DOI: 10.1002/ ((please add manuscript number))

Article type: Full Paper

Tunable Photodynamic Switching of DArE@PAF-1 for Carbon Capture

Richelle Lyndon, Kristina Konstas, Daniel J. Keddie, Matthew R. Hill and Bradley P. Ladewig**

R. Lyndon, Associate Professor B.P. Ladewig*
Department of Chemical Engineering, Monash University, VIC 3800 (Australia)
E-mail: bradley.ladewig@monash.edu

R. Lyndon, Dr K. Konstas, Dr M. R. Hill*
CSIRO Division of Materials Science and Engineering
Private Bag 33, Clayton South MDC, VIC 3169 (Australia)
E-mail: matthew.hill@csiro.au

Dr D. J. Keddie
Department of Chemistry, School of Science and Technology, University of New England,
NSW 2351 (Australia)

Associate Professor B. P. Ladewig
Department of Chemical Engineering, Imperial College London, Exhibition Road, London
SW7 2AZ (United Kingdom)

Keywords: metal organic frameworks, porous aromatic frameworks, carbon dioxide capture, photodynamic switching

Abstract

A new type of photodynamic carbon capture material with up to 26 wt% CO₂ desorption capacity is synthesized *via* incorporation of diarylethene (DArE) as guest molecules in Porous Aromatic Framework-1 (**PAF-1**). In these host-guest complexes, the carboxylic acid groups featured in **DArE** allow multiple non-covalent interactions to exist. **DArE** loadings ranging from 1 – 50 wt% are incorporated in **PAF-1** and the complexes characterized by UV-VIS spectroscopy, FT-IR spectroscopy, CO₂ and N₂ adsorption. Successful inclusion of **DArE** in **PAF-1** is indicated by the reduction of pore size distributions, and an optimum loading of 5 wt% is determined by comparing the percentage photoresponse and CO₂ uptake capacity at 1

bar. Mechanistic studies suggest that photoswitching modulates the binding affinity between **DArE** and CO₂ towards the host, triggering carbon capture and release. This is the first known example of photodynamic carbon capture and release in a PAF.

1. Introduction

In recent years, photodynamic switching has proven to be promising for low cost carbon capture and release, as reported for the first time in our previous study.^[1] Light is an attractive stimulus for triggering the capture and release of CO₂, owing to its natural abundance and capability for instantaneous delivery into materials. Harnessing light in this manner could potentially overcome the challenges encountered in conventional carbon capture technologies, where energy intensive vacuum, pressure or temperature swings were used to trigger the CO₂ release in order to regenerate the absorbents for the subsequent cycle. Previous reports have shown that light responsive properties can be introduced in porous materials through the use of light responsive pendant groups or guest molecules.^[2] More recently, localised bending of photoresponsive linkers within the framework can also display photoresponse properties, where photoresponsive linkers integrated within the metal organic framework were used to trigger CO₂ release, in which 64 % desorption capacity was obtained under dynamic conditions.^[1] More recently still, 76 % desorption capacity was observed under dynamic conditions.^[3] Thus, dynamic photoswitching is highly attractive for the efficient capture and release of CO₂, whilst lowering the energy required for adsorbent regeneration.

Porous materials remain one of the most intensively studied classes of adsorbents for gas storage and separation applications.^[4] Thus, they are the ideal candidates for developing light responsive materials for carbon capture. Porous aromatic frameworks (PAFs) are one of the most promising recent developments in the field of carbon capture materials.^[5] PAFs possess many of the inherent properties displayed in metal organic frameworks (MOFs) such as; high surface area, high gas selectivity, high porosity, high gas uptake capability and tunable

properties.^[6, 7, 8, 9] **PAF-1**, being one of the most porous versions of the PAF materials, can display BET surface areas of up to 5600 m²/g.^[7] Furthermore, unlike most MOF-based materials, PAFs have the additional advantage of exhibiting high thermal and hydrothermal stability.^[8, 9] Recent literature reports showed that optical properties could be introduced in PAFs through the use of photoresponsive pendant groups and photoresponsive linker molecules.^[10] However, to this date, dynamic photoresponsive PAF materials for CO₂ adsorption have not yet been reported. Thus further research was conducted in order to achieve dynamic photoswitching of PAFs containing light responsive groups for carbon capture.

