Supplementary information

Photo-responsive MOFs: Light-induced switching of porous single crystals containing photochromic diarylethene

Ian M. Walton,[a] Jordan Cox,[a] Jarrett Coppin,[a] Crysania Linderman,[a] Dinesh G. (Dan) Patel,[a] Jason Benedict*[a]

[a] *Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, New York 14260, USA*

Synthetic details:

DTE was synthesized as previously reported and its NMR spectra and UV-Vis spectrum matched that reported in the literature.[1] NMR spectra of the digested MOF samples, used to determine the amount of **DTE** present, were acquired on a Varian Inova 500 NMR spectrometer operating at 499.90 MHz with samples held at 25 °C during data acquisition.

MOF-5 crystals $[Zn_2(C_8H_4O_4)_2(C_6H_{12}N_2)]$ were grown initially following the previously reported solvatothermal synthesis.[2] To a thick walled, screw top pressure tube was added $Zn(NO_3)_2{\cdot}6H_2O$ (0.256 g, 0.84 mmol) terephthalic acid (0.140 g, 0.84 mmol), and 1,4-diazabicyclo[2.2.2]octane (0.046 g, 0.42 mmol) that was then dissolved with DMF (10 mL). With the lid tightly in place, the tube was heated to 130 °C for 2 days in a temperature controlled oven (Yamamoto, model# DKN402C). The reaction produced a powder product as well as crystals in a range of 50-60 μm in any linear direction. For larger crystals suitable for spectroscopic analysis, the concentration of the reactants was reduced while running the crystallization at lower temperature. Crystals with a size of up to 300 μm in any linear direction were formed along with powder product when $Zn(NO_3)_2{\cdot}6H_2O$ (0.125 g, 0.42 mmol), terephthalic acid (0.070 g, 0.42 mmol), and 1,4-diazabicyclo[2.2.2]octane (0.023 g, 0.21 mmol) were dissolved in DMF (10 mL) and heated to 100 °C for 2 days in a screw top pressure tube. All crystals were collected by suction filtration, washed with DMF, and dried overnight at 130 °C under vacuum to remove any DMF or H_2O molecules within the pores of the obtained **MOF-5**.

The crystals of **MOF-5@DTE** were prepared by adding **DTE** (10-30 mg) to evacuated **MOF-5** crystals (10 mg) in a small, sealed round bottom flask. The mixture was heated to 130 °C overnight. Attempts to reproduce the loading of the **DTE** into the **MOF-5** channels at temperatures lower than 130 °C were unsuccessful despite observed melting of the **DTE** crystals.

Figure S1: Images of a **MOF-5@DTE** crystal illustrating the persistence of the orange fatigue product in a crystal that was cycled by repeated UV and visible light irradiation. A) White light irradiation 5 min. B) White light irradiation 180 min. C) UV irradiation with 365 nm light for 3 min. The **DTE** remains photoswitchable. D) White light irradiation 20 min.

Characterization

Spectroscopy:

Absorption characterization of **MOF-5@DTE** crystals was carried out using an Olympus IMT-2 inverted microscope in which the side imaging port was coupled to a fiber optic. The spectral intensity of the output of the fiber was then measured with an Ocean Optics USB4000 spectrometer. The intensity measurements were converted to absorbance using MatLab.

Kinetics:

The sample was excited using a Thorlabs 365 nm LED (4.1 mW). For kinetic studies the LED was pulsed using a signal from a Stanford Research Systems delay generator, Model DG535. In a typical experiment the UV diode was switched on for a period of 10 s and then switched off for 240 s while the crystal's spectrum was being constantly measured using visible light from the microscope. After 240 s, the diode was then switched on for an additional 10 seconds and the cycle repeated. Spectra were recorded at a rate of five per second with an experiment typically lasting 2500 seconds (12500 scans) or 10 cycles of the UV irradiation. This experiment was performed on three separate crystals, each with the linear polarizer aligned with the *c*-axis of the **MOF-5** crystal.

