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Janus Triple Tripods Build up a Microporous Manifold for $HgCl_2$ and I_2 Uptake

Yonghe He,[a‡] Mengjiao Huang,[a‡] Xiangling Deng,[a] Shengxian Cheng,[c] Yan-Lung Wong,[c] Yun-Long Hou,[c] Matthias Zeller,[b] Jun He*[a] and Zhengtao Xu*[c]

[a] School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, Guangdong, China

[b] Department of Chemistry, Purdue University, 610 Purdue Mall, West Lafayette, Indiana 47907, United States.

[c] Department of Biology and Chemistry, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong, China.

* Corresponding author.

E-mail: junhe@gdut.edu.cn, zhengtao@cityu.edu.hk

‡These authors contributed equally.

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Experimental details

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. Nuclear magnetic resonance (NMR) spectra were recorded at 298 K on a 400 MHz Bruker superconducting magnet high-field NMR spectrometer, with working frequencies of 400 MHz for ^{1}H and 100 MHz for ^{13}C nuclei. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents, with tetramethylsilane (TMS) as the internal standard. 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 Hg^{2+}) were determined by using a PerkinElmer Optima™ 2100 DV ICP optical emission spectrometer.

Powder X-ray diffraction data were collected in the reflection mode at room temperature on an Inel Equinox 1000 X-ray diffractometer (Inel, France) equipped with 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. The Raman spectra were recorded at room temperature on a HORIBA Jobin Yvon Labram HR 800 Raman spectrometer with a 632.8 nm red laser in the range of 50～3500 cm^{-1}. The beam was focused on the sample through a confocal microscope using a 50 × objective lens.

Single crystal structure refinement details

Data for **GDUT-7** were collected using Bruker ApexII CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å. The instrument features a fine focus sealed tube X-ray source with graphite monochromator. Data for **GDUT-7-HgCl₂** were collected using Cu-Kα radiation (λ = 1.54178 Å) on a Bruker Quest diffractometer with kappa geometry, an I-μ-S microsource X-ray tube, laterally graded multilayer (Goebel) mirror single crystal for monochromatization, a Photon2 CMOS area detector. Both instruments are equipped with an Oxford Cryosystems low temperature device. Single crystals were mounted on Mitegen micromesh mounts using a trace of mineral oil and cooled in-situ to 100(2) K or 150(2) K for data collection. Data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX2 or Apex3 [1]. The space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs [2] and refined by full matrix least squares against F^2 with all reflections using Shelxl2018 [3] using the graphical interface Shelxle [4]. If not specified otherwise H atoms attached to carbon atoms were positioned geometrically and constrained to ride on their parent atoms. C-H bond distances were constrained to 0.95 Å for aromatic and alkene C-H moieties, and to 0.98 Å for aliphatic CH_3 moieties, respectively. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. Water H atom positions were refined and O-H distances were restrained to 0.84(2) Å. Where necessary, water H···H distances were restrained to 1.36(2) Å, and H atom positions were further restrained based on hydrogen bonding considerations. $U_{iso}(H)$ values were set to a multiple of $U_{eq}(C)$ with 1.5 for CH_3 and OH, and 1.2 for C-H units, respectively.

Additional data collection and refinement details, including description of disorder is given below for both structures. Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1888673 and 1888674 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

GDUT-7. A methyl thioether unit is disordered by rotation of the methyl group. The geometries of the two units were restrained to be similar to that of another not disordered thioether group. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.430(8) to 0.570(8).

A DMF molecule is disordered around a twofold axis. Two DMF molecules and a water molecule are disordered in general positions with a common occupancy ratio for the DMF molecules and one water molecule. The first moiety water molecule was found to be only partially occupied and its occupancy rate was refined independently. The disordered moieties were restrained to have a similar geometry as another not disordered Eu-coordinated DMF molecule. The O···N distances in the DMF molecules were restrained to be similar, and the DMF molecule of O9B was restrained to be close to planar. Water H atom positions were refined and O-H and H···H distances were restrained to 0.84(2) and 1.36(2) Å, respectively. Some water H atom positions were further restrained based on hydrogen bonding considerations. In the final refinement cycles some water H atoms were set to ride on their carrier atoms. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. A mild anti-bumping restraint was applied to keep minor moiety fragments from approaching the main framework too closely. Subject to these conditions the main occupancy ratio refined to 0.504(6) to 0.496(6). The occupancy of the partially occupied water molecule (of O13) refined to 0.295(13).

GDUT-7-HgCl$_2$. The structure is mostly isomorphous to **GDUT-7** and has been refined on a model based on that of **GDUT-7.**

A methyl thioether unit is disordered by rotation of the methyl group. The geometries of the two units were restrained to be similar to that of another not disordered thioether group. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.627(12) to 0.373(12).

Voids between the MOF-framework are occupied by $HgCl_2$ fragments and by ethanol molecules that are disordered with each other. The highest occupied $HgCl_2$ unit (Hg1, Cl1, Cl2) is found nearby sulfur atom S3 (ca. 3.1 Å Hg...S distance). This $HgCl_2$ unit is close to linear (159.7(3) degree angle) and close to symmetric (Hg-Cl distances are 2.267(5) and 2.266(6)). It was refined as disordered with three ethanol moieties (all weakly H bonded to nitrogen atom N3), and with another much less occupied $HgCl_2$ fragment. The second most prevalent $HgCl_2$ unit (Hg2, Cl3, Cl4) is disordered around a twofold axis and shares a site with an ethanol molecule that is also disordered around the twofold axis. Its geometry features a close to 90 degree angle (90.6(9)), and Hg-Cl distances differ (2.76(3) and 2.27(2)), but these values are unreliable to its low occupancy and the disorder. The least occupied $HgCl_2$ unit that is resolved is in proximity to an Eu-coordinated ethanol oxygen atom (O8...Hg3 = 2.66 Å). The Hg atom shares a site with an oxygen atom of a more prevalent solvate ethanol molecule. It's geometry also features a close to 90 degree angle but these values are unreliable to its low occupancy, the disorder and restraints applied (see below).

All ethanol molecules were restrained to have similar geometries (including the not disordered Eu-coordinated molecule). The close to linear $HgCl_2$ units (Hg1, Hg1B) were restrained to have similar geometries and Hg-Cl bond distances were restrained to be similar. ADPs of Hg1B, Cl1B and Cl2B were constrained to be identical. The angled $HgCl_2$ units were restrained to have similar geometries to each other. U^{ij} components of ADPs of all disordered ethanol and $HgCl_2$ units closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy rates of the $HgCl_2$ units refined to 0.2900(14) (Hg1), 0.0308(10) (Hg1B), 2 times 0.0873(13) (two copies of Hg2 around the twofold axis) and 0.0312(15) (Hg3). Occupancy ratios of disordered ethanol molecules refined to values between 0.674(7) (disordered with Hg3), two times 0.316(9) (two molecules disordered around two fold axis and disordered with Hg2) and 0.172(9) (the least occupied one of the three ethanol molecules disordered with Hg1).

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2) a) SHELXTL suite of programs, Version 6.14, 2000-2003, Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin: USA b) Sheldrick, G.M. (2008). Acta Cryst., A64, 112-122.

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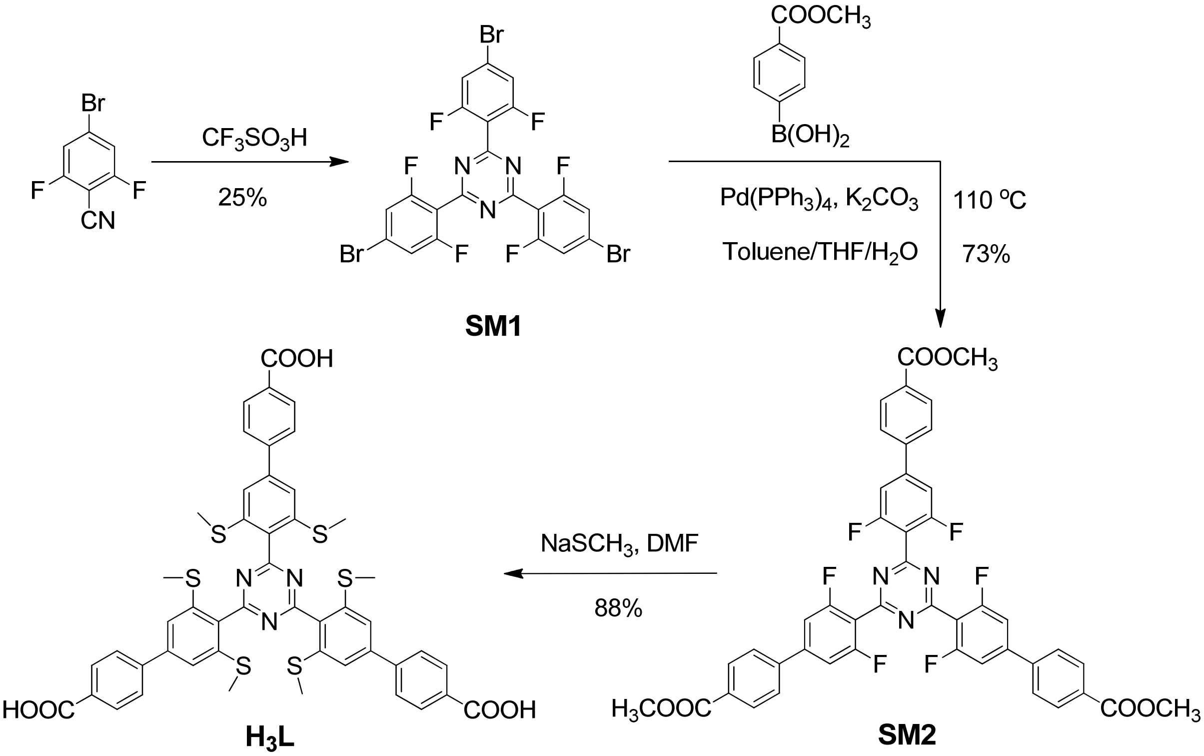

Fig. S1 The synthetic procedure for H_3**L**.