Amongst the various photochromic molecules, diarylethenes (**DArE**) are well known photochromic π -conjugated organic molecules.^[11] They contain two aromatic groups that are double bonded together through an alkene linkage. The photoswitching mechanism involves the cyclization of the open-ring and cycloreversion of the closed-ring isomers, following irradiation with UV and visible light respectively.^[12, 13] The photoresponse property of **DArE** derivatives are influenced by the conformation of their open-ring isomers, their substituents, conjugation length of the heteroaryl groups and the nature of the ethene bridge.^[14] Thus upon ring-closing, the colour generally changes from colourless to a wide range of colouration.^[12] The absorption band of the closed isomers in the visible region is due to the strongly conjugated system of the whole molecule, in which it can be further red-shifted by extending the conjugation length using various substituents such as long polyene chain, aryl groups and substituents attached in the 5-position of the thiophene rings.^[15, 16] Amongst **DArE** derivatives, dithienylperfluorocyclopentene-based **DArEs** are attractive guest molecules for photoswitching application due to their high sensitivity, fatigue resistance with respect to repeated switching cycles and thermal stability.^[12, 16, 17, 18, 19] The open ring isomer displays free rotation at the ethene and aryl groups, in which the two conformations, parallel and antiparallel forms exist and can exchange between each other, even at room temperature.^[20, 21]

However, photocyclization can only proceed through the antiparallel conformation.^[22-24]

Chemically gated photochromism can be introduced through the preparation of **DArE** derivatives with interlocking arms, such as those with carboxylic acid groups or mercaptoalkyl groups at the external positions of the heterocyclic rings.^[23] This would effectively lock the molecule in the non-photoactive parallel form. Upon disruption of the hydrogen bonds or disulfide linkages, the molecules can isomerize back to the antiparallel form, regaining its photoactivity. Thus, gated photochromism could modulate the binding affinity of host-guest systems. It has been shown that photoresponse can be achieved through the incorporation of diarylethene inside adsorbents.^[3, 25]

Figure 1. Dynamic photoswitching of light responsive DArE@PAF-1. Broadband light irradiation of the material resulted in a spontaneous CO₂ release. (a) PAF-1 is produced by a self-condensation of tetraphenylbromomethane (top left), which is then loaded with the diarylethene dye *o*-DArE (bottom left), which induces the release of adsorbed CO₂ upon exposure to visible light (bottom right). (b) The dye undergoes a reversible cyclization reaction which activates the PAF pores.

In this work, dithienylperfluorocyclopentene based **DArE** bearing carboxyl groups was chosen as the guest molecule for **PAF-1**. The presence of long π -conjugation length and interlocking arms could potentially offer multi non-covalent interactions in the host-guest complex, thereby affecting the photoswitching capabilities upon gas adsorption.

Herein we report **PAF-1** containing photoresponsive **DArE** guest molecules exhibits dynamic CO₂ capture and release properties upon broadband light irradiation (**Figure 1**). The inclusion of **DArE** guest molecules allows the host-guest complex to display up to 26 wt% desorption capacity at 50 wt% **DArE** loading. The observed photodynamicity was due to host-guest competition between **DArE** and CO₂ inside the sterically hindered pores of the PAF. Furthermore, the presence of carboxyl groups in **DArE**, along with the aromatic nature of the host and guest molecules, allowed multi non-covalent interactions (e.g., hydrogen bonding, aromatic interaction) upon light irradiation.^[26-29]