To test the extent to which the **DTE** back reaction is thermally driven at room temperature, the visible light source was blocked shortly after cessation of the UV irradiation. In a typical experiment, the crystal was irradiated with the 365 nm LED for 10 seconds then allowed to undergo a back reaction in visible light for 10 seconds. All light was then blocked from the sample for 120 seconds. Visible light irradiation was then continued. In all three crystals studied, the absorbance before and after the light blockage was statistically unchanged, thus the back reaction was stopped when the sample was isolated from all light. This study confirms that there is effectively no thermal back reaction for the **DTE** molecules incorporated within the **MOF-5** single crystal.

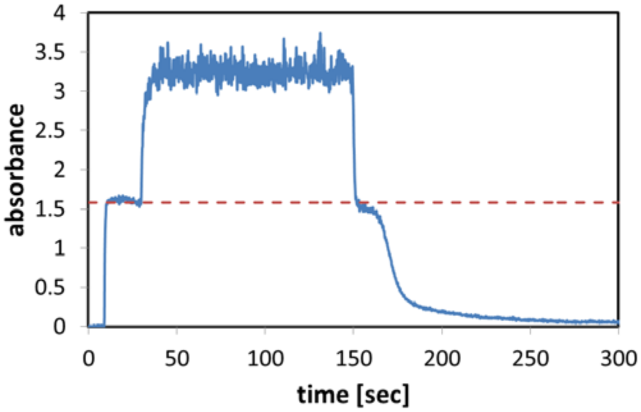

Figure S2: Results demonstrating the absence of a thermal back reaction on a minutes time scale for a **MOF-5@DTE** single crystal. After approximately 30 sec, the microscope light source was blocked which resulted in absorbance values above 3. After 2 minutes, the microscope light source was unblocked at which point the absorbance measurement and light induced back reaction were resumed. The dashed red line corresponds to the value of the absorbance prior to the light blockage, 1.58(5) to facilitate comparison with the value immediately after the light was unblocked, 1.56(5).

NMR Spectra of Digested MOF With and Without Diarylethene

To prepare samples for determination of the content of **DTE** in **MOF-5**, 3 mg of the loaded **MOF-5** was digested in 1 mL of DMSO-d_6 and 23 µL of DCl in D_2O (35% wt). The ^{1}H NMR spectra of several samples were compared to digested evacuated **MOF-5**. The peak at 8.02 ppm is attributed to the terephthalic acid linker while the peak at 6.77 ppm is attributed to thiophene ring protons and integrated to 2 H. The peak at ~6.25 ppm is due to the DABCO protons. Below we present representative spectra that show high variability in the amount of **DAE** incorporation.

