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

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

A new type of photodynamic carbon capture material with up to 26 wt% CO_2 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 noncovalent interactions to exist. DArE loadings ranging from 1 to 50 wt% are incorporated in PAF-1 and the complexes characterized by UV–vis spectroscopy, FT-IR spectroscopy, CO_2, and N_2 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 CO_2 uptake capacity at 1 bar. Mechanistic studies suggest that photoswitching modulates the binding affinity between DArE and CO_2 toward 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 CO_2, 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 CO_2 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, localized bending of photoresponsive linkers within the framework can also display photoresponse properties, where photoresponsive linkers integrated within the metal organic framework (MOF) were used to trigger CO_2 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 CO_2, 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. Brunauer-Emmett-Teller (BET) surface area is one of the most important physical properties that determine the quality of the materials. The BET theory is based on the multilayer adsorption assumption and the analyses can be performed using ASAP instruments. 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 MOFs such as high surface area, high gas selectivity, high porosity, high gas uptake capability, and tunable properties.[6–9] PAF-1, being one of the most porous versions of the PAF materials, can display BET surface areas of up to 5600 $m^2\ g^{-1}$.[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 CO_2 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

Dr. R. Lyndon, Dr. B. P. Ladewig
Department of Chemical Engineering
Monash University
VIC 3800, Australia
E-mail: b.ladewig@imperial.ac.uk

Dr. 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

Prof. R. A. Evans
CSIRO Molecular and Health Technologies
Bag 10, Clayton South, VIC 3169, Australia

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

Dr. B. P. Ladewig
Department of Chemical Engineering
Imperial College London
Exhibition Road, London SW7 2AZ, UK

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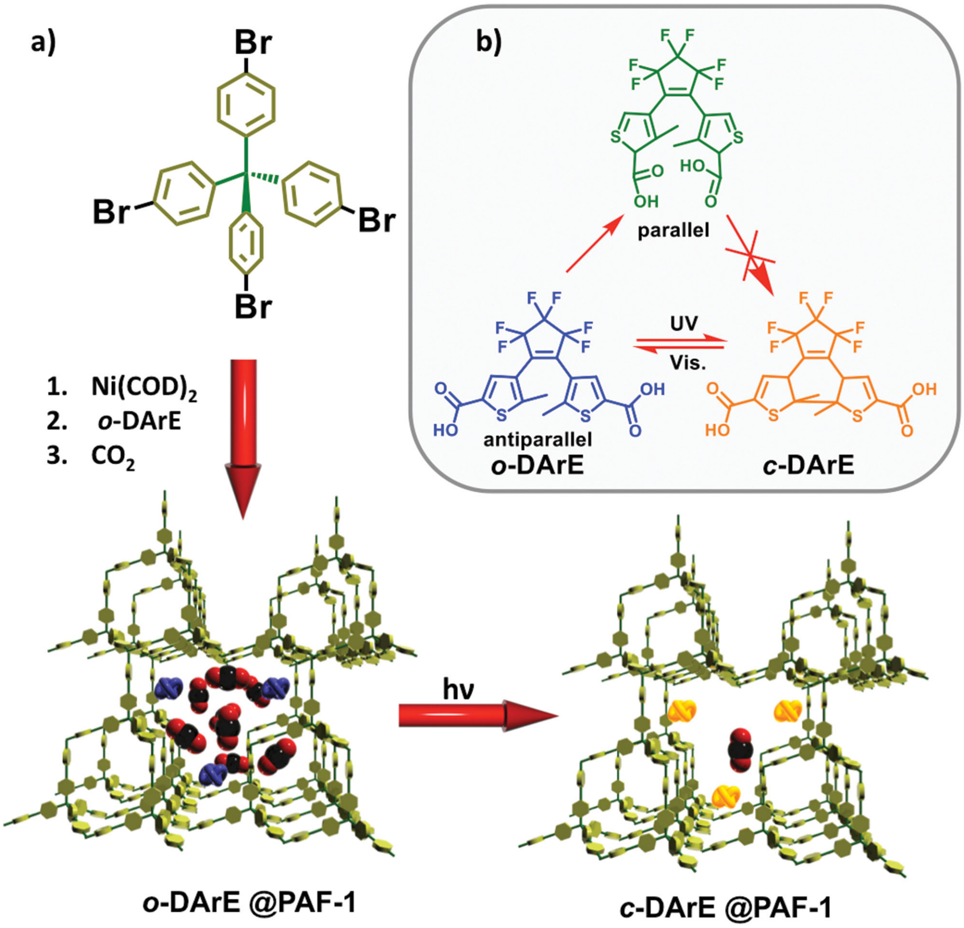