Synthesis of 2, 4, 6-tris (4-bromo-2, 6-difluorophenyl)-1, 3, 5-triazine (SM1).

To a two-neck round-bottomed flask (25 mL) loaded with a powder of 4-bromo-2,6-difluorobenzonitrile (5.0 g, 22.9 mmol) and a magnetic stirring bar, trifluoromethanesulfonic acid (5.0 g, 33.3 mmol) was added carefully under vigorous stirring. The reaction mixture was stirred at rt for 72 h, was then poured into 30 mL of water. The precipitate that immediately formed was collected by suction filtration and washed with water extensively. The precipitated solid was further purified by column chromatography (silica gel, with petroleum ether and ethyl acetate (20:1, V:V) as the eluent) to give a white solid (**SM1**, 1.25g, yield 25% based on 4-bromo-2,6-difluorobenzonitrile. ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.29 (d, *J* = 7.3 Hz, 6H).^{19}F NMR (400 MHz, CD_2Cl_2) δ = -111.19 (d, *J* = 7.5 Hz).^{13}C NMR (100 MHz, CD_2Cl_2) δ = 167.92, 162.29-159.63, 125.75-125.50, 116.69-116.40, 114.31. FT-IR (KBr pellet, ν/cm^{-1}): 3428 (w), 3083 (w), 3065 (w) ,1619 (s), 1571 (s), 1512 (s), 1419 (s), 1354 (s), 1291 (w), 1191 (m), 1149 (m), 1038 (s), 875(s), 848 (s),721 (w), 675 (s), 595 (w), 586 (m), 574 (m), 555 (m), 515 (m).

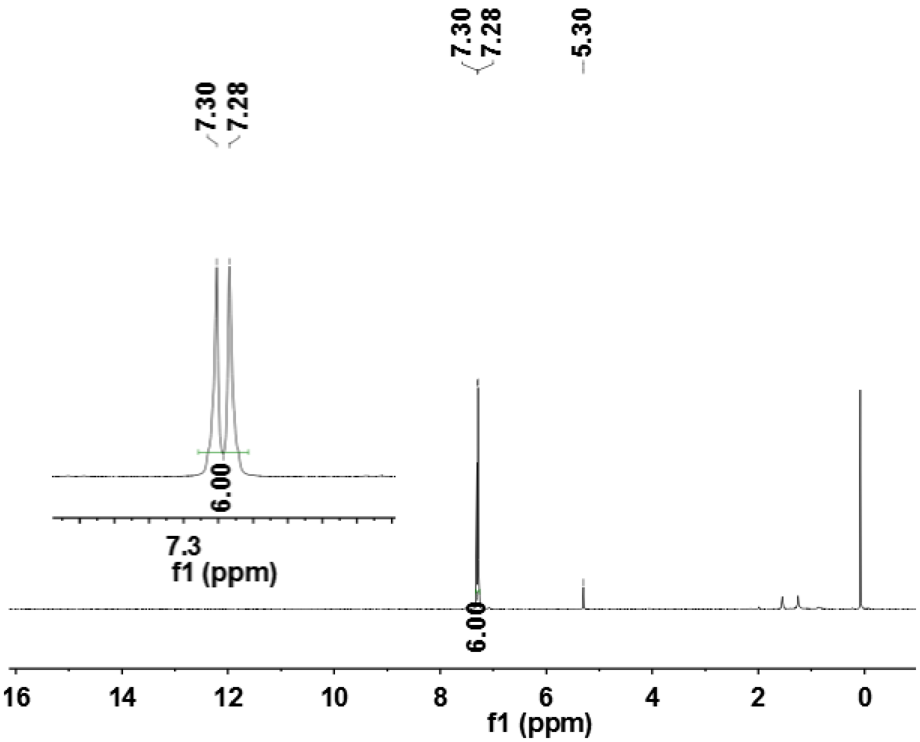

Fig. S2 The ^{1}H NMR spectrum of compound **SM1** in CD_2Cl_2.

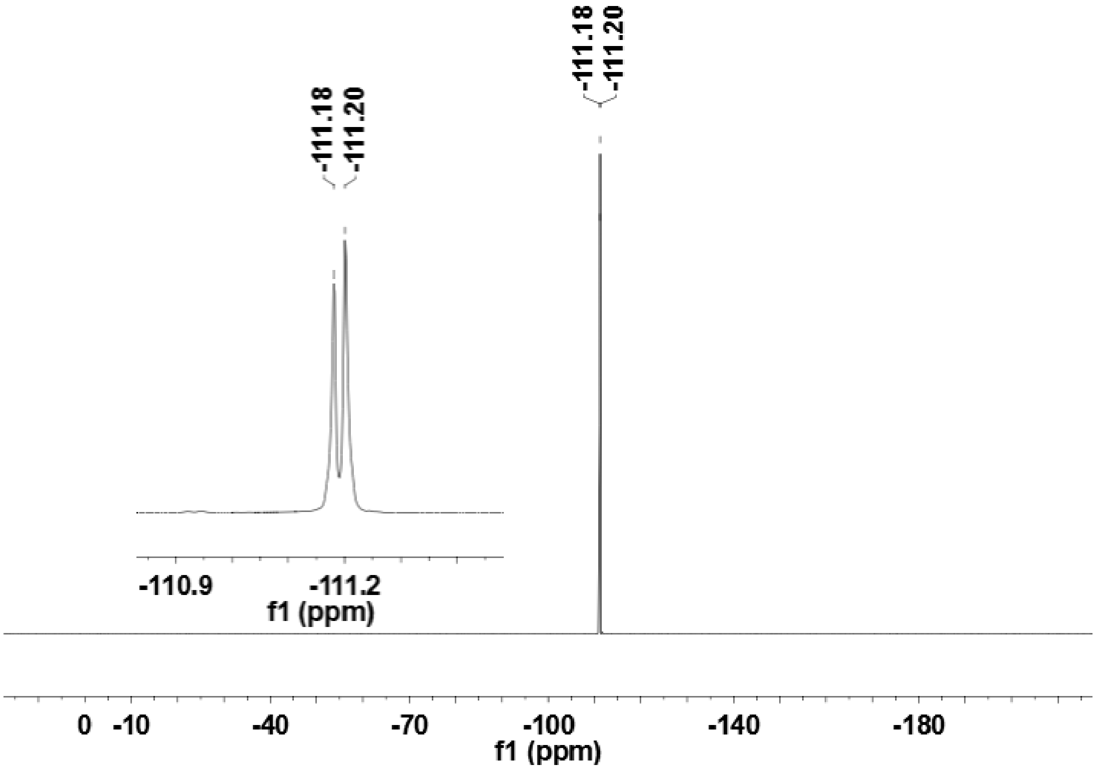

Fig. S3 The ^{19}F NMR spectrum of compound **SM1** in CD_2Cl_2.

