**Supporting Information** 

# An air-stable two-dimensional semiconducting metal-thiolate network and its exfoliation into ultrathin nanosheets †

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#### **Experimental details**

General procedure. Starting materials, reagents, and solvents were purchased from commercial sources (e.g., J&K, Aladdin, and Aldrich) and used without further purification. The elemental analyses (EA) were performed with a Vario Micro CUBE CHN elemental analyzer. Solution <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a 400 MHz Bruker superconducting magnet high-field NMR spectrometer at room temperature with tetramethylsilane (TMS) as internal standard. Thermogravimetric analyses (TGA) were carried out in a nitrogen stream using PerkinElmer Thermal analysis equipment (STA 6000) with a heating rate of 10 °C /min. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo Fisher XPS system (Escalab 250Xi) with a monochromatic Al Ka X-ray source. Fourier transform infrared (FT-IR) spectra were obtained using a Nicolet Avatar 360 FT-IR spectrophotometer. Powder X-ray diffraction data were collected at reflection mode on an Inel Equinox 1000 X-ray diffractometer (Inel, France) equipped with CPS 180 detector using monochromated Cu-K $\alpha$  ( $\lambda$  = 1.5406 Å) radiation. The X-ray tube operated at a voltage of 30 kV and a current of 30 mA. All of the magnetic data was obtained from a physical property measurement system (PPMS, DynaCool, Quantum Design Inc). The resistance data were measured on source meter equipment (Keithley 2400) with a single crystal solid or pellet achieved from pressing in a microtube, then electronic conductivity was determined by the function of  $\sigma = L / (R \cdot S)$ . Atomic force microscopy (AFM) measurement was carried out on a scanning probe microscope (Dimension FastScan, Bruker). High resolution transmission electron microscopy (HRTEM) data were measured on a field emission transmission electron microscope (Talos F200S, FEI). The electron paramagnetic resonance (EPR) spectrum was obtained at 100 K using a Bruker ER-420 spectrometer. The central magnetic field was 2890 G, and the modulation frequency was 100 kHz.

**Single crystal X-ray crystallography.** Single crystal X-ray diffraction data was collected on a Bruker APEX-II CCD diffractometer (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å) at T = 230 (2) K. The data was integrated using SAINT and corrected for absorption

and other systematic errors using SADABS program.<sup>[1]</sup> The structures were solved by direct methods with  $XS^{[2]}$  and refined by full-matrix least-squares on  $F_0^2$  using SHELXL<sup>[1]</sup>. Anisotropic temperature factors were applied to all non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and refined by applying riding models.

A dimethyl ammonium cation is disordered over four positions around a four-fold rotinversion axis. The two N-C bond distances were restrained to be similar in length (SADI command). *U*ij components of ADPs for disordered atoms closer to each other than 2.0 Angstrom were restrained to be similar. An ammonium cation is located in a general position. All N-H bond distances as well as all H $\cdots$ H distances were each restrained to be similar (SADI commands). A water molecule is disordered around a four-fold rotation axis, with four symmetry equivalent water H atom positions that are each half occupied. The O-H distances was restrained to 0.84(2) Angstroms, the H $\cdots$ H distance to the furthest away symmetry created H atom was restrained to 1.36(2) Angstroms, respectively.





Scheme S1 The synthetic procedure of H<sub>4</sub>dfdmt ligand.

**Synthesis of S1.** A round bottomed flask (100 mL) was loaded with a magnetic stirring bar, powder of tetrafluoroterephthalic acid (TFTP, 1.19 g, 5 mmol), 35 mL methanol

and 2 mL concentrated H<sub>2</sub>SO<sub>4</sub>. The flask was then connected to a condenser and the mixture was refluxed at 85 °C for 48 hours. After being cooled down to room temperature, 200 mL DI water was added into the reaction mixture, resulting in a large amount of white precipitate which was then filtered off by suction, washed extensively with water and dried in air (1.18 g, 89 % based on the TFTP). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  4.00 (s, 6H, CH<sub>3</sub>). FT-IR (KBr pellet, *v*/cm<sup>-1</sup>): 2965 (w), 1729 (s), 1631 (w), 1484 (s), 1438 (w), 1337 (s), 1266 (w), 1217 (m), 1180 (w), 1007 (m), 963 (m), 869 (w), 769 (w), 746 (m).



