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An air-stable anionic two-dimensional semiconducting metalthiolate network and its exfoliation into ultrathin few-layer nanosheets †

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The black, small-bandgap semiconducting framework Eu-dfdmat features extensive Eu<sup>3+</sup>-sulfur bridges from the linear linker 2,5difluoro-3,6-dimercaptoterephthalate (dfdmt). Each Eu center is chelated to four dfdmt linkers to form an anionic coordination sphere involving four carboxyl O and four mercapto S centers (EuO<sub>4</sub>S<sub>4</sub>), wherein the charge buildup can be alleviated by the electron-withdrawing fluoro groups. The extensive metal-linker bonding, together with a trace of Eu<sup>2+</sup> species, appears to boost electronic interaction in the 2D net, generating a small band gap of 1.31 eV (946 nm), albeit a modest conductivity (e.g., 10<sup>-6</sup> S m<sup>-1</sup>). The crystals also exhibit persistent EPR signals indicative of organic radicals (*g*=2.002). The Eu-dfdmt solid are stable in air and can be exfoliated into utrathin nanosheets (ca. 5 nm; 6-8 layers).

The structure-property relation remains a challenging topic in the study of metal-organic frameworks as electronic materials.<sup>1</sup> Because of the poor electronic coupling across metalcarboxylate and other popular linkages, MOFs as solid state materials had long been perceived as electronically inert; even though systematic efforts had been earlier made to unveil the feasibility of electronically integrating the metal centers and organic  $\pi$ -linkers, in order to clear the conceptual barrier to electronic MOF solids.<sup>2</sup> With the discoverv of conductive/metallic transport,<sup>3</sup> ferromagnetic,<sup>4</sup> superconductive<sup>5</sup> and topological insulator properties<sup>6</sup> (mostly

from the metal-dithiolene systems<sup>7</sup>), metal-linker electronic coupling in MOF solids has now proven a fruitful topic to pursue. To investigate structure-property relations, well-defined structures such as single crystals are crucial. As electronic coupling often involves strong links with significant covalent character (e.g., the less reversible metal-thiolate links) to promote orbital overlap, many electronic MOF materials are obtained as powder samples, and single crystals of 2D or 3D  $\pi$ -conjugated metal-thiolate networks remain rare, while related cases often involving metal-thiolate blocks linked via more labile (e.g., pyridinyl<sup>8</sup> and oxo<sup>9</sup>) donors.

In this context, lanthanide (Ln)-sulfur complexes are interesting. First, EuS and other RE chalcogenides are known for intriguing optical and electronic properties<sup>10</sup>; RE complexes with organic sulfur ligands including thiolates and thiocarboxylates have also been widely studied<sup>11</sup>, with some exhibiting dark colors<sup>12</sup> indicative of Ln-ligand electronic coupling (e.g., involving the Eu 4f and S 3p orbitals). Second, with RE(III) ions being hard acids and S donor soft bases, the RE-S links offer lability and reversibility for crystallizing the networks.

However, Ln-S links for MOF construction remain underexplored: most reported RE-S complexes are discrete, with only a few<sup>11a, 11c, 11d, 13</sup> being 1D polymeric structures. The underuse is perhaps (this is our speculation) due to the perceived ionicity and lability of the RE-S bond, which had swayed our vision, and made us think it unsuited for electronically bridging the organic moieties. For example, a 3D Nd-dithiocarbamate MOF crystal was recently made, but it is not  $\pi$ -conjugated, features light color and readily hydrolyses in air.<sup>14</sup>



Scheme 1 Linker dfdmt<sup>4-</sup>, its thiyl radical dfdmt-<sup>3-</sup> and two possible schemes for coordination with Eu<sup>3+</sup>.

