# A Bistable Dithienylethene-Based Metal-Organic Framework Illustrating Optically Induced Changes in Chemical Separations

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**ABSTRACT:** Dithienylethene-containing molecules have been examined due to their photo-switching capabilities. We have prepared a bistable, optically-triggered, Metal-Organic Framework containing a dithienylethene moiety which was synthesized and characterized. The advantage of this material is that, unlike other dithienylethene-containing MOFs, the properties of the pore can be changed via an optical trigger without the potential risk of structural damage to the framework. We illustrate the application of this MOF to chemical separations. With this class of materials, optically triggered conductivity, chemical storage and release, and sensing are possible.

Metal-organic frameworks (MOFs) are porous materials, consisting of metal clusters/ions (nodes), which are connected by organic ligands (linkers) to form a 3D porous framework.[1-3] The advantage of MOF chemistry is that with judicious choice of linker and node, MOFs can be tailored towards applications including, but not limited to, gas separations,[4] gas storage,[5,6] and catalysis.[7] For most of these applications, the fixed pore width, pore aperture, and pore chemistry are responsible for the behaviour of the MOF. If the pores can be designed to be more flexible or exist in more than one stable state, i.e., bistability,[8-10] then these properties can be turned on and off. For example, for gas separations it may be possible to obtain selective control over the rate of entry or retention in one form of the MOF. Switching the MOF to a different state can concomitantly change the rate of release of the guests in the pore.[11] It is for this reason that research in MOF chemistry has grown to include stimuli responsive MOFs.[12-23]

With applications in chemical separations, photoresponsive MOFs, one subgroup of stimuli responsive MOFs, have gained attention in recent years.[24-30] Perhaps the most notable example of photoresponsive MOFs include MOFs with an incorporated azobenzene linker (Figure S1 in the Supporting Information (SI)).[24,31] Under ambient conditions, the linker takes the trans-conformation. Upon UV-light irradiation, the azobenzene moiety undergoes a cis-trans isomerization. As such, azobenzene-containing MOFs have shown different separation selectivities depending on linker conformation.[24,31-33]

Another family of photoresponsive MOFs that have recently gained momentum incorporate dithienylethene switches (Figure 1).[22,34,35] With the applied stimulus of either UV or visible light, dithienylethene switches interconvert between the freely rotating ring-open isomer and the nearly-planar ring-closed isomer.[36] These molecules display desirable properties such as bistability between states, thermal stability, and remarkable resistance to fatigue.[37-39] Given this, these molecules are featured in a range of applications including optical memory switches,[36] and conducting materials.[40] As such, dithienylethene incorporated MOFs possess opportunities for designing conducting porous materials which have vast applications.[41]
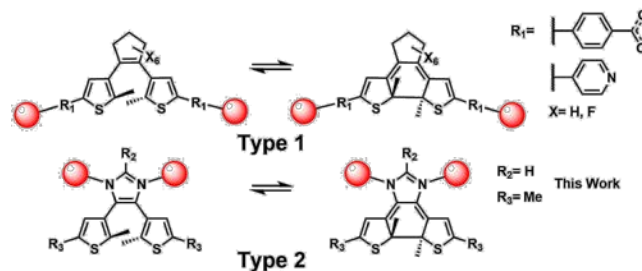


Figure 1. Dithienylethene-based linkers connecting metal nodes (spheres) either via the thienyl portions (Type 1), or the ethene portion of the dithienylethene moiety (Type 2).

As with azobenzene photoswitches (Figure S1), dithienylethene photo-switches can be incorporated in two different fashions (Figure 1). In the Type 1 fashion, the photo-switching MOF has the photo-active moiety incorporated via the thienyl portion of the linker. In this fashion, there is the potential long-term risk that the mechanical stress of the photo-isomerization could irreversibly damage the material.[42-44] In Type 2 photo-switching systems, the photo-active component is unencumbered in the pore. In the Type 2 fashion, the configuration potentially changes the properties of the pore without risk to the integrity of the MOF while also allowing the switch to be tailored towards applications without concern regarding the installation of node attachment points (e.g., pyridyl/carboxyl).

To date, of the hand full of dithienylethene-containing MOFs, the majority have been of the Type 1 motif where the thienyl moieties are directly attached to the framework (Figure 1 top).[31,45] These MOFs have shown tunable gas uptake as a function of photostimuli.[46] However, we hypothesize that a Type 2 dithienylethene-based MOF (Figure 1 bottom) would be more tunable and structurally robust. To that end, we report the first example of a Type 2 photo-switching MOF (PSZ-1 based on an imidazole backbone, Figure 2) that illustrates reversible photo-switching with a concomitant shift in host-guest interactions.

