CHEMISTRY
A European Journal

Supporting Information

A Boiling-Water-Stable, Tunable White-Emitting Metal–Organic Framework from Soft-Imprint Synthesis

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General Procedure. Starting materials, reagents, and solvents were purchased from commercial sources (J&K, Aldrich and Acros) and used without further purification. Elemental analysis was performed with a Vario Micro CUBE CHN elemental analyzer. FT-IR spectra were obtained using a Nicolet Avatar 360 FT-IR spectrophotometer. Solution ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker superconducting magnet high-field NMR spectrometer at room temperature, with tetramethylsilane (TMS) as the internal standard. The determinations of photoluminescence (PL) were conducted on a Horiba Jobin Yvon Florolog-3-TCSPC spectrophotometer. Thermogravimetric analyses (TG) were carried out in a nitrogen stream using PerkinElmer Thermal analysis equipment (STA 6000) with a heating rate of 10 °C/min.

The ratios of the metal ions (between Eu^{3+} and Tb^{3+}) were determined by using a PerkinElmer Optima™ 2100 DV ICP optical emission spectrometer. Scanning electron microscope (SEM) images were collected using Philips XL30 ESEM. Powder X-ray diffraction data for the samples were collected in reflection mode at room temperature on an Inel Equinox 1000 X-ray diffractometer (Inel, France) equipped with a CPS 180 detector using monochromated Cu-Kα1 (λ = 1.5406 Å) radiation. The X-ray tube was operated at a voltage of 30 kV and a current of 30 mA.

X-ray photoelectron spectroscopy (XPS) spectra were recorded with a Perkin Elmer PHI5000C system equipped with a hemispherical electron energy analyzer. The spectrometer was operated at 15 kV and 20 mA, and an aluminum anode (Al Kα, hν = 1486.6 eV) was used. The C1s line (284.6 eV) was used as the reference to calculate binding energies (BE).

The porosity and surface area analysis was performed using a Quanta chrome Autosorb iQ gas sorption analyzer. The sample was outgassed at 0.03 torr with a 5 °C/min ramp to 110 °C and held at 110 °C for 60 hours. The sample was then held at vacuum until the analysis was run. Pore analysis was performed using N_2 at 77 K (P/P_0 range of 1×10^{-5} to 0.995). Initial data analysis was done using the AS1Win and Quadra Win 5.05 software (both of Quanta chrome instruments). High purity gases were used throughout the analysis.

The overall quantum yield was measured with an absolute photoluminescence quantum yield measurement system (Hamamatsu, C11347-11). This system consists of a Xe arc lamp, a monochromator, an integrating sphere, a multichannel detector, and a personal computer. A

monochromatic light source was used as the excitation light source, which mounted a xenon lamp with a lamp rating of 150 W. The overall quantum yield $\Phi_{overall}$ is given by

$$\Phi_{overall} = \frac{S(Em)}{S(Abs)} = \frac{\int \frac{\lambda}{hc}\left[I_{em}^{sample}(\lambda) - I_{em}^{reference}(\lambda)\right]d\lambda}{\int \frac{\lambda}{hc}\left[I_{ex}^{reference}(\lambda) - I_{ex}^{sample}(\lambda)\right]d\lambda}$$

where S(Abs) is the number of photons absorbed by a sample and S(Em) is the number of photons emitted from a sample, λ is the wavelength, h is Planck's constant, c is the velocity of light, $I_{sample\ (ex)}$ and $I_{reference\ (ex)}$ are the integrated intensities of the excitation light with and without a sample respectively, $I_{sample\ (em)}$ and $I_{reference\ (em)}$ are the photoluminescence intensities with and without a sample, respectively.

Single crystal X-ray diffraction data for **1** and **2-Eu** were collected on a Bruker AXS Smart Apex CCD diffractometer (Mo Kα radiation, λ = 0.71073 Å) at T = 100 (2) K. The data were integrated using SAINT and corrected for absorption and other systematic errors using SADABS. The structures were solved and refined by full-matrix least-squares on F_o^2 using SHELXL-2014/7 (Sheldrick, G. M. 2014), and SHELXLE Rev714 (Hübschle, C. B.; et al., 2011).

Compound **1** crystallized in the space group *Fddd*, but with severe disorder and some indication of additional non-translational ordering as indicated by diffuse streaks visible in planes perpendicular to the h-direction (e.g. 0kl, 1kl, 2kl, etc).

