

NJC

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

The role of atropisomers on the photo-reactivity and fatigue of diarylethene-based metal-organic frameworks

Ian M. Walton^a, Jordan M. Cox^a, Cassidy A. Benson,^a Dinesh (Dan) G. Patel^b, Yu-Sheng Chen^c, Jason B. Benedict^{*,a}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Photo-responsive metal-organic frameworks (MOFs) are one example of light controlled smart materials for use in advanced sensors, data storage, actuators and molecular switches. Herein we show the design, synthesis and characterization of a photo-responsive linker that is subsequently reacted to yield MOF single crystals. The photo-responsive properties of the resulting UBMOF-2 arise from the photo-induced cyclization of the diarylethene moiety designed into the linker. Computational modeling to assess the relative energies of linker atropisomers reveals a large energetic barrier preventing facile interconversion between key species. The role of this barrier on the observed photo-induced fatigue provides useful insight into the development of advanced photo-responsive nanoporous materials.

Introduction

Photochromic technologies have the potential to transform traditionally passive materials into active materials which change their chemical or electronic properties in response to light stimulus. New photochromic materials are being synthesized and reported at an extremely rapid rate driven in large part by the numerous potential applications for these advanced materials including molecular switches,¹⁻⁴ sensors,⁵⁻¹⁰ data storage,¹¹⁻¹³ photomechanical devices¹⁴⁻¹⁷, and even biological switches.¹⁸⁻²⁰ One of the newest emerging applications for photochromic technologies is the development of photo-responsive metal-organic frameworks (MOFs).²¹⁻³¹

Diarylethenes (DAE) remain one of the most promising and popular photochromic systems as they typically exhibit bi-directional photoswitching, strong optical disparity between the open and closed forms, and excellent resistance to fatigue in the single crystalline phase. While DAE-based MOFs have been prepared using guest exchange methods,²⁷ the design and synthesis of DAE-based linkers provides greater control over the location and composition of the photoswitchable group within the photochromic framework.^{28,32} Given the importance of reducing our dependence on non-

renewable resources, these advanced materials should be engineered with sustainability in mind.³³⁻³⁵ Designing materials with engineered resistance to fatigue (entering a photoirreversible state) will directly increase the useful lifetime of these photo-responsive materials. In the diarylethene class of molecules, the rate at which the molecular switches fatigue is often highly dependent on the structural rigidity and permeability of the local photochrome microenvironment. Neat close-packed crystalline materials often possess very high resistance to fatigue, while solutions and films (formats which are easily processed) of the same molecule exhibit (sometimes rapid) degradation.³⁶ Herein we report the synthesis and characterization of a new diarylethene-based ditopic linker (9,10-bis(2-methyl-3-phenylthiophen-3-yl)-phenanthrene-2,7-dicarboxylate, **PhTPDC** and a photo-responsive MOF prepared from this

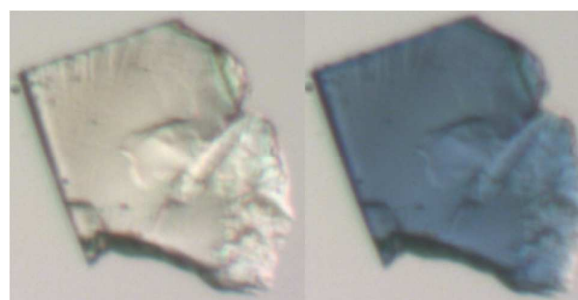
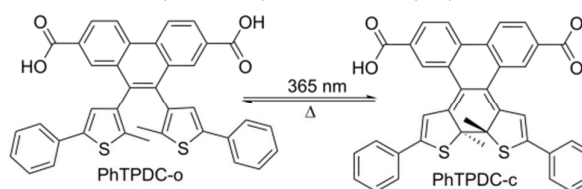


Figure 1. Ring-opened and -closed structures of the photochromic MOF linker PhTPDC (upper). Images of a UBMOF-2 single crystal prior to irradiation with UV light (left), following UV irradiation (right).

^a Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, New York, 14260-3000, USA

^{b, b} Department of Chemistry, 76 University Drive, the Pennsylvania State University, Hazleton, PA, 18202, USA

^c Center for Advanced Radiation Sources, The University of Chicago, Argonne, IL 60439

Full details of the synthesis and characterization of **PhTPDC**, the reaction intermediates, and the synthesis of **UBMOF-2**, crystal structure and refinement data, details of acid digestion experiments
See DOI: 10.1039/x0xx00000x

linker, **UBMOF-2** (Figure 1). Repeated photo-cycling of **UBMOF-2** results in the loss of photo-responsivity. Analysis of the fatigued framework suggests that the degradation is the result of the formation of photo-inactive atropisomers of **PhTPDC** which are stabilized by the framework. The stabilization of these atropisomers is likely a property unique to microenvironments which place moderate constraints on molecular reorganization, as is the case in MOFs. Understanding and ultimately controlling atropisomer formation remains a key design challenge for conformationally-flexible DAE-based photo-responsive materials.

