Functional Materials

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Photoswitching CO_2 Capture and Release in a Photochromic Diarylethene Metal–Organic Framework**

Feng Luo, Cong Bin Fan, Ming Biao Luo, Xiao Liu Wu, Yan Zhu, Shou Zhi Pu, Wen-Yuan Xu, and Guo-Cong Guo**

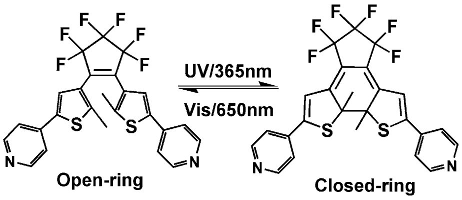
Abstract: *We demonstrate herein a promising pathway towards low-energy CO_2 capture and release triggered by UV and visible light. A photosensitive diarylethene ligand was used to construct a photochromic diarylethene metal–organic framework (DMOF). A local photochromic reaction originating from the framework movement induced by the photoswitchable diarylethene unit resulted in record CO_2-desorption capacity of 75 % under static irradiation and 76 % under dynamic irradiation.*

Diarylethene derivatives are one of the most promising families of photochromic compounds. They undergo photoinduced isomerization involving ring-opening/closing reactions triggered by UV and visible light, mainly as a result of their fatigue-resistant and thermally irreversible properties. They have potential for application in optoelectronic devices, such as ultrahigh-density optical data storage, logic gates, molecular wires, and sensors.[1–3] Diarylethene derivatives have been reported as switching materials, including fluorescent molecular switches, photochromic chiral switches, photocontrolled conductivity switches, and liquid-crystal switches.[4–6] The photostability of these derivatives was also found to be very high, with more than 10^4 photoinduced coloration/decoloration cycles and a lifetime of more than a thousand years at 30 °C.[2]

Another family of compounds, metal–organic frameworks (MOFs), show unique potential as sorbents for CO_2 capture and release in view of their structurally designable nature and large capacity to selectively absorb CO_2.[7–9] However, in essence the use of MOF adsorbents relies on pressure, temperature, and/or vacuum swings, thus implying that the release process of adsorbed CO_2 mainly depends on vacuum or heating operations, which are very energy-consuming. The search for new stimuli with a lower or even zero energy cost for triggering CO_2 release is therefore an urgent task and a big challenge. In this regard, light, and especially sunlight, is the best choice.

Recent advances reveal that the incorporation of light-sensitive azobenzene units into the metal–organic framework could enable this goal to be reached.[10–12] The choice of the azobenzene unit lies in the fact that under UV irradiation it can undergo reversible *trans*-to-*cis* isomerization with a distance change between the *para* carbon atoms from 9 to 5.5 Å. The structural change greatly facilitates CO_2 release. In a recent finding by Hill and co-workers, up to 64 % desorption capacity was observed.[12] For true low-energy CO_2 capture and release, the development of new MOF materials with similar responses in the visible region is imperative.

Taking these points into account, we have developed a distinct strategy in this respect. A diarylethene derivative (L; Scheme 1) with two N-donor sites was used to construct a diarylethene MOF (DMOF). The photoresponsive diarylethene unit undergoes an exquisite change triggered by UV and visible light between open-ring and closed-ring isomers, and the large skeletal structure provides a chance to construct porous DMOFs. To our best of knowledge, DMOFs have not been reported previously, although an earlier study showed that MOFs with diarylethene derivatives as isolated molecules in channels showed photoresponsive and photochromic behavior under polarized light.[13] In our study, to construct a neutral porous DMOF, we adopted a strategy of combining mixed N- and O-donor ligands with the commonly selected dicarboxylate ligand of biphenyl-4,4′-dicarboxylic acid (H_2bpdc).



Scheme 1. Photochromic reaction of the diarylethene derivative (L) under UV and visible light.

The photoswitchable DMOF, namely, Zn(L)(bpdc)·solvents (**1**), was synthesized solvo(hydro)thermally

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[*] Prof. Dr. F. Luo, Prof. Dr. G.-C. Guo
State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences
Fuzhou, Fujian 350002 (China)
E-mail: gcguo@fjirsm.ac.cn

Prof. Dr. F. Luo, M. B. Luo, Dr. X. L. Wu, Y. Zhu, W.-Y. Xu
College of Biology, Chemistry and Material Science
East China Institute of Technology
Fuzhou, Jiangxi 344000 (China)

Prof. Dr. C. B. Fan, S. Z. Pu
Jiangxi Key Laboratory of Organic Chemistry
Jiangxi Science and Technology Normal University
Nanchang 330013 (China)
E-mail: pushouzhi@tsinghua.org.cn

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from $Zn(NO_3)_2{\cdot}6H_2O$, H_2bpdc, and L (see Scheme 1) in a ratio of 1:1:1. The disordered solvent molecules in **1** could not be exactly determined by single-crystal X-ray diffraction, and their presence was further confirmed by thermogravimetric (TG) and elemental analyses, which indicated their identity as two dimethylformamide (DMF) molecules and one water molecule.