2. Results and Discussion

2.1. N₂ Adsorption Isotherm Measurement

The successful inclusion of **DArE** molecules in **PAF-1** was first suggested by the decrease in N₂ adsorption capacity, as shown in **Figure 2a**. In its natural state, **DArE** displays an open-ring structure, with a molecular diameter of 0.9 – 1.3 nm. The pore size distribution calculated from the N₂ adsorption isotherm at 77 K indicated that **PAF-1** had a pore width in the range of 1.2 – 3.0 nm, with the majority of surface area arising from pores in the range 1.2 – 1.7 nm, as shown in **Figure 2b**. Further analyses of the isotherm supported the result, indicated by the decrease in pore size distribution intensities (**Figure 2b**), surface areas (**Figure 2c**) and total

pore volume (**Figure 2d**) as the **DrAE** loading increased from 1 – 50 wt%.^[12] The result was expected as it indicated that the guest molecules progressively occupied more of the vacant sites within the **PAF-1**.

Figure 2. N₂ adsorption isotherm of PAF-1 (black) and DArE@PAF-1 (1 wt%, red; 5wt %, blue; 20 wt%, green; 50 wt%, magenta) at 77 K (a), showing the effects of DArE loading on the pore size distributions (b), BET surface areas (c), and total pore volumes (d) of PAF-1.

2.2. Carbon Capture and Release Under Dynamic Photoswitching Conditions

To examine the potential of dynamic carbon capture and release in **DArE@PAF-1**, a photoswitching experiment was conducted at room temperature with CO₂, the results of which are presented in **Figure 3**.

Figure 3. CO₂ adsorption isotherms of PAF-1 and DArE@PAF-1 at 303 K under photoswitching conditions showed that CO₂ capture and release occurred reversibly in the absence and presence of light respectively (a), CO₂ sorption isotherms were normalised for clarity, showing that greater photoresponse was obtained with higher DArE loading (b), trade-off between photoresponse (c), and CO₂ uptake capacity at 1 bar (d). Photoswitching occurs approximately every 15 minutes to allow clear detection of CO₂ capture and release. Photoresponse effect can be observed within 1-2 minutes.

The observed photoresponse was similar to our recent study,^[1] as CO₂ capture and release occurred reversibly in the absence and presence of light respectively. The adsorption isotherm obtained under static irradiation matched those irradiated parts of the isotherm obtained under dynamic conditions (**Figure S1**). Such dynamicity was likely due to the presence of **DArE** molecules in the PAF, in which the intermolecular interactions between CO₂ molecules and the adsorption sites occurred, triggering instantaneous CO₂ release.^[1, 26, 27, 30, 31] However, it was found that with varying **DArE** loading, there was a trade-off between photoresponse (**Figure 3c**) and CO₂ uptake capacity. To correlate photoactivity and CO₂ adsorption, CO₂

uptake capacity at 1 bar, which showed the largest photoresponse, was calculated and compared (**Figure 3d**). When not irradiated, the CO₂ uptake capacity increased at higher loading concentration, but reduced when the loading concentration exceeded 5 wt%, indicating an optimal loading concentration. This suggested competitive interactions between **DArE** and CO₂ with the host, preventing CO₂ from occupying the adsorption sites. The increase in dynamic photoresponse during the CO₂ adsorption measurement with higher **DArE** loading concentrations corresponded to the increase in photoactivity of **DArE** in **PAF-1** (**Figure 3c**). Furthermore, CO₂ adsorption in the presence of light did not follow the Dubinin–Radushkevich (D-R) model and the change in pore size could not be determined (**Figure S3**). This was due to gas adsorption at the surface being disturbed by the presence of UV light.^[32] A photoswitching experiment was also performed on unloaded **PAF-1** as a control study to ensure that the photodynamicity was mainly due to the presence of **DArE** molecules (**Figure 3a**). The low photoresponse exhibited by **PAF-1** was due to the aromatic nature of its framework.

Figure 3. Kinetic studies of CO₂ desorption at 303 K and 273 K at a pressure range of 0.6-1 bar, showing the effects of different DArE loadings (a) and temperature with 50 wt% DArE@PAF-1 (b).