Figure 1. Dynamic photoswitching of light responsive DArE@PAF-1. Broadband light irradiation of the material resulted in a spontaneous CO$_2$ release. a) PAF-1 is produced by a self-condensation of tetraphenylbromomethane (top left), which is then loaded with the diarylethene dye *o*-DArE (bottom left), which induces the release of adsorbed CO$_2$ upon exposure to visible light (bottom right). b) The dye undergoes a reversible cyclization reaction which activates the PAF pores.

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 color generally changes from colorless to a wide range of coloration.[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 redshifted by extending the conjugation length using various substituents such as long polyene chain, aryl groups, and substituents attached in the five-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.[12,16–19] 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 nonphotoactive 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]

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 multiple noncovalent 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 CO$_2$ capture and release properties upon broadband light irradiation (**Figure 1**). The

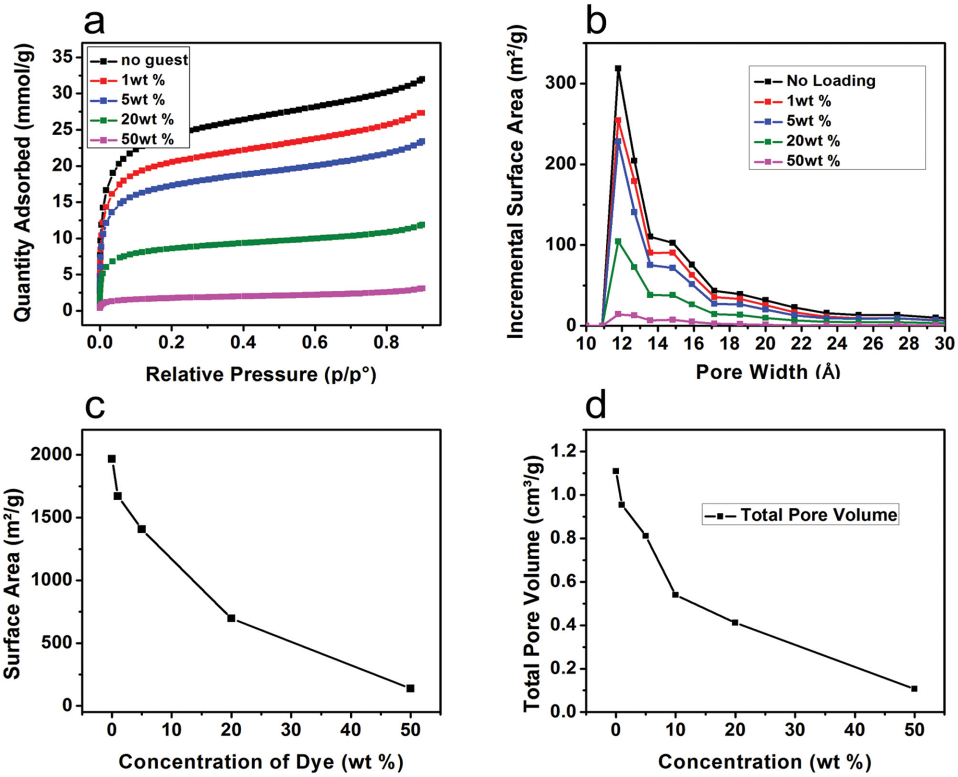

Figure 2. N_2 adsorption isotherm of PAF-1 (black) and DArE@PAF-1 (1 wt%, red; 5wt%, blue; 20 wt%, green; 50 wt%, magenta) at 77 K a), showing the effects of DArE loading on the pore size distributions b), BET surface areas c), and total pore volumes d) of PAF-1.