The structure of **1** gives a chiral $P2_12_12_1$ space group with a Flack factor of 0.017(17), thus implying spontaneous resolution from an achiral source. The chiral character of **1** was further confirmed by solid-state circular dichroism (CD), which gave a positive Cotton effect at $\lambda = 224$ nm and a negative Cotton effect at $\lambda = 385$ nm (see Figure S1 in the Supporting Information). The Zn^{II} site is four-coordinated by two $bpdc^{2-}$ oxygen atoms and two L nitrogen atoms, thus creating a tetrahedral geometry (Figure 1 a). The L ligand adopts the open-ring form. The two $bpdc^{2-}$ ligands (in the bis(monodentate) mode) and the two L ligands are each linked to two Zn^{II} ions. Such connectivity generates a four-connected **dia** net with fivefold interpenetration (Figure 1 b,c).[14] Consequently, the solvent-accessible volume is largely reduced, but considerable free volume is also observed (36.9 % of the cell volume),[15] indicative of a porous framework of **1**. To the best of our knowledge, compound **1** is the first porous DMOF.

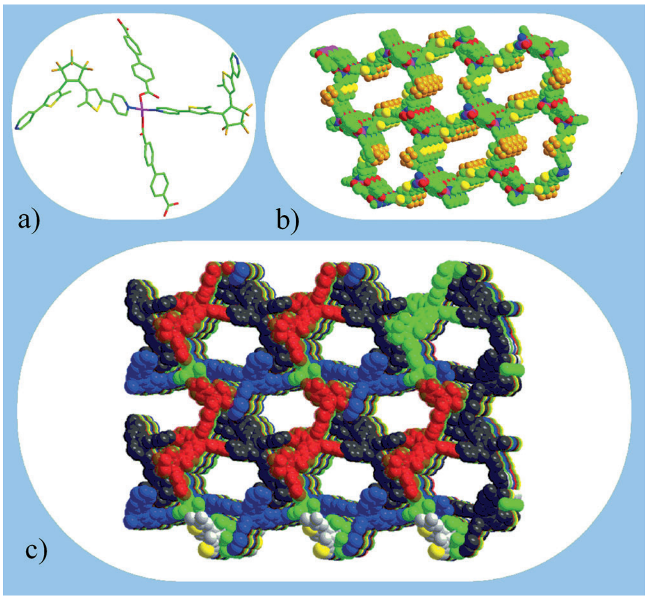

Figure 1. a) Coordination environment of the metal ions in **1** (all hydrogen atoms are omitted for clarity). Color code: C green, N blue, O red, Zn purple, S yellow, F orange. b) View of the 3D **dia** net of **1** along the *b* axis. c) View along the *b* axis of the fivefold interpenetrating **dia** net of **1** with solvent-free channels (8.4×10.8 Å^2; each color represents one identical **dia** net).

As observed in other diarylethene derivatives,[1–6] the single crystal of **1** underwent a fast photochromic reaction (Figure 2). Upon UV irradiation, it turned blue, whereas the blue color disappeared upon irradiation with visible light. Generally speaking, the photochromic mechanism for diarylethene derivatives is derived from the transformation between the open-ring and closed-ring forms, as the two forms show different absorption characteristics (strong UV absorption in the open-ring form but strong visible-light absorption in the closed-ring form), which result in the different colors observed. The similarity observed between the absorption properties of **1** and the L ligand suggests that the corresponding photochromic reaction, with the color change from buff to blue, is directly related to the structural transformation of the L ligand from the open-ring to the closed-ring conformation. To confirm this hypothesis, we recorded the UV/Vis spectrum of **1** in the solid. As shown in Figure 3, solid **1** displays an absorption maximum at around 330 nm, which is characteristic of the π–π* transitions of the L ligand.[16] Upon irradiation with 300 nm light for 1 min, the sample changed color to blue, and two absorption bands with peaks around 330 and 629 nm were observed. This result indicates that the open-ring form is transformed into the closed-ring form, but that the transformation is not completed,[17] as evidenced by the coexistence of the absorption peaks around 330 and 629 nm. Moreover, with respect to the L ligand in the solid, the blue-shift of the absorption bands (330 and 629 nm) indicates a significant electronic effect related to the coordination of the pyridine ring.[16]

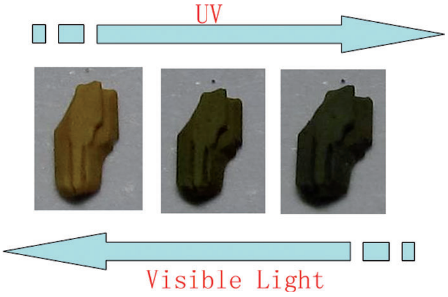

Figure 2. Photographs showing the photochromic reaction upon the exposure of a single crystal of **1** to UV and visible light.

