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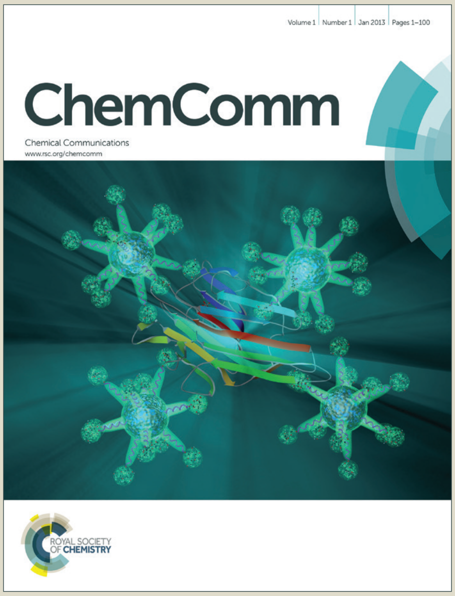

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Photoresponsive Porous Materials: The Design and Synthesis of Photochromic Diarylethene-based Linkers and a Metal-organic Framework

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The synthesis and characterization of novel photochromic diarylethene-based linkers for use in metal-organic frameworks is described including crystal structure analysis of nearly all reaction intermediates. The bis-carboxylated dithien-3-ylphenanthrenes can be prepared under relatively mild conditions in high yield and were subsequently used to create a photoresponsive metal-organic framework, UBMOF-1. While the photochromism of the ligand TPDC in solution is fully reversible, the cycloreversion reaction is suppressed when this linker is incorporated into the crystalline framework of UBMOF-1.

Constructed from transition metal building blocks bridged by organic linkers, metal-organic frameworks (MOFs) remain an extremely promising area of research given their enormous potential impact on separation science, chemical sensing, gas storage, and drug delivery.[1-5] While MOFs have traditionally been employed as passive materials, next generation active materials will be capable of undergoing structural reorganization upon application of external stimuli including light, heat, or changes in pH.[6-8]

Photochromic molecules, compounds that change their molecular and electronic structure upon application of light, remain ideal candidates for sensors, switches, and optical data storage media and have been reviewed extensively.[9-15] More recently, photochromic technologies have been pursued for use in MOFs in hopes of affording photonic control over the physical properties of the crystalline host.[16-19]

Although several instances of MOFs containing non-covalently attached photochromic molecules have been reported,[16, 20, 21] the lack of control over guest orientation and concentration diminishes the utility of this method. By using photoactive linkers, the photochromic groups are covalently attached to the framework leading to MOFs with well-defined stoichiometry. To date, photoswitchable MOF linkers consist entirely of conventional MOF linkers with an appended azobenzene group capable of exhibiting photoinduced *cis-trans* isomerization.[17-19, 22] In this report, we introduce a new class of photoswitchable linkers based upon the highly popular diarylethene photochromes.[10, 23-25]

The prevalence of diarylethenes in photochromic research is due in large part to their excellent thermal stability, large optical differences between ring open and ring closed forms, and resistance to fatigue.[10] The core of the multi-functional diarylethene linker consists of a *bis*-thien-3-yl substituted phenanthrene (**BT3P**) as shown in Figure 1. A linker suitable for the preparation of light-responsive MOFs is obtained by incorporating carboxylic acid groups on either the phenanthrene or the thiophene units, although other binding groups are also possible (Figure 1). Carboxylation of the 2,7 positions of the phenanthrene unit is a unique especially promising route as this leads to a structurally rigid ditopic linker which strongly resembles several common MOF linkers and ultimately leads to photo-responsive MOFs which are isostructural with the MOFs which utilize non-photochromic linkers.