Adsorption kinetic studies showed that desorption capacities at 1 bar can increase by 65 % from 5 wt% to 50 wt% within 4 minutes of light irradiation (**Figure 4**). Some CO₂ was re-

adsorbed beyond this point, indicating that perhaps there was a small shift in the equilibrium, resulting in a slight preferential binding of CO₂ with the host. However, the equilibrium was shifted significantly towards **DArE-PAF-1** interactions at lower temperature, resulting in a complete CO₂ desorption within 9 minutes of irradiation (**Figure 4b**).

2.3. Photoswitching Mechanism Studied Using Solid-State UV-Vis and FT-IR

Further photoresponse studies were conducted to assess the dynamic properties of **PAF-1** during dynamic gas adsorption. Solid-state UV-VIS and FT-IR revealed the possible photoswitching mechanism. Upon UV (340 nm) and visible (480 nm) excitation of the free **DArE** molecule, absorption peaks which correspond to the closed-ring (**c-DArE**) and opening ring **DArE** (**o-DArE**) at 460 and 580 nm, and 370 nm respectively were observed (**Figure X**).^[19, 33] These peaks were also observed in the sample prepared, confirming the presence of **DArE** within **PAF-1** (**Figure S4**). To further analyse the photoresponse mechanism, the peak intensities at 460 and 370 nm exhibited by the free **DArE** and **DArE@PAF-1** during UV-VIS experiments were monitored by continually irradiating the materials with alternating UV and visible light. From the result, the peak intensities of **c-DArE@PAF-1** at 460 nm remained constant, whereas the peak intensities of **o-DArE@PAF-1** at 370 nm gradually decreased over several cycles (**Figure S4f**). Similar trends were observed in the free **o-DArE** molecule (**Figure S4e**). The slight decrease in peak intensities at 370 nm indicated that perhaps photocyclization was inhibited.

Figure 5. Full FT-IR spectra of **DArE** in the absence (black) and presence (red) of light irradiation.

FT-IR results revealed the photoisomerization behaviours of **DArE@PAF-1** in more detail.

Upon light irradiation, the FT-IR spectrum of host-free **DArE** showed that the photogeneration of the closed ring isomer can be detected by the formation of 2 additional weak C-F absorption bands at 966 and 1013 cm⁻¹ (**Figure 5**).^[34] However, these two signals were not observed in the FT-IR spectrum of **DArE@PAF-1** (**Figure 6**).

Figure 6. Full FT-IR spectra of **DArE@PAF-1** in the absence (black) and presence (red) of light irradiation.

This may be due to the peaks associated with **DArE** photoresponse being too weak to be detected and had been masked by the PAF's peaks. Instead, the C=O (1688 cm^{-1}) and O-H (3000 cm^{-1}) peaks showed considerable broadening, suggesting that multiple intermolecular non-covalent interactions may be involved.^[35] Upon light irradiation, the formation of *c*-**DArE** exhibited a planar geometry which is less bulky compared to its twisted open structure.^[29, 31, 36] Thus aryl-perfluoraryl interactions became more favourable between the guest molecules and the host, and hence the peak broadening at 1688 cm^{-1} .^[26-28, 30] With the aromatic stacking occurring, the movements due to photocyclization upon light irradiation would be suppressed. This was also confirmed in FT-IR spectra of irradiated **DArE@PAF-1** and free **DArE**, as shown by the reduction in peak intensities at 810, 985, 1035, 1140 and 1548 cm^{-1} regions (**Figure 5 and Figure 6**). These peaks correspond to the vibration modes

of the thiophene and cyclopentene groups in **DArE**.^[34, 37] The reduction in peak intensities was due to the loss of aromatic character of two thiophene rings in **DArE** upon ring closure.^[18, 38] Furthermore, the restricted movement of **DArE** guest molecules inside the pores of **PAF-1** also enhanced the ring bending vibration of the aryl and ethene groups around 500-600 cm⁻¹ region (Figure 6).^[21, 39] In conjunction with the aromatic stacking, H-bonding was also detected at 3000 cm⁻¹.^[26] This was only observed in the FT-IR spectra of **DArE@PAF-1**, which suggested the formation of the parallel *o*-**DArE** conformer, where intramolecular H-bonding between the carboxylic acid of the guest molecules may occur (shown in **Figure S5**), a known phenomenon reported in the literature.^[21-23] The stable intramolecular H-bonds are unlikely to be broken without H-bond breaking agents.^[21-23] As **DArE** can exist in three conformers, the antiparallel *o*-**DArE** (**Figure S6**) and *c*-**DArE** conformers (**Figure S7**) may interconvert reversibly under broadband light irradiation, but some parallel *o*-**DArE** conformers may form in the process.^[22, 23, 40]