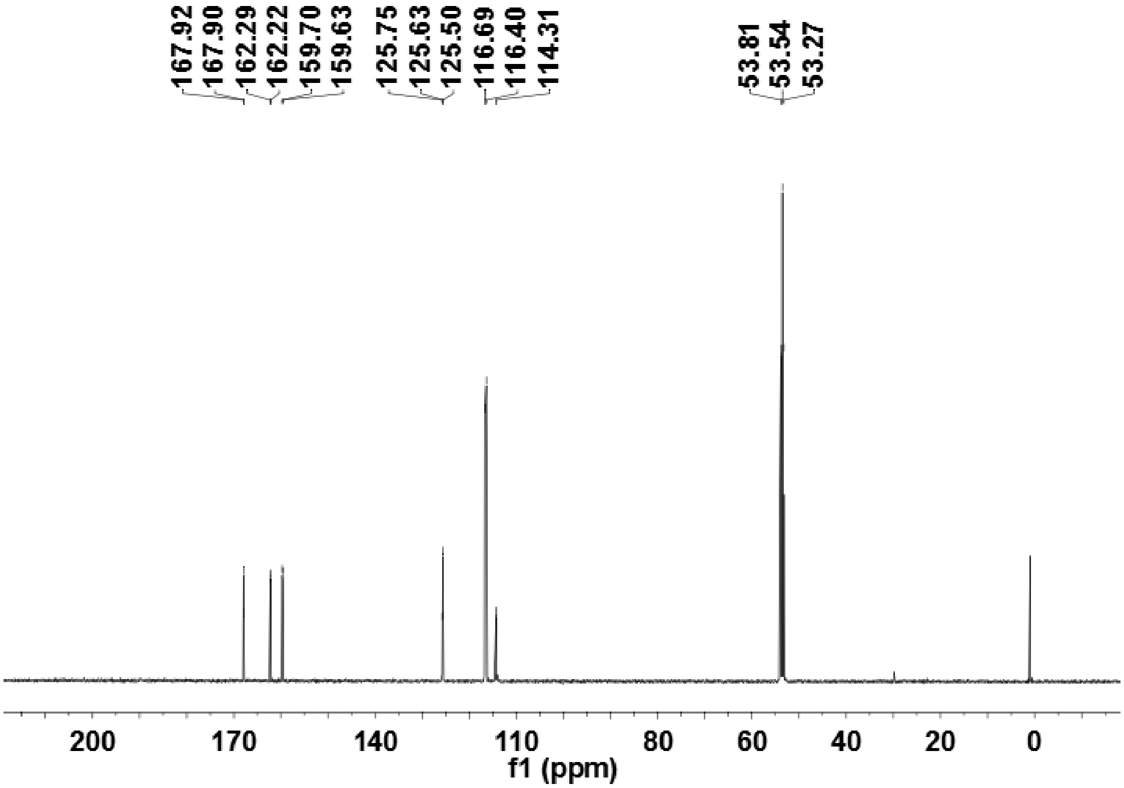

Fig. S4 The ^{13}C NMR spectrum of compound **SM1** in CD_2Cl_2.

Synthesis of trimethyl 4',4''',4'''''-(1,3,5-triazine-2,4,6-triyl)tris(3',5'-difluoro-[1,1'-biphenyl]-4-carboxylate) (SM2).

A two-neck round-bottomed flask (50 mL) was loaded with a magnetic stirring bar, powders of **SM1** (0.654 g, 1.0 mmol), 4-methoxyl carbonylphenyl boronic acid (1.080 g, 6.0 mmol), potassium carbonate (1.660 g, 12.0 mmol) and (triphenylphosphine) palladium (0.120 g, 0.1 mmol), and was then evacuated and refilled with N_2 thrice. Solvents of toluene, tetrahydrofuran (THF) and water (V:V:V = 1:1:1, 18 mL) were degassed and injected *via* cannula under N_2 into the flask. The flask was then connected to a condenser and the mixture was refluxed for 48 h under N_2 protection. After the reaction mixture was cooled to room temperature, the mixture was poured into water (50 mL) and extracted by ethyl acetate (3 × 50 mL). The combined organic layer was then washed with water (3 × 50 mL), dried over anhydrous $MgSO_4$, and the organic solvent was removed with a rotary evaporator. The residue was further purified by column chromatography (silica gel, with PE and EA as the eluent) to afford a white solid (**SM2**, 0.60 g, yield 73 % based on **SM1**). ^1H NMR (400 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 8.4 Hz, 6H), 7.69 (d, *J* = 8.4 Hz, 6H), 7.35 (d, *J* = 8.8 Hz, 6H), 3.95 (s，9H,). ^{19}F NMR (400 MHz, $CDCl_3$) δ = -111.36 (d, *J* = 8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.15, 166.25, 162.69-160.13, 145.17, 142.29, 130.65, 130.43, 127.08, 114.37, 111.19-110.94, 52.32. FT-IR (KBr pellet, ν/cm^{-1}): 3432 (w), 3071 (w), 2949 (w), 2919 (w), 2848 (w), 1718 (s), 1634 (s), 1584 (m), 1560 (s), 1510 (s), 1438 (s), 1397 (m), 1355 (s), 1280 (s), 1187 (m), 1108 (s), 1033 (s), 958 (w), 893 (m), 858 (s), 827 (m), 771 (s), 723 (w), 697 (w), 584 (w), 555 (m).

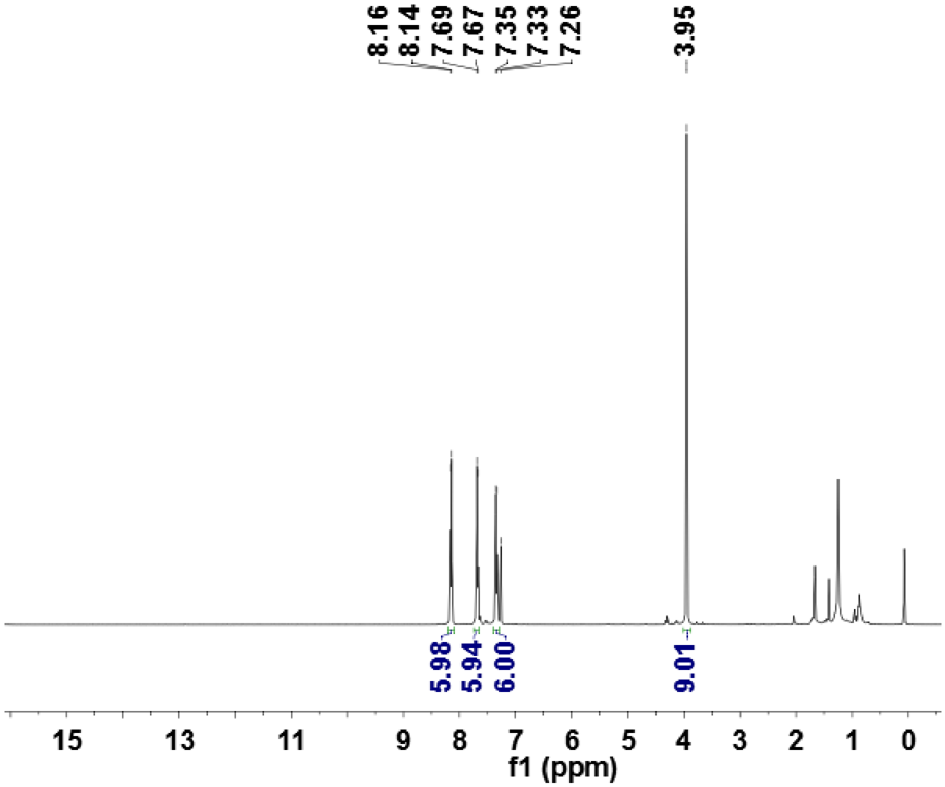

Fig. S5 The ^{1}H NMR spectrum of compound **SM2** in CDCl$_3$.

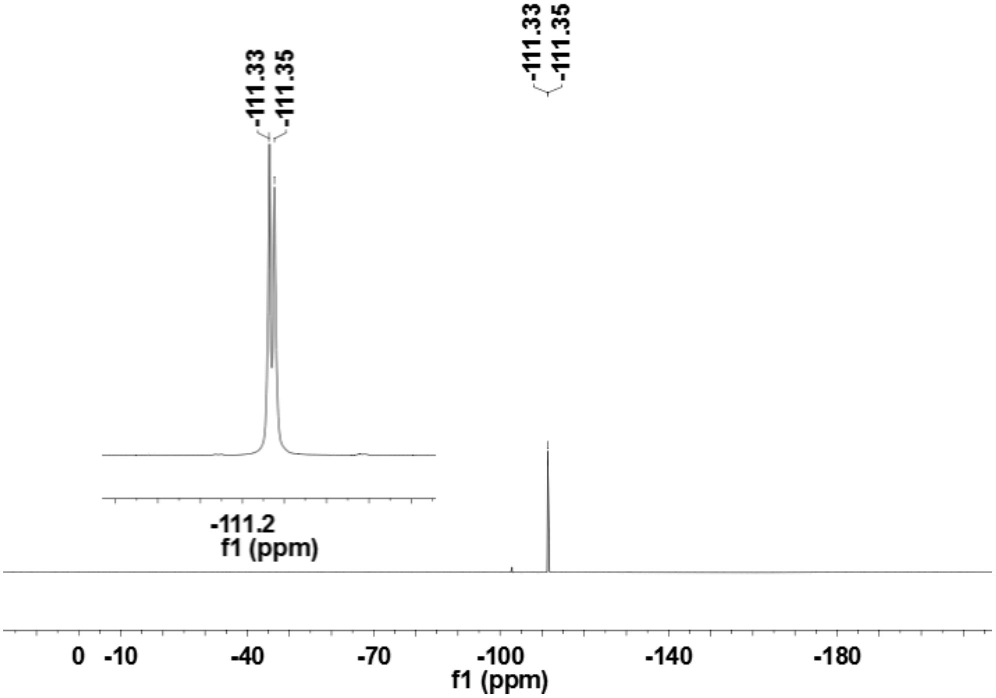

Fig. S6 The ^{19}F NMR spectrum of compound **SM2** in CDCl$_3$.