The model given here is based on the Bragg reflections only. In the model there are two types of unique ligands. One is split into two moieties that are shifted sideways by nearly one Ångstrom from each other (this is the ligand with the lower atom numbers, i.e. O1 to O4, S1 to S4 etc). This ligand is in addition disordered with another set of two moieties, rotated by around 60 degrees with regard to the first two sets. The atoms of both sets are thus half occupied plus additionally split by an occupancy ratio, but the four moieties together represent one fully occupied ligand. The other ligand (made up of O5 to O8, S5 to S8 etc) is located nearly exactly on a center of symmetry but is in addition intersecting with another ligand of the same kind and the atoms are thus only one quarter occupied. The intersecting happens at the S-substituted

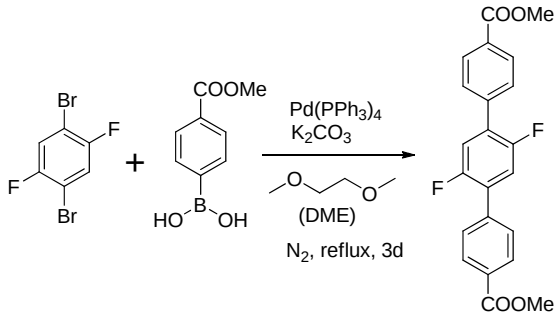
central ring. For the major moiety of the first ligand and for the second ligand the S and methyl groups are again 1:1 disordered and have half the occupancy of the ligand they are bonded to.

The ratio of Eu to ligand is 1:1.5, which is also consistent with results of elemental analysis, i.e., EDX measurement indicated no Cl present in the sample (see Figure S6 below); chemical analysis of the product $Eu(C_{22}H_{16}O_4S_2)_{1.5}(H_2O)_{0.5}$ yielded the following: calcd [C (51.23%), H (3.26%), S (12.43%)], found [C (51.29%), H (3.54%), S (12.04%)].

Due to the severe disorder and the large thermal movement of the ligands a range of restraints and constraints was applied in order to obtain a stable and chemically meaningful model: all aromatic rings were constrained to resemble ideal hexagons with C-C distances of 1.39 Ångstrom; all other equivalent C-C, all C-O and C (phenyl)-S distances were each restrained to be similar. S-C (methyl) distances were restrained to be 1.75(2) Ångstrom. S···S distances of neighboring S atoms were restrained to be similar. O···O distances in symmetry related carboxylate units were restrained to be similar. Distances of methyl carbon atoms to next phenyl carbon atoms were restrained to be not less than 2.80(2) Ångstrom. All atoms expected to lie in a plane of an aromatic ring were restrained to reside within this plane and carboxylate units were restrained to be planar. C-C distances between phenyl rings were restrained to be 1.50(2) Ångstrom. All C and O atoms were restrained to have ADPs similar to those of their neighbors, and all C, S and O atoms to be isotropic within a standard deviation of 0.05 Angstroms squared. The ADPs of the following atoms were constrained to be each identical: O2 and O4; S5, S6, S7 and S8; S1, S2, S3 and S4.

All non-metal atoms were subjected to a rigid bond restraint (RIGU) and to be approximately isotropic (ISOR), and Uij components of ADPs of C and O atoms (but not S atoms) were restrained to be similar if closer than 1.7 Ångstroms (SIMU). H atoms were set as riding. Where not possible due to disorder and limits of the program Shelxl to handle disorder within disorder the riding was simulated using appropriate distance restraints. Standard deviations for restraints used are SHELXL default values where not mentioned otherwise. Subject to these conditions the occupancies obtained were as follows: 0.3680 (10) for the major moiety of the first ligand (O1 to O4, S1 to S4 etc), 0.1320 (10) for the minor moiety of the same ligand. 0.1950 (14) and 0.173 (14) for the additional SMe to H disorder of the major moiety.