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Electronic Supplementary Information (ESI) available: Experimental details and general procedures; XRD, IR, EPR, XPS, TGA, optical absorption spectrum and temperature dependent I-V curves. CCDC 1941723 contains the supplementary crystallographic data for Eu-dfdmt. See DOI: 10.1039/x0xx00000x
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The 2D MOF Eu-dfdmt was crystallized by solvothermally reacting  $H_4dfdmt$  (Scheme 1; see ESI for synthesis) and EuCl<sub>3</sub>·6H<sub>2</sub>O in N,N-dimethylformamide (DMF), water and acetonitrile (1:1:1, v/v/v). Single-crystal X-ray diffraction (SCXRD) revealed the connectivity and composition Eu(dfdmt)<sub>2</sub> for the anionic net (Fig. 1a and 1b). The structure is tetragonal (P4/n; Table S1, ESI), with ½ dfdmt and ¼ Eu in the asymmetric unit. The Eu<sup>3+</sup> is 8-coordinated (EuO<sub>4</sub>S<sub>4</sub>), with the  $C_4$ -related carboxyl O (2.384 Å) and thiolate S (2.988 Å) donors forming a square antiprism (Fig. 1a): the multiple S atoms bonded to Eu(III) here therefore contrast with the known EuDMBD framework (DMBD, 2,5-dimercapto-1,4-benzenedicarboxylic acid),16 wherein the -SH groups remain unbonded to the metal center. The Eu(III) is thus chelated to four dfdmt bridges in the resulted puckered square net (Fig. 1b), featuring neighboring Eu square antiprisms in opposing orientations. The Eu-S links afford a rare example of single crystalline 2D  $\pi$ -conjugated metal-thiolate net (Fig. S10; cf an unconjugated Eu-sulfur sheet<sup>14</sup>).

The precise charge on the 2D net of Eu(dfdmt)<sub>2</sub>, however, is



**Fig. 1** Single crystal structure of Eu-dfdmt: a) Coordination environment of Eu; b) a 2D layer and the imbedded  $[(CH_3)_2NH_2]^+$  guests viewed along the *c* axis; c) a side view of the layered structure (along the *a* axis), showing also the intercalated NH<sub>4</sub><sup>+</sup> and water molecules (H atoms were omitted for clarity.)

less defined, mainly because dfdmt is partially oxidized into radicals (e.g., as the thiyl dfdmt·<sup>3-</sup>; Scheme 1) as revealed in electron paramagnetic resonance (EPR) and other studies. The degree of linker oxidation is hard to quantify by SCXRD, e.g., by charge balancing from the NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub> and (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub><sup>+</sup> cations (formed from acetonitrile and DMF hydrolysis), as the data generally do not locate the light H atoms. Elemental analysis results (i.e., C 26.49, H 3.09, N 8.55, S 15.52%) also lacks the precision to pinpoint the degree of protonation. The fitting formula Eu(dfdmt)<sub>2</sub>·(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>·<sup>7</sup>/<sub>3</sub>NH<sub>4</sub>·<sup>5</sup>/<sub>3</sub>NH<sub>3</sub>·H<sub>2</sub>O (calculated C Page 2 of 4

26.69, H 3.11, N 8.65, S 15.83%) is derived<sub>vi</sub>from<sub>ble</sub>X<sub>5</sub> (av photoelectron spectroscopy (XPS).

XPS reveals two types of sulfur centers, with the signals of S  $2p_{3/2}$  at 161.4 and  $2p_{1/2}$  162.6 eV in one (major) set,<sup>21</sup> and 163.7 and 164.9 eV (respectively) in the other (minor) set (Fig. S7c). The major type can be ascribed to the anionic thiolate S centers (RS<sup>-</sup>, lower binding energies), and the minor type, thiyl radicals (RS·). Deconvolution of the peaks indicate the RS<sup>-</sup>/RS· molar ratio to be 7:5. The RS<sup>-</sup>/RS· and NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub> ratios, however, are variable in this system; as XPS is surface sensitive, its results may not reflect the bulk composition. The occupancy of the associated H atoms was therefore not crystallographically refined using the XPS NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub> ratio.

XPS also indicates Eu to be mostly trivalent, accompanied by a trace of Eu<sup>2+</sup>: i.e., the prominent Eu(III)  $3d_{3/2}$  (1165.9 eV) and  $3d_{5/2}$  (1136.4 eV) peaks (Fig. S7b)<sup>17</sup>, and the weak Eu(II) peaks at lower binding energies of 1158.2 and 1126.9 eV.<sup>18</sup> Lanthanides commonly being trivalent, the Eu<sup>2+</sup> is stabilized by its half-filled,  $4f^7$  configuration. The Eu(II) fraction is however small (below 5% as per XPS), and its impact on the overall charge of the Eu(dfdmt)<sub>2</sub> net is insignificant. The Eu<sup>2+</sup> likely arises from Eu<sup>3+</sup> reduction by the electron-rich dfdmt<sup>4-</sup> linkers, which also forms the radical anion dfdmt.<sup>3-</sup> mentioned above.