Results and Discussion

Phenanthrene-based diarylethenes exhibit reversible photocyclization in solution,^{37,38} while simultaneously possessing a rigid backbone capable of supporting functional groups for use in the construction of MOFs.³⁹ The 5-phenyl 2-methyl thiophene derivative was targeted for synthesis as the phenyl group has been shown to bathochromically shift the absorption band in related DAEs.³⁷ We were also interested in assessing the influence of the bulkier functional group on the chemical and physical properties of subsequently derived MOFs. In addition to potentially exhibiting a greater impact on the cavity or pore size in these materials and thus a greater impact on the porosity and selectivity, the larger aromatic group should also exhibit enhanced intermolecular interactions potentially impacting the distribution of thiophene orientations within the lattice.

In a solution of methanol, the ring-open form, **PhTPDC-o**, is readily converted to the closed form **PhTPDC-c** upon irradiation with UV light (365 nm). The initially colourless solution turns blue following irradiation and the formation of the ring closed species can be monitored by the appearance of new absorption bands in the UV/Visible spectrum of the solution (Figure 2). Upon exposure to visible light (>495 nm), the blue solution reverts back to colourless and the original spectrum is obtained. The presence of an isosbestic point at 317 nm indicates the photochemical reaction does not generate any side products. While ring closed isomers of DAEs generally exhibit excellent thermal stability, in the absence of visible light, the **PhTPDC** coloured solution slowly reverts back to a colourless solution indicating the presence of a back

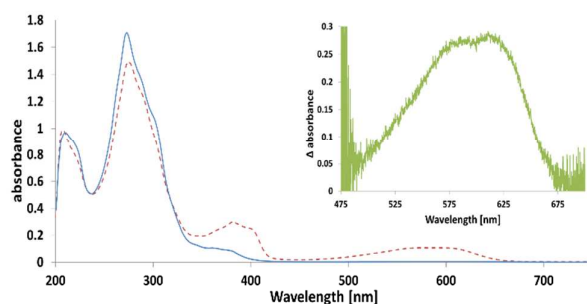


Figure 2. Top: UV/Visible absorption spectra of the open (solid blue line) and closed form (dashed red line) of **PhTPDC** (2.5×10^{-5} M in MeOH). Inset: The difference absorption spectrum of a **UBMOF-2** single crystal following irradiation with 365 nm light.

reaction which is thermally accessible at room temperature.³⁶ A fit of the time-dependent absorbance of a solution of **PhTPDC-c** at room temperature was well-modelled using single exponential decay with a rate constant of $1.43(4) \times 10^{-3} \text{ s}^{-1}$ for a 3.27×10^{-3} M solution in MeOH. Thus for **PhTPDC** in solution, the cycloreversion reaction is driven by both light and heat. It remains unknown if thermally activated back reactions are a general property of phenanthrene based DAEs as previous reports have not specifically examined this property.^{37,38}

UBMOF-2 structure and photophysical properties

The solvothermal reaction of **PhTPDC**, with zinc(II) nitrate in dimethylformamide yielded large photo-responsive single crystals of **UBMOF-2** suitable for X-ray diffraction structure determination and spectroscopic characterization (Figure 1). In these crystals, deprotonated **PhTPDC** coordinates to Zn4O secondary building units (SBUs) to form frameworks of $\text{Zn}_4\text{O}(\text{PhTPDC})_3$, which was named **UBMOF-2** (University at Buffalo MOF-2, Figure 1). Single crystal X-ray diffraction experiments revealed that **UBMOF-2** crystallizes in the cubic space group $Fm\bar{3}m$ ($a=34.250 \text{ \AA}$) and is isostructural with **UBMOF-1**, **IRMOF-10**, and **IRMOF-14**.^{39,40}

Similar to **UBMOF-1**, the low symmetry linker **PhTPDC** in **UBMOF-2** resides on a high site symmetry position ($mm2$). While atomic positions of the metal SBU and the phenanthrene portion of the linker were crystallographically resolvable, the strong disorder of the photo-reactive thiophene groups prevented reliable refinement of their positions on both irradiated and non-irradiated crystals. Acid digestion experiments performed on **UBMOF-2** confirmed that the **PhTPDC** linker remained chemically intact throughout the MOF synthesis and subsequent acid digestion (See supporting information).

Upon irradiation with 365 nm light, single crystals of **UBMOF-2** readily transform from colourless to dark blue (Figure 1). Visible absorption spectra of irradiated individual single crystals confirmed the presence of an absorption band identical to that of the **PhTPDC-c** in solution (Figure 2).

Shown in Figure 3 are traces of the time-dependent absorbance at 600 nm of a single crystal of **UBMOF-2** following irradiation with UV light (365 nm) at four different temperatures. Following the cessation of irradiation with UV light, the absorbance of a photoisomerized single crystal, **UBMOF-2-c**, slowly decays back to that of the original crystal containing only the ring-open species, **UBMOF-2-o**. In order to assess the degree to which the ring-opening reaction is light or thermally driven, the light of the microscope which is used to monitor the reaction (and could potentially drive the cycloreversion reaction) was blocked for a short amount of time during the decay measurement. As shown in Figure 3, the 'light blocked' traces are nearly identical to the traces in which the light of the microscope illuminates the sample for the entire duration of the measurement at all temperatures. These experiments indicate that the cycloreversion reaction in **UBMOF-2** is entirely thermally driven.

