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

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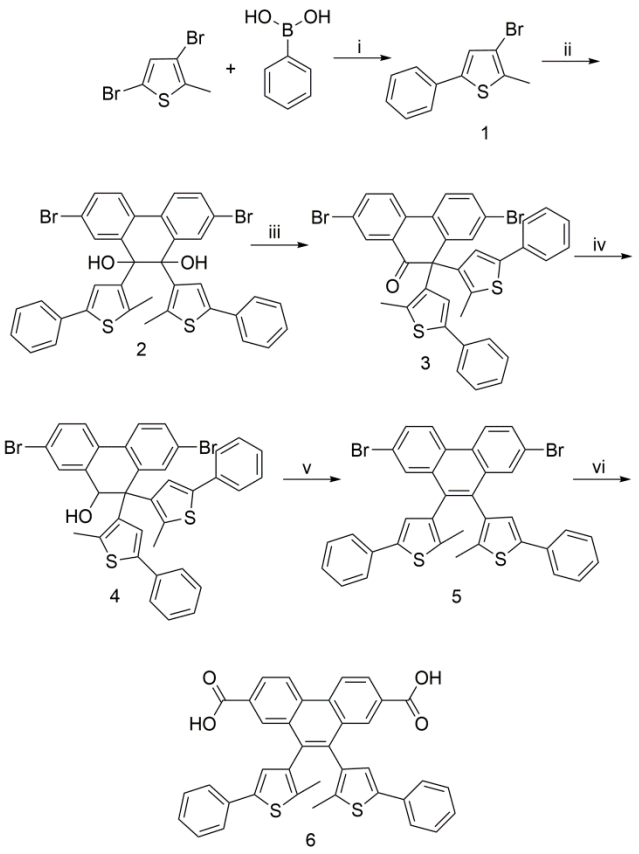
Synthetic Procedure:

Synthesis of 1: To a 100 mL schlenk tube, 10 ml of water, 10 mL of toluene, 2,5-dibromo-5-methylthiophene (1.5 g, 5.8 mmol), phenylboronic acid (.7145 g, 5.859 mmol), and Na_2CO_3 (4.23 g, 39.9 mmol). The solution was degassed by three freeze/pump/thaw cycles. 3 mg of tetrakis(triphenylphosphene) palladium(0) was added under N_2 flow, followed by two freeze/pump/thaw cycles. The biphasic solution was then refluxed under N_2 at 100 °C for 24 hours. The reaction was then cooled; the aqueous phase was then extracted with Et_2O. The combined organic layers were then washed with H_2O (2 x 20 mL) and sat. brine solution (2 x 20 mL). The organic phase was dried over $MgSO_4$, and then the solvent was removed under reduced pressure. The resulting solid was dissolved in Et_2O and passed through a silica plug to remove impurities. 1.4058 g of **1** was recovered for a 95 % yield. MP: 107-110 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.508 (d, 2H, J = 7.81 Hz), 7.367 (t, 2H, J= 7.81 Hz), 7.281 (t, 1H, J= 7.32 Hz), 2.421 (s, 3H); HRMS (EI) calculated for $C_{11}H_9Br_1S_1$ 251.9603, found m/z 251.96083.



Scheme S1: PhTPDC synthesis i. $Pd(PPh_3)_4$, Na_2CO_3, Toluene/H_2O, Reflux for 24 hr. ii. 1) *n*-BuLi, THF, -78 °C 2) 2,7–dibromo-9,10-phenanthrenedione -78 to RT. iii. pTSOH, Toluene relflux, 24 hr. iv. $NaBH_4$, MeOH/THF relflux. v. pTSOH, Toluene reflux vi. 1) *n*-BuLi, ThF, -78 °C 2) Dry CO_2, -78 °C to RT 3) HCl

Synthesis of 2: To a flame dried 250 mL round-bottom flask, **1** (1.5 g, 5.9 mmol) was added. The white solid was placed under high vacuum for 60 min followed by backfilling with N_2. Under nitrogen dry THF (60 mL) was added. The resulting solution was cooled to -78 °C in a dry ice/acetone bath followed by the slow addition of 1.5 M n-buyllithium in hexanes (4.0 mL, 5.9 mmol) over 30 min. The reaction was stirred at -78 °C for 1 hour and immediately followed by the addition of 2,7–dibromo-9,10-phenanthrenedione (1.098 g, 2.999 mmol) in a single portion. The reaction was allowed to slowly warm to room temperature and stirred for 20 hours. The reaction was then refluxed for 2 hours under N_2 atmosphere, then cooled to room temperature and quenched by slow addition of 1 M HCl. The product was then extracted with Et_2O (2 x 30 mL) and the combined organic layers were washed with 10% aqueous NaS_2O_3 (2 x 30 ml), H_2O (2 x 30 mL), and brine (2 x 30 mL). The organic layer was dried over $MgSO_4$ and the solvent removed by rotary evaporation. The product was isolated by column chromatography as a white solid (1.05 g, 49 % yield). MP: 137 °C (decomp.) ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.827 (d, 2H, J= 2.44 Hz), 7.748 (d, 2H, J= 8.3 Hz), 7.562 (dd, 2H, J= 1.95, J= 8.3 Hz), 7.231 (t, 4H, J= 8.71), 7.15 (m, 6H, J= 7.32 Hz), 6.326 (s, 2H), 2.812 (s, 6H); HRMS (EI) calculated for $C_{36}H_{26}O_2Br_2S_2$ 713.9715, found m/z 713.97150.