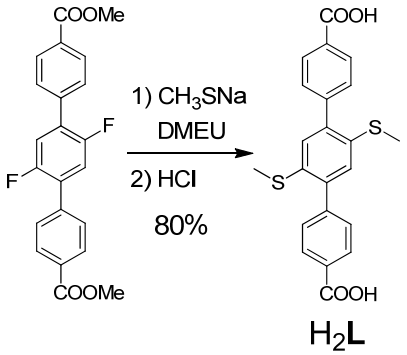
In compound **2**-Eu, 35% of the unit cell volume consists of solvate filled voids. No meaningful solvate model could be developed for these regions and the electron density therein was instead corrected for with back Fourier transform methods using the SQUEEZE procedure implemented in the program Platon. Squeeze corrected for 331.9 electrons within a volume of 796.6 cubic Ångstrom. Due to the small crystal size and the diffraction power of the crystals the data quality is quite low and all C and O atoms were subjected to a rigid bond restraint (RIGU in Shelxl).



S1

Synthesis of 2',5'-difluorine-[1,1':4',1''-terphenyl]-4,4''-dimethyl ester (S1). A two-neck round-bottomed flask (250 mL) was loaded with a magnetic stirring bar, powders of 1,4-dibromo-2,5-difluoro-benzene (1.36 g, 5.00 mmol), 4-methoxycarbonylphenylboronic acid (2.16 g, 12.00 mmol, 2.4 equiv), potassium carbonate (4.15g, 30.00 mmol, 6 equiv), and tetrakis (triphenyl phosphine) palladium (0.14 g, 0.12 mmol), which was then evacuated and refilled with N_2 thrice. Ethylene glycol dimethyl ether (DME, 80 mL) was degassed and injected *via* cannula under N_2 into the flask. The flask was then connected to a condenser and the mixture was heated to reflux of the solvent for 72 h under N_2 protection. After the reaction mixture was cooled to room temperature, the solvent was removed with a rotary evaporator and the residue was washed with a large amount of water (200 mL). The residue was further purified by column chromatography (silica gel, with CH_2Cl_2 as the eluent) to give a white solid (**S1**, 1.47 g, 77% yield based on 1,4-dibromo-2,5-difluoro-benzene). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.04-8.06 (d, 4H, CHAr), 7.60-7.62 (d, 4H, CHAr), 7.24-7.28 (t, 2H, CHAr), 3.85 (s, 6H, CH_3). FT-IR (KBr pellet, ν/cm^{-1}): 3055 (w), 2952 (m), 1720 (s), 1610 (s), 1491 (s), 1436 (s), 1436 (m), 1395 (s), 1286 (s), 1192 (m), 1170 (s), 1114 (s), 1014 (s), 907 (m), 854 (s), 795 (s), 769 (s), 706 (s), 465

(m). Chemical analysis of the product (**S1**) yielded the following: Calcd [C (69.11%), H (4.22%)]; Found [C (69.08%), H (4.38%)].



Synthesis of 2',5'-dimethylthio-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid (H_2**L).** In a nitrogen-filled glovebox, sodium thiomethoxide (0.35 g, 5.00 mmol) was loaded into a 50-mL two-neck flask equipped with a septum and a magnetic stirring bar. After the flask was taken out of the glovebox, DMEU (1,3-dimethyl-2-imidazolidinone, 8 mL) was injected *via* cannula under N_2. When the sodium thiomethoxide was completely dissolved in DMEU, **S1** (0.38 g, 1.00 mmol) was added. The reaction mixture was then stirred and heated at 90 ^oC under N_2 protection. After 2 days, the reaction mixture was poured into 100 mL of water, and HCl (10%) was added slowly with vigorous stirring. After the pH was reduced to below 2, the resultant yellowish solid product was isolated by suction filtration [0.33 g, 80% based on **S1**]. The solid product thus obtained was pure and was used for crystal growth without further purification. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.07 (s, 2H, COOH), 8.02-8.04 (d, 4H, CHAr), 7.59-7.61 (d, 4H, CHAr), 7.18 (s, 2H, CHAr), 2.39 (s, 6H, SCH_3). ^{13}C NMR (DMSO-d_6, 100MHz): δ 167.75, 144.24, 139.86, 133.66, 130.54, 129.91, 129.69, 127.27, 15.80. FT-IR (KBr pellet, ν/cm^{-1}): 3448 (w), 2917 (m), 2665 (m), 2545 (m), 1682 (s), 1607 (m), 1565 (w), 1423 (m), 1319 (m), 1287 (s), 1180 (w), 1114 (w), 1014 (m), 855 (w), 755 (w), 706 (w), 550 (w). Chemical analysis of the product (H_2**L**) yielded the following: Calcd [C (64.37%), H (4.42%), S (15.62%)]; Found [C (64.08%), H (4.28%), S (15.35%)].