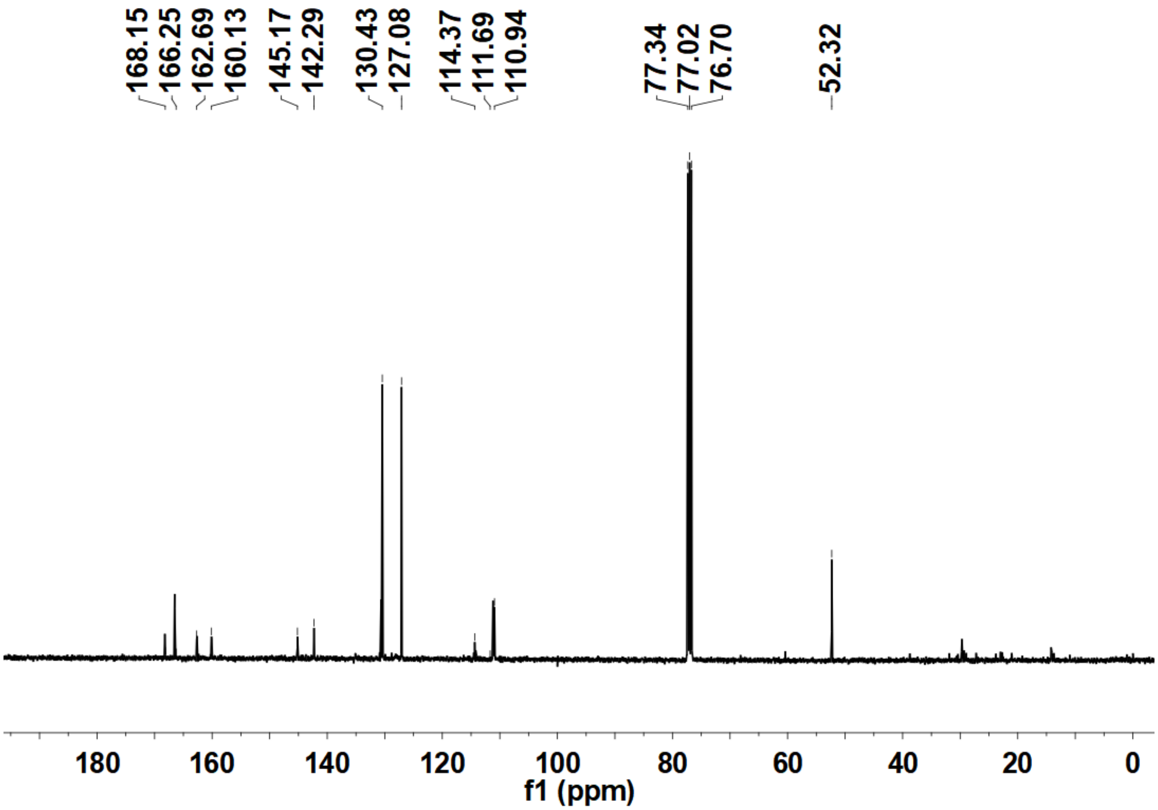

Fig. S7 The ^{13}C NMR spectrum of compound **SM2** in $CDCl_3$.

Synthesis of 4',4''',4'''''-(1,3,5-triazine-2,4,6-triyl)tris(3',5'-bis(methylthio)-[1,1'-biphenyl]-4-carboxylic acid) (H_3L).

Powders of **SM2** (0.327 g, 0.4 mmol) and CH_3SNa (0.420 g, 6.0 mmol) and a magnetic stir bar were loaded into a 25 mL two-neck round-bottom flask under N_2 protection. The flask was connected to a Schlenk line, and 10 mL degased DMF was then transferred into the flask via cannula. After being stirred at room temperature for 24 h, the mixture was poured into water (100 mL) and HCl (10%) 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. Yield: 0.333 g (88%, based on **SM2**). The product thus obtained was pure as indicated by NMR and was used for crystal growth without further purification. ^1H NMR (400 MHz, DMSO-d_6) δ = 13.08 (s, 3H), 8.05-8.07 (d, J = 8.3 Hz, 6H), 7.95-7.97 (d, J = 8.3 Hz, 6H), 7.55 (s, 6H), 2.53 (s， 18H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 173.76, 167.14, 143.37, 141.15, 139.16, 134.72, 130.36, 129.97, 127.49, 122.25, 16.40. FT-IR (KBr pellet, ν/cm^{-1}): 3428 (s), 3068 (w), 2985 (w), 2955 (w), 2919 (s), 2854 (w), 2642 (w), 2526 (w), 1687 (s), 1607 (s), 1577 (s), 1526 (s), 1506 (s), 1413 (s), 1381 (m), 131 (m), 1318 (m), 1259 (s), 1175 (m), 1160 (m), 1098 (m), 1012 (m), 968 (m), 846 (m), 806 (s), 770 (s) ,702 (w), 658 (w).

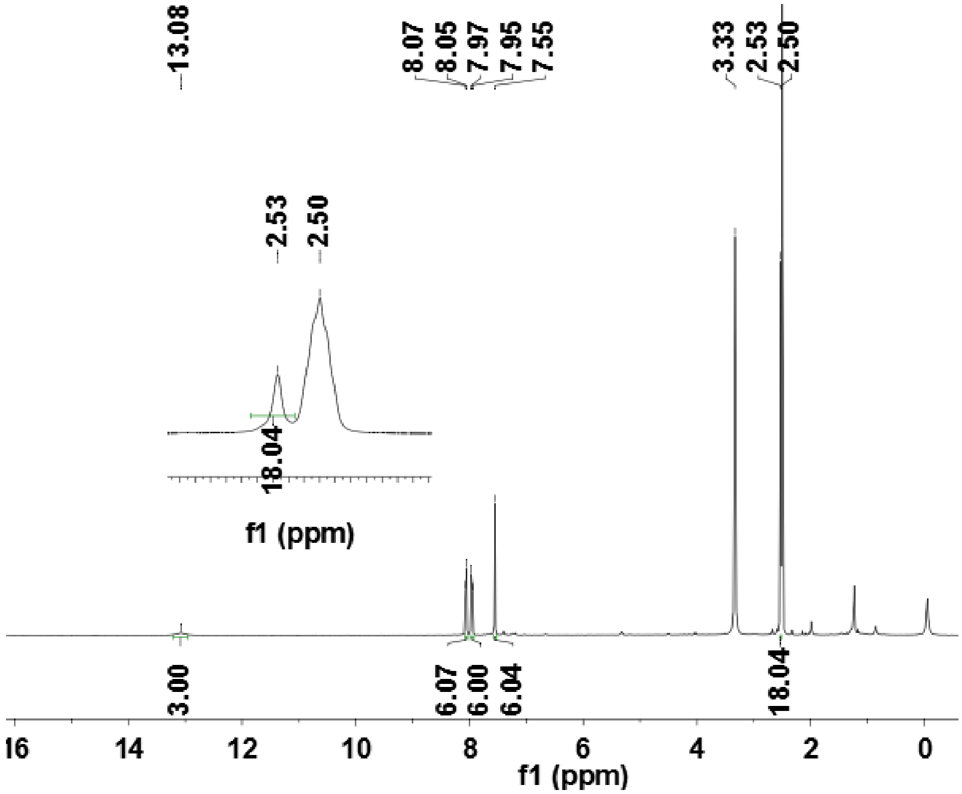

Fig. S8 The ^{1}H NMR spectrum of **H$_3$L** in DMSO-d_6.

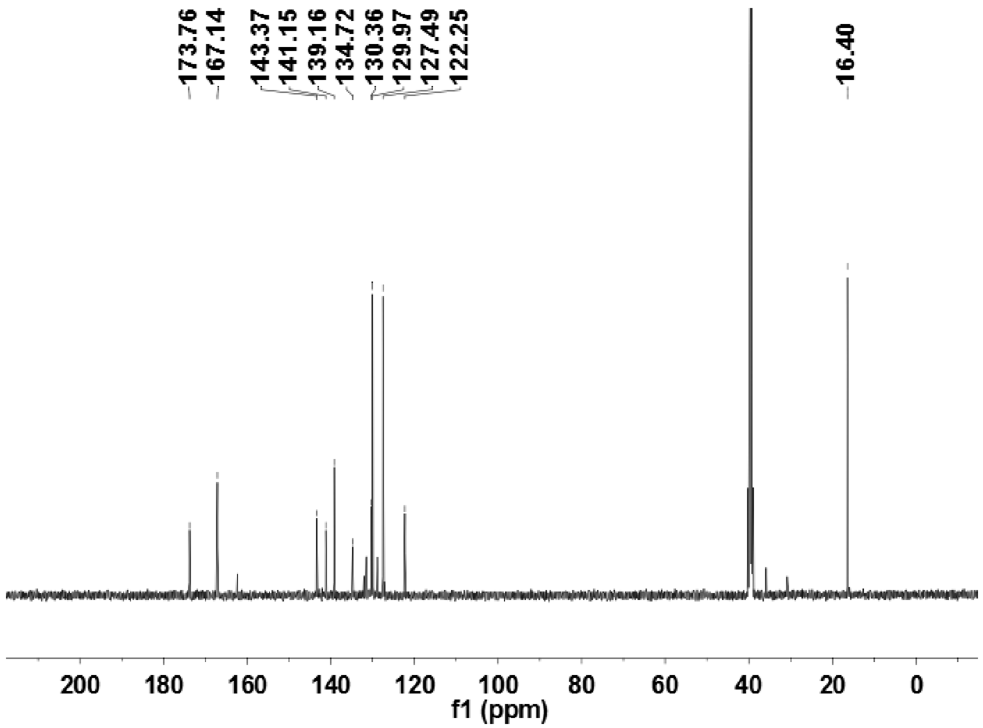

Fig. S9 The ^{13}C NMR spectrum of **H_3L** in DMSO-d_6.