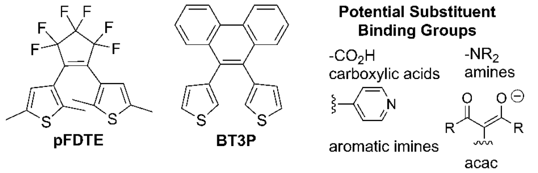
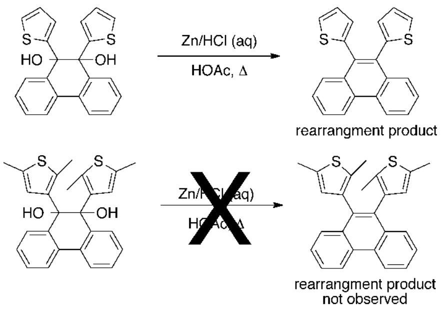


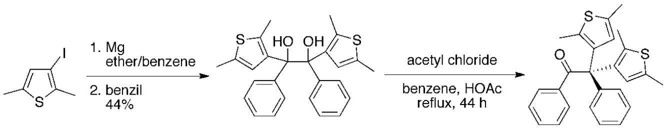
Figure 1. Molecular structures of the prototypical diarylethene, **pFDTE**, of parent compound in this study, **BT3P**, and of potential metal binding substituent groups suitable for MOFs.

Using the work of Geng[26] as a starting point, we set out to utilize the pinacol rearrangement of a thien-3-yl substituted phenanthrene diol in a one-pot synthesis to give the desired diarylethene (Scheme 1). Geng and coworkers explored the one-pot rearrangement and reduction of a thien-2-yl substituted phenanthrene diol (Scheme 1, top) by including both a strong acid to promote rearrangement and zinc dust to afford the necessary reduced product. However, several attempts at forcing this rearrangement for our model system consisting of a 2,5-dimethylthien-3-yl substituted diol led only to the recovery of starting material (Scheme 1, bottom).



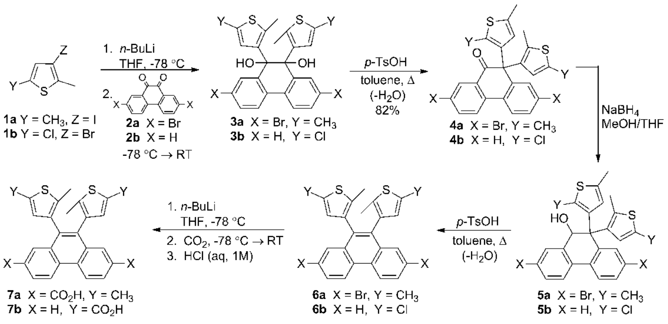
Scheme 1. A one pot reaction allows for the double pinacol rearrangement of a thien-2-yl substituted phenanthrene diol (top) while the thien-3-yl substituted diol explored in this study does not react (bottom).

To our knowledge, only one report exists where a 2,5-dimethylthien-3-yl substituted diol was used as a substrate in the pinacol rearrangment, and harsh conditions were required to carry out this transformation (Scheme 2).[27] The use of refluxing acetyl chloride is not compatible with many functional groups including alcohols and amines, both of which could find use as ligands.



Scheme 2. Conversion of 3-iodo-2,5-dimethylthiophene to the corresponding Grignard reagent followed by reaction with benzil affords the corresponding diol. The pinaol rearrangement of this diol is acheived by treatment with acetyl chloride in refluxing benzene/acetic.

To preclude the need for the harsh conditions required to achieve a pinacol rearrangment with our systems, we chose a stepwise synthetic route which starts with the formation of the requisite phenanthrene diol (Scheme 3). A 3-halosubstituted thiophene **1** is lithiated and then treated with the appropriate phenanthrene-9,10-dione **2** to afford diol **3**. Compound **2b** is available commercially while compound **2a** is available in a single step and reasonable yield by treating **2b** with *N*-bromosuccinimide (NBS) in sulfuric acid.[28] The crystal structure of diol **3a** was found to be the *trans* isomer as predicted by Cram's Rule.[29]



Scheme 3. Synthetic route to *bis*-carboxylated phenanthrene dithienylethenes **7a** and **7b**. Single crystal XRD structures were obtained for **3a**, **4a**, **6a**, and **7b**.

