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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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Supporting Information:

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Synthetic Methods:

Unless otherwise specified, all chemicals were purchased from commercial sources and used without further purification. THF was dried over sodium/benzophenone and stored over dried 4 Å molecular sieves prior to use. Immediately before use, *n*-butyllithium was titrated with 1,3-diphenyl acetone *p*-toluenesulfonyl hydrazine in THF at 0 °C.[1] ^{1}H-NMR spectra were recorded on an Inova 500 MHz instrument referenced to residual solvent signal. Abbreviations used are: s=singlet d=doublet t=triplet m=multiplet dd=doublet of doublets td=triplet of doublets bs=broad singlet bt=broad triplet bm=broad multiplet. Solution electronic absorption spectra were recorded on a Perkin-Elmer Lambda 12 spectrophotometer in 1-cm quartz cuvettes using spectroscopic grade solvents purchase from Aldrich. High-resolution mass spectra were obtained at the University at Buffalo's mass spectrometry facility on a ThermoFinnigan MAT XL spectrometer.

Synthesis of 3a: To a flame dried 250 ml round-bottom flask, 4-iodo-2,5-dimethylthiophene (2.619 g, 11.0 mmol) was added. The pale yellow oil 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 (9.0 mL, 13.5 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 (2.000 g, 5.5 mmol) in a single portion. The reaction was allowed to slowly warm to room temperature and stirred for 20 hours, then quenched by slow addition of 1 M HCl. The product was then extracted with diethyl ether (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 (2.14 g, 66% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.78 (d, 2H, *J*=2.5 Hz), 7.65 (d, 2H, *J*=10.5 Hz), 7.51 (dd, 2H, *J*=5 Hz, 2.5Hz), 5.68 (s, 2H), 2.71 (s, 6H), 2.07 (s, 6H); HRMS (EI) calculated for $C_{26}H_{22}O_2Br_2S_2$ 589.940, found m/z 589.94250

Synthesis of 4a: **3a** (1.00 g, 1.69 mmol) was dissolved in toluene (50 mL) in a 100 mL round bottom flask. Para-toluene sulfonic acid (0.032 g, 0.17 mmol) was added to the solution. The flask was capped with a Barrret trap and a reflux condenser. The reaction was refluxed for 20 hours at 140 °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 (0.799g, 82% yield). The product was pure by NMR. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.98 (d, 1H, *J*=3 Hz), 7.75 (d, 1H, *J*=10.5 Hz), 7.72 (d, 1H, *J*=11 Hz), 7.67 (dd, 1H, *J*=10.5 Hz, 3 Hz), 7.54 (dd, 1H, *J*=10.5 Hz, 3 Hz), 6.99 (d, 1H, *J*=3 Hz), 5.92 (bs, 2H), 2.28 (s, 6H), 1.84 (s 6H); HRMS (EI) calculated for $C_{26}H_{20}O_1Br_2S_2$ 571.9296, found m/z: 571.93054.

Synthesis of 5a: Compound **4a** (0.750 g, 1.31 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 $NaBH_4$ (0.050 g, 1.31 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 (2x25 mL). The combined organic phases were washed with H_2O (2x30 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 (0.634, 84% yield).^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.59 (d, 1H, *J*=10 Hz), 7.51 (d, 1H, *J*=2.5 Hz), 7.47 (d, 1H, *J*=10.5 Hz), 7.40 (dd, 1H, *J*=10 Hz, 2.5 Hz), 7.24 (d, 1H, *J*=2 Hz), 7.09 (bs, 1H), 6.26 (bt, 2H), 5.49 (bs, 1H), 5.32 (bs, 1H), 2.32 (bm, 6H),

1.91 (bs, 1H), 1.81 (bs, 2H), 1.57 (bs, 3H); HRMS (EI) calculated for $C_{26}H_{22}O_1Br_2S_2$ 573.9453, found m/z 573.94519.

Synthesis of 6a: 5a (0.600 g, 1.04 mmol) was dissolved in toluene (50 mL) in a 100 mL round bottom flask. Para-toluene sulfonic acid (0.020 g, 0.10 mmol) was added to the solution. The flask was capped with a Barrret 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 (0.384 g, 66% yield). The solid was pure by NMR.^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.55 (d, 2H, *J*=6 Hz), 7.77 (dd, 2H, *J*=16 Hz, 2 Hz), 7.73 (t, 2H, *J*=2 Hz), 6.31 (d, 1H, *J*=0.8 Hz), 6.30 (d, 1H, *J*=0.8 Hz), 2.39 (s, 3H), 2.38 (s, 3H), 2.00 (s, 3H). 1.96 (s, 3H); HRMS (EI) calculated for $C_{26}H_{20}Br_2S_2$ 555.9347, found m/z 55.93561.

Synthesis of 7a: 6a (0.200 g, 0.35 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 (0.49 mL, 0.73 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 (2x30 mL). The combined organic layers were washed with 10% by wt. NaS_2O_3 (2x30 ml), H_2O (2x30 mL), and brine (2x30 mL). The organic layer was dried over $MgSO_4$, and the solvent removed by rotorary evaporation. The product was isolated by column chromatography, eluted with 5% acetic acid and 95% ethyl acetate as a grey solid (0.122 g, 70% yield). ^{1}H NMR (Acetone-d6, 500 MHz) δ 9.12 (d, 2H, *J*=11 Hz), 8.43 (dd, 2H, *J*=28 Hz, 2 Hz), 8.34 (d, 2H, *J*=11 Hz), 6.55 (s, 1H) 6.52 (s, 1H), 2.4 (s, 3H), 2.38 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H); HRMS (EI) calculated for $C_{28}H_{22}O_4S_2$ 486.0954, found m/z 486.09500

Synthesis of 3b: 2-chloro-4-iodo-5-methylthiophene (2.0 g, 8.4 mmol) was added to a flame dried 100 mL round-bottom flask. The oil was held under vacuum for 1 hour, the reaction vessel was then back-filled with N_2. Under nitrogen dry THF (60 mL) was added. The solution was cooled to -78 °C in a dry ice/acetone bath. 1.5 M n-buyllithium in hexanes (5.74 mL, 8.6 mmol) was added at -78 °C over 20 min. The reaction was then stirred at -78 °C for 15 min. 2,7–dibromo-9,10-phenanthrenedione (1.54 g, 4.2 mmol) was added all at once under nitrogen. 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 diethyl ether (2x30 mL). The combined organic layers were washed with 10% by wt. NaS_2O_3 (2x30 ml), H_2O (2x30 mL), and brine (2x30 mL). The organic layer was dried over $MgSO_4$, and the solvent removed by rotary evaporation. The product was passed through a silica plug with 100% CH_2Cl_2 to remove impurities. The solvent was removed under reduced pressure to afford an off white solid (0.973 g, 39% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.87 (dd, 2H, *J*=7 Hz, 1 Hz), 7.59 (dd, 2H, *J*=7 Hz, 1 Hz), 7.44 (td, 2H, *J*=9 Hz, 1.5 Hz), 7.32 (td, 2H, *J*=6.5 Hz, 1 Hz), 5.99 (s, 2H), 2.64 (s, 6H); HRMS (EI) calculated for $C_{24}H_{18}O_2Cl_2S_2$ 472.0120, found m/z 472.01196.

Synthesis of 4b: 3b (1.40 g, 2.96 mmol) was dissolved in toluene (60 mL) in a 100 mL round bottom flask. Para-toluene sulfonic acid (0.056 g, 0.30 mmol) was added to the solution. The flask was capped

with a Barrret trap and a reflux condenser. The reaction was refluxed for 20 hours. The solvent was removed under reduced pressure. The reaction residue was passed through a silica gel plug and eluted with 4:1 Hexanes:CH_2Cl_2 the solvent was removed with reduced pressure to afford a tan solid (1.308 g, 97 % yield) The product was pure by NMR. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.95 (d, 1H, *J*=10 Hz), 7.91 (d, 1H, *J*=10.5 Hz), 7.88 (dd, 1H, *J*=10.5 Hz, 2 Hz), 7.62 (td, 1H, *J*=8 Hz, 2 Hz) 7.44 (td, 1H, *J*=9 Hz, 1.5 Hz) 7.37 (td, 1H, *J*=9.5 Hz, 1.5 Hz) 7.29 (td, 1H, *J*=10 Hz, 1.5 Hz) 6.87 (d, 1H, *J*=10 Hz), 6.16 (s, 2H), 1.86 (bs, 6H); HRMS (EI) calculated for $C_{24}H_{16}O_1Cl_2S_2$ 454.0014, found m/z 454.00143.

Synthesis of 5b: 4b (1.20 g, 2.63 mmol) was dissolved in THF (20 mL) and methanol (20 mL) in a 100 mL round bottom flask. The reaction was capped with a reflux condenser and heated at 60 °C. $NaBH_4$ (0.109 g, 2.9 mmol) was added in four portions over 4 hours with heating. The reaction was then heated at 60 °C 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 (2x25 mL). The combined organic phases were washed with H_2O (2x30 mL) and sat. brine solution (2x30 mL). The organic phase was then dried over $MgSO_4$ and the solvent removed with reduced pressure to afford a brown solid (1.077 g, 89% yield). The product was pure by NMR. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.82 (bt, 1H), 7.70 (t, 1H *J*=6.5 Hz), 7.58 (m, 1H, *J*=6.5 Hz), 7.44 (bt, 1H), 7.32 (m, 2H, *J*=7 Hz), 7.11 (d, 1H, *J*=7.5 Hz), 6.08 (bs, 1H), 5.49 (s, 1H), 5.27 (s, 1H), 1.91 (s, 3H), 1.62 (s, 3H); HRMS (EI) calculated for $C_{24}H_{18}O_1Cl_2S_2$ 456.0171, found m/z 456.01529

Synthesis of 6b: 5b (1.00 g, 2.18 mmol) was dissolved in toluene (65 mL) in a 100 mL round bottom flask. Para-toluene sulfonic acid (0.042 g, 0.22 mmol) was added to the solution. The flask was capped with a Barrret trap and a reflux condenser. The reaction was refluxed for 20 hours. 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 affored a brown solid (0.791 g, 83% yield). The product was pure by NMR. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.79 (d, 2H, *J*= 8 Hz), 7.70 (t, 2H, *J*=8 Hz), 7.62 (t, 2H, *J*=8 Hz), 7.57 (d, 2H, *J*=8 Hz), 6.56 (s, 1H), 6.55 (s, 1H), 2.03 (s, 3H), 1.99 (s, 3H), 1.55 (s, 6H); HRMS (EI) calculated for $C_{24}H_{16}Cl_2S_2$ 438.0065, found m/z 438.00632.

Synthesis of 7b: 6a (0.690 g, 1.57 mmol) was added to a flame dried 100 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 (25 mL) was added. The solution was cooled to -78 °C in a dry ice/acetone bath. 1.5 M n-buyllithium in hexanes (2.1 mL, 3.14 mmol) was added at -78 °C over 30 min. The reaction was then stirred at -78 °C for 2 hours. 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 1M HCl, the product was then extracted with ethyl acetate (2x30 mL). The combined organic layers were washed with 10% by wt. NaS_2O_3 (2x30 ml), H_2O (2x30 mL), and brine (2x30 mL). The organic layer was dried over $MgSO_4$, and the solvent removed by rotorary evaporation. The product was isolated by column chromatography, eluted with 5% acetic acid and 95% ethyl acetate as a tan solid (0.114 g,16% yield). ^{1}H NMR (DMSO d6, 500 MHz) δ 9.00 (d, 2H, *J*=8.5 Hz), 7.78 (t, 2H, *J*=7.5 Hz), 7.64 (t, 2H, *J*=8 Hz), 7.41 (d, 2H, *J*=8.5 Hz), 7.39 (s, 2H), 2.10 (s, 6H); HRMS (EI) calculated for $C_{24}H_{18}O_4S_2$ 458.0641, found m/z 458.06409.

Synthesis of UBMOF-1: To a 15 mL pressure tube **7a** (0.010 g, 0.02mmol), $Zn(NO_3)_2{\cdot}6H_2O$ (0.006 g, 0.02 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 300-500 μm along each axis. Single crystal X-ray diffraction revealed the framework consisted of Zn_4O tetrahedron capped by deprotonated **7a**. 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 verify the ligand did not decompose during the synthesis of UBMOF-1, 4 mg of UBMOF-1 was digested in 23 μL of DCl in D_2O (35% wt.) and added to 1 mL of DMSO-d_6. The ^{1}H-NMR spectrum of the digested sample was then compared to a sample of **7a** dissolved in 1 mL of DMSO-d_6. The digested framework showed peaks consistent with product **7a**, and residual solvent from the solvothermal reaction.

