemble the shape of anthracene crystals grown with co-sublimation methods (Fig. 2.4 (b)). All the mesas

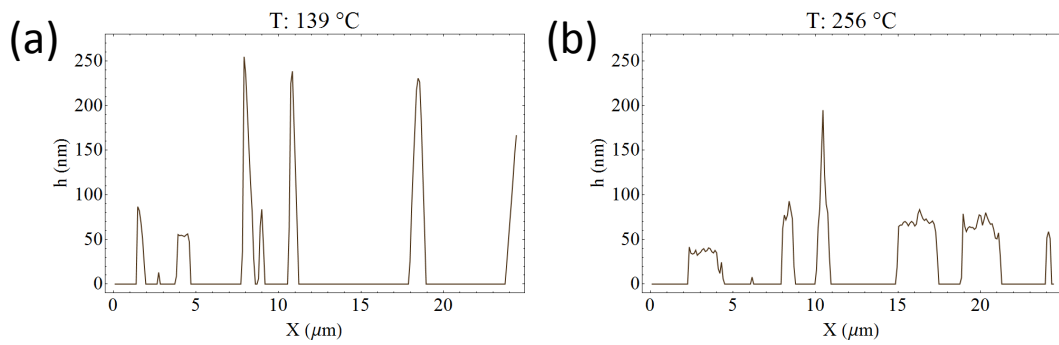


Figure 2.12: Cut through Fig. 2.11 (a) and Fig. 2.11 (f) showing the difference between crystals thin and elongated in cross section (a) and flat wide mesas (b).

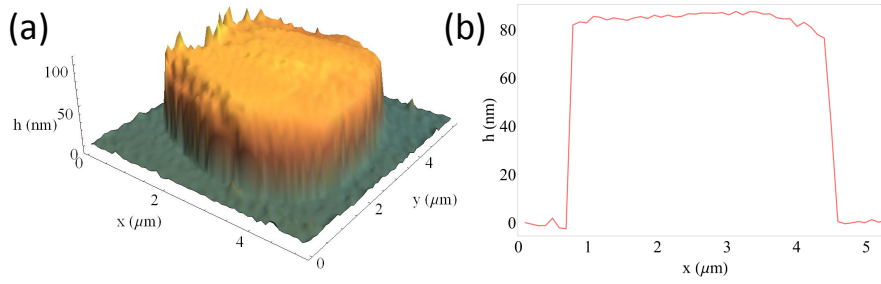


Figure 2.13: (a) A 3-dimensional atomic-force microscopy plot of a flat anthracene crystal grown with the bottom temperature of the vial set to 243 °C. (b) Cut-through along x of the crystal in (a). From this image one can see that the crystal exhibits a flat top ~ 85 nm thick with a very low roughness limited by the resolution of the microscope.

appear more randomly shaped. However, the crystal shows a very homogeneous flat top and sharp edges. These features are shown better in Fig. 2.13 (b), which is a cut through the centre along x of the image in (a). The roughness measured on the top of the mesa is 1.1 nm rms, which is at the level of the noise in the microscope itself. The thickness is ~ 85 nm which makes it ideal for applications to photonic devices. A small variation in thickness of only 10% is also generally observed over several crystals within a 3×3 mm area in the same sample.

Fig. 2.14, shows the height of the flat mesas as function of the growth time. Each point represents the mean height of several crystals within the atomic-force image (typically $50 \times 50 \mu\text{m}$), the error bars being derived from the standard deviation of the height histogram of each image. The growth time refers to the period over which the glass cover is kept on top of the vial. The time was varied between 10 and 60 s. One can see a linear increase in thickness at short times, which saturates after about 30 s, the red line being a guide to the eye. The maximum thickness I made was ~ 140 nm, I think this saturation is due to the cover glass heating up over 25 °C. This changes the thermodynamics of the crystal growth as I explain in the next section. I conclude that this method can produce crystals with a very uniform thickness ranging from 40 to 140 nm with a surface coverage of 0.4 DBT per square micron, which makes them ideal for the evanescent coupling to a waveguide.

2.5.3 Protecting the crystals with PVA

Because anthracene sublimates at room temperature, the crystals gradually shrank in area and disappeared in less than a day. We were able to prevent this by overcoating them with

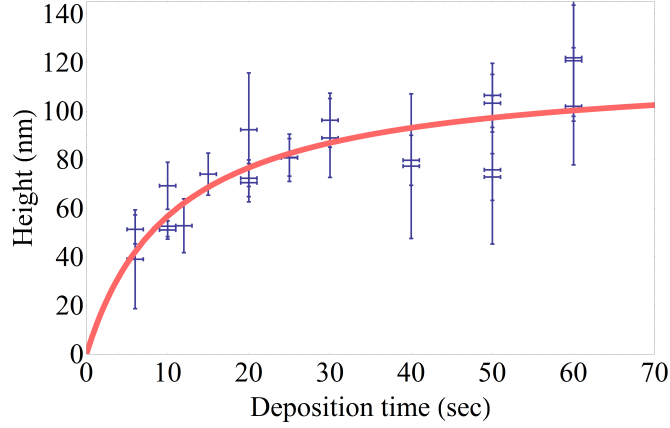


Figure 2.14: Thickness of the anthracene crystal grown at a temperature of the bottom of the vial of 243 °C as function of the evaporation time. One can see a linear relation at times between 10 and 30 s with a saturation behaviour for longer ones.

a poly-vinyl-alcohol film. This was prepared by mixing 0.08 g of PVA powder (341584-25G, Sigma-Aldrich) in 2 ml deionised water and heating at 65 °C for about an hour until the powder dissolved completely. The PVA film was formed by spinning 20 μ l of this solution on top of the anthracene, then ramping up to 3000 rpm and back down again over a minute. The coated crystals lasted for many months at room temperature. Over this time, the crystals aggregated and annealed to form larger, regular structures shaped as in Fig. 2.4 (b).

Before investigating the properties of the DBT molecules embedded in these crystals, I digress to comment on the thermodynamics of the crystal growth.

2.6 Theory of thin film crystal growth

In this section I discuss briefly why the crystals start to grow as flat mesas, rather than growing out of the surface, once the temperature of the copper block is high enough. The crystal growth is driven by the difference in the chemical potential between the vapour at the top of the vial (μ_v) and the anthracene crystal (μ_{ac}), which we can express as $\Delta\mu = \mu_v - \mu_{ac}$. The chemical potential is the energy required to change the number of particles of a system, N , by one. In terms of the free energy F it can be written as:

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} \quad (2.1)$$

with T and V denoting the temperature and the volume of the system respectively. It can be shown [121] that

$$\mu = -k_B T \ln \frac{p_Q}{p} \quad (2.2)$$

with k_B being the Boltzmann constant, p and T the pressure and the temperature of the system and p_Q the quantum pressure defined as $p_Q = \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{\frac{3}{2}} k_B T$. The chemical potential of the vapour at the top of the vial where growth occurs can be therefore written as

$$\mu_v = -k_B T_t \ln \frac{p_Q}{p_t} \quad (2.3)$$

with p_t and T_t being the pressure and the temperature at the top respectively. Similarly, the chemical potential of an infinitely large anthracene surface at T_t is

$$\mu_{ac} = -k_B T_t \ln \frac{p_Q}{p_0(T_t)} \quad (2.4)$$

with $p_0(T_t)$ denoting the vapour pressure of anthracene at the top temperature. The difference between these chemical potentials is

$$\Delta\mu = \mu_v - \mu_{ac} = k_B T_t \ln \frac{p_t}{p_0(T_t)}. \quad (2.5)$$

In order to estimate p_t , let us treat the anthracene vapour as an ideal gas. Then this pressure at the top of the vial is related to that at the bottom by

$$p_t = \sqrt{\frac{T_t}{T_b}} p_0(T_b), \quad (2.6)$$

where we take the pressure at the bottom to be the vapour pressure of the solid at temperature T_b . Eq. 2.5 then becomes

$$\Delta\mu = k_B T_t \ln \frac{\sqrt{T_t} p_0(T_b)}{\sqrt{T_b} p_0(T_t)}. \quad (2.7)$$

The chemical potential difference is zero when the temperature $T_b = T_t$. In this case there is no growth and the crystal is in equilibrium with the vapour. However, as the temperature at the bottom of the vial increases, so does the chemical potential difference and crystals start growing, adopting the geometry that minimises their surface energy

[122, 123]. As the temperature increases above a critical value, the chemical potential difference provides enough free energy for the crystals to start growing in wide and flat mesas. As shown in Fig. 2.11, that critical value lies somewhere between 220° C and 240° C. At these temperatures, the ratio of vapour pressures, $\frac{p_0(T_b)}{p_0(T_t)}$, is in the range $(0.4-3.4) \times 10^7$ [124, 125, 126], and the corresponding chemical potential difference between the vapour at the top and the infinite crystal is 0.41 ± 0.02 eV.

Following section 4 of [127], as detailed in Appendix B, we expect this transition to occur at a chemical potential difference of

$$\Delta\mu = 2ab(2\gamma_{001} - \sigma). \quad (2.8)$$

where ab is the area of the (001) plane of the unit cell, while γ_{001} and σ are the surface energies per unit area of the (001) plane and the interface with the substrate, respectively. From [115, 128] the values are $ab = 51.7 \text{ \AA}^2$, $\gamma_{001} = 3.3 \text{ meV/\AA}^2$. Comparing this theory with our measurement, we conclude that the energy per unit area of the anthracene binding to the glass is $\sigma = 2.6 \pm 0.2 \text{ meV/\AA}^2$. This binding energy with glass, not previously reported in the literature, is somewhat lower than the values for pentacene, $\sigma = 4.8 \text{ meV/\AA}^2$, tetracene, $\sigma = 5.9 \text{ meV/\AA}^2$ and perylene, $\sigma = 4.6 \text{ meV/\AA}^2$ [123] perhaps due to the smaller size of the anthracene molecule.

2.7 The anisotropy of crystal evaporation

As seen in the section 2.4.3, crystals were protected by a thin layer of polyvinyl-alcohol immediately after the growth. Without the protective layer, they would evaporate within hours as shown in the 3-dimensional atomic-force microscope images in Fig. 2.15. The label of each image corresponds to the time the crystals were left to evaporate at room temperature, starting from the first (image (a)), captured immediately after the growth, to the last (image (i)), which was captured after 317 minutes. As one can see, in the last image most of the crystals have sublimed. When protecting the crystals with a thin layer of polyvinyl-alcohol on the other hand they lasted for months. Fig. 2.15 also highlights the anisotropy of the crystal evaporation. Crystals in fact predominantly evaporate from the sides, keeping their height mostly constant. Thermodynamically, evaporation can be

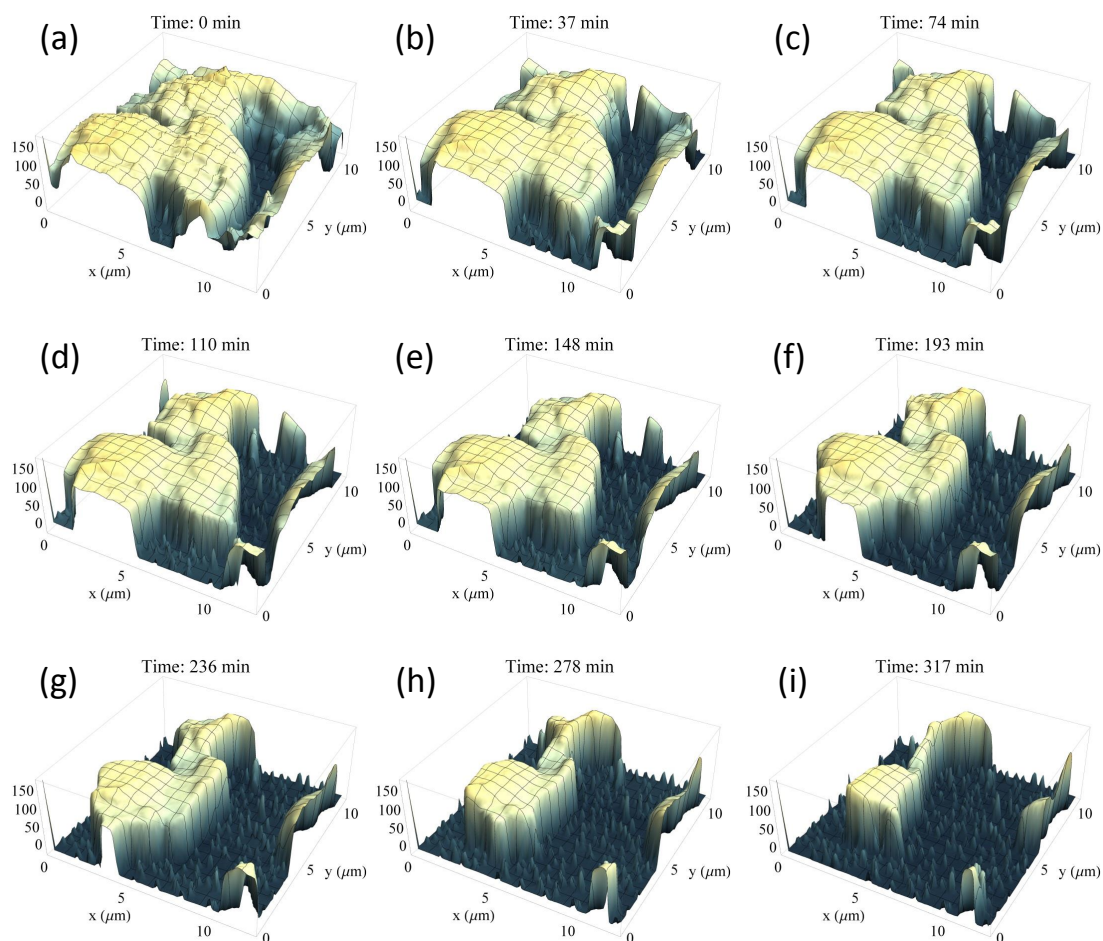


Figure 2.15: Series of AFM images of anthracene crystals grown with the thin film evaporation method let evaporate at room temperature. The first image, (a), was taken immediately after the growth, while the last one, (i), after ~ 5 hours. During this time the crystals were exposed to air and let to sublime. The scale on all images is the same to highlight the fact that the evaporation occurs from the lateral sides while the crystals keep the same height.

seen as the inverse process of growth and since such growth is mostly 2-dimensional, so is the evaporation of the crystals.

I used the images in Fig. 2.15 to estimate the value of the vapour pressure of anthracene, p_v , at room temperature, $\sim 25^\circ$ C. By definition, this is the pressure exerted by the anthracene vapour in thermodynamic equilibrium with the crystal at a given temperature in a closed system (in our case the casing surrounding the atomic-force-microscope probe. In the theory section I showed that the vapour pressure has a profound effect on the crystal growing process. Numerous research groups have measured it by measuring the mass loss of bulk anthracene at various temperatures, but so far no measurement at room temperature, has been reported.

I assume the following model. At thermodynamic equilibrium, the number of anthracene molecules in the vapour striking the crystal is equal to the number of molecules evaporating from a crystal. Let us consider a surface of area A . The number N of molecules leaving as a function of time t is

$$\frac{dN}{dt} = \frac{1}{4}n\bar{v}A, \quad (2.9)$$

where $\bar{v}$ is the mean velocity and n the number density in the saturated vapour, $n = \frac{N}{V}$. In terms of n , Eq. 2.9 can be expressed as

$$n = \frac{4}{\bar{v}A} \frac{dN}{dt}. \quad (2.10)$$

Assuming the saturated vapour to behave as an ideal gas, the mean velocity can be expressed as $\bar{v} = \sqrt{\frac{8k_B T}{\pi m}}$, with m being the mass of one anthracene molecule, k_B the Boltzmann constant and T the temperature in K. Hence Eq. 2.10 becomes

$$n = \frac{4}{A} \sqrt{\frac{\pi m}{8k_B T}} \frac{dN}{dt}. \quad (2.11)$$

Because of the assumption of the saturated anthracene vapour to behave as an ideal gas, the pressure p_v can be expressed as

$$p_v = nk_B T. \quad (2.12)$$

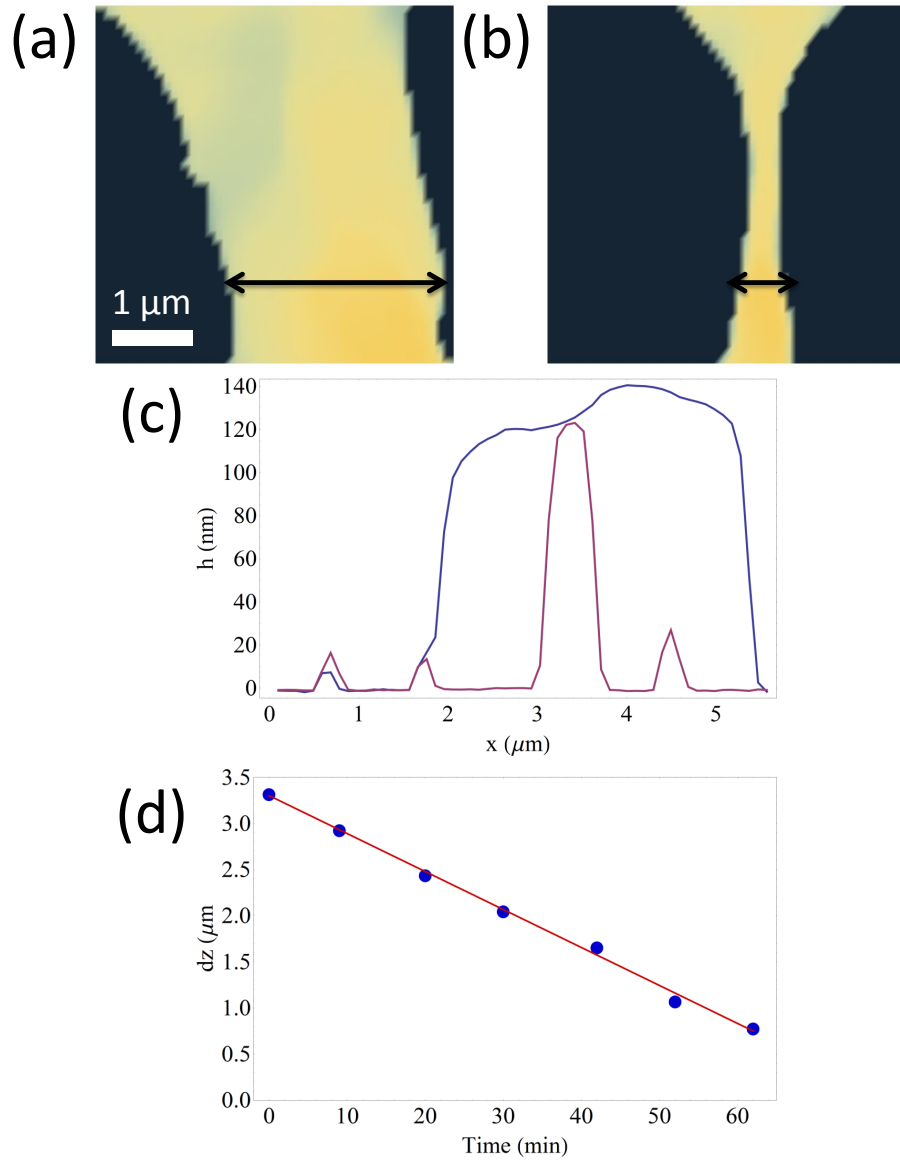


Figure 2.16: (a)-(b) AFM images showing a region of a crystal grown with the thin film evaporation method (light yellow) shrinking in mostly in one direction, as highlighted by the black arrow. (c) Cut-through along the black line of the image in (a) (blue line) and (b) (red line). (d) Blue dots: experimental data of the width of the crystal as a function of time. A fit to a straight line, red, leads to the rate of evaporation in one dimension when crystal exposed to air.

Substituting n with Eq. 2.11,

$$p_v = \sqrt{2\pi k_B T m} \frac{1}{A} \frac{dN}{dt}. \quad (2.13)$$

Because of the result from Fig. 2.15 of the crystals evaporating only from the sides, the rate of loss of molecules over an area A can also be expressed as

$$\frac{dN}{dt} = \frac{\rho A dz}{m dt}. \quad (2.14)$$

Here ρ is the density of the anthracene crystals. Hence

$$\frac{1}{A} \frac{dN}{dt} = \frac{\rho}{m} \frac{dz}{dt}, \quad (2.15)$$

which leads to the following expression for p_v ,

$$p_v = \sqrt{2\pi k_B T m} \frac{\rho}{m} \frac{dz}{dt}. \quad (2.16)$$

I analysed the atomic-force microscope images looking at the regions where the crystals evaporated, such as Fig. 2.16 (a) and (b). Fig 2.16 (b) was taken after ~ 1 hour from Fig. 2.16 (a) and shows the crystal shrinking in one direction. By monitoring the width of the crystal (Fig. 2.16 (c)) as a function of time I extrapolated the data presented by the blue dots in Fig. 2.16 (d). A fit to a straight line, shown in red leads to a rate of evaporation of $\frac{dz}{dt} = 20.58 \pm 0.54$ nm/min. Using the density of anthracene of 1.28 g/cm³ and a molecular weight of 178.229 g [126], I estimate a vapour pressure at room temperature of $p_{v,\text{Single cr.}} = 0.130 \pm 0.003$ mPa.

Repeating the measurement over many regions I estimate the vapour pressure of anthracene at room temperature to be $p_v = 0.136 \pm 0.017$ mPa. Let us compare this value with the vapour pressure one can compute for similar temperatures using the Antoine coefficients found in the literature [125, 129, 130, 132, 131, 133]. I should point out that these coefficients were measured for temperatures between 40°C and 100°C and all the curves were extrapolated to room temperature. They were measured by monitoring the mass loss of high-purity anthracene in powder, not the crystalline form as in my measurement. The result is shown in Fig. 2.17 on a natural logarithmic scale. It shows a big discrepancy between my measurement, magenta dot, with the literature, solid lines. This

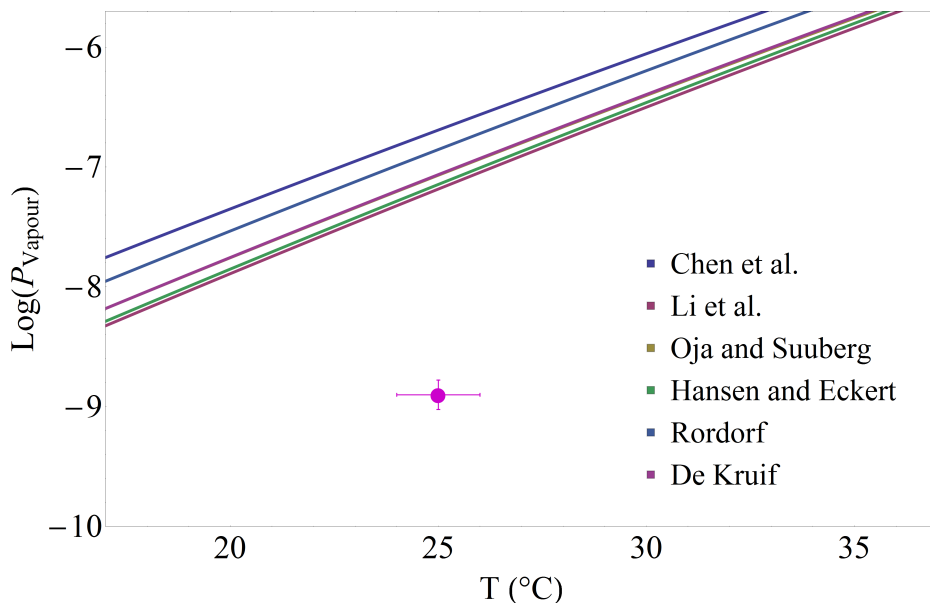


Figure 2.17: Magenta dot: vapour pressure as measured by monitoring the evaporation of the anthracene crystals at room temperature. Solid lines: vapour pressure estimated using the Antoine coefficients found in the literature and measured by Chen *et al.* [125], Li *et al.* [129], Oja and Suuberg [130], Hansen and Eckert [131], Rordorf [132], and De Kruif [133].

is probably due to the fact that because I was monitoring crystalline anthracene, there needs to be an efficiency with which molecules stick on a crystal when they hit it. If the system is in equilibrium then the number arriving (and sticking) to a crystal must equal the number leaving, so this efficiency will also be a factor in the number leaving. Let us call this factor ϵ . The vapour pressure is then proportional to $\frac{1}{\epsilon}$. Taking the various vapour pressures at room temperature using the Antoine coefficients from the literature [125, 129, 130, 132, 131, 133], I estimate the sticking efficiency of the anthracene molecules, or ϵ , to be between 0.11 and 0.18.

Chapter 3

Optical system

3.1 Introduction

Having grown the thin anthracene crystals I went on to investigate the optical properties of the DBT molecules. It was important to establish whether the DBT molecules embedded in the thin anthracene crystals could stably emit single photons at a high rate for use in photonic devices. In order to study the molecules' emission I built a confocal microscope designed to illuminate a sample with the smallest possible spot scanned across a region of interest. Once a molecule was located the spot could be positioned directly on top of it to carry out further studies. A schematic diagram of the microscope can be seen in Fig. 3.1.

3.2 Principles of confocal microscopy

Before describing in detail how the scanning optical microscope in Fig. 3.1 works, it is worth spending some time reviewing the history of confocal microscopy. This starts with the 19th century German physicist Abbe who, together with Otto Schott and Carl Zeiss is sometimes considered to be the founder of modern optics. Abbe made important contributions to microscopy such as the development of the apochromatic lens and the refractometer. He also postulated the famous resolution limit, called the Abbe criterion. This states that the image of a point source, formed by an objective of numerical aperture NA, is limited by the diffracted Airy pattern to a resolution of

$$d_{\text{Abbe}} = \frac{\lambda}{2NA}, \quad (3.1)$$

with λ being the wavelength of the light. It wasn't until the middle of the 20th century though that Abbe's criterion of resolution was put to a test with the development of the first confocal microscopes. In 1939 a paper appeared by the Swiss scientist Hans Goldmann on a novel instrument to examine the human eye. This instrument, called a slit lamp, was built so that both light rays of the illumination and the image passed through a semicircular slit [134]. After a decade, in 1951, the Japanese physicist Hiroto Naora published an article clearly describing a confocal microscope used for microspectrophotometry of nucleic acids. In his setup he used two irises, one in the excitation path and one just before the photomultiplier tube used for detection [135]. In his setup the sample was kept still. The first scanning confocal microscope was built by the cognitive scientist Marvin Minsky who filed a patent in 1957 about it [136].

The key idea is to have two pinholes, one in excitation and one in detection. The excitation pinhole provides spatial filtering of the excitation light. Nowadays this is achieved by coupling laser light into a single-mode optical fibre [137]. At the output of the optical fibre, light is generally sent to an infinity corrected, high numerical aperture (NA) objective lens by a dichroic mirror or a beamsplitter. The objective lens focuses the light to a diffraction limited spot on the sample and excites the specimens - in our case, the DBT molecules. The emitted fluorescence and backscattered laser light are collected and collimated using the same objective lens. The reflected laser light is blocked using a dichroic mirror or long pass filters. Fluorescence light on the other hand is focused to a pinhole placed in front of a photodetector. The role of the pinhole is to reject light which originates from points outside the focal plane [137, 138]. It therefore provides higher axial resolution than a normal microscope. This is known as the confocal advantage. The diameter of the pinhole plays an important role determining the depth of field of the image [138, 139]. Normally, its size should be between 0.5 and 2 of the Airy-disc diameter [138]. Confocal images are created either by raster scanning the sample, held on top of a piezo-controlled stage underneath the laser spot [138], or by moving the laser spot using a scanning mirror.

3.3 Laser system

The experiments in this thesis used five different laser systems. (i) My investigation of the optical properties of the DBT molecules on top of glass, chapter 4, was mainly

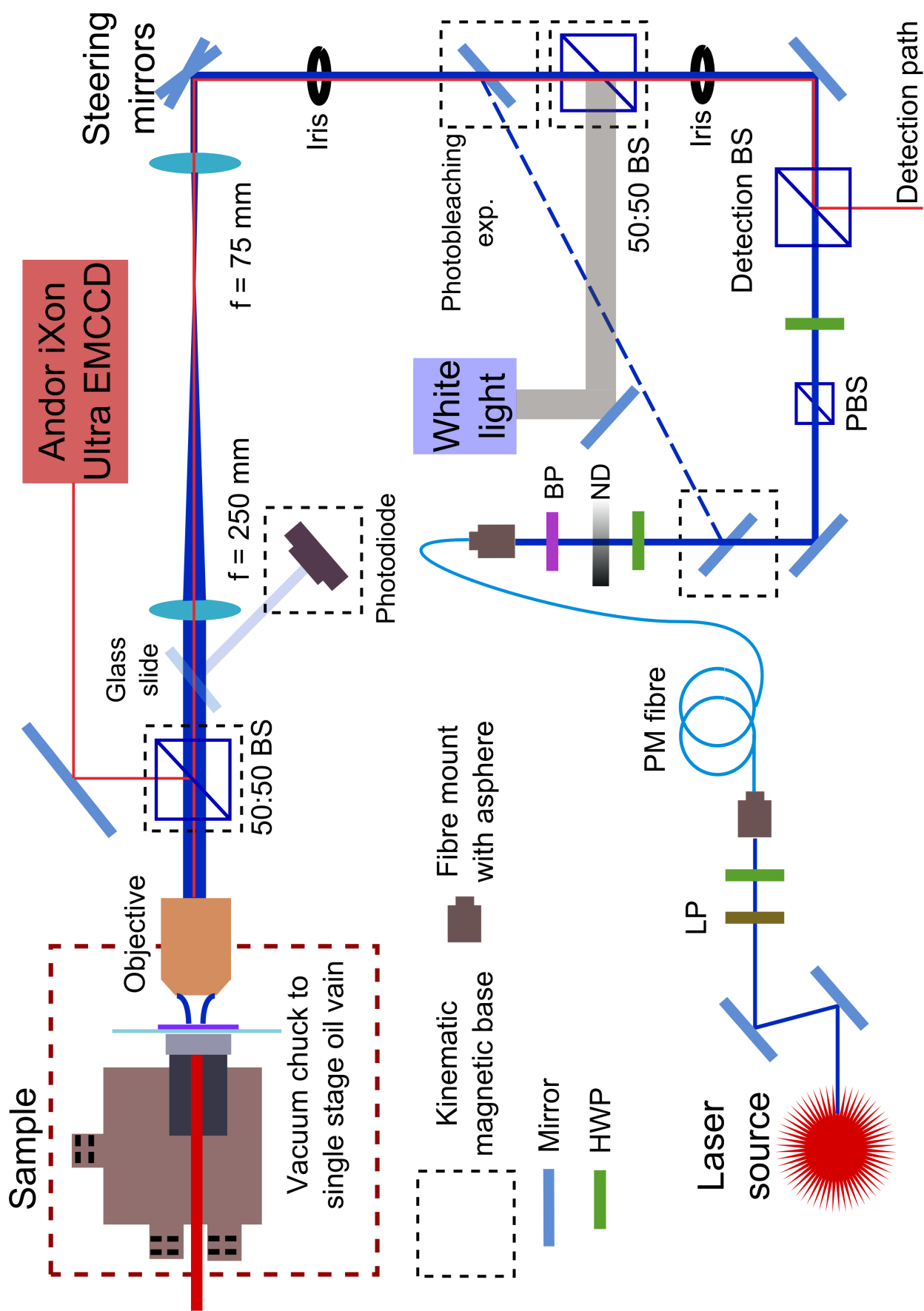


Figure 3.1: Schematics of the main optical setup.

Laser	Wavelength (nm)	Max. output power
Lynx	780 CW	8 mW
Toptica how power	780 CW	3 W
Ti:Sapphire	780 CW	500 mW
Toptica low power	780 CW	33 mW
Picoquant	755 pulsed (typically 40 MHz)	4.7 mW

Table 3.1: The lasers used during the course of the PhD

carried out using an external-cavity continuous-wave diode laser (TEC 100 Littrow-Lynx controlled with the MLD-1000 Modular Laser Driver System, Sacher Lasertechnik). This laser produced ~ 8 mW at 780 nm. (ii) For the photobleaching measurement, a higher power was needed, and I used a continuous-wave diode laser (TA 100 Pro laser, Toptica) with output power of ~ 3 W at 780 nm. (iii) An alternative high-power source was the single-frequency Ti:Sapphire laser (MBR110, Coherent) used at 780 nm. The Ti:Sapphire laser was used predominantly when imaging the DBT molecules on top of lithium niobate, chapter 6, and when investigating the narrowing of the second-order correlation function at high intensity, section 4.7.2. (iv) For the waveguide experiment, chapter 5, given that a low-NA objective was used because of its long working distance, I replaced the Littrow-Lynx laser with a similar external-cavity continuous-wave diode laser (controlled with the DCC110 and DTC110 Laser Drivers, Toptica). This laser could deliver up to 33 mW at 780 nm. (v) When pulsed excitation was required, for example when measuring the lifetime of the molecules by time-correlated single-photon counting (TCSPC), I used a pulsed diode laser (LDH-P-760 controlled with the PDL 800-B Laser Driver System, Picoquant). I measured a maximum output power of 4.7 mW at 755-756 nm and a repetition rate of 40 MHz. The repetition rate could be adjusted from 2.5 MHz to 40 MHz and according to the manufacturer the laser's minimum temporal width was 83 ps.