The formation of the parallel conformer prevented photocyclization back to its antiparallel form.^[22, 23, 40] This would explain the incomplete ring opening process suggested in solid UV-VIS result (**Figure S4**). Thus, the presence of multiple interactions in light irradiated **DArE@PAF-1** may be responsible for triggering spontaneous CO₂ release. The competitive interaction between **DArE** and CO₂ molecules with the host would occur as adsorption took place within a sterically demanding environment.^[26-28, 30]

3. Conclusion

Photodynamic CO₂ capture and release from PAF containing photoactive guest molecules has been demonstrated for the first time. Light can be switched on and off to trigger CO₂ desorption and adsorption respectively. Such dynamicity is likely due to the increase in host-guest interactions upon the formation of the parallel *o*-**DArE** conformer, as shown in the UV-VIS and FT-IR results. During photoirradiation, aromatic stacking and H-bonding occurred,

resulting in the inhibition of **DArE** photocyclisation in a sterically hindered environment. Thus, it promoted the formation of its parallel **o-DArE** conformer, featuring interlocking arms due to H-bonding interactions. The **PAF-1-DArE** and **CO₂-PAF-1** interactions compete with each other, weakening the intermolecular interactions between CO₂ molecules and the adsorption sites, triggering instantaneous CO₂ release. The results of this study also demonstrate the level of photoresponse can be modulated through the use of different **DArE** loadings. A stronger photoresponse, of up to 26 %, can be obtained at higher loadings (50 wt %), but beyond the optimum concentration of 5 wt %, the CO₂ uptake capacity gradually reduced. The ability to modulate the photoresponse could offer greater control for carbon capture and release in industrial applications.

4. Experimental Section

Materials: **DArE** from was prepared by adaption of relevant literature procedures^[41] (for experimental details see Supporting Information). **PAF-1** was prepared as per the published literature method.^[9]

*Preparation of **DArE@PAF-1**:* Different concentrations of **DArE** were loaded in **PAF-1** (weight percentage diarylethene loading) in ~5 mL dry diethyl ether in Quartz ASAP tube. The solution was sonicated for 1 h to allow even loading distribution within the PAF. The solvent was then evaporated under N₂ atmosphere.

UV-VIS Spectroscopy: UV-VIS spectra were obtained using FlexStation® 3 Benchtop Multi-Mode Microplate Reader. The solid samples used were activated accordingly prior to measurements. Excitation and emission wavelengths of the sample in solid state were read in a Corning black flat clear bottom microplate in fluorescence reading mode at room temperature. For photoresponse analyses, the sample was irradiated with light for a certain period of time and the spectra were recorded immediately after irradiation.

FT-IR Spectroscopy: Infrared spectra were obtained on Thermoscientific Nicolet 6700 in powder form using the attenuated total reflectance method (ATR). Time-resolved photoresponse experiments were conducted by irradiating the solid sample for a certain period of time and the spectra were recorded immediately after or during irradiation. The solid samples used were activated accordingly prior to measurements.