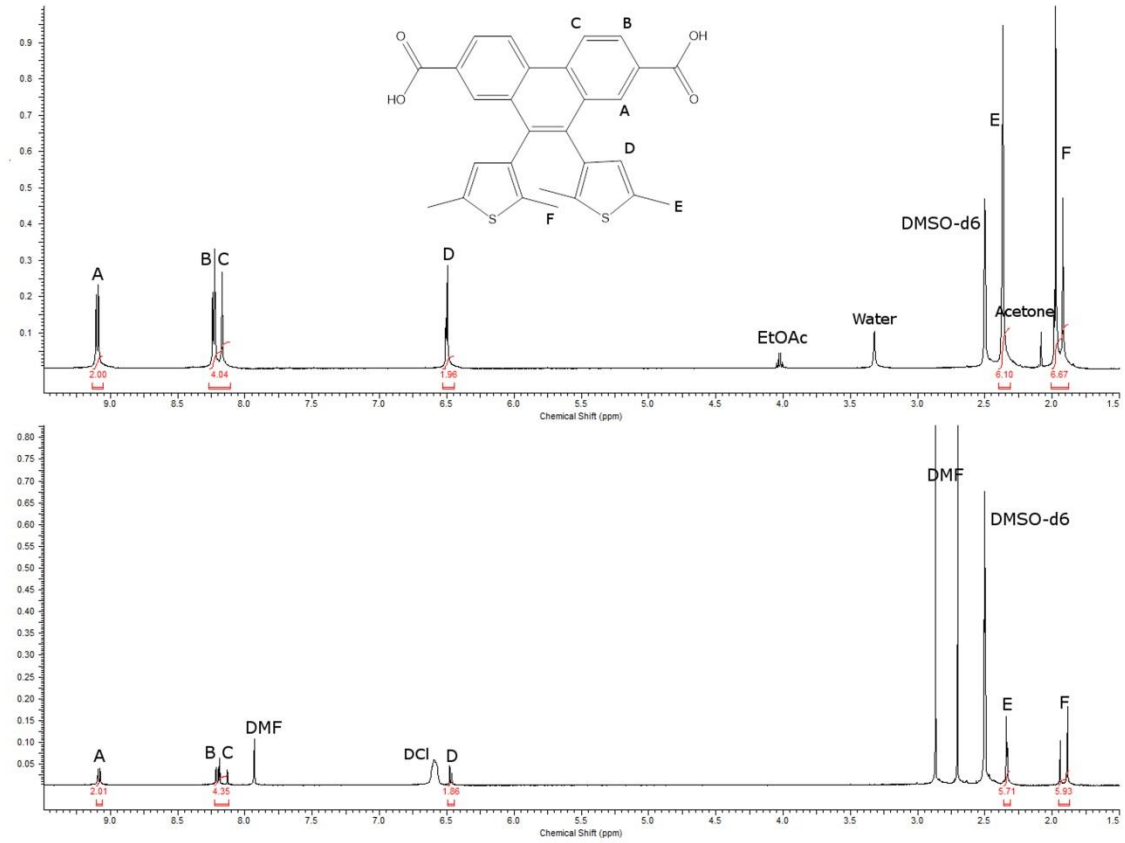

Figure S1. ^{1}H-NMR spectrum of **7a** (upper) and digested **UBMOF-1** (lower) in DMSO-d_6. Signals from the ligand and residual solvents are identified.

MOF Digestion UV-vis: 3 mg of **UBMOF-1** was irradiated for 30 min with a 365 nm diode. The sample was then digested (in the dark) in 1 mL of dry DMSO and 23 μL of conc. HCl and the UV/Vis spectrum was recorded. The digested sample was then irradiated with a white light source for 20 min with a spectrum recorded after 10 and 20 min. The sample was then irradiated with 365 nm diode for 10 min

and the final spectrum was recorded. These experiments indicate that the irreversible photochemistry observed in the UBMOF-1 crystal becomes fully reversible once the crystals are digested.

UBMOF-1 single crystal UV/Vis: Freshly grown UBMOF-1 crystal, measuring 100 μm along each axis was mounted on a glass slide in oil in the dark. Images and UV-vis absorption spectra were obtain of the crystal prior to irradiation (line a). The crystal was then irradiated with a 365 nm diode for 5 min. Images and spectra of the irradiated crystal were then taken, showing a strong increase in absorption at 550 nm (line b). To best quantify the change in absoption of the photochromic UBMOF-1, the difference in the non-irradiated crystal (line b) and irradiated crystal (line b) was calculated to give the corrected spectra (line c).

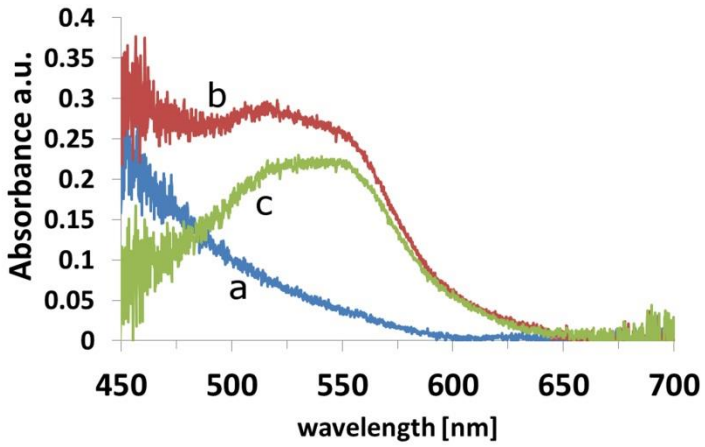

Figure S2. Single crystal absorption spectrum of **UBMOF-1** before irradiation (a, blue line), after irradiation with 365 nm light (b, red line), and the difference between the two spectra (c, green line, c = b - a).

Single Crystal X-ray Diffraction:

X-ray diffraction data for all samples were 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. Generally five sets of data (360 frames in each set) were collected for each compound, nominally covering complete reciprocal space.

Details of the single crystal structure determination of 3a:

Single crystals of $C_{26}H_{22}Br_2O_2S_2$ [3a] were crystallized from ethyl acetate layered with methanol. A suitable crystal was selected and mounted on a glass capillary with oil on a Bruker APEX2 microfocus rotating anode diffractometer. The crystal was kept at 90 K during data collection. Using Olex2,[2] the structure was solved with the XS structure solution program using Direct Methods and refined with the XL refinement package using Least Squares minimisation.[3]

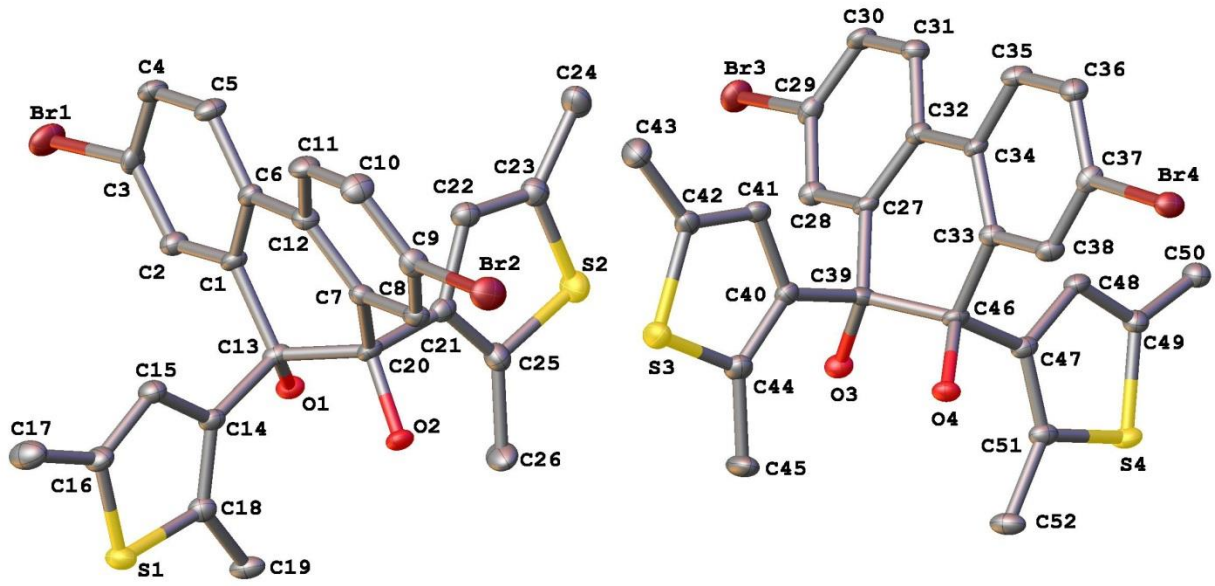

Figure S3. ORTEP drawing of the asymmetric unit of **3a** at the 50% probability level including numbering. Hydrogen atoms have been omitted for clarity.

Table S1. Crystal data and structure refinement for 3a

Identification code	3a
Empirical formula	$C_{26}H_{22}Br_2O_2S_2$
Formula weight	590.37
Temperature/K	90
Crystal system	triclinic
Space group	P-1
a/Å	9.2188(14)
b/Å	14.566(2)
c/Å	19.104(3)
α/°	107.302(3)
β/°	92.630(3)
γ/°	104.290(3)
Volume/Å^3	2353.5(6)
Z	4
ρ_{calc}mg/mm^3	1.666
m/mm^{-1}	3.644
F(000)	1184.0
Crystal size/mm^3	0.2 × 0.2 × 0.02
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection	4.326 to 57.694°

Index ranges	$-12 \leq h \leq 12$, $-19 \leq k \leq 16$, $-22 \leq l \leq 25$
Reflections collected	22906
Independent reflections	12122 [R_{int} = 0.0405, R_{sigma} = 0.0782]
Data/restraints/parameters	12122/0/589
Goodness-of-fit on F^2	1.008
Final R indexes [I>=2σ (I)]	R_1 = 0.0439, wR_2 = 0.1014
Final R indexes [all data]	R_1 = 0.0720, wR_2 = 0.1113
Largest diff. peak/hole / e $Å^{-3}$	1.20/-1.08

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*Y*	*z*	U(eq)
Br1	-176.1(4)	3916.9(3)	1515.6(2)	29.04(10)
Br2	11460.3(4)	6221.8(3)	4009.1(2)	26.54(10)
Br3	1686.4(4)	8292.9(3)	7093.4(2)	23.50(9)
Br4	13254.3(4)	10095.8(2)	9619.0(2)	18.74(9)
S1	6786.1(10)	7140.0(6)	770.4(5)	19.85(19)
S2	4825.2(11)	8284.8(7)	5167.0(5)	24.0(2)
S3	9089.1(10)	8450.7(7)	5452.0(5)	21.8(2)
S4	8315.6(10)	13215.4(6)	9105.3(5)	17.98(18)
O1	4126(3)	7297.4(16)	2684.5(13)	16.1(5)
O2	7425(3)	7924.6(16)	3247.0(13)	16.8(5)
O3	7059(3)	10591.7(17)	6999.1(13)	16.5(5)
O4	10253(2)	10951.0(16)	7607.4(13)	14.7(5)
C1	4144(4)	5589(2)	2494.0(19)	15.7(7)
C2	2685(4)	5289(2)	2139.8(19)	18.7(7)
C3	1794(4)	4331(2)	2041.8(19)	18.3(7)
C4	2316(4)	3677(3)	2316(2)	21.0(8)
C5	3798(4)	3967(2)	2643(2)	19.9(8)
C6	4757(4)	4920(2)	2725.2(18)	15.9(7)
C7	7168(4)	6236(2)	3264.0(18)	15.4(7)
C8	8672(4)	6521(2)	3560.5(18)	17.0(7)
C9	9400(4)	5810(3)	3604.7(19)	19.2(7)
C10	8649(4)	4798(3)	3353(2)	22.3(8)
C11	7138(4)	4515(2)	3066(2)	20.1(8)
C12	6360(4)	5216(2)	3019.4(19)	16.2(7)
C13	5096(4)	6647(2)	2578.5(19)	14.6(7)
C14	5781(4)	6664(2)	1869.9(19)	15.9(7)
C15	6233(4)	5829(2)	1415.0(19)	18.8(7)
C16	6794(4)	5976(2)	803(2)	20.2(8)