Light leaving the laser was coupled into a polarisation-maintaining single-mode fibre (P3-780PM-FC-2, Thorlabs), labelled PM fibre in Fig. 3.1, in order to filter the spatial mode of the laser. The linear polarizer made sure that light was linearly polarised and the half-wave-plate (HWP) allowed me to adjust the polarization axis so that the light would only couple to a principal axis of the fibre. At the output of the optical fibre I placed a band-pass filter (labelled BP in Fig. 3.1). This blocked any light at a wavelength longer than 785 nm, coming either from the laser or from Raman scattering in the optical

fibre. When using the continuous-wave lasers at 780 nm, a 780 nm bandpass filter was used (D780/10X, Chroma Technologies). When however the 755 nm pulsed diode laser was used, I replaced the 780 nm filter with a 760 nm one (760/12 Brightline, Semrock). The 780 nm filter was placed at a normal incidence, and the 760 nm one was placed at $\sim 20^\circ$ of incidence in order to decrease its central wavelength towards 755 nm [140].

3.4 Description of the confocal microscope

3.4.1 Excitation

After passing through the band-pass filter, the light went through a continuously variable neutral-density filter, labelled ND in Fig. 3.1, having an optical density of 0-2.0 (NDC-50C-2, Thorlabs). This allowed me to vary the excitation power and measure the saturation intensity of the molecules. Light then passed through a half-wave plate, a broadband dielectric mirror (BB1-E03, Thorlabs) and a polarising beamsplitter (PBS052, Thorlabs). The half-wave plate was used to rotate the linear polarisation axis until the electric field was p-polarised (i.e. horizontally polarised). This was done to match the transmission of the polarising beamsplitter which transmits p-polarised light with $>90\%$ efficiency. After the polarising beamsplitter, the light entered a zero-order half-wave plate (WPH10M-780, Thorlabs) which was carefully rotated using a motorised rotation stage controlled with LABVIEW (KPRM1E/M, Thorlabs). Light was then transmitted through a beamsplitter (see Detection section for details) to another broadband dielectric mirror (BB1-E03, Thorlabs) and then through two irises placed in the beam path for alignment. To illuminate the sample with white light, for example when choosing which crystal to investigate, I used a white LED (MCWHL5, Thorlabs). Light from the LED was collimated (ACP2520-A, Thorlabs) and directed to a one-inch silver mirror and a 50:50 pellicle beamsplitter (BP145B2, Thorlabs). The beamsplitter was mounted on top of a magnetic kinematic base (KB75/M, Thorlabs) so it could be easily removed when the white light illumination was not required. Light emerging through the second iris was incident on a steering mirror (GVSM002/M, Thorlabs), whose galvanometers were controlled with a LABVIEW software. This steered the angle at which the light entered the objective thereby translating the position of the focussed spot on the sample. I used two lenses, with focal lengths $f=75$ mm and $f=250$ mm separated by 325 mm to expand the collimated

Objective	Description	Experiment
60 $\times$ oil	Oil-immersion, NA= 1.40, 0.13 WD, Plan Apo	Glass
100 $\times$ air	Air, NA= 0.9, 0.51 WD, Plan Apo	Lithium niobate
20 $\times$ air	Air, NA= 0.45, 4.5 WD, LU Plan	Waveguides

Table 3.2: The objective lenses used in the optical setup together with their description and the specific experiment they were used for. (NA = Numerical Aperture, Plan Apo = Apochromatic and Flat Field correction, LU = Luminous Universal, i.e. brightfield, darkfield, and polarized light, WD = Working distance in mm).

beam size from 2 mm to 6.7 mm and completely fill the back aperture of the objective lens. When measuring the orientation of the dipole of the molecules, I placed a glass slide in the beam path (angle of incidence 30°) to reflect 6% of the light onto a silicon photodiode detector (DET10A/M, Thorlabs). This allowed me to record the laser power as the polarization of the light was varied and to monitor the excitation intensity when measuring the molecules' saturation. After the lenses, laser light then passed through a 50:50 non-polarising beamsplitter cube also mounted on top of a magnetic kinematic base (GVSM002/M, Thorlabs) used to image the sample with the iXon Ultra camera (Andor, Oxford Instruments). The light entered the microscope objective and was focused down to a nearly diffraction-limited spot on the sample. Three different objective lenses were used, as summarised in the Table 3.2, all of them infinity-corrected. They were used in different experiments for different substrates where the DBT molecules were deposited. When using the oil objective, 50 μ l of oil for immersion lenses (Nikon 50 Type NF) with refractive index $n= 1.515$ was deposited on the cover slip. The oil-objective was also corrected for the 160 μ m thickness of the cover slips. For the photobleaching experiment, the first lens after the galvo mirrors, with $f=75$ mm, was removed. This caused the second lens to focus the laser light on the back aperture of the objective lens, creating a wide laser spot, which illuminated many molecules at the same time. Given the wider laser spot, more power was required to achieve the same intensity. I therefore mounted two extra mirrors (highlighted in Fig. 3.1 by two dashed boxes around them) on top of two kinematic platforms. When confocal images were acquired, the normal setup was used. When the molecules were illuminated with the wider beam, I placed both mirrors in the setup using the kinematic mounts, thus avoiding the losses in the detection beamsplitter optics. With the light at the output of the fibre being linearly polarised, I adjusted the first HWP to excite the molecules with light polarised along the direction of their dipole.

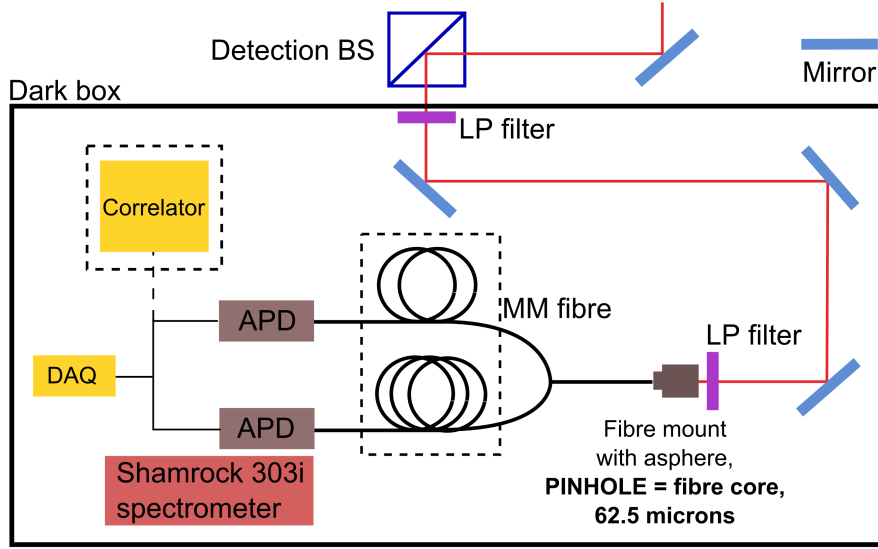


Figure 3.2: Schematics of the detection part of the confocal microscope.

3.4.2 Detection

The fluorescence that we detected from the molecules was of longer wavelength than the excitation light and retraced the path of the confocal microscope, as highlighted in Fig. 3.1 by the red line. Light then entered the detection beamsplitter. I used a 90:10 (R:T) non-polarising cube beamsplitter (BS029, Thorlabs) when investigating the optical properties of the DBT molecules on top of glass and lithium niobate and a 50:50 (R:T) beamsplitter cube (BS017, Thorlabs) in the waveguide experiment, which allowed higher intensities before the objective lens. At the detection (Fig. 3.2) beamsplitter the reflected part entered the dark box shown in Fig. 3.2 through an aperture a few millimetres in diameter. The box was constructed from aluminium struts (Bosch Rexroth) and black plastic sheets intended to exclude room light. After entering the box, light from the molecules passed through a long-pass filter that rejected the scattered excitation light. When using the continuous-wave diode lasers at 780 nm, a 792 nm long-pass filter was used (RET792lp, Chroma Technologies). This rejected the excitation light as well as the zero-phonon line, but it transmitted the more red-shifted sidebands of the THz-wide room temperature fluorescence. When the pulsed diode laser at 755 nm was used, I replaced the 792 nm filter with a 770 nm long-pass one (ET770lp, Chroma Technologies) and in this case I could detect light from the zero-phonon line (section 4.2). After being filtered, the light was directed to another long-pass filter and then be coupled into a multimode

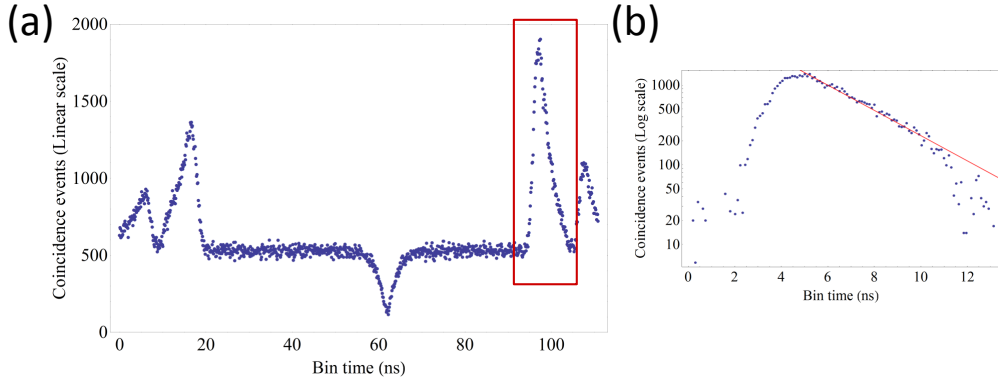


Figure 3.3: (a) Second-order correlation measurement with the TimeHarp 200 card, showing the second-order correlation dip, as described in section 4.7 together with four ‘flashes’ caused by the APDs at its sides. I eliminated them with the aid of extra fibres in the detection. (b) Zoom in the ‘flash’ with most coincidence counts in (a). Histogram of the arrival time of the emitted photons from an APD to the other in the HBT setup.

optical fibre, labelled MM in Fig. 3.2 (GIF625 with FT038-BK reinforced jacket tubing, Thorlabs). The fibre core diameter of $62.5\ \mu\text{m}$ acts as a pinhole and this is why the whole system is a confocal microscope which provided good signal-to-background when looking at single molecule fluorescence. For our pinhole diameter of $62.5\ \mu\text{m}$ the axial resolution one could achieve was $d_{axial} = 95.6\ \mu\text{m}$. This was three orders of magnitude higher than the thickness of the anthracene crystals containing the DBT molecules and therefore did not limit the detection of these molecules. When two detectors were used, for example when measuring the molecules’ second-order correlation function, the light was split using a 1×2 multimode coupler (FCMM625-50A, Thorlabs) with extra multimode fibres, 2 m and 3 m respectively, butt-coupled to it in a typical Hanbury-Brown-Twiss (HBT) setup [141].

The fibres were connected to two avalanche photodiodes (APD) used for single photon detection in Geiger mode (SPCM-AQRH-15-FC, Perkin Elmer). According to the manufacturer, these APDs have a photon detection efficiency of $\sim 50\%$ at 800 nm and a dark count rate of 50 counts/second. I observed that when the APDs are used in Geiger mode, the avalanche of carriers is accompanied by photon emission, as previously demonstrated by Kurtsiefer et al. [142]. This was a problem when measuring the second-order correlation function because a photon emitted from the avalanche in one APD, could back-scatter off the fibre coupler and be detected by the other APD. The arrival times of these

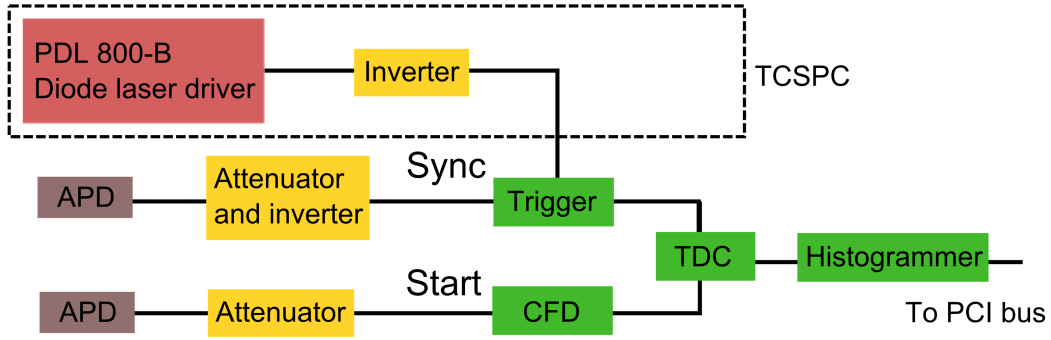


Figure 3.4: A schematic of the Timeharp 200 used for TCSPC and correlation measurements on single molecules [143].

photons were, of course, correlated and in the histogram created by the time-correlation card appeared as peaks, as shown by the four peaks, two at each side of the second-order correlation dip in Fig. 3.3 (a). The strongest of these peaks, highlighted by the red box in Fig. 3.3 (a), is shown in Fig. 3.3 (b) on a logarithmic scale. The peak shows a rise time of 1 ns and an exponential decay of 2.74 ± 0.03 ns which is in agreement with [142]. These peaks, known as ‘flashes’, were separated in time because of the extra lengths of fibres highlighted by the dashed box in Fig. 3.2, leaving a wide window in the time-correlated counting card histogram to measure a second-order correlation function. The spectrum of the emission from the APDs ranges from 700 to 1000 nm [142] and matches the fluorescence spectrum of the molecules.

The TTL signals from the APDs were sent to a DAQ card (NI USB 6343, National Instruments) and the data acquisition was performed using LABVIEW (2014, SP1, National Instruments). When measuring the lifetimes of molecules by time-correlated single-photon counting (TCSPC) or when measuring the second-order correlation function, the signal from the APDs was directed to a time-correlated counting card, labelled correlator (Timeharp 200, Picoquant) in Fig. 3.2. A schematic diagram in Fig. 3.4 shows the building blocks of the Timeharp 200. The 5 V TTL signal from the lower APD in Fig. 3.2 was sent to a 14 dB RF attenuator because the Timeharp card required an input voltage step between 50 and 1500 mV. It was then sent to the ‘start’ input of the card which used a constant fraction discriminator (CFD) in order to give a constant trigger time, independent of the pulse height [143]. The card was designed mainly to perform TCSPC and the ‘sync’ signal coming from a laser driver has usually a well-defined shape. Therefore in

the ‘sync’ channel, the signal was sent to a simple settable comparator (Trigger) [143]. In my case I sent the signal from the pulsed laser driver after passing it through an inverter (SI 100, Picoquant). When measuring the second-order correlation function on the other hand, both signals from the APDs were sent to the card. The one sent to the ‘sync’ was inverted and attenuated (SIA 400, Picoquant), after being split with a power splitter (ZAPD-21-S+, Mini-Circuits) in order to monitor the single counts using the DAQ card. In the TimeHarp 200 card both signals from the CFD and the Trigger were fed to a Time to Digital Converter (TDC). The TDC measures a voltage proportional to the time difference between the two signals and converts it to a digital time which is fed to the histogrammer [143]. The card acts as a stopwatch. For TCSPC the ‘start’ signal is provided by the APD detector not the laser driver, because the laser has a repetition rate of 10-40 MHz. Since the card takes between 300 and 2000 ns to convert the start pulses, it cannot keep up with the laser rate. Hence the engineers at PicoQuant reversed the start and stop signal and the card starts counting every time a photon is detected. It therefore measures the time between the detection of the photon emitted by a molecule and the next excitation pulse.

3.4.3 Calibration of the confocal microscope

After the optical setup was aligned, an image was acquired of an empty glass slide while raster scanning the steering mirrors across their full travel range. This determined where the centre of the scan was in relation to the input voltage of the galvo mirrors. To know the size of the confocal images when raster-scanning the galvo mirrors, I imaged an empty metallic grid (G2786N 2000 Mesh Grid, Nikel, Agar Scientific) after having removed the long-pass filters in the excitation and having attenuated the laser to ~ 1 nW in order to avoid saturation of the APDs. A typical image of the grid, acquired using the high NA oil objective is shown in Fig. 3.5. The empty metallic grid had 2000 lines/inch, which meant a distance between lines of $12.7\ \mu\text{m}$. The images were analysed using Mathematica to relate the position on the scan to the voltages on the galvo mirrors. The relation turned out to be linear. Fig. 3.6 (a) shows a confocal image of a sample with a sparse distribution of molecules, taken with the same 1.4 NA oil-objective. The excitation intensity was set to well below the saturation of the molecules to avoid any power broadening effect. The signal from the well isolated fluorescence spot highlighted by the white circle was fitted to

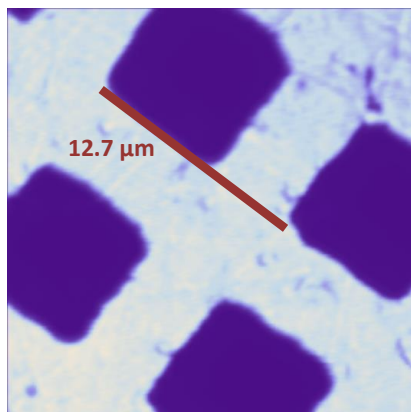


Figure 3.5: Confocal image of an empty metallic grid acquired by detecting the backscattered laser light. This picture was used to calibrate the size of the images when raster scanning the steering mirrors.

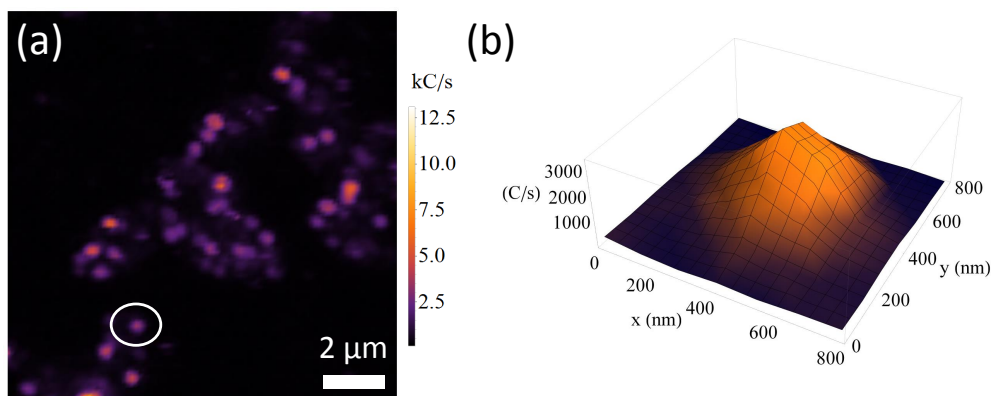


Figure 3.6: (a) Confocal microscope image of a sample with a sparse distribution of molecules. (b) Signal from the fluorescence spot highlighted by the white circle in (a).

a 3-D Gaussian:

$$Ae^{-\left(\frac{(x-\alpha)^2}{2\sigma_x^2} + \frac{(y-\beta)^2}{2\sigma_y^2}\right)} + B. \quad (3.2)$$

In this equation, α and β are the coordinates of the centre of the peak, A is the amplitude, B is the background signal and σ_x and σ_y characterise the dimensions of the spot. The signal from the highlighted molecule in Fig. 3.6 (a) is plotted in Fig. 3.6 (b). A fit according to Eq. 3.2 leads to $\sigma_x = 133 \pm 4$ nm and $\sigma_y = 153 \pm 4$ nm. Taking the average of the two, the full width half maximum (FWHM) of the laser spot is:

$$d = 336 \pm 4 \text{ nm}. \quad (3.3)$$

We can compare this with the Abbe's resolution criterion from Eq. 3.1, which for 780 nm light reads $d_{\text{Abbe}} = 279$ nm. The higher spot size I measured could be possibly due to the fluorescence spot being two or more molecules slightly close to each other. This might also explain the difference between σ_x and σ_y .

3.4.4 Imaging and spectroscopy

As shown in Fig. 3.1, the iXon Ultra camera was used to image the field of view in the microscope. This was mainly to check the focusing of the samples and to check that the correct illumination was being provided during the photobleaching experiment. It was occasionally used to image the fluorescence of the molecules. When doing so, the CCD chip was cooled by an internal peltier to -60°C and the electron multiplying (EM) gain was set to its maximum value of 255. Sending light to a grating spectrometer, instead of to an APD, allowed me to measure the room temperature spectrum of the molecules. I used a Shamrock 303i grating turret spectrograph together with a Newton EMCCD Camera (Andor, Oxford Instruments). The spectrograph has 3 gratings with different characteristics, as shown in the table below.

Grating	Description	Resolution (nm)
1	300 l/mm - Blaze 760 nm	0.688
2	1200 l/mm - Blaze 750 nm	0.130
3	1200 l/mm -Blaze 850 nm	0.133

To calibrate the spectrograph I used a neon lamp, a source of light with a well-known typical spectrum (6032 Spectral Calibration Lamp, Newport). The lamp was set to shine light directly into the spectrograph and the room lights were switched off. When measuring the spectrum of the molecules, I cooled the sensor of the Newton camera to -80°C with the aid of 16°C cooling water, and used the 755 nm laser together with 770 nm long-pass filters, allowing the collection of light from the zero-phonon line of the molecules.

3.4.5 Sample mount

Initially, cover slips coated with anthracene crystals were taped on top of a glass microscope slide (crystal side down). The slide was positioned in a custom made or commercial (MAX3SLH, Thorlabs) holder in front of the objective lens. The holder was on top of a Nanomax stage with differential drives and closed-loop piezos (MAX311/M, Thorlabs) connected to a 3-axis piezo controller (BPC303, Thorlabs). However, since the sample was kept vertical, gravity would cause a small constant drift, especially when using the oil-immersion objective. In order to increase the stability of the microscope, I designed a vacuum chuck which was fitted inside a stage (HMM001, Thorlabs) mounted on top of the Nanomax. The glass slides with cover slips or waveguide chips would be held by the constant vacuum being created by a single-stage oil pump (West Technologies).

Chapter 4

Optical properties of the dibenzoterrylene molecules in a thin film

4.1 Introduction

In this chapter I first show and comment on the spectrum I measured at room temperature and show confocal images of the DBT molecules inside anthracene thin films grown with the method described in chapter 2. I investigate the direction of the dipole of these molecules. I then show a measurement of the excited state lifetime of the DBT molecules and compare it to the ones found in the literature. I also measure the saturation intensity of the DBT molecules. I prove that molecules in the thin crystals are single quantum emitters by measuring antibunching under pulsed and continuous-wave excitation. I investigate the stability of molecular emission, and observe that large fraction of them remain optically active even after more than 10^{12} excitations, while some of the molecules undergo a photochemical reaction known as photo-bleaching. Finally I measure the lifetime of the triplet state of a DBT molecule by looking at the times when it stops fluorescing. Most of the results shown here have been published in [104].

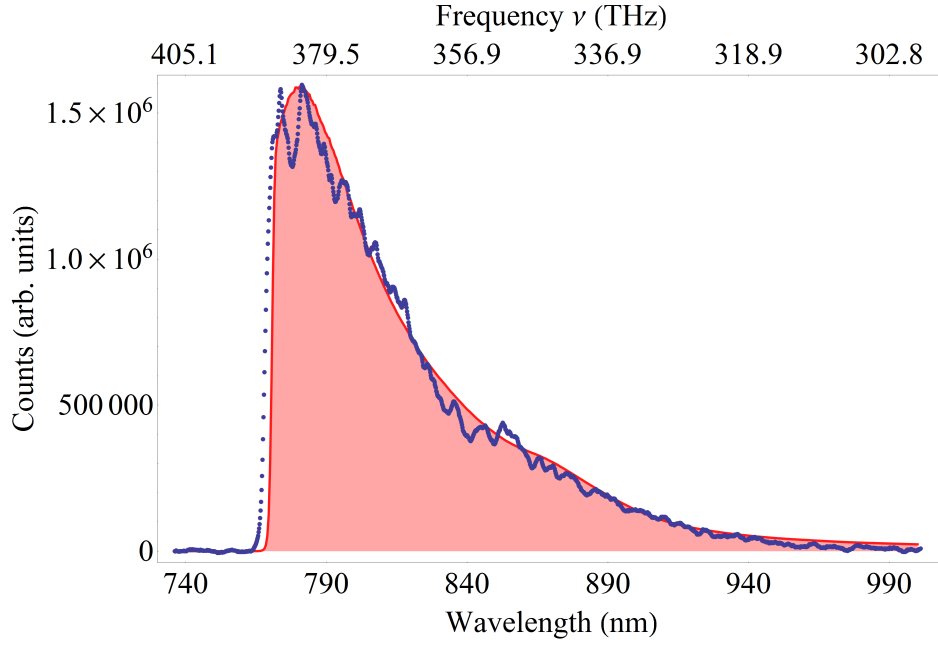


Figure 4.1: Emission spectrum of DBT in a thin anthracene crystal at room temperature. Blue dots: experimental data. Red thin line: Fitting to the sum of Lorentzian profiles (in frequency) peaked around the transitions measured by Nicolet *et al.* [80] all broadened by ~ 20 THz. This sum was multiplied by the transmission spectrum of the long-pass filter.

4.2 Room temperature spectrum

I began by investigating the fluorescence spectrum of DBT in an anthracene crystal grown by the supersaturated vapour method described in chapter 2. A large number of molecules were simultaneously illuminated at room temperature by an excitation laser at 755 nm, and the fluorescence was dispersed by Grating 1 of the Andor spectrometer (see section 3.4.4) which provided a resolution of 0.688 nm. The excitation light was blocked by 770 nm long-pass filters as in Fig. 3.2. The spectrum of this fluorescence is shown by the blue dots in Fig. 4.1. It shows a very broad peak at ~ 781 nm, corresponding to a frequency of ~ 383.9 THz. It also shows various smaller peaks appearing at different wavelengths. These are due to the effect of various optical elements in the confocal microscope. One can however clearly discern a second, broad feature at ~ 848 nm. To fit the data I used the frequencies of the transitions Γ_{ZPL} and $\Gamma_{1,v}$ measured by Nicolet *et al.* [80] and simulated by Major [102]. In terms of wavelength λ these are $\lambda_i \sim 784$ nm, 802 nm, 805 nm, 817 nm, 872 nm, and 894 nm. The sum of each Lorentzian profile centered at

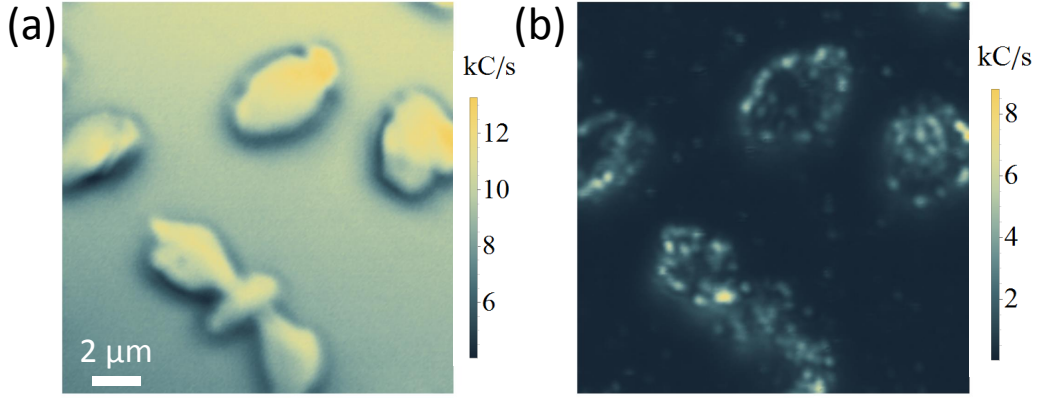


Figure 4.2: Scans taken with the confocal microscope. (a) Anthracene crystals imaged by removing the long-pass filters and detecting the reflected excitation light. (b) DBT molecules imaged with the long-pass filters in the detection path. Almost every bright spot is a single DBT molecule. The two images perfectly match suggesting that the DBT molecules are well-inserted into the anthracene crystals.

each optical transition, λ_i , is, in terms of frequency ν

$$f(\nu) = A \sum_i \alpha_i \frac{\frac{1}{2}w}{\left(\nu - \frac{c}{\lambda_i}\right)^2 + \left(\frac{1}{2}w\right)^2}. \quad (4.1)$$

Here A is a normalisation constant, α_i the branching ratio of the transition i and w the width of the transition at room temperature. This function was multiplied by the transmission spectrum of the 770 nm long-pass filters (according to the manufacturer, Chroma Technologies) and fitted to the data. This is shown by the red line in Fig. 4.1. The fit leads to a width of ~ 20 THz, or ~ 40 nm in terms of wavelength. The fit confirmed the theory that thermal broadening increases the linewidth to tens of THz and that the impurities inside the anthracene crystals were DBT molecules whose transitions in [80, 102] match the spectrum in Fig. 4.1.

4.3 Orientation of individual molecules

Next, I began to look at single DBT molecules. The sample was held by the mount in the oil-objective confocal microscope (see Fig. 3.1) and illuminated with ~ 1 nW of 780 nm excitation light. I monitored the strong back-scattered excitation light, without the long-pass filters while scanning the laser over an area of $16 \times 16 \mu\text{m}$ with a resolution of 200

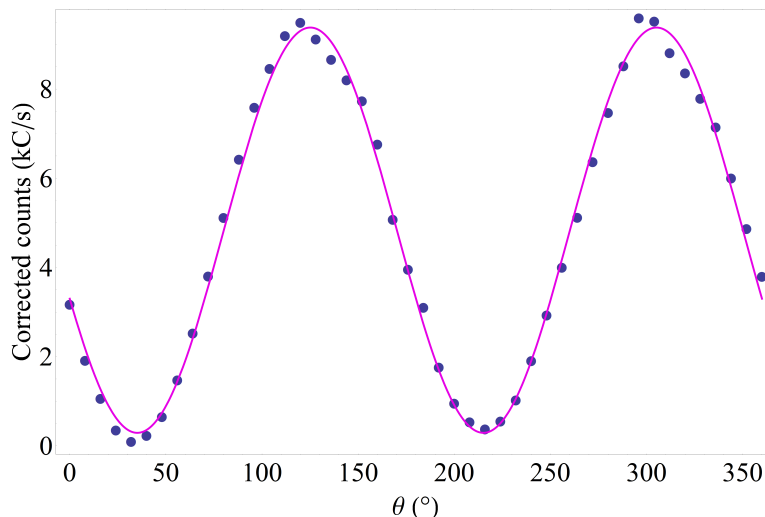


Figure 4.3: A trace of the detected photons emitted by a single molecule as the polarisation of the incident light was varied. After subtracting the background the data was normalised to the incident power which lead to an almost unity visibility.

$\times 200$ pixels. A typical image is shown in Fig. 4.2 (a). Here we see individual anthracene crystals whose sharp edges cause a decrease in the back-scatter compared with that from the flat surfaces of glass or anthracene. These images also demonstrate the relative flatness of the crystals' top surfaces. Having imaged the crystals, I then placed two 792 nm long-pass filters in the detection path and increased the intensity of the excitation by four orders of magnitude. This allowed me to image the DBT molecules, as shown in Fig. 4.2 (b). Many of these bright spots are single DBT molecules. By comparing the two images one can see that the DBT molecules lie within the anthracene crystals.