**Fig. S1** The <sup>1</sup>H NMR spectrum of **S1** in CDCl<sub>3</sub>.

Synthesis of S2. A two-necked and round-bottom flask charged with 2-ethylhexyl-3mercaptopropionate (1.9 mL, 8.3 mmol) and potassium carbonate (2.208 g, 16 mmol) was connected to a nitrogen manifold. *N*,*N*-dimethylformamide (DMF, 15 mL) was bubbled with N<sub>2</sub> for 10 minutes and transferred via cannula into the flask followed by stirring. Compound S1 (1.064 g, 4 mmol) was added under nitrogen and the reaction mixture was stirred at room temperature for 6 hours. Afterward, the mixture was poured into an ice-water bath (200 mL) and extracted with ethyl acetate (EA,  $3 \times 100$  mL). The combined organic mixture was washed by DI water ( $3 \times 100$  mL) and subjected to flash column chromatography (eluent: *n*-hexane/EA 50 to 1 then 30 to 1) to acquire the colourless liquid (1.80 g, 68% based on S1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  4.03 – 3.96 (m, 4H, CH<sub>2</sub>), 3.95 (s, 6H, CH<sub>3</sub>), 3.13 (t, 4H, CH<sub>2</sub>), 2.59 (t, 4H, CH<sub>2</sub>), 1.54 (dd, 2H, CH), 1.30 (dt, 16H, CH<sub>2</sub>), 0.91 – 0.83 (m, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 171.42, 163.23, 156.52, 153.98, 129.44, 122.78, 67.55, 53.37, 38.92, 35.00, 30.55, 29.10, 23.93, 23.12, 14.19, 11.12. FT-IR (KBr pellet, *v*/cm<sup>-1</sup>): 2958 (s), 2930 (s), 2865 (m), 1743 (s), 1631 (w), 1596 (w), 1444 (m), 1406 (s), 1353 (m), 1267 (s), 1191 (s), 1149 (s), 1044 (w), 972 (m), 886 (w), 826 (w), 722 (w).



Fig. S2 The <sup>1</sup>H NMR spectrum of S2 in CDCl<sub>3</sub>.



Fig. S3 The <sup>13</sup>C NMR spectrum of S2 in CDCl<sub>3</sub>.

**Synthesis of H<sub>4</sub>dfdmt.** Compound **S2** (1.8 g, 2.72 mmol) was placed in a two-neck flask charged with a magnetic stir bar. The flask was evacuated and refilled by N<sub>2</sub> (cycle repeated 3 times) to ensure the flask was under N<sub>2</sub> atmosphere. A KOH solution (1.6 M, 20 mL in EtOH/H<sub>2</sub>O, v/v=1/1) was bubbled by N<sub>2</sub> for 10 minutes and then transferred into the two-neck flask via cannula under N<sub>2</sub> protection. After being heated at 90 °C for 36 hours, the reaction mixture was cooled to room temperature, and HCl (10% in water, 12 mL) was then added slowly with vigorous stirring. After the pH value of the mixture became lower than 2, the precipitate was collected by suction filtration and washed with water extensively, and dried on a filter paper under suction with a nitrogen stream to afford H<sub>4</sub>dfdmt as a pale yellow solid (0.506 g, 70% based on **S2**). The product thus obtained was pure as indicated by NMR and used for crystal growth without further purification. <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  162.63, 155.10, 152.56, 129.25. FT-IR (KBr pellet, *v*/cm<sup>-1</sup>): 2598 (w), 2530 (w), 1680 (s), 1443 (s), 1413 (s), 1256 (s), 1186 (m), 930 (m), 861 (m), 809 (m), 774 (w), 647 (w).



Fig. S4 The <sup>1</sup>H NMR spectrum of H<sub>4</sub>dfdmt in DMSO- $d_6$ .



Fig. S5 The <sup>13</sup>C NMR spectrum of  $H_4$ dfdmt in DMSO- $d_6$ .