PSZ-1 was synthesized via the solvent assisted linker exchange[47-51] (SALE) method between ZIF-70 – a MOF formed from Zn(II), imidazole, and 2-nitroimidazole – and the imidazolate-based dithienylethene linker, HL1 (see SI for further details). ZIF-70 was chosen due to the presence of a 1.59 nm pore which could accommodate L1.[52] In looking at the crystal structure of ZIF-70 (Figure 2), only one of the four structurally inequivalent imidazolate linkers point into the large pore. As such, we estimate that only a maximum of 25

% of the linkers can be substituted by **L1** in PSZ-1. The incorporation of **L1** to form PSZ-1 was confirmed by ^{1}H NMR (Figure 3).[53] The NMR of dissolved crystals of PSZ-1 showed the presence of **L1** at a ratio of 0.27:1.00:0.70 **L1**:imidazolate:nitro-imidazolate. Further SALE with a fresh solution of H**L1** did not increase the loading of **L1** indicating that only an eighth of the total linkers, or half of the linkers that point into the large pore, could be substituted. To further investigate, a crystal of PSZ-1 was investigated by single crystal X-ray diffraction. As shown in the SI, only the imidazole pointing into the large pore shows evidence of **L1** with roughly 50 % **L1** incorporated. Furthermore, the powder X-ray diffractogram (PXRD) of PSZ-1 match with that of the crystal structure (Figure S5). We thus propose that half of the linkers around the large pore of PSZ-1 were selectively substituted (Figure 2e).[54]
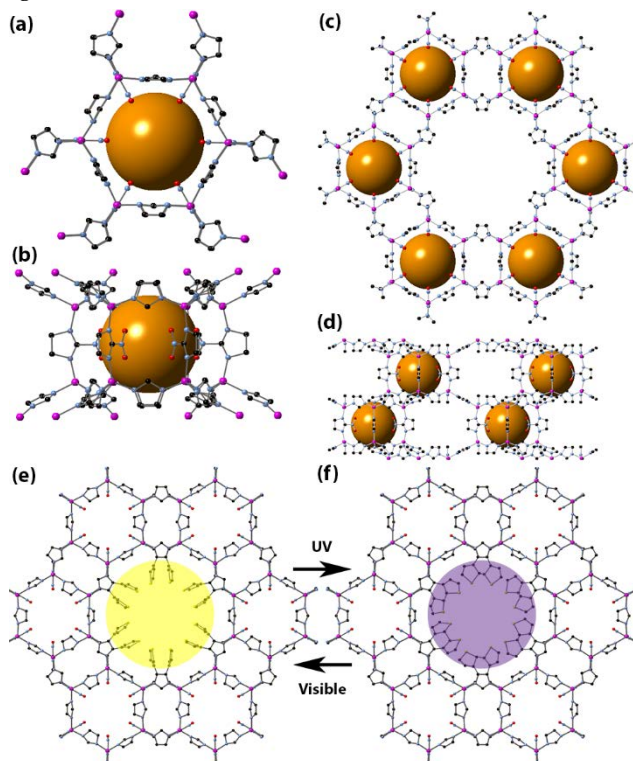


Figure 2: (a/b) the smallest hexagonal pore of ZIF-70 viewed down the c-axis, and perpendicular to the c-axis respectively; 3 of the 4 unique imidazoles form this pore. The 4th imidazole connects each small pore to three adjacent pores above and three adjacent pores below. In this connectivity, a larger pore (d) and a ca. 1.59 nm pore (c) are formed. PSZ-1, formed via the solvent-assisted linker exchange (SALE) process with **L1** and ZIF-70 shown in both the open (e) and closed (f) conformation (incorporation of **L1** in (e) and (f) modeled in crystal maker; crystallographic data of the open form can be found in the SI).