The decay of the absorption band at 600 nm follows bi-exponential kinetics with both measured decay rates

exhibiting similar temperature dependence (Figure 3). An Arrhenius plot of the decay rates indicated that the activation barriers associated with the two constants are 56.2 kJ/mol and 65.7 kJ/mol, respectively (Figure 3). The bi-exponential behaviour of the thermal back reaction of the **PhTPDC** ligand

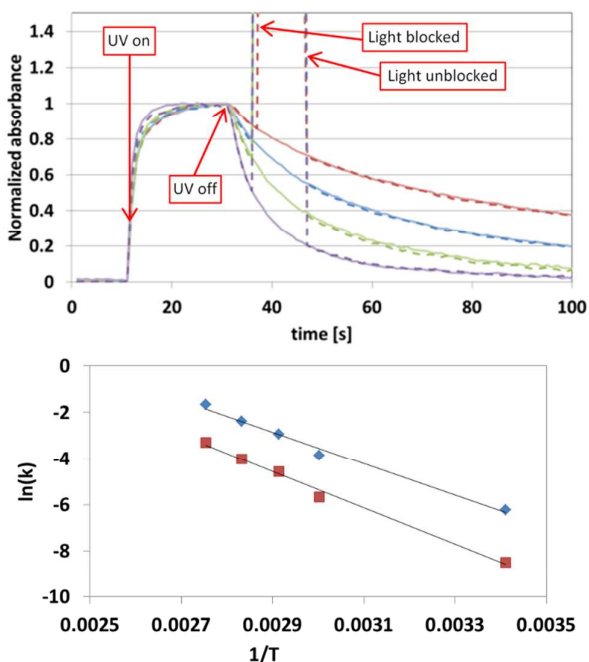


Figure 3. Top: Normalized Thermal Back reaction of UBMOF-2 by temperature at 600 nm. Light blocked for 10 sec after 5 sec of back reaction (dotted line), full back reaction (full line). 90° C (red), 80° C (blue), 70° C (green), 60° C (purple) Bottom: Arrhenius plot of k_1 (blue diamonds) and k_2 (red squares).

within the framework may arise from local chemical inhomogeneity as is often observed in solid-state photochromic systems.⁴¹

Fatigue and Atropisomerization in UBMOF-2

Cycling experiments were performed in order to assess the robustness of the photo-switching process within the **UBMOF-2** lattice. In these experiments, a single **UBMOF-2** crystal is irradiated with a controlled dose of UV light and then allowed to thermally relax back to the ring-open form (Figure 4). With each cycle, the maximum change in absorbance is lower than the previous indicating a reduction in the photochemical activity of the crystal due to the formation of a photochemically inactive fatigue product. With prolonged cycling or irradiation, single crystals of **UBMOF-2** eventually reach a fully fatigued state and cease turning blue and remain colourless upon irradiation with UV light.

Fatigue in the diarylethene class of molecules is often a consequence of chemical degradation, primarily photo-oxidation or methyl rearrangement of the ring-closed form of the molecule that leads to highly coloured and chemically distinct species that are easily observed by optical spectroscopy.^{36,42-44} The lack of permanent visible coloration of the fully fatigued **UBMOF-2** crystals indicates that the

fatigue product is not one of the aforementioned coloured reaction by-products. The ¹H-NMR spectra of neat **PhTPDC** and solutions of acid digested fresh and fully fatigued **UBMOF-2** crystals were nearly identical further confirming that the linker was not photo-chemically degraded (Figure S3). An additional key observation is that solutions of digested fully fatigued **UBMOF-2** crystals are photochromic. When the acid used for digestion is added to fully fatigued crystals being irradiated by 365 nm light, the solution surrounding the crystals immediately turns blue. As photochromic activity in diarylethenes is highly dependent on molecular conformation, the digestion experiments suggest that the fatigue product is likely due to the linker adopting a photo-inactive conformation following ring-opening and that this species is able to rapidly relax back to a photo-active conformer once released from the lattice.

Shown in Figure 5 is the potential energy surface (PES) corresponding to the rotation of one thiophene group 360° about the thiophene-phenanthrene bond in 2° steps; the geometry was optimized at each step. Examination of this PES reveals a number of intriguing features including the presence of four local minima, each one being a distinct conformer of the ring-open isomer of **PhTPDC**.