Crystal growth

Preparation of single crystals of GDUT-7. H_3L (5.0 mg, 5.3 μmol) and $EuCl_3 \cdot 6H_2O$ (5.0 mg, 13.6 μmol) were loaded into a heavy-wall glass tube (10 mm OD, 6 mm ID), and then a solution of water and DMF (1.0 mL, 1:1, V/V) was added. The tube was flame-sealed and heated to 130 °C in a programmable oven for 72 h, followed by slow cooling (0.2 °C/min) to room temperature, during which single crystals suitable for single-crystal X-ray diffraction were formed (6.0 mg, yield 80% based on **H_3L**). FT-IR (KBr pellet, ν/cm^{-1}): 3404 (m), 2910 (m), 1604 (s), 1580 (s), 1532 (s), 1494 (s), 1401 (s), 1342 (s), 1160 (w), 1107 (w), 1009 (w), 964 (w), 845 (s), 780 (s), 699 (w), 673 (w). X-ray powder diffraction of the bulk sample indicated a pure phase consistent with the single-crystal structure. Elemental analysis found [C (49.60%), H (4.22%), N (6.25%)]; a fitting formula can be determined to be $Eu(C_{48}H_{36}N_3O_6S_6)_5 \cdot (C_3H_7NO)_{3.5} \cdot (H_2O)_4$ (mw 1423), which gives a calculated profile as [C (49.37%), H (4.85%), N (6.40%)]. The quantification of the C_3H_7NO (DMF) and the water guests are also supported by the ^{1}H NMR spectrum (see Fig. S10 and the TGA plot of Fig. S11). The ^{1}H NMR spectrum of a solution obtained from dissolving crystals of **GDUT-7** in DCl (38% in D_2O)/DMSO-d_6 (1:4, v:v).

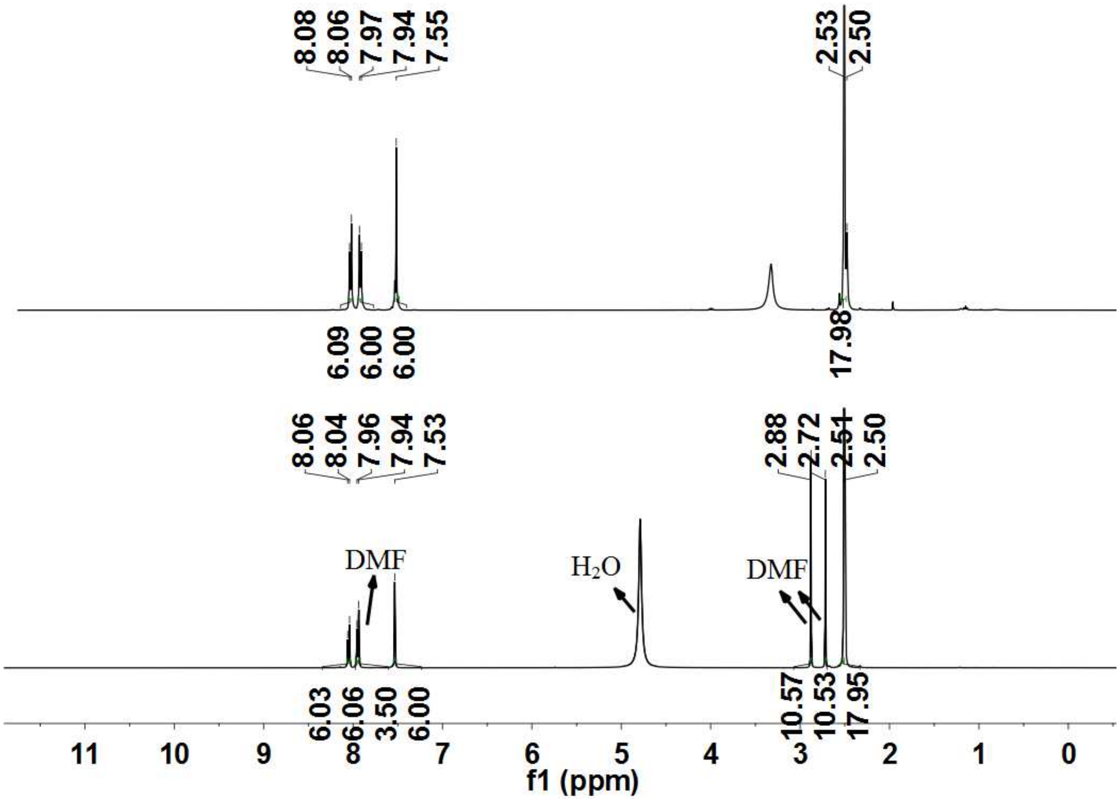

Fig. S10 Solution ^{1}H-NMR spectra of the ligand H_3**L** in DMSO-d_6 (top) and the as-made sample of **GDUT-7** dissolved in DCl (38% in D_2O)/DMSO-d_6 (1:4, v:v) (bottom).

Activation of crystals of GDUT-7. Freshly prepared crystals (5.0 mg) were stored in a 10 mL glass vial with DMF (5.0 mL) at rt for 4 h. The DMF solution was decanted and the crystals were washed with acetonitrile (5.0 mL × 9 — each time, the crystals were allowed to soak for 8 hours before the acetonitrile was decanted).

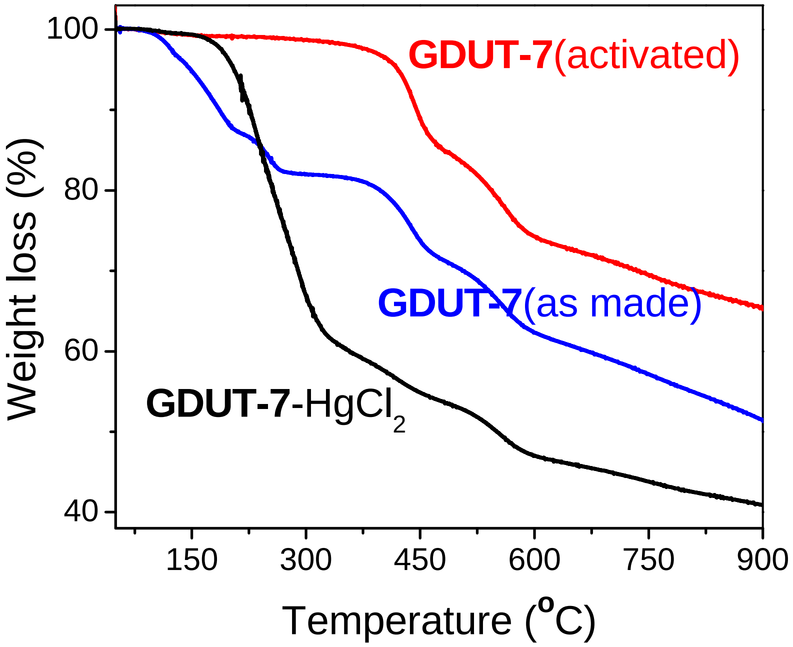

Fig. S11 Thermogravimetric analysis (TGA) plots of an as-made sample of **GDUT-7** (blue), an activated sample of **GDUT-7** (red) and a $HgCl_2$-loaded sample of **GDUT-7** (black). The initial weight loss (e.g., under 260 °C) of about 17.6% in plot of **GDUT-7** (blue) can be ascribed to the departure of the guests of DMF and water. The ensuing weight loss of 36% from 370 °C to 900 °C could be due to decomposition of the organic ligands.