C17	7368(4)	5270(3)	196(2)	28.7(9)
C18	6013(4)	7440(2)	1585.6(19)	17.7(7)
C19	5681(4)	8441(2)	1851(2)	20.2(8)
C20	6361(4)	7033(2)	3263.1(19)	15.8(7)
C21	5698(4)	7322(2)	3988.3(19)	16.5(7)
C22	5227(4)	6647(3)	4403.5(19)	18.5(7)
C23	4731(4)	7051(3)	5048(2)	19.9(7)
C24	4178(4)	6581(3)	5615(2)	26.0(8)
C25	5529(4)	8251(3)	4341(2)	21.2(8)
C26	5874(5)	9210(3)	4145(2)	28.3(9)
C27	6336(4)	9337(2)	7608.1(19)	14.3(7)
C28	4874(4)	9141(2)	7295.1(19)	15.9(7)
C29	3696(4)	8552(2)	7534.0(19)	18.0(7)
C30	3980(4)	8156(2)	8080.9(19)	18.5(7)
C31	5455(4)	8350(2)	8394.7(19)	17.0(7)
C32	6668(4)	8943(2)	8166.7(19)	15.1(7)
C33	9353(4)	9932(2)	8374.1(18)	14.4(7)
C34	8243(4)	9160(2)	8499.2(18)	14.0(7)
C35	8690(4)	8656(2)	8953.1(19)	17.2(7)
C36	10169(4)	8906(2)	9289.5(19)	18.5(7)
C37	11223(4)	9686(2)	9160.6(19)	15.2(7)
C38	10820(4)	10194(2)	8712.1(19)	15.9(7)
C39	7611(4)	9947(2)	7303.2(19)	16.3(7)
C40	8137(4)	9231(2)	6657.7(19)	15.2(7)
C41	8020(4)	8207(2)	6598.3(19)	16.2(7)
C42	8478(4)	7688(2)	5976.5(19)	17.2(7)
C43	8457(4)	6602(3)	5713(2)	24.6(8)
C44	8716(4)	9476(3)	6069(2)	20.2(8)
C45	9028(5)	10430(3)	5874(2)	27.9(9)
C46	8956(4)	10569(2)	7927.4(19)	14.6(7)
C47	8568(4)	11475(2)	8447.8(19)	15.1(7)
C48	7768(4)	11412(2)	9063.4(18)	15.9(7)
C49	7546(4)	12288(2)	9475.3(19)	16.5(7)
C50	6690(4)	12469(2)	10124.1(19)	19.8(7)
C51	8927(4)	12419(2)	8393.9(19)	17.1(7)
C52	9768(4)	12859(2)	7860(2)	21.1(8)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}

Br1	17.6(2)	25.1(2)	38.6(3)	10.89(18)	-5.83(17)	-3.89(15)
Br2	16.27(19)	32.1(2)	32.5(2)	14.25(18)	-0.95(16)	4.90(15)
Br3	13.03(18)	25.57(19)	27.5(2)	7.19(16)	-0.61(15)	-0.42(14)
Br4	14.78(17)	20.70(17)	22.47(19)	10.92(15)	0.13(14)	3.42(14)
S1	23.3(5)	17.3(4)	21.2(5)	9.7(4)	6.9(4)	4.6(4)
S2	29.6(5)	22.0(4)	20.5(5)	4.9(4)	5.7(4)	9.3(4)
S3	25.9(5)	19.4(4)	18.3(5)	5.7(4)	6.9(4)	2.8(4)
S4	20.9(5)	11.8(4)	23.0(5)	7.7(4)	7.0(4)	4.2(3)
O1	17.0(13)	12.5(11)	20.1(14)	6.5(10)	3.8(10)	4.7(9)
O2	15.9(12)	12.4(11)	20.2(13)	6.9(10)	1.4(10)	-1.5(9)
O3	15.7(12)	14.7(11)	20.2(13)	7.2(10)	2.5(10)	4.3(10)
O4	13.0(12)	14.6(11)	18.4(13)	8.4(10)	5.4(10)	2.6(9)
C1	15.7(17)	11.3(15)	18.4(18)	5.2(14)	2.9(14)	-0.4(13)
C2	19.7(18)	14.8(16)	20.9(19)	7.1(15)	1.3(15)	1.9(14)
C3	12.7(17)	19.1(17)	17.4(19)	2.9(14)	-2.2(14)	-1.4(14)
C4	20.0(19)	16.3(17)	24(2)	9.0(15)	1.9(15)	-3.0(14)
C5	19.1(18)	12.6(16)	27(2)	8.6(15)	1.4(15)	1.2(14)
C6	17.1(18)	12.9(15)	15.2(18)	3.7(14)	3.5(14)	0.3(13)
C7	15.8(17)	16.3(16)	15.4(18)	8.1(14)	3.0(14)	2.9(13)
C8	19.5(18)	14.7(16)	16.7(18)	6.8(14)	5.1(14)	2.1(14)
C9	14.3(18)	23.9(18)	20.6(19)	8.7(15)	2.8(14)	5.1(14)
C10	19.5(19)	21.4(18)	29(2)	10.1(16)	1.3(16)	8.6(15)
C11	25(2)	12.7(15)	24(2)	8.7(15)	3.6(16)	4.0(14)
C12	17.2(17)	15.1(16)	18.2(18)	7.4(14)	3.6(14)	4.7(13)
C13	13.8(17)	9.8(14)	20.7(18)	5.6(13)	3.6(14)	2.9(13)
C14	15.0(17)	13.1(15)	18.5(18)	6.1(14)	2.2(14)	0.8(13)
C15	22.2(19)	13.7(16)	20.2(19)	6.6(15)	3.5(15)	2.9(14)
C16	26(2)	12.9(16)	22(2)	5.2(15)	4.7(16)	4.9(14)
C17	36(2)	19.3(18)	33(2)	8.7(17)	14.8(19)	8.4(17)
C18	16.4(18)	16.7(16)	20.2(19)	6.9(15)	3.5(14)	3.5(14)
C19	20.0(19)	14.6(16)	29(2)	10.6(15)	9.5(16)	5.1(14)
C20	16.7(17)	10.4(15)	17.8(18)	4.4(13)	0.6(14)	-0.5(13)
C21	14.5(17)	14.1(16)	19.9(19)	5.9(14)	-1.7(14)	2.4(13)
C22	16.7(18)	17.8(17)	21.4(19)	7.9(15)	2.8(15)	3.2(14)
C23	18.6(18)	21.6(17)	19.8(19)	7.4(15)	1.7(15)	5.1(15)
C24	24(2)	30(2)	21(2)	7.9(17)	5.3(16)	0.6(16)
C25	26(2)	21.2(18)	16.3(19)	6.6(15)	2.8(15)	6.3(15)
C26	47(3)	14.2(17)	24(2)	5.9(16)	4.2(19)	10.8(17)
C27	14.2(17)	9.1(14)	18.3(18)	4.5(13)	3.7(14)	0.2(13)
C28	14.7(17)	14.3(16)	19.4(18)	6.1(14)	3.2(14)	3.9(13)
C29	14.0(17)	15.5(16)	19.7(19)	1.6(14)	1.3(14)	0.7(13)
C30	15.0(17)	15.0(16)	23(2)	7.7(15)	3.1(15)	-1.8(13)
C31	17.3(18)	15.5(16)	19.1(19)	8.5(14)	2.9(14)	2.4(14)

C32	15.2(17)	11.5(15)	17.6(18)	4.7(14)	2.3(14)	1.6(13)
C33	13.5(17)	13.5(15)	17.7(18)	6.8(14)	4.0(14)	3.9(13)
C34	14.9(17)	9.1(14)	16.2(18)	4.0(13)	1.1(13)	0.4(13)
C35	17.1(18)	12.1(15)	24(2)	8.7(14)	5.1(15)	3.2(13)
C36	22.1(19)	14.5(16)	19.6(19)	7.1(14)	2.3(15)	4.0(14)
C37	10.6(16)	14.3(15)	19.8(18)	3.4(14)	2.1(13)	4.3(13)
C38	12.9(17)	14.4(15)	21.1(19)	7.8(14)	4.1(14)	1.7(13)
C39	16.3(17)	16.1(16)	18.2(18)	11.1(14)	1.5(14)	1.1(13)
C40	14.1(17)	13.0(15)	16.0(18)	4.0(14)	0.4(13)	0.3(13)
C41	13.7(17)	16.3(16)	18.2(18)	8.6(14)	1.7(14)	-0.5(13)
C42	13.8(17)	18.4(16)	16.5(18)	5.9(14)	1.2(14)	-1.1(14)
C43	32(2)	19.0(18)	22(2)	5.5(16)	3.1(17)	6.6(16)
C44	19.8(19)	18.2(17)	20.3(19)	6.7(15)	4.1(15)	0.0(14)
C45	42(2)	18.9(18)	23(2)	11.4(16)	10.8(18)	1.7(17)
C46	12.6(16)	11.7(15)	19.4(18)	7.7(14)	2.8(14)	-0.1(13)
C47	13.4(17)	12.2(15)	19.5(18)	6.8(14)	0.0(14)	1.8(13)
C48	18.1(17)	11.0(15)	18.4(18)	6.6(14)	2.4(14)	1.3(13)
C49	19.6(18)	14.6(16)	16.1(18)	6.6(14)	2.0(14)	4.1(14)
C50	24.4(19)	16.9(16)	18.6(19)	7.5(15)	4.1(15)	4.2(15)
C51	15.2(17)	15.7(16)	21.3(19)	9.0(14)	2.5(14)	2.0(13)
C52	24(2)	17.6(17)	27(2)	13.0(16)	11.9(16)	7.1(15)

Table S4. Bond Lengths for 3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C3	1.898(3)	C16	C17	1.516(5)
Br2	C9	1.895(3)	C18	C19	1.506(4)
Br3	C29	1.899(3)	C20	C21	1.526(5)
Br4	C37	1.902(3)	C21	C22	1.439(4)
S1	C16	1.717(3)	C21	C25	1.371(5)
S1	C18	1.725(3)	C22	C23	1.351(5)
S2	C23	1.723(4)	C23	C24	1.490(5)
S2	C25	1.725(4)	C25	C26	1.515(5)
S3	C42	1.721(3)	C27	C28	1.375(5)
S3	C44	1.727(4)	C27	C32	1.409(4)
S4	C49	1.723(3)	C27	C39	1.537(4)
S4	C51	1.722(3)	C28	C29	1.394(4)
O1	C13	1.434(4)	C29	C30	1.378(5)
O2	C20	1.430(4)	C30	C31	1.387(5)
O3	C39	1.419(4)	C31	C32	1.406(4)
O4	C46	1.433(4)	C32	C34	1.477(5)
C1	C2	1.381(5)	C33	C34	1.407(4)
C1	C6	1.402(4)	C33	C38	1.382(5)
C1	C13	1.531(4)	C33	C46	1.528(4)
C2	C3	1.386(4)	C34	C35	1.399(4)
C3	C4	1.383(5)	C35	C36	1.393(5)
C4	C5	1.384(5)	C36	C37	1.393(4)
C5	C6	1.410(4)	C37	C38	1.379(4)
C6	C12	1.467(5)	C39	C40	1.544(5)
C7	C8	1.386(5)	C39	C46	1.565(5)
C7	C12	1.411(4)	C40	C41	1.437(4)
C7	C20	1.526(4)	C40	C44	1.370(5)
C8	C9	1.385(4)	C41	C42	1.353(4)
C9	C10	1.388(5)	C42	C43	1.505(5)
C10	C11	1.387(5)	C44	C45	1.507(5)
C11	C12	1.404(4)	C46	C47	1.530(4)
C13	C14	1.524(4)	C47	C48	1.430(4)
C13	C20	1.577(5)	C47	C51	1.369(4)
C14	C15	1.436(4)	C48	C49	1.354(4)
C14	C18	1.370(4)	C49	C50	1.492(4)
C15	C16	1.352(5)	C51	C52	1.507(4)

Table S5. Bond Angles for 3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C16	S1	C18	93.26(16)	C21	C25	C26	132.1(3)
C23	S2	C25	93.28(17)	C26	C25	S2	117.2(3)
C42	S3	C44	93.49(16)	C28	C27	C32	120.8(3)
C51	S4	C49	93.35(16)	C28	C27	C39	118.4(3)
C2	C1	C6	120.7(3)	C32	C27	C39	120.6(3)
C2	C1	C13	117.8(3)	C27	C28	C29	120.0(3)
C6	C1	C13	121.3(3)	C28	C29	Br3	119.2(3)
C1	C2	C3	119.7(3)	C30	C29	Br3	120.1(3)
C2	C3	Br1	118.9(3)	C30	C29	C28	120.7(3)
C4	C3	Br1	119.9(3)	C29	C30	C31	119.3(3)
C4	C3	C2	121.3(3)	C30	C31	C32	121.4(3)
C3	C4	C5	118.7(3)	C27	C32	C34	120.3(3)
C4	C5	C6	121.5(3)	C31	C32	C27	117.7(3)
C1	C6	C5	117.9(3)	C31	C32	C34	122.0(3)
C1	C6	C12	119.8(3)	C34	C33	C46	121.6(3)
C5	C6	C12	122.3(3)	C38	C33	C34	120.3(3)
C8	C7	C12	119.8(3)	C38	C33	C46	117.8(3)
C8	C7	C20	119.7(3)	C33	C34	C32	118.9(3)
C12	C7	C20	120.3(3)	C35	C34	C32	123.3(3)
C9	C8	C7	120.5(3)	C35	C34	C33	117.8(3)
C8	C9	Br2	119.6(3)	C36	C35	C34	122.4(3)
C8	C9	C10	121.1(3)	C35	C36	C37	117.8(3)
C10	C9	Br2	119.2(3)	C36	C37	Br4	120.5(3)
C11	C10	C9	118.2(3)	C38	C37	Br4	118.3(2)
C10	C11	C12	122.2(3)	C38	C37	C36	121.2(3)
C7	C12	C6	119.6(3)	C37	C38	C33	120.4(3)
C11	C12	C6	122.4(3)	O3	C39	C27	110.0(3)
C11	C12	C7	118.1(3)	O3	C39	C40	106.0(3)
O1	C13	C1	108.7(3)	O3	C39	C46	110.0(3)
O1	C13	C14	107.0(3)	C27	C39	C40	109.2(3)
O1	C13	C20	109.5(3)	C27	C39	C46	110.5(3)
C1	C13	C20	110.5(3)	C40	C39	C46	110.8(3)
C14	C13	C1	110.0(3)	C41	C40	C39	123.0(3)
C14	C13	C20	111.0(3)	C44	C40	C39	124.7(3)
C15	C14	C13	122.2(3)	C44	C40	C41	112.3(3)
C18	C14	C13	125.4(3)	C42	C41	C40	114.2(3)
C18	C14	C15	112.4(3)	C41	C42	S3	110.0(2)
C16	C15	C14	113.7(3)	C41	C42	C43	129.1(3)
C15	C16	S1	110.5(3)	C43	C42	S3	120.9(3)
C15	C16	C17	128.8(3)	C40	C44	S3	110.1(3)
C17	C16	S1	120.7(3)	C40	C44	C45	132.3(3)

