## Supplementary Information

## Coordination-directed self-assembly of a simple benzothiadiazole-fused tetrathiafulvalene to low-bandgap metallogels

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## Experimental

Materials and methods All reagents were purchased from commercial sources and used without further purification. 4,5-Bis(propylsulfanyl)-1,3-dithiol-2-thione and [1,3]dithiolo[4,5-f]-2,1,3-benzothiadiazole-6-one were synthesized as previously published.<sup>1</sup> <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 300 spectrometer operating at 300 MHz and 75.5 MHz, respectively. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent peak (chloroform,  ${}^{1}\text{H} = 7.26$  ppm,  ${}^{13}\text{C} = 77.0$  ppm). Coupling constants (J) are given in hertz (Hz). Peak multiplicities are described in the following way: s, singlet; t, triplet; m, multiplet. HRMS data was obtained with ESI (electrospray ionization) mode. FTIR spectra were recorded on a Perkin Elmer One FTIR spectrometer. Differential scanning calorimetry was performed in a MettlerToledo DSC823e under N<sub>2</sub> at a heating rate of 5 °C/min. Powder X-ray diffraction in reflection geometry was carried out. The patterns as a function of temperature were measured with Cu K $\alpha$  radiation ( $\lambda = 1.54$  Å) in a 0.3 mm capillary in Debye-Scherrer geometry on a STOE StadiP powder diffractometer. The patterns are shown with 20 mm offset on the intensity scale. Energy dispersive Xray spectroscopy (EDX) analysis of xerogels was obtained on a Noran SIX NSS200 dispersive X-ray detector. Scanning electron microscopy (SEM) measurements were carried out on Hitachi S-3000 N. Magnetic susceptibility measurements were made on a Quantum Design MPMS SQUID-XL magnetometer under an applied magnetic field of 10<sup>3</sup> Oe between 300 and 2 K. EPR spectra were obtained with an X-Band Bruker ELEXYS 500 spectrometer equipped with a rectangular cavity operating in a T102 mode, a Bruker variable temperature unit, a field frequency lock system, and an NMR gaussmeter. The modulation amplitude was kept well below the line width, and the microwave power was well below saturation.

Synthesis of 6-[4,5-bis(propylthio)-1,3-dithiol-2-ylidene][1,3]dithiolo[4,5-f]-2,1,3benzothiadiazole (1) To a 10-20 ml microwave vial (Biotage) was added [1,3]dithiolo[4,5-f]-2,1,3-benzothiadiazole-6-one (0.64)2.8 mmol). 4.5g, bis(propylsulfanyl)-1,3-dithiol-2-thione (1.60 g, 5.66 mmol), toluene (4 mL), and triethylphosphite (5 mL). Ar was bubbled through the mixture for 10 minutes. The mixture was then submerged in an oil bath at 130 °C for 30 minutes. After cooling down to room temperature, the reaction mixture was poured into methanol (75 mL). The crude precipitate was recovered by filtration and rinsed copiously with methanol. Pure compound 1 was obtained after column chromatography on silica gel with gradient elution of dichloromethane and hexane in 61% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.78 (s, 2H), 2.82 (t, J = 7.23 Hz, 4H), 1.68 (m, J = 7.28 Hz, 4H) 1.03 (t, J = 7.33 Hz, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 153.52, 142.73, 127.84, 116.06, 111.80, 38.35, 23.16, 13.15; HRMS (ESI) m/z calculated for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>S<sub>7</sub>, 459.9353; found. 459.9343.

**General Procedure for Preparation of Metallogels** For a typical gel formation reaction, 0.04 mmol of **1** was dissolved in 1 mL of solvent in a vial. Then, 0.1 mL of an ethanol solution of metal(II) salt at concentration of 0.4 M was added. The vial was closed with a screw cap and left at room temperature. The gelation was found to occur in less than 5 minutes. To make films of the gel, 11.5 mg of ligand **1** was dissolved in 0.5 mL of *o*-dichlorobenzene to which was added a solution of 4.26 mg of copper chloride in 0.05 mL of ethanol. A loose gel formed. It was put in between two glass

slides and compressed firmly and the slides were rubbed together. The gel particles broke down and blended together. Then the glass slides were slid apart in one motion and left to dry.

**Preparation of Samples for Electrical Resistivity Measurements** A sample of the xerogel was deposited onto a flat  $SiO_2$  wafer by drop-casting (total area was around 0.7 cm<sup>2</sup>) and was exposed to iodine vapors for 2 minutes. Temperature resistance dependence was measured using a standard four-probe dc method. Four annealed platinum wires (20 µm in diameter) were attached to the surface of the xerogel (which had an average thickness of 0.4 µm according to atomic force microscopy) using conductive graphite paste. The current used for measurements was 1 µA.

**AFM Experiments** CS AFM studies were performed on a 5500LS SPM system from Agilent Technologies using the Resiscope module. A contact mode with a bias voltage applied to the sample while scanning with a grounded conducting Pt-Ir coated silicon tip (force constant around 1.2 N/m) were used. Contact to the sample was made through the graphite substrate.

**Crystal Structure Determination** A crystal of **1** was mounted with Paratone-N on a glass needle and used for X-ray structure determination at -100 °C. All measurements were made on a Oxford Diffraction SuperNova area-detector diffractometer<sup>2</sup> using mirror optics monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The unit cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of 7789 reflections in the range  $1.74^{\circ} < \theta < 28.12^{\circ}$ . A total of 1743 frames were collected using  $\omega$  scans, 80 seconds exposure time and a rotation angle of 0.5° per frame, and a crystal-detector distance of 65.0 mm.