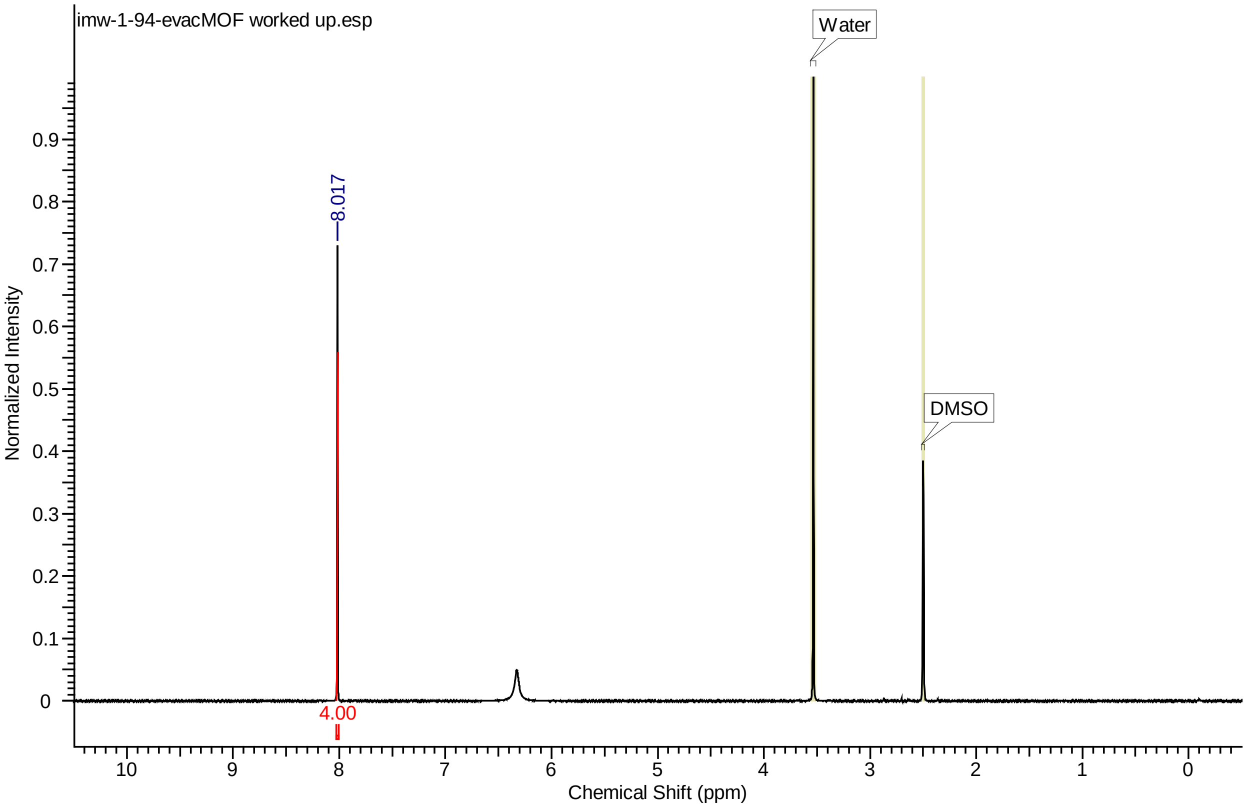

Figure S3. ^{1}H NMR spectrum of evacuated **MOF-5** digested in 1 mL of DMSO-d_6 and 23 µL of DCl in D_2O (35% wt) used as a reference.