Key diol **3** is subjected to the first of two pinacol rearrangements by refluxing in toluene containing 10 mol % *p*-toluenesulfonic acid (*p*-TsOH) to give ketone product **4**. While mineral acids are typically used for such rearrangements and dehydration, *p*-TsOH is known to avoid oxidizing sensitive substrates while other acids are not.[30] Water is removed by means of a Dean-Stark trap. Reduction of **4** to the corresponding alcohol **5** is achieved in a 1:1 solvent system of THF and methanol using sodium borohydride added in portions over several hours. The alcohol obtained is spectroscopically pure but can be further purified by column chromatography. The last pinacol rearrangement, giving photochromic *bis*-thien-3-yl substituted phenanthrene **6** proceeds as before by treating alcohol **5** with *p*-TsOH in refluxing toluene with concomitant removal of water.

While photochromes **6a** and **6b** are interesting in their own right, in order to make them suitable for MOF inclusion they must be lithiated and then treated with carbon dioxide followed by protonation with dilute acid. The resulting dicarboxylic acids maintain photochromic activity; the electronic absorption spectra for the open and closed forms of **7a** are presented in Figure 2.

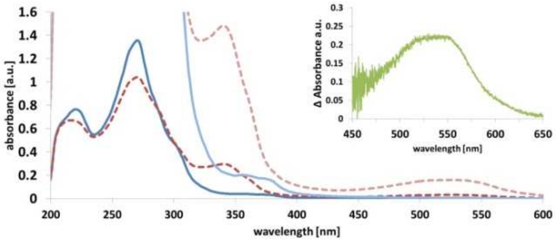


Figure 2. UV visible spectra (1.4 x 10^{-5} M in methanol) of the open (solid blue line) and closed form (dashed red line) of **7a**. The absorbance has been multiplied by a factor of 5 (pale blue and red line) to emphasize the absorption bands above 350 nm. Inset: The difference absorption spectrum (before and after irradiation at 365 nm) of a **UBMOF-1** single crystal.

Initial attempts to synthesize a framework using **7b** have been unsuccessful, potentially due in part to the conformational flexibility and non-linearity of the carboxylate binding groups. The solvothermal reaction of **7a**, which is a rigid linear ditopic linker, with zinc nitrate in dimethylformamide yields large photochromic single crystals. In these crystals, deprotonated **7a** (9,10-bis(2,5-dimethylthiophen-3-yl)-phenanthrene-2,7-dicarboxylate, **TPDC**) coordinates to zinc metal centers to form frameworks of Zn_4O(**TPDC**)$_3$, which we label as **UBMOF-1 (University at Buffalo MOF-1)**. The structure of **UBMOF-1**, which was determined by single crystal XRD, is isomorphous with the previously reported frameworks IRMOF-10 and IRMOF-14.[31] That the three structures are isomorphous is not surprising as all three structures possess an identical oxide-centered Zn_4O tetrahedron, and the known structures utilize the linkers biphenyl-4,4'-dicarboxylate and pyrene-2,7-dicarboxylate, which are similar in length to the phenanthrene-dicarboxylate backbone of **TPDC**.

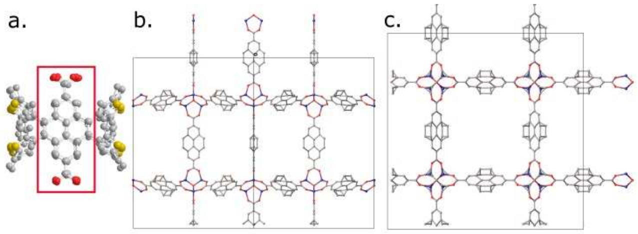


Figure 3. a. Image of the superposition of eight distinct confirmations of TPDC resulting from the high site symmetry of the ligand. The crystallographically refined portion of the ligand is boxed in red. Images of the packing of **UBMOF-1**

viewed along [110] (b) and [100] (c). Color scheme of atoms is as follows: zinc (blue), oxygen (red), carbon (grey), and sulfur (yellow).