Generally, only two conformers (atropisomers) are considered when assessing the photoactivity of a diarylethene: the parallel and anti-parallel rotamers. In the *parallel* (para) conformer, the methyl groups attached to the reactive carbon atoms reside on the same side of a plane containing the central double bond and the bonds to the aryl groups. In the case of **PhTPDC**, this plane necessarily contains the phenanthrene portion of the molecule. For the *anti-parallel* (anti) conformer, the methyl groups attached to the reactive carbon atoms reside on opposite sides of the plane. While the para rotamer is never photoactive, the anti conformer is only photoactive when the reactive carbon atoms of the two thiophene rings are within 4.2 Å.⁴⁵

The potential energy wells for the para and anti isomers exhibit similar topology. The structures at the centre of the

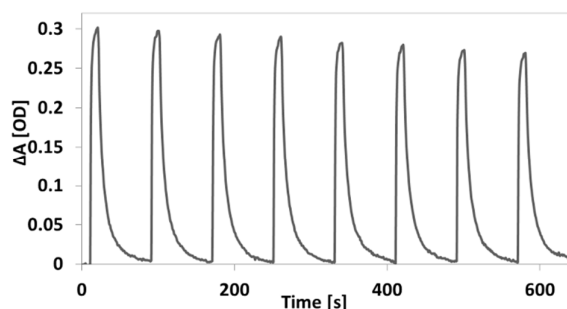


Figure 4. Trace of the absorbance at 600 nm of a single crystal of UBMOF-2 cycling experiment at 363.15 K (as described in the text) showing the gradual loss of the maximal photo-induced coloration.

wells (Figure 5, b and e) are local maxima which correspond to molecular geometries in which the planes of the thiophene groups are oriented approximately perpendicular to the phenanthrene plane. The local minima found on either side of the maxima (Figure 5, a, c, d, and f) correspond to molecular

geometries in which the two thiophene groups are rotated between 20° and 30° from perpendicular to the phenanthrene plane. In all six geometries, the two thiophene planes are approximately parallel. This suggests that the parallel (*meso*) isomer proposed previously for related phenanthrene-based

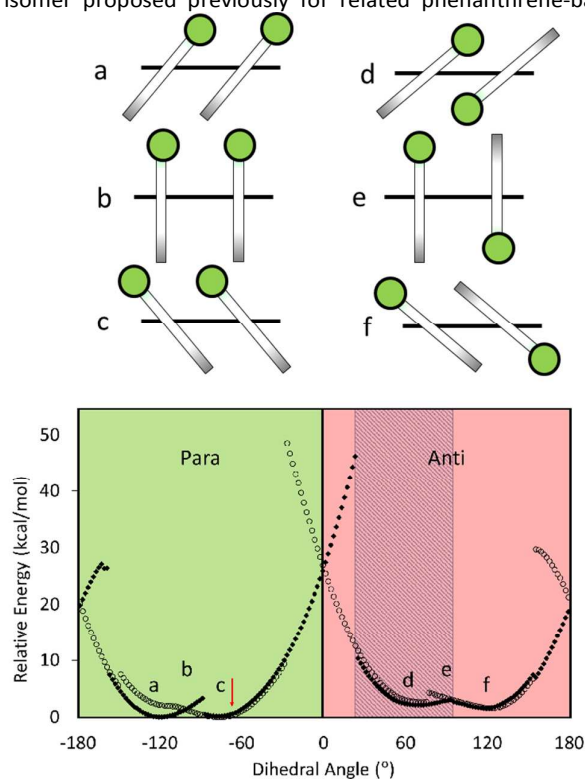


Figure 5 . Illustration of the conformers of PhTPDC (upper) along with the calculated potential energy surface for the dihedral rotation of one thiophene ring (lower). The black line in the illustrations represents the phenanthrene plane and the bars represent the orientation of the thiophene groups relative to the plane. The green circles correspond to the location of the photo-active carbon atoms within the thiophene group. The diagonally shaded region in the graph corresponds to molecular geometries which should exhibit photoactivity, i.e. anti-conformers in which the reactive carbon-carbon distance is 4.2 Å or less. The closed and open circles correspond to calculations in which the thiophene group is rotated clockwise and counter-clockwise, respectively.

diarylethenes may not be the lowest energy parallel conformer.³⁷

Of the four low energy structures, only conformer d is expected to be photoactive, thus, conformers a, c, and f are considered likely fatigue species. A large energetic barrier exists between the anti and para forms which suggests that the conversion between the anti and para isomers ($c \leftrightarrow d$ or $a \leftrightarrow f$) should be slow relative to the conversion between isomers of the same type ($a \leftrightarrow c$ or $d \leftrightarrow f$). In related phenanthrene-based diarylethenes, the activation energy for conversion between anti and para isomers was determined to be approximately 110 kJ mol⁻¹ leading to half-lives for the individual isomers of several thousand hours.³⁷

The ratio of para and anti isomers in solution can be determined by NMR spectroscopy using the slight difference in chemical shift of the thiophene methyl groups. If the fatigue species is a para isomer, NMR spectroscopy performed on fatigued crystals immediately following digestion should reveal a ratio of isomers which is enriched in the para species relative to a digested sample of photochemically active **UBMOF-2** crystals. Interestingly, this was not what was observed. Instead, the ratio between the para and anti isomers of **PhTPDC** was the same between freshly digested **UBMOF-2**, as well as the digested fully fatigued **UBMOF-2**. These results combined with the observation that the fatigued crystals immediately regain photoactivity upon digestion suggest that conformer f, in which the thiophenes remain anti-parallel to one another yet adopt a photo-inactive geometry is the most likely candidate for the fatigue product. Future work will attempt to identify features unique to the lattice that are responsible for the formation of the fatigue species.