The paramagnetic organic radical and Eu(II) species are also detected by EPR measurement (at 100 K) on the powder sample of Eu-dfdmt. The asymmetric signal at g=2.002 is typical of organic radicals (Fig. S8). The EPR signal was persistent even in air, which is consistent with the general stability of thiyl radicals.<sup>19</sup> EPR also discriminates Eu<sup>2+</sup> from Eu<sup>3+</sup>: the 4*f*<sup>6</sup> Eu<sup>3+</sup> ion is diamagnetic with the <sup>7</sup>*F*<sub>0</sub> a ground state, and is therefore EPR silent,<sup>20</sup> while the 4*f*<sup>7</sup>, paramagnetic Eu<sup>2+</sup> is EPR-active (e.g., with g  $\approx$  2.0, 2.8, 3.4, 4.5 and 6.0 observed of Eu<sup>2+</sup> in glassy systems<sup>21</sup>). In our case, the EPR features of g  $\approx$  2.03, 2.8 and 4.3 can be ascribed to Eu<sup>2+</sup>,<sup>22</sup> with the split peak around g = 2.0 also indicating the contribution from the organic radicals.

The molar magnetic susceptibility  $(\chi_M)$  data (at an applied field of 1000 Oe and in the 2-300 K range; with  $\chi_M T$  and  $\chi_M^{-1}$ plotted against temperature in Fig. S9) features  $\chi_M T = 2.1 \text{ cm}^3$ mol<sup>-1</sup> K at 300 K, slightly greater than the value of 1.5 cm<sup>3</sup> mol<sup>-1</sup> K for a Eu(III) ion calculated from the Van Vleck equation allowing for population of the excited state.23 The higher observed  $\chi_M T$  at 300 K can be ascribed to the contribution from organic radicals. The  $\chi_M T$  value decreases continuously at lowering temperature, and approaches zero at 2K. The observed graphs (Fig. S9) can be modelled by the depopulation of Stark levels for a single Eu(III) ion, which takes a J = 0 ground state (<sup>7</sup>F<sub>0</sub>) at 2 K to render  $\chi_M T$  close to zero. With thermally populated excited states, the magnetic susceptibility follows the Curie-Weiss law in the temperature range of 180-300 K. Alternatively, the graphs are also in accord with a single Eu<sup>3+</sup> center in strong antiferromagnetic coupling with two free radicals (S =  $\frac{1}{2}$ ), i.e., (RS·)Eu<sup>3+</sup>(·SR), 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. Structurally, the isolated Eu<sup>3+</sup> center corresponds to a (RS<sup>-</sup>)₄Eu<sup>3+</sup> coordination node (Scheme 1) with four thiolate ligands, while the second magnetic model of (RS·)Eu<sup>3+</sup>(·SR) corresponds to a (RS<sup>-</sup>)<sub>2</sub>(RS·)<sub>2</sub>Eu<sup>3+</sup> node containing Published on 17 February 2020. Downloaded by Universite Paris Descartes on 2/17/2020 12:42:53 PM

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Fig. 2 Powder X-ray diffraction patterns (Cu K $\alpha$ ,  $\lambda$  = 1.5418 Å) of Eu-dfdmt: a) calculated from the single crystal structure; b) measured from a fresh powder sample at room temperature; c) from a powder exposed in air for one month.

two neutral thiyl RS· radicals and two thiolate anions (Scheme 1). The 7:5 RS<sup>-</sup>/RS· ratio (e.g., as found above by XPS) in the Eudfdmt solid suggests that the  $(RS^{-})_{4}Eu^{3+}$  and  $(RS^{-})_{2}(RS\cdot)_{2}Eu^{3+}$  nodes exist in 1:5 ratio to fit the magnetic data.

Together with the carboxylate O donors, the two corresponding  $EuO_4S_4^{5-}$  and  $EuO_4S_4^{3-}$  anionic nodes can be formally deduced [even though at room temperature (rt) the charges are likely averaged out in the 2D net], to match the charge-balanced formula  $Eu(dfdmt)_2 \cdot (CH_3)_2 NH_2 \cdot \frac{7}{_3} NH_4 \cdot \frac{5}{_3} NH_3 \cdot H_2O$  determined above. As shown Figs. 1b and 1c, the organic cations  $(CH_3)_2 NH_2^+$  are located in the cavities of the coordination layer, while the interlayer space is filled by the  $NH_4^+/NH_3$  and  $H_2O$  species, further stabilizing the anionic host via electrostatics/H-bonds (Table S2). A N<sub>2</sub> sorption test (77 K) on a sample activated at 100 °C indicated no porosity (Fig. S11), consistent with the compact X-ray crystal structure.