With the MOF in hand, we turned our attention to examining the photo-isomerization of PSZ-1. As shown in Figure S2 & S3, in solution, H**L1** is capable of switching to the closed form when exposed to $\lambda < 254$ nm light. The closed form of H**L1** displays a new absorption at 550 nm. In PSZ-1, (Figure 4, Figure S11), yellow crystals of PSZ-1-open convert to violette crystals of PSZ-1-closed upon exposure to UV-light ($\lambda < 254$ nm). As with H**L1** in solution, the colour change observed for PSZ-1 was accompanied by a new absorption band at 550 nm. If PSZ-1-closed is subsequently exposed to

visible light ($\lambda > 515$ nm), then the spectra returns to that of PSZ-1-open. ZIF-70 did not show any changes in absorption upon exposure to UV-light (Figure S4).
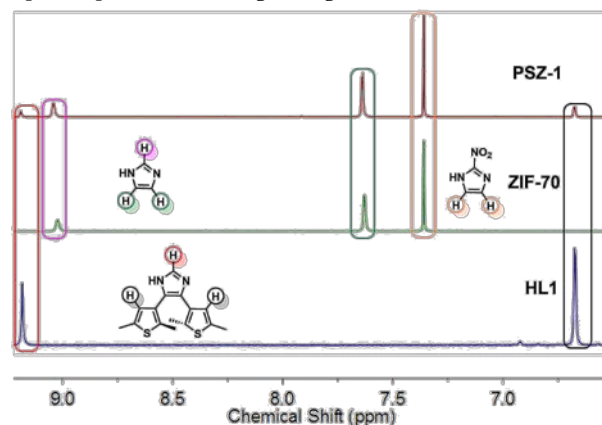


Figure 3. Solution-phase NMR of dissolved PSZ-1 (top), ZIF-70 (middle), and H**L1** (bottom) in a DMSO-$d_6$ and sulfuric acid-$d_2$ solution; the new peaks at 6.64 and 9.11 ppm illustrate that **L1** has been incorporated into ZIF-70 to form PSZ-1.
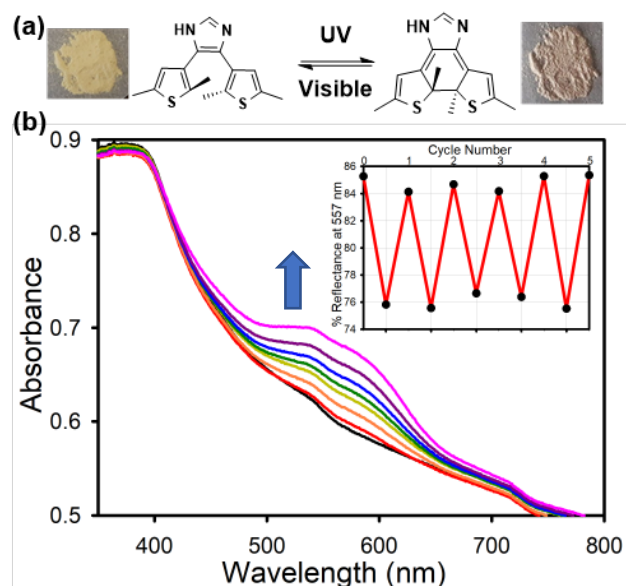


Figure 4. (a) PSZ-1-open (left) and PSZ-1-closed (right) illustrating the photochromic behaviour of PSZ-1. (b) Solid State UV-Vis spectra of 1% w/w PSZ-1 in KBr as a function of UV-light exposure time (1 min exposures up to 5 min, then a 5 min exposure to 10 min followed by a 10 min exposure, totaling to 20 min total exposure time). The inset illustrates the reversible nature of the photo-switching material PSZ-1.

To illustrate the reversibility of the photo-isomerization of PSZ-1, the MOF was exposed to 5 open/close UV/Visible cycles (Figure 4, Table S1, and Figure S7). Unlike H**L1** in solution, based on the reflectance spectra and NMR, there is no evidence of any decay of PSZ-1 to a photo-bleached or otherwise photo-inactive state (See Figure S10).

To further illustrate the stability of PSZ-1 to photo-switching, we investigated the the $N_2$ (77 K) gas-adsorption of PSZ-1 in the open and closed form. As shown in Figure 5, ZIF-70 has a Brunauer–Emmett–Teller (BET) surface area of 2000 m²/g.[55] For PSZ-1, the BET surface area expectedly decreases to 1250 m²/g. Furthermore (Figure 5 & S8), the BET surface

area doesn't change after 5 open-close cycles. PXRD of PSZ-1 indicates that cycling (5x) the MOF between the open and closed isomer has little-to-no structural change (Figure S5). Thus, PSZ-1 is not being bleached or otherwise damaged during photo-isomerization.
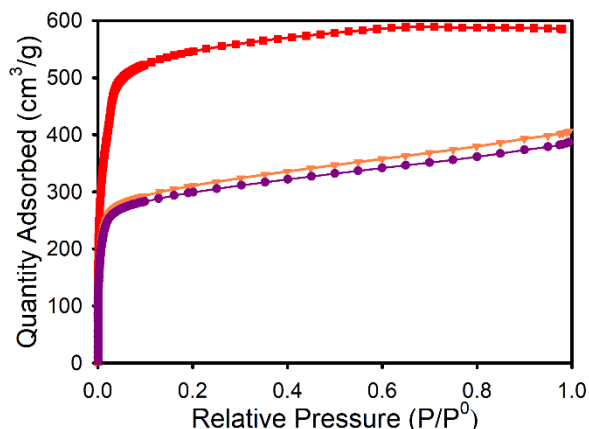