Synthesis of 3: **2** (1.050 g, 1.470 mmol) was dissolved in toluene (50 mL) in a 100 mL round bottom flask. Para-toluene sulfonic acid (0.028 g, 0.147 mmol) was added to the solution. The flask was capped with a Barret trap and a reflux condenser. The reaction was refluxed for 20 hours at 145 °C. The solvent was removed under reduced pressure. The reaction residue was passed through a silica gel plug and eluted with CH_2Cl_2. The solvent was removed under reduced pressure to afford an off white solid (0.821 g, 80 % yield). The product was pure by NMR. MP: 134 °C (decomp.) ^{1}H NMR ($CDCl_3$, 500 MHz) Major conformer; δ 8.022 (d, 1H, J= 1.47 Hz), 7.807 (d, 1H, J= 8.79 Hz), 7.747 (d, 1H, J= 8.3 Hz), 7.686 (dd, 1H, J= 1.95, J= 8.79 Hz), 7.603 (dd, 1H, J= 8.3 Hz, J= 1.46 Hz), 7.300 (m, 7H, J= 8.79 Hz), 7.211 (m, 3H, J= 6.84 Hz), 7.15 (d, 1H, J= 1.96 Hz), 6.842 (bs, 1H), 6.328 (bs, 1H), 2.091 (bs, 3H), 1.879 (bs, 3H) ; HRMS (EI) calculated for $C_{36}H_{24}OBr_2S_2$ 695.9609, found m/z 695.96277.

Synthesis of 4: Compound **3** (0.270 g, .387 mmol) was dissolved in THF (15 mL) and methanol (15 mL) in a round bottom flask outfitted with a water-cooled reflux condenser. The reaction was heated to 60 °C capped and $NaBH_4$ (0.015 g, 0.396 mmol) was added in four portions over 4 hours with heating. Heating at 60 °C was continued for 20 hours. The reaction was cooled to 0 °C and quenched with the slow addition of 1 M HCl (30 mL). The product was then extracted with CH_2Cl_2 (2 x 25 mL). The combined organic phases were washed with H_2O (2 x 30 mL) and sat. brine solution (2x30 mL). The organic phase was the dried over $MgSO_4$ and the solvent removed with reduced pressure. The product was isolated by column chromatography as an off white solid (0.2100 g, 79% yield). MP: 126 °C (decomp.) ^{1}H NMR ($CDCl_3$, 500 MHz) Major conformer; δ 7.787 (bs, 1H), 7.646 (bt, 1H), 7.515 (bm, 5H), 7.415 (dd, 1H, J= 1.95, J= 8.3 Hz), 7.330 (bm, 7H), 7.231 (bm, 3H), 5.638 (bs, 1H), 5.429 (bs, 1H), 2.394 (bs, 1H), 2.106 (bs, 1H), 1.952 (bs, 3H), 1.760 (bs, 2H); HRMS (EI) calculated for $C_{36}H_{26}OBr_2S_2$ 697.9766, found m/z 697.97510.

Synthesis of 5: 4 (0.2666 g, 0.3819 mmol) was dissolved in toluene (50 mL) in a 100 mL round bottom flask. Para-toluene sulfonic acid (0.0072 g, 0.0378 mmol) was added to the solution. The flask was capped with a Barret trap and a reflux condenser. The reaction was refluxed for 20 hours. The solvent was removed under reduced pressure, and then diluted with CH_2Cl_2. The product solution was washed with sat. aq. $NaHCO_3$ (50 mL), water (50 mL) and sat. brine (50 mL). The combined organic phase was dried over $MgSO_4$, filtered and the solvent removed under reduced pressure to afford a white solid (0.140 g, 54 % yield). The solid was pure by NMR. MP: 128 °C (decomp.). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.602 (dd, 2H, J= 8.79 Hz, J= 2.44 Hz), 7.921 (d, 1H, J= 1.95 Hz), 7.821 (d, 1H, J= 2 Hz), 7.791 (dt, 2H, J= 8.79 Hz, J= 1.95 Hz), 7.490 (t, 1H, J= 1.46 Hz), 7.475 (d, 1H, J= 0.98 Hz), 7.454 (t, 1H, J= 1.46 Hz), 7.439 (d, 1H, J= 0.98 Hz), 7.341 (t, 2H, J= 7.81 Hz), 7.260 (m, 6H), 6.985 (s, 1H), 6.955 (s, 1H), 2.168 (s, 3H), 2.089 (s,3H); HRMS (EI) calculated for $C_{36}H_{24}Br_2S_2$ 679.9660, found m/z 679.96619.