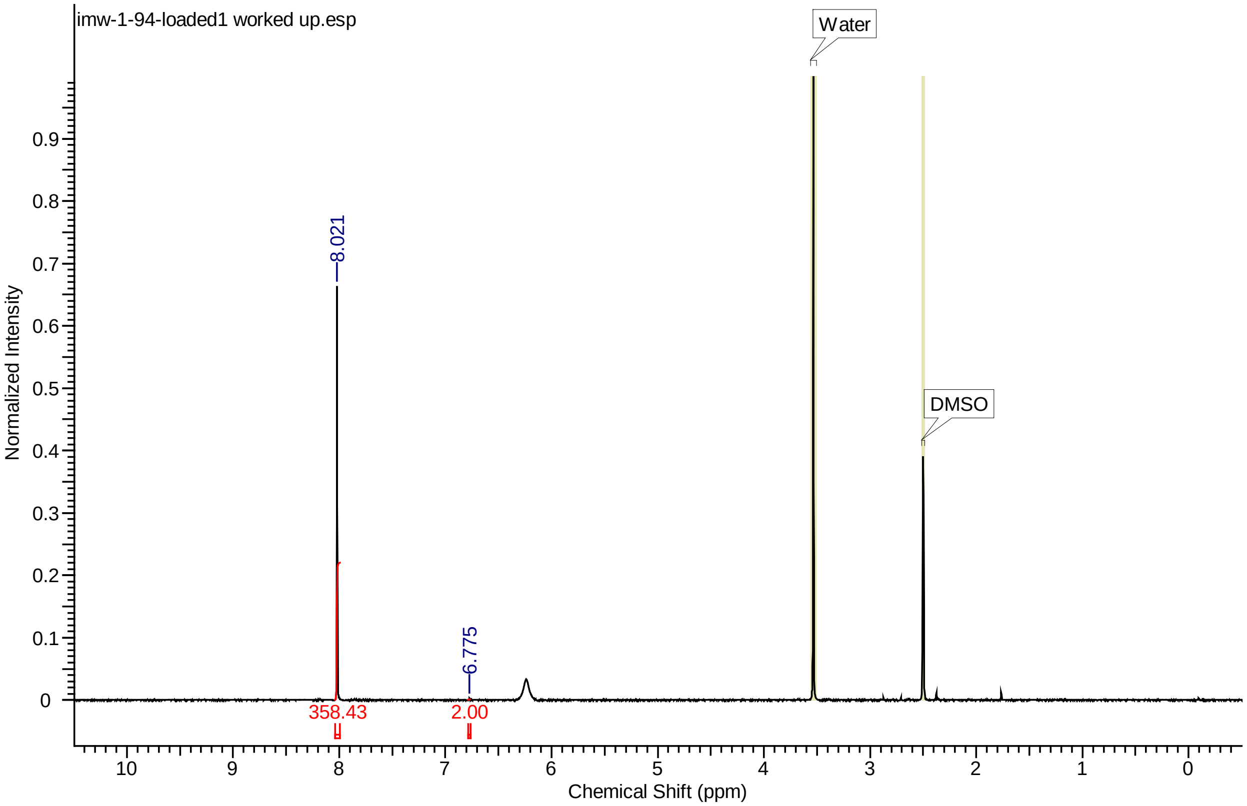

Figure S4. ^{1}H NMR spectrum of a digested sample of **MOF-5** loaded with **DAE**. Integration of the terephthalic acid protons and the **DAE** thiophene protons indicate a ratio of ~90:1.