At this point I wanted to establish whether the molecules remain under the crystal, stuck on the glass surface, or if they are incorporated into the anthracene during the growth process. To do so I measured the orientation of the absorbing dipole direction, similarly to the experiment carried out by Major [102]. As mentioned in chapter 2, Nicolet *et al.* proved that when embedded in the main anthracene site, the $S_0 \rightarrow S_1$ transition dipole moment, is polarised along the b axis of the crystal. When a molecule sits in the red site, the transition dipole moment is rotated by 7° with respect to the b axis [80]. I therefore measured the fluorescence as a function of the linear polarisation angle of the excitation light to see whether the DBT molecules shared a common dipole orientation. In each crystal, I selected a few molecules well isolated from each other. I then rotated the HWP in the optical setup (Fig. 3.1) whilst monitoring the molecule fluorescence as function of

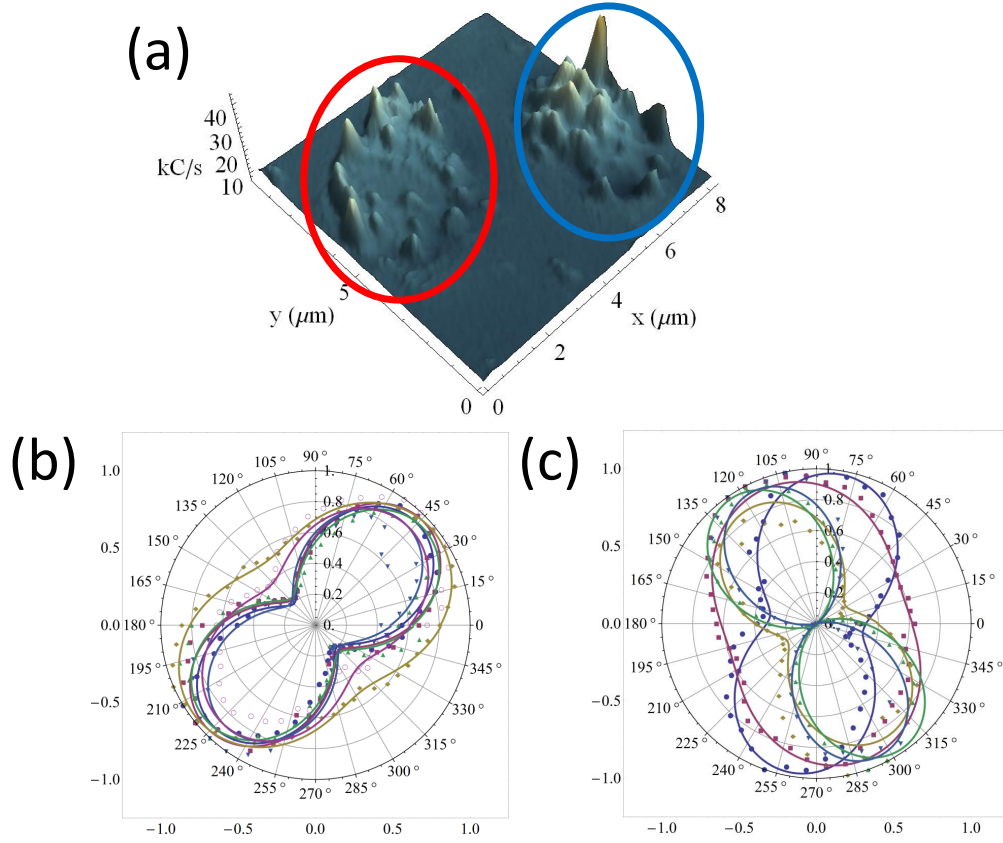


Figure 4.4: (a) 3-D confocal scan showing fluorescence from DBT molecules in two anthracene nanocrystals. (b) Normalised polar plots of molecule fluorescence as function of the polarization of the excitation light for the crystal on the left highlighted in red and (c) for the crystal on the right highlighted in blue. The experimental data is shown by the points while the fits according to Eq. 4.2 are shown by the solid lines. In (b) all six optical dipoles share a common orientation while in (c) one molecule shows a different orientation with respect to the other four.

the linear polarization angle of the pump light, θ . The background, measured by repeating the measurement in a region of the crystal with no DBT, was subtracted from the data. The background-subtracted fluorescence was then normalised to the incident intensity by reflecting a small amount of the light with a glass slide placed in front of the objective lens and monitoring the power as function of θ with a photodiode. The optical components most sensitive to the polarization of light, such as pellicle beamsplitters or dichroic mirrors, were not used in the setup. Still, I could observe some sensitivity of the setup to the polarization of the light which was taken into account by the normalisation. A typical plot of the emitted fluorescence from a single molecule as function of the polarization of the excitation light is shown in Fig. 4.3. The blue dots are the normalised data while the solid magenta line is a fit of the form

$$A \cos^2 (\theta \pm \phi) + B. \quad (4.2)$$

Here A is amplitude of the oscillation, B is an offset that takes into account any residual background light and ϕ is the absorbing dipole direction. The polarization of the emitted photons could also be measured, but the emission spectrum is very broadband and the measurement is less reliable. In the case of the data in Fig. 4.3, B is negligible, demonstrated by a visibility of 0.98 in the fluorescence modulation. I observed that the absorbing dipoles of molecules in the same crystal are closely aligned with each other. As an example, let us look at the two crystals in Fig. 4.4 (a). The polar plots for the left hand crystal indicated in red are shown in Fig. 4.4 (b). All six molecules have a similar orientation. The four molecules in the right hand crystal, highlighted in blue, all show the same orientation, with one showing a slight variation (Fig. 4.4 (c)). Overall I looked at 58 molecules in 12 separate crystals over a wide region of the same sample. The molecules in each separate crystal shared a similar orientation with respect to each other. This can be seen in the histogram in Fig. 4.5. The graph shows a small spread in the orientation of the molecules relative to the mean orientation. By fitting a Gaussian, I estimate a standard deviation of 12° . This is a little more than the deviation reported by Nicolet *et al.* [81], perhaps because they used much thicker co-sublimated crystals but still constitutes strong evidence that during the crystal growth the DBT molecules are incorporated inside the anthracene. It also suggests that the fluorescence emission of the molecules should be sta-

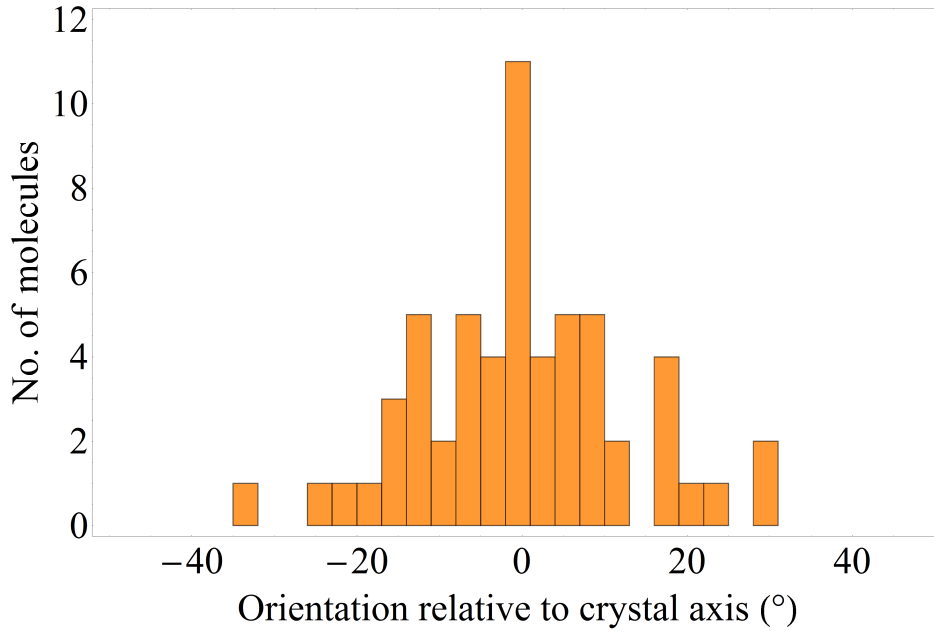


Figure 4.5: Histogram of the phase of the dipoles of 58 molecules in 12 anthracene crystals relative to the mean orientation. It shows a peak at 0° indicating that all the DBT molecules align in the same direction along the b axis of the anthracene crystals.

ble, as the molecules are embedded within the crystal. We note that molecules in the red insertion site are oriented 7° away from the b axis of the crystal, but only 1% of molecules are expected in that site [81], so we do not think the angular distribution is significantly influenced by the occupation of the red site. An investigation at cryogenic temperatures, where spectral selection of the molecules in the red site is possible, will show this more definitely.

4.4 Lifetime of dibenzoterrylene molecules in a thin film of anthracene

In order to measure the lifetime of the $S_{1,0}$ state, I excited a single molecule using the 755 nm pulsed laser described in section 3.3, with a repetition rate of 20 MHz and a temporal pulse width of 83 ps. The arrival time of the subsequent fluorescence photon was recorded by the TimeHarp counting module with a temporal resolution of 26.7 ps. A typical histogram of the arrival of times is shown in Fig. 4.6 (a) by the green line. We expect this to be a convolution of the instrument response function (a Gaussian peak

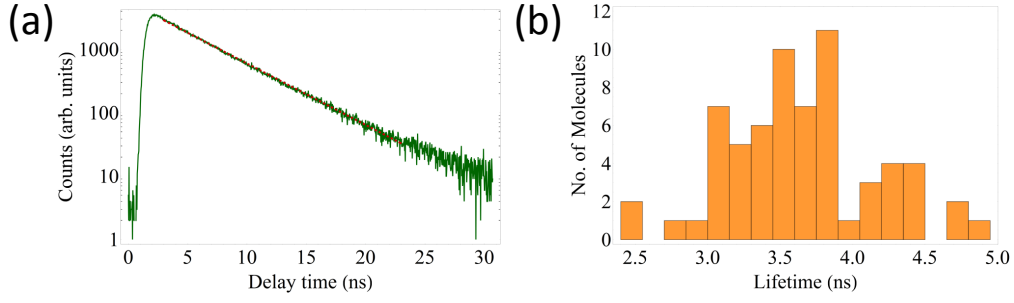


Figure 4.6: (a) Green line: typical histogram in a logarithmic scale of a time-correlated single photon counting lifetime measurement of a single molecule. The data is a convolution of the instrument response function and the single exponential decay of the excited state population. The fit, shown by the red dashed line, leads to a lifetime of 4.64 ± 0.24 ns. (b) Histogram of the lifetimes of 65 molecules in six different thin anthracene crystals showing a spread in lifetimes from 2.5 to 5 ns peaked at ~ 3.7 ns, in agreement with the literature [85, 112].

with a width of 83 ps) with the single exponential denoting the decay of the upper state population. To gather information on the excited state lifetime of the molecule, τ , I plot the data on a logarithmic scale and I then fit it to a straight line with a slope equal to $-\frac{1}{\tau}$. In the case of the molecule in Fig. 4.6 (a) this led to the straight line shown by the red line. The measured excited state lifetime is 4.64 ± 0.24 ns. I measured the lifetime of 65 molecules in six different anthracene crystals using this method. Their lifetimes ranged from 2.5 to 5 ns, with the distribution shown in Fig. 4.6 (b), which peaks at ~ 3.7 ns. These values are in agreement with the lifetimes measured by Toninelli *et al.* for DBT molecules in spin coated anthracene thin films which ranged between 3.3 and 5.7 ns [85]. They are also in agreement with the lifetimes measured for much thicker crystals grown by the co-sublimation method [80, 82, 112].

4.5 Saturation of the fluorescence

I have investigated the fluorescence from a single molecule, illuminated by a cw laser beam at a wavelength of 780 nm, as a function of the peak intensity I_0 incident on the surface of the anthracene crystal. The value I_0 was deduced from the power P measured entering the microscope objective and the measured FWHM spot size on the sample, according to

$$I_0 = \frac{4 \ln(2) P}{\pi FWHM^2}. \quad (4.3)$$

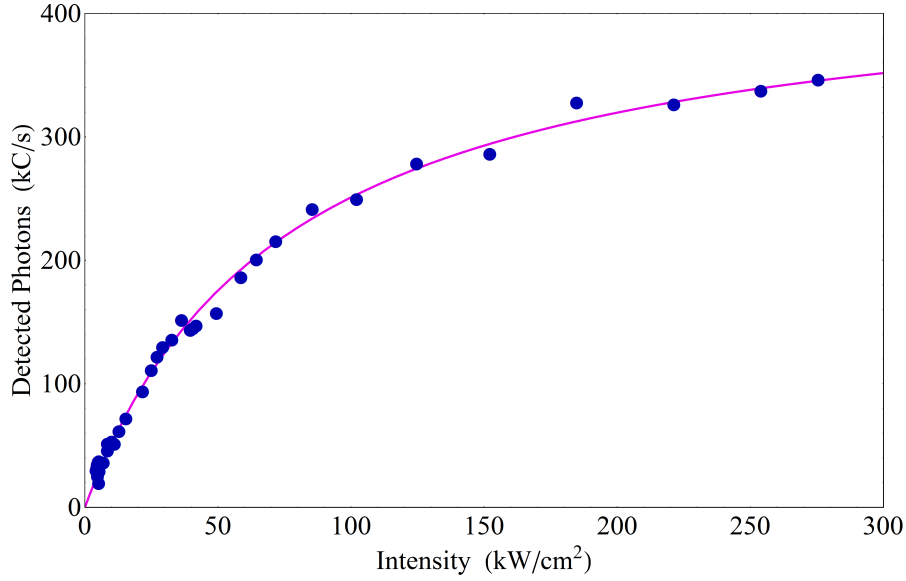


Figure 4.7: Blue dots: number of detected photons (10^3 APD counts/second, kC/s) from a single molecule collected in the laboratory for various illumination intensities. Magenta solid line: fit according to Eq. 4.9 which leads to a saturation intensity $I_{\text{sat}} = 75.1 \pm 2.6$ kW/cm 2 .

The background light level was determined by measuring the photon rate when illuminating a part of the crystal with no molecules. The background-subtracted photon rates are shown by the blue dots in Fig. 4.7. These points are well described by a fit to the saturation function

$$R_{\text{flu}} = R_{\text{max}} \frac{I}{I + I_{\text{sat}}}, \quad (4.4)$$

where R_{flu} is the number of detected photons or fluorescence rate, I is the laser intensity at the molecule, I_{sat} is the saturation intensity, and R_{max} is the limiting rate at high intensity. The solid line shows the fit, with $I_{\text{sat}} = 75.1 \pm 2.6$ kW/cm 2 and $R_{\text{max}} = 440$ kC/s. It is worth recalling the main transitions as in section 4.3: $\lambda_i \sim 784$ nm, 802 nm, 805 nm, 817 nm, 872 nm, and 894 nm. I calculated the detunings for excitation at 780 nm. Because of the 20 THz homogenous broadening I seem to be exciting up to about the fifth vibrational level, $v = 5$.

In order to understand this behaviour more fully, we build a simple model shown in Fig 4.8. The excitation laser, at 780 nm, is tuned ~ 2 THz to the blue of the ZPL, while the homogeneous width of the transitions $S_{0,0} \rightarrow S_{1,v}$ is ~ 20 THz, as measured in section 4.3. This laser excites a number of the states $S_{1,v}$ (up to approximately $v = 5$) at a total

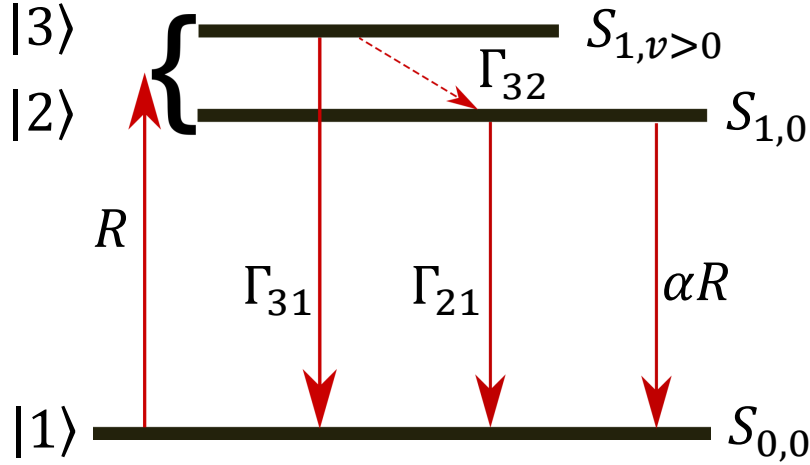


Figure 4.8: The approximated 3-level diagram for a DBT molecule in an anthracene crystal.

rate R . Those excited molecules that have $v \neq 0$ relax to the state $S_{1,0}$, over a few ps at rate Γ_{32} . This is so fast that we can neglect the spontaneous decay rate Γ_{31} . We can also neglect any stimulated decay from the state $|3\rangle$ to $|1\rangle$, because we work in a regime where $R \ll \Gamma_{32}$. The excited molecule therefore accumulates a population n_2 in the state $S_{1,0}$. This decays radiatively with a spontaneous rate Γ_{21} and a stimulated rate αR . The value of α depends on the details of the blue detuning and the relaxation rates of the system, so we make no assumption about it, except that $\alpha \leq 1$. Some of the decays from $S_{1,0}$ go to vibrationally excited sidebands of the state S_0 , but these decay non-radiatively within a few ps to $S_{0,0}$, replenishing the population n_1 of that state at a rate equal to

$$n_2 (\Gamma_{21} + \alpha R) \quad (4.5)$$

With this model the rate equations for the excited state population are

$$\begin{aligned} \frac{dn_2}{dt} &= Rn_1 - (\Gamma_{21} + \alpha R) n_2 \\ n_1 + n_2 &= 1 \end{aligned} \quad (4.6)$$

which lead to the time-dependent solution

$$n_2(t) = \frac{R}{R(1+\alpha) + \Gamma_{21}} \left(1 - e^{-(R(1+\alpha) + \Gamma_{21})t} \right). \quad (4.7)$$

Thus in the steady state or $t \rightarrow \infty$, the population is

$$n_2 = \frac{R}{R(1 + \alpha) + \Gamma_{21}}. \quad (4.8)$$

The excitation rate R is proportional to the laser intensity I , so let us write $R = \beta I$, where β is a constant. Since the detected fluorescence rate R_{flu} is proportional to n_2 , we have

$$R_{\text{flu}} \propto \frac{I}{I + I_{\text{sat}}}, \quad (4.9)$$

with

$$I_{\text{sat}} = \frac{\Gamma_{21}}{\beta(1 + \alpha)}. \quad (4.10)$$

This is the form to which the data are fitted in Fig. 4.7. We note that in the simple 2-level case, where $\alpha = 1$ this gives us $I_{\text{sat}} = \frac{1}{2} \frac{\Gamma_{21} I}{R}$, which is the standard result. By contrast, when all the population is excited via level $|3\rangle$, $\alpha = 0$ and $I_{\text{sat}} = \frac{\Gamma_{21} I}{R}$, which is twice as large. The difference is easily understood. At low intensity the population $n_2 \sim \frac{R}{\Gamma_{21}}$ for both cases, but as the intensity is increased the coherently-pumped population saturates at $\frac{1}{2}$, whereas the incoherently pumped population saturates at 1. The saturation intensity given by the data is $75.1 \pm 2.6 \text{ kW/cm}^2$. I am not aware of any other determination of this parameter, but note that closely related data are also measured by Toninelli *et al.* [85]. The rate of detected photons at saturation is given by the data as $R_{\text{max}} = 440 \times 10^3 \text{ s}^{-1}$. This is to be compared with the saturated emission rate given by $\frac{\Gamma_{21}}{1 + \alpha}$. The lifetime of this particular molecule was measured to be 3.9 ns, giving a saturated rate in the range $(1.3\text{-}2.6) \times 10^8 \text{ s}^{-1}$. Thus we conclude that the net detection efficiency for the fluorescence in this apparatus was between (0.2-0.3)%.

4.6 Correlation measurements

In this section I show that a fluorescent point in the confocal microscope image is a single molecule by measuring antibunching of the photons both under pulsed and continuous-wave excitation [144, 141]. The degree of second-order temporal coherence, often called second-order correlation function, $g^{(2)}(\tau)$, is the normalised probability of detecting a photon from a source (a molecule in this case) at a time $t + \tau$ having already detected a

photon at a time t . I carried out this measurement of $g^{(2)}(\tau)$ for DBT molecules in an anthracene crystal (Fig. 4.2). Light from a molecule with intensity I_I is sent through a beam splitter. Part of it (R) is reflected and sent to a detector that measures its intensity at time $I_R(t)$. Similarly, part of the light (T) is transmitted and sent to a detector that measures the intensity $I_T(t)$. The temporal correlation between these intensities is the $g^{(2)}(\tau)$ and can be written as [144, 145, 146]

$$g^{(2)}(\tau) = \frac{\langle I_T(t+\tau)I_R(t) \rangle}{\langle I_T(t+\tau) \rangle \langle I_R(t) \rangle} \quad (4.11)$$

with $\langle \dots \rangle$ denoting the time-averages. Following Beck [144], Eq. 4.11 can be simplified by writing the intensities at the two detectors in terms of the input intensity $I_I(t)$, given that $I_T(t) = TI_I(t)$ (and similarly $I_R(t) = RI_I(t)$). Hence, we can write

$$g^{(2)}(\tau) = \frac{\langle I_I(t+\tau)I_I(t) \rangle}{\langle I_I(t+\tau) \rangle \langle I_I(t) \rangle}. \quad (4.12)$$

At time $\tau = 0$, Eq. 4.12 becomes

$$g^{(2)}(\tau = 0) = \frac{\langle I_I^2(t) \rangle}{\langle I_I(t) \rangle^2}. \quad (4.13)$$

So far I have not mentioned the quantum nature of light. In the quantum picture, one has to replace the intensities by their operators. The quantization of the radiation field leads to the result that for a polarized plane wave, the intensity operator $\hat{I}$ is

$$\hat{I} = 2\epsilon_0 c \hat{E}^- \hat{E}^+ \quad (4.14)$$

In Eq. 4.14, ϵ_0 is the permittivity of free space, c the speed of light and $\hat{E}^\pm$ are the raising and lowering electric field operators. They are related to the creation ($a^\dagger$) and annihilation (a) quantum operators by

$$\begin{aligned} \hat{E}^- &= \sum_{\vec{k}} \sqrt{\frac{\hbar\omega_k}{2\epsilon_0 V}} a_{\vec{k},\vec{\epsilon}}^\dagger \vec{\epsilon} e^{+i\vec{k}\cdot\vec{r}} \\ \hat{E}^+ &= \sum_{\vec{k}} \sqrt{\frac{\hbar\omega_k}{2\epsilon_0 V}} a_{\vec{k},\vec{\epsilon}} \vec{\epsilon} e^{-i\vec{k}\cdot\vec{r}} \end{aligned} \quad (4.15)$$

where $\vec{k}$ is the wavevector of the mode of light, V the volume of the mode, $\vec{\epsilon}$ the polarization of the light and $\vec{r}$ the direction of propagation. By substituting Eq. 4.15 in 4.14 and then into Eq. 4.12, we can write the degree of second-order coherence at $\tau = 0$ in terms of the creation ($a^\dagger$) and annihilation (a) quantum operators,

$$g^{(2)}(\tau = 0) = \frac{\langle (a^\dagger)^2 a^2 \rangle}{\langle (a^\dagger) a \rangle^2} \quad (4.16)$$

For a Fock or number state $|n\rangle$ with n -photons, for which

$$\begin{aligned} a^\dagger |n\rangle &= \sqrt{n+1} |n+1\rangle \\ a |n\rangle &= \sqrt{n} |n-1\rangle \end{aligned} \quad (4.17)$$

Eq. 4.16 becomes

$$g^{(2)}(\tau = 0) = \frac{\langle n | a^\dagger a^\dagger a a | n \rangle}{\langle n | a^\dagger a | n \rangle^2} = \frac{n(n-1)}{n^2} = 1 - \frac{1}{n}. \quad (4.18)$$

Eq. 4.18 shows that for a Fock state the degree of second-order temporal coherence is bounded with an upper limit of 1, $g^{(2)}(\tau = 0) < 1$. This is a violation of classical theory of light. Assuming a classical picture, following Loudon and using the Cauchy-Schwarz inequality [146], two measurements of the intensity of light at two different times t_1 and t_2 have to obey

$$|\langle I(t_1) I(t_2) \rangle|^2 \leq \langle I(t_1) \rangle^2 + \langle I(t_2) \rangle^2. \quad (4.19)$$

Applying this to N measurements one derives that $\langle I(t) \rangle^2 \leq \langle I^2(t) \rangle$ and therefore Eq. 4.13 reads that $g^{(2)}(\tau = 0) \geq 1$, which is the opposite result as for a Fock state. It is not however possible to set an upper limit for a $g^{(2)}(\tau = 0)$ of a classical source, therefore $\infty > g^{(2)}(\tau = 0) \geq 1$.

In the case of a single-photon source, for which the number state is known and equal to unity, $g^{(2)}(\tau = 0) = 0$. A source for which the second-order correlation does not behave as in the classical theory is said to be antibunched. In this case

$$g^{(2)}(\tau = 0) < g^{(2)}(\tau). \quad (4.20)$$

This implies that the probability of emitting a successive photon is higher at longer times

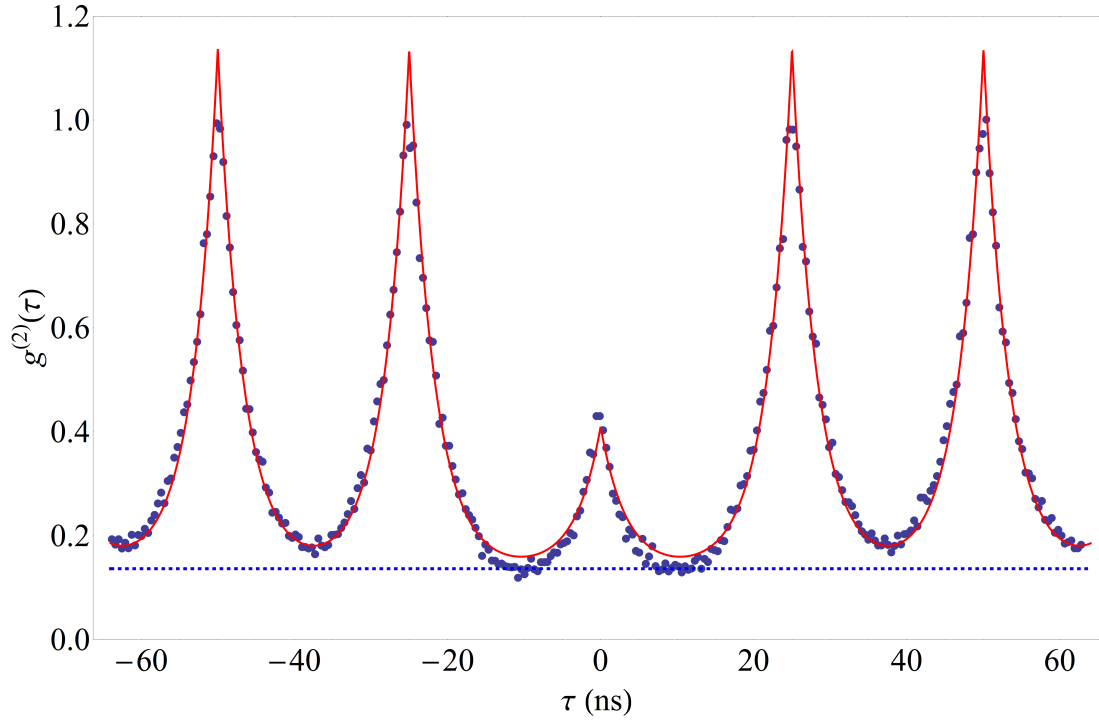


Figure 4.9: Second-order correlation function of light from a single DBT molecule within a thin anthracene crystal under pulsed excitation. The significant reduction of the central peak is proof of the quantum nature of the detected light meaning that the detected photons were generated by a single DBT molecule. The blue dots are the normalised data collected with the timing card over 30 minutes. The red line is a fit to Eq. 4.24. The blue dashed line is the background level deduced from the fitted function.

than at shorter time intervals. DBT molecules are an example of an antibunched, or quantum, source of light.

4.6.1 Second-order correlation function under pulsed excitation

My first measurement of the second order correlation function, as in Eq. 4.16, was carried out exciting the molecules with the pulsed 755 nm laser every 25 ns. The photons were detected using APDs, as in Fig. 3.2 and the correlation with the Picoquant Timeharp200 as in Fig. 3.4 set with a timing resolution of 106.9 ps. The measurement lasted ~ 30 mins and with an average power of the pulsed laser of $16 \mu\text{W}$ the count rate was of the order of 40 kC/s in each detector. The result is shown in the blue dots in Fig. 4.9. The data shows peaks separated by 25 ns of approximately the same height, except for the central peak whose height is significantly reduced compared to the others. For clarity I plotted the average of every four data points, corresponding to a timing resolution of 427.6 ps. Given

that this is much shorter than the $S_{1,0}$ upper state lifetime τ_0 , the exponential decay of the excited state can be well resolved. Following excitation we expect the mean intensity to decay as

$$e^{-\frac{|t|}{\tau_0}}. \quad (4.21)$$

For multiple peaks, each separated by a time Δt , the fitting function is just the sum of these decays,

$$B + \sum_{p=-\infty}^{\infty} e^{-\frac{|t-p\Delta t|}{\tau_0}}, \quad (4.22)$$

provided the time between excitations is long compared to τ_0 . That is satisfied because we use $\Delta t = 25$ ns. The constant B is added because of the background due to the dark counts in the detector. The integer p labels each excitation pulse. The central peak however is significantly reduced by the quantum nature of the molecules. As stated before, it should be zero in case for a number of molecules $m = 1$. The central peak at time $t = 0$, can be fitted by the function

$$B + \left(1 - \frac{1}{m}\right) e^{-\frac{|t|}{\tau_0}}. \quad (4.23)$$

Putting this together with Eq. 4.22, one expects the second order correlation function to be well described by the function

$$g^{(2)}(\tau) = B + \sum_{p=-\infty}^{\infty} \left(1 - \frac{\delta_{0p}}{m}\right) e^{-\frac{|t-p\Delta t|}{\tau_0}}. \quad (4.24)$$

Here, δ_{0p} is the Kronecker delta function. In order to fit the data with the fewest free parameters, I fixed the lifetime τ_0 to a value I determined independently for this same molecule by measuring the time a photon is detected after the molecule is excited (time-correlated single-photon counting, TCSPC). This leads to the exponential decay of the excited state population as presented in the previous section. For the single molecule investigated in Fig. 4.9, the measured exponential decay, shown by the green dots in Fig. 4.10, gives an excited state lifetime of 3.28 ± 0.03 ns. Having fixed Δt and τ_0 in Eq. 4.24, I fitted the data in Fig. 4.9 leaving only the background B and the number of molecules m as free parameters. The fit is shown by the red solid line, with the background of 0.14 highlighted by the blue dashed line. The fit gives the number of molecules as $m = 1.37 \pm 0.01$ and therefore a second order correlation function $g^{(2)}(0) = 0.27 \pm 0.01$.

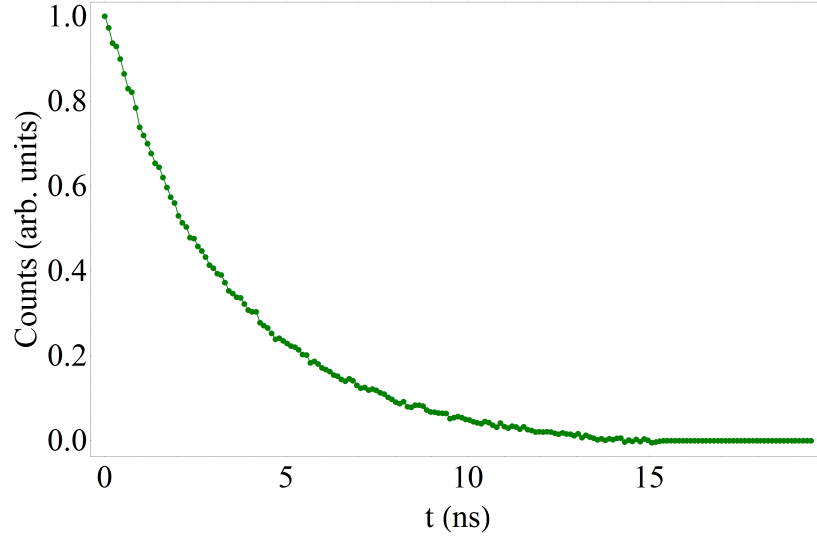


Figure 4.10: Background-subtracted exponential decay of the excited state population of the single molecule investigated in Fig. 4.9 measured by time-correlated single-photon counting.

Being less than 0.5, this value confirms that the bright spot in the confocal scan is indeed a single molecule. Most probably, the value is not zero because of a small amount of light scattered by nearby molecules within the same nano-crystal.

4.6.2 Second-order correlation function under continuous-wave excitation

When a photon emitted by a molecule is detected, the molecule is prepared in the ground state. Then the probability of detecting another photon is directly proportional to the probability $n_2(\tau)$ of the molecule being in the excited state, $S_{1,0}$. By normalising for long times, when another photon must have been re-emitted and detected, the second order correlation function can be written as

$$g^{(2)}(\tau) = \frac{n_2(\tau)}{n_2(\tau \rightarrow \infty)}. \quad (4.25)$$

Using the time-dependent expression for the population $n_2(\tau)$ from Eq. 4.7, Eq. 4.25 becomes

$$g^{(2)}(\tau) = 1 - e^{-(R(1+\alpha)+\Gamma_{21})\tau}. \quad (4.26)$$

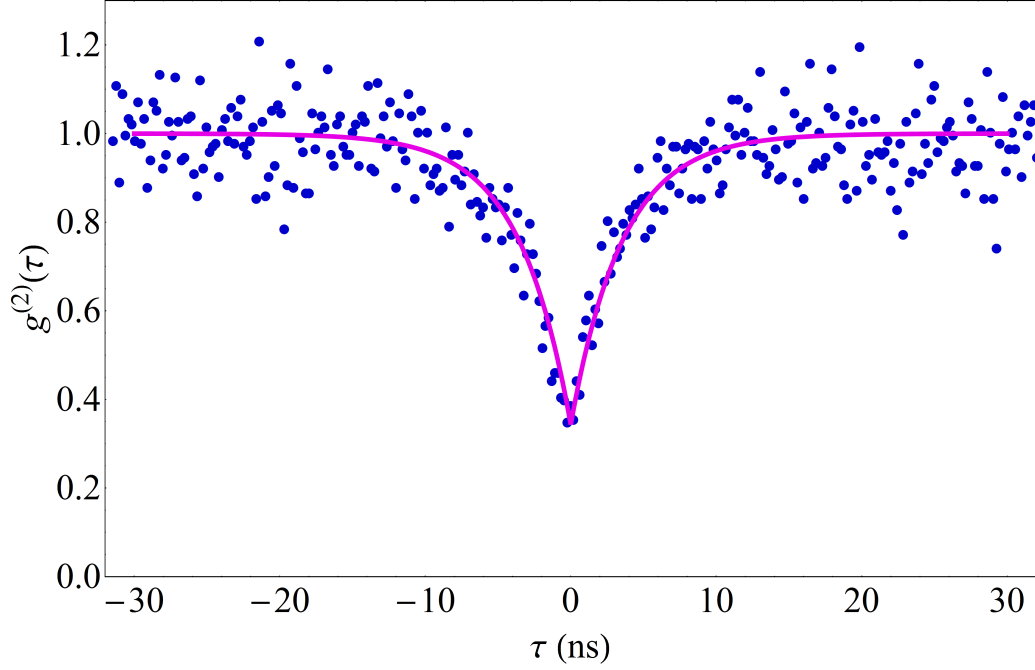


Figure 4.11: Blue dots: second-order correlation function or $g^{(2)}(\tau)$ of a single DBT molecule in a thin anthracene crystal grown with the saturated vapour method. The data was collected exciting the molecule with $s = 0.1$, estimated because of having measured the saturation intensity of such molecule (4.7). The saturation parameter was fixed when fitting the data to Eq. 4.27. Such fit is shown by the solid magenta line.

In terms of the saturation parameter $s = \frac{I}{I_{\text{sat}}}$ and the excited state lifetime of the molecule $\tau_0 = \frac{1}{\Gamma_{21}}$, this expression becomes

$$g^{(2)}(\tau) = 1 - e^{-(1+s)\frac{\tau}{\tau_0}}. \quad (4.27)$$

This expression is the same as the one derived for the case of a quantum dot by Lounis *et al.* [147]. It is also the same formula one can derive when considering a two-level system in the strong dephasing regime [88].