Synthesis of 6: 5 (0.125 g, 0.183 mmol) was added to a flame dried 25 mL round-bottom flask. The solid was held under vacuum for 1 hour, the reaction vessel was then back-filled with N_2. Under nitrogen dry THF (20 mL) was added. The solution was cooled to -78 °C in a dry ice/acetone bath. 1.5 M n-buyllithium in hexanes (0.27 mL, 0.40 mmol) was added at -78 °C over 30 min. The reaction was then stirred at -78 °C for 1 hour. Dry CO_2 was then bubbled through the solution for 2 hours. The reaction was allowed to warm to room temperature and stirred for 20 hours. The reaction was quenched by slow addition of 1 M HCl, the product was then extracted with ethyl acetate (2 x 30 mL). The combined

organic layers were washed with 10% by wt. NaS_2O_3 (2 x 30 ml), H_2O (2 x 30 mL), and brine (2 x 30 mL). The organic layer was dried over $MgSO_4$, and the solvent removed by rotary evaporation. The product was isolated by column chromatography, eluted with 5% acetic acid and 95% ethyl acetate as a grey solid (0.03 g, 27 % yield). MP: 253 °C (decomp.) ^{1}H NMR (DMSO-d6, 500 MHz) δ 9.177 (d, 2H, J= 8.3 Hz), 8.301 (m, 4H, J= 10.3 Hz), 7.536 (d, 4H, J= 7.32 Hz), 7.450 (s, 2H) 7.373 (t, 2H, J= 7.81 Hz), 7.309 (t, 4H, J= 7.81 Hz), 7.246 (m, 2H, J= 7.81 Hz), 2.161 (s, 2H), 2.063 (s, 4H); HRMS (EI) calculated for $C_{38}H_{26}O_4S_2$ 610.1267, found m/z 610.12708.

UBMOF-2 Synthesis: To a 15 mL pressure tube **PhTPDC** (0.010 g, 0.016 mmol), $Zn(NO_3)_2{\cdot}6H_2O$ (0.006 g, 0.020 mmol) and DMF (5 mL) was added. The pressure tube was sealed with a Teflon screw top and heated at 110 °C for 2 days. The resulting crystals were 100-300 µm along each axis. Single crystal X-ray diffraction revealed the framework consisted of Zn_4O tetrahedron capped by deprotonated PhTPDC. The voids of the lattice are presumed to consist of DMF solvent, although no attempt was made to refine these molecules. The chemical stability of the ligand was verified through digestion experiments described below.

Physical Measurements:

MOF Digestion: To further confirm the composition of UBMOF-2 and the nature of the fatigue product of the incorporated **PhTPDC** linker, acid digestion experiments were performed. Approximately 10 mg of **UBMOF-2** was digested in 30 µL of DCl in D_2O (35% wt.) in 1 g of DMSO-d_6 the mixture was then agitated. The UBMOF-2 crystals broke apart into the organic linker, PhTPDC, and the metal SBUs. The ^{1}H-NMR spectrum of the digested sample was then compared to a sample of **6** dissolved in 1 mL of DMSO-d_6. The digested framework showed peaks consistent with product **6**, and residual solvent from the solvothermal reaction. **UBMOF-2** crystals following repeated cyclization and thermal cycloreversion were digested under identical conditions to freshly synthesized **UBMOF-2** crystal digestions. The digestion of fatigued crystals was monitored visually to determine the return of photo-activity to the liberated **PhTPDC** linkers.