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 CO_2 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 multiple noncovalent interactions (e.g., hydrogen bonding and aromatic interaction) upon light irradiation.[26–29]

2. Results and Discussion

2.1. N_2 Adsorption Isotherm Measurement

The successful inclusion of DArE molecules in PAF-1 was first suggested by the decrease in N_2 adsorption capacity, as shown in **Figure 2**a. 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 N_2 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 to 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.

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 CO_2, the results of which are presented in **Figure 3**.

The observed photoresponse was similar to our recent study,[1] as CO_2 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, Supporting Information). Such dynamicity was likely due to the presence of DArE molecules in the PAF, in which the intermolecular interactions between CO_2 molecules and the adsorption sites occurred, triggering instantaneous CO_2 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 CO_2 uptake capacity. To correlate photoactivity and CO_2 adsorption, CO_2 uptake capacity at 1 bar, which showed the largest photoresponse, was calculated and compared (Figure 3d). When not irradiated, the CO_2 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 CO_2 with the host, preventing CO_2 from occupying the adsorption sites. The increase in dynamic photoresponse during the CO_2 adsorption measurement with higher DArE loading concentrations corresponded to the increase in photoactivity of

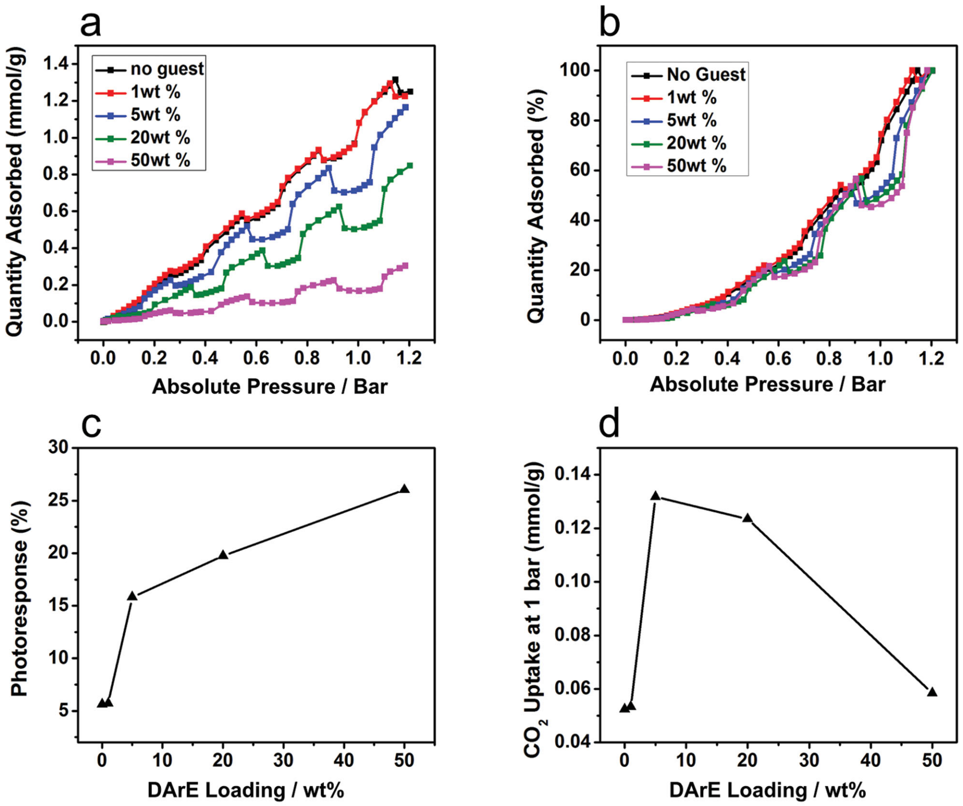

Figure 3. CO_2 adsorption isotherms of PAF-1 and DArE@PAF-1 at 303 K under photoswitching conditions showed that CO_2 capture and release occurred reversibly in the absence and presence of light, respectively a), CO_2 sorption isotherms were normalized for clarity, showing that greater photoresponse was obtained with higher DArE loading b), trade-off between photoresponse c), and CO_2 uptake capacity at 1 bar d). Photoswitching occurs approximately every 15 min to allow clear detection of CO_2 capture and release. Photoresponse effect can be observed within 1–2 min.