Crystal growth

Preparation of single crystals of 1. H_2**L** (8.2 mg, 20.0 μmol) and $EuCl_3 \cdot 6H_2O$ (20.0 mg, 54.0 μmol) were loaded into a heavy-wall glass tube (10 mm OD, 6 mm ID), and then a solution of

water and acetonitrile (2.0 mL, 1:1, v/v) was added. The tube was then flame-sealed and heated at 140 °C in a programmable oven for 48 hours, followed by slow cooling (0.1 °C/min) to room temperature, during which single crystals suitable for single-crystal X-ray diffraction were formed (7.5 mg, yield 65% based on H_2**L**). Chemical analysis of the product $Eu(C_{22}H_{16}O_4S_2)_{1.5}(H_2O)_{0.5}$ yielded the following: calcd [C (51.23%), H (3.26%), S (12.43%)], found [C (51.29%), H (3.54%), S (12.04%)]. FT-IR (KBr pellet, ν/cm^{-1}): 3442 (w), 2916 (w), 1610 (s), 1582 (s), 1536 (s), 1407 (w), 1371 (m), 1176 (w), 1139 (m), 1102 (w), 1031 (w), 1011 (m), 950 (w), 857 (m), 780 (m), 737 (m), 710 (m), 601 (w), 521 (w), 454 (w). X-ray powder diffraction of the bulk sample indicated a pure phase consistent with the single-crystal structure (see Figure S8). EDX elemental analysis indicates that no chlorine was present in the sample (see Figure S6 below).

Preparation of single crystals of 2-Eu. H_2**L** (8.2 mg, 20.0 μmol), $EuCl_3·6H_2O$ (20.0 mg, 54.0 μmol) and CuI (16.0 mg, 84.0 μmol) were loaded into a heavy-wall glass tube (10 mm OD, 6 mm ID), and then a solution of water and acetonitrile (2.0 mL, 1:1, v/v) was added. The tube was then flame-sealed and heated at 120 °C in a programmable oven for 48 hours, followed by slow cooling (0.1 °C/min) to room temperature, during which single crystals suitable for single-crystal X-ray diffraction were formed (6.8 mg, yield 53% based on H_2**L**). Chemical analysis of the product $Eu(C_{22}H_{16}O_4S_2)_{1.5}(CuI)(H_2O)_6$ yielded the following: calcd [C (41.50%), H (2.53%), S (10.07%)], found [C (41.37%), H (2.75%), S (10.42%)]. IR (ν/cm^{-1}): 3447 (w), 3063 (w), 2908 (w), 2202 (w), 1633 (s), 1601 (s), 1583 (s), 1536 (m), 1495 (m), 1419 (s), 1372 (s), 1294 (w), 1265 (s), 1228 (m), 1137 (w), 1098 (m), 1084 (w), 1013 (w), 818 (m), 781 (m), 745(w), 651 (w), 525 (w). X-ray powder diffraction of the bulk sample indicated a pure phase consistent with the single-crystal structure. An isoreticular structure with **2**-Eu could also be obtained by using $TbCl_3$ instead of $EuCl_3$ as the metal source under similar reaction conditions as above, affording the crystalline samples of **2**-Tb, which was also confirmed by PXRD.

Preparation of the white-light-emitting sample 2-Eu/Tb. H_2**L** (8.2 mg, 20.0 μmol), $TbCl_3·6H_2O$ (20.0 mg, 54.0 μmol), $EuCl_3·6H_2O$ (1.0 mg, 3.0 μmol), and CuI (16.0 mg, 84.0 μmol) were loaded into a heavy-wall glass tube (10mm OD, 6mm ID), and then a solution of water and acetonitrile (2.0 mL, 1:1, v/v) was added. The tube was then flame-sealed and heated at 120 °C in a programmable oven for 48 hours, followed by slow cooling (0.1 °C/min) to room

temperature, during which single crystals were formed (7.0 mg, yield ca. 50% based on H_2**L**). IR (ν/cm^{-1}): 3396 (s), 2919 (w), 1607 (s), 1584 (s), 1535 (s), 1411 (s), 1185 (w), 1104 (w), 1032 (w), 1013 (m), 970 (w), 864 (w), 788 (s), 727 (w), 710 (w), 597 (w), 552 (w), 521 (w). X-ray powder diffraction of the bulk sample indicated the framework was consistent with the single-crystal structure of **2**-Eu. The ratio between Tb^{3+} and Eu^{3+} for the sample was determined by ICP and EDX, which revealed that 9.5% of the Tb^{3+} centers have been replaced by Eu^{3+} centers.