C14	C18	S1	110.2(2)	C45	C44	S3	117.6(3)
C14	C18	C19	131.5(3)	O4	C46	C33	109.3(3)
C19	C18	S1	118.3(2)	O4	C46	C39	109.7(3)
O2	C20	C7	110.0(3)	O4	C46	C47	106.8(2)
O2	C20	C13	109.9(3)	C33	C46	C39	111.1(3)
O2	C20	C21	105.8(3)	C33	C46	C47	109.3(3)
C7	C20	C13	110.8(3)	C47	C46	C39	110.6(3)
C7	C20	C21	109.1(3)	C48	C47	C46	122.1(3)
C21	C20	C13	111.1(3)	C51	C47	C46	125.7(3)
C22	C21	C20	123.2(3)	C51	C47	C48	112.2(3)
C25	C21	C20	125.2(3)	C49	C48	C47	114.4(3)
C25	C21	C22	111.5(3)	C48	C49	S4	109.7(2)
C23	C22	C21	114.7(3)	C48	C49	C50	128.0(3)
C22	C23	S2	109.8(3)	C50	C49	S4	122.2(2)
C22	C23	C24	129.2(3)	C47	C51	S4	110.4(3)
C24	C23	S2	121.0(3)	C47	C51	C52	132.2(3)
C21	C25	S2	110.7(3)	C52	C51	S4	117.4(2)

Table S6. Torsion Angles for 3a.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
Br1	C3	C4	C5	174.7(3)	C21	C22	C23	S2	0.1(4)
Br2	C9	C10	C11	179.4(3)	C21	C22	C23	C24	-179.3(4)
Br3	C29	C30	C31	179.8(2)	C22	C21	C25	S2	0.6(4)
Br4	C37	C38	C33	-179.2(2)	C22	C21	C25	C26	179.1(4)
O1	C13	C14	C15	-151.6(3)	C23	S2	C25	C21	-0.5(3)
O1	C13	C14	C18	27.2(5)	C23	S2	C25	C26	-179.2(3)
O1	C13	C20	O2	-72.2(3)	C25	S2	C23	C22	0.2(3)
O1	C13	C20	C7	166.1(2)	C25	S2	C23	C24	179.7(3)
O1	C13	C20	C21	44.6(3)	C25	C21	C22	C23	-0.5(5)
O2	C20	C21	C22	-147.3(3)	C27	C28	C29	Br3	179.9(2)
O2	C20	C21	C25	30.0(4)	C27	C28	C29	C30	-0.4(5)
O3	C39	C40	C41	-146.3(3)	C27	C32	C34	C33	13.9(5)
O3	C39	C40	C44	31.6(4)	C27	C32	C34	C35	-168.0(3)
O3	C39	C46	O4	-71.1(3)	C27	C39	C40	C41	-27.7(4)
O3	C39	C46	C33	167.9(2)	C27	C39	C40	C44	150.1(3)
O3	C39	C46	C47	46.4(3)	C27	C39	C46	O4	167.1(2)
O4	C46	C47	C48	-154.9(3)	C27	C39	C46	C33	46.1(3)
O4	C46	C47	C51	24.8(5)	C27	C39	C46	C47	-75.4(3)
C1	C2	C3	Br1	-177.3(2)	C28	C27	C32	C31	-0.5(5)
C1	C2	C3	C4	2.4(5)	C28	C27	C32	C34	-179.9(3)
C1	C6	C12	C7	17.9(5)	C28	C27	C39	O3	27.7(4)

C1	C6	C12	C11	-161.7(3)	C28	C27	C39	C40	-88.4(3)
C1	C13	C14	C15	-33.7(4)	C28	C27	C39	C46	149.4(3)
C1	C13	C14	C18	145.1(3)	C28	C29	C30	C31	0.1(5)
C1	C13	C20	O2	168.1(3)	C29	C30	C31	C32	0.0(5)
C1	C13	C20	C7	46.4(3)	C30	C31	C32	C27	0.2(5)
C1	C13	C20	C21	-75.2(3)	C30	C31	C32	C34	179.6(3)
C2	C1	C6	C5	-5.4(5)	C31	C32	C34	C33	-165.5(3)
C2	C1	C6	C12	172.7(3)	C31	C32	C34	C35	12.6(5)
C2	C1	C13	O1	34.5(4)	C32	C27	C28	C29	0.6(5)
C2	C1	C13	C14	-82.4(4)	C32	C27	C39	O3	-155.9(3)
C2	C1	C13	C20	154.7(3)	C32	C27	C39	C40	88.1(4)
C2	C3	C4	C5	-4.9(5)	C32	C27	C39	C46	-34.1(4)
C3	C4	C5	C6	2.3(5)	C32	C34	C35	C36	-176.9(3)
C4	C5	C6	C1	2.8(5)	C33	C34	C35	C36	1.3(5)
C4	C5	C6	C12	-175.3(3)	C33	C46	C47	C48	-36.8(4)
C5	C6	C12	C7	-164.0(3)	C33	C46	C47	C51	142.9(3)
C5	C6	C12	C11	16.3(5)	C34	C33	C38	C37	1.7(5)
C6	C1	C2	C3	3.0(5)	C34	C33	C46	O4	-154.1(3)
C6	C1	C13	O1	-149.5(3)	C34	C33	C46	C39	-32.8(4)
C6	C1	C13	C14	93.7(4)	C34	C33	C46	C47	89.4(4)
C6	C1	C13	C20	-29.3(4)	C34	C35	C36	C37	-0.1(5)
C7	C8	C9	Br2	179.7(2)	C35	C36	C37	Br4	178.4(2)
C7	C8	C9	C10	0.2(5)	C35	C36	C37	C38	-0.3(5)
C7	C20	C21	C22	-29.0(4)	C36	C37	C38	C33	-0.5(5)
C7	C20	C21	C25	148.3(3)	C38	C33	C34	C32	176.2(3)
C8	C7	C12	C6	178.3(3)	C38	C33	C34	C35	-2.0(5)
C8	C7	C12	C11	-2.0(5)	C38	C33	C46	O4	31.8(4)
C8	C7	C20	O2	27.6(4)	C38	C33	C46	C39	153.0(3)
C8	C7	C20	C13	149.3(3)	C38	C33	C46	C47	-84.7(3)
C8	C7	C20	C21	-88.0(4)	C39	C27	C28	C29	177.0(3)
C8	C9	C10	C11	-1.1(5)	C39	C27	C32	C31	-176.9(3)
C9	C10	C11	C12	0.4(5)	C39	C27	C32	C34	3.7(5)
C10	C11	C12	C6	-179.2(3)	C39	C40	C41	C42	177.2(3)
C10	C11	C12	C7	1.2(5)	C39	C40	C44	S3	-177.5(3)
C12	C7	C8	C9	1.4(5)	C39	C40	C44	C45	0.9(6)
C12	C7	C20	O2	-157.5(3)	C39	C46	C47	C48	85.8(4)
C12	C7	C20	C13	-35.8(4)	C39	C46	C47	C51	-94.5(4)
C12	C7	C20	C21	86.9(4)	C40	C39	C46	O4	45.8(3)
C13	C1	C2	C3	179.0(3)	C40	C39	C46	C33	-75.2(3)
C13	C1	C6	C5	178.6(3)	C40	C39	C46	C47	163.3(3)
C13	C1	C6	C12	-3.2(5)	C40	C41	C42	S3	0.8(4)
C13	C14	C15	C16	179.0(3)	C40	C41	C42	C43	-177.2(3)
C13	C14	C18	S1	-179.1(3)	C41	C40	C44	S3	0.6(4)

C13	C14	C18	C19	-0.8(6)	C41	C40	C44	C45	178.9(4)
C13	C20	C21	C22	93.5(4)	C42	S3	C44	C40	-0.1(3)
C13	C20	C21	C25	-89.2(4)	C42	S3	C44	C45	-178.8(3)
C14	C13	C20	O2	45.8(3)	C44	S3	C42	C41	-0.4(3)
C14	C13	C20	C7	-76.0(3)	C44	S3	C42	C43	177.7(3)
C14	C13	C20	C21	162.5(3)	C44	C40	C41	C42	-0.9(5)
C14	C15	C16	S1	0.1(4)	C46	C33	C34	C32	2.2(5)
C14	C15	C16	C17	-179.5(4)	C46	C33	C34	C35	-176.0(3)
C15	C14	C18	S1	-0.2(4)	C46	C33	C38	C37	175.9(3)
C15	C14	C18	C19	178.1(4)	C46	C39	C40	C41	94.3(4)
C16	S1	C18	C14	0.3(3)	C46	C39	C40	C44	-87.8(4)
C16	S1	C18	C19	-178.3(3)	C46	C47	C48	C49	178.7(3)
C18	S1	C16	C15	-0.2(3)	C46	C47	C51	S4	-178.5(3)
C18	S1	C16	C17	179.4(3)	C46	C47	C51	C52	-0.8(6)
C18	C14	C15	C16	0.1(5)	C47	C48	C49	S4	0.4(4)
C20	C7	C8	C9	176.3(3)	C47	C48	C49	C50	176.4(3)
C20	C7	C12	C6	3.4(5)	C48	C47	C51	S4	1.2(4)
C20	C7	C12	C11	-176.9(3)	C48	C47	C51	C52	178.9(4)
C20	C13	C14	C15	89.0(4)	C49	S4	C51	C47	-0.9(3)
C20	C13	C14	C18	-92.2(4)	C49	S4	C51	C52	-178.9(3)
C20	C21	C22	C23	177.2(3)	C51	S4	C49	C48	0.3(3)
C20	C21	C25	S2	-177.0(3)	C51	S4	C49	C50	-176.0(3)
C20	C21	C25	C26	1.5(7)	C51	C47	C48	C49	-1.0(5)

Table S7. Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3a.

Atom	*X*	*y*	*z*	U(eq)
H1	3790	7340	3079	24
H2	7753	7820	2847	25
H3	6838	11020	7331	25
H4A	10426	10491	7284	22
H2A	2303	5727	1968	22
H4	1684	3054	2281	25
H5	4169	3522	2813	24
H8	9197	7195	3731	20
H10	9146	4323	3376	27
H11	6623	3840	2898	24
H15	6148	5243	1530	23
H17A	6558	4889	-195	43
H17B	7742	4826	392	43
H17C	8167	5650	6	43
H19A	6219	8809	2336	30
H19B	4617	8343	1870	30

H19C	5997	8808	1517	30
H22	5260	5985	4241	22
H24A	4764	6964	6086	39
H24B	4277	5911	5476	39
H24C	3136	6564	5647	39
H26A	5261	9621	4390	42
H26B	5659	9054	3620	42
H26C	6921	9562	4301	42
H28	4671	9401	6924	19
H30	3190	7763	8238	22
H31	5646	8083	8764	20
H35	7974	8136	9033	21
H36	10444	8562	9590	22
H38	11540	10717	8637	19
H41	7661	7926	6956	19
H43A	7785	6266	5260	37
H43B	8117	6300	6081	37
H43C	9456	6548	5630	37
H45A	9983	10541	5687	42
H45B	9055	10980	6308	42
H45C	8244	10377	5504	42
H48	7429	10820	9172	19
H50A	7149	13125	10464	30
H50B	6704	11980	10366	30
H50C	5664	12417	9959	30
H52A	9639	13512	7925	32
H52B	9380	12436	7363	32
H52C	10822	12909	7951	32

Details of the single crystal structure determination of 4a:

Single crystals of $C_{26}H_{20}Br_2OS_2$ [4a] were crystallized from toluene. A suitable crystal was selected and mounted with oil on a glass capillary on a Bruker APEX2 microfocus rotating anode diffractometer. The crystal was kept at 90 K during data collection. Using Olex2,[2] the structure was solved with the XS structure solution program using Direct Methods and refined with the XL refinement package using Least Squares minimisation.[3] Electron density associated with a strongly disordered solvent molecule was removed from the structure using SQUEEZE. The electron count for the void was determined to be 40.9 which is close to 50, the number of electrons in a single toluene molecule.