Conclusions

In summary, we report the synthesis and characterization of a novel photo-responsive phenanthrene-based diarylethene linker and metal-organic framework, **UBMOF-2**. While the linker exhibits bi-directional photoswitching in solution, the cycloreversion process in **UBMOF-2** was found to be entirely thermally driven. Cycling experiments revealed that **PhTPDC**, the photoactive species within the lattice, was gradually converted to a photo-inactive atropisomer. The rapid regeneration of photoactivity upon digestion and lack of spectroscopic evidence of a permanent photodegradation by-product supports a model in which the thiophene groups adopt a photoinactive orientation following thermally driven cycloreversion which is stabilized by the framework lattice. An analysis of the potential energy surface associated with rotation of one thiophene group reveals a number of key energetic minima, only one of which is expected to be photoactive. Future photo-responsive MOFs will utilize the unique microenvironment of void spaces to stabilize select atropisomers for advanced light-responsive crystalline materials.

Methods

Optical Spectroscopy: Solution UV/Visible spectra were collected using quartz cuvettes (1 cm path length) on a Perkin Elmer Lambda 35 spectrometer. Visible absorption spectroscopy on single crystal samples were measured using an inverted microscope (Olympus model IMT-2) coupled through a fibre optic cable to a spectrometer (Ocean Optics USB4000-UV-VIS). All experiments were performed using the tungsten lamp of the microscope with a 495 nm long pass filter to prevent cyclization by shorter wavelengths. Samples were irradiated using a 365 nm UV diode (Thor Labs, M365F1, 3.0 mW). To prevent sample degradation, all measurements were performed on crystals in a dimethylformamide (DMF) solution

in a sealed rectangular glass capillary (2 x 0.2 mm, Vitrocom). A microscopy cryostat (Cryoindustries, RC102-CFM) was used for temperature control throughout the experiments. The single crystals examined varied in size from 50 to 200 μm in thick.

Theoretical Calculations: DFT calculations utilizing the ωB97XD long-range and dispersion corrected functional were performed on PhTPDC with a 6-31G* basis set to qualitatively study the energetic barriers of rotation of the thiophenes. By employing a dispersion-corrected functional, the interactions of the thiophenes with the phenanthrene backbone and with each other were taken into account, and these interaction were observed in the resultant energies of rotation. The model was first geometry optimized in the anti-parallel conformation, then, starting from the optimized geometry, one thiophene group was rotated 360° in 2° steps. At each step the molecule was allowed to relax, with the exception of the dihedral angle which defines the thiophene rotation. Due to the observed hysteresis of the energy of PhTPDC with respect to rotation, two calculations were performed with the thiophene group rotating in opposite directions.

Acknowledgements

Partial support of this work was provided by the University at Buffalo, The State University of New York. ChemMatCARS Sector 15 is principally supported by the Divisions of Chemistry (CHE) and Materials Research (DMR), National Science Foundation, under Grant Number NSF/CHE-1346572. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract Number DE-AC02-06CH11357.

Supplementary Information

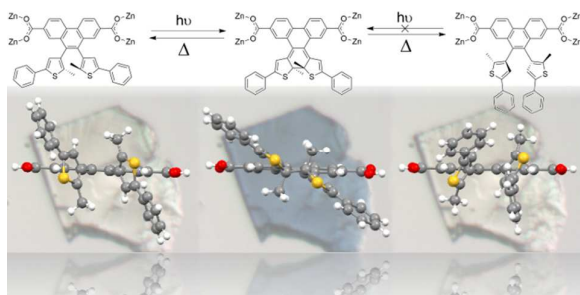
Full details of the synthesis and characterization of PhTPDC, the reaction intermediates, and the synthesis of UBMOF-2, crystal structure and refinement data, details of acid digestion experiments

Notes and references

- Kenji, M.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 7195.
- Kumar, S.; Watkins, D. L.; Fujiwara, T. *Chem. Commun. (Cambridge, U. K.)* **2009**, 4369.
- Martin, S.; Haiss, W.; Higgins, S. J.; Nichols, R. J. *Nano Lett.* **2010**, *10*, 2019.
- Wagner, K.; Byrne, R.; Zanoni, M.; Gambhir, S.; Dennany, L.; Breukers, R.; Higgins, M.; Wagner, P.; Diamond, D.; Wallace, G. G.; Officer, D. L. *J. Am. Chem. Soc.* **2011**, *133*, 5453.
- Davis, D. A.; Hamilton, A.; Yang, J. L.; Cremer, L. D.; Van Gough, D.; Potisek, S. L.; Ong, M. T.; Braun, P. V.; Martinez, T. J.; White, S. R.; Moore, J. S.; Sottos, N. R. *Nature* **2009**, *459*, 68.
- Ferri, V.; Elbing, M.; Pace, G.; Dickey, M. D.; Zharnikov, M.; Samori, P.; Mayor, M.; Rampi, M. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 3407.