Fabrication of Light-emitting LED. By a simple and efficient dip coating procedure, a thin film of **2**-Eu/Tb (or **2**-Eu, **2**-Tb) can be easily applied onto a commercially available UV-LED lamp, and thus accomplish the conversion into a new LED. Specifically, an as-made crystalline sample (about 5 mg) was loaded into an agate mortar and manually ground with the pestle for 20 min to afford a fine powder. Ethanol (1.0 mL, ABS) was then added to the mortar. Further grinding (for about 1 min) was applied until a significant portion of the alcohol has evaporated and a homogeneous slurry was achieved. A commercial 360 nm UV-LED lamp (Le Group Fox, Inc.) was then dipped into the slurry, held therein for several seconds, and then taken out for the coating to dry in air. This dip coating process can be repeated to further ensure an even and continuous coating on the lens/housing of the LED.

Treatment of 2-Eu **by H_2S gas.** Upon exposure to H_2S gas at room temperature for 1 h, the colorless crystals of **2**-Eu become black (see Figure S4 for details). Chemical analysis of the product $Eu_2(C_{22}H_{16}O_4S_2)_3(CuI)_2(H_2O)_{14}(H_2S)_2$ yielded the following: calcd [C (35.54%), H (3.61%), S (11.50%)], found [C (35.07%), H (3.97%), S (11.22%)].

Detection of H_2S. A **2**-Eu crystal sample (1 mg) was evenly divided into four 15-mL vials. Into each of vials was then added 10 mL of each of the following NaSH solutions: 0 ppm, 1 ppm, 2 ppm, 20 ppm. The resultant mixtures inside were heated at 80 °C for 2 hours.

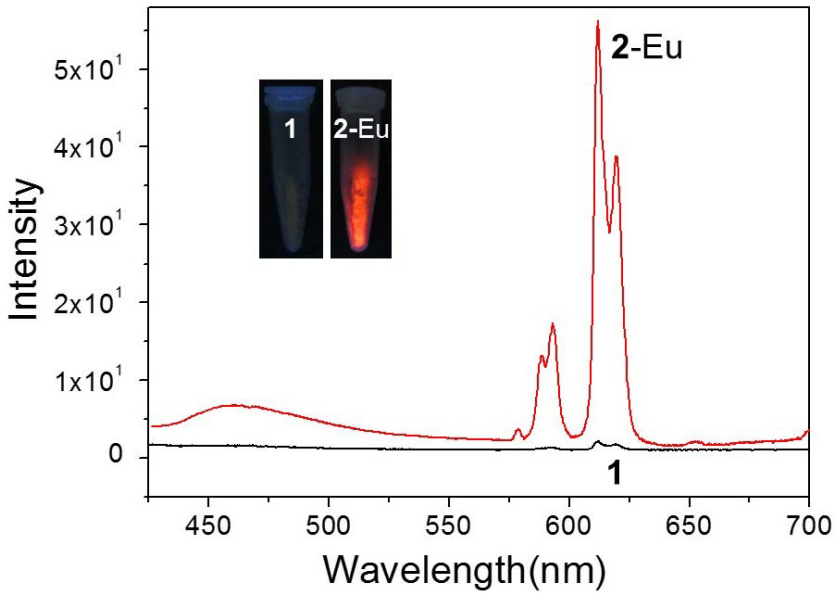


Figure S1. Room-temperature solid-state emission spectra from (black) a crystalline sample of **1**, (red) a crystalline sample of **2**-Eu. The inset shows photographs of the samples of **1** and **2**-Eu.