Figure 5. $N_2$ gas-adsorption isotherm at 77 K of ZIF-70 (Red squares: BET surface area = 2000 m²/g), PSZ-1-open (Orange triangles) and PSZ-1-closed (Purple circles); BET surface area = 1250 m²/g for both.
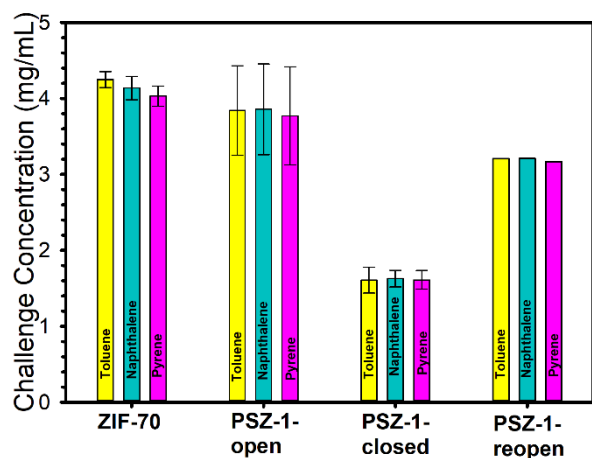


Figure 6. Concentration of aromatic hydrocarbon filtrate through the MOF filters; toluene (Yellow), naphthalene (Turquoise), and pyrene (Purple)

Type 2 photo-switching MOFs have the potential to alter the environment of the pore/pore aperture without significantly altering the framework of the. To demonstrate that PSZ-1 possesses different pore properties between the open and closed conformer, we examined the separation of a 1:1:1 weight % solution (5 mg/mL) of toluene, naphthalene and pyrene through the MOFs. As shown in Figure 6, when ZIF-70 is used as a filter, there is little retention of analytes. When PSZ-1-open is utilized as a filter, then a slight increase in analyte retention is observed. However, when PSZ-1-closed is used as a filter, a large retention of analytes is observed indicating that the switching has change the pore characteristics. The lack of any differences between analytes indicates that the effects in the MOF is likely electronic and not steric in origin.[56] When PSZ-1-closed is irradiated with visible light, the filtering properties are similar to PSZ-1-open indicating reversible behaviour.

In summary, a Type 2 photo-switch MOF based on

dithienylethene was synthesized and characterized. PSZ-1 shows a reversible photo-isomerization between the UV-only absorbing open conformation (PSZ-1-open) and the visible-light absorbing closed conformation (PSZ-1-closed). We demonstrated that light can be used to change the host-guest interactions in order to alter elution rates..

With PSZ-1 and the tailorability of dithienylethene photoswitches, new functionalities can be introduced into the pore without the need to necessarily consider the synthetic challenges of introducing carboxylate or pyridyl groups onto the thienyl moieties. We are presently investigating the applications of these MOFs towards tuning electronic and steric separations, and investigating photo-switching conducting MOFs.

## Supporting Information

Experimental details, UV and visible measurements of ZIF-70 and PSZ-1, powder X-ray diffractograms, single crystal diffraction, ¹H NMR of post-SALE solutions, and photo-cycling tests on PSZ-1 can be found in the supporting information.

## Acknowledgments

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(54) To further illustrate that the ligand was incorporated into the MOF, rather than being trapped in the pore, we examined the mother liquor from the SALE reaction. NMR analysis of the solution indicated the presence of nitro-imidazole as well as imidazole (Figure S6 in the SI). We further examined PSZ-1 post SALE by soaking PSZ-1 in MeOH for 24h; analysis by NMR indicated no evidence of any imidazole linkers in the solvent phase.

(55) The surface area of ZIF-70 ranges from 1700-2000 $m^2$/g. The origin of the variation is unknown. In our experience, crystals of ZIF-6 have, at times, been observed intermixed with ZIF-70.

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