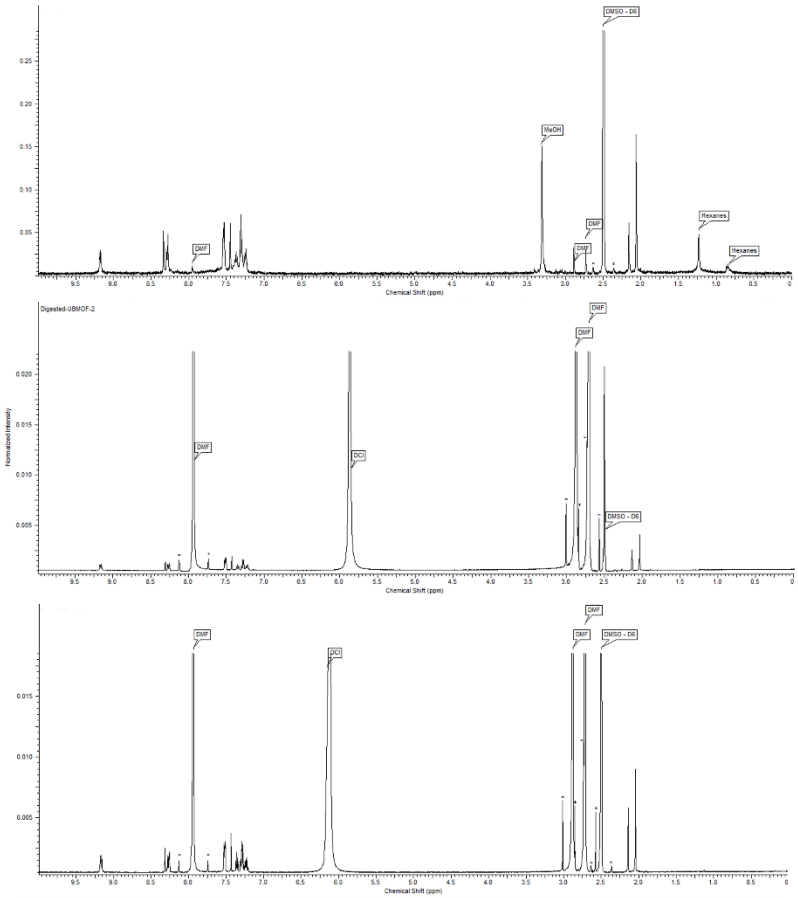


Figure S2: Top: PhTPDC NMR in DMSO –D6. Middle: UBMOF-2 digestion NMR in DMSO-D6. Bottom: Fatigued UBMOF-2 NMR in DMSO-D6. Asterisk marked peaks indicate ^{13}C satellite peaks.

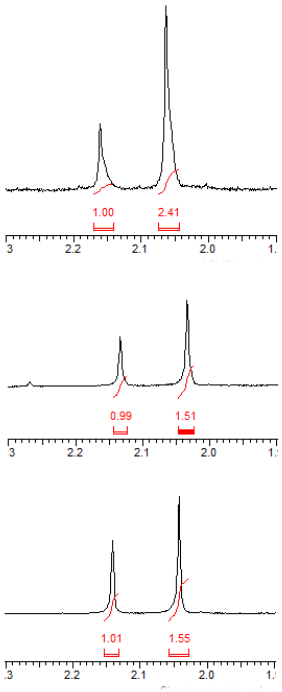


Figure S3: Thiophene methyl of the PhTPDC (Top), digested UBMOF-2 (Middle), and digested fatigued UBMOF-2 (Bottom). The up field peak is attributed to the para rotomer, and the downfield peak is attributed to the slightly shielded anti rotomer.

UBMOF-2 single crystal UV/Vis: Freshly grown UBMOF-2 crystals, were taken up into a 2 x .2 mm capillary in fresh DMF, UBMOF-2 crystals ranged in size from 50 µm to 250 µm on each side. Images and UV-vis absorption spectra were obtain of the crystal prior to irradiation. The crystal was then irradiated with a 365 nm diode (Thor Labs, M365F1, 3.0 mW) for 5 min. Images and spectra of the irradiated crystal were then taken, showing a strong increase in absorption at 600 nm. To best quantify the change in absorption of the photochromic UBMOF-2, the difference in the non-irradiated crystal and irradiated crystal was calculated to give the corrected spectra.