DArE in PAF-1 (Figure 3c). Furthermore, CO_2 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, Supporting Information). 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.

Adsorption kinetic studies showed that desorption capacities at 1 bar can increase by 65% from 5 to 50 wt% within 4 min of light irradiation (**Figure 4**). Some CO_2 was readsorbed beyond this point, indicating that perhaps there was a small shift in the equilibrium, resulting in a slight preferential binding of CO_2 with the host. However, the equilibrium was shifted

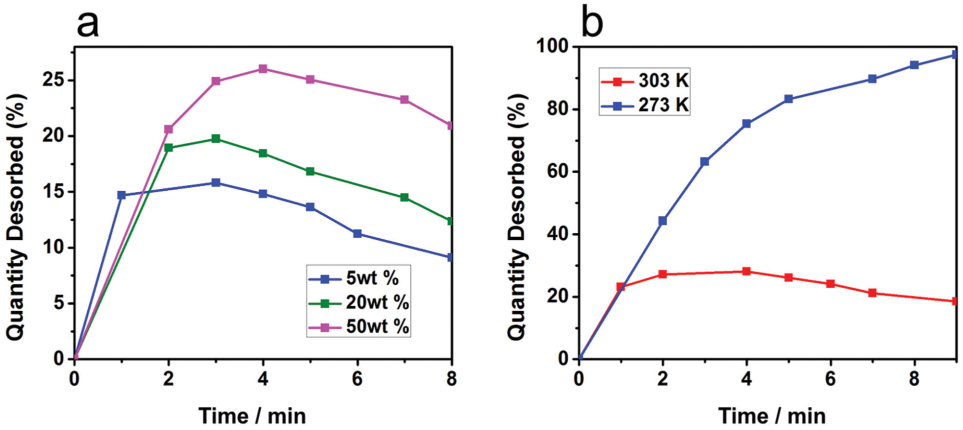

Figure 4. Kinetic studies of CO_2 desorption at 303 and 273 K at a pressure range of 0.6–1 bar, showing the effects of different DArE loadings a) and temperature with 50 wt% DArE@PAF-1 b).

significantly toward DArE-PAF-1 interactions at lower temperature, resulting in a complete CO_2 desorption within 9 min of irradiation (Figure 4b).

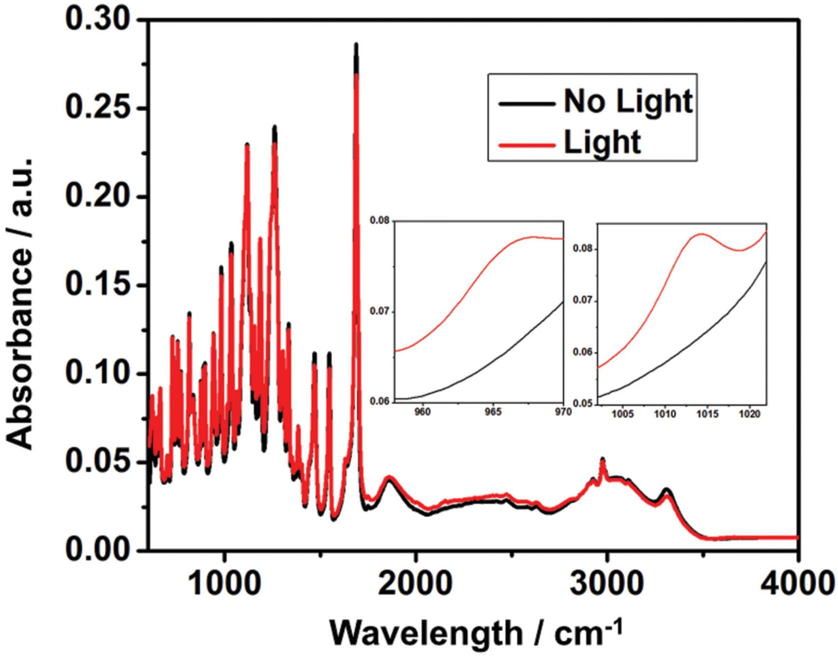

Figure 5. Full FT-IR spectra of DArE in the absence (black) and presence (red) of light irradiation.