Preparation of single crystals of Eu-dfdmt. H<sub>4</sub>dfdmt (5.3 mg, 20.0 µmol) and EuCl<sub>3</sub>·6H<sub>2</sub>O (16.0 mg, 44.0 µmol) were loaded into a heavy-wall glass tube (10 mm OD, 6 mm ID), and then a solution of N,N-dimethylformamide, water and acetonitrile (0.6 mL, v/v/v=1/1/1) was added. The tube was then flame-sealed and heated at 140 °C in a programmable oven for 72 hours followed by cooling (1 °C/min) to room temperature. The resulted single crystals (suitable for single-crystal X-ray diffraction) were then retrieved by filtration (5.0 mg, 31 % based on H<sub>4</sub>dfdmt). FT-IR (KBr pellet, v/cm<sup>-1</sup>): 3396 (w), 3211 (w), 2954 (m), 2812 (m), 2432 (w), 1698 (w), 1655 (w), 1554 (s), 1456 (m), 1428 (s), 1359 (s), 1262 (m), 1175 (w), 1014 (w), 899 (w), 846 (m), 754 (m), 674 (m), 634 (m), 620 (w), 427 (w). X-ray powder diffraction of the bulk sample indicated a pure phase consistent with the single-crystal structure (see Fig. 2 in the text). Elemental analysis of the activated product  $C_{18}H_{26}F_4N_5O_9S_4Eu$ , i.e., Eu(dfdmt)<sub>2</sub>·4NH<sub>4</sub>·(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>·H<sub>2</sub>O found (%) C 26.49, H 3.09, N 8.55, S 15.52; calculated (%): C 26.57, H 3.20, N 8.61, S 15.75.

**Exfoliation of Eu-dfdmt into nanosheets.** In a typical process, an Eu-dfdmt crystal sample (ca. 2.0 mg) was mixed with 10 mL of DMF and sealed in a ball mill jar (25 mL) containing dozens of balls (total weight of the balls: 80 g). The jar was then fitted into a ball mill (DECO-PBM-AD-0.25L, Changsha Deco Equipment Co.) for operation at a horizontal speed of 500 rpm and rotational speed of 50 rpm for 12 h. A colloidal

suspension of nanosheets was achieved. For SEM and AFM studies, 0.10 mL of the suspension was pipetted into a small vial, diluted to 0.50 mL by DMF. After being left to stand still for 2 hours, 0.010 mL of the resulted suspension was then dropped onto a silicon plate and used for SEM and AFM studies (vacuum was applied to remove the residual solvent). For TEM (including HRTEM) measurement, 0.010 mL of the nanosheet suspension was dropped via a pipet onto a carbon-coated copper mesh, and vacuum was applied to remove the residual solvent.

### Structure and characterizations



Fig. S6 The IR spectra of H<sub>4</sub>dfdmt ligand (a) and Eu-dfdmt (b).



**Fig. S7** A full view of the XPS spectrum (panel a) of a sample of Eu-dfdmt, and the close-ups for Eu 3d peaks (panel b), S 2p peaks (panel c) and O 1s peaks (panel d). The binding energies of O 1s at 531.8 eV in panel d is characteristic of anionic O species (see for example, Cai, Y.; Li, X.; Wu, K.; Yang, X. *Anal. Chim. Acta* **2019**, *1062*, 78-86).



**Fig. S8** Solid-state electron paramagnetic resonance (EPR) spectrum of Eu-dfdmt at 100 K. The split peak around g = 2.0 can be ascribed to the combined result of organic radicals and Eu<sup>2+</sup> ions.



**Fig. S9** Temperature dependence of the  $\chi_M T$  and the  $\chi_M^{-1}$  products at 1000 Oe in the temperature range of 2-300 K.

The magnetic data can be fitted with a model based on isolated Eu(III) centers. Alternatively, the plots are also in accord with a formula unit containing a single Eu(III) center in strong antiferromagnetic coupling with two free radicals (S =  $\frac{1}{2}$ ), with the spin-orbit coupling constant modeled to be 370(6)cm<sup>-1</sup>, and  $\theta$  = -104 (2) K in the Curie-Weiss expression.



Fig. S10 The distinct Eu-S network with  $\pi$ -conjugated linkers in Eu-dfdmt (without showing the Eu-O bonds).



Fig. S11 The adsorption and desorption isotherms of Eu-dfdmt for  $N_2$  at 77 K (measured by a Micrometrics ASAP 2020 Surface Area and Porosity Analyzer).