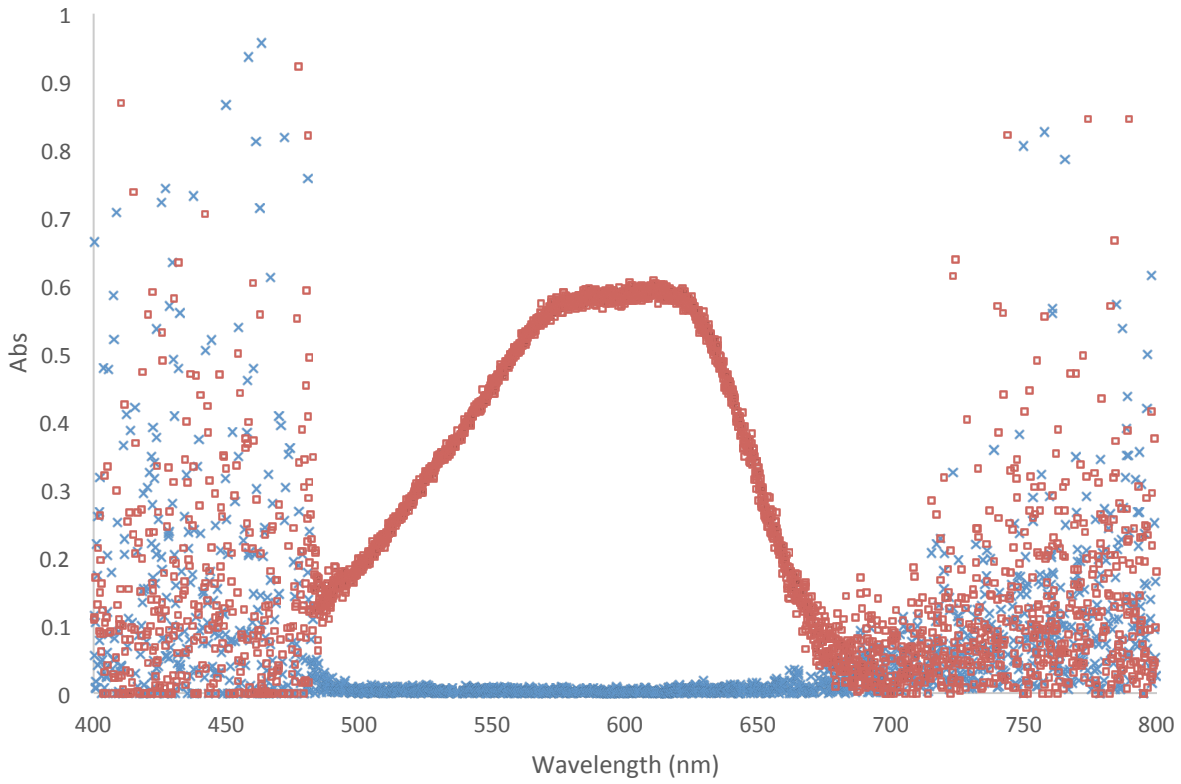


Figure S4: Raw data for inset of Figure 2. Single Crystal UV-vis spectra of UBMOF-2 prior to irradiation (blue x) and the crystal following irradiation with 365nm light (red □).

UBMOF-2 Kinetic Studies: To study the thermally driven cycloreversion of UBMOF-2, single crystals of the framework ranging from 100 to 300 µm per side were sealed in a glass capillary in fresh DMF. The capillary was mounted on a temperature controlled microscope stage (Cryo Industries of America) and heated to 385, 375, 365, 355, and 395 K. At each temperature a single crystal was aligned and the change in absorbance upon irradiation was recorded at 600 nm. Once a steady absorbance was reached UV irradiation (365 nm) was ceased and the decrease in absorbance was measured over time until the original absorbance was achieved. Plots of the decrease of absorbance at 600 nm were fit to a bi-exponential decay. The rate or thermal cycloreversion was found to be dependent on the temperature of the measurement.

PhTPDC (6) UV/Vis Studies: Pure PhTPDC ligand was dissolved into MeOH to form a $2.5X10^{-4}$ M solution suitable for solutions state UV/Vis studies. The absorption was measured in a Perkin Elmer Lambda 35 UV-vis spectrometer.