The high site symmetry (mm2) of the photochromic linker (which itself possesses no internal symmetry) in **UBMOF-1** gives rise to strong crystallographic disorder of the low symmetry ligand and prevents reliable refinement of the dimethylthiophene groups. It should be noted that crystallographic symmetry imposed upon the ligand causes the phenanthroline backbone of **TPDC** to resemble pyrene (see Figure 3 and discussion in the supplementary information).

To verify that no significant ligand decomposition occurs during the course of the solvothermal synthesis, a sample of **UBMOF-1** was digested using DCl/DMSO-d_6 and analyzed by ^{1}H-NMR spectroscopy. As the spectrum of the digested **UBMOF-1** is virtually identical to that of **7a** in DMSO-d_6, we conclude that the ligand remains intact throughout the solvothermal synthetic process and subsequent digestion.

Figure 4. Images of a **UBMOF-1** single crystal: (a) before exposure to UV light, (b) after irradiation with 365 nm light, and (c) after irradiation with visible light for >2 hours

While the photochromism of **7a** is fully reversible (the red solutions of the closed photoproduct return to the initial colorless state upon application of visible light), crystals of **UBMOF-1** do not completely revert back to their initial state upon irradiation with visible light (Figure 4). After more than two hours of irradiation with visible light, the red coloration persists. Two possibilities exist for the persistent coloration: the local chemical environment of the **TPDC** in the framework is suppressing the ring-opening reaction or the **TPDC** has undergone an undesirable photochemical reaction leading to a colored fatigue product which is photochemically inert.[10, 32, 33] Dissolving irradiated **UBMOF-1** crystals provides an opportunity to distinguish between these two possibilities. A photochemically inert fatigue product will not revert back to the colorless ring open form, whereas, a solution of the ligand will be photochromic.

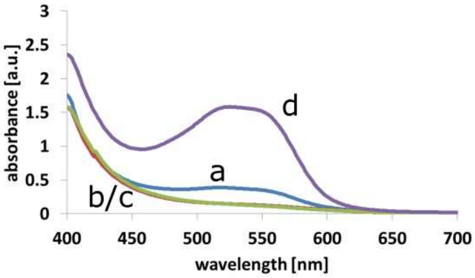


Figure 5. UV/Vis absorption spectra of (a, blue line) digested irradiated **UBMOF-1** single crystals, (b, red line) digested solution after exposure to 10 min of white light, (c, green line) digested solution after 20 min of white light, (d, purple line) digested solution after 10 min of exposure to 365 nm light.

Digestion of a sample of UV irradiated **UBMOF-1** yields a pale red solution that turns pale yellow upon exposure to visible light (Figure 5). Exposing the pale yellow solution to 365 nm light causes the sample to revert back to a red color consistent with the ring-closed photoproduct. As the solutions of digested **UBMOF-1** retain their reversible photochromism, this suggests that the persistent coloration is a consequence of the local chemical environment as opposed to the formation of a photochemical fatigue product. Similar stabilization of the photoproduct has been observed in the azobenzene derivatized MOFs,[16, 17] although the precise origin of stabilization has not been determined.

Conclusions

In conclusion, the synthesis and characterization of a new class of photochromic metal-organic framework linkers based on diarylethenes is described. The first framework synthesized with the photoswitchable ligands, **UBMOF-1**, is isostructural with the previously reported IRMOF-10 and -14. This result reinforces the supposition that additional functionality, such as photoswitching, can be designed into a ligand without affecting the topology of MOFs created using the new ligands. The suppression of the ligand ring-opening reaction in the MOF relative to solution highlights the challenges and opportunities present in this new class of materials.

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Notes and references

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The authors declare no competing financial interests.

†Electronic Supplementary Information (ESI) available: Synthetic details, digestion experiment results, additional UV/Vis spectra, crystallographic data, crystallographic refinement details. See DOI: 10.1039/c000000x/

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