- Inouye, M.; Akamatsu, K.; Nakazumi, H. *J. Am. Chem. Soc.* **1997**, *119*, 9160.
- O'Bryan, G.; Wong, B. M.; McElhanon, J. R. *ACS Appl. Mater. Interfaces* **2010**, *2*, 1594.
- Park, I. S.; Jung, Y.-S.; Lee, K.-J.; Kim, J.-M. *Chem. Commun. (Cambridge, U. K.)* **2010**, *46*, 2859.
- Shao, N.; Jin, J. Y.; Wang, H.; Zhang, Y.; Yang, R. H.; Chan, W. H. *Anal. Chem.* **2008**, *80*, 3466.
- Evans, R. A.; Hanley, T. L.; Skidmore, M. A.; Davis, T. P.; Such, G. K.; Yee, L. H.; Ball, G. E.; Lewis, D. A. *Nat. Mater.* **2005**, *4*, 249.
- Irie, M.; Uchida, K. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 985.
- Raymo, F. M.; Giordani, S.; White, A. J. P.; Williams, D. J. *J. Org. Chem.* **2003**, *68*, 4158.
- Koshima, H.; Ojima, N.; Uchimoto, H. *J. Am. Chem. Soc.* **2009**, *131*, 6890.
- Morimoto, M.; Irie, M. *J. Am. Chem. Soc.* **2010**, *132*, 14172.
- Terao, F.; Morimoto, M.; Irie, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 901.
- Yu, Y. L.; Nakano, M.; Ikeda, T. *Nature* **2003**, *425*, 145.
- Shimoboji, T.; Larenas, E.; Fowler, T.; Kulkarni, S.; Hoffman, A. S.; Stayton, P. S. *Proc. Natl. Acad. Sci. U. S. A.* **2002**, *99*, 16592.
- Chandrasekaran, V.; Lindhorst, T. K. *Chem. Commun. (Cambridge, U. K.)* **2012**, 48.
- Al-Atar, U.; Fernandes, R.; Johnsen, B.; Baillie, D.; Branda, N. R. *J. Am. Chem. Soc.* **2009**, *131*.
- Yanai, N.; Uemura, T.; Inoue, M.; Matsuda, R.; Fukushima, T.; Tsujimoto, M.; Isoda, S.; Kitagawa, S. *J. Am. Chem. Soc.* **2012**, *134*, 4501.
- Park, J.; Yuan, D.; Pham, K. T.; Li, J.-R.; Yakovenko, A.; Zhou, H.-C. *J. Am. Chem. Soc.* **2011**, *134*, 99.
- Modrow, A.; Zargarani, D.; Herges, R.; Stock, N. *Dalton Trans.* **2011**, *40*, 4217.
- Bernt, S.; Feyand, M.; Modrow, A.; Wack, J.; Senker, J.; Stock, N. *Eur. J. Inorg. Chem.* **2011**, *2011*, 5378.
- Hermann, D.; Emerich, H.; Lepski, R.; Schaniel, D.; Ruschewitz, U. *Inorg. Chem.* **2013**, *52*, 2744.
- Brown, J. W.; Henderson, B. L.; Kiesz, M. D.; Whalley, A. C.; Morris, W.; Grunder, S.; Deng, H.; Furukawa, H.; Zink, J. I.; Stoddart, J. F.; Yaghi, O. M. *Chemical Science* **2013**, *4*, 2858.
- Walton, I. M.; Cox, J. M.; Coppin, J. A.; Linderman, C. M.; Patel, D. G. D.; Benedict, J. B. *Chem. Commun. (Cambridge, U. K.)* **2013**, *49*, 8012.
- Patel, D. G. D.; Walton, I. M.; Cox, J. M.; Gleason, C. J.; Butzer, D. R.; Benedict, J. B. *Chem. Commun. (Cambridge, U. K.)* **2014**, *50*, 2653.
- Luo, F.; Fan, C. B.; Luo, M. B.; Wu, X. L.; Zhu, Y.; Pu, S. Z.; Xu, W.-Y.; Guo, G.-C. *Angew. Chem., Int. Ed.* **2014**, *53*, 9298.
- Collins, T. *Science* **2001**, *291*, 48.
- Fiksel, J. *Environ. Sci. Technol.* **2003**, *37*, 5330.
- Grassian, V. H.; Meyer, G.; Abruña, H.; Coates, G. W.; Achenie, L. E.; Allison, T.; Bruntschwig, B.; Ferry, J.; Garcia-Garibay, M.; Gardea-Torresdey, J.; Grey, C. P.; Hutchison, J.; Li, C.-J.; Liotta, C.; Raguskas, A.; Minter, S.; Mueller, K.; Roberts, J.; Sadik, O.; Schmehl, R.; Schneider, W.; Selloni, A.; Stair, P.; Stewart, J.; Thorn, D.; Tyson, J.; Voelker, B.; White, J. M.; Wood-Black, F. *Environ. Sci. Technol.* **2007**, *41*, 4840.
- Irie, M. *Chem. Rev.* **2000**, *100*, 1685.
- Wanko, M.; Feringa, B. L. *Chem. Commun. (Cambridge, U. K.)* **2007**, *0*, 1745.
- He, J.; Wang, T.; Chen, S.; Zheng, R.; Chen, H.; Li, J.; Zeng, H. *Journal of Photochemistry and Photobiology A: Chemistry* **2014**, *277*, 45.
- Patel, D. G.; Walton, I. M.; Cox, J. M.; Gleason, C. J.; Butzer, D. R.; Benedict, J. B. *Chem. Commun. (Cambridge, U. K.)* **2014**, *50*, 2653.