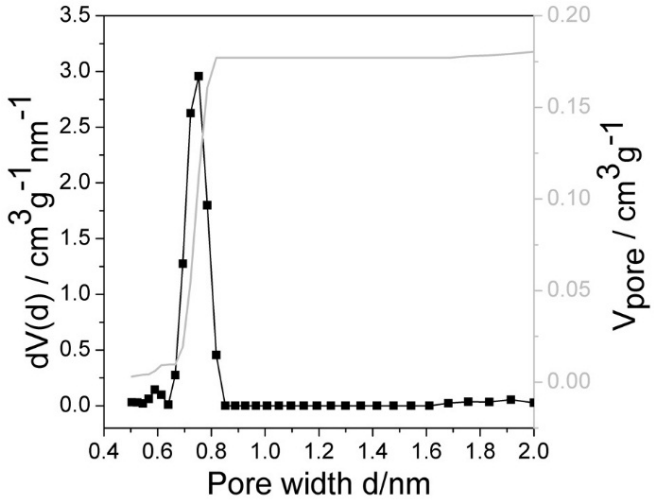


Figure S2. Pore size distribution and pore volume of **2**-Eu (N_2 gas at 77 K; DFT model).

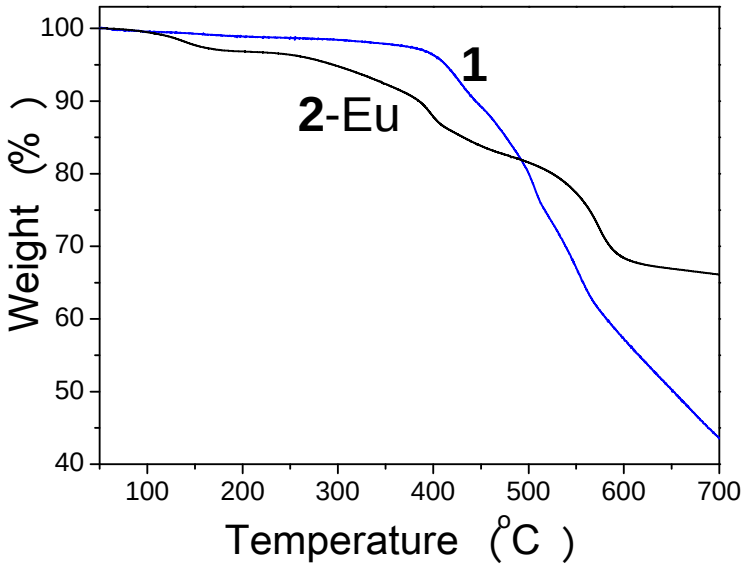


Figure S3. Thermogravimetric analysis (TGA) plots of **1** (blue line) and **2**-Eu (black line).

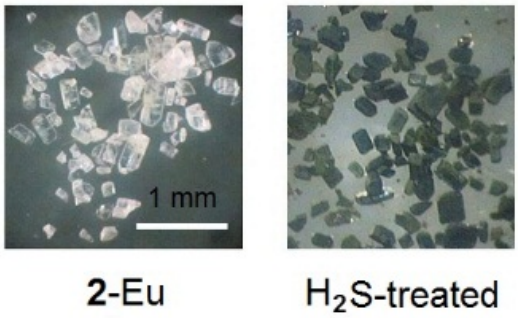


Figure S4. Photographs of (left) as-made single crystals of **2**-Eu; (right) sample from (a) after treatment in H_2S gas for 1 hour.

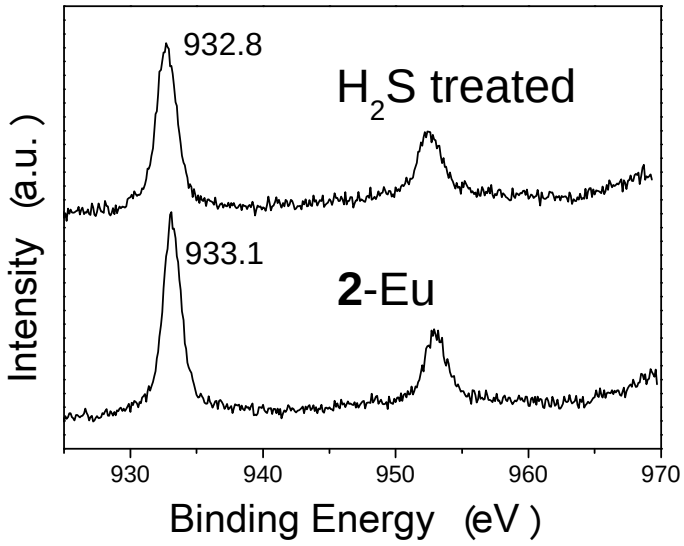


Figure S5 XPS (X-ray photoelectron spectroscopy) spectra for solid samples of **2**-Eu and after H_2S treatment. The peaks around 933 and 952 eV correspond to the states of $2P_{3/2}$ and $2P_{1/2}$ of the Cu atoms respectively.