I measured the second-order correlation function for DBT molecules embedded in an anthracene crystal with the method described in chapter 3, exciting the molecules with a continuous-wave laser. I looked at the same molecule for which I measured a saturation intensity of $I_{\text{sat}} = 75.1 \pm 2.6 \text{ kW/cm}^2$. The second order correlation function for this molecule is shown in Fig. 4.11. Before gathering the data, I measured the laser power in front of the objective lens. This allowed me to estimate that the molecule was being excited at a saturation $s = \frac{I}{I_{\text{sat}}} = 0.1$. By fixing this parameter, the function in Eq. 4.27

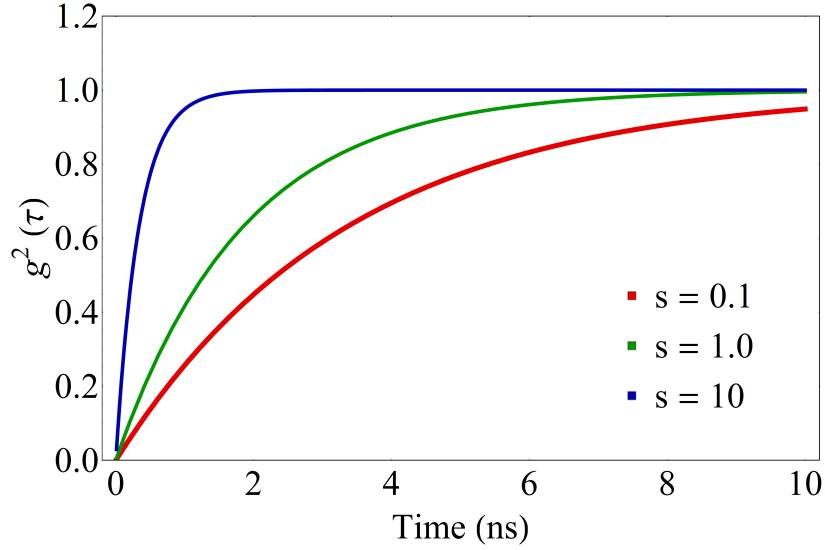


Figure 4.12: $g^{(2)}(\tau)$ as in Eq. 4.27 for various saturation parameters s assuming an excited state lifetime of 3.7 ns. As s increases, there is a clear narrowing of the $g^{(2)}(\tau)$ function.

was fitted to the data, leaving only the lifetime τ_0 as free parameter. The fit led to a lifetime of the molecule of 3.89 ± 0.22 ns and, more importantly, a $g^{(2)}(0) = 0.34 \pm 0.03$. Because $g^{(2)}(0) < 0.5$, this measurement proves that the bright spot in the confocal image was indeed a single molecule delivering a stream of single photons.

Fig. 4.12 shows Eq. 4.27 for increasing values of the saturation parameter s . As the intensity of the light exciting the molecules increases, more population is brought from the ground state to the first excited state and this results in a higher probability of detecting a photon at short times. This shows in the second-order correlation function as a narrowing of the dip. To demonstrate this aspect, the $g^{(2)}(\tau)$ of a single molecule was measured at increasing excitation intensities. The result is shown in Fig. 4.13 (a). For better clarity, the data was grouped by taking the average every three points. One sees that the $g^{(2)}(\tau)$ narrows when the excitation power is increased (higher s), as predicted by the theory. In Fig. 4.13 (b) the single $g^{(2)}(\tau)$ from Fig. 4.13 (a) are plotted. The red lines Fig. 4.13 are derived from the theory. They show the convolution of Eq. 4.27 with the temporal response function of the apparatus (I assume this molecule has the same saturation as the molecule in Fig. 4.11). This instrument response function is modelled by a Gaussian with a 455 ps standard deviation. At high intensities, more photons are generated by the molecule and are detected by the APDs, and their finite time response affects the second-order correlation function. I then fixed s to the values displayed in the image, leaving only

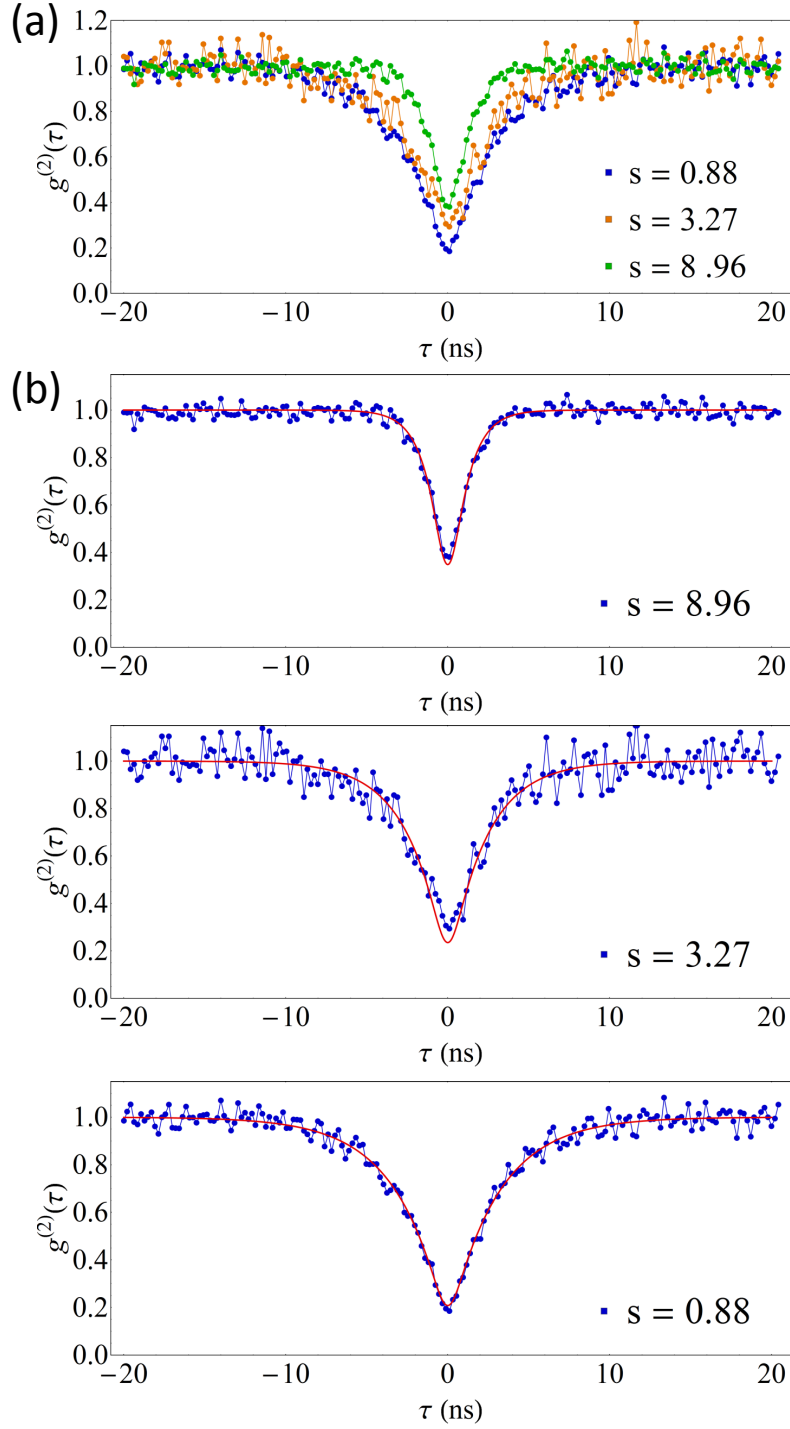


Figure 4.13: (a) Second-order correlation function of a single DBT molecule in a thin anthracene crystal for increasing excitation intensities. When exciting the molecule with a high power, the $g^{(2)}(\tau)$ narrows as predicted by the theoretical model shown in Fig. 4.12. (b) Individual second-order correlation functions from (a). The fits shown by the solid red line are a convolution of Eq. 4.27 and the temporal response function of the apparatus.

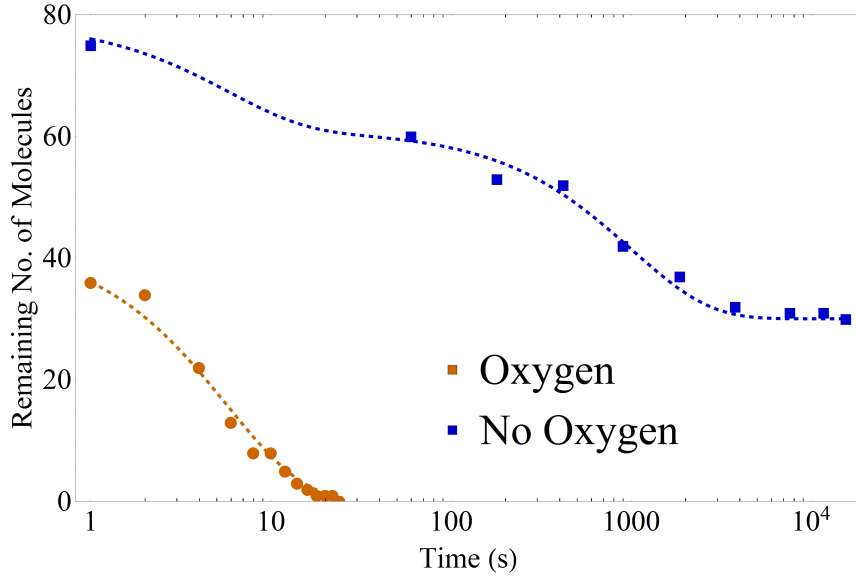
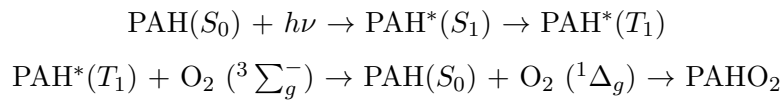


Figure 4.14: Photo-bleaching of DBT molecules inside thin films of anthracene. In orange the data collected after carrying out the crystal growth in air and exciting the molecules at 780 nm using an intensity of 10 kW/cm² incident on the anthracene. This data can be well approximated by a single exponential decay with a lifetime of 5.7 s (orange-dashed line). In blue I show the data collected growing the crystals in an oxygen-depleted environment exciting the molecules with a high intensity of 130 kW/cm². This data is approximated by the simple empirical formula in Eq. 4.28 (blue-dashed line).

τ_0 as a common free parameter to all data sets. The fit of each $g^{(2)}(\tau)$ is shown by the red solid lines and shows good agreement for each data set. Note that for $s = 0.88$, $g^{(2)}(0) = 0.22$ leaving no doubt that with the new growth method I could deposit single molecules inside anthracene nano-crystals.

4.7 Photostability of the molecule emission

To use single DBT molecules in a thin anthracene crystal for real applications to photonic devices, one needs to ensure they constantly deliver bright streams of single photons. It is known however that polycyclic aromatic hydrocarbons (PAH) can undergo an irreversible conversion into a non-fluorescent product. This process, known as photo-bleaching, can be summarised by the following sequence [148, 77]:



where S_0 denotes the electronic ground state of the molecule, S_1 the singlet excited state, T_1 the triplet excited state, $^3\Sigma_g^-$ the triplet ground state of the oxygen molecule and $^1\Delta_g$ the singlet excited state of the oxygen. In words, following [149], this sequence reads that when a molecule is excited to the S_1 state from the ground state (S_0), it can decay to the triplet state T_1 . For many polycyclic aromatic hydrocarbons this process occurs with a high probability, but in the case of DBT in anthracene [80] the inter-system crossing probability is exceptionally low at $\sim 10^{-7}$. Because the triplet state of the organic molecule, T_1 , is long-lived, there is a high probability of triplet-triplet annihilation to produce oxygen in its singlet state. Normally the oxygen molecule is in its ground electronic state $^3\Sigma_g^-$. In this configuration, oxygen is inert. It becomes however highly reactive when in the singlet excited state $^1\Delta_g$. Once the oxygen is in its singlet state, it can react with the dye molecule to form the dioxide. The result of this photo-chemical reaction is a non-fluorescent product. To prove that oxygen plays an important role for the stability of the molecule emission, I carried out a crystal growth as discussed in the previous chapter with the growth setup exposed to air. I then illuminated one molecule at a time using the continuous-wave Littrow-Lynx laser at 780 nm with an intensity incident on the anthracene film of 10 kW/cm². Using the saturation intensity measured in the previous section, this intensity corresponds to $s \sim 0.13$. When exciting each molecule I recorded fluorescence intensity traces and measured how long each DBT survived before photobleaching. The orange circles in Fig. 4.14 show how many of the 36 molecules studied remained fluorescent as a function of the illumination time. The dashed orange line is a fit according to a single exponential decay with a lifetime of 5.7 s. Given the excitation intensity, this corresponds to a DBT molecule being excited $\sim 10^7$ times per second. Since the branching ratio to the triplet state is of order 10^{-7} [80], this suggests that the molecule has roughly a 1-in-6 chance of oxidising each time it passes through its triplet state. This agrees with the measurement in [149].

In order to increase the photostability of the dye molecules the crystal growth was generally carried out inside a glove bag filled with nitrogen. In this case we find that the molecules are extremely photostable. To measure their bleaching time, I removed the $f = 75$ mm lens in the optical setup in Fig. 3.1. The $f = 250$ mm lens would then focus the excitation light onto the back aperture of the oil-objective lens creating a spot of 9.3 μm (FWHM) in the sample plane. In order to achieve a high intensity on the sample

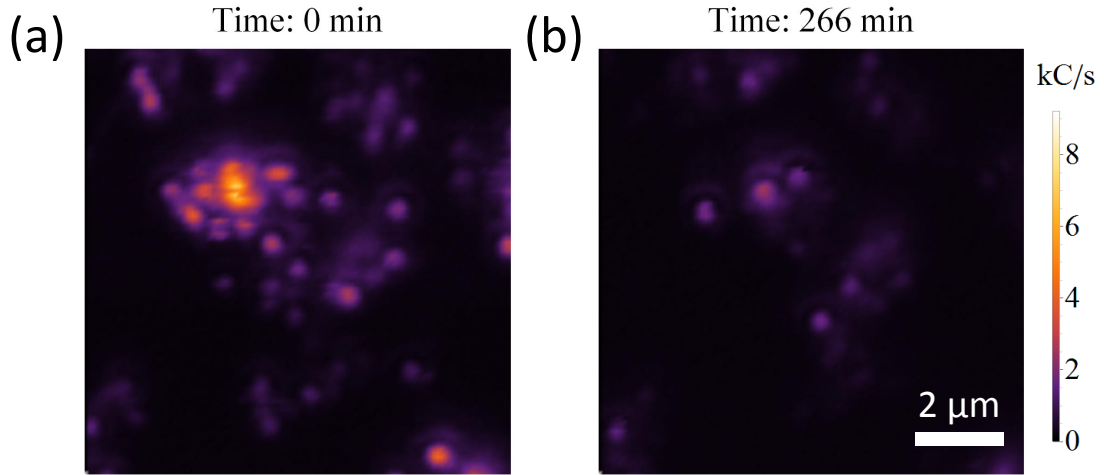


Figure 4.15: (a) Confocal image of DBT molecule in a thin anthracene crystal before illuminating them with the wide laser spot. (b) Confocal image of the molecules in (a) that remained after illuminating them for more than 4 hours.

the high power Toptica TA 100 Pro was used. This delivered 125 mW in front of the objective lens at 780 nm. The peak intensity incident on the anthracene was 130 kW/cm^2 , which corresponds to $s \sim 1.7$. A confocal image of the molecules at the beginning of the measurement is shown in Fig. 4.15 (a). I then illuminated the molecules with the high intensity wide spot for more than 4 hours, checking once in a while how many remained unbleached with a confocal scan. As shown in Fig. 4.15 (b), after 4 hours and 26 minutes, more than a third of the molecules remained unbleached. This is also shown by the blue squares in Fig. 4.14, where I summed the data collected over three different crystals, all illuminated for the same amount of time. An initial population of 75 molecules decays to 60 after one minute, 32 after one hour and 30 after 4 hours and 26 minutes. This evolution cannot be described by a single exponential such as in the oxygen case. Instead, the empirical formula

$$f(x) = 15e^{-\frac{t}{5.7}} + 31e^{-\frac{t}{10^3}} + 30 \quad (4.28)$$

provided an adequate description of the data. The initial decay time of 5.7 s is presumably due to a few molecules entering the triplet state, and reacting with residual oxygen in the crystal. The second decay of 10^3 s has not previously been observed and suggests another bleaching mechanism. In Fig. 4.14 one can see that 30 molecules survive more than 10^{12} excitations at the end of the measurement proving them suitable for applications in real photonic devices. This is more than a third of the initial population, which could perhaps

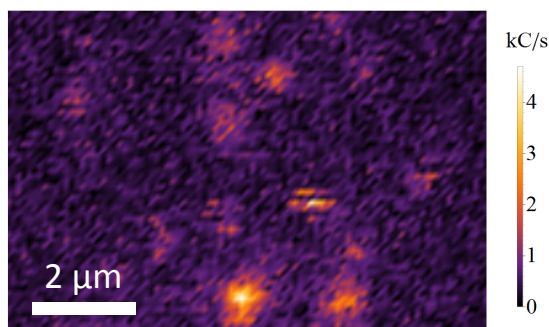


Figure 4.16: Confocal image of DBT molecules embedded in anthracene crystals with the co-evaporation method. The emission from the molecules shows intermittence during the confocal scan which is a sign of photo-blinking and not stable emission.

be increased even further by a more serious effort to remove the oxygen from the growth environment such as in the chamber built by Major *et al.* [112], who did not observe photobleaching.

The photo-blinking of DBT molecules in thin anthracene films was also observed when monitoring the scattering of photons from molecules over time, similar to the data presented by Deperasinska *et al.* [77]. The photo-blinking occurred mainly for molecules embedded in crystals grown in the presence of air. These molecules showed strong blinking and intermit scattering of photons just before photo-bleaching. According to [77, 149] the photo-blinking and photo-bleaching are both processes related to the presence of oxygen in the dye's matrix and my observation seems to confirm this.

It is also worth mentioning the poor photostability of DBT molecules in anthracene films created by co-evaporation. I developed this method while finding the optimal recipe for growing DBT-doped thin anthracene crystals. Instead of spin coating a solution of DBT in toluene and diethyl ether on a cover slip, 50 μ l of the 1 mMol solution of DBT in toluene were poured in the vial on top of the anthracene. The crystal growth was then carried out with the recipe as in section 2.4.2 in an oxygen-depleted environment. The molecules were then imaged using the confocal microscope, as shown in Fig. 4.16. In this image we can see a photo-blinking molecule, which exhibits dark stripes across the bright spot due to the temporary disappearance of fluorescence during the raster scan. I surmise that these blinking molecules were not well-inserted in the anthracene.

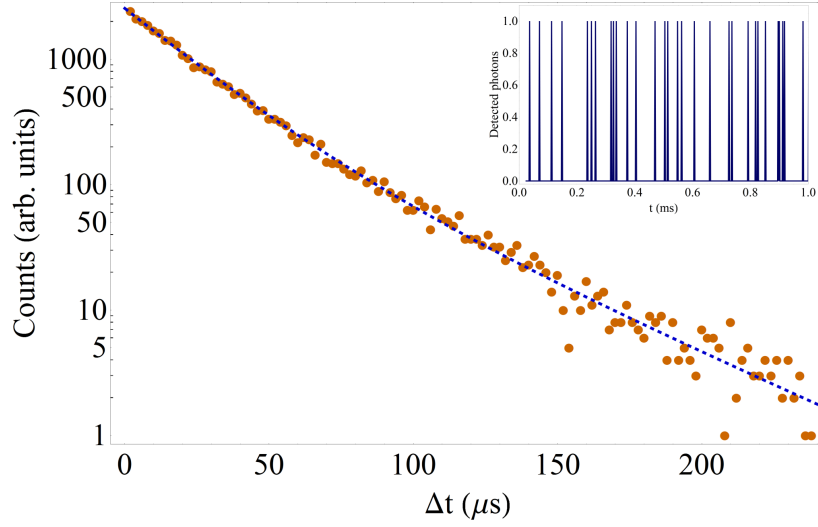


Figure 4.17: Orange circles: histogram of the time intervals between sequential photon detections while continuously exciting a single molecule. In a logarithmic scale, a double exponential decay can be seen. The fast initial decay is related to the detection efficiency of the confocal microscope while the longer decay appearing in the tail is related to the triplet state decay. A double exponential function of the form of Eq. 4.29 is fitted and shown by the dashed blue line. Inset: detected photons from a single molecule as function of time, sampling every $2 \mu\text{s}$.

4.8 Triplet state lifetime

The triplet state, T_1 of the DBT molecule is very long-lived in comparison with the singlet S_1 . This means that when the molecule enters the triplet state it stops fluorescing for a while. In order to measure the triplet state lifetime I continuously pumped a single molecule with intensity equal to the saturation intensity and looked at the periods when no fluorescence was detected. Simultaneously, I recorded the number of photons detected by the APD in a time window of $2 \mu\text{s}$. Typical data is shown in the inset of Fig. 4.17. This image shows that every once in a while the APD does not detect a photon. From this data I measured the time intervals between successive detections of photons. These intervals were histogrammed and are shown in Fig. 4.17. As one can see, two decays appear in the logarithmic scale. There is a fast decay due to the normal fluorescence rate of the S_1 state, reduced by the imperfect collection efficiency of the confocal microscope, and a slower decay appearing at later times. The long interval is the time when the molecule stopped fluorescing because of it being in the triplet state. I fitted to the data a double

exponential of the form

$$f(t) = Ae^{-\beta_{\text{microscope}} \frac{t}{\tau_0}} + Be^{-\frac{t}{\tau_{\text{triplet}}}}, \quad (4.29)$$

where A and B are constants, $\beta_{\text{microscope}}$ refers to the efficiency of the confocal microscope, τ_0 the single excited state lifetime and τ_{triplet} is the lifetime of the triplet state. I measure this to be $\tau_{\text{triplet}} = 42.6 \pm 4.2 \mu\text{s}$. This agrees with the triplet state lifetimes in the range 40-200 μs reported by Nicolet *et al.* [80] and with the value of $70 \pm 30 \mu\text{s}$ measured by Major [102], but is much more precise than these previous values.

Chapter 5

Coupling dibenzoterrylene molecules to a silicon nitride waveguide

5.1 Introduction

In this chapter I describe the coupling of DBT molecules to optical waveguides. I discuss the geometry of the waveguides and the method I used to characterize their losses. I move on to show the method of depositing of DBT-doped anthracene crystals on top of the waveguides. I successfully coupled photons from DBT molecules and transmitted them over a waveguide distance of ~ 10 mm. I show the results analysing the radiation from the molecules coupled to the waveguide to infer their presence on the waveguide. I finally calculate the mean coupling efficiency of these molecules and compare it to the theory.

5.2 Minimising the effective mode area

Fig. 5.1 illustrates our geometry for coupling a molecule to a waveguide, as proposed by Hwang and Hinds [89]. It is shown in chapter 1 of the thesis that a molecule in the evanescent field of a waveguide should send a fraction β of its photons into the guided mode. This fraction is given by Eq. 1.11:

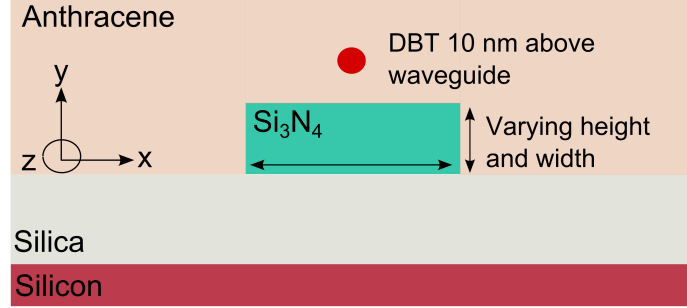


Figure 5.1: Sketch of the simulations geometry. I varied the height and width of a silicon nitride waveguide (Si_3N_4) on top of $1\ \mu\text{m}$ of silica on silicon. A layer of anthracene infinitely thick surrounded the waveguide. Anthracene was assumed to have refractive indices $n_x=1.82$, $n_y=2.22$ and $n_z=1.57$ [118, 102]. The DBT molecule was placed 10 nm above the waveguide because we think that with the new growth method the molecules sit close to the surface.

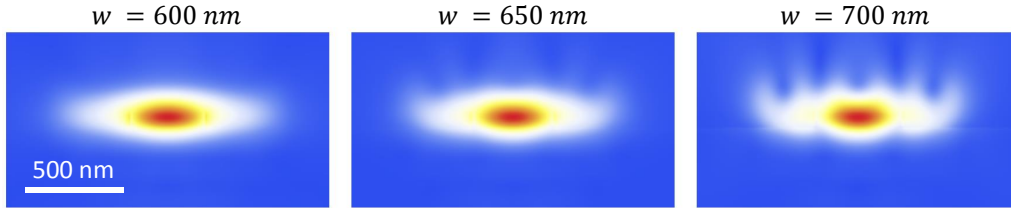


Figure 5.2: TE modes amplitudes for silicon nitride waveguides of various widths. One can see that above 650 nm there is a transition from single-mode to multi-mode.

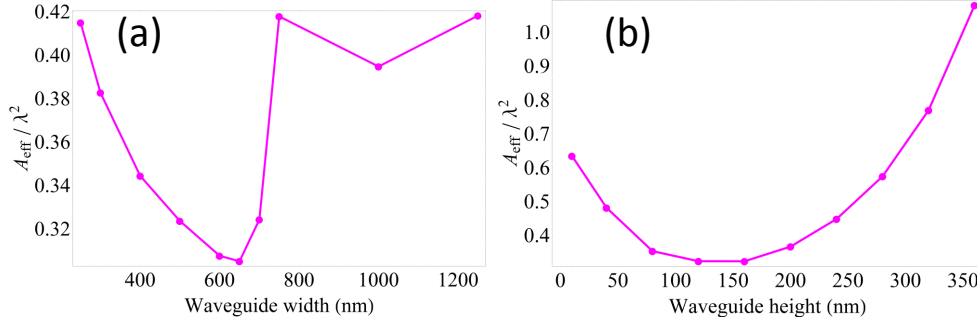


Figure 5.3: Effective area A_{eff} normalised to the wavelength squared as function of (a) the width of the waveguide (fixing its height to 120 nm) and (b) its height (fixing its width to 500 nm). In (a) one can see a clear minimum between 500 and 700 nm. Above 650 nm though, the operation of the waveguide becomes multi-mode. In (b), the minimum occurs for a height of 120 nm. Waveguides were fabricated 120 nm tall and between 300 and 700 nm wide.

$$\beta = \frac{1}{4} \frac{\left(\frac{3\lambda^2}{2\pi n^2} \right) \frac{c}{n}}{A_{eff} v_g}. \quad (5.1)$$

The highest coupling is therefore achieved for small effective mode areas A_{eff} , defined in Eq. 5.1. Hwang and Hinds [89] calculated that the waveguide should be 600 nm wide and 120 nm tall for an N-Hexadecane or PMMA host matrix. To check whether this is still the case for anthracene I simulated the behaviour of a molecule 10 nm above a silicon nitride waveguide and surrounded by an infinitely thick layer of anthracene, as shown in Fig. 5.1. The DBT molecule was assumed to be perfectly aligned with the b-axis of the anthracene and that axis was taken to be transverse to the waveguide, along x in Fig. 5.1. For the refractive index, I took the value $n_x = 1.82$, which is appropriate for this polarisation [118, 102]. The molecule was assumed to radiate at a frequency of ~ 383 THz (free-space wavelength 783.73 nm [88]). The simulations were carried out using Lumerical FDTD Solutions. First, as shown in Fig. 5.2, above a width of 650 nm, the operation of the waveguide becomes multi-mode. This behaviour was also calculated by Hwang and Hinds [89]. I then varied this width looking to minimise the effective area, A_{eff} in Eq. 5.1. Fig. 5.3 (a) shows that the smallest effective area, and therefore the highest coupling, is achieved for a width between 500 and 600 nm. Similarly, I varied the height of the waveguide and found a minimum in the effective area for a height of 120 nm (Fig. 5.3 (b)). These parameters motivated the geometry of the waveguides built by the group.

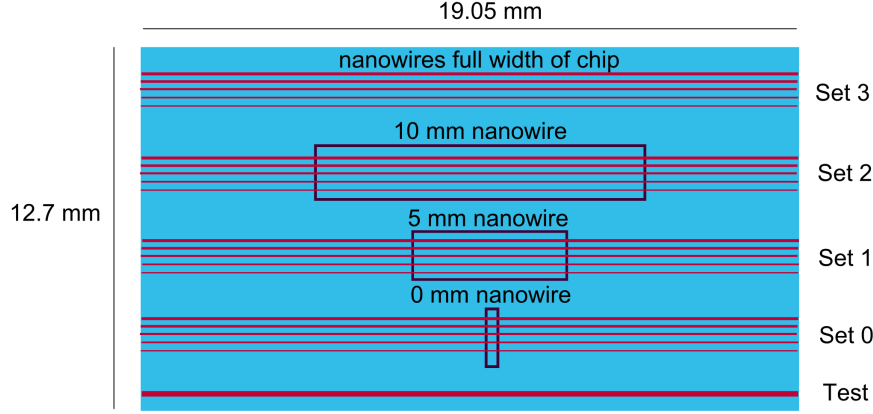


Figure 5.4: Schematics of the silicon nitride chip where I deposited DBT molecules to be coupled to waveguides.

5.3 The silicon nitride waveguides

Our starting wafers for the fabrication of the waveguides consisted of $525 \pm 25 \mu\text{m}$ thick monocrystalline Czochralski silicon, with $1 \mu\text{m}$ of silica (SiO_2) deposited on top. This was followed by 120 nm of low pressure chemical vapour deposited (LPCVD) silicon nitride (Si_3N_4). According to the company (Active Business Company GmbH), the uncertainty in the thickness of the silicon nitride was only 5%. The circular wafers were sent to the University of Southampton, where they were sliced to form chips of dimensions $19.05 \text{ mm} \times 12.7 \text{ mm}$. Waveguides were then made by creating a mask by e-beam lithography and reactive ion etching. A schematic of the chip is shown in Fig. 5.4.

Four sets of waveguides were etched, together with a test waveguide. The test waveguide, displayed at the bottom of Fig. 5.4, was $5 \mu\text{m}$ wide throughout the chip and it was used as a baseline to characterise the losses of the other waveguides. Each of the sets contained five different waveguides with five different widths in the central part. These widths varied from 300 to 700 nm in 100 nm steps. This central part is defined as the nanowire region. Set 0 had waveguides with 0.0 mm of taper, which meant that the nanowire region had zero length. Sets 1 and 2 were tapered to give 5.0 and 10.0 mm lengths of nanowire respectively. The taper ratio was $500:1$. This means that for every 500 nm in length, the widths of the waveguides would reduce by 1 nm . Set 3 on the other hand had no $5 \mu\text{m}$ wide region and nanowires throughout the 19.05 mm of the chip. After the waveguides were etched, the chips were cleaved and the facets - i.e. the ends of the waveguides - were polished.

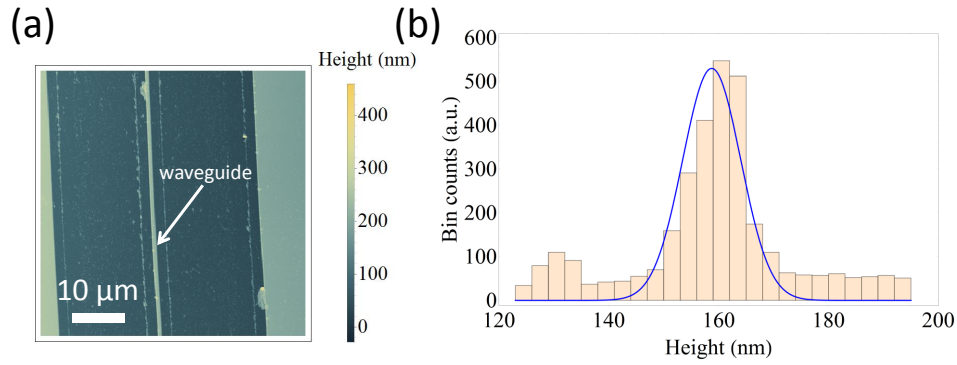


Figure 5.5: (a) Atomic force microscope image of a waveguide. (b) Histogram of the height of each pixel of the central region in (a). A peak appears at 160 nm.

I imaged the empty waveguides with the AFM in order to investigate the surface roughness and the actual height of the silicon nitride. A typical image is shown in Fig. 5.5 (a). The waveguides were created by etching away the silicon nitride layer, leaving 20 μm wide trenches each side. One can immediately see them on the sides, as well as the waveguide in the middle of the image. The waveguide was supposed to be 500 nm wide and 120 nm tall. On the waveguide it is possible to observe imperfections in the etching which appear as straight dotted lines. To measure the height of the waveguide, I put the height of each of its pixels into the histogram shown in Fig. 5.5 (b). Each bin is 3 nm, chosen because that is the resolution of the instrument. I fitted a Gaussian function to that histogram, as shown in blue, with a mean of 159 nm and a FWHM of 13 nm. The height of the waveguide is much higher than the expected one of 120 nm. There could be two reasons. First, the LPCVD nitride layer might be thicker than Active Business Company GmbH specified. Second, the etching at the University of Southampton might have removed more material than expected. In other words, 120 nm of silicon nitride was removed as well as ~ 40 nm of the silica buffer underneath. It was not possible to know which was the actual reason, but the latter seems more likely.