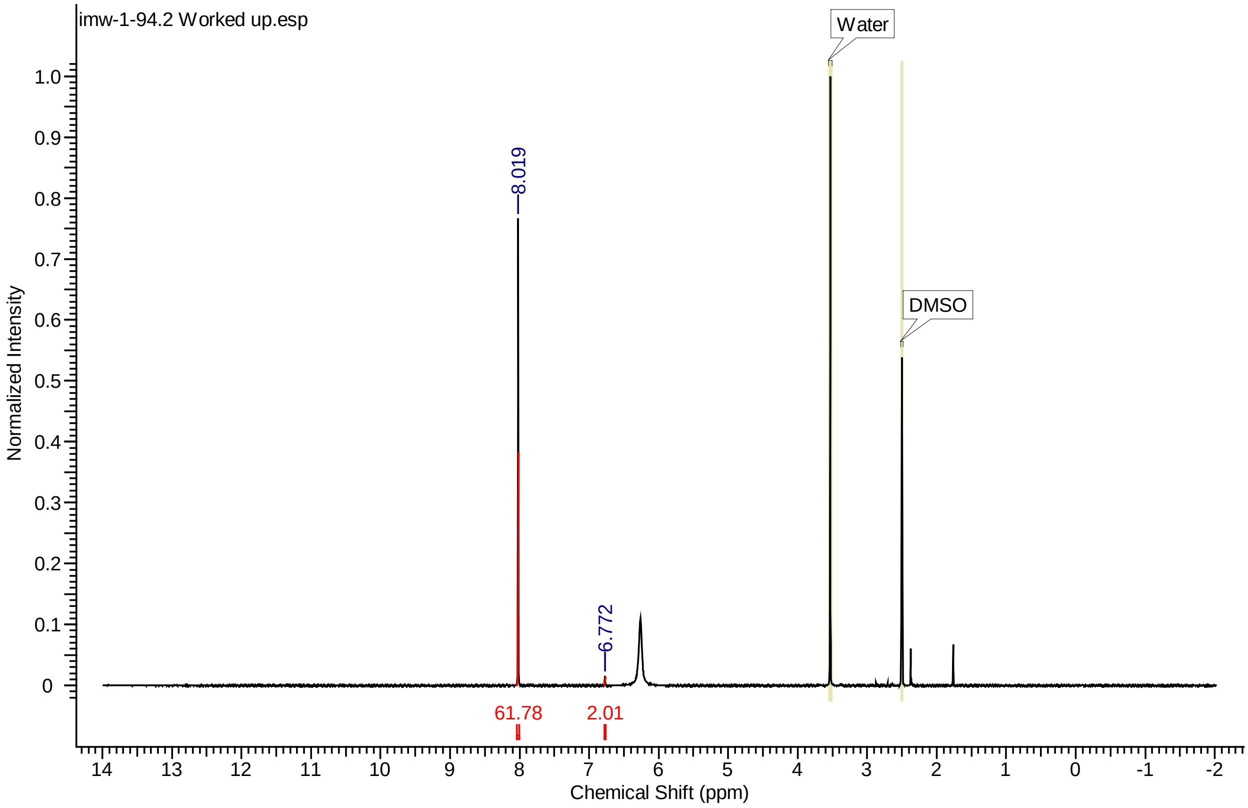

Figure S5. ^{1}H NMR spectrum of a second sample of digested **MOF-5** loaded with **DAE**. Integration of the terephthalic acid protons and the **DAE** thiophene protons indicate a ratio of ~15:1.