Sample treatment: 105 mg **Eu-dfdmt** crystals were added to a 25-mL flask containing 20 mL of methanol at room temperature, and the methanol was refreshed every 10 hours for three times. The solid sample was collected by centrifugation and dried under vacuum at 60 °C for 24 h, and then further heated (e.g., for activation) at 100 °C for 24 h on the Analyser prior to the sorption test.



**Fig. S12** Thermogravimetric curve of Eu-dfdmt from room temperature to 1000 °C (in nitrogen atmosphere with a heating rate of 10 °C/min).

The steep step of weight loss of 16% at ca 270 °C corresponds to the departure of  $4NH_3$  +  $(CH_3)_2NH + H_2O$  (fw 131) from the formula  $Eu(dfdmt)_2 \cdot 4NH_4 \cdot (CH_3)_2NH_2 \cdot H_2O$  (fw 812); Calculated weight fraction: 131/812 = 16.1%. The residual weight of 24.2% corresponds to the formation of  $Eu_2O_3$ ; calculated weight fraction: 176/812 = 21.7%.



Fig. S13 *I-V* voltammetric curve of Eu-dfdmt based on top-down surfaces at room temperature.



Fig. S14 AFM image (a) and the height distribution (b) along the line in (a).



Fig. S15 The PXRD patterns of Eu-dfdmt: a) bulk crystals and b) nanosheets after exfoliation.



Fig. S16 The FT-IR spectra of Eu-dfdmt: a) bulk crystals and b) nanosheets after exfoliation.



Fig. S17 *I-V* voltammetric curve of nanosheets of Eu-dfdmt at room temperature.

Compound	Eu-dfdmt
Chemical formula	$C_{18}H_{26}F_{4}N_{5}O_{9}S_{4}Eu$
Formula weight	812.64
Temperature (K)	230(2)
Crystal size (mm <sup>3</sup> )	$0.16 \times 0.086 \times 0.06$
Crystal system	Tetragonal
Space group	P4/n
<i>a</i> (Å)	12.7820(15)
<i>b</i> (Å)	12.7820(15)
<i>c</i> (Å)	8.4363(2)
$\alpha$ (deg)	90.00
$\beta$ (deg)	90.00
γ (deg)	90.00
$V(Å^3)$	1378.32(7)
Ζ	2
$\rho_{\text{calcd}}$ (g/cm <sup>3</sup> )	1.958
GOF	1.059
$R_1^a[I \ge 2\sigma(I)]$	0.0214
$wR_2^b$ [all data]	0.0510

 Table S1 Crystal data and structure refinement parameters for Eu-dfdmt.

 ${}^{a} R_{1} = \sum \|F_{o}| - |F_{c}|| / \sum (|F_{o}|) \quad {}^{b} WR_{2} = \{\sum [W(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [W(F_{o}^{2})^{2}] \}^{1/2}$ 

<b>D</b> –H····A	D–H(Å)	H····A(Å)	D…A(Å)	D-H···A(°)
$N2-H2A\cdots O2^i$	0.856	1.986	2.842	177
$N2-H2B\cdots S1^{ii}$	0.857	2.586	3.423	166
$N2-H2B\cdots F1^{ii}$	0.857	2.474	2.915	113
N2-H2A…F1 <sup>iii</sup>	0.856	2.636	2.900	100
N2-H2C···O2 <sup>iv</sup>	0.863	1.957	2.806	168
N2-H2D…O1	0.851	2.203	2.997	155
N1-H1A…S1	0.900	2.528	3.372	157
N1-H1B…S1 <sup>v</sup>	0.900	2.561	3.423	161
O3-H3····S1 <sup>vi</sup>	0.851	2.666	3.488	163

**Table S2** Hydrogen bond geometrical parameters (Å, °) in Eu-dfdmt (D–H···A = Donor-Hydrogen···Acceptor).

Symmetry code: (i) -x+1, -y+1, -z+1; (ii) y, -x+1/2, z+1; (iii) 1/2-x, 1/2-y, z; (iv) y, -x+1/2, z; (v) -y+1, x+1/2, -z; (vi) -y+1/2, x, z.

#### References

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