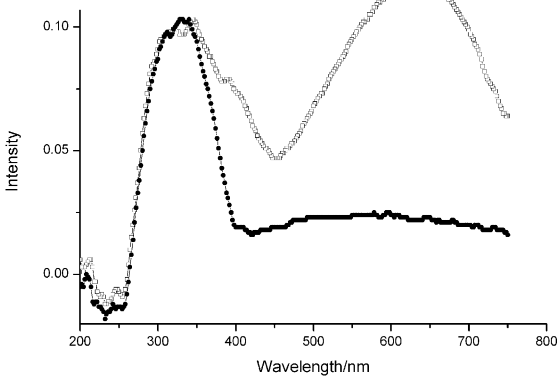

Figure 3. Absorption spectra of **1** in the solid. □: sample under UV for 1 min; ●: sample.

Considering the d^{10} Zn^{II} metal ion, the luminescence performance of organic ligands, and the photochromism of

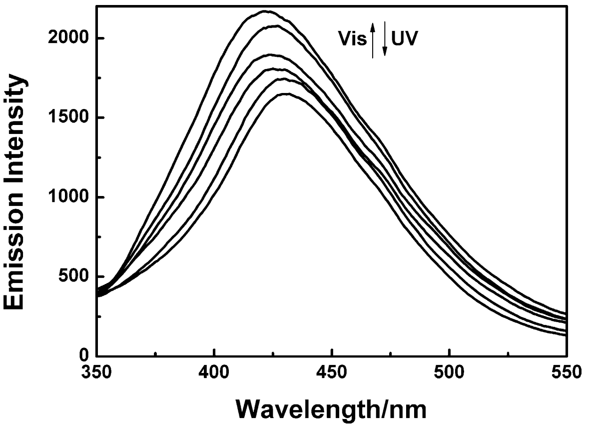

Figure 4. Photocontrolled tunable luminescence performance of **1** in the solid under UV and visible light (the spectrum was recorded of the samples under visible or UV light every 5 s).

the L ligand, we tested the photocontrolled luminescence of **1**. As shown in Figure 4, compound **1** in the solid shows strong blue emission at 421 nm when excited at 285 nm. Interestingly, photocontrolled tunable luminescence was observed under the trigger of UV or visible light. The strength of the blue emission of **1** was gradually reduced under UV irradiation at 300 nm, but could be recovered under visible light. This behavior is indicative of reversible photocontrolled tunable luminescence. In contrast to the solvent-dependent or excitation-wavelength-based tunable luminescence observed previously in MOFs,[18,19] our system displays photodependent tunable luminescence.

To evaluate the thermostability of the skeleton of **1** and to confirm the permanent porosity of this material, we carried out thermogravimetric (TG) analysis, various-temperature PXRD (powder X-ray diffraction) studies, and N_2-adsorption analysis. The first weight loss of 16.7 % below 220 °C should correspond to the loss of all solvent molecules (two DMF molecules plus one water molecule, calcd: 16.5 %). Then, below 300 °C, a platform suggesting no weight loss was observed. The following major weight loss above 300 °C indicates the chemical decomposition of organic ligands (see Figure S2). The PXRD pattern of **1** (see Figure S3) also indicates high thermostability below 300 °C, even after the loss of all solvent molecules. The unit cell could still be determined by single-crystal X-ray diffraction after **1** had been heated at 300 °C, and was comparable with the unit cell of **1**, but the final structure could not be solved owing to decreased single crystallinity. Further evidence for the remarkable stability of this crystalline material is that the crystallinity of the samples of **1** were well-maintained after the repetitious experiments of N_2 and CO_2 adsorption, and could be solved well by single-crystal X-ray diffraction.