- 37 Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, 295, 469.
- 38 Sworakowski, J.; Janus, K.; Nešpůrek, S. *Adv. Colloid Interface Sci.* **2005**, 116, 97.
- 39 Irie, M.; Lifka, T.; Uchida, K.; Kobatake, S.; Shindo, Y. *Chem. Commun. (Cambridge, U. K.)* **1999**, 747.
- 40 Higashiguchi, K.; Matsuda, K.; Yamada, T.; Kawai, T.; Irie, M. *Chem. Lett.* **2000**, 29, 1358.
- 41 Higashiguchi, K.; Matsuda, K.; Kobatake, S.; Yamada, T.; Kawai, T.; Irie, M. *Bull. Chem. Soc. Jpn.* **2000**, 73, 2389.
- 42 Kobatake, S.; Uchida, K.; Tsuchida, E.; Irie, M. *Chem. Commun. (Cambridge, U. K.)* **2002**, 2804.
- 43
- 44 (1)Kenji, M.; Irie, M. *J. Am. Chem. Soc.* **2000**, 122, 7195.
- 45 (2)Kumar, S.; Watkins, D. L.; Fujiwara, T. *Chem. Commun. (Cambridge, U. K.)* **2009**, 4369.
- 46 (3)Martin, S.; Haiss, W.; Higgins, S. J.; Nichols, R. J. *Nano Lett.* **2010**, 10, 2019.
- 47 (4)Wagner, K.; Byrne, R.; Zanon, M.; Gambhir, S.; Dennany, L.; Breukers, R.; Higgins, M.; Wagner, P.; Diamond, D.; Wallace, G. G.; Officer, D. L. *J. Am. Chem. Soc.* **2011**, 133, 5453.
- 48 (5)Davis, D. A.; Hamilton, A.; Yang, J. L.; Cremer, L. D.; Van Gough, D.; Potisek, S. L.; Ong, M. T.; Braun, P. V.; Martinez, T. J.; White, S. R.; Moore, J. S.; Sottos, N. R. *Nature* **2009**, 459, 68.
- 49 (6)Ferri, V.; Elbing, M.; Pace, G.; Dickey, M. D.; Zharnikov, M.; Samori, P.; Mayor, M.; Rampi, M. A. *Angew. Chem., Int. Ed.* **2008**, 47, 3407.
- 50 (7)Inouye, M.; Akamatsu, K.; Nakazumi, H. *J. Am. Chem. Soc.* **1997**, 119, 9160.
- 51 (8)O'Bryan, G.; Wong, B. M.; McElhanon, J. R. *ACS Appl. Mater. Interfaces* **2010**, 2, 1594.
- 52 (9)Park, I. S.; Jung, Y.-S.; Lee, K.-J.; Kim, J.-M. *Chem. Commun. (Cambridge, U. K.)* **2010**, 46, 2859.
- 53 (10)Shao, N.; Jin, J. Y.; Wang, H.; Zhang, Y.; Yang, R. H.; Chan, W. H. *Anal. Chem.* **2008**, 80, 3466.
- 54 (11)Evans, R. A.; Hanley, T. L.; Skidmore, M. A.; Davis, T. P.; Such, G. K.; Yee, L. H.; Ball, G. E.; Lewis, D. A. *Nat. Mater.* **2005**, 4, 249.
- 55 (12)Irie, M.; Uchida, K. *Bull. Chem. Soc. Jpn.* **1998**, 71, 985.
- 56 (13)Raymo, F. M.; Giordani, S.; White, A. J. P.; Williams, D. J. *J. Org. Chem.* **2003**, 68, 4158.
- 57 (14)Koshima, H.; Ojima, N.; Uchimoto, H. *J. Am. Chem. Soc.* **2009**, 131, 6890.
- 58 (15)Morimoto, M.; Irie, M. *J. Am. Chem. Soc.* **2010**, 132, 14172.
- 59 (16)Terao, F.; Morimoto, M.; Irie, M. *Angew. Chem., Int. Ed.* **2012**, 51, 901.
- 60 (17)Yu, Y. L.; Nakano, M.; Ikeda, T. *Nature* **2003**, 425, 145.
- 61 (18)Shimoboji, T.; Larenas, E.; Fowler, T.; Kulkarni, S.; Hoffman, A. S.; Stayton, P. S. *Proc. Natl. Acad. Sci. U. S. A.* **2002**, 99, 16592.
- 62 (19)Chandrasekaran, V.; Lindhorst, T. K. *Chem. Commun. (Cambridge, U. K.)* **2012**, 48.
- 63 (20)Al-Atar, U.; Fernandes, R.; Johnsen, B.; Baillie, D.; Branda, N. R. *J. Am. Chem. Soc.* **2009**, 131.
- 64 (21)Yanai, N.; Uemura, T.; Inoue, M.; Matsuda, R.; Fukushima, T.; Tsujimoto, M.; Isoda, S.; Kitagawa, S. *J. Am. Chem. Soc.* **2012**, 134, 4501.
- 65 (22)Park, J.; Yuan, D.; Pham, K. T.; Li, J.-R.; Yakovenko, A.; Zhou, H.-C. *J. Am. Chem. Soc.* **2011**, 134, 99.