Gas Adsorption: N₂ and CO₂ adsorption isotherms of samples were recorded at low pressure (0-1.2 bar) by a volumetric method using Micromeritics ASAP 2420 or Tristar II 3020 instruments respectively. Prior to measurement, the sample was activated under vacuum and heat. The sample was activated at 150 °C under dynamic vacuum at 10⁻⁶ Torr for a certain period of time to remove any solvent molecules. Approximately 100 mg of dried activated sample was weighed in a pre-dried and weighed ASAP tube. Multiple replicate weights of the activated sample were taken and an average weight was calculated for both the empty tube and the added sample. Quartz ASAP tubes were used for experiments involving UV light and glass ASAP tubes were used for visible light switching experiments. An accurate weight of the degassed sample was calculated prior to analysis. Gas adsorption measurements were performed using ultra-high purity (99.999 %) CO₂ and N₂ gas. Pre-weighed and dried custom made aluminium foiled quartz or glass ASAP tube was used for light switching experiments. A custom made light cell was used to contain the BET tube and light guide to allow maximum light exposure and coverage on the sample when the light was switched on. A Cole Palmer Model BT 15 heated circulating bath was used to maintain the temperature at 303 K or 273 K throughout the experiment. A temperature probe was wedged inside the light cell between the ASAP tube and light guide to monitor the temperature.

Photoresponse Studies: Acticure® 4000 containing a high pressure 100 Watt mercury vapour short arc lamp was used as a UV-VIS light source to trigger the sample's light response during analysis. The light was fixed at the highest intensity output with no filter (200-500 nm, corresponding to 24,600 mW/cm²).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This research is supported by the Science and Industry Endowment Fund.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

- [1] R. Lyndon, K. Konstas, B. P. Ladewig, P. D. Southon, P. C. J. Keper, M. R. Hill, *Angewandte Chemie International Edition* 2013, 52, 3695.
- [2] N. Yanai, T. Uemura, M. Inoue, R. Matsuda, T. Fukushima, M. Tsujimoto, S. Isoda, S. Kitagawa, *Journal of the American Chemical Society* 2012, 134, 4501.
- [3] F. Luo, C. B. Fan, M. B. Luo, X. L. Wu, Y. Zhu, S. Z. Pu, W. Y. Xu, G. C. Guo, *Angewandte Chemie International Edition* 2014, 53, 9298.
- [4] D. M. D'Alessandro, T. McDonald, *Pure and Applied Chemistry* 2011, 83, 57; D. M. D'Alessandro, B. Smit, J. R. Long, *Angewandte Chemie International Edition* 2010, 49, 6058; M. E. Davis, *Nature* 2002, 417, 813.
- [5] S. J. Garibay, M. H. Weston, J. E. Mondloch, Y. J. Colon, O. K. Farha, J. T. Hupp, S. T. Nguyen, *CrystEngComm* 2013, 15, 1515.
- [6] J.-R. Li, R. J. Kuppler, H.-C. Zhou, *Chemical Society Reviews* 2009, 38, 1477; S. Ma, H.-C. Zhou, *Chemical Communications* 2010, 46, 44; S. Ma, D. Sun, J. M. Simmons, C. D. Collier, D. Yuan, H.-C. Zhou, *Journal of the American Chemical Society* 2008, 130, 1012; Y. Zhu, H. Long, W. Zhang, *Chemistry of Materials* 2013, 25, 1630.
- [7] R. Babarao, S. Dai, D.-e. Jiang, *Langmuir* 2011, 27, 3451.