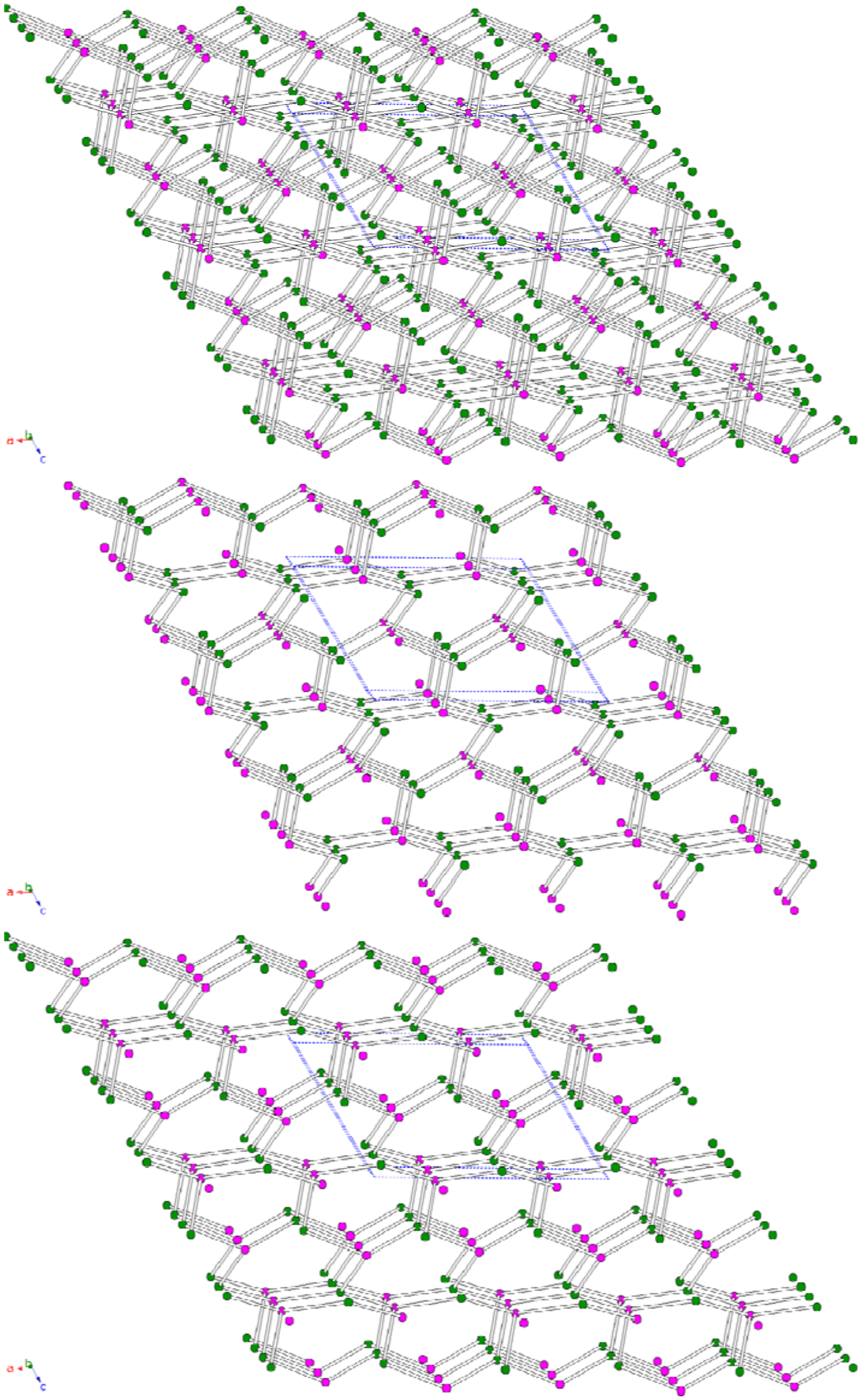

Fig. S12 Overall topology of the Eu-carboxyl net: purple sphere, center of Eu cluster; green sphere, center of linker **L** (top panel), which can be deconstructed into two intersecting subnets, both being of the $ThSi_2$, i.e., (10, 3)-b topology (middle and bottom panels). The two subnets intersect at the purple nodes to create the 6-connected node.

Hg(II) sorption isotherm measurement.

Mercury(II) chloride solutions of various concentrations (10, 50, 100, 200, 400 and 800 mg L^{-1}) were prepared using a KH_2PO_4/Na_2HPO_4 buffer solution (pH = 6.8), and used in the following adsorption procedure. A freshly made sample of **GDUT-7** (6.0 mg) was washed with DMF (3 × 1.0 mL) and soaked in acetonitrile (3 × 3.0 mL) for 3 hours each time. The acetonitrile was then decanted, and the crystals were washed twice with water to remove residual acetonitrile, and immediately afterward mixed with the $HgCl_2$ solution (3.0 mL). After the mixture was shaken at 150 rpm and room temperature for about 48 hours using an IKA KS 501 Digital Orbital shaker, the crystals were separated by centrifugation and the concentration of the remaining Hg in the supernatant was determined by ICP-AES. Based on the Langmuir adsorption equation (see below), the saturated Hg(II) adsorption capacity q_{max} was calculated to be 85 mg/g.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}}$$

where a plot of C_e/q_e to C_e (see Fig. 6 inset) yields the sorption capacity q_{max} (mg g^{-1}) as the reciprocal of the slope.

The distribution coefficient (K_d) is defined as $K_d = \frac{C_i - C_f}{C_f} \times \frac{V}{m}$, where C_i is the initial metal ion concentration, C_f is the equilibrium metal ion concentration, V is the volume of the sample solution (mL) and m is the amount of the sorbent (g). The K_d of **GDUT-7** was calculated to be 7.5×10^2 mL g^{-1}.

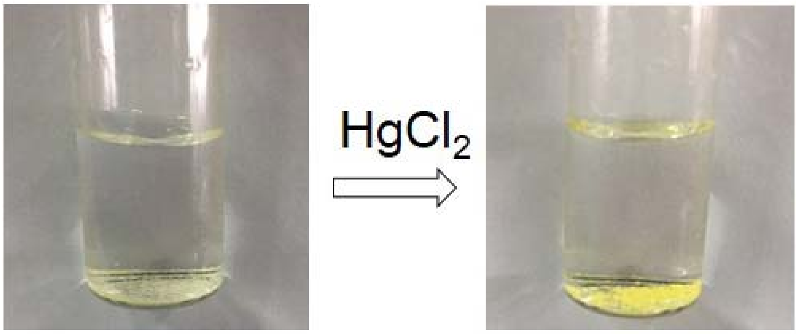

Fig. S13 Photographs of single crystals of **GDUT-7** before (left) and after (right) aqueous $HgCl_2$ solution treatment (15 ppm). The color of the crystals turns from colorless to light yellow.

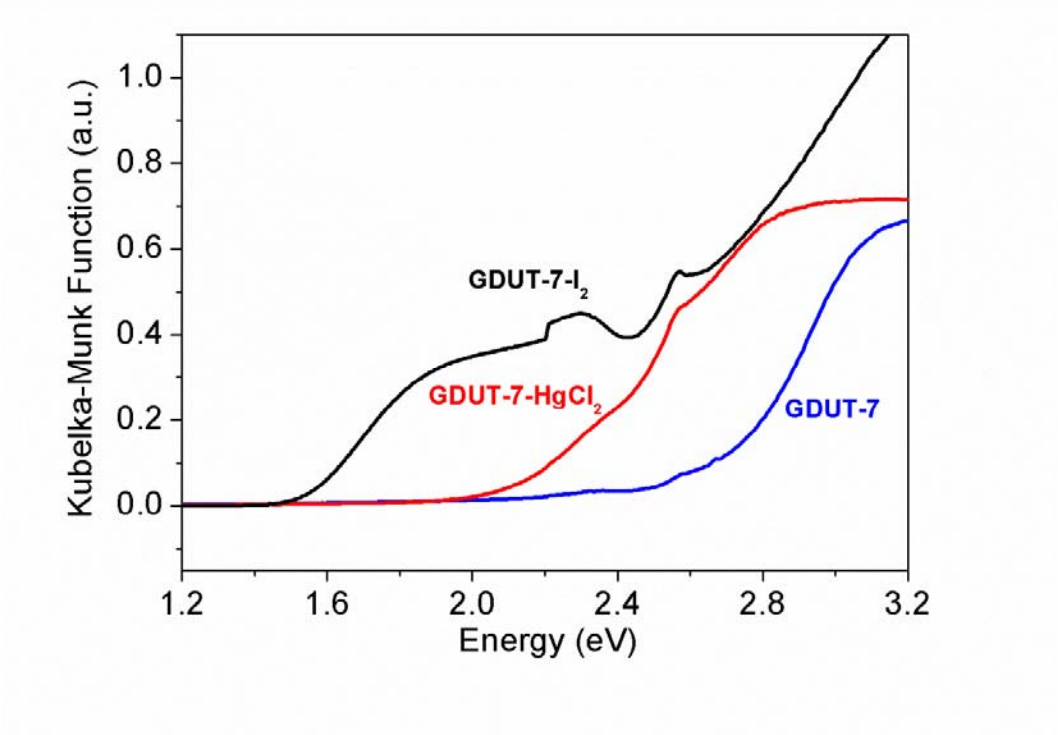

Fig. S14. Room temperature optical absorption spectra for solid samples of **GDUT-7** (2.7 eV), **GDUT-7-**$HgCl_2$ (2.1 eV) and **GDUT-7-**I_2 (1.6 eV).

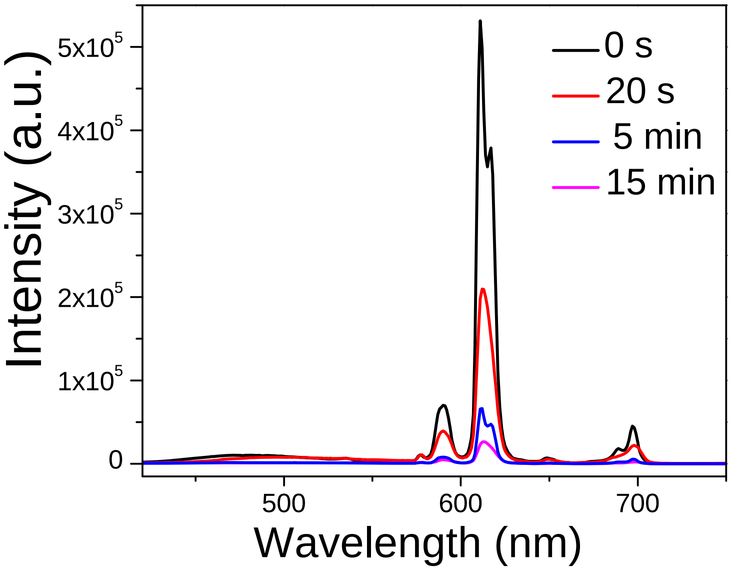

Fig. S15 Room-temperature solid-state emission spectra of activated single crystals of **GDUT-7** (black) and a sample of **GDUT-7** after a treatment with saturated $HgCl_2$ (in ethanol) for 20 s (red), 5 min (blue) and 15 min (pink).