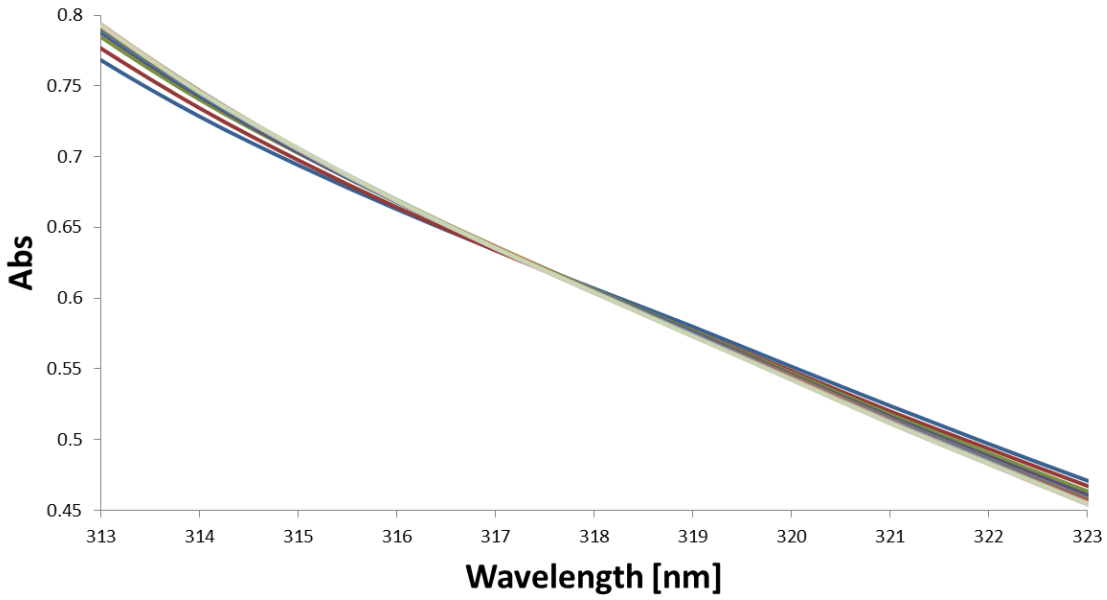


Figure S5: Isosbestic point of PhTPDC (6) confirming the conversion of o-PhTPDC to c-PhTPDC.

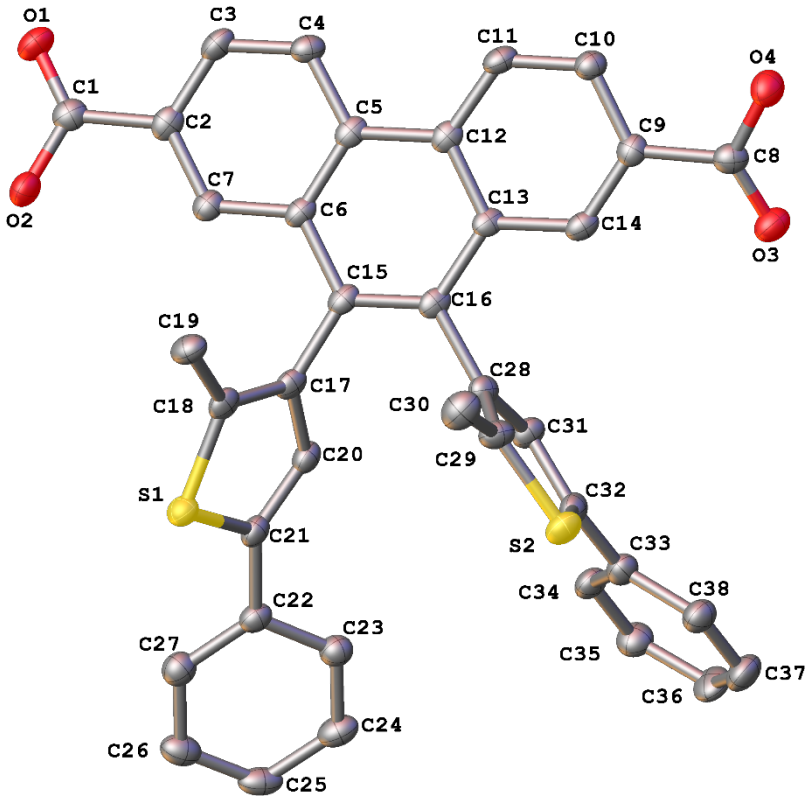


Figure S6. ORTEP drawing of the asymmetric unit of PhTPDC at the 50% probability level including numbering. Hydrogen atoms and two fully ordered methanol solvent molecules have been omitted for clarity.

Single Crystal X-ray Diffraction:

PhTPDC

X-ray diffraction data was collected using a Bruker SMART APEX2 CCD diffractometer installed at a rotating anode source (MoKα radiation, λ=0.71073 Å), and equipped with an Oxford Cryosystems (Cryostream 700) nitrogen gas-flow apparatus. The data were collected by the rotation method with 0.5° frame-width (ω scan) and 60 sec exposure time per frame. Five sets of data (360 frames in each set) were collected for this compound, nominally covering complete reciprocal space.

Crystal Structure of PhTPDC

Table 1 Crystal data and structure refinement for PhTPDC.

Identification code	PhTPDC
Empirical formula	$C_{40}H_{34}O_6S_2$
Formula weight	674.79
Temperature/K	90
Crystal system	triclinic
Space group	P-1
a/Å	9.994(2)
b/Å	10.490(3)
c/Å	16.062(4)
α/°	103.726(7)
β/°	94.369(7)
γ/°	98.139(7)
Volume/Å^3	1608.8(7)
Z	2
ρ_{calc}g/cm^3	1.393
μ/mm^{-1}	0.216
F(000)	708.0
Crystal size/mm^3	0.03 × 0.02 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.06 to 52.94
Index ranges	$-12 \le h \le 12$, $-13 \le k \le 13$, $-20 \le l \le 20$
Reflections collected	26867
Independent reflections	6632 [R_{int} = 0.0937, R_{sigma} = 0.0895]
Data/restraints/parameters	6632/0/441
Goodness-of-fit on F^2	1.014
Final R indexes [I>=2σ (I)]	R_1 = 0.0645, wR_2 = 0.1521
Final R indexes [all data]	R_1 = 0.1125, wR_2 = 0.1789
Largest diff. peak/hole / e Å^{-3}	1.00/-0.62