The width of the waveguide could not be measured by the AFM because of its low scanning resolution (1-2 μm). Instead I used the confocal microscope to illuminate a 600 nm wide waveguide with 780 nm light using the 0.9 NA air objective. With this objective, the size of the laser spot on the sample was 585 nm (FWHM of a fitted Gaussian, details in the calibration section of chapter 3). For this measurement, the long-pass filters in the detection were removed in order to observe the structure of the waveguide and the laser

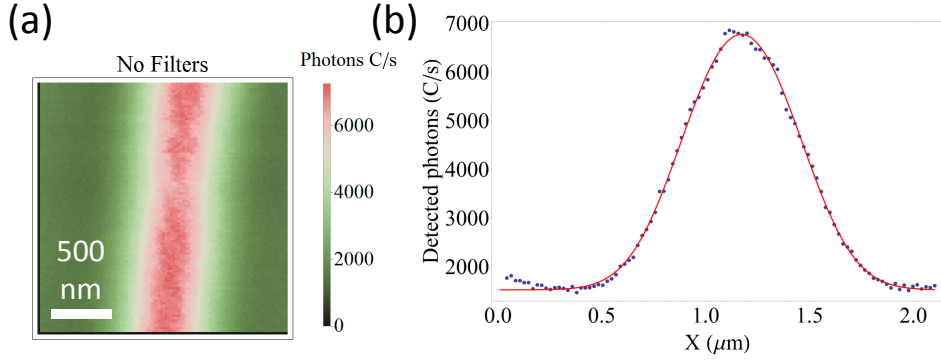


Figure 5.6: a) Confocal image with long-pass filters removed. Waveguide 600 nm wide viewed in reflected excitation light. b) Cut-through of the centre of the image fitted with Eq. 5.3

power was attenuated to 1 nW to avoid saturation of the APDs. The confocal image is shown in Fig. 5.6 (a). The waveguide can be clearly seen in red in the middle of the image. This is because according to Fresnel's law, the reflectivity of the silicon nitride is 11.1% (assuming normal incidence of 780 nm light). This is almost three times the reflectivity of the silica buffer underneath of 3.4%. Hence when the laser was scanned on top of the waveguide it was reflected three times more than on top of the silica. Fig. 5.6 (b) is a cut through of the confocal image. A clear peak appears at the position of the waveguide. In order to determine the width of the waveguide I have fitted a function to this peak, which is the convolution of the Gaussian laser spot $g(x)$ having FWHM ~ 585 nm. This was convoluted with the top hat function

$$f(x) = \begin{cases} 0 & \text{if } x < -\frac{W}{2} \\ 1 & \text{if } -\frac{W}{2} < x < +\frac{W}{2} \\ 0 & \text{if } x > +\frac{W}{2}, \end{cases} \quad (5.2)$$

W being the width of the waveguide. The result of the convolution is

$$\int_{-W/2}^{W/2} g(x - x_0) f(x) dx \propto \text{Erf} \left(\frac{\frac{W}{2} - x_0}{FWHM \ln(2)} \right) + \text{Erf} \left(\frac{\frac{W}{2} + x_0}{FWHM \ln(2)} \right). \quad (5.3)$$

The fitted function, shown in Fig. 5.6 (b) by the red line, fits the data very well with $W = 564 \pm 4$ nm. I repeated the fitting process for 100 cuts through of the waveguide which

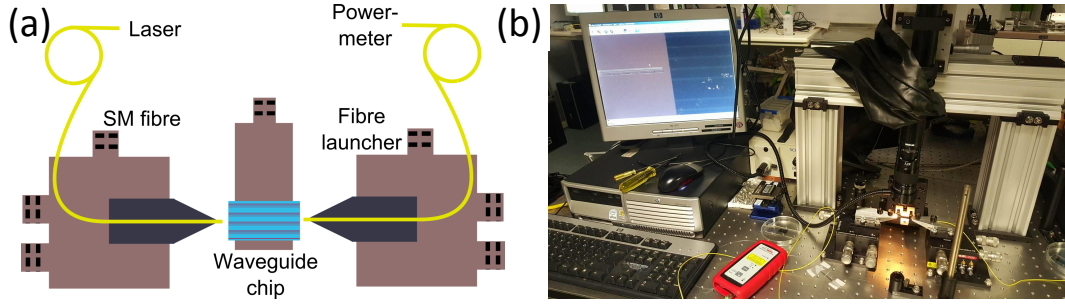


Figure 5.7: (a) Schematics of the optical setup used to characterise the transmission losses. Light from a laser is coupled to one of the waveguides on the chip with a single-mode fibre. After being transmitted through the chip it is collected and sent to a power-meter. (b) The picture of the optical setup as depicted in (a) together with the imaging system.

gave an average width of $W = 579 \pm 14$ nm, not far from the design value of 600 nm.

5.4 Characterizing the losses and coupling efficiency to the silicon nitride waveguide

5.4.1 Method

To characterise the losses of the silicon nitride waveguides and measure how much light could be transmitted through each waveguide on the chip, I built the setup shown in Fig. 5.7 (a). The chip was glued with epoxy on top of a glass microscope slide. I then protected both side facets of the chip with a finely-cut elastomer (Sylgard 184 silicone elastomer, Dow Corning). This was done to avoid depositing the anthracene and the DBT solution on the facets during the crystal growth. Before placing it on the waveguide, the elastomer film was cut so that only the central region of the waveguide chip would be exposed. While characterising the losses, I also covered the central part using a thin cover slip, in order to avoid the deposition of any dust. The protected waveguide was subsequently put on a compact 5-axis platform (PY005/M, Thorlabs) to vary its position and inclination. The stage holding the waveguide was placed between two Nanomax stages (MAX311/M and MAX312/M, Thorlabs) holding two tapered v-groove fibre holders (HFV002, Thorlabs). Single-mode fibres (780HP, Thorlabs) were cut, stripped and cleaved (FC-6RS cleaver, Sumimoto Electric). I checked that the cleave was perpendicular to the fibre core using the imaging capabilities of a fusion splicer (71 C splicer, Sumimoto

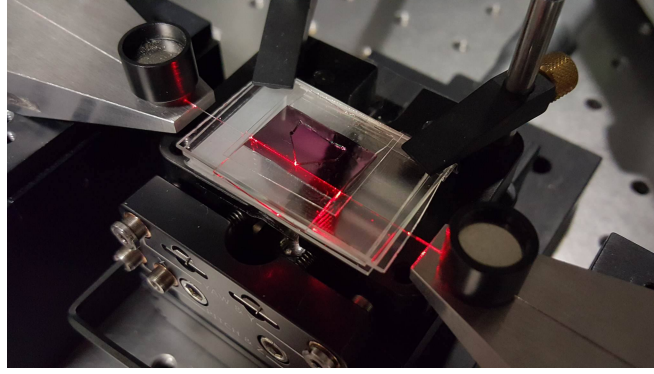


Figure 5.8: A picture of a silicon nitride waveguide chip while a transmission measurement was carried out. Scattering from red light coupled to a waveguide and transmitted through the chip can be observed. The chip was covered with an elastomer leaving only the central part exposed. A glass cover slip covered the entire chip while characterising the losses to avoid the deposition of dust.

Electric). The fibre was then inserted in the v-groove holders next to the chip, as shown in Fig. 5.7 (a). A fibre next to a chip is shown in the screen in Fig. 5.7 (b). Coupling was achieved first by moving the single mode fibres held by the Nanomax stages looking to maximise the scattering of red light from a handheld laser source at 635 nm (HLS635, Thorlabs), such as in Fig 5.8. The scattering was observed on a computer screen with the aid of a camera (UI-1240LE, IDS Imaging) connected to a 12 $\times$ zoom system (1-50486AD, Navitar). After that preliminary coupling, infrared light at 785 nm was sent from one of the fibres to the chip (LDC 201 C laser diode controller with LPS-785-FC single mode fiber-pigtailed laser diode, Thorlabs). The output power from the fibre at the other end of the waveguide was monitored with a power meter (PM100D power meter), with the fibre tip directly connected to the S150C or S120C heads (Thorlabs). The micrometers of the Nanomax stages were rotated until the optical power on the monitor was maximised. Because the propagating mode of the waveguide is linearly polarised, manual fibre polarization controllers were used (FPC030, Thorlabs) to adjust the polarization of the incident light. These work by causing stress-induced birefringence in the single-mode fibres looped around them. A 2-4-2 configuration of loops was used to emulate a quarter-half-quarter wave-plate system. The typical scattering of red light when it was transmitted through a waveguide can be seen in Fig. 5.8.

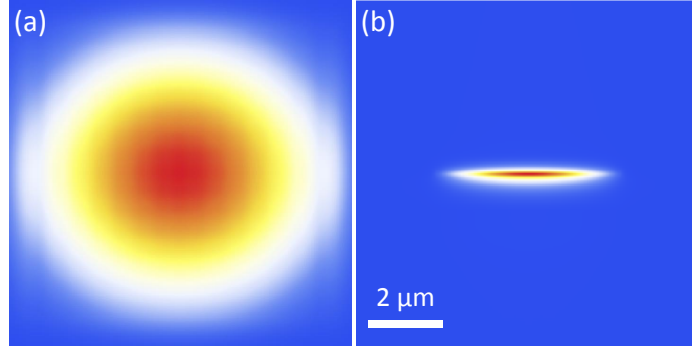


Figure 5.9: (a) The magnitude of the field of the fundamental mode of the 780 HP single-mode fibre. (b) The magnitude of the guided fundamental mode in a silicon nitride waveguide 5 μm wide and 120 nm high.

5.4.2 Simulations of coupling efficiencies

In order to separate the propagation loss in the waveguide from the coupling loss I calculated the optimum coupling efficiency between a single-mode fibre and a waveguide. To do so, I first calculated the field distributions in the modes of the fibre and waveguide using Lumerical FDTD Solutions, with a 785 nm light source. According to the manufacturer (Thorlabs), the 780 HP fibre has a 4.4 μm -wide core made of a material with refractive index of 1.46. The cladding is 125 μm -wide and has a refractive index of 1.45. For the silicon nitride waveguide I took a width of 5 μm and a height of 120 nm. The width of the waveguide allowed multimode propagation but I considered only the coupling to the fundamental mode. The magnitudes of the guided fields are both shown in Fig. 5.9. From these fields I calculated the optimum coupling efficiency given by

$$\eta = \frac{\left| \int E_{\text{WG}}^* E_{\text{Fibre}} dA \right|^2}{\int |E_{\text{WG}}|^2 dA \int |E_{\text{Fibre}}|^2 dA} \quad (5.4)$$

This gives $\eta = 10.28\%$. Hence at each end of the waveguide there is a transmission of ~ 0.1028 just from mode overlaps. On top of this, one needs to consider Fresnel losses of 0.14 at each facet due to the air glass-air-silicon nitride interfaces. The fibre was in fact not in contact with the waveguide to avoid damage and index-matching glues were not used.

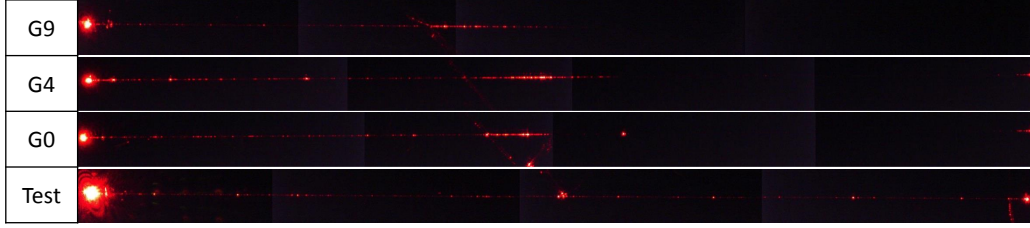


Figure 5.10: Scattering from red light from various silicon nitride waveguides throughout their entire length. One can see the transmission through G9, the waveguide with 700 nm-wide and 5 mm long taper, stops in the middle of the image and the same behaviour is observed in all the waveguides of Set 1, 2 and 3.

5.4.3 Results

By using the setup described in section 5.4.1 I was able to characterise the transmission efficiencies through the waveguides. Unlike Set 0, Sets 1, 2 and 3 did not transmit any light. As an example consider Fig. 5.10, which shows images of scattering of red light when transmitted through various waveguides. Light was sent from the left with a single-mode fibre as described in the previous section and shown in Fig. 5.7 (a). In the test waveguide (the one 5 μm -wide with no taper), one can observe scattering throughout the image, with a bright spot showing light coming out at the other end on the right. The same spot appears for the G0 and the G4 waveguides, belonging to Set 0, although the scattering significantly fades away after the middle. It is not the case for the G9 waveguide. This is the widest waveguide of Set 1, with 700 nm-wide and 5 mm long taper. In this case scattering fades away completely in the middle and transmission is completely lost. I could observe the same behaviour for all the waveguides in Set 1, 2 and 3, leaving only Set 0 as the set I could use to couple photons from the dye molecules.

To quantify the transmission efficiencies I measured the power entering the waveguide from the fibre on the left and compared it to the power measured at the output of the fibre from the right. First, I looked at the test waveguide. The input power was 11.7 mW while at the output I measured 17.2×10^{-3} mW. This means that only 0.15% of the input photons were transmitted to the fibre at the other end of the chip. In other words the transmission efficiency was $\eta_t = 1.47 \times 10^{-3}$. To separate this into propagation efficiency, η_p and coupling efficiency, η_c , I make use of the optimum coupling efficiency between a single-mode fibre and a waveguide calculated in the previous section. This was given by $\eta \sim 0.1$. I also mentioned the Fresnell losses because of the air gap between the fibre

Waveguide	Description	Transmission efficiency, η_t ($\times 10^{-4}$)
Test	Test guide	14.70
G0	300 nm wide	0.09
G1	400 nm wide	1.45
G2	500 nm wide	0.13
G3	600 nm wide	1.80
G4	700 nm wide	4.22

Table 5.1: Transmission efficiencies of Set 0 of the silicon nitride chip used for coupling DBT molecules.

and the waveguide. These amount to 0.85, giving a coupling efficiency per fibre of $\eta_c = 0.086$. The propagation efficiency through the chip can then be calculated as $\eta_p = \frac{\eta_t}{\eta_c} = 0.20$. Because of the length of the waveguide, the transmission efficiency per centimeter is 0.38/cm. Let us digress and compare this with values for similar silicon nitride waveguides found in the literature. Many groups fabricate silicon nitride waveguides and characterise their transmission efficiencies at telecom wavelengths. For studies at wavelengths nearer to 785 nm though, one needs to look at optical waveguides used as biosensors. In their interferometric biosensor, Muellner *et al.* reported a transmission of 0.82/cm at 850 nm [150] and Prieto *et al.* 0.94-0.96/cm at 633 nm [151]. These waveguides were fabricated by plasma-reactive ion-etching silicon nitride deposited using plasma-enhanced chemical vapour deposition. This process is known to lead to losses between 0.80-0.98/cm at 633 nm [152]. All the waveguides mentioned above were embedded in a medium with high refractive index. The waveguides from Southampton however did not have any cladding and were exposed to air. For unclad waveguides, Daldosso *et al.* measured losses of 0.50-0.80 dB/cm at 780 nm [153]. Similar losses were also reported by Subramanian *et al.* for the same wavelength [154].

Similarly as for the test guide, I measured the transmission efficiencies in the infrared for Set 0, the set with no length of taper. They are summarised in Table 5.1. At first one can note that for certain waveguides the losses were much higher than for the test waveguide. These waveguides were excluded and the coupling of dye molecules was attempted only for the G1, G3 and G4 guides which showed on average a difference of less than an order of magnitude compared to the test waveguide.

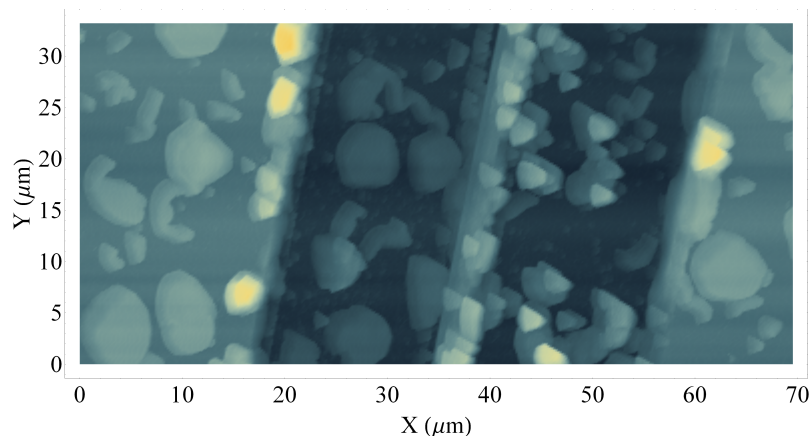


Figure 5.11: An atomic force microscope image of the 700 nm-wide waveguide taken after the crystal growth. Many crystals grew on top of the waveguide as well as in the trenches.

5.5 Method for growing dibenzoterrylene-doped anthracene crystals on the waveguide

5.5.1 Anthracene crystals on top of the waveguide

As discussed in section 2.3, crystals need to be thin in order to achieve a good coupling of DBT molecules to the waveguide. In order to see if thin films of anthracene formed well on top of a silicon nitride waveguide I carried out a supersaturated vapour growth on a chip. The method was similar to that in chapter 2, with 3.39 g of anthracene (8 20109 Merck Millipore, Anthracene for synthesis) in a vial heated at 240°C. The growth was carried out for 60 seconds in order to have good surface coverage. An AFM image taken after the growth is shown in Fig. 5.11. Similarly to Fig. 5.5 the waveguide is at the centre of the image. This time though small crystals only a few microns across, shaped as in chapter 2, appear. They aggregate on top of the waveguide. The waveguide is G19 in set 3, the 700 nm-wide waveguide throughout the length of the chip.

For the particular experiment where I managed to couple photons from dye molecules to the silicon nitride waveguide, the parameters used during the growth were similar to those mentioned above in order to have a similar coverage of anthracene crystals on the waveguide. In fact, if a growth did not provide good crystals with DBT molecules inside, the chip would have been ruined. The cleaning of the chip was not possible because the strong solvents such as toluene or acetone left traces of fluorescent molecules or impurities.

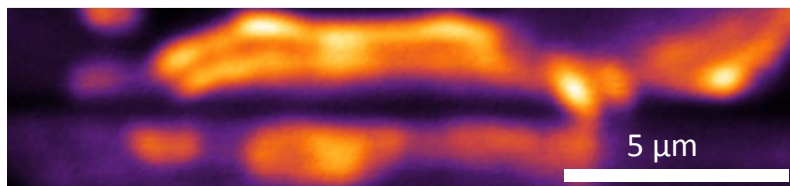


Figure 5.12: Fluorescence confocal image of DBT molecules inside thin anthracene crystals deposited on top of the silicon nitride chip with the spin coating method. The dark line in the middle of each image is the thin waveguide, where not many molecules could be deposited with the spin coating method.

5.5.2 Depositing the dibenzoterrylene molecules: spincoating

I attempted to deposit the DBT molecules on top of the silicon nitride ridge waveguide using the method described in chapter 2. I diluted the 1 mMol solution of DBT in toluene with diethyl ether at a ratio of 1:100 (volume). I placed 20 μl of the solution on top of the waveguide chip, which was glued with epoxy on a glass slide. I then spin coated the whole sample, ramping up to 2000 rpm over 5 s, holding for 60 s before ramping down suddenly. I then grew a thin film of anthracene overcoating the DBT molecules by the supersaturated vapour method. I placed 3.3 g of anthracene inside a vial heated to 243°C. When the anthracene reached that temperature I placed the sample on top of the vial so that thin anthracene crystals overcoated the waveguide and the DBT molecules. The growth was carried out for one minute in the presence of oxygen. Once anthracene crystals were grown, I looked at the position of the DBT molecules with respect to the waveguide using the confocal microscope described in chapter 3. The laser spot stayed on any one molecule for a maximum of 80 ms with very low power (continuous wave 780 Toptica laser with $\sim 6 \mu\text{W}$ in front of the objective lens) so bleaching was not an issue here. For this measurement I used the 0.9 NA objective. A typical confocal image for this sample is shown in Fig. 5.12. The waveguide was in the middle of the image (dark line), surrounded by the molecule fluorescence. This means that although crystals grew well on top of the waveguide, molecules didn't aggregate there. During the spin coating process, molecules were thrown into the trenches and trapped at the bottom of the waveguide where the guided mode has no strong evanescent field they can couple to. A new DBT deposition method was needed.

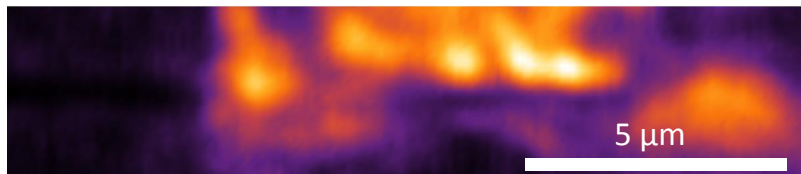


Figure 5.13: Fluorescence confocal image of DBT molecules inside thin anthracene crystals deposited on top of the silicon nitride chip with the spraying method. In this case some of the molecules sit on top of the waveguide, as by the strong fluorescence interrupting the dark horizontal line.

5.5.3 Depositing the dibenzoterrylene molecules: spraying

I found experimentally that the best way of depositing the DBT molecules was to spray a solution on top of the middle of the chip whose facets were protected by an elastomer. I diluted the 1 mMol solution of DBT in toluene with diethyl ether at a ratio of 1:1000 (volume) and placed 10 ml of the new solution into a spray diffuser (K-2311, Koehler Technische Produkten). I then held the spray 10 cm away from the waveguide, at an inclination of approximately 60° . I sprayed the solution 8 times and let the diethyl ether and toluene evaporate for 15 minutes. After the growth I looked at the molecules' fluorescence with the confocal microscope (Fig. 5.13). One can see that the waveguide (positioned horizontally in the middle of the image), has some fluorescence on top, meaning that after spraying, with this method, molecules would sit on top of ridge structures.

The sprayed DBT molecules showed good photostability proved by the lack of photoblinking in Fig. 5.13 and the observation of a constant rate of emitted photons. When depositing the molecules using this method, the spray diffuser created bubbles with clusters of DBTs. When the toluene and diethyl ether evaporated, they left clusters of DBT molecules that then got incorporated into anthracene crystals.

5.6 Coupling DBT molecules to a silicon nitride waveguide

5.6.1 Method

Next, I set about showing that some of the DBT fluorescence was coupled into the silicon nitride waveguide. For this, I built the setup shown in Fig. 5.14 (a). A 3-axis positioning stage (Nanomax, Thorlabs) was placed next to the sample stage. They both appear in light brown in Fig. 5.14 (a). On top of the newly added stage, I positioned a cleaved (FC-

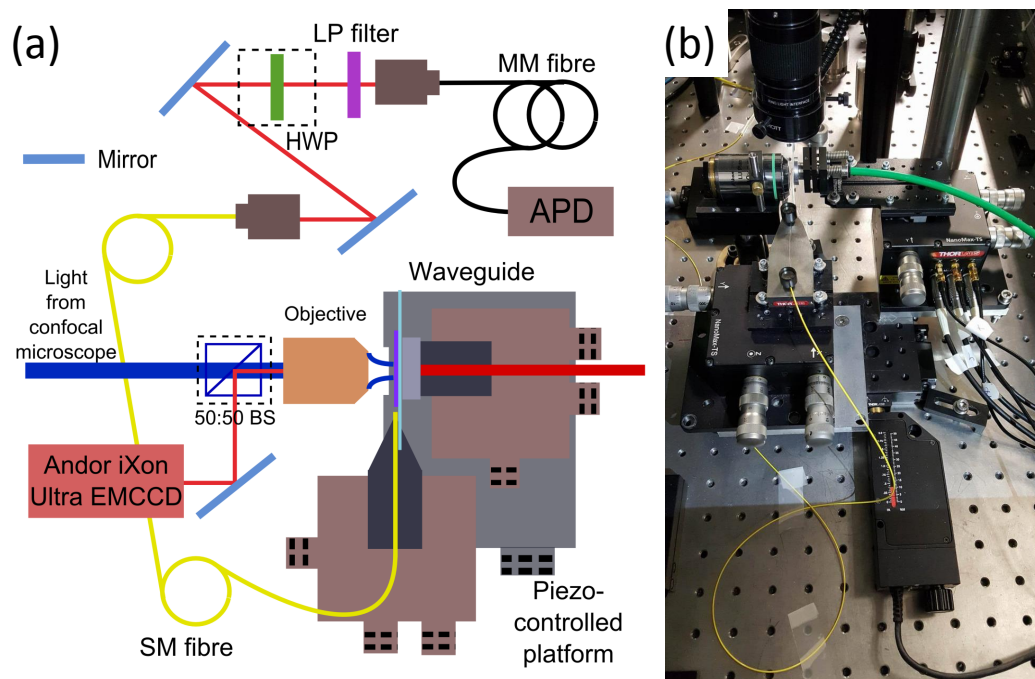


Figure 5.14: (a) Schematics of the setup used to detect light coupled to the waveguide from the molecules using a single-mode optical fibre placed at its facet. Light from the fibre would then be filtered in free space and sent to an APD. (b) A photo of the corresponding setup

6RS cleaver, Sumitomo Electric) single-mode fibre, appearing in yellow in Fig. 5.14 (a), (780HP, Thorlabs), supported by a tapered v-groove fibre holder (HFV002, Thorlabs). This launched light into a waveguide. Both the sample stage and the fibre stage were bolted on top of a single-axis piezo-controlled platform (PT1/M, Thorlabs). Its travel range of 25 mm was longer than the length of the waveguide and it was moved using a motor (8500 actuator, Newport) connected to a high-precision motion controller (ESP300, Newport). Once the waveguide was mounted in the confocal microscope sample mount and its inclination adjusted until parallel to the optical table, 785 nm light was coupled to it via the single-mode optical fibre. A laser (LDC 201 C laser diode controller with LPS-785-FC single mode fiber-pigtailed laser diode, Thorlabs) generated light which was coupled to a multimode fibre. Light was then sent to a waveplate to couple to the guided mode of the waveguide. It was then coupled to the single-mode optical fibre using two mirrors. In order to prove the coupling, the scattering of the light from the waveguide was monitored with the iXon Ultra camera and a camera placed on top of the setup (UI-1240LE, IDS Imaging) connected to a 12 $\times$ zoom system body tube (1-50486AD, Navitar). This zooming system does not appear in Fig. 5.14 (a) however can be seen on the top of Fig. 5.14 (b). Once light was coupled to the silicon nitride waveguide, I moved the whole platform. Given that the waveguide and the fibre were both on top of the same stage, coupling was maintained during this process. The single-axis stage was moved until it reached the centre of the waveguide. Molecules were excited through the confocal microscope and the light coupled to the waveguide was collected by the single-mode optical fibre and sent to an extra detection channel. The single-mode optical fibre was terminated by an FC/PC connector. Light travelled in free space to a long-pass filter. When detecting light from molecules, the HWP was no longer needed and it was removed. Light was then coupled to the multi-mode optical fibre. At the other end, the fibre was connected to an APD instead of the laser for the detection of the molecules' fluorescence.

Finally it needs to be mentioned that for this experiment, I used the 20x, 0.45 NA objective lens (Nikon), which had a longer working distance compared to the previously mentioned objectives. The laser spot achieved with this lens had a FWHM of $\sim 1.4 \mu\text{m}$, and a standard deviation $\sigma = 588 \text{ nm}$.

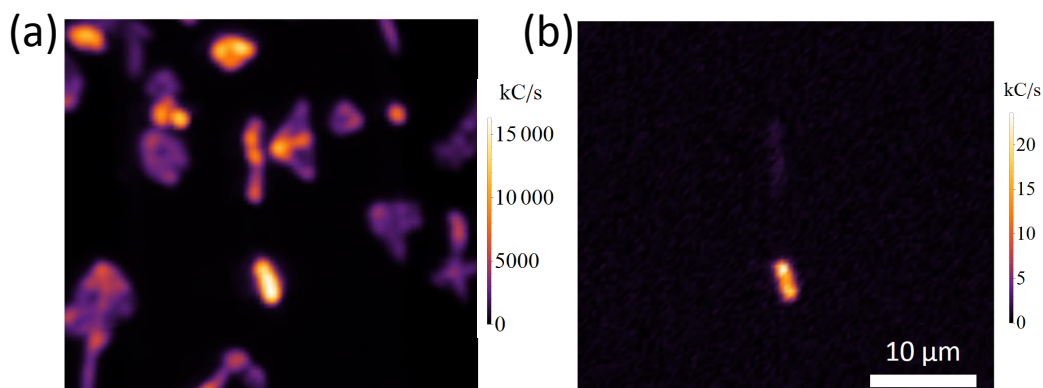


Figure 5.15: (a) Confocal image of molecules on top of the waveguide. (b) Waveguide output after a long-pass filter when scanning the laser over the same region as in (a). The scale of the two images is different because of the much stronger signal in the confocal image compared to the waveguide one.

5.6.2 Confocal images

I grew the anthracene crystals on top of the waveguide chip I had previously characterised. After the growth, I removed the elastomer which was protecting the facets of the chip and I placed the chip in the confocal microscope. Once the chip was in place, I coupled light from a cleaved fibre to the G1, G3 and G4 waveguides in Set 0, one at a time. Every time light was coupled to one of these, I would move the fibre and the chip until reaching the centre of the waveguide, where from 5 μm the width would taper down to the nanowire region. Even though for Set 0 the nanowire region had a length of 0.0 mm, I expected an evanescent field that would couple the molecules due to the tapered region which was 4.3-4.7 mm long depending on the waveguide width.

By steering the galvo mirrors of the confocal microscope I then imaged the molecules on top of the waveguide. I used the 780 nm external-cavity continuous-wave diode laser that could deliver up to 33.2 mW of power. In the confocal detection setup I collected the emission using an APD, filtering out the laser light with two 792 nm long-pass filters. The detection of light coupled to the waveguide when moving the laser spot across the sample was carried out with another APD with filters at the same wavelength. The confocal image acquired scanning the laser over the G1 waveguide is shown in Fig. 5.15 (a). The corresponding waveguide output is shown in Fig. 5.15 (b). One sees that one of the bright regions seen in (a) is reproduced in (b), indicating that the light from those molecules

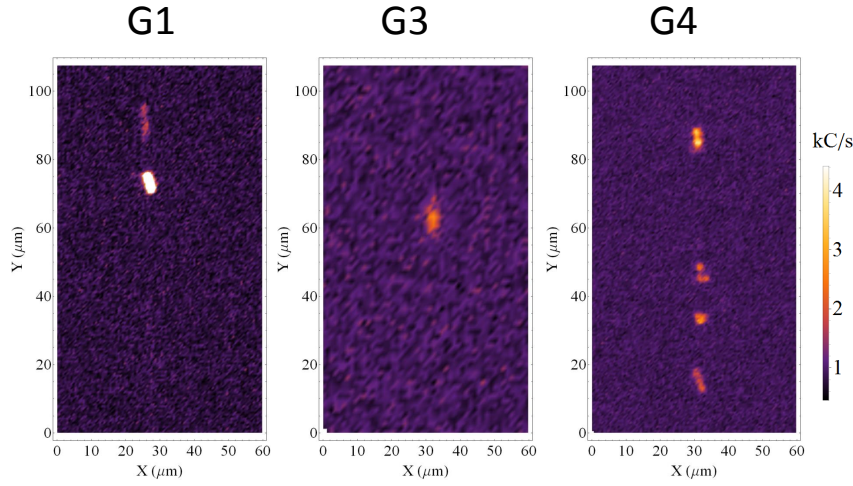


Figure 5.16: Waveguide output after a long-pass filter when scanning the laser over the G1, G3 and G4 waveguides. All images have the same scale. The strongest signal was detected for the G1 waveguide.

was partially coupled into the waveguide, as desired. At this position, the waveguide was ~ 866 nm wide. I analysed Fig. 5.15 (a) to determine whether the bright region, i.e. the crystal with molecules coupled to the waveguide, was wider or thinner than the waveguide. As one can see the crystal presents a homogeneous fluorescence indicating the presence of many molecules. I assumed that these molecules were evenly distributed across the crystal whose shape is similar to the one measured using the atomic-force-microscope, with very sharp edges and a flat top. Mathematically the shape of the crystal is a top hat function. While scanning the laser spot across the bright region in Fig. 5.15 (a) the detected fluorescence is the convolution of this top hat function and the Gaussian laser spot. Fitting the data similarly to section 5.3, I estimate that the crystal is 2.6 ± 0.1 μm wide. This results suggests that the crystal was three times wider than the waveguide and about twice the FWHM of the laser beam (~ 1.4 μm).

Similarly to the G1 waveguide, I also found molecules coupled to the G3 and G4 waveguides. Again, the microscope made a raster scan of the excitation light over each waveguide, while the light emerging from the waveguide was collected by the single-mode 780HP fibre. The waveguide outputs are all shown on the same scale in Fig. 5.16. Because all the images have the same scale, the signal from the molecules coupled to the G1 waveguide appears over-saturated compared to the signal from the other two waveguides. At the bright region, the G1 waveguide is 866 nm wide. In contrast, the width of the

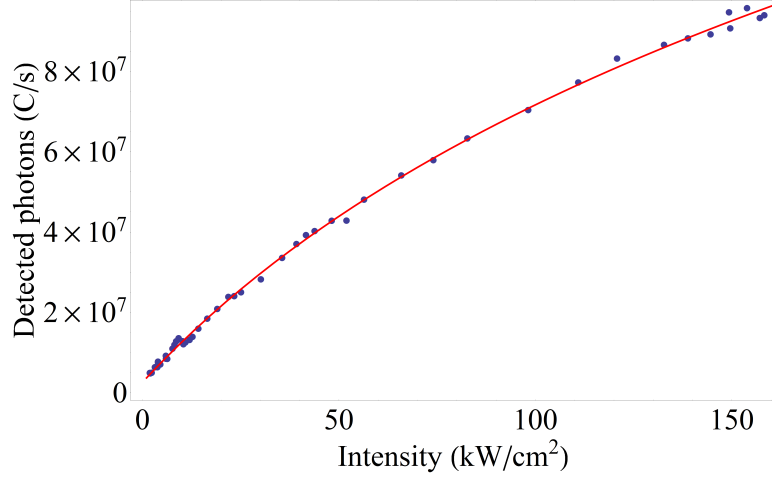


Figure 5.17: Detected emission as function of illumination intensities of the molecules on top of the G3 waveguide. The fit gives a saturation intensity equal to 81 ± 4 kW/cm².