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 open-ring DArE (*o*-DArE) at 460 and 580, 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, Supporting Information). To further analyze 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, Supporting Information). Similar trends were observed in the free *o*-DArE molecule (Figure S4e, Supporting Information). The slight decrease in peak intensities at 370 nm indicated that perhaps photocyclization was inhibited.

FT-IR results revealed the photoisomerization behaviors 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 two 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**).

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 noncovalent 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–perfluoaryl interactions became more favorable 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 (Figures 5 and 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 (as shown in Figure S5 in the Supporting Information), 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, Supporting Information) and *c*-DArE conformers (Figure S7, Supporting Information) 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, Supporting Information). Thus, the presence of multiple interactions in light irradiated DArE@PAF-1 may be responsible for triggering spontaneous CO_2 release. The competitive interaction between DArE and CO_2 molecules with the host would occur as adsorption took place within a sterically demanding environment.[26–28,30]

3. Conclusion

Photodynamic CO_2 capture and release from PAF containing photoactive guest molecules has been demonstrated for the

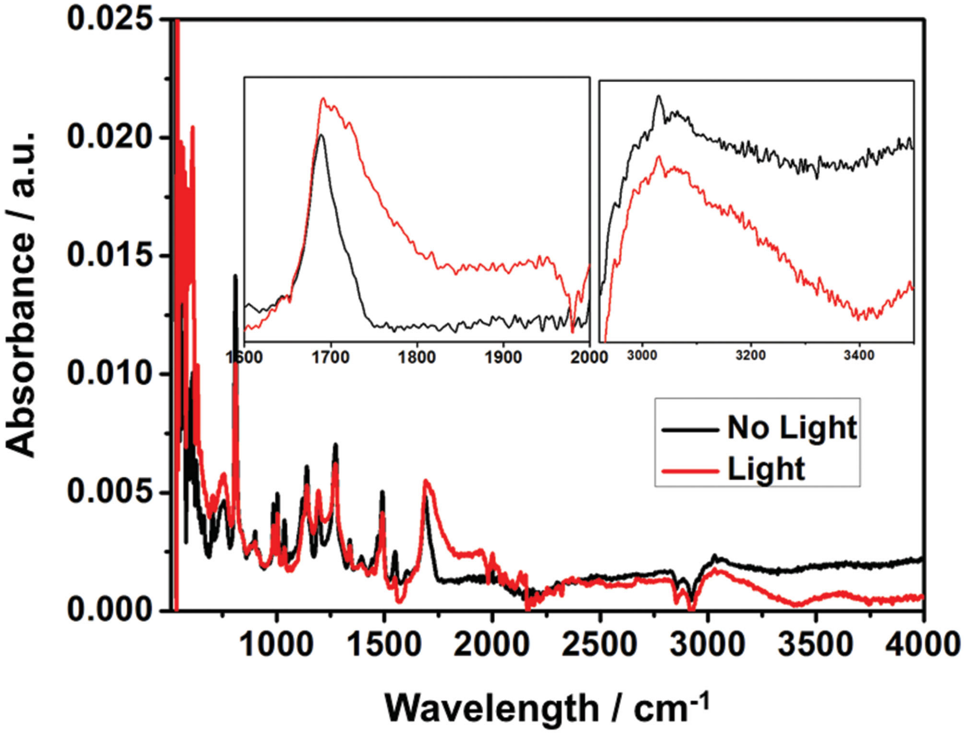

Figure 6. Full FT-IR spectra of DArE@PAF-1 in the absence (black) and presence (red) of light irradiation.

first time. Light can be switched on and off to trigger CO_2 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 photocylization 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 CO_2-PAF-1 interactions compete with each other, weakening the intermolecular interactions between CO_2 molecules and the adsorption sites, triggering instantaneous CO_2 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 CO_2 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 was prepared by adaption of relevant literature procedures[41] (for experimental details see the 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 N_2 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. 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: N_2 and CO_2 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 predried 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 ultrahigh purity (99.999%) CO_2 and N_2 gas. Preweighed and dried custom made aluminum 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 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 W mercury vapor 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 cm^{-2}).

Supporting Information

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

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