- [8] T. Ben, S. Qiu, CrystEngComm 2013, 15, 17; T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu, G. Zhu, Angewandte Chemie International Edition 2009, 48, 9457.
- [9] K. Konstas, J. W. Taylor, A. W. Thornton, C. M. Doherty, W. X. Lim, T. J. Bastow, D. F. Kennedy, C. D. Wood, B. J. Cox, J. M. Hill, A. J. Hill, M. R. Hill, Angewandte Chemie International Edition 2012, 51, 6639.
- [10] P. K. Kundu, G. L. Olsen, V. Kiss, R. Klajn, Nature Communications 2014, 5; H. A. Patel, S. Hyun Je, J. Park, D. P. Chen, Y. Jung, C. T. Yavuz, A. Coskun, Nature Communications 2013, 4, 1357; Y. Zhu, W. Zhang, Chemical Science 2014, 5, 4957.
- [11] K. Matsuda, M. Irie, Journal of Photochemistry and Photobiology, C: Photochemistry Reviews 2004, 5, 169.
- [12] M. Irie, Photochemical & Photobiological Sciences 2010, 9, 1535.
- [13] S. Kobatake, Y. Matsumoto, M. Irie, Angewandte Chemie International Edition 2005, 44, 2148; F. Terao, M. Morimoto, M. Irie, Angewandte Chemie International Edition 2012, 51, 901.
- [14] K. Yuan, J. Boixel, H. Le Bozec, A. Boucekkine, H. Doucet, V. Guerchais, D. Jacquemin, Chemical Communications 2013, 49, 7896.
- [15] S. Castellanos, L. Grubert, R. Stößer, S. Hecht, The Journal of Physical Chemistry C 2013, 117, 23529; J. Ern, A. T. Bens, H.-D. Martin, K. Kuldova, H. P. Trommsdorff, C. Kryschi, The Journal of Physical Chemistry A 2002, 106, 1654; J. Ern, A. T. Bens, H. D. Martin, S. Mukamel, D. Schmid, S. Tretiak, E. Tsiper, C. Kryschi, Chemical Physics 1999, 246, 115; S. L. Gilat, S. H. Kawai, J.-M. Lehn, Chemistry - A European Journal 1995, 1, 275; E. Kim, M. Kim, K. Kim, Bulletin of the Korean Chemical Society 2008, 29, 827; A. Thomas Bens, D. Frewert, K. Kodatis, C. Kryschi, H.-D. Martin, H. P. Trommsdorff, European Journal of Organic Chemistry 1998, 1998, 2333.

- [16] A. R. Santos, R. Ballardini, P. Belser, M. T. Gandolfi, V. M. Iyer, L. Moggi, *Photochemical & Photobiological Sciences* 2009, 8, 1734.
- [17] C. Brieke, F. Rohrbach, A. Gottschalk, G. Mayer, A. Heckel, *Angewandte Chemie International Edition* 2012, 51, 8446; M. Irie, T. Lifka, S. Kobatake, N. Kato, *Journal of the American Chemical Society* 2000, 122, 4871; M. Irie, K. Uchida, *Bulletin of the Chemical Society of Japan* 1998, 71, 985; K. Uchida, T. Matsuoka, S. Kobatake, T. Yamaguchi, M. Irie, *Tetrahedron* 2001, 57, 4559; J. Yuan, Z. Li, M. Hu, S. Li, S. Huang, J. Yin, S. H. Liu, *Photochemical & Photobiological Sciences* 2011, 10, 587.
- [18] M. Irie, *Chemical Reviews* 2000, 100, 1683; M. Irie, M. Mohri, *Journal of Organic Chemistry* 1988, 53, 803.
- [19] M. Morimoto, M. Irie, *Chemistry - A European Journal* 2006, 12, 4275.
- [20] H. Tian, S. Yang, *Chemical Society Reviews* 2004, 33, 85.
- [21] C. C. Warford, V. Lemieux, N. R. Branda, in *Molecular Switches*, Vol. 1 (Eds: B. L. Feringa, W. R. Browne), Wiley-VCH, Weinheim, Germany 2011, 1.
- [22] M. Irie, O. Miyatake, K. Uchida, *Journal of the American Chemical Society* 1992, 114, 8715.
- [23] M. Irie, O. Miyatake, R. Sumiya, M. Hanazawa, Y. Horikawa, K. Uchida, *Molecular Crystals and Liquid Crystals Science and Technology Section A* 1994, 246, 155.
- [24] K. Shibata, K. Muto, S. Kobatake, M. Irie, *The Journal of Physical Chemistry A* 2001, 106, 209.
- [25] H. Okada, N. Nakajima, T. Tanaka, M. Iwamoto, *Angewandte Chemie* 2005, 117, 7399; I. M. Walton, J. M. Cox, J. A. Coppin, C. M. Linderman, D. G. Patel, J. B. Benedict, *Chemical Communications* 2013, 49, 8012.
- [26] M. Morimoto, M. Irie, *Chemical Communications* 2005, 0, 3895.
- [27] M. Morimoto, S. Kobatake, M. Irie, *Chemical Record* 2004, 4, 23.