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for PhTPDC. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	1561.1(9)	3818.0(9)	9141.1(5)	24.2(2)
S2	4634.1(9)	-442.1(9)	8676.7(6)	28.3(2)
O1	-4519(2)	2196(2)	5743.0(16)	31.7(6)
O2	-3080(2)	3336(2)	6897.2(16)	30.8(6)
O3	3033(2)	-4975(2)	5982.2(15)	30.8(6)
O4	2657(3)	-5207(3)	4554.3(15)	32.3(6)
C1	-3481(3)	2323(3)	6234(2)	24.5(8)

C2	-2557(3)	1314(3)	6116(2)	22.9(7)
C3	-2778(3)	324(3)	5348(2)	24.2(8)
C4	-1946(3)	-620(3)	5203(2)	23.0(7)
C5	-865(3)	-610(3)	5827(2)	20.6(7)
C6	-625(3)	400(3)	6604(2)	20.1(7)
C7	-1515(3)	1344(3)	6737(2)	21.5(7)
C8	2523(3)	-4656(3)	5361(2)	25.0(8)
C9	1645(3)	-3603(3)	5464(2)	21.8(7)
C10	696(3)	-3564(3)	4779(2)	22.9(7)
C11	-131(3)	-2615(3)	4909(2)	22.8(7)
C12	-13(3)	-1636(3)	5686(2)	20.3(7)
C13	989(3)	-1636(3)	6362(2)	19.3(7)
C14	1771(3)	-2673(3)	6233(2)	21.3(7)
C15	481(3)	435(3)	7264(2)	20.2(7)
C16	1224(3)	-582(3)	7146(2)	20.0(7)
C17	799(3)	1531(3)	8063(2)	21.5(7)
C18	1192(3)	2863(3)	8089(2)	22.6(7)
C19	1389(4)	3518(3)	7367(2)	27.1(8)
C20	809(3)	1329(3)	8911(2)	22.7(7)
C21	1207(3)	2445(3)	9562(2)	22.6(7)
C22	1351(3)	2578(3)	10500(2)	22.7(7)
C23	1740(3)	1534(3)	10822(2)	25.5(8)
C24	1855(4)	1624(4)	11699(2)	30.3(8)
C25	1601(4)	2751(4)	12277(2)	31.0(9)
C26	1241(4)	3798(4)	11965(2)	31.6(9)
C27	1109(4)	3696(4)	11087(2)	27.7(8)
C28	2326(3)	-644(3)	7814(2)	22.3(7)
C29	3638(3)	-29(4)	7884(2)	26.2(8)
C30	4224(4)	891(4)	7376(2)	34.0(9)
C31	2137(3)	-1457(3)	8404(2)	22.9(7)
C32	3286(4)	-1441(3)	8925(2)	25.3(8)
C33	3402(3)	-2121(3)	9624(2)	25.4(8)
C34	2324(3)	-2262(3)	10115(2)	25.8(8)
C35	2398(4)	-2897(4)	10775(2)	31.7(9)
C36	3566(4)	-3398(4)	10963(2)	33.8(9)
C37	4657(4)	-3252(4)	10496(2)	35.7(9)
C38	4588(4)	-2614(4)	9830(2)	29.4(8)
O6	4737(3)	5000(3)	2960.9(18)	53.2(9)
C40	5089(4)	4356(4)	2146(2)	35.6(9)
O5	5687(3)	6908(3)	5553.1(16)	37.4(7)
C39	5574(4)	7897(4)	6306(2)	32.9(9)

UBMOF-2

X-ray diffraction data for UBMOF-2 was collected using a Bruker SMART APEX2 CCD diffractometer installed at the APS beamline ID-15B (λ=0.41328 Å), and equipped with a [APS cryo info] nitrogen gas-flow apparatus. The data were collected by the rotation method with 0.5° frame-width (ϕ scan) and 1 sec exposure time per frame. Three sets of data (one set of 720 frames, two sets of 360 frames) were collected, nominally covering complete reciprocal space.