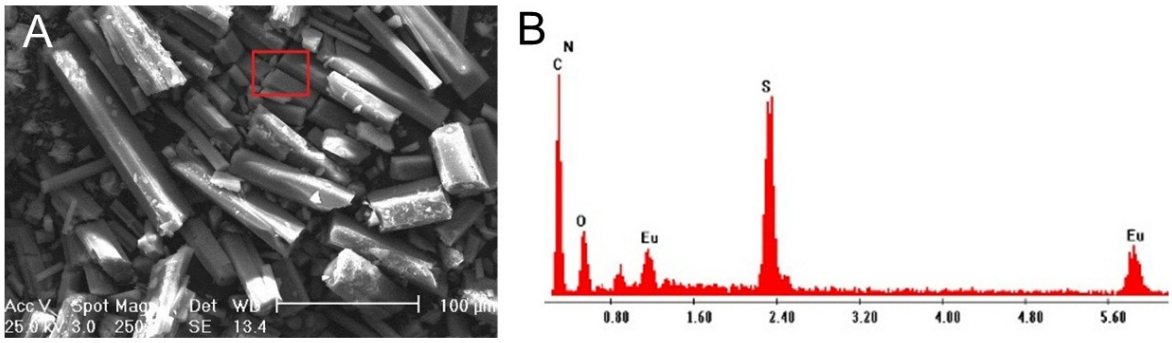


Figure S6 SEM image (A) and the corresponding energy-dispersive X-ray (EDX) spectrum (B) of as-synthesized compound **1**.

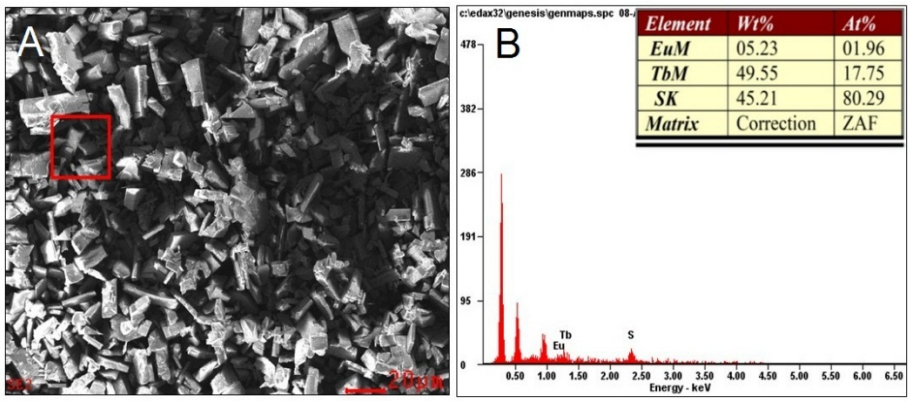


Figure S7 The SEM image (A) and the corresponding energy-dispersive X-ray (EDX) spectrum (B) of as-synthesized compound **2**-Eu/Tb.

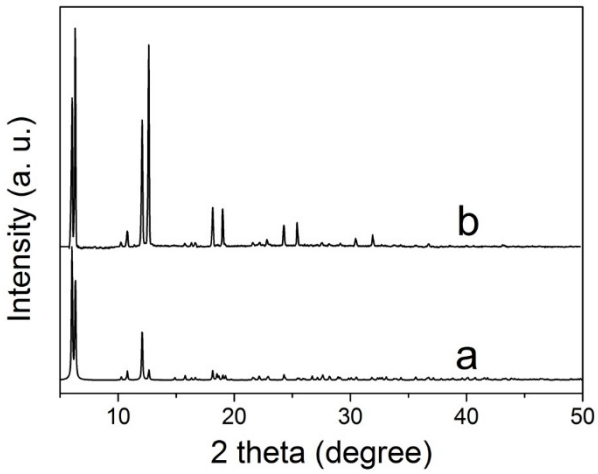


Figure S8. X-ray diffraction patterns (Cu Kα, λ = 1.5418 Å) of **1**: (a) calculated from the single-crystal structure at 100K; (b) observed for a powder solid sample at room temperature.