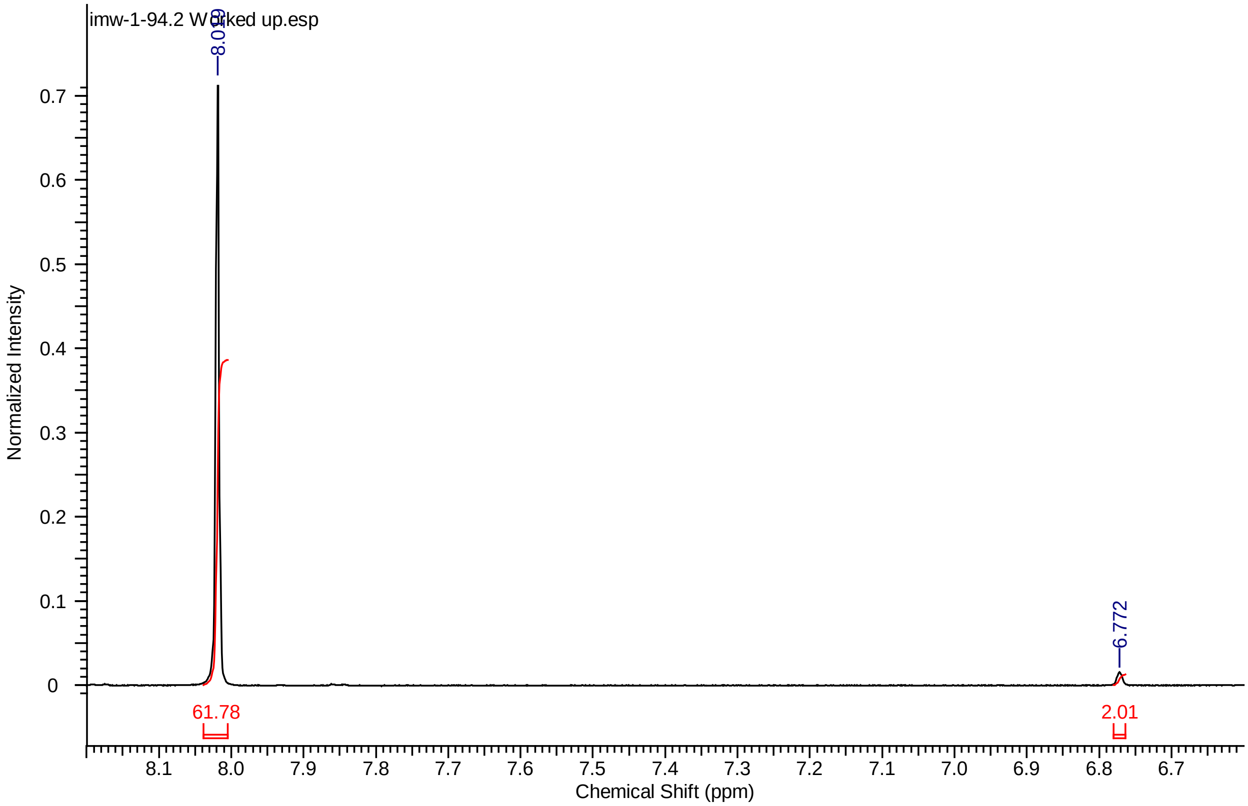

Figure S6. Zoomed in image of the spectrum from Figure S5.

X-ray diffraction:

The X-ray diffraction data was collected both at our home source and at a synchrotron source. The home source data was collected at a temperature of 245 K on **MOF-5@DTE** crystals approximately 50-80 μm in any linear dimension using a Bruker microfocus turbo rotating anode source (Mo, λ=0.71073 Å). The synchrotron data was collected on beamline 15-IDB (30 keV, λ=0.41328 Å) at the Advanced Photon Source at Argonne National Laboratory at a temperature of 243 K on crystals measuring approximately 10-30 μm in any linear dimension.

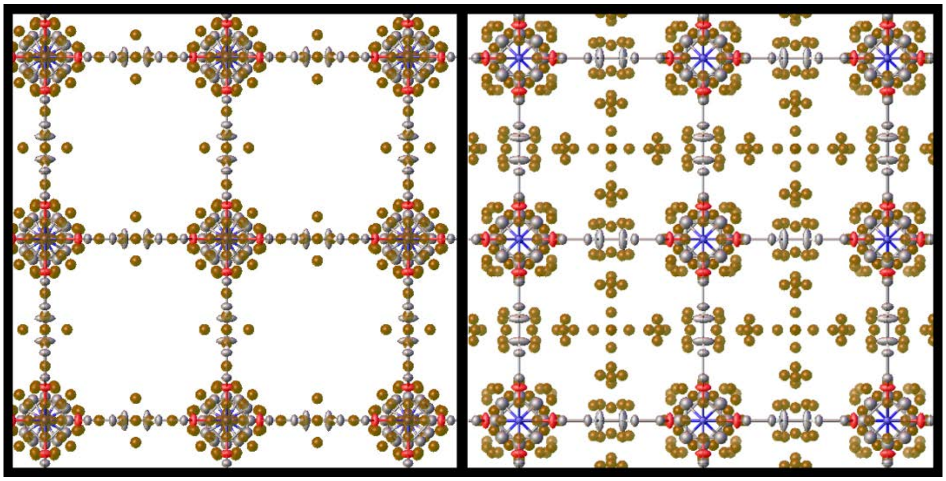

Figure S7. Images illustrating the 15 highest peaks of residual electron density for an evacuated MOF-5 single crystal (left) and a **MOF-5@DTE** single crystal (right) viewed down the *c*-axis. Protons have been omitted for clarity. In the **MOF-5@DTE** structure, residual density is located within the channel indicating the presence a chemical species within this region, however, the structure of the species (presumably **DTE**) could not be refined.

1. S. Kobatake, T. Yamada, K. Uchida, N. Kato and M. Irie, *J. Am. Chem. Soc.*, 1999, **121**, 2380-2386.
2. D. N. Dybtsev, H. Chun and K. Kim, *Angew. Chem., Int. Ed.*, 2004, **43**, 5033-5036.