G3 waveguide was ~ 1162 nm while the width of G4 was ~ 1184 nm. Because of the smaller width and strongest signal I focus the majority of the rest of the chapter on the investigation of the optical properties of molecules coupled to the G1 waveguide. The lifetime of the molecules coupled to the G3 waveguide will also be presented in section 5.6.8. The shape of the crystal on top of the G3 waveguide in fact allowed for a direct comparison between the lifetime of molecules coupled and not coupled to the waveguide within the same anthracene crystal.

5.6.3 Saturation intensity of molecules collected via the confocal

For the rest of this chapter I will go through the optical properties of molecules coupled to the G1 waveguide in order to estimate the coupling efficiency, β in Eq. 1.11. This was done by first measuring the collection efficiency of the confocal microscope and then comparing the number of fluorescence photons detected in the microscope with the number in the waveguide.

To measure the collection efficiency of the confocal microscope I first determined the saturation intensity of the molecules on top of a silicon nitride sample and their excited state lifetime using the method already described in chapter 4. I positioned my laser spot on top of molecules on the G1 waveguide and recorded the fluorescence count with the confocal microscope as a function of the intensity of the resonant, cw, 780 nm excitation light. Given that there were many molecules on the sample (the antibunching curve did

not show any dip), the signal detected by the confocal microscope was so strong that I had to place an ND 2.0 filter in front of the APD. The background is negligible compared with the signal from the molecules. The result is shown by the blue dots in Fig. 5.17. In order to fit the data and estimate the saturation intensity of molecules on top of the waveguide, one had to use a more generalised formula than Eq. 4.9. Let us consider the laser intensity at the sample position given by a 2D Gaussian with amplitude I_0 and $\text{FWHM} = 2\sqrt{2\ln(2)}\sigma$, written in polar coordinates as:

$$I(r) = I_0 e^{-\frac{r^2}{2\sigma^2}}. \quad (5.5)$$

Within the laser spot, each molecule is excited with a different illumination intensity. Hence the total detected scattering rate is given by the sum of each molecule's scattering rate as

$$R = \sum_i \frac{I(r_i)}{I(r_i) + I_{\text{sat},i}} R_{\text{max},i} \eta_{\text{confocal}} + C, \quad (5.6)$$

with the index i denoting the i^{th} molecule. $R_{\text{max},i}$ is the maximum limiting rate and η_{confocal} the detection efficiency of the confocal microscope. C is a constant given by the detected counts at zero intensity. I assume that the molecules have similar saturation intensities and limiting rate. This is justified by the small variation in the molecules' lifetime shown in the previous chapter. I further make the reasonable approximation that the molecules are uniformly distributed over a region larger than the spot size of the excitation light. This is justified by the fact that I measured the crystal to be twice as wide as the FWHM of the laser spot. I can then replace the sum with an integral:

$$\begin{aligned} R &= 2\pi R_{\text{max}} \eta_{\text{confocal}} n_{\text{mol}} \int_0^\infty r \frac{I(r)}{I(r) + I_{\text{sat}}} dr + C \\ &= 2\pi R_{\text{max}} \eta_{\text{confocal}} n_{\text{mol}} \int_0^\infty r \frac{I_0 e^{-\frac{r^2}{2\sigma^2}}}{I_0 e^{-\frac{r^2}{2\sigma^2}} + I_{\text{sat}}} dr + C \\ &= 2\pi R_{\text{max}} \eta_{\text{confocal}} n_{\text{mol}} \sigma^2 \ln \left(\frac{I_{\text{sat}} + I_0}{I_{\text{sat}}} \right) + C, \end{aligned} \quad (5.7)$$

where n_{mol} is the number density of molecules. I fitted the data in Fig. 5.17 by leaving R_{max} , η_{confocal} , n_{mol} , I_{sat} and C as free parameters, with the result $I_{\text{sat}} = 81 \pm 4 \text{ kW/cm}^2$. This is consistent with the value $75 \pm 3 \text{ kW/cm}^2$ that I measured for individual molecules

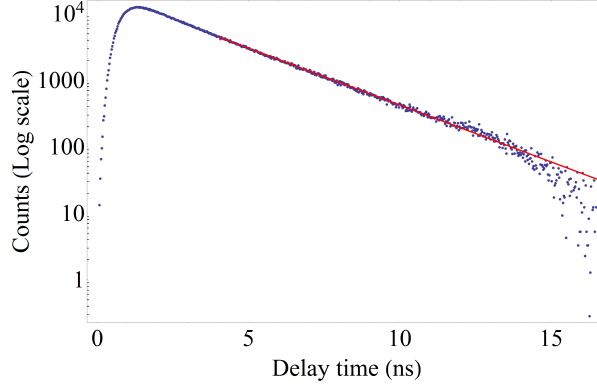


Figure 5.18: Time-correlated single-photon counting data of molecules coupled to the G1 waveguide. The fit according to Eq. 5.9 is shown in red.

in chapter 4 and published in [104].

5.6.4 Lifetime of molecules coupled to a waveguide

Having gathered information on the saturation intensity, I measured the excited state lifetime of the molecules on top of the G1 waveguide. For this, I used the 755 nm pulsed laser with 40 MHz repetition rate and a pulse width of 83 ps. I then collected the fluorescence of the molecules from the facet of the waveguide filtering the laser light with a 770 nm long-pass filter. Given that there were many molecules within the FWHM of the laser and that for each one the population of the excited state decayed as a single exponential, the short excitation pulse causes the fluorescence to decay as

$$C = C_0 \sum_j e^{-\frac{t}{\tau_j}}. \quad (5.8)$$

In this equation, t is the time, C_0 is a normalising factor and τ_j is the excited state lifetime of the j^{th} molecule. However, we know from chapter 4 that the lifetime of the molecules in the thin anthracene crystals follows a normal distribution with mean of 3.7 ns and a standard deviation of 0.4 ns. This variation of $\sim 12\%$ is small, so I approximate Eq. 5.8 as

$$C = C_0 e^{-\frac{t}{\tau_0}}, \quad (5.9)$$

where τ_0 is the mean lifetime. A fitting of the data in Fig.5.18 gives a mean lifetime of 2.57 ± 0.05 ns. This value is nearly three standard deviations away from the value measured

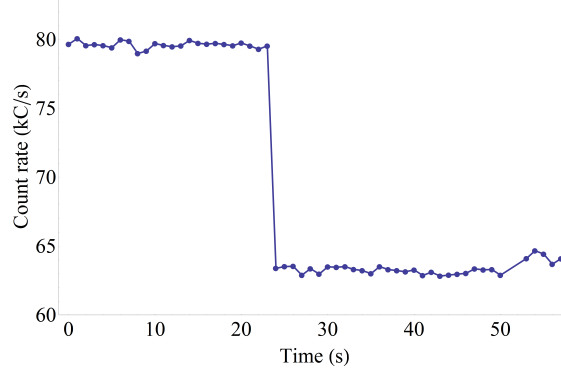


Figure 5.19: Emission from a single molecule as a function of time (in seconds). After ~ 25 seconds the molecule photobleached and the count rate suddenly dropped in a single step.

in chapter 4. This is most likely due to the molecules being on top of silicon nitride and coupled to the waveguide. The short lifetime suggests an enhancement of the emission, which will be studied in more depth in section 5.6.8.

5.6.5 Efficiency of the confocal microscope

As mentioned before, the purpose of section 5.6 is to estimate the coupling efficiency of the molecules to the waveguide. To this end I needed to know how many photons per second the APD in the confocal path was detecting from a single molecule. Because I measured the lifetime of the molecules and their saturation intensity, this can lead to an estimate of the detection efficiency of the confocal microscope. A simple method to measure how many photons per second I was able to detect from a single molecule is to look at the number of counts before and after a molecule bleached. In order to encourage bleaching I grew a new sample in an atmosphere of oxygen rather than nitrogen. Apart from that the method was as described in chapter 2. I used the cw 780 nm Toptica laser to drive these molecules resonantly, with 1.96 mW in front of the 0.45 NA air objective, which according to the previously measured saturation intensity, corresponded to $\frac{I_0}{I_{\text{sat}}} = s \sim 1.12$ at the centre of the laser spot. After carrying out a confocal scan, I collected fluorescence from a single spot as a function of time, and waited for a bleaching event. A typical trace is shown in Fig. 5.19. After ~ 25 s, the counts dropped from ~ 80 kC/s to ~ 63 kC/s. After repeating this for a few molecules I found that with the 0.45 NA air objective setup the APD detects $R = (17.5 \pm 2.3) \times 10^3$ photons per second from a single molecule. Now

Description of loss	Efficiency
Molecule to fibre	0.012
Splice	0.98
LP filter	0.44
APD	0.5
Total efficiency $\eta_{\text{WG, G1}}$	2.6×10^{-3}

Table 5.2: Breakdown of contributions to the total efficiency $\eta_{\text{WG, G1}}$ for detection of a photon that has been emitted by a molecule into the waveguide.

Eq. 5.6 gives

$$R = \frac{s}{1+s} R_{\text{max}} \eta_{\text{confocal}}. \quad (5.10)$$

For this resonant cw excitation, $R_{\text{max}} = \frac{1}{2\tau_0}$ where $\tau_0 = 2.57 \pm 0.05$ ns is the lifetime measured in section 5.6.4. Hence I find that $\eta_{\text{confocal}} = (1.7 \pm 0.2) \times 10^4$. This value will be important later on when I will discuss the coupling efficiency of the molecules to the silicon nitride waveguides.

Knowing the emission from a single molecule, I can now use Eq. 5.7 to estimate the number density of molecules in the crystal on top of the G1 waveguide that produced the bright spot below the centre of Fig. 5.15 (a), $n_{\text{mol}} = 1.6 \times 10^{14}$ molecules/m². Hence, the number of molecules within the FWHM of the laser spot on top of the G1 waveguide was 184.

5.6.6 Estimating the mean coupling of molecules to the waveguide

Let us define β as the probability that a photon emitted by a molecule will be coupled into the G1 waveguide, and let us define $\eta_{\text{WG, G1}}$ as the probability that this photon will be subsequently detected. In order to determine the value of β from the fluorescence rate detected through the waveguide, we need to find $\eta_{\text{WG, G1}}$. To do so, I calculate all the factors that contribute to the detection efficiency. The transmission along the whole G1 waveguide, including the coupling losses to the fibre at each end, was 1.45×10^{-4} (see Table 5.1). Since the molecules were close to the middle of the guide, assuming symmetric losses throughout the chip, I estimate 0.012 transmission from propagating along the guide and coupling into the fibre (the yellow fibre in Fig. 5.14 (a)). A splice in the fibre added a loss corresponding to a transmission of 0.98. After the fibre, light travelled to the detector with negligible loss except from the long-pass filter. From the fluorescence spectrum I

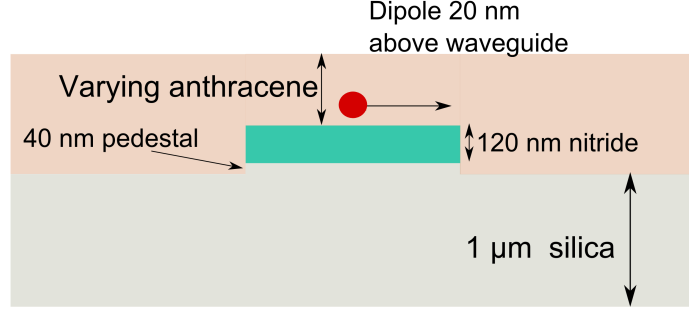


Figure 5.20: Sketch of the geometry used to simulate the behaviour of a molecule as function of its position across the waveguide. $1\ \mu\text{m}$ of silica was deposited on top of an infinitely thick silicon substrate. On top of this, a silica pedestal $40\ \text{nm}$ thick and the silicon nitride waveguide, $120\ \text{nm}$ thick. Both were $866\ \text{nm}$ wide, because I estimated that was the width of the waveguide at the molecules' position following the 500:1 taper ratio. A dipole radiating at $792\ \text{nm}$ (the cut-off wavelength of the long-pass filter) was placed $20\ \text{nm}$ above the top of the waveguide inside an anthracene crystal. I estimated the dimensions of the crystal by looking at the confocal images. In the simulations I varied the thickness of the crystal as well as the position of the dipole within the FWHM of the excitation spot.

derived in chapter 4 (shown red in Fig. 4.1), I calculate that the transmission through the $792\ \text{nm}$ long-pass filter is 44% of the total fluorescence. Lastly the APD has a detection efficiency of 50% at $800\ \text{nm}$. All these transmission efficiencies, summarised in Table 5.2 amount to a net detection efficiency for photons coupled into the waveguide of $\eta_{\text{WG}, G1} = 2.6 \times 10^{-3}$. The coupling β is computed as

$$\beta = \frac{N_{\text{WG}, G1}}{N_{\text{confocal}}} \times \frac{\eta_{\text{confocal}}}{\eta_{\text{WG}, G1}}. \quad (5.11)$$

At the centre of the bright spot in Fig. 5.15 (b) the count rate detected via the waveguide is $N_{\text{WG}, G1} = 23.6\ \text{kC/s}$. At the same position, the rate in Fig. 5.15 (a) is $N_{\text{confocal}} = 13.3 \times 10^3\ \text{kC/s}$. We have determined in section 5.6.5 that $\eta_{\text{confocal}} = (1.7 \pm 0.2) \times 10^{-4}$ and as previously mentioned $\eta_{\text{WG}, G1} = 2.6 \times 10^{-3}$. This gives

$$\beta_{G1} = (1.2 \pm 0.1) \times 10^{-4} \quad (5.12)$$

5.6.7 Comparing the coupling with simulations

Let us now compare the measured coupling, β_{G1} , with the coupling from simulations carried out using Lumerical FDTD Solutions (Version 8.16, Academic KX License, Lumerical

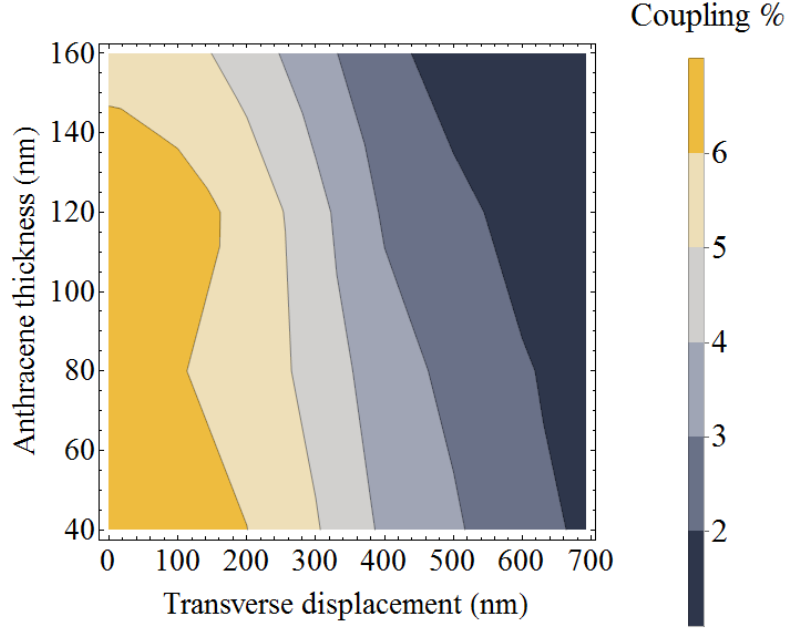


Figure 5.21: Coupling efficiency when varying dipole's transverse position on the waveguide and the thickness of the anthracene crystal.

Solutions Inc.). The geometry used for the simulations is shown in Fig. 5.20. I placed a dipole emitting at $\lambda = 792$ nm (the cut-off wavelength of the long-pass filter in the detection) 20 nm above the top of the G1 waveguide inside an anthracene crystal. The length and width of the crystal were 7.2 and 2.6 μm respectively (taken from the image in Fig. 5.15) and the thickness was fixed at a value between 40 nm and 160 nm. The waveguide was 160 nm high and, at the molecules' position, 866 nm wide. As mentioned in section 5.3, I believe that during the etching process, 120 nm of silicon nitride was removed as well as ~ 40 nm of the silica underneath. The direction of the dipole was parallel to the guided field, and the laser was centred on the waveguide. The coupling was computed by evaluating the power transmitted through a plane situated ~ 16 μm (~ 20 λ) away from the molecule, as fraction of the total radiated power. The results are plotted in Fig. 5.21 for a range of molecule position and anthracene thickness. As a simple check, I compared these values with the coupling given by inserting the numerically calculated A_{eff} and v_g into Eq. 1.11 very close agreement ($\sim 5\%$) [90]. An average taken over the range of displacements in Fig. 5.21 gives a mean coupling of $\sim 4\%$. This is roughly the same as taking an average over the region excited by the laser spot, whose FWHM is 1.4

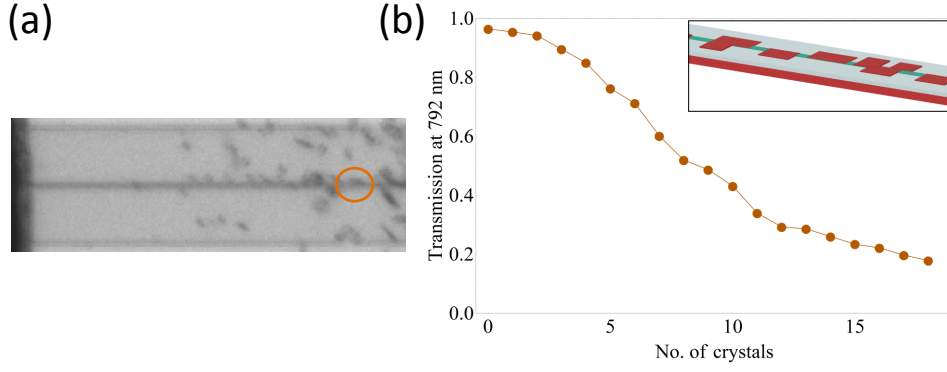


Figure 5.22: (a) Optical microscope image of the G1 waveguide with the crystal where coupling was measured highlighted by the orange circle. The crystals that sit on top of the waveguide cause some additional loss through their coupling to the evanescent field. (b) Transmission at 792 nm after light passes an integer number of crystals. Inset on top right: the simulated structure with small thin crystals randomly distributed on top of the waveguide.

μm . Thus we conclude that the coupling efficiency β_{G1} derived from the experiment should be a few percent. This is two orders of magnitude higher than the value we obtained, so we need to consider what factors might have compromised the experiment.

In the Lumerical calculation, I assume that the optical dipole was parallel to the guided field, but the orientation of the crystal was not controlled, so there is an unknown projection factor of $\cos^2(\theta)$ that should be included in the estimate of β . A second uncertainty concerns the transmission of the guide, which was measured prior to depositing the crystals. Fig 5.22 (a) shows a microscope image of G1 taken just after the anthracene deposition. There are roughly 11 crystals sitting on top of the guide between the crystal where I measured the coupling, circled in orange, and the end where the light was coupled out. In order to check whether they might have changed transmission, I put crystals of similar shape and size into the Lumerical model, adding them one at a time, and plotting the output as function of the number of crystals. The result is shown in Fig. 5.22 (b). For the 11 crystals seen in Fig. 5.22 (a) the additional attenuation factor is of order 0.3. Of course, it would have been good to check the transmission after growing the crystals, but their sublimation is so rapid that there was no time to do so. Finally, I note that there could have been a strong asymmetry in the transmission of the guide. Because the transmission from end to end was $\sim 10^{-4}$, we took a value of 10^{-2} from the centre (see first line of Table 5.2). However, it is entirely possible that the transmission was 10^{-3} in the

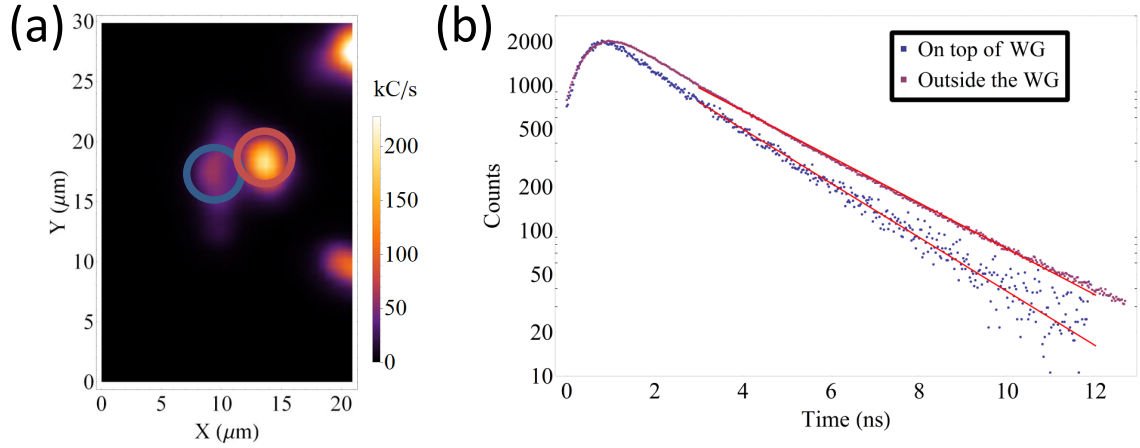


Figure 5.23: (a) Confocal image of molecules on top (blue circle) and in the vicinity (red circle) of the G3 waveguide. (b) Time-correlated single-photon counting data of molecules coupled to the G3 waveguide (blue). This is compared to the data acquired for molecules outside the waveguide (red).

half used and 10^{-1} in the other half. Indeed we see in Fig. 5.10 that the guides typically have loss from a small number of scattering centres. This could have been checked by moving the detector to the other end of the guide, but again the short lifetime of the crystals prevented us from doing so. In future experiments of this type we will monitor both ends simultaneously, and we will use waveguides where the crystals can be prevented from subliming by using a protective overcoating. In light of these uncertainties, we decided to determine the coupling by a different method, which is described in the next section.

5.6.8 Lifetime of molecules on top and outside the waveguide

The result in section 5.6.4 (Fig. 5.18), showed that molecules on top of the G1 waveguide have significantly shorter lifetime than those measured in chapter 4 (Fig. 4.6) on top of glass. We summarised that this was due to the additional density of photons modes provided by the waveguide. The coupling into the guide increases the total radiation rate from the unassisted value Γ_1 to a faster value Γ'_1 . Our coupling parameter β is the fraction of radiation that couples into the guide, so

$$\beta = \frac{\Gamma'_1 - \Gamma_1}{\Gamma'_1}. \quad (5.13)$$

Thus an alternative way to determine β is to measure the radiative decay rates for

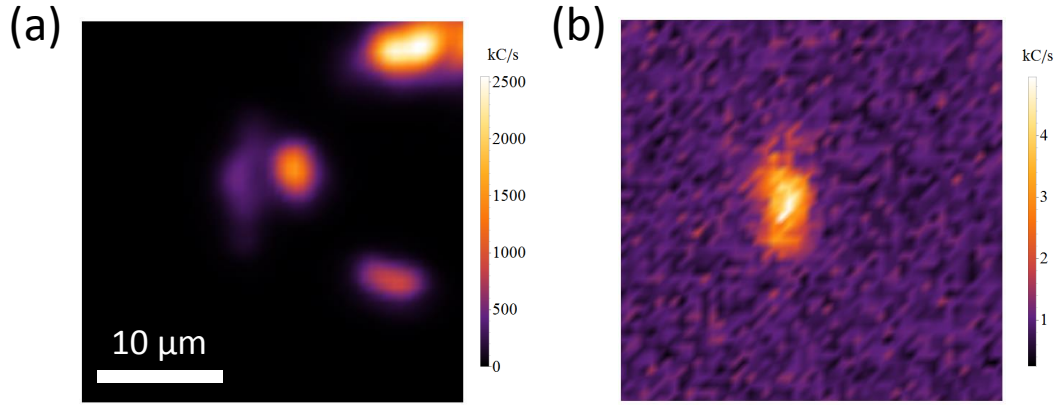


Figure 5.24: (a) Confocal image of molecules on top of the G3 waveguide. (b) Waveguide output after a long-pass filter when scanning the laser over the same region as in (a).

molecules on top of the guide (Γ'_1) and for those off to the side (Γ_1). Fig. 5.23 (a) shows DBT molecules on top of a G3 guide, circled blue and those off to the side, circled red. Each group was excited by short pulses at 755 nm and the fluorescence was detected to measure the decay curve. In Fig. 5.23 (b) the red dots show the decay of fluorescence seen through the confocal microscope after exciting the molecules sitting off to the side of the guide. The data shows the exponential decay of the excited state population convoluted with the instrument response function due to the finite temporal width of the laser pulse. To fit the data, I plotted it on a logarithmic scale and I fitted to it a straight line starting at 3 ns to exclude any contribution from the laser pulse. The fit to the red dots, shown by the red solid line, gives $\Gamma_1 = (3.57 \pm 0.03) \times 10^8 \text{ s}^{-1}$. Similarly I fitted the blue dots, which show the fluorescence detected through the G3 guide. The fit gives $\Gamma'_1 = (4.22 \pm 0.09) \times 10^8 \text{ s}^{-1}$. Together these yield the coupling efficiency $\beta = 15 \pm 2 \%$.

I simulated the G3 guide using Lumerical, exactly as described in section 5.6.7 for G1, and obtained a calculated coupling of 7.1% into each direction of the guide, making a total of 14.2%. There may be other factors that would contribute to an enhancement of the excited state lifetime. The part of the crystal on top of the waveguide may be thinner hence causing an enhancement. Moreover, molecules on top of the waveguide sit on silicon nitride, while molecules in the trenches on silica. According to Eq. 1.10, this difference in refractive indices can contribute to an enhancement. Still, the data is an average of many molecules and definitely shows an increased decay rate on the waveguide which qualitatively suggests a coupling to the waveguide mode, proved by the confocal

image in Fig. 5.24. This figure, similarly to Fig. 5.15, shows a confocal image acquired scanning the laser over the G3 waveguide. The waveguide output is shown in Fig. 5.24 (b). One sees that the molecules with a higher spontaneous decay rate as in Fig. 5.23 (a) are indeed partially coupled into the waveguide.

5.7 A summary of problems yet to be solved

Two problems need to be addressed before it is possible to make practical quantum photonic devices using DBT molecules in anthracene. The first is the random orientation of the anthracene crystal relative to the guide, which in turn determines the orientation of the DBT optical dipoles. It would be very helpful to have a substrate on which the anthracene automatically grows with a specific orientation, and this led to the idea that a strongly polar material, such as lithium niobate, might be able to achieve that. In chapter 6, I show some first results on the growth of anthracene on lithium niobate.

The second problem is that good coupling to molecules on the surface of the waveguide, requires the guided mode to have strong evanescent field. While such modes can be designed, as shown in this thesis, they do not propagate well because the evanescent field also couples to defects and contaminants on the surface, resulting in a very high propagation loss. For this reason it would be desirable to place the DBT molecules inside the guide, rather than on the surface, so that the mode could be well confined and yet the molecules could still interact with a strong field. One way to achieve this is to etch a narrow slot in the waveguide. In chapter 7, I suggest a geometry for slotted waveguides and show our first results putting DBT molecules inside nano-slots.

Chapter 6

Dibenzoterrylene molecules on top of lithium niobate

6.1 Introduction

In this chapter I will discuss the efforts to control the alignment of DBT molecules on top of photonic structures. A poor directionality of the emission of the molecules with respect to a waveguide has profound negative effects on the coupling efficiency. When the dipole of a molecule is not transverse to a waveguide the coupling is reduced in proportion to $\cos^2(\theta)$, with θ being the angle between the dipole transition matrix element and the vacuum electric field of the waveguide mode. As seen in chapter 4, DBT molecules sit with a well-defined alignment when they are properly embedded inside the anthracene matrix, so if we control the orientation of the crystal on a waveguide, we also control the molecules. With this in mind, I have grown anthracene-doped crystals on top of lithium niobate (LiNbO_3), to see if the crystals are aligned by the surface charges of that material. The lithium niobate samples were fabricated in collaboration with Prof. Gallo at KTH Royal Institute of Technology, Stockholm.

Congruent lithium niobate is a ferroelectric material used extensively in the integrated and guided-wave photonic industry [155]. It was synthesised and studied in its crystal form at Bell laboratories in the 1960s [156, 157, 158, 159, 160]. As shown in Fig. 6.1 (a), it consists of many planar sheets of Li and O, shown by the blue and red balls, that form octahedra at the centre of which Nb atoms, the green ball, is positioned [161, 162]. What

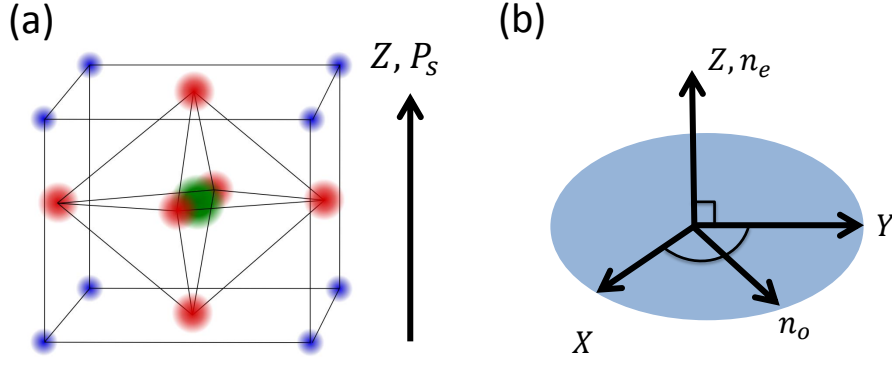


Figure 6.1: (a) Positions of the lithium atoms (blue) and the niobium atoms (green) centred between the oxygen octahedra (red) when lithium niobate is below the Curie temperature. The direction of the spontaneous polarization is along the Z-axis and indicated by the black arrow. (b) The direction of the ordinary and the extraordinary refractive indices with respect to the directions of the three major axes. The X-Y plane is highlighted by the blue ellipsoid.

makes this material particularly interesting is the high spontaneous polarization P_s along the Z (or c) axis, at temperatures below the Curie temperature (T_C). $P_s = 70 \mu\text{C}/\text{cm}^2$ [162, 163], and is generally consistent across different wafers and suppliers. The spontaneous polarization is due a shift in the positions of the Li and Nb atoms which occurs below $T_C = 1483 \text{ K}$ [162]. Above that, the material loses its permanent electromagnetic properties. Congruent lithium niobate is generally cut as a wafer, whose normal is one of the X, Y or Z axes of Fig. 6.1 (b). Following Weis and Gaylord [161], the Z axis is parallel to the direction of the spontaneous polarization. The X axis is perpendicular to a crystal mirror plane and along one equivalent translation vector of the unit cell [162]. A Z-cut wafer has electric polarisation normal to the surface therefore has surface charges.

Lithium niobate is also birefringent. The principal extraordinary index (n_e) is along the same direction as the Z axis. The principal ordinary refractive index (n_o) lies between the X and the Y axes, as depicted by Fig. 6.1 (c) [164]. Using the Sellmeier coefficients of congruent lithium niobate measured in the infrared by Zelmon *et al.* [165], I have computed these indices at 783.73 nm, the wavelength of the ZPL of the DBT molecules [88], using the Sellmeier coefficients from [165], to be $n_e = 2.177$ and $n_o = 2.257$ [166, 167]. The birefringence of the material, defined as $n_e - n_o$, is 0.08.

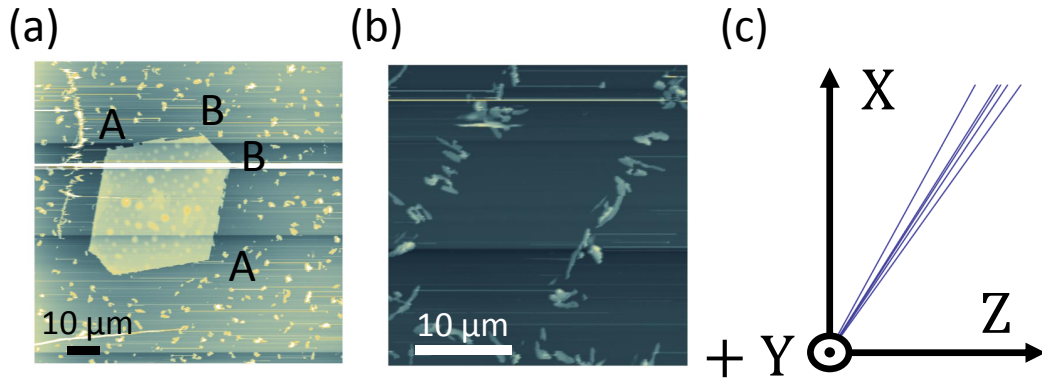


Figure 6.2: (a) Atomic-force microscope image of anthracene crystals on top of a Y-cut substrate grown with the supersaturated vapour method. Among many flat small crystals of only 1-3 μm across a much bigger crystal was formed. This crystal has the particular shape of anthracene described by Major *et al.* [112], with specific angles at vertices A and B. (b) Atomic-force microscope image showing crystals growing preferentially along specific sets of lines. (c) The direction of 5 such drifts of crystals, together with the crystal axes of lithium niobate. These lines are oriented at $\sim 60^\circ$ to the Z axis.