Powder X-ray diffraction (PXRD) indicates a pure crystalline phase for the air-stable Eu-dfdmt solid (Fig. 2). Thermogravimetric analysis (TGA) found a steep weight loss (ca 16%; between 235 and 270 °C) attributable to the departure of one dimethylamine, four ammonia and one water molecules from the formula  $Eu(dfdmt)_2 \cdot (CH_3)_2 NH_2 \cdot \frac{7}{3} NH_4 \cdot \frac{5}{3} NH_3 \cdot H_2 O$  (calcd. 16.1%; Fig. S12).

Diffuse reflection measurement reveals a small band gap of 1.31 eV (946 nm), as per the tangent method<sup>24</sup> (Fig. 3a). The electrical conductivity was measured by the two-probe method on a single crystal (rectangular block: 1.31 × 0.75 × 0.32 mm). At rt, the I-V curve (from -5 to 5 V) in the left-right direction (in plane of the 2D net) indicates a conductivity [ $\sigma = L/(R \cdot S)$ ] of 4.56  $\times$  10<sup>-6</sup> S m<sup>-1</sup> (Fig. 3b), while lower conductivity was found along the top-down direction (through planes of the 2D net; Fig. S13): 1.78 × 10<sup>-6</sup> S m<sup>-1</sup>. The limited conductivity can be due to the noncoplanar arrangement of the dfdmt linkers, which may hinder in-plane charge transport. The stable currents at rt point to electronic conduction, which is consistent with the negligible rt ionic conductivity (below 10<sup>-12</sup> S m<sup>-1</sup> as per impedance measurement). The conductivity increases at rising temperature (Fig. 3c), reaching  $1.02 \times 10^{-5}$  S m<sup>-1</sup> at 120 °C, although ionic conductivity remains to be further studied under these heated conditions.



**Fig. 3** A diffuse reflectance spectrum (a), an *I-V* voltammetric curve based on leftright surfaces at room temperature (b, inset: photograph of a single crystal, scale bar: 1 mm), and at different temperatures (c), and the Arrhenius plot with linear fitting (d) for Eu-dfdmt (with a formally fitted activation energy of 0.25 eV).



**Fig. 4** An AFM image (a) and height profile (b) of a nanosheet of Eu-dfdmt, TEM and HRTEM images under different resolutions (c and d), periodic lattice fringes found in panel d (e), and electron diffraction spots of corresponding fast-Fourier-transform (FFT) pattern (f) for nanosheets at 300 kV.

MOF nanosheets offer advantages of high aspect ratio, large surface area and numerous exposed active sites<sup>15</sup>. Notably, Eudfdmt can be exfoliated into ultrathin and few-layer nanosheets (Fig. 4) by simple ball-milling. Atomic force microscopy (AFM) height profile diagrams of two randomly selected nanosheets indicate the respective thicknesses to be 5.0 and 6.6 nm (Fig. 4b and Fig. S14): i.e., those of 6-8 layers (a single layer being 0.84 nm thick; Fig. 1). The lateral dimensions feature 324 and 476 nm, highlighting the ultrathin morphology and high aspect ratios. TEM and HRTEM (high-resolution transmission electron microscopy) images reveal translucent, crystalline thin morphology (Figs. 4c and 4d), with distinct lattice fringes (Fig. 4e) corresponding to  $d_{031}$  (0.380 nm), and the fast-Fouriertransform (FFT) pattern indexed to the Eu-dfdmt lattice (e.g., 031, 012 and 02-1, Fig. 4f). PXRD and FT-IR (Figs. S15 and S16) also verifies sample stability in the exfoliation process. The conductivity of nanosheets  $(2.36 \times 10^{-6} \text{ S} \text{ m}^{-1} \text{ at room})$ temperature, see Fig. S17) was found to be slightly lower than the in-plane value of the bulk crystal, which might be partly due to the structural defects and traps caused by exfoliation.

In conclusion, by taking our early design of thiol-carboxyl combination into the fluorination domain, we have discovered the highly anionic 2D Eu-dfdmt network as a rare example of

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conjugated lanthanide-sulfur framework. The Eu ions were found to be mostly trivalent (3+), but the small amount of Eu(II) ions may likely impact electronic properties, e.g., to reduce the band gap to generate the black color. In spite of the substantial thiyl radical species (accounting for 42% of the S atoms), the solid sample of Eu-dfdmt are stable in air. The electrical conductivity, however, appears to be quite modest (e.g.,  $10^{-6} - 10^{-5}$  S m<sup>-1</sup> from room temperature to 120 °C), so that doping and alloying with various other transition metal ions may be needed to improve the electronic properties.

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# **Conflicts of interest**

There are no conflicts to declare.

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