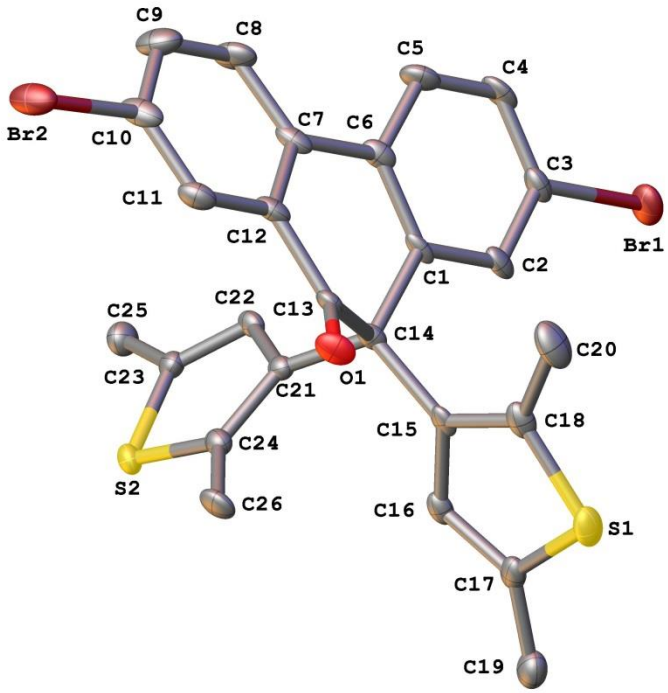

Figure S4. ORTEP drawing of the asymmetric unit of **4a** at the 50% probability level including numbering. Hydrogen atoms have been omitted for clarity.

Table S8. Crystal data and structure refinement for 4a

Identification code	4a
Empirical formula	$C_{26}H_{20}Br_2OS_2$
Formula weight	572.36
Temperature/K	90
Crystal system	triclinic
Space group	P-1
a/Å	9.9642(4)
b/Å	11.4661(4)
c/Å	11.6872(4)
α/°	89.5730(11)
β/°	85.9664(11)
γ/°	76.2250(12)
Volume/Å^3	1293.59(8)
Z	2
ρ_{calc}mg/mm^3	1.469
m/mm^{-1}	3.310
F(000)	572.0
Crystal size/mm^3	0.1 × 0.05 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	3.494 to 52.816°
Index ranges	$-12 \leq h \leq 12$, $-14 \leq k \leq 14$, $-14 \leq l \leq 14$

Reflections collected	23952
Independent reflections	5329 [R_{int} = 0.0622, R_{sigma} = 0.0609]
Data/restraints/parameters	5329/6/284
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0455, wR_2 = 0.0966
Final R indexes [all data]	R_1 = 0.0753, wR_2 = 0.1056
Largest diff. peak/hole / e $Å^{-3}$	0.69/-0.44

Table S9. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 4a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*X*	*y*	*z*	U(eq)
Br1	3139.8(5)	6694.2(4)	1833.4(3)	29.18(14)
Br2	9203.0(5)	7844.9(5)	-5982.5(4)	33.33(15)
S2	2790.2(11)	6211.3(9)	-5042.4(8)	19.1(2)
S1	441.5(12)	10868.8(9)	-1257.9(9)	25.7(3)
O1	4327(3)	9858(2)	-3590(2)	23.4(7)
C3	4223(4)	6860(3)	462(3)	19.7(9)
C13	4675(4)	8869(3)	-3174(3)	15.3(8)
C10	8198(4)	7617(4)	-4584(4)	25(1)
C7	6646(4)	7220(4)	-2602(3)	19.9(9)
C1	4381(4)	7613(3)	-1451(3)	15.3(8)
C17	-137(4)	9735(4)	-1871(3)	20.3(9)
C2	3593(4)	7499(3)	-446(3)	18.1(9)
C8	7986(4)	6515(4)	-2871(4)	26.9(10)
C21	3470(4)	7273(3)	-3338(3)	14.7(8)
C24	2914(4)	7520(4)	-4388(3)	17.5(8)
C16	968(4)	8874(3)	-2295(3)	17.5(9)
C11	6891(4)	8327(4)	-4360(3)	21.8(9)
C4	5614(4)	6344(4)	398(3)	23.3(10)
C18	2164(4)	10180(3)	-1570(3)	21.3(9)
C23	3536(4)	5321(4)	-3953(3)	17.8(9)
C9	8759(4)	6703(4)	-3848(4)	32.2(11)
C12	6103(4)	8124(3)	-3377(3)	18.6(9)
C22	3840(4)	6011(3)	-3123(3)	16.3(8)
C6	5812(4)	7092(3)	-1535(3)	18.2(9)
C5	6408(4)	6462(4)	-595(3)	24(1)
C26	2466(4)	8695(4)	-4994(3)	23.1(10)
C15	2288(4)	9110(3)	-2138(3)	15.8(8)
C14	3660(4)	8245(3)	-2496(3)	15.5(8)
C20	3253(5)	10778(4)	-1217(4)	33.2(11)
C25	3748(4)	3976(4)	-3994(4)	24.3(10)
C19	-1635(4)	9776(4)	-1886(4)	28.1(10)

Table S10. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 4a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	41.3(3)	28.1(3)	13.8(2)	6.63(17)	-1.91(19)	0.2(2)
Br2	21.6(2)	49.8(3)	29.7(3)	19.3(2)	-3.92(19)	-10.6(2)
S2	21.0(5)	23.6(6)	12.2(5)	-3.4(4)	-1.8(4)	-3.9(4)
S1	38.2(7)	15.6(5)	19.8(5)	-2.2(4)	-2.9(5)	0.7(5)
O1	30.4(17)	19.3(15)	22.5(15)	11.7(12)	-10.1(13)	-7.7(13)
C3	33(2)	16(2)	11.3(19)	1.7(16)	-6.2(17)	-6.0(18)
C13	18.4(15)	17.9(15)	10.3(14)	2.1(12)	-6.7(12)	-4.0(13)
C10	22(2)	36(3)	23(2)	14.6(19)	-8.1(18)	-17(2)
C7	24(2)	23(2)	18(2)	7.5(17)	-11.1(18)	-13.7(19)
C1	29(2)	10.1(19)	9.5(18)	4.6(15)	-9.1(16)	-7.2(17)
C17	27(2)	19(2)	10.6(19)	2.7(16)	-1.2(17)	1.6(18)
C2	30(2)	12(2)	13.4(19)	0.0(15)	-9.1(17)	-5.1(18)
C8	22(2)	33(3)	25(2)	16(2)	-8.9(19)	-4(2)
C21	12.5(19)	18(2)	12.3(18)	1.5(16)	-0.5(15)	-2.2(16)
C24	16(2)	22(2)	13.9(19)	0.3(16)	-1.3(16)	-3.8(17)
C16	28(2)	12(2)	11.7(18)	2.5(15)	-5.5(17)	-3.4(18)
C11	23(2)	23(2)	22(2)	8.5(18)	-9.9(18)	-8.0(19)
C4	36(3)	21(2)	15(2)	7.9(17)	-14.2(19)	-6(2)
C18	35(3)	15(2)	14(2)	3.7(16)	-5.6(18)	-5.0(19)
C23	15(2)	21(2)	14.7(19)	-1.4(16)	0.5(16)	-0.1(17)
C9	17(2)	41(3)	37(3)	13(2)	-4(2)	-2(2)
C12	23(2)	19(2)	18(2)	5.5(16)	-10.7(17)	-9.5(18)
C22	16(2)	23(2)	10.0(18)	3.0(16)	-1.5(16)	-4.6(17)
C6	25(2)	14(2)	18(2)	5.8(16)	-8.7(17)	-8.0(18)
C5	24(2)	23(2)	26(2)	9.6(18)	-13.4(19)	-3.1(19)
C26	27(2)	29(2)	14(2)	8.1(17)	-9.6(18)	-6(2)
C15	26(2)	14(2)	7.8(18)	4.1(15)	-5.9(16)	-4.0(17)
C14	20(2)	13(2)	13.6(19)	4.0(15)	-6.5(16)	-4.0(17)
C20	55(3)	23(2)	26(2)	-2.0(19)	-10(2)	-15(2)
C25	26(2)	22(2)	24(2)	-4.3(18)	-3.4(19)	-3.7(19)
C19	31(3)	31(3)	19(2)	-1.1(19)	1.3(19)	-1(2)

Table S11. Bond Lengths for 4a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C3	1.902(4)	C1	C14	1.548(5)
Br2	C10	1.905(4)	C17	C16	1.358(5)
S2	C24	1.724(4)	C17	C19	1.484(6)
S2	C23	1.723(4)	C8	C9	1.377(6)
S1	C17	1.722(4)	C21	C24	1.382(5)
S1	C18	1.724(4)	C21	C22	1.431(5)
O1	C13	1.212(4)	C21	C14	1.546(5)
C3	C2	1.386(5)	C24	C26	1.503(5)
C3	C4	1.368(6)	C16	C15	1.428(5)
C13	C12	1.479(5)	C11	C12	1.395(5)
C13	C14	1.544(5)	C4	C5	1.382(6)
C10	C11	1.370(6)	C18	C15	1.375(5)
C10	C9	1.388(6)	C18	C20	1.497(6)
C7	C8	1.402(6)	C23	C22	1.352(5)
C7	C12	1.405(5)	C23	C25	1.507(5)
C7	C6	1.476(5)	C6	C5	1.399(5)
C1	C2	1.389(5)	C15	C14	1.519(5)
C1	C6	1.405(5)			

Table S12. Bond Angles for 4a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C23	S2	C24	93.32(19)	C17	C16	C15	114.9(4)
C17	S1	C18	93.6(2)	C10	C11	C12	119.4(4)
C2	C3	Br1	119.6(3)	C3	C4	C5	119.3(4)
C4	C3	Br1	118.9(3)	C15	C18	S1	110.3(3)
C4	C3	C2	121.5(4)	C15	C18	C20	130.4(4)
O1	C13	C12	121.4(4)	C20	C18	S1	119.3(3)
O1	C13	C14	123.5(3)	C22	C23	S2	110.0(3)
C12	C13	C14	114.9(3)	C22	C23	C25	128.6(4)
C11	C10	Br2	118.6(3)	C25	C23	S2	121.3(3)
C11	C10	C9	121.3(4)	C8	C9	C10	119.1(4)
C9	C10	Br2	120.1(3)	C7	C12	C13	120.6(4)
C8	C7	C12	117.6(4)	C11	C12	C13	118.6(3)
C8	C7	C6	123.4(4)	C11	C12	C7	120.8(4)
C12	C7	C6	118.9(4)	C23	C22	C21	114.5(3)
C2	C1	C6	119.8(3)	C1	C6	C7	119.6(3)
C2	C1	C14	119.6(4)	C5	C6	C7	121.7(4)
C6	C1	C14	120.4(3)	C5	C6	C1	118.7(4)
C16	C17	S1	109.3(3)	C4	C5	C6	121.1(4)

C16	C17	C19	128.9(4)	C16	C15	C14	123.8(3)
C19	C17	S1	121.7(3)	C18	C15	C16	111.8(4)
C3	C2	C1	119.7(4)	C18	C15	C14	124.2(4)
C9	C8	C7	121.7(4)	C13	C14	C1	108.4(3)
C24	C21	C22	111.8(3)	C13	C14	C21	103.8(3)
C24	C21	C14	124.0(3)	C21	C14	C1	108.5(3)
C22	C21	C14	124.2(3)	C15	C14	C13	112.5(3)
C21	C24	S2	110.2(3)	C15	C14	C1	111.8(3)
C21	C24	C26	130.3(4)	C15	C14	C21	111.5(3)
C26	C24	S2	119.5(3)				