- [28] S. Yagai, K. Ohta, M. Gushiken, K. Iwai, A. Asano, S. Seki, Y. Kikkawa, M. Morimoto, A. Kitamura, T. Karatsu, *Chemistry - A European Journal* 2012, 18, 2244.
- [29] X. Zhou, Y. Duan, S. Yan, Z. Liu, C. Zhang, L. Yao, G. Cui, *Chemical Communications* 2011, 47, 6876.
- [30] S. Meejoo, B. M. Kariuki, K. D. M. Harris, *ChemPhysChem* 2003, 4, 766; M. Morimoto, S. Kobatake, M. Irie, *Photochemical & Photobiological Sciences* 2003, 2, 1088; S. Yagai, K. Iwai, M. Yamauchi, T. Karatsu, A. Kitamura, S. Uemura, M. Morimoto, H. Wang, F. Würthner, *Angewandte Chemie International Edition* 2014, 53, 2602.
- [31] S. Yagai, K. Ishiwatari, X. Lin, T. Karatsu, A. Kitamura, S. Uemura, *Chemistry - A European Journal* 2013, 19, 6971.
- [32] R. K. Motkuri, P. K. Thallapally, S. K. Nune, C. A. Fernandez, B. P. McGrail, J. L. Atwood, *Chemical Communications* 2011, 47, 7077.
- [33] L. N. Lucas, J. J. D. De Jong, J. H. Van Esch, R. M. Kellogg, B. L. Feringa, *European Journal of Organic Chemistry* 2003, 155.
- [34] J. J. D. De Jong, W. R. Browne, M. Walko, L. N. Lucas, L. J. Barrett, J. J. McGarvey, J. H. Van Esch, B. L. Feringa, *Organic & Biomolecular Chemistry* 2006, 4, 2387.
- [35] L. Ma, Q. Wang, G. Lu, R. Chen, X. Sun, *Langmuir* 2009, 26, 6702.
- [36] T. Hirose, K. Matsuda, M. Irie, *Journal of Organic Chemistry* 2006, 71, 7499; D. Kitagawa, H. Nishi, S. Kobatake, *Angewandte Chemie International Edition* 2013, 52, 9320.
- [37] A. Takata, S. Yokojima, H. Nakagawa, Y. Matsuzawa, A. Murakami, S. Nakamura, M. Irie, K. Uchida, *Journal of Physical Organic Chemistry* 2007, 20, 998.
- [38] S. Kobatake, H. Hasegawa, K. Miyamura, *Crystal Growth & Design* 2011, 11, 1223.
- [39] H. Jean-Ruel, M. Gao, M. A. Kochman, C. Lu, L. C. Liu, R. R. Cooney, C. A. Morrison, R. J. D. Miller, *Journal of Physical Chemistry B* 2013, 117, 15894; K. Matsuda, K. Higashiguchi, in *Supramolecular Soft Matter: Applications in Materials and Organic Electronics*, (Ed: T. Nakanishi), John Wiley & Sons, Inc., Hoboken, New Jersey 2011, 215.

[40] S.-Z. Pu, F.-S. Zhang, F. Sun, R.-J. Wang, Z.-H. Zhou, S.-K. Chan, Tetrahedron Letters 2003, 44, 1011.

[41] S. Hiroto, K. Suzuki, H. Kamiya, H. Shinokubo, Chemical Communications 2011, 47, 7149; S. Kawamorita, H. Ohmiya, M. Sawamura, Journal of Organic Chemistry 2010, 75, 3855.

Dynamic light-activated carbon capture and release in Porous Aromatic Framework-1 is achieved by successfully loading DArE as a guest molecule. Up to 26 wt% CO₂ desorption capacity is possible with 50wt% **DArE** loading. The observed photodynamicity is due to host-guest competition between **DArE** and CO₂ inside the sterically hindered pores of **PAF-1**.

Carbon Capture

Richelle Lyndon, Kristina Konstas, Daniel J. Keddie, Matthew R. Hill* and Bradley P. Ladewig*

Tunable Photodynamic Switching of DArE@PAF-1 for Carbon Capture