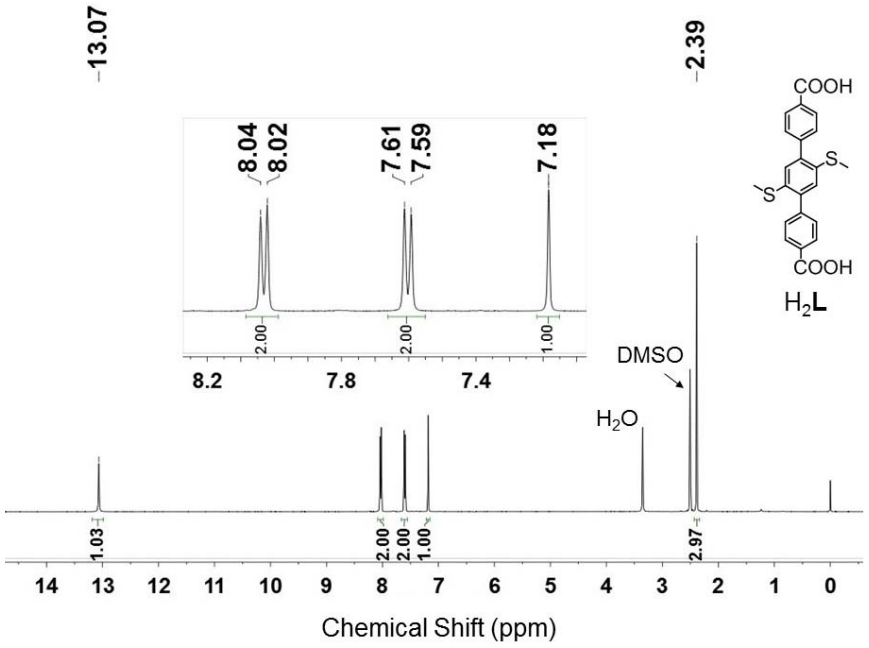


Figure S9. The ^{1}H NMR spectrum of H_2**L** in DMSO-d_6.

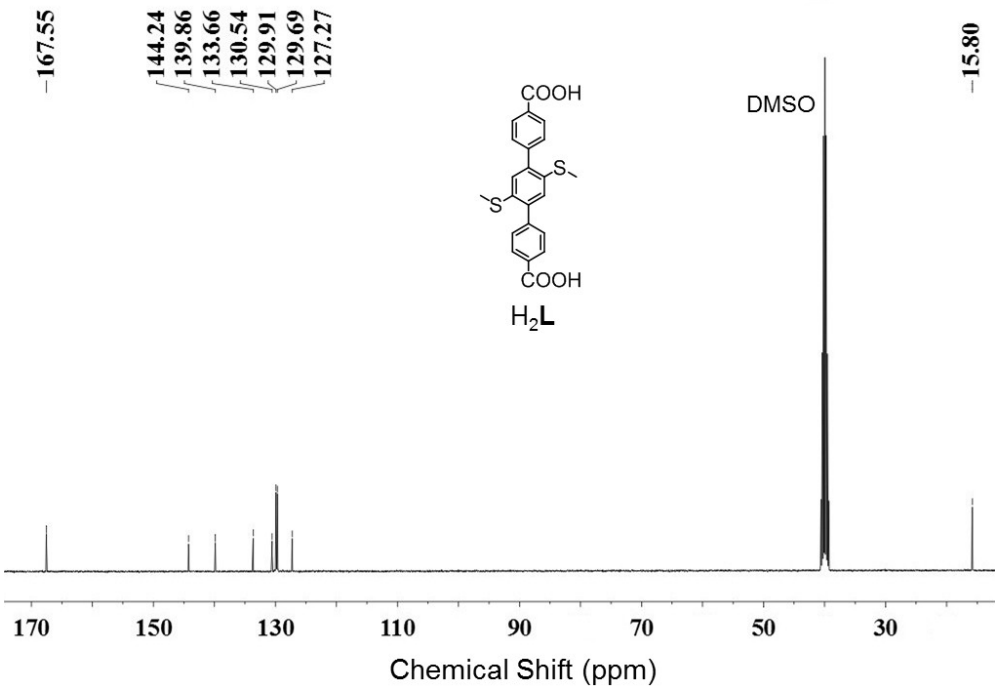


Figure S10. The ^{13}C NMR spectrum of H_2**L** in DMSO-d_6.