Table S13. Torsion Angles for 4a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C3	C2	C1	-179.5(3)	C16	C15	C14	C21	16.0(5)
Br1	C3	C4	C5	-179.9(3)	C11	C10	C9	C8	-0.4(7)
Br2	C10	C11	C12	175.9(3)	C4	C3	C2	C1	0.6(6)
Br2	C10	C9	C8	-176.7(3)	C18	S1	C17	C16	-0.2(3)
S2	C23	C22	C21	0.5(4)	C18	S1	C17	C19	179.7(3)
S1	C17	C16	C15	-0.2(4)	C18	C15	C14	C13	-51.6(5)
S1	C18	C15	C16	-0.6(4)	C18	C15	C14	C1	70.7(5)
S1	C18	C15	C14	-177.2(3)	C18	C15	C14	C21	-167.7(3)
O1	C13	C12	C7	156.6(4)	C23	S2	C24	C21	-2.2(3)
O1	C13	C12	C11	-24.3(6)	C23	S2	C24	C26	176.7(3)
O1	C13	C14	C1	-139.3(4)	C9	C10	C11	C12	-0.4(7)
O1	C13	C14	C21	105.5(4)	C12	C13	C14	C1	46.1(4)
O1	C13	C14	C15	-15.1(5)	C12	C13	C14	C21	-69.1(4)
C3	C4	C5	C6	-0.5(6)	C12	C13	C14	C15	170.2(3)
C10	C11	C12	C13	-177.6(4)	C12	C7	C8	C9	0.8(6)
C10	C11	C12	C7	1.5(6)	C12	C7	C6	C1	18.0(6)
C7	C8	C9	C10	0.2(7)	C12	C7	C6	C5	-161.9(4)
C7	C6	C5	C4	-179.7(4)	C22	C21	C24	S2	2.8(4)
C1	C6	C5	C4	0.4(6)	C22	C21	C24	C26	-175.9(4)
C17	S1	C18	C15	0.5(3)	C22	C21	C14	C13	118.3(4)
C17	S1	C18	C20	-179.7(3)	C22	C21	C14	C1	3.2(5)
C17	C16	C15	C18	0.5(5)	C22	C21	C14	C15	-120.3(4)
C17	C16	C15	C14	177.2(3)	C6	C7	C8	C9	-176.6(4)
C2	C3	C4	C5	0.0(6)	C6	C7	C12	C13	-5.0(6)
C2	C1	C6	C7	-179.7(3)	C6	C7	C12	C11	175.9(4)
C2	C1	C6	C5	0.2(6)	C6	C1	C2	C3	-0.7(6)
C2	C1	C14	C13	148.8(3)	C6	C1	C14	C13	-35.1(5)
C2	C1	C14	C21	-99.0(4)	C6	C1	C14	C21	77.1(4)

C2	C1	C14	C15	24.3(5)	C6	C1	C14	C15	-159.6(3)
C8	C7	C12	C13	177.4(4)	C14	C13	C12	C7	-28.7(5)
C8	C7	C12	C11	-1.7(6)	C14	C13	C12	C11	150.5(3)
C8	C7	C6	C1	-164.6(4)	C14	C1	C2	C3	175.5(3)
C8	C7	C6	C5	15.5(6)	C14	C1	C6	C7	4.2(5)
C24	S2	C23	C22	0.9(3)	C14	C1	C6	C5	-175.9(3)
C24	S2	C23	C25	179.9(3)	C14	C21	C24	S2	-177.0(3)
C24	C21	C22	C23	-2.2(5)	C14	C21	C24	C26	4.3(7)
C24	C21	C14	C13	-61.9(5)	C14	C21	C22	C23	177.6(4)
C24	C21	C14	C1	-177.1(4)	C20	C18	C15	C16	179.6(4)
C24	C21	C14	C15	59.4(5)	C20	C18	C15	C14	3.0(6)
C16	C15	C14	C13	132.2(3)	C25	C23	C22	C21	-178.3(4)
C16	C15	C14	C1	-105.6(4)	C19	C17	C16	C15	-180.0(4)

Table S14. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4a.

Atom	*x*	*y*	*z*	U(eq)
H2	2627	7857	-381	22
H8	8370	5891	-2365	32
H16	870	8168	-2667	21
H11	6524	8953	-4870	26
H4	6029	5909	1029	28
H9	9664	6214	-4016	39
H22	4265	5684	-2451	20
H5	7375	6110	-640	29
H26A	3275	8897	-5399	35
H26B	2039	9327	-4431	35
H26C	1793	8626	-5547	35
H20A	3512	11261	-1852	50
H20B	4070	10166	-1018	50
H20C	2890	11298	-549	50
H25A	2851	3767	-3866	36
H25B	4353	3614	-3395	36
H25C	4179	3671	-4746	36
H19A	-2081	9956	-1113	42
H19B	-1751	8996	-2144	42
H19C	-2061	10402	-2413	42

Table S15. Solvent masks information for 4a.

Number	X	Y	Z	Volume	Electron count	Content
1	0.000	0.500	0.000	45.6	40.9	toluene

Details of the single crystal structure determination of 6a:

Single crystals of $C_{26}H_{20}Br_2S_2$ [6a] were grown by slow cooling of a warm dimethylformamide solution. A suitable crystal was selected and mounted on a glass capillary with oil on a Bruker APEX2 microfocus rotating anode diffractometer. The crystal was kept at 90 K during data collection. Using Olex2,[2] the structure was solved with the XS structure solution program using Direct Methods and refined with the XL refinement package using Least Squares minimisation.[3]

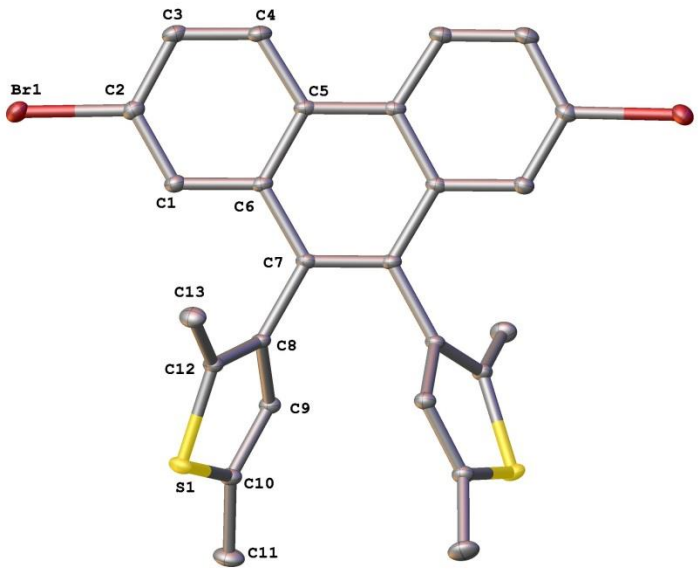

Figure S5. ORTEP drawing of the grown unit of **6a** at the 50% probability level including numbering of the asymmetric unit. Hydrogen atoms have been omitted for clarity.

Table S16. Crystal data and structure refinement for 6a

Identification code	6a
Empirical formula	$C_{26}H_{20}Br_2S_2$
Formula weight	556.36
Temperature/K	90
Crystal system	monoclinic
Space group	C2/c
a/Å	9.3043(3)
b/Å	21.4919(8)
c/Å	11.0020(4)
α/°	90
β/°	94.3179(8)

γ/°	90
Volume/Å^3	2193.79(13)
Z	4
ρ_{calc}mg/mm^3	1.684
m/mm^{-1}	3.897
F(000)	1112.0
Crystal size/mm^3	0.05 × 0.04 × 0.02
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection	3.79 to 66.308°
Index ranges	-10 ≤ h ≤ 14, -26 ≤ k ≤ 32, -16 ≤ l ≤ 16
Reflections collected	17072
Independent reflections	4186 [R_{int} = 0.0258, R_{sigma} = 0.0209]
Data/restraints/parameters	4186/0/138
Goodness-of-fit on F^2	1.085
Final R indexes [I>=2σ (I)]	R_1 = 0.0219, wR_2 = 0.0560
Final R indexes [all data]	R_1 = 0.0255, wR_2 = 0.0577
Largest diff. peak/hole / e Å^{-3}	0.63/-0.27

Table S17. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 6a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	-74.0(2)	3389.5(2)	4607.8(2)	16.08(4)
S1	2016.8(3)	6072.4(2)	2690.8(3)	12.86(6)
C1	2324.4(13)	3926.9(5)	3567.7(10)	11.81(19)
C3	2275.0(14)	2799.1(6)	3533.5(11)	14.2(2)
C4	3572.6(14)	2794.6(5)	3008.7(10)	13.4(2)
C6	3643.4(13)	3926.3(5)	3005.6(10)	10.45(18)
C9	4232.8(12)	5575.6(5)	3787(1)	10.98(18)
C8	3623.4(12)	5111.8(5)	2964.3(10)	9.91(18)
C5	4302.2(13)	3351.1(5)	2750(1)	10.73(18)
C10	3489.5(13)	6122.8(5)	3738.9(10)	11.64(19)
C7	4336.3(12)	4507.4(5)	2735.3(10)	10.10(18)
C2	1674.6(13)	3373.7(5)	3826.6(10)	12.8(2)
C12	2400.6(12)	5314.0(5)	2308.3(10)	10.87(18)
C11	3826.5(16)	6714.7(6)	4422.4(12)	18.9(2)
C13	1496.0(14)	4985.6(6)	1320.1(11)	15.7(2)

Table S18. Anisotropic Displacement Parameters (Å^2×10^3) for 6a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	15.48(6)	12.48(6)	20.68(6)	2.96(4)	3.99(4)	-2.02(4)
S1	13.12(12)	8.55(12)	16.30(12)	-1.83(9)	-2.96(9)	2.58(9)
C1	12.9(5)	9.0(5)	13.5(4)	0.5(3)	0.3(4)	-0.9(4)
C3	18.3(5)	9.2(5)	15.0(5)	1.4(4)	0.5(4)	-2.6(4)
C4	17.9(5)	7.6(5)	14.6(5)	-0.1(4)	0.2(4)	-1.2(4)
C6	12.8(5)	7.4(4)	10.8(4)	0.2(3)	-1.0(3)	-1.1(3)
C9	12.3(5)	8.7(5)	11.6(4)	-0.1(3)	-1.2(3)	-0.3(4)
C8	11.1(4)	6.3(4)	12.2(4)	0.3(3)	0.0(3)	-0.6(3)
C5	14.5(5)	6.8(4)	10.6(4)	0.4(3)	-1.2(3)	-0.5(3)
C10	13.2(5)	8.8(5)	12.6(4)	-1.3(3)	-1.0(4)	-0.4(4)
C7	11.9(5)	6.7(4)	11.5(4)	0.2(3)	-0.8(3)	0.4(3)
C2	14.3(5)	11.0(5)	13.0(4)	1.5(4)	0.3(4)	-1.5(4)
C12	10.9(4)	7.9(4)	13.6(4)	-1.2(3)	-0.3(4)	-0.3(4)
C11	24.2(6)	11.2(5)	20.4(5)	-5.5(4)	-4.4(5)	0.9(4)
C13	16.4(5)	12.6(5)	17.4(5)	-2.7(4)	-4.1(4)	-0.9(4)

Table S19. Bond Lengths for 6a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C2	1.8967(12)	C6	C7	1.4466(15)
S1	C10	1.7266(12)	C9	C8	1.4342(15)
S1	C12	1.7273(11)	C9	C10	1.3633(16)
C1	C6	1.4152(16)	C8	C7	1.4886(15)
C1	C2	1.3735(16)	C8	C12	1.3713(15)
C3	C4	1.3770(18)	C5	C5[1]	1.448(2)
C3	C2	1.4028(17)	C10	C11	1.4989(17)
C4	C5	1.4147(16)	C7	C7[1]	1.375(2)
C6	C5	1.4175(16)	C12	C13	1.5002(16)

[1]1-X,+Y,1/2-Z

Table S20. Bond Angles for 6a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	S1	C12	93.08(5)	C6	C5	C5[1]	119.27(7)
C2	C1	C6	119.97(11)	C9	C10	S1	110.27(8)
C4	C3	C2	118.65(11)	C9	C10	C11	128.78(11)
C3	C4	C5	121.84(11)	C11	C10	S1	120.93(9)
C1	C6	C5	119.32(10)	C6	C7	C8	120.49(10)
C1	C6	C7	120.24(10)	C7[1]	C7	C6	120.29(6)
C5	C6	C7	120.41(10)	C7[1]	C7	C8	119.22(6)
C10	C9	C8	113.56(10)	C1	C2	Br1	118.97(9)
C9	C8	C7	123.59(10)	C1	C2	C3	121.69(11)
C12	C8	C9	112.63(10)	C3	C2	Br1	119.34(9)

C12	C8	C7	123.37(10)	C8	C12	S1	110.45(8)
C4	C5	C6	118.44(11)	C8	C12	C13	129.07(10)
C4	C5	C5[1]	122.29(7)	C13	C12	S1	120.36(9)

[1]1-X,+Y,1/2-Z

Table S21. Torsion Angles for 6a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C6	C5	C4	3.35(16)	C5	C6	C7	C7[1]	-2.15(19)
C1	C6	C5	C5[1]	-175.91(12)	C10	S1	C12	C8	-0.25(9)
C1	C6	C7	C8	-4.28(16)	C10	S1	C12	C13	-176.60(10)
C1	C6	C7	C7[1]	175.64(13)	C10	C9	C8	C7	172.04(10)
C3	C4	C5	C6	-2.12(17)	C10	C9	C8	C12	-0.83(14)
C3	C4	C5	C5[1]	177.11(13)	C7	C6	C5	C4	-178.84(10)
C4	C3	C2	Br1	-177.57(9)	C7	C6	C5	C5[1]	1.90(19)
C4	C3	C2	C1	2.12(18)	C7	C8	C12	S1	-172.25(9)
C6	C1	C2	Br1	178.83(8)	C7	C8	C12	C13	3.69(19)
C6	C1	C2	C3	-0.86(18)	C2	C1	C6	C5	-1.92(17)
C9	C8	C7	C6	119.24(12)	C2	C1	C6	C7	-179.73(10)
C9	C8	C7	C7[1]	-60.67(18)	C2	C3	C4	C5	-0.58(18)
C9	C8	C12	S1	0.64(12)	C12	S1	C10	C9	-0.21(9)
C9	C8	C12	C13	176.58(11)	C12	S1	C10	C11	178.15(11)
C8	C9	C10	S1	0.62(13)	C12	C8	C7	C6	-68.64(15)
C8	C9	C10	C11	-177.58(12)	C12	C8	C7	C7[1]	111.45(15)
C5	C6	C7	C8	177.94(10)					

[1]1-X,+Y,1/2-Z

Table S22. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 6a.