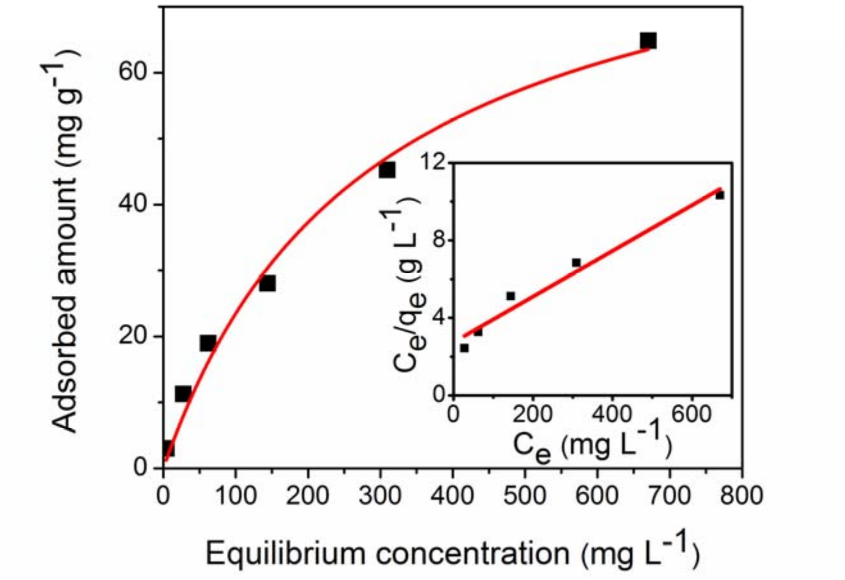

Fig. S16 The Hg(II) adsorption isotherm for GDUT-7. Inset: linear expressions fitted with Langmuir model

Crystal sample of GDUT-7 treated with excess $HgCl_2$. The activated crystals were placed into a saturated EtOH solution (3.0 mL) of mercury (II) chloride at room temperature for 2 days. Elemental analysis found [C (29.99%), H (2.64%), N (2.31%), S (9.57%)]; a fitting formula can be determined to be $Eu(C_{48}H_{36}N_3O_6S_6)_5\cdot(HgCl_2)_{2.8}\cdot(EtOH)_{0.9}\cdot(H_2O)_{5.5}$, which gives a calculated profile as [C (29.97%), H (2.65%), N (2.11%), S (9.64%)].

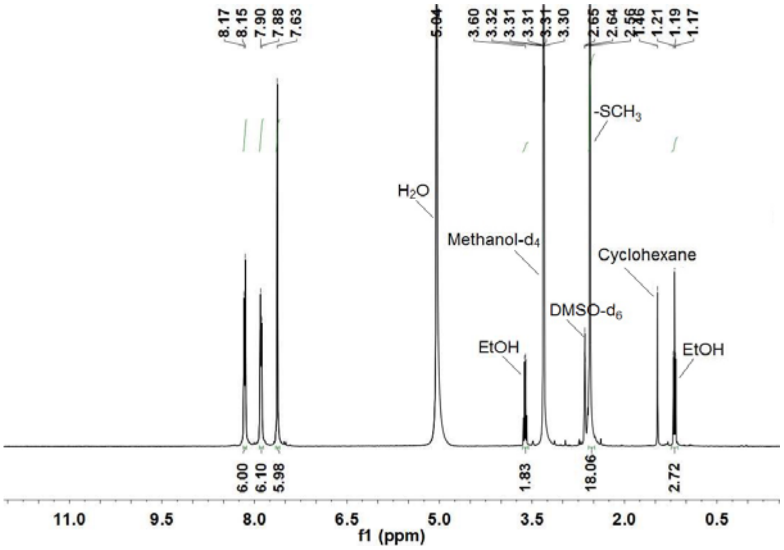

Fig. S17 The ^{1}H NMR spectrum of compound **GDUT-7**·$HgCl_2$ in MeOH-d_4/DCl/DMSO-d_6 solvents.

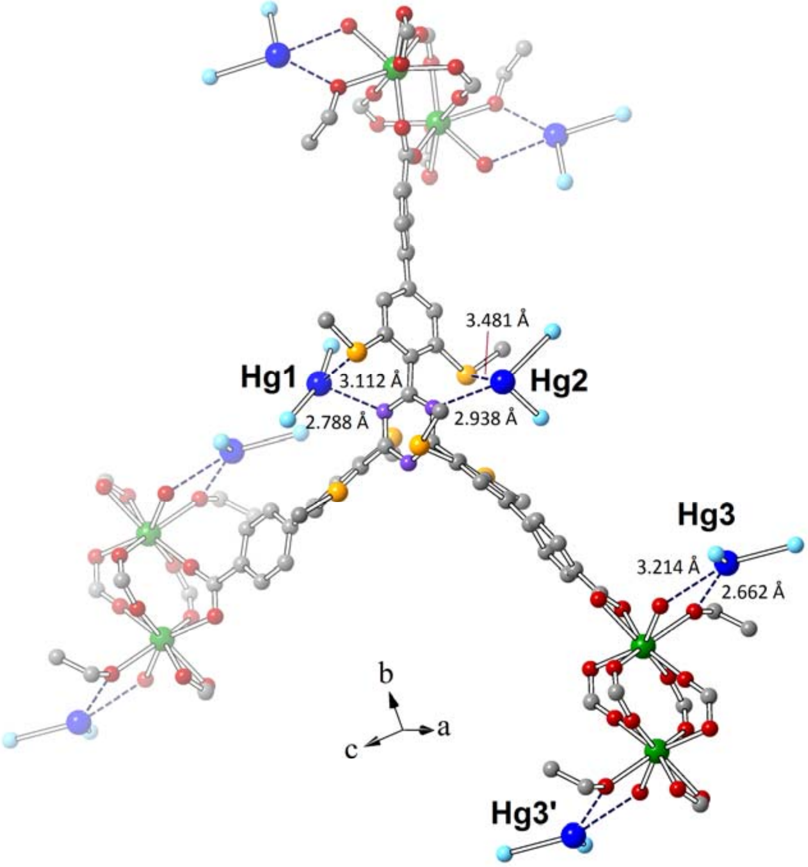

Fig. S18 Linker **L**, the three associated Eu(III) clusters and the $HgCl_2$ guests found in the crystal structure of **GDUT-7**-$HgCl_2$.

Uptake of I_2 vapor by GDUT-7. A small plastic vial containing as made crystals of **GDUT-7** (5.0 mg) was placed into a larger vial containing crystallites of I_2 (100 mg), and the larger vial was then capped and heated up at 95 °C for 2 hs for the I_2 vapor diffusion. The resultant crystals were copiously washed with $CHCl_3$ (to remove I_2 on the exterior; until the filtrate became colorless, then left in air to dry. Chemical analysis of the **GDUT-7**$\cdot(I_2)_{2.6}$ samples thus obtained, $Eu(C_{48}H_{36}N_3O_6S_6)\cdot(I_2)_{2.6}$, corresponding to **GDUT-7**$\cdot(I_2)_{2.6}$, yielded the following: calcd [C (32.85%), H (2.18%), N (2.39%), S (10.96%)]; found [C (33.17%), H (2.39%), N (2.64%), S (10.70%)].

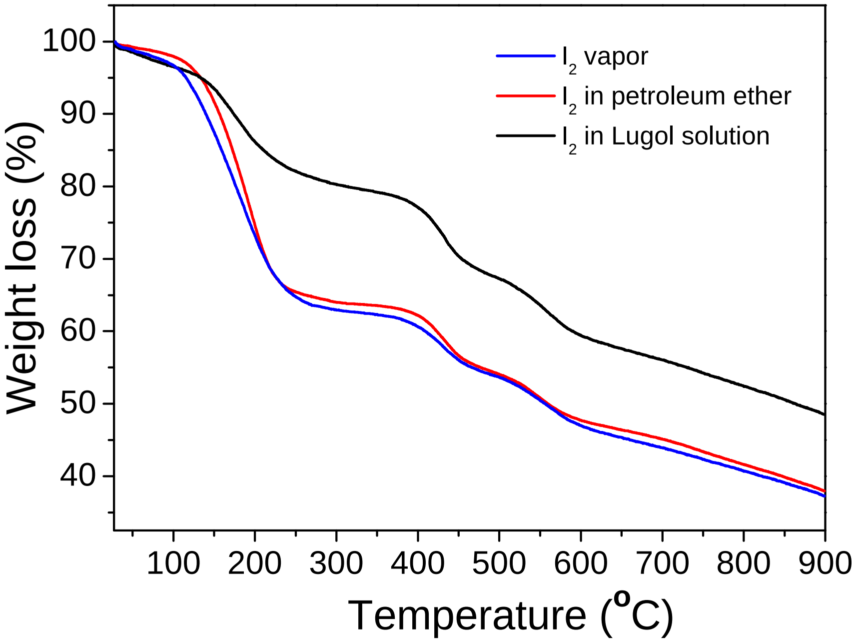

Fig. S19 Thermogravimetric analysis (TGA) plots of the I_2-loaded samples of **GDUT-7-I_2** from the treatment with I_2 vapor (blue), in water (Lugol solution, black) and in petroleum ether (red).