6.2 Anthracene thin films grown on top of lithium niobate

6.2.1 Z-cut

Following the method described in chapter 2, thin films of anthracene were grown on top of X-, Y-, and Z-cuts from optical grade congruent lithium niobate (Conex Systems Technology, Inc.) with parallelism better than 20 arcseconds. Bound surface charges with a density of $\pm 0.7 \times 10^{-3} \text{ C/m}^2$ were expected to be present at the surface of the Z-cut samples [168]. With this cut, I could observe no growth of anthracene crystals on the surface. I previously measured the bonding energy of the anthracene to glass, in section 2.5 to be $\sim 2.6 \text{ meV/\AA}^2$. The fact that anthracene could not deposit on the sample suggests (see Eq. 2.8) that the energy per unit area of the anthracene binding to Z-cut lithium niobate is much lower than $2.6 \text{ meV/\AA}^2$. Hence the chemical potential difference achieved by the temperature gradient along the vial was not sufficient to drive the crystal growth.

6.2.2 X-cut and Y-cut

I was able to grow thin films of anthracene on top of X- and Y-cut wafers. On a Y-cut surface, one particular growth produced huge crystals some tens of microns across, that

exhibited the characteristic shape of anthracene, as shown in Fig. 6.2 (a). These crystals were deposited among other small, flat mesas only 1-3 μm across. Following Major *et al.* [112], one can immediately recognise the vertices A and B, whose angles are expected to be 109.757° and 125.122° , respectively [112]. From these images I measured $110^\circ \pm 4^\circ$ and $126^\circ \pm 4^\circ$ leaving no doubt that these are flat anthracene crystals. When the anthracene is doped with DBT, the molecules orient their optical dipole along the line connecting the A vertices, called the b-axis. Generally the growths did not produce such huge crystals but it was observed that small crystals grew preferentially on quite specific sets of lines. As an example of that one can see the two parallel lines of crystals in the microscope image of Fig. 6.2 (b). On the right of Fig. 6.2 (b), I plot the orientation of the lithium niobate axes (as provided by Prof. Gallo) together with the directions of 5 such drifts of crystals, shown in blue. These lines of growth are oriented at $\sim 60^\circ$ to the Z axis.

Some flat mesas were seen to lie on specific lines also on top of X-cuts. However in these samples a large fraction of the crystals grew perpendicular to the surface, and could be seen edge-on, as in Fig. 2.11 (a)-(c). This type of growth is typical when the binding energy of the anthracene to the surface is not strong enough to achieve 2-dimensional growth. It could well be that the surfaces of the X and Y-cut substrates have different overall binding energies and growth of flat mesas is more favourable on Y-cut samples.

6.3 Measuring the orientation of dibenzoterrylene molecules in anthracene grown on top of lithium niobate

I turn now to a direct measurement of the alignment of DBT molecules in anthracene crystals grown on top of lithium niobate. In particular, given the promising results from the previous section, I focused on the Y-cut substrates. On those samples where growth lines were observed, I left the crystals to evaporate and then grew DBT-doped crystals. The growth method was the same as previously described in chapter 2. As a starting point though, I grew DBT-doped anthracene crystals on top of glass and used the confocal microscope with the 0.9 NA objective and the Ti:Sapphire laser to investigate the dipole orientation.

As expected, I found that molecules within the same crystal were oriented all in a similar direction (presumably the b-axis), but that the crystals themselves had no preferred

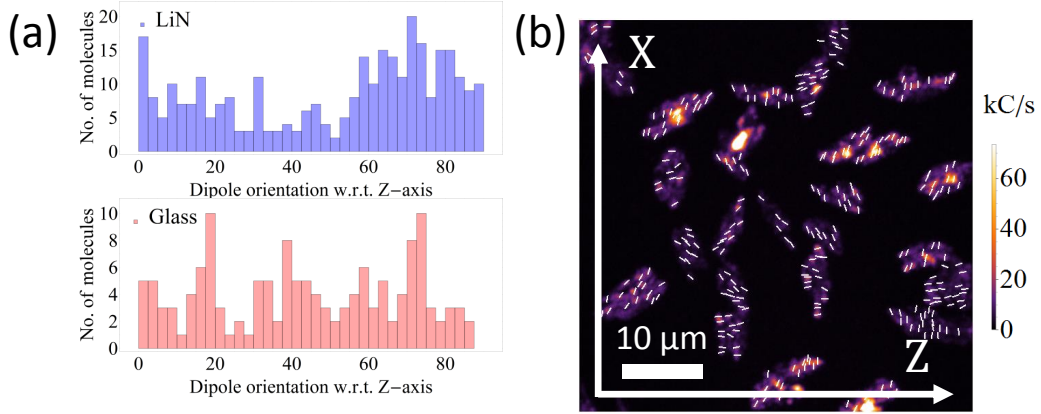


Figure 6.3: (a) Histogram of the orientation of the dipole of DBT molecules embedded in anthracene crystals on top of a Y-cut substrate and glass. In this case the dipole orientation is with respect to the Z axis. There is a flat random distribution of molecules on top of glass but a preferential alignment of molecules on top of lithium niobate. (b) Fluorescence image of single DBT molecules on top of lithium niobate. The white lines show the orientation of the dipoles. For reference, the axes of lithium niobate are also shown.

orientation, as shown by the lower histogram in Fig. 6.3 (a). On repeating the measurement for DBT molecules on top of lithium niobate, I obtained the image in Fig. 6.3 (b), of 315 molecules, which all show relatively good visibility in the emission as function of the polarisation angle of excitation light. In this image the white lines show the measured orientation of the dipole of the DBT molecules, with the white arrows highlighting the Z and X axes of lithium niobate. One has the immediate impression that there are preferred orientations of the molecules, and that impression persists in the upper histogram of Fig. 6.3 (a), where there is a broad peak between 60° and 80° . This crystal growth did not yield obvious lines of crystals, but it is striking that the preferred direction for the DBT molecules (and thus for the b-axis of the anthracene) is quite close to that of the growth lines seen in Fig. 6.2 (b). It seems that the crystals may tend to have their b-axis parallel to the lines of preferred growth.

Before moving on to discuss growth on top of lithium niobate structures and possible waveguide geometries, I will digress to consider what physical mechanisms might align the anthracene on top of lithium niobate. The polarizabilities of the anthracene molecule along each of the three axes have been studied computationally by Hinchliffe *et al.* [169] and agree with the experimental measurements of Cheng *et al.* [170]. Along the long axis of this molecule, the polarizability is $p_L = 238 \text{ a.u.}$, compared to only $p_S = 103 \text{ a.u.}$

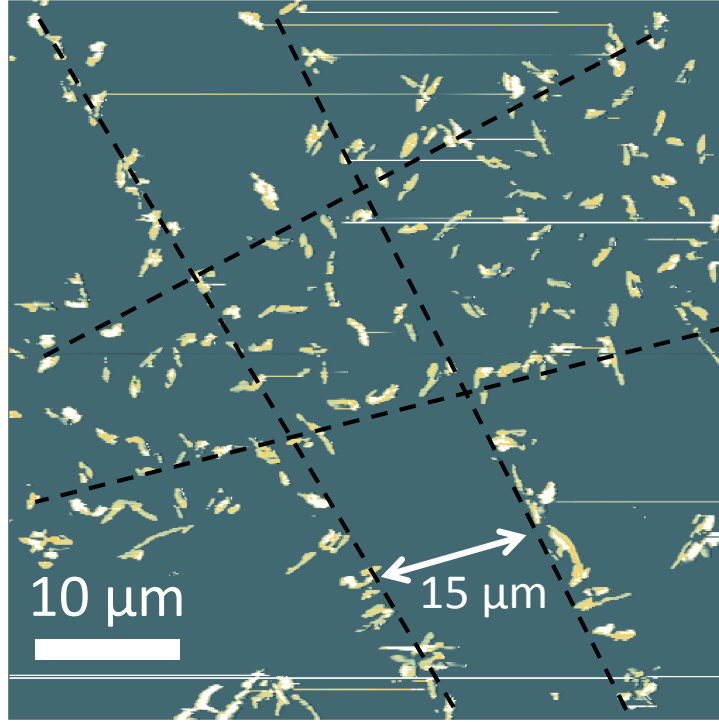


Figure 6.4: Atomic-force microscope image of anthracene crystals grown on top of a Y-cut substrate of lithium niobate. They both show crystals growing on specific lines, highlighted by the dashed black lines, the longest of which are separated by $\sim 15 \mu\text{m}$.

of the short axis. It could be that this difference in polarizability causes a torque when the molecule is exposed to an external electric field. The surface charge on the Y-cut substrates is as big as $\frac{1}{3}$ of the surface charge on the Z-cut substrates [162]. As measured by Jungk *et al.* this charge is $\sigma_Z = 0.7 \times 10^{-3} \text{ C/m}^2$ [168]. Hence the surface charge on the Y-substrate is $\sigma_Y = 0.23 \times 10^{-3} \text{ C/m}^2$. Assuming the sample was an infinite sheet of charge, the electric field would be $E = 1.3 \times 10^7 \text{ V/m}$. The maximum electric potential energy associated with such electric field and molecule's polarizability is

$$U_E = \frac{1}{2} p_L E^2. \quad (6.1)$$

Inserting the numbers leads to an energy $U_E = 2.1 \mu\text{eV}$, which is four orders of magnitude smaller than the thermal energy associated with the molecules being at room temperature (25 meV). It seems therefore unlikely that the anthracene molecules align in a specific direction due to surface charges.

A more plausible reason for the observations presented here is a small angle between

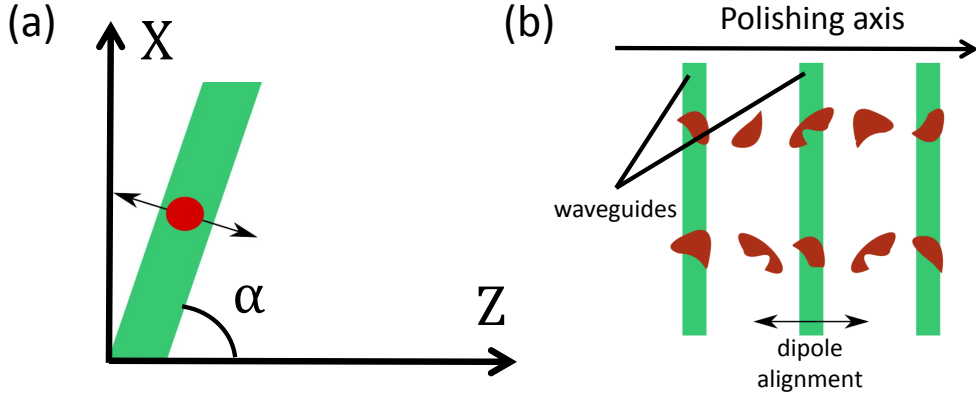


Figure 6.5: (a) Ideal orientation of a lithium niobate waveguide for the coupling of single DBT molecules. The waveguide should be etched out of a Y-cut substrate and be oriented such that the angle between the waveguide and the Z axis is $\alpha \sim 18^\circ$. (b) Anthracene crystals on top of lithium niobate waveguides whose sample was polished at a tilt around the direction shown by the blue arrow. Based on preliminary results, this may cause the anthracene crystals to align the DBT dipoles as shown perpendicular to the waveguides.

the plane of the lithium niobate crystal and the plane of the wafer cut. This could cause a large-scale pattern of terraces on the surface, with a step each time the cut passes through a new plane of the crystal. It is possible that the anthracene crystals aggregate along these steps. This hypothesis is supported by the atomic-force microscope image in Fig. 6.4. One can see two lines of anthracene crystals separated by $\sim 14.7 \mu\text{m}$. According to Conex Systems Technology, Inc., the company that supplied the wafers, the parallelism of the wafers better than 20 arcseconds. The top two layers of the Y-cut surfaces can be separated by a distance of 0.67-2.69 Å. This range is due to different possibilities in the combinations of the top two layers. From these distances, and assuming a cutting angle error of 20 arcseconds, one expects a large-scale spacing of 7-28 μm which might explain the lines of growth shown in Fig. 6.4. Confirmation of this hypothesis would require a more careful investigation with wafers cut at different angles, and that is beyond the scope of this thesis.

6.4 Fabricating lithium niobate waveguides

Having control over the orientation of the anthracene crystals on top of lithium niobate, and therefore the orientation of the dipole of the molecules, it would be possible to fabricate waveguides or photonic structures that would guarantee a high coupling. These structures

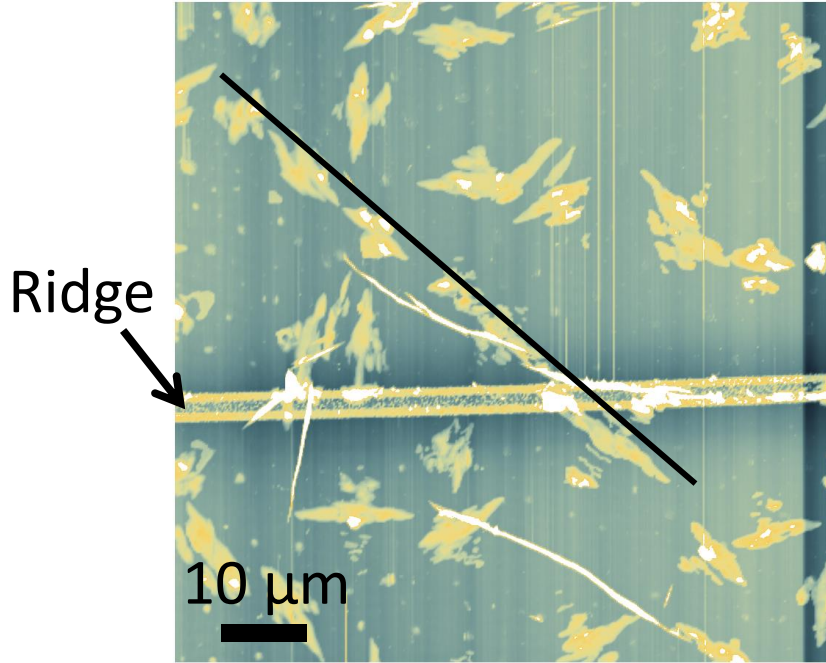


Figure 6.6: Anthracene crystals on top of a ridge structure etched in a Y-cut sample. The ridge structure was 80 nm tall and 3 μm wide. Again, anthracene crystals tend to align $\sim 60^\circ$ with respect to the Z axis as in the previous images.

should be designed to have the dipole of the molecules transverse to the guide. As seen in the previous section, the Y-cut substrates of lithium niobate might be a promising candidate achieving this. The ideal waveguide should be designed as in Fig. 6.5 (a). In the specific case studied here the molecules' dipoles align at $\sim 72^\circ$ to the Z axis. The waveguide should be perpendicular to these dipoles and therefore the etching should be done, according to Fig. 6.5 (a) at an angle $\alpha \sim 18^\circ$. Instead of etching the waveguides at this angle given by the polishing error, it might be better to polish a sample with an intentional rotation around an axis perpendicular to the guides, as shown by the black arrow in Fig. 6.5 (b). This might then create the series of crystals highlighted in Fig. 6.5 (b), with the DBT dipoles perpendicular to the waveguides, giving maximum coupling.

I tested the growth of anthracene crystals on top of a ridge structure etched in a Y-cut substrate of lithium niobate. This structure was 80 nm tall and 3 μm wide and can be seen in just below the middle of Fig. 6.6. Although the background is flat, the top surface is rough with an rms height variation of 57 nm. Since this measurement was

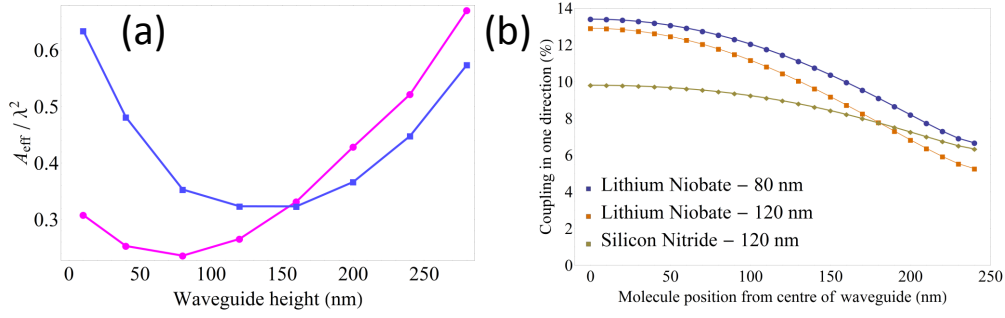


Figure 6.7: (a) Effective area A_{eff} normalised to the wavelength as function of the height of a silicon nitride (blue) and lithium niobate (magenta) waveguide. While for the case of silicon nitride the minimum occurs for a height of 120 nm, for lithium niobate the minimum is at 80 nm. (b) Analytical coupling efficiency in one direction as function of the molecule's position along away from the centre of the waveguide. The coupling was computed using Eq. 1.11 for different waveguides, all 500 nm wide. In blue and orange a waveguide made of a Y-cut lithium niobate, 80 nm and 120 nm tall respectively. In brown a waveguide made of silicon nitride.

taken, improvements in the fabrication process have been made in Prof. Gallo's group. Although the ridge was rough in this measurement, anthracene crystals grew in thin flat mesas. Moreover one can see that the crystals grew along a specific line, highlighted in black. This line lies at roughly the same angles to the Z axis as shown in the previous atomic-force microscope images.

In order to estimate the expected coupling for a waveguide made of lithium niobate, I simulated the behaviour of a molecule 10 nm above a waveguide made by etching a Y-cut wafer using Lumerical FDTD Solutions to calculate the effective mode area and group velocity. The geometry for this simulation is the same as in Fig. 5.1, except the silicon nitride waveguide has been replaced by Y-cut lithium niobate. Given the birefringence of lithium niobate [165, 166, 167], I set $n_x = 2.177$ and $n_y = n_z = 2.257$ (where the axes are the same as in Fig. 5.1). The first thing I checked was for which thickness of the waveguide the evanescent field is maximised at the position of the molecule. In other words, following section 5.2, for which thickness the effective area A_{eff} is minimum. The result is plotted in Fig. 6.7 in magenta and compared with the corresponding result for silicon nitride in blue. It shows that the effective area is minimum for a waveguide 80 nm thick, the same as the ridge structures in Fig. 6.5 (b). The effective area is much smaller than for silicon nitride hence a higher coupling is expected for waveguides etched in lithium niobate. This is because the refractive indices of lithium niobate are higher than for silicon nitride. In

Fig. 6.7 (b) I show the coupling efficiency β calculated for a range of lateral positions of the molecule, always placed 10 nm above the top of the ridge. This was obtained from the numerically calculated mode area and group velocity according to Eq. 1.11. Recall,

$$\beta = \frac{\Gamma_{\text{wg}}}{\Gamma_{\text{rad}}} = \frac{1}{4} \frac{\left(\frac{3\lambda^2}{2\pi n^2}\right) \frac{c}{n}}{A_{\text{eff}} v_g}. \quad (6.2)$$

Blue and orange curves are the results for a waveguide made of a Y-cut lithium niobate, 80 nm and 120 nm tall respectively. In light brown the results for the 120 nm tall silicon nitride waveguide of chapter 5. These results show an increase of the maximum coupling into one direction from $\sim 10\%$ for silicon nitride to $\sim 13\%$ for lithium niobate. Near the centre, the two thicknesses of lithium niobate give almost the same coupling, but a significant difference appears as the molecule is moved further away from the centre. Beyond 250 nm, the molecule is outside the waveguide and this field was not simulated. This plot shows how important depositing the molecules near the maximum of the guided field is, and that is the topic of the next chapter.

Chapter 7

Dibenzoterrylene molecules in silicon nitride slots

7.1 Introduction

In the previous chapter I discussed a possible method to align the molecules in order to achieve good coupling between the optical dipole and the waveguide. In this chapter I tackle the other aspect of good coupling: placing the molecules near the maximum of the guided field. The idea is to put them in a slot cut into the guide [89]. Slots offer the possibility of trapping DBT molecules during the spin coating step of the method described in chapter 2. This could force the molecules to sit in the waveguide rather than aggregating in the trench at its base as in 5.12. Moreover one could position the slot such that the molecules would sit at the maximum of the guided field and therefore achieve a higher coupling than in the evanescent case. A second benefit of this method is that it would not require crystals to sit on top of the guide and this could greatly improve transmission. All of this is discussed in detail in this chapter where I also show preliminary data on the emission of DBT molecules inside nanoslots etched in a silicon nitride wafer.

7.2 Slot waveguides: design

In chapter 5, we saw how spin coated molecules were trapped in the corners of the trenches on either side of the ridge waveguide. In order to avoid this, the new slotted waveguide is constructed as shown in Fig. 7.1. Here, a nanoslot is etched in a silicon nitride waveguide,

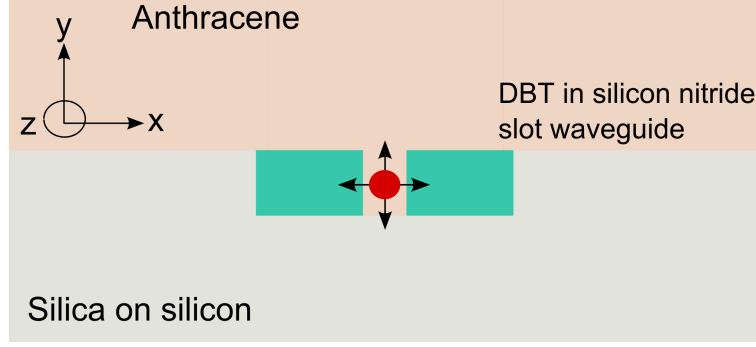


Figure 7.1: Sketch of the slotted silicon nitride waveguide for coupling dye molecules. The nanoslot is etched in a silicon nitride waveguide embedded in silica. A DBT molecule in an anthracene crystal is deposited in the nanoslot.

which is in turn embedded in silica. The waveguide has similar dimensions to the one fabricated in chapter 5, being 500 nm wide with a height of 120 nm. During the spin coating, molecules should enter the nanoslot. An anthracene crystal is then grown in the slot and is intended to take up the molecule. Anthracene also grows on top of the guide. I simulated the coupling of a molecule to the slot waveguide using Lumerical FDTD Solutions. For these simulations, the width of the waveguide was kept constant while the slot cut completely through the guide and was square in the y-z plane (Fig. 7.1). The width of the slot was varied as was the position of the molecule within the slot. The anthracene on top of the waveguide was assumed to be infinitely thick and to have the refractive indices as in Fig. 5.1. The molecule's dipole was taken as perfectly aligned with respect to the guided electric field. First, as shown in Fig. 7.2 (a), I computed the effective area A_{eff} for a molecule in the slot at the position of the maximum of the propagating mode. I found that $A_{eff} \sim 0.15 \lambda^2$, less than half of the effective area in case of ridge waveguides ($\sim 0.32 \lambda^2$). A very weak minimum of the effective area occurs for a square with a width of 90 nm, but a slot of this size perturbs the propagating mode significantly. I therefore investigated the coupling of a molecule inside a smaller slot only 50 nm wide, using Eq. 1.11, with the group velocity being calculated using Lumerical FDTD Solutions. Fig. 7.2 shows the coupling as a function of the molecule's position with respect to the centre of the slot. The asymmetry in the vertical direction is to be expected because the SiO_2 at the bottom has a refractive index of 1.45 while at the top there is anthracene with a much higher refractive index. The maximum coupling is 20.3% in each direction, which is twice as much as the coupling one could achieve with a molecule on top of a ridge

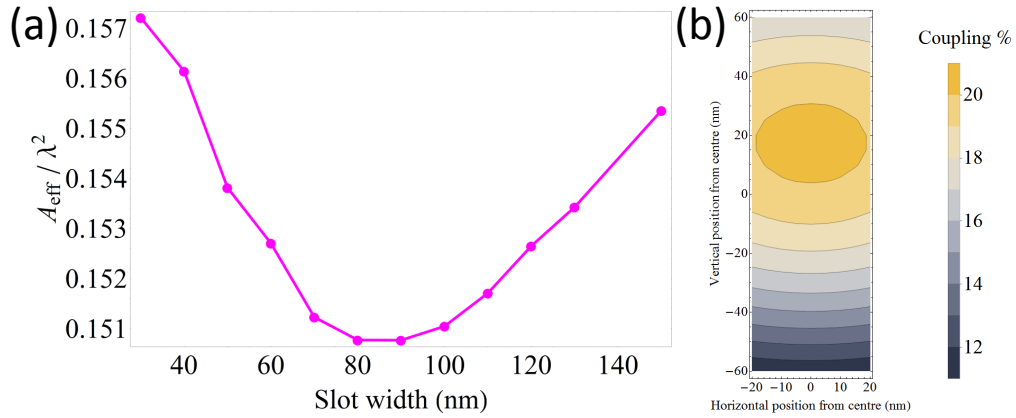


Figure 7.2: (a) Effective area A_{eff} normalised to the wavelength as function of the side length of the slot. A weak minimum appears for a slot whose side is 90 nm. (b) Coupling efficiency as function of the molecule’s position inside a 50×50 nm slot. The slot was 120 nm deep, as much as the waveguide in Fig. 7.1.

waveguide. The main reason for this is that the field is enhanced by the square of the ratio of the permittivities of the waveguide and the slot [171]. In order to achieve this excellent coupling, the molecule has to be placed ~ 75 nm from the bottom of the slot. The DBT molecules are initially spin coated onto the guide, and although they do become incorporated into the anthracene, we do not expect them to move far inside. Therefore, to achieve maximum coupling, it may be preferable to etch the slot less deep. A study of that is now in progress.

7.3 Slot waveguides: preliminary experiments

7.3.1 Anthracene crystal in a slot

Slots were etched by e-beam lithography at the University of York in collaboration with Prof. Krauss and Dr. Reardon. The silica wafer had a ~ 150 nm thick layer of silicon nitride, in which slots of various height and width were made, spaced by a distance which allowed them to be resolved using the confocal microscope. In chapter 2, I showed that the anthracene flat-mesa crystals sublime from their sides, not from the top. After growing a thin film of anthracene on top of the slot sample with the method from chapter 2, I let the crystals sublime in the hope only the anthracene in the slots would remain. Fig. 7.3 (a) shows four atomic force microscope images taken ~ 30 minutes apart. After ~ 80 minutes, crystals on the top have mostly sublimed to reveal the slots. Fig. 7.3 (b) magnifies the

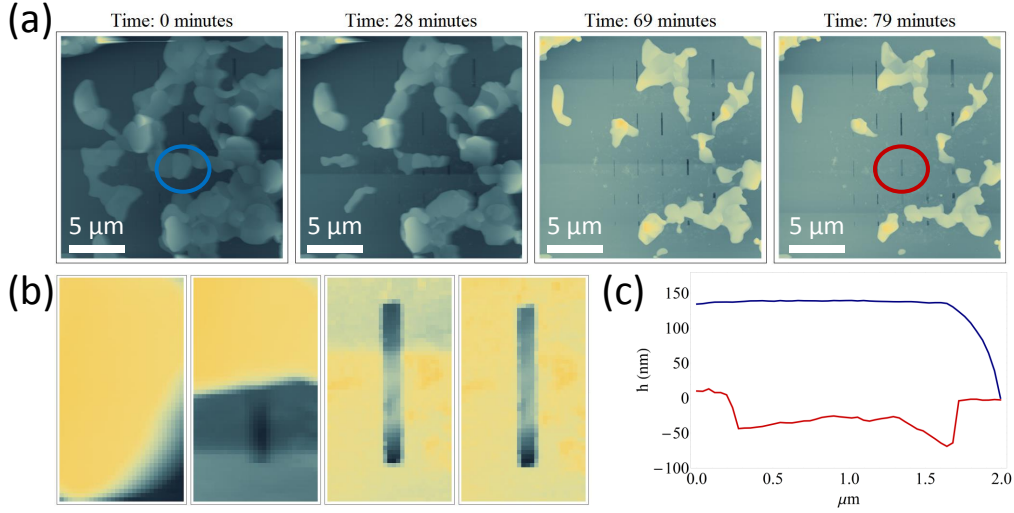


Figure 7.3: (a) Atomic force microscope image of anthracene crystals on top of the slot test-sample. The first three images were taken after ~ 30 minutes from one another to allow the crystals to evaporate. The last two images show the presence of anthracene in the slots with the crystals around them mostly evaporated. This is shown better in (b), which is a zoom-in of the 186 nm-wide slot highlighted in the last image in (a). Here, after 70 minutes, the crystal has evaporated leaving only the anthracene inside the slot. (c) Section through the centre of (b) along the vertical direction at time 0 (blue) and after ~ 79 minutes (red).

four images in (a) to zoom in on the slot highlighted by blue and red circles in (a). The third and fourth images in (b) have a clearly different height from the background level, but we see at once that they are not empty because the false-colour mapping exhibits a variation along the slot. This is seen more directly in Fig. 7.3 (c) which plots the height profile along the centre of the slot at zero time (blue) and after 79 minutes (red). The red curve shows that the anthracene has sunk below the background level, but only by ~ 50 nm. By contrast, the crystals that have sublimed away were initially ~ 150 nm thick. This suggests that the binding of the anthracene to the sides of the slots forced it to evaporate at a slower rate. This particular slot was 1500 nm long and 186 nm wide (as measured by scanning electron microscope at the University of York). These dimensions are bigger than the ones used in the simulations but still allow for a much higher coupling than in the evanescent case.

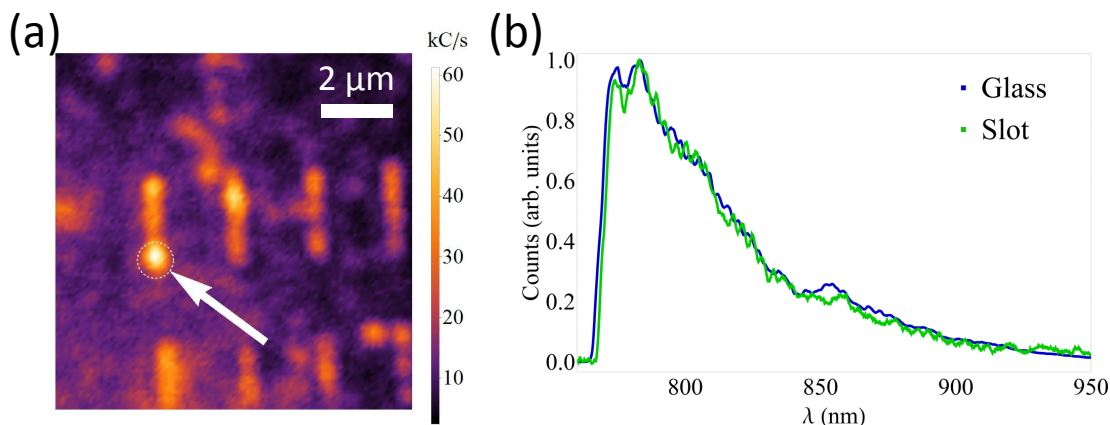


Figure 7.4: (a) Confocal images of a series of slots filled with DBT molecules excited at 780 nm in anthracene crystals. The molecules indicated by the arrow were deposited in the 279 nm-wide slot. Their fluorescent spectrum (measured when using the 755 nm pulsed laser) is shown in (b). Here a fluorescence spectrum of molecules on top of glass is also displayed for comparison. The small mismatch is due to different tilt angles of the long-pass filter during the two different measurements. There is no doubt that these molecules inside the slots were DBT.

7.3.2 Dibenzoterrylene molecules in a slot

Having proven that anthracene can grow inside a slot, I then turned to look at whether DBT molecules can be inserted inside the anthracene. To test that, I grew DBT-doped anthracene crystals on the slot sample. I used a dropper to deposit on the surface 20 μ l of the 1 mMol solution of DBT molecules in toluene, diluted with diethyl ether at a ratio of 1:100 (volume). This higher concentration and the fact that the solution was not spun increased the probability of introducing DBT molecules into the slots. Once the diethyl ether and toluene evaporated, I overcoated the sample with anthracene then allowed the anthracene on top to evaporate before capping the sample with PVA in order to prevent further evaporation. The sample was then placed in the confocal microscope and the molecules were imaged using the 0.9 NA air objective. Fig. 7.4 (a) is a confocal image of the fluorescing molecules taken using the Toptica 780 nm cw laser, which appear as bright features in the slots. To prove that this fluorescence was due to DBT molecules in anthracene and not to other impurities or defects, I measured its optical properties. Fig. 7.4 (b) shows the dispersed fluorescence spectrum of the bright spot highlighted by the arrow in Fig. 7.4 (a). For this measurement I used the 755 nm pulsed laser to excite the molecules and collect their fluorescence above 770 nm using a long-pass filter. This

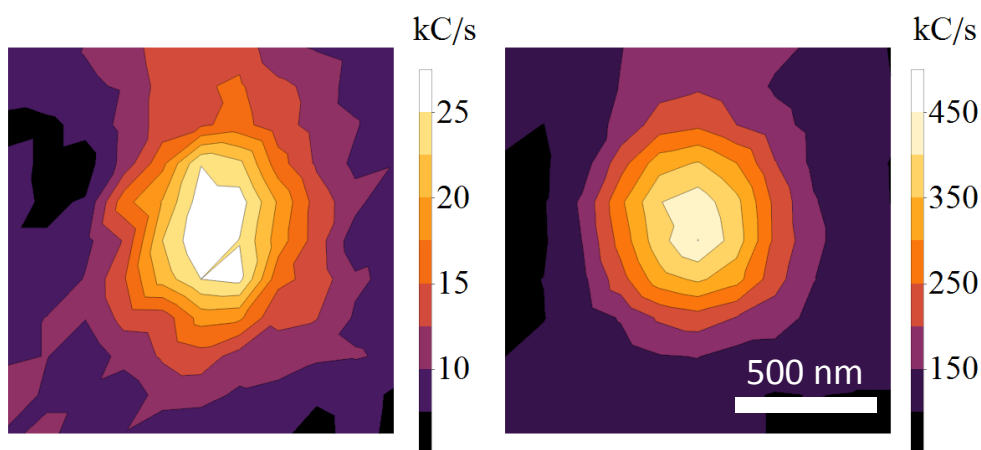


Figure 7.5: Confocal images of DBT molecules inside a nanoslot. On the left, the 780 nm CW laser was scanned across the sample at an intensity of $\sim 4.88 \text{ kW/cm}^2$, while on the right of $\sim 113.15 \text{ kW/cm}^2$. As the intensity increases, more photons are being scattered by the molecules.

fluorescence was sent to grating 1 of the spectrometer (see chapter 3). The spectrum of molecules in the slots is shown in green and it perfectly matches the spectrum of DBT molecules on glass (blue), already presented in chapter 4. The two spectra have a peak at $\sim 383.9 \text{ THz}$ ($\sim 781 \text{ nm}$) and are very well matched throughout the broad red-detuned fluorescence indicating that the molecules inside the slots are indeed DBT molecules in anthracene.