Atom	*x*	*y*	*z*	U(eq)
H1	1898	4302	3762	14
H3	1806	2429	3690	17
H4	3981	2415	2819	16
H9	5056	5509	4304	13
H11A	3677	7062	3880	28
H11B	4813	6708	4748	28
H11C	3206	6753	5077	28
H13A	955	4660	1672	24
H13B	2109	4810	746	24
H13C	845	5277	910	24

Details of the single crystal structure determination of 7b:

Single crystals of $C_{26}H_{18}O_4S_2$ [7b] were grown by slow evaporation of an ethyl acetate solution. A suitable crystal was selected and mounted on glass capilary with oil on a Bruker APEX2 microfocus rotating anode diffractometer. The crystal was kept at 90 K during data collection. Using Olex2,[2] the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the XL refinement package using Least Squares minimisation.[3] Electron density associated with strongly disordered solvent molecules was removed from the structure using SQUEEZE. The electron count for the void was determined to be 107. As the number of electrons in ethyl acetate is 42 and 10 for water, the void likely contains approximately 2 ethyl acetate molecules and a water molecule (94 electrons).

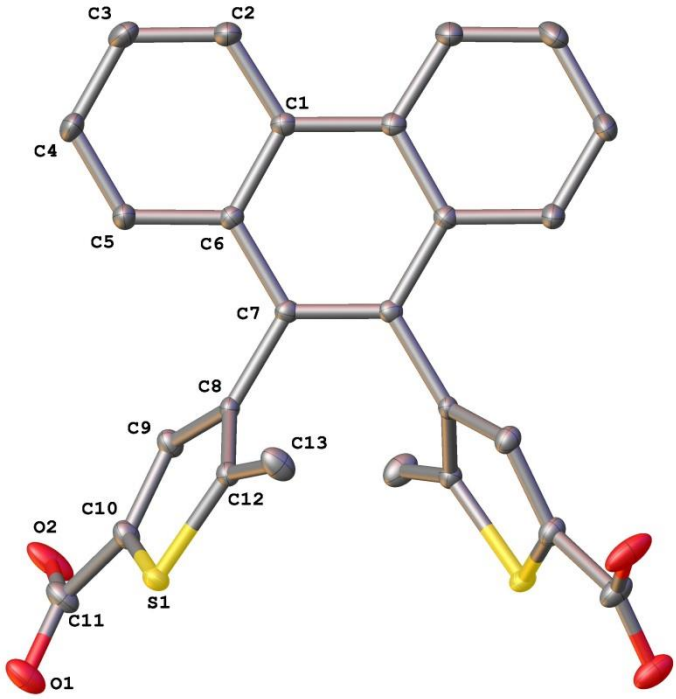

Figure S6. ORTEP drawing of the grown unit of **7b** at the 50% probability level including numbering of the asymmetric unit. Hydrogen atoms have been omitted for clarity.

Table S23. Crystal data and structure refinement for 7b

Identification code	7b
Empirical formula	$C_{26}H_{18}O_4S_2$
Formula weight	458.52
Temperature/K	90
Crystal system	monoclinic
Space group	P2/c
a/Å	7.3757(3)
b/Å	11.0027(5)
c/Å	17.9502(8)
α/°	90

β/°	96.2569(14)
γ/°	90
Volume/Å^3	1448.03(11)
Z	2
ρ_{calc}mg/mm^3	1.052
m/mm^{-1}	0.208
F(000)	476.0
Crystal size/mm^3	0.2 × 0.1 × 0.025
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	3.702 to 57.446°
Index ranges	-9 ≤ h ≤ 9, -14 ≤ k ≤ 14, -24 ≤ l ≤ 24
Reflections collected	31209
Independent reflections	3746 [R_{int} = 0.0390, R_{sigma} = 0.0241]
Data/restraints/parameters	3746/0/147
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0423, wR_2 = 0.1140
Final R indexes [all data]	R_1 = 0.0530, wR_2 = 0.1193
Largest diff. peak/hole / e Å^{-3}	0.83/-0.21

Table S24. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 7b. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*X*	*y*	*z*	U(eq)
S1	4668.4(5)	8767.6(3)	3883.6(2)	13.88(11)
O1	7829.7(16)	9910.6(11)	4780.9(7)	24.1(3)
O2	9896.1(16)	8498.3(12)	4541.2(8)	30.0(3)
C7	5179.0(19)	5536.1(12)	2884.0(7)	11.2(3)
C6	5331.0(19)	4399.3(12)	3294.8(8)	12.7(3)
C8	5369.1(19)	6700.3(12)	3310.8(7)	11.4(3)
C9	7027(2)	7103.4(13)	3713.3(8)	14.4(3)
C1	5141(2)	3280.5(13)	2907.5(8)	14.0(3)
C5	5618(2)	4389.3(13)	4089.7(8)	16.9(3)
C12	3967.0(19)	7511.0(13)	3360.3(8)	12.6(3)
C13	2018(2)	7414.7(15)	3034.6(9)	19.9(3)
C4	5690(2)	3312.6(14)	4482.1(9)	20.9(3)
C10	6861(2)	8211.8(13)	4047.8(8)	15.3(3)
C2	5193(2)	2193.5(14)	3328.4(8)	19.6(3)
C11	8244(2)	8948.3(14)	4492.1(9)	19.2(3)
C3	5455(3)	2205.3(14)	4100.1(9)	23.3(4)

Table S25. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 7b. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	16.71(19)	10.77(17)	13.70(18)	-2.64(12)	-0.39(13)	1.07(13)
O1	19.3(6)	22.1(6)	29.8(6)	-12.8(5)	-3.1(5)	1.5(4)
O2	17.6(6)	28.7(7)	41.5(8)	-22.3(6)	-5.7(5)	1.0(5)
C7	11.6(6)	9.6(6)	11.9(7)	0.2(5)	-0.8(5)	0.0(5)
C6	14.9(7)	10.7(6)	12.1(6)	0.6(5)	-0.3(5)	1.3(5)
C8	15.0(7)	10.7(6)	7.9(6)	0.6(5)	-1.2(5)	-0.6(5)
C9	14.3(7)	15.0(7)	13.3(6)	-2.6(5)	-1.2(5)	0.3(5)
C1	17.5(7)	10.9(6)	13.3(7)	0.5(5)	0.5(5)	1.5(5)
C5	24.9(8)	13.4(7)	12.0(7)	-0.3(5)	-0.1(6)	2.1(6)
C12	15.0(7)	11.9(6)	10.7(6)	0.0(5)	0.0(5)	-0.5(5)
C13	13.6(7)	21.7(8)	23.4(8)	-7.2(6)	-2.4(6)	1.8(6)
C4	33.7(9)	16.9(7)	11.5(7)	3.1(6)	0.5(6)	4.1(6)
C10	14.9(7)	15.8(7)	14.6(7)	-3.5(5)	-0.9(5)	-0.3(5)
C2	32.5(9)	11.1(7)	14.9(7)	0.7(5)	1.0(6)	1.8(6)
C11	18.4(7)	18.6(7)	20.2(7)	-8.0(6)	0.6(6)	-1.0(6)
C3	38.5(10)	14.2(7)	17.1(7)	4.4(6)	2.5(7)	4.7(7)

Table S26. Bond Lengths for 7b.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C12	1.7192(14)	C8	C12	1.376(2)
S1	C10	1.7238(15)	C9	C10	1.371(2)
O1	C11	1.2319(19)	C1	C1[1]	1.455(3)
O2	C11	1.309(2)	C1	C2	1.413(2)
C7	C7[1]	1.375(3)	C5	C4	1.376(2)
C7	C6	1.4502(18)	C12	C13	1.495(2)
C7	C8	1.4913(19)	C4	C3	1.399(2)
C6	C1	1.4132(19)	C10	C11	1.469(2)
C6	C5	1.419(2)	C2	C3	1.378(2)
C8	C9	1.4216(19)			

[1]1-X,+Y,1/2-Z

Table S27. Bond Angles for 7b.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C12	S1	C10	91.66(7)	C4	C5	C6	120.95(14)
C7[1]	C7	C6	120.37(8)	C8	C12	S1	111.91(11)
C7[1]	C7	C8	120.80(7)	C8	C12	C13	128.76(13)
C6	C7	C8	118.81(12)	C13	C12	S1	119.33(11)
C1	C6	C7	120.20(12)	C5	C4	C3	120.19(14)
C1	C6	C5	118.93(13)	C9	C10	S1	111.57(11)

C5	C6	C7	120.84(12)	C9	C10	C11	129.71(14)
C9	C8	C7	123.82(13)	C11	C10	S1	118.71(11)
C12	C8	C7	124.11(13)	C3	C2	C1	121.49(14)
C12	C8	C9	112.07(12)	O1	C11	O2	124.65(14)
C10	C9	C8	112.78(13)	O1	C11	C10	120.87(14)
C6	C1	C1[1]	119.36(8)	O2	C11	C10	114.48(13)
C2	C1	C6	118.60(13)	C2	C3	C4	119.81(14)
C2	C1	C1[1]	122.02(8)				

[1]1-X,+Y,1/2-Z

Table S28. Torsion Angles for 7b.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C10	C11	O1	4.3(2)	C8	C9	C10	S1	0.70(17)
S1	C10	C11	O2	-175.15(12)	C8	C9	C10	C11	-178.28(15)
C7[1]	C7	C6	C1	1.0(2)	C9	C8	C12	S1	0.81(16)
C7[1]	C7	C6	C5	-177.14(17)	C9	C8	C12	C13	-178.53(14)
C7[1]	C7	C8	C9	-113.55(19)	C9	C10	C11	O1	-176.76(16)
C7[1]	C7	C8	C12	66.3(2)	C9	C10	C11	O2	3.8(3)
C7	C6	C1	C1[1]	2.2(2)	C1	C6	C5	C4	-0.8(2)
C7	C6	C1	C2	-176.40(14)	C1[1]	C1	C2	C3	-179.75(18)
C7	C6	C5	C4	177.35(14)	C1	C2	C3	C4	-0.5(3)
C7	C8	C9	C10	178.87(13)	C5	C6	C1	C1[1]	-179.59(17)
C7	C8	C12	S1	-179.04(10)	C5	C6	C1	C2	1.8(2)
C7	C8	C12	C13	1.6(2)	C5	C4	C3	C2	1.5(3)
C6	C7	C8	C9	68.05(18)	C12	S1	C10	C9	-0.21(12)
C6	C7	C8	C12	-112.11(16)	C12	S1	C10	C11	178.90(13)
C6	C1	C2	C3	-1.2(2)	C12	C8	C9	C10	-0.98(18)
C6	C5	C4	C3	-0.8(3)	C10	S1	C12	C8	-0.35(11)
C8	C7	C6	C1	179.44(13)	C10	S1	C12	C13	179.05(12)
C8	C7	C6	C5	1.3(2)					

[1]1-X,+Y,1/2-Z

Table S29. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 7b.

Atom	*x*	*y*	*z*	U(eq)
H2	10627	8988	4773	45
H9	8131	6653	3747	17
H5	5764	5137	4355	20
H13A	1221	7619	3419	30
H13B	1765	6582	2859	30

H13C	1791	7980	2613	30
H4	5899	3321	5014	25
H2A	5044	1437	3074	24
H3	5476	1464	4372	28

Table S30. Solvent masks information for 7b.