Data reduction was performed using the CrysAlisPro<sup>2</sup> program. The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multi-scan method using SCALE3 ABSPACK in CrysAlisPro<sup>2</sup> was applied.

The structure was solved by direct methods using SIR92,<sup>3</sup> which revealed the positions of all non-hydrogen atoms of the title compound. The non-hydrogen atoms were refined anisotropically. The H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 Ueq of its parent atom (1.5 Ueq for the methyl groups). Refinement of the structure was carried out on  $F^2$  using full-matrix least-squares procedures, which minimized the function  $\Sigma w (F_0^2 - F_c^2)^2$ . The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. All calculations were performed using the SHELXL-97<sup>4</sup> program.

Crystallographic data of **1**, CCDC 1005516, can be obtained free of charge from the Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data\_request/cif</u>.

**Table S1.** Gelation test in different transition metal chlorides (0.04 mmol of **1** in 1 mL of  $CHCl_3$ , 0.04 mmol of metal salt in 0.1 mL of ethanol, except for 0.15 mL of ethanol for  $CdCl_2$ ).

metal salt	phase
ZnCl <sub>2</sub>	solution
MnCl <sub>2</sub> ·4H <sub>2</sub> O	solution
FeCl <sub>2</sub> ·4H <sub>2</sub> O	solution
CoCl <sub>2</sub> ·6H <sub>2</sub> O	loose gel
CuCl <sub>2</sub> ·2H <sub>2</sub> O	gel
$CdCl_2$	gel

**Table S2.** Gelation ability of copper salts with different counteranions (0.03 mmol of 1 in 1 mL of  $CH_2Cl_2$ , 0.03 mmol of metal salt in 0.1 mL of ethanol except for  $CuBr_2$ , with 0.04 mmol of 1 in 1 mL of  $CHCl_3$  and metal salt, 0.08 mmol in 0.15 mL ethanol).

metal salt	phase
$CuF_2 \cdot 2H_2O$	solution
$Cu(NO_3)_2 \cdot 3H_2O$	initially solution, then gel formed as solvent
	began to evaporate.
$Cu(ClO_4)_2 \cdot 6H_2O$	solution
CuBr <sub>2</sub>	loose gel
$CdBr_2 \cdot 4H_2O$	loose gel
CoBr <sub>2</sub> hydrate	loose gel



Figure S1. DSC traces of two heating and cooling curves of a  $CuCl_2$  xerogel of 1.



Figure S2. <sup>1</sup>H NMR spectra of 1 in CDCl<sub>3</sub> (blue line) and a CdBr<sub>2</sub> gel (black line).



Figure S3. FTIR spectra of 1 and its MCl<sub>2</sub> xerogels



Figure S4. Powder X-ray diffraction of 1 and a CuCl<sub>2</sub> xerogel at room temperature.



**Figure S5.** Magnetic susceptibility plot as  $\chi T$  vs T of a CuCl<sub>2</sub> xerogel of **1**.



**Figure S6.** SEM images of  $CuCl_2$  xerogel samples made by varying the solvent used to dissolve **1**. (a)  $CH_2Cl_2$ , (b)  $CHCl_3$ , (c) chlorobenzene, and (d) *o*-dichlorobenzene.



Figure S7. SEM of gels made from 1 in chloroform and metal salt as follows: left,  $CdBr_2 \cdot 4H_2O$ , and right,  $CoCl_2 \cdot 6H_2O$ , both in ethanol.



**Figure S8.** Photographs of a  $CuCl_2$  gel of **1** on a glass microscope slide, (a) xerogel; (b) after washing with ethanol; and (c) after washing with dichloromethane. Washing with ethanol removes metal ions, revealing uncoordinated **1**. Washing then with dichloromethane removes the outermost layers of **1**, revealing a new layer of gel and a return to the blue color.



**Figure S9.** SEM of a  $CuCl_2$  gel of 1. (a) gel as synthesized, (b) after washing with dichloromethane, (c) after washing with ethanol.



**Figure S10.** A schematic representation of the possible formation of the CuCl<sub>2</sub>-coordinated complex gel showing 1-D molecular stacking along the coordination bonds as the primary structure of the gel.



Figure S11. a) SEM of a thin film of  $CuCl_2$  gel of 1. b) Thin film immediately after deposition. c) The same film after drying.



**Figure S12.** Graph showing the room temperature EPR signals of (a) an un-doped, (b) iodine doped, and (c) annealed doped copper chloride-based coordination xerogel of **1**.



Figure S13. The change of temperature vs time during the annealing of a doped CuCl<sub>2</sub> xerogel of 1.



**Figure S14.** Low angle part of the diffraction patterns of undoped (a) and doped (b) Cu xerogel of **1** as a function of temperature (green curve at 175 °C, red curve at 150 °C, blue curve at 100 °C).



**Figure S15.** In (a) SEM image of a freshly doped copper chloride-based xerogel of **1** and in (b) SEM image of the same sample after the annealing cycle was applied.



Figure S16. An ORTEP (50% probability ellipsoids) structure (top) and packing diagram (down) of 1.

The crystal of **1** is twinned by inversion with a ratio of 0.63:0.37. There are two molecules per asymmetric unit (Figure S16). One *n*-propyl moiety of each molecule is disordered over two sites with occupancies 0.599:0.401 and 0.607:0.393. There are two molecules per asymmetric unit. In the crystal lattice, the molecules are stacked in a head-to-tail manner along *b*-axis through N•••S contacts of 3.282 Å. There are no S•••S close contacts, however, some C•••S close contacts of 3.472 Å and unconventional intermolecular hydrogen bonds C-H•••N in a range of 3.298 to 3.444 Å are observed.

## **Reference:**

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