Looking at 20 such bright spots, I used time-correlated single photon counting to measure the lifetime of DBT molecules inside the slots, with a mean of 3.3 ns and a standard deviation of 0.2 ns. This lifetime is marginally shorter than the 3.7 ns mean lifetime of DBT on top of glass (chapter 4), presumably because of the difference between the two nanoenvironments. Fig. 7.5 shows one such spot, which has been scanned at 780 nm using cw excitation light of two different intensities: 4.88 kW/cm^2 on the left and 113.15 kW/cm^2 on the right. The size of the spot is just half the excitation laser (I measure 535 nm FWHM), so the fluorescing molecules are confined to a region that is small on that scale. This fluorescence did not exhibit a $g^2(0)$ dip, so I consider that the source is made up of several DBT molecules in a small region.

In Fig. 7.6 I plot the count rate of scans at 13 different peak excitation intensities, each scan being integrated over a 540-nm square region, by adding the pixels. In the object

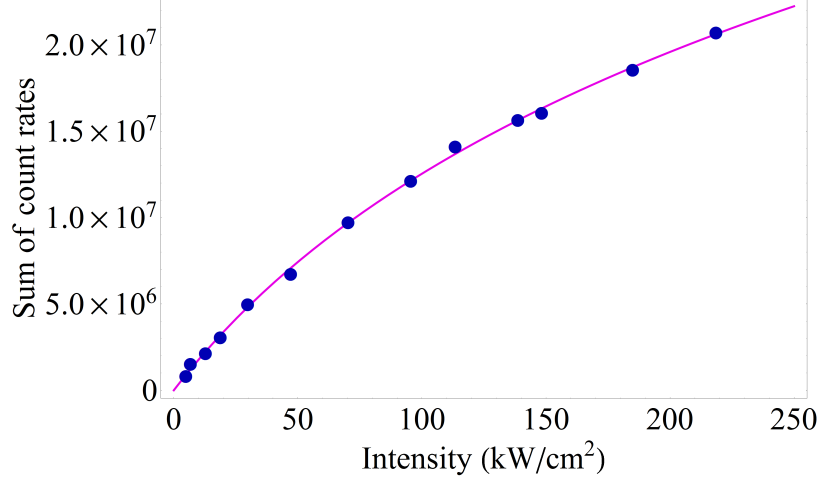


Figure 7.6: Blue dots: sum of the detected photons per second scattered by a bright spot when the laser was scanned over a 540 nm square region around it. The experimental data was gathered for various excitation intensities, showing a saturation intensity of $I_{\text{sat}} = 88.1 \pm 6.6 \text{ kW/cm}^2$. Magenta solid line: fit according to Eq. 7.2.

plane each pixel is a 135 nm square. In order to determine a saturation intensity from this plot, I note that at each pixel of Fig. 7.5, the detected count rate is proportional to the scattering rate of the molecule. This is $R_{\text{max}} \frac{I(r)/I_{\text{sat}}}{1+I(r)/I_{\text{sat}}}$, where R_{max} is the limiting rate at high intensities, I is the laser intensity at the molecule, r is the displacement of the laser beam centre from the molecule and I_{sat} is the saturation intensity. $I(r)$ is given by the 3D gaussian

$$I(r) = I_0 e^{-\frac{r^2}{2\sigma^2}}. \quad (7.1)$$

The sum of pixels (each with an area ΔA over one bright spot is well approximated by the integral

$$R = \frac{1}{\Delta A} R_{\text{max}} \int_0^\infty 2\pi r \frac{I_0 e^{-\frac{r^2}{2\sigma^2}}}{I_0 e^{-\frac{r^2}{2\sigma^2}} + I_{\text{sat}}} dr = \propto \ln \left(\frac{I_{\text{sat}} + I_0}{I_{\text{sat}}} \right). \quad (7.2)$$

This equation was used to fit the curve in Fig. 7.6, with the result that $I_{\text{sat}} = 88.1 \pm 6.6 \text{ kW/cm}^2$. I repeated the measurement for a total of 30 bright spots inside 14 different slots of various lengths. The average of these gives $I_{\text{sat}} = 96.2 \text{ kW/cm}^2$ and there is a standard deviation of 21 kW/cm^2 as a result of variation between one bright spot to another. This I_{sat} is about 10% higher than the measured in chapter 4 for a single DBT

molecule above a glass substrate, perhaps corresponding to the 10% shorter lifetime we observe. The bright spot in the slots is clearly due to DBT molecules and the fact that they exhibit excellent photostability, leaves us no doubt that the molecules are properly incorporated into the anthracene. The smallest slot with DBT molecules was 104 nm wide. This is very promising for the photon source as we have calculated that such a slot gives more than 20% coupling in each direction. A narrower slot would be even better in order to avoid reflection of the propagating mode from the slot. This scheme also looks better than evanescent coupling from the perspective of loss because the high losses due to the presence of the anthracene crystals could be overcome by letting them evaporate hence avoiding transmission losses as in Fig. 5.22 (b).

Chapter 8

Summary and Outlook

8.1 Summary

The aim of this thesis was to show (i) that a DBT molecule in an anthracene matrix is an excellent candidate to be a bright and stable source of single photons and (ii) that it could be integrated into a photonic device, to deliver the photons to a waveguide, as proposed in [89].

To serve this purpose, we needed to develop a method for producing thin crystals of anthracene with a controlled concentration of dopant DBT molecules. Crystals grown by the commonly-known co-sublimation method proved too thick for coupling. Crystals I made by spin coating replicated the thickness reported by Toninelli et al. [85]. The silicon nitride photonic waveguides were however not amenable to spin coating because they had ridges. I therefore developed a novel crystal growing method which relies on the formation of anthracene crystals in two dimensions from a supersaturated vapour. With this method I produced extremely flat, DBT-doped crystals with very sharp edges. By adjusting the growth time, I could control the thickness between 40 and 140 nm. This method consists of depositing a solution of DBT molecules in toluene and diethyl ether on a substrate and subsequently over coating them with the anthracene. Finally the crystals are protected against sublimation by a thin film of polyvinyl alcohol. I measured that unprotected crystals evaporate within a few hours at room temperature while protected ones last for months (at least). I observed that crystals evaporate mainly from the sides instead of from the top. By comparing the rate of evaporation with measured values of the

vapour pressure I was able to make an estimate of the sticking probability for anthracene during the crystal growth.

I built a confocal microscope to image and characterise the fluorescence emission from the DBT molecules. By imaging the fluorescence from DBT molecules in the anthracene crystals I was able to determine the alignment of the transition dipole relative to the crystal axes. The photostability of the molecules, together with their alignment, indicated that they had moved inside the anthracene during the growth and replaced three anthracene molecules along the b axis. I measured the lifetime of DBT molecules on top of glass and for the first time I determined their saturation intensity of $\sim 75 \text{ kW/cm}^2$ incident on the surface of the anthracene. I proved that the new growth method could control the concentration of the DBT molecules down to 0.4 molecules per square micron. I measured the degree of second order coherence, $g^{(2)}(\tau)$ both under pulsed excitation and continuous wave. In the continuous wave case I observed a narrowing of the dip of $g^{(2)}(\tau)$ for high intensities. Both the correlation measurements and the saturation intensities are explained by solving the rate equations with a combination of resonant and blue pumping. The stability of the fluorescence emission was proved by continuously exciting them and finding that even in a thin crystal, a large fraction of the emitters can be excited more than 10^{12} times at saturation without photo-bleaching. I also measured the lifetime of the triplet state to be $42.6 \pm 4.2 \mu\text{s}$, which was previously an uncertain quantity.

In order to test the coupling between DBT molecules and a waveguide, I changed the microscope to have a longer working distance and added optics to couple into the waveguide. I also changed the way the DBT was introduced to the chip from spin coating to spray coating in order to avoid having molecules collecting in corners of the waveguide structure. Initially I used the silicon nitride ridge waveguides, built following the design proposed by Hwang and Hinds [89], as a proof of concept for the coupling of photons from dye molecules to photonic structures. The coupling was tested by scanning the laser across the waveguide while monitoring the output at its facet. I found that these waveguides had high losses of up to 15 dB/cm, probably due to the strong evanescent fields. With such high losses, the coupling of single photons from a single molecule could not be detected through the waveguide, but I was able to see ~ 200 molecules coupling. After estimating this number and determining the orientation of their transition dipoles and their lifetime I found the mean coupling efficiency. This did not match the coupling efficiency estimated

using Lumerical FDTD solutions even after taking into account the additional propagation losses due to anthracene crystals on top of the guide. That discrepancy remains to be understood.

One limitation still to be addressed is the random orientation of the anthracene crystals with respect to the waveguide structure. This could possibly be overcome by using a substrate that aligns the anthracene crystals. Our first attempt in this direction was to grow anthracene on a lithium niobate surface. Crystals did not grow on Z-cut lithium niobate substrates, but on top of X-cuts and Y-cuts they were observed to grow along a specific direction. The origin of this effect is a topic for further study, but we propose that it may be related to terraces formed by cutting the lithium niobate at a small angle with respect to the crystal planes. A key area for improvement is the propagation loss that comes with having a large evanescent field at the surface of the waveguide, which scatter from impurities or contaminants. This problem can be solved by inserting a narrow slot into the ridge and growing the DBT-doped crystal inside the slot.

In the last chapter I proposed a design for such a slot waveguide and showed that anthracene and DBT can be inserted into the slots.

8.2 Outlook

8.2.1 Proposal for a good photonic structure for coupling to DBT molecules

Using the results from the last two chapters I propose a new photonic structure using a lithium niobate waveguide to collect photons from a single DBT molecule. The geometry is illustrated in Fig. 8.1 (a). A small slot is etched into the waveguide, so that a single molecule can sit at the maximum of the guided field. The waveguide has a height of 250 nm and a width of 600 nm and sits on top of a 1 μm -thick layer of silica on silicon. The dimensions of the waveguide were chosen in order to have good single-mode confinement together with little evanescent field which would otherwise cause high propagation losses. The waveguide is surrounded by a layer of Poly(methyl methacrylate) (PMMA) that covers up the corners outside the base of the ridge. This is necessary if we are to use spin coating because otherwise, as shown in Fig. 5.12, molecules aggregate in the corners. The nano-slot can be etched in the PMMA layer as well as the lithium niobate, by means of wet etching for the PMMA and reactive ion etching or UV etching for the lithium niobate.

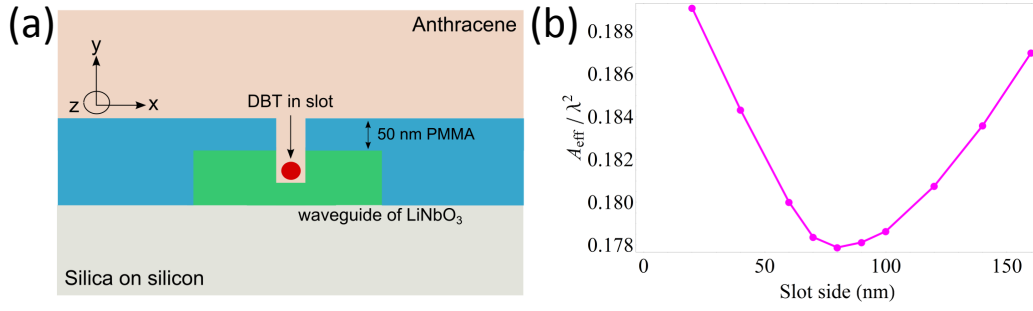


Figure 8.1: (a) An optimised photonic structure to couple single photons from DBT molecules to a waveguide. A lithium niobate slot is etched in a waveguide 600 nm wide and 250 nm high. This sits on top of silica and is surrounded by a thin layer of PMMA to facilitate the molecules' deposition. An infinitely thick layer of anthracene embeds the whole structure. (b) Effective area A_{eff} normalised to the wavelength as function of the side of the slot. A minimum appears for a square slot with a width of 80 nm.

The bottom of the slot would lie ~ 125 -150 nm above the silica so that DBT falling into the bottom of the slot will sit close to the maximum of the guided mode, thereby having maximum coupling. As in chapter 7, I used Lumerical FDTD Solutions to vary the slot size and minimise the effective mode cross section A_{eff} for a molecule at the centre of the slot, 5 nm above its bottom. As shown in Fig. 8.1 (b), the effective area is minimum for a square slot with a side of ~ 80 nm in length. For such a slot one can achieve a coupling efficiency in one direction of 21.13%. Although this is no better than we calculated for the silicon nitride slot in chapter 7, lithium niobate is a promising alternative for silicon nitride and recent progress in Prof. Gallo's fabrication methods could allow us a fast production of waveguides with a high degree of precision.

I propose to double the number of photons coupled into one direction by constructing a Bragg reflector at one end of the trench, as illustrated in Fig. 8.2. The Bragg period for the DBT (free space) wavelength of $\lambda = 783.73$ is ~ 211 nm. Following Wang [172, 173, 174], for a stepwise effective index as in Fig. 8.2, the grating bandwidth is

$$\Delta\lambda = \frac{\lambda^2}{\pi n_g} \sqrt{\kappa^2 + \left(\frac{\pi}{L}\right)^2} \quad (8.1)$$

where L is the total length of the grating, n_g the group index and κ the coupling between the forward and backwards propagating mode per unit length. This coupling denotes the

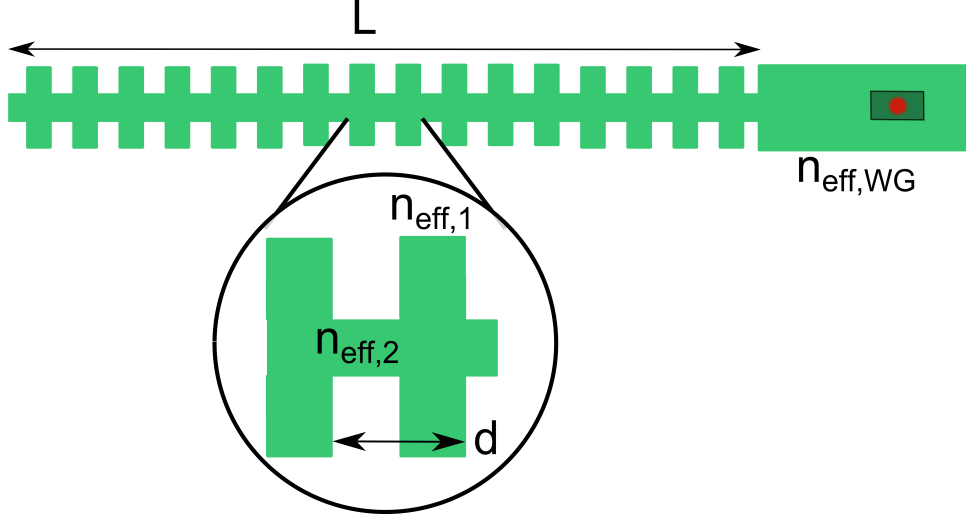


Figure 8.2: A slot waveguide with a Bragg grating on one side in order to reflect the molecule's emission and deliver a high yield of photons in one direction of the waveguide. A Bragg grating is a periodic variation of the effective refractive index of the waveguide. Here the variation is achieved by periodically varying the width of the waveguide over a period d .

strength of the grating, and is proportional to the reflection at each interface,

$$\kappa = \frac{2(n_{eff,1} - n_{eff,2})}{\lambda_B}, \quad (8.2)$$

where $n_{eff,1}$ and $n_{eff,2}$ are the two effective refractive indices as highlighted in Fig. 8.2. Using Lumerical MODE solutions I varied the widths of the two regions of the Bragg grating to maximise κ and found a maximum for widths of 800 and 340 nm, for which $n_{eff,1} \sim 1.89$ and $n_{eff,2} = 1.67$. Taking 45 such periods, Eq. 8.1 gives a bandwidth of ~ 53 nm. This is almost as broad as the molecules' emission, as shown in section 4.3 in Fig. 4.1. Hence, with such geometry, the majority of the molecules' emission is reflected with unity yield and one can achieve a coupling in one direction estimated to be more than 40%.

8.2.2 Will the molecules be stable at cryogenic temperatures?

A question which remains unanswered is whether the DBT molecules in the slot will be photo-stable at low temperature. In co-sublimated thick crystals, DBT molecules show an extremely stable central emission frequency with very little spectral diffusion [80, 88]. However this might not be the case in the slot where the crystal is very thin.

Gmeiner *et al.* studied the effect of thickness on photostability for the case of DBATT molecules in naphthalene [175]. The group used melt growth to fill nanochannels of known depth by capillary forces. They observed that although 60% of the molecules showed a lifetime-limited linewidth at 1.5 K in nanochannels 730 nm deep, fewer than 10% had a narrow linewidth in channels with depths ranging between 60-135 nm. Such behaviour is due to strains induced in the crystal and the vicinity of the boundaries. If that were true for DBT in the slot, only a small fraction of molecules could be used for applications in quantum information, where lifetime limited linewidths are required. This needs to be tested by experiment.

Photostability also requires the molecules to be well-inserted into the organic matrix. We believe this is true for DBT in anthracene because of their well-defined polarisation with respect to the b-axis of the anthracene. We observe a slightly bigger spread in the orientation distribution compared to the result of Nicolet *et al.*[81], but, if necessary, that can be improved by having the crystals undergo cycles of annealing (cycles of heating and cooling the crystals). Simulated annealing showed that DBT molecules would end up sitting in a very stable configuration with their transition dipole moment oriented along the b-axis [84]. Recently, co-sublimated DBT-doped anthracene crystals were mounted in a closed-cycle cryostation at 4 K by our group and the molecules showed narrow linewidths [88]. In the near future the thin crystals will also be placed in the same setup and the DBT linewidths will be studied. If a broad spectrum is measured, the crystals could be annealed in cycles until a lifetime-limited molecule is found. In case annealing does not produce lifetime-limited molecular linewidths one can think about changing the host matrix. A new host for DBT, para-Dichlorobenzene (pDCB), was recently studied by Verhart *et al.* [78]. In this matrix, DBT molecules showed near-infrared emission at 744.34 nm with very narrow lifetime-limited linewidths of ~ 30 MHz at cryogenic temperatures. This host is a promising alternative to anthracene since it has a much lower melting point, 53°C compared to 217°C. When exposed to this lower temperature, photonic structures do not get damaged. One could use this to fill nanoslot waveguides by capillary forces with a melting growth method similar to the one used for DBATT in naphthalene. Molecules in these crystals have a high probability to be well-inserted in the matrix, and therefore show lifetime-limited emission.

Because of their well-defined polarization though, even the single photons generated at

room temperature by a single DBT molecule are useful. One can easily encode information in their well-defined polarization degree of freedom and once coupled to a fibre or a waveguide they can be excellent carriers of quantum information for quantum communication applications.

In summary, this thesis research has made a very encouraging first investigation into the use of DBT in anthracene as an integrated source of photons on demand. In particular the DBT is well incorporated into the anthracene above glass and lithium niobate substrates, and exhibits extremely good photostability in thick samples. Waveguide loss argues against evanescent coupling to molecules on the surface, but the use of a slot in the guide offers a promising alternative and we have already seen that the molecules can be inserted into a slot. Our initial choice of silicon nitride did not yield well-polarised molecules, so we will pursue lithium niobate next. While there remains an uncertainty about the low temperature performance, we have every reason for optimism on the basis of the low temperature data taken with thick samples, and we expect that the next thesis from this group will demonstrate a working, integrated single-photon source.

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Appendices

A. Derivation of the spontaneous emission rate of a two-level molecule in the vicinity of a waveguide

In this first appendix I will explicitly and fully derive the spontaneous emission rate of a molecule in the vicinity of a waveguide to then arrive at the coupling result in Eq. 1.11.

Before considering the case of a molecule radiating in the presence of a waveguide, let us consider what happens when the molecule emitting light when inside a homogenous and transparent dielectric medium. This is the simple case of a DBT molecule emitting inside bulk anthracene. The expression for the spontaneous emission rate of a molecule with transition dipole matrix element $\vec{d}$ into the transverse electric field mode i based on first order perturbation theory (Fermi's golden rule) is [91, 92]

$$\Gamma_{\text{rad}} = \frac{2\pi}{\hbar^2} \sum_i [dE_i(r_0) \cos(\theta)]^2 D_i(\omega). \quad (3)$$

In this equation, d is the magnitude of the dipole transition matrix element $\vec{d}$, $E_i(r_0)$ the magnitude of the vacuum electric field at the position of the molecule r_0 and θ the angle between the two. In Eq. 3, $D_i(\omega)$ is the density of modes having transverse mode i . Eq. 3 can be expressed it in terms of the coupling, g_i , to the i^{th} electric field mode. Mathematically the coupling can be written as

$$g_i = \frac{1}{\hbar} |dE_i(r_0) \cos(\theta)|. \quad (4)$$

Hence Fermi's golden rule becomes

$$\Gamma_{\text{rad}} = 2\pi \sum_i g_i^2 D_i. \quad (5)$$

In order to calculate the coupling g_i , let us consider a travelling field of one mode and polarization x [176, 177, 145], and restrict our analysis to a box of length L much longer than the wavelength of the light. The field can be written as

$$E_{x,i} = i\sqrt{\frac{\hbar\omega}{2\epsilon_r\epsilon_0 L^3}} \left(\hat{a}e^{ik_x x} - \hat{a}^\dagger e^{-ik_x x} \right) \quad (6)$$

Here I assumed that the dielectric material is homogeneous with relative permittivity ϵ_r .

The coupling for this particular polarization is then [89]

$$g_x = \frac{1}{\hbar} \sqrt{\frac{\hbar\omega}{2\epsilon_r\epsilon_0 L^3}} d_x = \sqrt{\frac{d_x^2 \omega}{2\hbar\epsilon_r\epsilon_0 L^3}}, \quad (7)$$

where d_x is the component of the transverse matrix element parallel to the polarization x . We are left to calculate the mode density $D_i(\omega)$. Let us consider first the density of modes in one direction and then expand our theory for the 3D case. Over the length L , the electric field acquires a phase kL . Because of periodic boundary conditions, the spacing between the modes is constant:

$$\partial k = \frac{2\pi}{L}. \quad (8)$$

The number of modes per unit wavevector is then

$$dN = \frac{L}{2\pi} dk. \quad (9)$$

When considering three dimensions, the density of states simply becomes

$$dN = \frac{L^3}{8\pi^3} d^3k. \quad (10)$$

Each wavevector supports two transverse polarizations. Using spherical coordinates, one can simplify $d^3k = 4\pi k^2 dk$. Substituting these results in Eq. 10 leads to

$$dN = 2 \frac{L^3}{8\pi^3} 4\pi k^2 dk = \frac{L^3}{\pi^2} k^2 dk. \quad (11)$$

In a homogenous dielectric, the group and phase velocities are the same and $dk = \frac{n}{c} d\omega$, with n being the refractive index. Hence the mode density in terms of frequency is:

$$D_i(\omega) = \frac{dN}{d\omega} = \frac{L^3 \omega^2 n^3}{\pi^2 c^3}, \quad (12)$$

For the mode density in one polarization x , given that all polarizations are equally probable, one only needs an extra factor of $1/3$:

$$D_{x,i}(\omega) = \frac{dN_x}{d\omega} = \frac{L^3 \omega^2 n^3}{3\pi^2 c^3}, \quad (13)$$

Putting this and Eq. 7 together, we can derive the expression for the spontaneous rate of emission of a molecule inside a dielectric

$$\Gamma_{x,\mathbf{rad}} = \frac{n^3}{\epsilon_r} \frac{d_x^2 \omega^3}{3\pi\hbar\epsilon_0 c^3}, \quad (14)$$

Or summing over all the three polarisations [89]

$$\Gamma_{\mathbf{rad}} = n \frac{d^2 \omega^3}{3\pi\hbar\epsilon_0 c^3} = n\Gamma_0. \quad (15)$$

In the last step, $\epsilon_r = n^2$ and $d^2 = d_x^2 + d_y^2 + d_z^2$. As pointed out by many authors in the literature, one has to correct Eq. 15 taking into account an extra factor due to local field effects [93]. Let us take $\Gamma_{rad} = n\Gamma_0 f(n)$, where $f(n)$ is the correction factor. Here I consider the correction factor generally used for impurities, such as molecules, in non-absorbing dielectric media [94, 95]. Such Lorentz local-field approach leads to a correction factor equal to [94, 95, 96, 97]:

$$f(n) = \left(\frac{n^2 + 2}{3} \right)^2 \quad (16)$$

Hence

$$\Gamma_{\mathbf{rad}} = n \frac{d^2 \omega^3}{3\pi\hbar\epsilon_0 c^3} \left(\frac{n^2 + 2}{3} \right)^2. \quad (17)$$

Now let us consider what happens when the molecule, still inside the same dielectric material, is placed in the vicinity of a waveguide. This is the case of a DBT molecule inside an anthracene crystal on top of a waveguide. The photonic structure alters the local density of states and part of the molecule's radiation is coupled to the guided mode. Similarly to the derivation above, one can use Fermi's golden rule to compute the rate of spontaneous emission of an atom or a molecule into a nearby waveguide:

$$\Gamma_{\mathbf{wg}} = \frac{2\pi}{\hbar^2} \sum_i [dE_i(r_0) \cos(\theta)]^2 D_i(\omega). \quad (18)$$

In this case though, $dk = \frac{1}{v_g} d\omega$, with v_g being the group velocity. This is the speed at which the envelope of the electric field propagates. The longitudinal mode density in one direction just follows:

$$D_{x,i}(\omega) = \frac{dN_x}{d\omega} = \frac{L}{2\pi v_g}. \quad (19)$$

For a mode i , the electric field is

$$E_i = i\sqrt{\frac{\hbar\omega}{2\epsilon_r\epsilon_0 LA_{eff}}} \left(\hat{a}e^{i\vec{k}\cdot\vec{r}} - \hat{a}^\dagger e^{-i\vec{k}\cdot\vec{r}} \right), \quad (20)$$

with A_{eff} being the effective area of the mode, defined as [89, 90]

$$A_{eff} = \frac{\int \int \epsilon_r(r) \epsilon_0 E_i^2(r) dA}{\epsilon_r(r_0) \epsilon_0 E_i^2(r_0)} \quad (21)$$

Combining all of the equations above, and again noting that only the transition matrix element d_x of the molecule couples to the i^{th} mode with x polarisation,

$$\Gamma_{\mathbf{wg}} = \frac{d_x^2 \omega}{2\hbar n^2 \epsilon_0 A_{eff} v_g} \left(\frac{n^2 + 2}{3} \right)^2. \quad (22)$$

The factor of $\left(\frac{n^2+2}{3}\right)^2$ is again the local-field correction [91]. We can now define the coupling of the molecules to the waveguide as the ratio between the rate of radiation of a molecule to the waveguide, Eq. 22, and the rate of radiation to its surrounding dielectric medium, Eq. 17. The coupling is generally denoted by β :

$$\beta = \frac{\Gamma_{\mathbf{wg}}}{\Gamma_{\mathbf{rad}}} = \frac{1}{4} \frac{\left(\frac{3\lambda^2}{2\pi n^2}\right) \frac{c}{n}}{A_{eff} v_g}. \quad (23)$$

In the last step I assumed that the molecule only aligns with one axis of the dielectric material, such that $d = d_x$. Note that $\frac{3\lambda^2}{2\pi n^2}$ is the the optical cross section for the ZPL transition of the DBT molecule inside a crystal of refractive index n .

B. Derivation of the chemical potential difference required for growth of anthracene crystals

In this Appendix I will follow section 4 of [127] to arrive at the chemical potential difference in Eq. 2.8.

Let us first consider the change in free energy ΔG during a 3-dimensional nucleation of a crystal from a vapour. In the growth process I could in fact observe that crystals

form from the anthracene vapour. Mathematically, ΔG can be expressed as:

$$\Delta G = -n_{cr}\Delta\mu + \sum_i \gamma_i S_i + (\gamma_j - \sigma) S_j, \quad (24)$$

with the first term being the free energy associated with the transition from the vapour to the crystal, given that n_{cr} is the number of molecules in the crystal and $\Delta\mu$ the chemical potential difference. The second term in Eq. 24 is the total surface free energy of the crystal [127], with γ_i being the energy per unit area of facet i , S_i the area and σ the binding energy of the surface j to the substrate. By looking at Fig. 3, one can easily substitute in Eq. 24 the specific surface energies for the anthracene:

$$\Delta G = -n_{cr}\Delta\mu + 4\gamma_{110}S_{110} + 4\gamma_{111}S_{111} + 2\gamma_{20\bar{1}}S_{20\bar{1}} + (2\gamma_{001} - \sigma) S_{001}, \quad (25)$$

Here I made use of the symmetries of the crystal to group facets with the same surface energies. Given that it is hard, even for thick crystals [112], to discern the facets 110 and 111, we can group them to a single term S_l and simplify Eq. 25 even further:

$$\Delta G = -n_{cr}\Delta\mu + 4\gamma_l S_l + 2\gamma_{20\bar{1}}S_{20\bar{1}} + (2\gamma_{001} - \sigma) S_{001}, \quad (26)$$

The index l denoting the side facets at the A angle. Following Campione *et al.* [178], one can express the surface areas in terms of the number of anthracene unit cells n_b , n_c and n_d (along the 110 facet) and the lattice constants a , b and c :

$$S_l = n_d n_c \sqrt{a^2 + b^2} c \quad (27a)$$

$$S_{20\bar{1}} = n_b n_c b c \quad (27b)$$

$$S_{001} = ab (2n_b + n_d) n_d. \quad (27c)$$

One can substitute these in Eq. 26:

$$\Delta G = -n_{cr}\Delta\mu + 4\gamma_l n_d n_c \sqrt{a^2 + b^2} c + 2\gamma_{20\bar{1}} n_b n_c b c + (2\gamma_{001} - \sigma) ab (2n_b + n_d) n_d. \quad (28)$$

The number of molecules in the crystal is related to the number of molecules in a unit cell

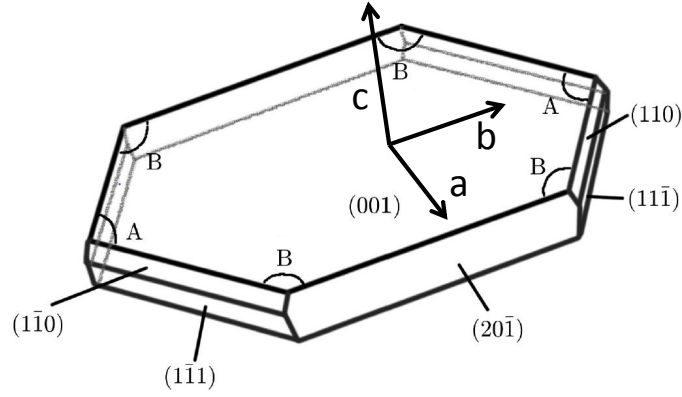


Figure 3: Diagram of the anthracene crystal structure as it appears when crystals are grown with the co-sublimation method. The a , b and c crystal axes are shown for reference. Figure adapted from [112].

Z by:

$$n_{cr} = n_c (2n_b n_d + n_d^2) Z. \quad (29)$$

For the case of anthracene, $Z = 2$, leading to

$$\Delta G = -2n_c (2n_b n_d + n_d^2) \Delta\mu + 4\gamma_l n_d n_c \sqrt{a^2 + b^2} c + 2\gamma_{20\bar{1}} n_b n_c b c + (2\gamma_{001} - \sigma) a b (2n_b + n_d) n_d. \quad (30)$$

The simultaneous search of stationary points with respect to the number of cells leads to the following set of equations:

$$4\gamma_l n_c \sqrt{a^2 + b^2} c - 2(n_b + n_d) [2n_c \Delta\mu + a b (\sigma - 2\gamma_{001})] = 0 \quad (31a)$$

$$-4n_c n_d \Delta\mu + 2b [c n_c \gamma_{20\bar{1}} + a n_d (\sigma - 2\gamma_{001})] = 0 \quad (31b)$$

$$4\gamma_l n_d \sqrt{a^2 + b^2} c + 2b c n_b \gamma_{20\bar{1}} - 2n_d (2n_b + n_d) \Delta\mu = 0 \quad (31c)$$

Solving these equations one can calculate the critical vertical dimension n_c^* [127]:

$$n_c^* = \frac{a b (2\gamma_{001} - \sigma)}{\Delta\mu}. \quad (32)$$

When growing the mesas wide and flat such as in the vapour method described above, the quantity n_c^* is fixed to $\frac{1}{2}$. This is because, following Sassella *et al.* 2D nucleation occurs when the critical dimension along the c direction corresponds to a monomolecular layer

[127]. The chemical potential difference matching this constraint is

$$\Delta\mu = 2ab(2\gamma_{001} - \sigma) . \tag{33}$$