- 66 (23)Modrow, A.; Zargarani, D.; Herges, R.; Stock, N. *Dalton Trans.* **2011**, 40, 4217.
- 67 (24)Bernt, S.; Feyand, M.; Modrow, A.; Wack, J.; Senker, J.; Stock, N. *Eur. J. Inorg. Chem.* **2011**, 2011, 5378.
- 68 (25)Hermann, D.; Emerich, H.; Lepski, R.; Schaniel, D.; Ruschewitz, U. *Inorg. Chem.* **2013**, 52, 2744.
- 69 (26)Brown, J. W.; Henderson, B. L.; Kiesz, M. D.; Whalley, A. C.; Morris, W.; Grunder, S.; Deng, H.; Furukawa, H.; Zink, J. I.; Stoddart, J. F.; Yaghi, O. M. *Chemical Science* **2013**, 4, 2858.
- 70 (27)Walton, I. M.; Cox, J. M.; Coppin, J. A.; Linderman, C. M.; Patel, D. G. D.; Benedict, J. B. *Chem. Commun. (Cambridge, U. K.)* **2013**, 49, 8012.
- 71 (28)Patel, D. G. D.; Walton, I. M.; Cox, J. M.; Gleason, C. J.; Butzer, D. R.; Benedict, J. B. *Chem. Commun. (Cambridge, U. K.)* **2014**, 50, 2653.
- 72 (29)Park, J.; Feng, D.; Yuan, S.; Zhou, H.-C. *Angew. Chem., Int. Ed.* **2015**, 54, 430.
- 73 (30)Li, H.-Y.; Wei, Y.-L.; Dong, X.-Y.; Zang, S.-Q.; Mak, T. C. W. *Chem. Mater.* **2015**, 27, 1327.
- 74 (31)Aulakh, D.; Varghese, J. R.; Wriedt, M. *Inorg. Chem.* **2015**, 54, 1756.
- 75 (32)Luo, F.; Fan, C. B.; Luo, M. B.; Wu, X. L.; Zhu, Y.; Pu, S. Z.; Xu, W.-Y.; Guo, G.-C. *Angew. Chem., Int. Ed.* **2014**, 53, 9298.
- 76 (33)Collins, T. *Science* **2001**, 291, 48.
- 77 (34)Fiksel, J. *Environ. Sci. Technol.* **2003**, 37, 5330.
- 78 (35)Grassian, V. H.; Meyer, G.; Abruña, H.; Coates, G. W.; Achenie, L. E.; Allison, T.; Brunschwig, B.; Ferry, J.; Garcia-Garibay, M.; Gardea-Torresdey, J.; Grey, C. P.; Hutchison, J.; Li, C.-J.; Liotta, C.; Raguskas, A.; Minter, S.; Mueller, K.; Roberts, J.; Sadik, O.; Schmehl, R.; Schneider, W.; Selloni, A.; Stair, P.; Stewart, J.; Thorn, D.; Tyson, J.; Voelker, B.; White, J. M.; Wood-Black, F. *Environ. Sci. Technol.* **2007**, 41, 4840.
- 79 (36)Irie, M. *Chem. Rev.* **2000**, 100, 1685.
- 80 (37)Walko, M.; Feringa, B. L. *Chem. Commun. (Cambridge, U. K.)* **2007**, 0, 1745.
- 81 (38)He, J.; Wang, T.; Chen, S.; Zheng, R.; Chen, H.; Li, J.; Zeng, H. *Journal of Photochemistry and Photobiology A: Chemistry* **2014**, 277, 45.
- 82 (39)Patel, D. G.; Walton, I. M.; Cox, J. M.; Gleason, C. J.; Butzer, D. R.; Benedict, J. B. *Chem. Commun. (Cambridge, U. K.)* **2014**, 50, 2653.
- 83 (40)Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, 295, 469.
- 84 (41)Sworakowski, J.; Janus, K.; Nešpůrek, S. *Adv. Colloid Interface Sci.* **2005**, 116, 97.
- 85 (42)Irie, M.; Lifka, T.; Uchida, K.; Kobatake, S.; Shindo, Y. *Chem. Commun. (Cambridge, U. K.)* **1999**, 747.
- 86 (43)Higashiguchi, K.; Matsuda, K.; Yamada, T.; Kawai, T.; Irie, M. *Chem. Lett.* **2000**, 29, 1358.
- 87 (44)Higashiguchi, K.; Matsuda, K.; Kobatake, S.; Yamada, T.; Kawai, T.; Irie, M. *Bull. Chem. Soc. Jpn.* **2000**, 73, 2389.
- 88 (45)Kobatake, S.; Uchida, K.; Tsuchida, E.; Irie, M. *Chem. Commun. (Cambridge, U. K.)* **2002**, 2804.
- 89
- 90



Stabilization of unfavorable rotational isomers within the nanoporous crystalline matrix reduces the useful lifetime of this photo-switchable material.