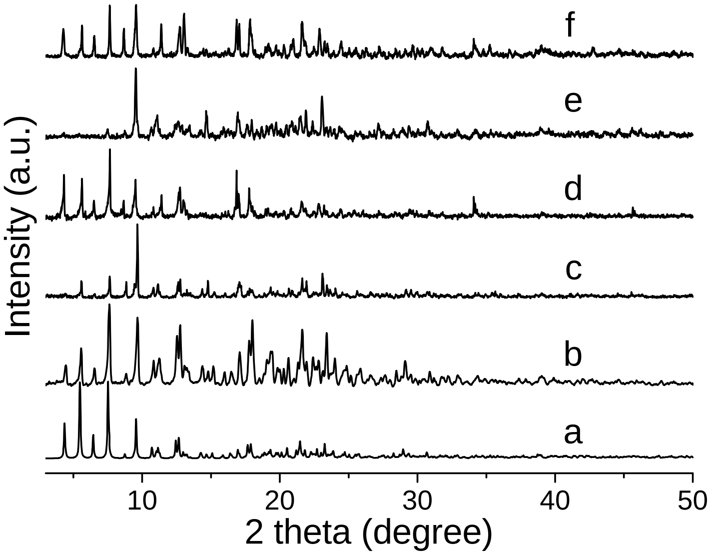

Fig. S20 PXRD patterns. (a) Calculated from the single-crystal structure of GDUT-7; (b) as-made bulk sample of GDUT-7; (c) sample from (b) after treatment in I_2 vapor at 95 °C for 2 h; (d) sample from (c) washed with EtOH; sample from (b) after six cycles of I_2 loading (e) and eluting (f).

Uptake from water and organic solvents. Aside from the vapor phase, water also presents an interesting medium in which to test the uptake of I_2. **GDUT-7** stands out as a robust MOF system that efficiently removes I_2 from aqueous solutions. For example, an I_2-KI solution (5.0 mL, containing 50 mg, 0.1975 mmol of I_2 and 100 mg of KI) was shaken with crystals of **GDUT-7** (5 mg) overnight, the resultant crystals were copiously washed with $CHCl_3$ (to remove I_2 on the exterior; until the filtrate becomes colorless, then left in air to dry. Chemical analysis of the **GDUT-7**$\cdot(I_2)_{1.2}$ samples thus obtained, $Eu(C_{48}H_{36}N_3O_6S_6)\cdot(I_2)_{1.2}$, corresponding to **GDUT-7**$\cdot(I_2)_{1.2}$, yielded the following: calcd [C (41.19%), H (2.59%), N (3.00%), S (13.74%)]; found [C (41.13%), H (2.19%), N (3.25%), S (13.28%)].

When a similar experiment was carried out with the I_2 dissolved in non-polar solvents (e.g., petroleum ether or cyclohexane), the uptake amount seems larger than from water media. Chemical analysis of the **GDUT-7**$\cdot(I_2)_{2.25}$ samples thus obtained, $Eu(C_{48}H_{36}N_3O_6S_6)\cdot(I_2)_{2.25}$, corresponding to **GDUT-7**$\cdot(I_2)_{2.25}$, yielded the following:

calcd [C (34.60%), H (2.18%), N (N2.51%), S (11.55%)]; found [C (34.96%), H (2.35%), N (2.76%), S (11.20%)].

Release of the I_2 guests from the host of **GDUT-7**, however, can be readily enabled by polar solvents like ethanol, methanol or acetonitrile, as these solvents instantaneously take on the distinct colors of molecular iodine upon contact with the loaded crystalline samples of **GDUT-7**.

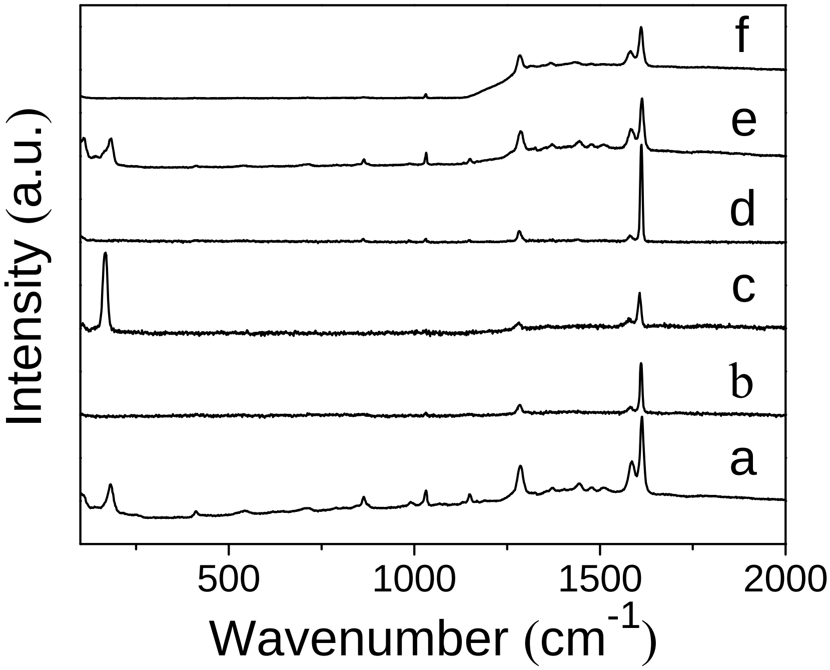

Fig. S21. The Raman spectra of (a) a sample of **GDUT-7**-I_2 (from treatment by I_2 vapor); (b) sample (a) washed by EtOH to elute the I_2 guests; (c) **GDUT-7**-I_2 (from treatment by the petroleum ether solution); (d) sample (c) washed by EtOH to elute the I_2 guests; (e) **GDUT-7**-I_2 (from treatment by Lugol's solution); (f) sample (e) washed by EtOH to elute the I_2 guests. The Raman peak of the I_2 guests at 180 cm^{-1} is similar to that of I_2 solid.

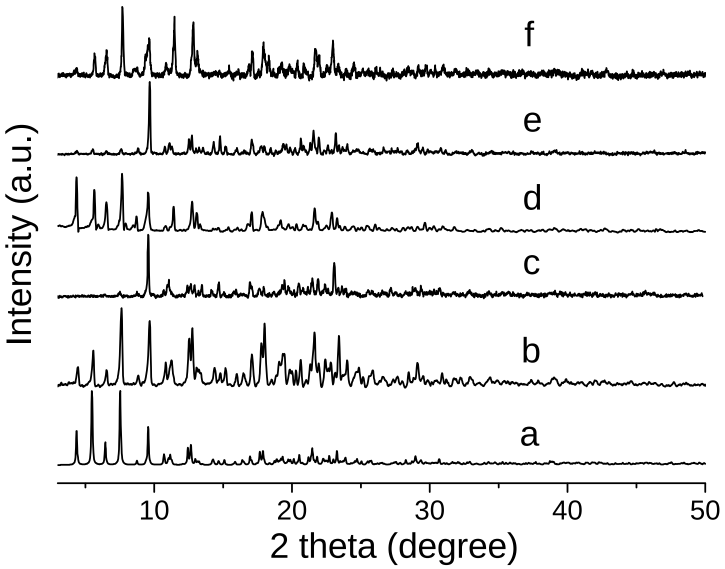

Fig. S22 PXRD patterns. (a) Calculated from the single-crystal structure of GDUT-7; (b) as-made bulk sample of GDUT-7; (c) sample from (b) after treatment in petroleum ether solution of I_2 (2.4 mg/mL); (d) sample from (c) washed with EtOH; (e) sample from (b) after treatment in a Lugol solution (I_2-KI in water, containing 1% I_2); (f) sample from (e) washed with EtOH.

Table S1. Crystallographic data of **GDUT-7** and **GDUT-7-HgCl₂**.

	GDUT-7	**GDUT-7-HgCl₂**
Empirical formula	$C_{51}H_{45}EuN_4O_8S_6\cdot(C_3H_7NO)_{2.5}\cdot(H_2O)_{0.792}$	$C_{50}H_{43.97}EuN_3O_8S_6\cdot(HgCl_2)_{0.44}\cdot(C_2H_6O)_{2.61}$
Formula weight	1383.23	1398.69
Temperature/K	100(2)	150(2)
Wavelength/Å	0.7107	1.54178
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*
a/Å	48.151(12)	47.818(3)
b/Å	9.652(2)	9.5341(6)
c/Å	32.614(8	32.3065(17)
α/°	90	90
β/°	122.942(4)	122.338(3)
γ/°	90	90
V/Å³	12720(5)	12444.2(13)
Z	8	8
Dc/g.cm⁻³	1.445	1.493
μ/mm⁻¹	1.245	11.790
F(000)	5679	5647
R_1[a][I>2σ (I)]	0.0408	0.0417

wR_2[b] (all data)	0.0968	0.1169
GOF	1.009	1.041

[a] $R_1=\sum(||F_0|-|F_c||)/\sum|F_0|$; [b] $wR_2=[\sum w(F_0^2-F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$