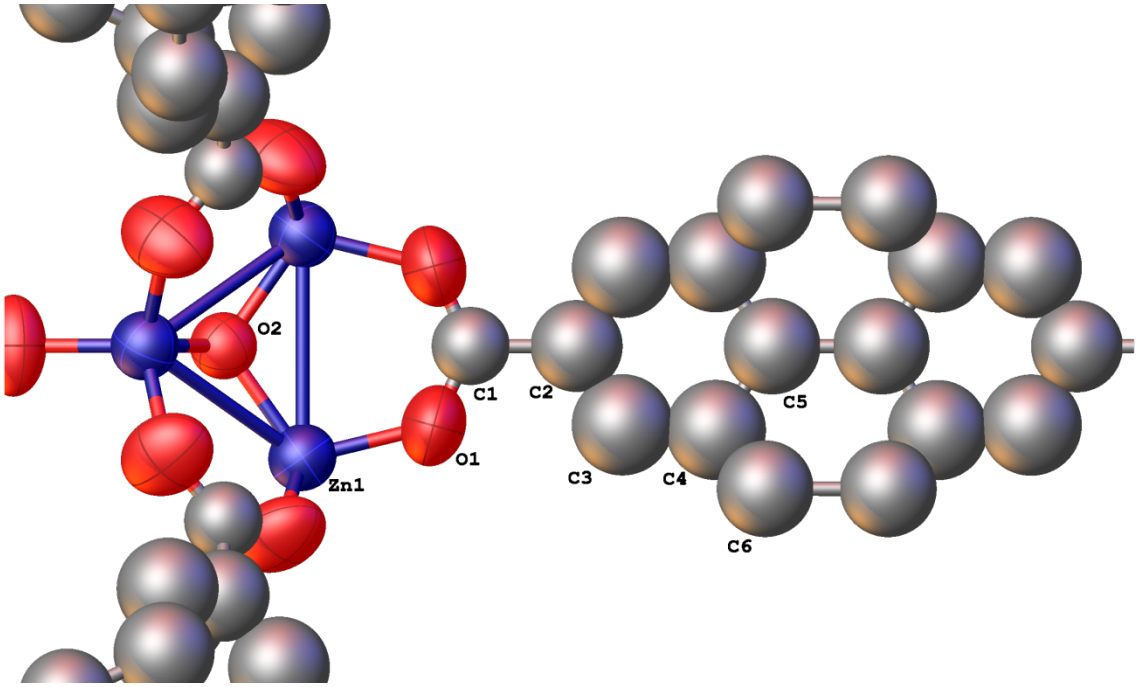


Figure S7. ORTEP drawing of the grown unit of **UBMOF-2** at the 50% probability level including numbering of the asymmetric unit. Hydrogen atoms have been omitted for clarity.

Table 3 Crystal data and structure refinement for UBMOF-2.

Identification code	UBMOF-2
Empirical formula	$C_{12}H_3O_{3.25}Zn$
Formula weight	264.51
Temperature/K	100.0
Crystal system	cubic
Space group	Fm-3m
a/Å	34.001(3)
b/Å	34.001(3)
c/Å	34.001(3)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	39307(5)
Z	32
ρ_{calc}g/cm^3	0.358
μ/mm^{-1}	0.497
F(000)	4192.0
Crystal size/mm^3	0.05 × 0.05 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.98 to 35.26
Index ranges	$-28 \leq h \leq 28$, $-28 \leq k \leq 28$, $-28 \leq l \leq 28$
Reflections collected	86799
Independent reflections	698 [R_{int} = 0.2267, R_{sigma} = 0.0237]
Data/restraints/parameters	698/0/44
Goodness-of-fit on F^2	2.297
Final R indexes [I>=2σ (I)]	R_1 = 0.1655, wR_2 = 0.4709
Final R indexes [all data]	R_1 = 0.1850, wR_2 = 0.4923
Largest diff. peak/hole / e Å^{-3}	0.93/-0.35

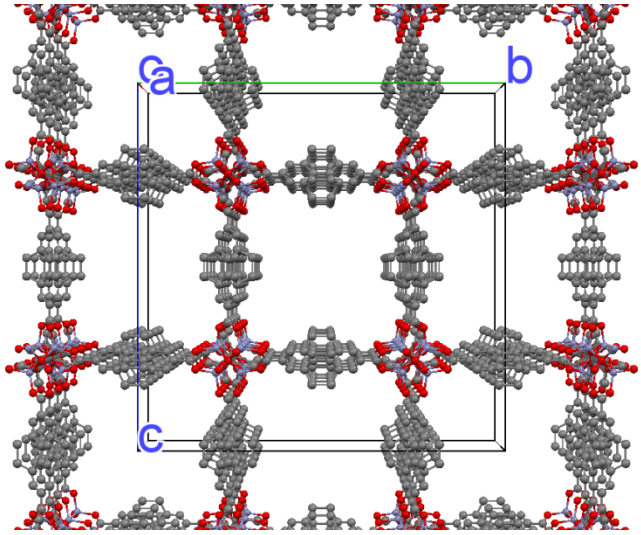


Figure S8. Perspective packing diagram of UBMOF-2 viewed along [100].