Before the N_2- and CO_2-adsorption experiments were carried out, the solid samples of **1** were treated by immersion in methanol for 2 days, and the solvent-exchanged samples were then degassed under high vacuum at 100 °C for 12 h.[20] To confirm that the solvent had been completely removed, we carried out a TG experiment. It was clear that below 300 °C there was no detectable weight loss, thus indicating the complete removal of solvents. In a N_2-adsorption experiment at 77 K, almost no N_2 adsorption was observed (see Figure S4). However, a remarkable feature were the CO_2 isotherms at 196, 273, and 298 K, which reveal a type I behavior typical for microporous materials (see Figure S4).[8] This selective CO_2 adsorption over N_2 adsorption may be ascribed to the special quadrupole moment of CO_2 (13.4 $C\,m^2$), which has been attested to be a big contributor to the high affinity between CO_2 molecules and the MOF skeleton and the excellent CO_2-adsorption capability.[8,9] By contrast, the N_2 molecule has a smaller quadrupole moment (4.7 $C\,m^2$) and consequently negligible contact with the MOF skeleton; it cannot be effectively adsorbed on the pore surface. The CO_2-adsorption capacity at 1 atm was found to be 32.3 (196 K), 14.3 (273 K), and 5.0 $cm^3\,g^{-1}$ (298 K). These values are comparable with reported values.[8,9]

Notably, after UV irradiation, the blue samples of **1** showed significant CO_2 adsorption, and the adsorption amount was significantly increased, up to 20.1 $cm^3\,g^{-1}$ (298 K), which is equal to four times that without UV irradiation (5.0 $cm^3\,g^{-1}$) and suggests a 75 % desorption capacity with static irradiation. The desorption capacity is much greater than the earlier reported 42 % desorption capacity under static irradiation and 64 % desorption capacity under dynamic conditions,[12] thus creating a record in this field. The significant results with respect to the reversible photochromic properties of **1** prompted us to explore the CO_2-release behavior controlled by a light trigger. An in situ dynamic CO_2-adsorption experiment under light irradiation was designed (Figure 5). The adsorption segment of the experiment was always carried out under UV light (300 nm), whereas the desorption segment was always carried out under visible light (600 nm). In these experiments, dynamic photoswitching CO_2 release was observed: instantaneous CO_2 release with a 76 % desorption capacity, which is consistent with the value found under static irradiation. We also investigated the CO_2 release under ambient conditions without any additional light. This in situ dynamic CO_2-adsorption experiment was designed similarly, whereby the adsorption segment was carried out under UV irradiation, but the

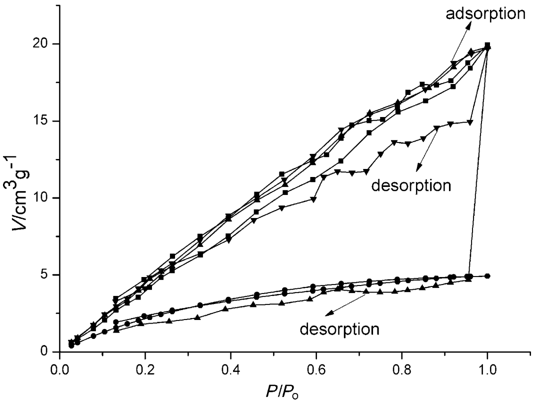

Figure 5. The static and dynamic CO_2 isotherms of **1**. ■: under UV irradiation; ●: under ambient conditions; ▲: adsorption under UV, desorption under visible light; ▼: adsorption under UV, desorption under ambient CO_2, 298 K.

desorption segment under ambient light. Under these conditions, a 24% desorption capacity was found. The results indicate that the CO_2-desorption capacity of this material can be well modulated, depending on the distinct triggers.

Characterization of the interpenetrating framework, Zn(L)(bpdc), demonstrated that the skeleton was well-retained even after heating at 300°C, thus suggesting that no obvious framework expansion, reduction, or shift had occurred. However, all evidence discussed above pointed to the photocontrolled transformation of the L ligand between the open-ring and closed-ring conformers in **1**; thus, local framework movement should occur, and is proposed to be responsible for the large variations in static CO_2 uptake and dynamic CO_2 release. Similarly, as discovered in the azobenzene MOFs,[10–12] *trans*-to-*cis* isomerization of azobenzene creates local framework flexibility and photoresponse towards CO_2 adsorption/release.

In conclusion, a protocol based on a diarylethene derivative was proposed for the first time for the design and preparation of a porous DMOF. The results reveal that the photochromic performance of the diarylethene ligand can be maintained well, and the local framework movement derived from the photochromic diarylethene ligand should enable low-energy CO_2 capture and release. The new DMOF has a record high desorption capacity of 75% with static irradiation and 76% with dynamic irradiation, and the photochromic behavior of the material was controlled for the first time by irradiation with visible light.

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