Number	X	Y	Z	Volume	Electron count	Content
1	0.000	0.500	-0.153	180.5	107.0	Ethyl acetate and water

Details of the single crystal structure determination of UBMOF-1:

Single crystals of $C_{48}H_{42}O_{13}Zn_4$ [UBMOF-1] were crystallized out of a solvothermal synthesis reaction in dimethylformamide. A suitable crystal was selected and mounted on a glass capillary with oil on a Bruker APEX2 microfocus rotating anode diffractometer. The crystal was kept at 90.0 K during data collection. Using Olex2,[2] the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the XL refinement package using Least Squares minimisation.[3] Due to strong disorder the dimethyl thiophene groups could not be refined. The carbon of the ethylene bridge was refined with a chemical occupancy of 1/4. As the multiplicity of this site was 8, the refinement resulted in a total of 2 carbon atoms disordered over the 8 sites. Solvent was *not* removed from this structure using SQUEEZE, as this method is only reliable when high-resolution data is available (which was not the case for this particular compound).

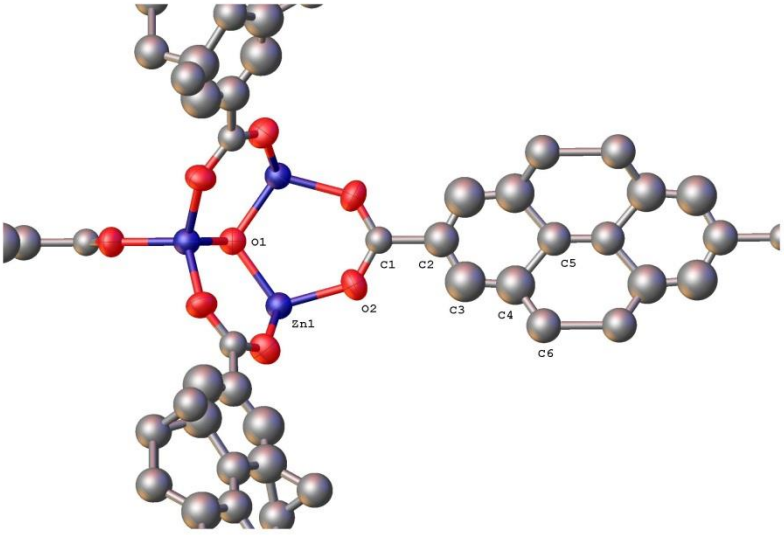

Figure S7. ORTEP drawing of the grown unit of **UBMOF-1** at the 50% probability level including numbering of the asymmetric unit.

Table S31. Crystal data and structure refinement for UBMOF-1

Identification code	UBMOF-1
Empirical formula	$C_{48}H_{42}O_{13}Zn_4$
Formula weight	1088.30
Temperature/K	90.0
Crystal system	cubic
Space group	Fm-3m
a/Å	34.250(19)
b/Å	34.250(19)
c/Å	34.250(19)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	40176(68)
Z	8
ρ_{calc}mg/mm^3	0.360
m/mm^{-1}	0.487
F(000)	4432.0
Crystal size/mm^3	0.25 × 0.25 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	3.364 to 29.446°
Index ranges	-24 ≤ h ≤ 24, -24 ≤ k ≤ 24, -24 ≤ l ≤ 24
Reflections collected	46698
Independent reflections	444 [R_{int} = 0.1136, R_{sigma} = 0.0168]
Data/restraints/parameters	444/0/28
Goodness-of-fit on F^2	2.901
Final R indexes [I>=2σ (I)]	R_1 = 0.1937, wR_2 = 0.5153
Final R indexes [all data]	R_1 = 0.2123, wR_2 = 0.5539
Largest diff. peak/hole / e Å^{-3}	0.62/-0.65

Table S32. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for UBMOF-1. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*X*	*y*	*z*	U(eq)
Zn1	2829.2(11)	2170.8(11)	2170.8(11)	109(7)
O1	2500	2500	2500	110(20)
O2	2726(5)	2274(5)	1630(6)	131(10)
C3	2714(16)	2286(16)	830(20)	250(30)
C2	2500	2500	1000(30)	190(30)
C1	2500	2500	1450(20)	113(19)
C5	2500	2500	192(12)	170(20)
C4	2733(13)	2267(13)	470(20)	240(20)
C6	3080(40)	2200(30)	270(30)	180(50)

Table S33. Anisotropic Displacement Parameters (Å^2×10^3) for UBMOF-1. The Anisotropic displacement

factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn1	109(7)	109(7)	109(7)	0(2)	0(2)	0(2)
O1	110(20)	110(20)	110(20)	0	0	0
O2	143(13)	143(13)	110(20)	20(11)	-20(11)	-5(14)

Table S34. Bond Lengths for UBMOF-1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1	O1	1.953(6)	C2	C3[3]	1.19(7)
Zn1	O2	1.92(2)	C2	C1	1.53(6)
Zn1	O2[1]	1.92(2)	C1	O2[3]	1.26(3)
Zn1	O2[2]	1.92(2)	C5	C5[6]	1.32(8)
O1	Zn1[3]	1.953(6)	C5	C4[3]	1.48(5)
O1	Zn1[4]	1.953(6)	C5	C4	1.48(5)
O1	Zn1[5]	1.953(6)	C4	C6[7]	1.38(12)
O2	C1	1.25(3)	C4	C6	1.38(12)
C3	C2	1.19(7)	C6	C6[8]	1.9(2)
C3	C4	1.23(7)	C6	C6[7]	1.3(2)

[1]1/2-Z,1/2-X,+Y; [2]1/2-Y,+Z,1/2-X; [3]1/2-X,1/2-Y,+Z; [4]+Y,1/2-X,1/2-Z; [5]1/2-Y,+X,1/2-Z; [6]1/2-X,1/2-Y,-Z; [7]1/2-Y,1/2-X,+Z; [8]+X,+Y,-Z

Table S35. Bond Angles for UBMOF-1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2[1]	Zn1	O1	110.1(8)	C3[3]	C2	C1	119(7)
O2[2]	Zn1	O1	110.1(8)	O2	C1	O2[3]	121(6)
O2	Zn1	O1	110.1(8)	O2[3]	C1	C2	119(3)
O2[1]	Zn1	O2[2]	108.8(8)	O2	C1	C2	119(3)
O2[1]	Zn1	O2	108.8(8)	C5[6]	C5	C4[3]	130(4)
O2[2]	Zn1	O2	108.8(8)	C5[6]	C5	C4	130(4)
Zn1	O1	Zn1[3]	109.5	C4	C5	C4[3]	99(7)
Zn1[4]	O1	Zn1[3]	109.471(1)	C3	C4	C5	126(8)
Zn1[5]	O1	Zn1[3]	109.5	C3	C4	C6[7]	123(7)
Zn1	O1	Zn1[4]	109.471(2)	C3	C4	C6	123(7)
Zn1	O1	Zn1[5]	109.471(1)	C6[7]	C4	C5	103(6)
Zn1[4]	O1	Zn1[5]	109.5	C6	C4	C5	103(6)
C1	O2	Zn1	135(4)	C6	C4	C6[7]	57(8)
C2	C3	C4	124(10)	C4	C6	C6[8]	120(5)
C3[3]	C2	C3	121(10)	C6[7]	C6	C4	62(4)
C3	C2	C1	119(6)	C6[7]	C6	C6[8]	89.996(13)

[1]1/2-Z,1/2-X,+Y; [2]1/2-Y,+Z,1/2-X; [3]1/2-X,1/2-Y,+Z; [4]1/2-Y,+X,1/2-Z; [5]+Y,1/2-X,1/2-Z; [6]1/2-X,1/2-Y,-Z; [7]1/2-Y,1/2-X,+Z; [8]+X,+Y,-Z

Table S36. Torsion Angles for UBMOF-1.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Zn1	O2	C1	O2[1]	0.000(11)	C5[4]	C5	C4	C3	180.000(7)
Zn1	O2	C1	C2	180.000(7)	C5[4]	C5	C4	C6[3]	-29(4)
C3	C2	C1	O2[1]	180.000(6)	C5[4]	C5	C4	C6	29(4)
C3	C2	C1	O2	0.000(5)	C5	C4	C6	C6[2]	-26(4)
C3[1]	C2	C1	O2	180.000(6)	C5	C4	C6	C6[3]	-97(4)
C3[1]	C2	C1	O2[1]	0.000(6)	C4	C3	C2	C3[1]	0.000(12)
C3	C4	C6	C6[2]	-177(4)	C4	C3	C2	C1	180.000(6)
C3	C4	C6	C6[3]	111(6)	C4[1]	C5	C4	C3	0.000(8)
C2	C3	C4	C5	-0.001(12)	C4[1]	C5	C4	C6[3]	151(4)
C2	C3	C4	C6	145(6)	C4[1]	C5	C4	C6	-151(4)
C2	C3	C4	C6[3]	-145(6)	C6[3]	C4	C6	C6[2]	72(4)

[1]1/2-X,1/2-Y,+Z; [2]+X,+Y,-Z; [3]1/2-Y,1/2-X,+Z; [4]1/2-X,1/2-Y,-Z

Table S37. Atomic Occupancy for UBMOF-1.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
C6	0.25				

Additional details regarding the UBMOF-1 refinement:

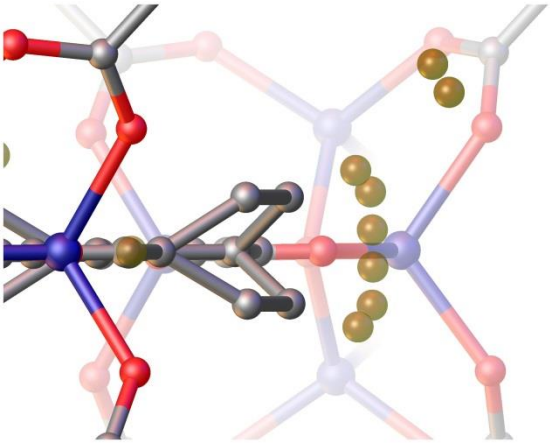

Figure S8. Image of the highest residual electron density peaks for UBMOF-1 near the ethylene bridge of the TPDC ligand illustrating the smeared out electron density located near the presumed position of the dimethylthiophene groups.

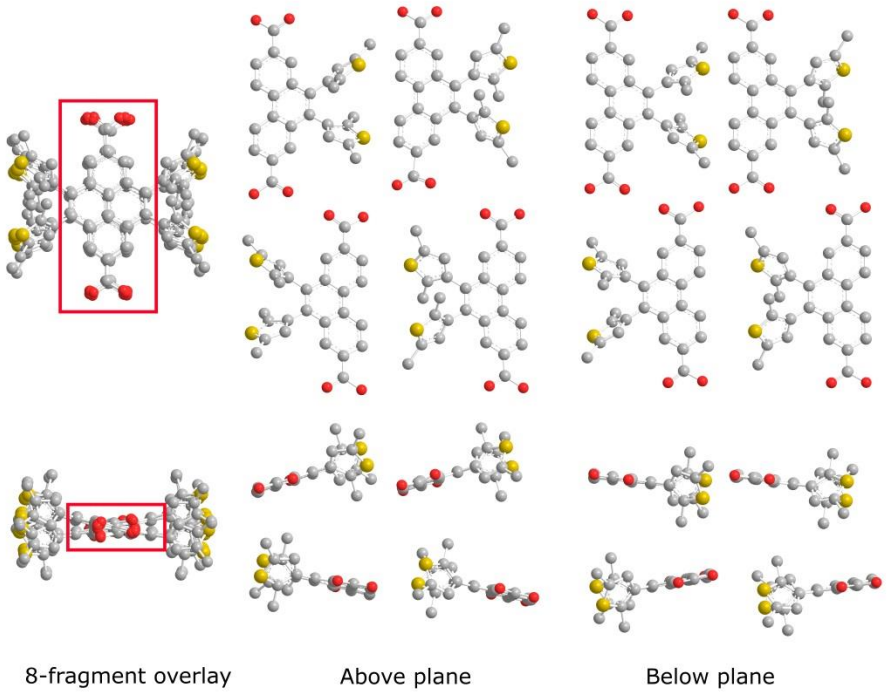

Figure S9. Image of the overlay of the eight TPDC ligands generated by the high crystallographic site symmetry for this ligand. The geometry of the ligand was optimized using mm2 methods contained in the Chem3D Pro Software suite.

References:

(1) F. Lipton, M.; M. Sorensen, C.; C. Sadler, A.; H. Shapiro, R. *J. Organomet. Chem.* 1980, *186*, 155.

(2) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* 2009, *42*, 339.

(3) Sheldrick, G. *Acta Crystallographica Section A* 2008, *64*, 112.