Syntheses, structures and luminescent properties of decorated lanthanide metal-organic frameworks of (E)-4,4'-(ethene-1,2-diyl)dibenzoic acids[†]

Yu Li and Datong Song*

Received 30th August 2010, Accepted 5th November 2010 DOI: 10.1039/c0ce00750a

The functionalized ligand (*E*)-4,4'-(1,4-bis(methylthio)but-2-ene-2,3-diyl)dibenzoic acid (H₂L_S) and four metal-organic frameworks, $[M_2(L_H)_3(DMSO)_4] \cdot xDMSO$ (6 and 7 for $M = Tb^{3+}$, Eu^{3+} respectively; $L_H = (E)$ -4,4'-(ethene-1,2-diyl)dibenzoate) and $[M_2(L_S)_3(DMF)_2(H_2O)_2]$ (8 and 9 for $M = Eu^{3+}$, Tb^{3+}) have been synthesized and characterized. All four MOFs adopt the anticipated connectivity, but the fold of interpenetration in each MOF crystal varies as a result of different solvent inclusion and ligand functionality. Compounds 6 and 7 contain a large amount of solvent molecules and tend to lose solvent in air. Compounds 8 and 9 are stable crystals without lattice solvent molecules in the crystals; the coordinating solvent molecules can be reversibly removed and replenished with the skeletons intact. All four MOFs show mainly the ligand-based luminescence, while 8 also displays metal-based luminescence.

Introduction

A large number of metal-organic frameworks (MOFs) with different functionalities have been reported in the past decade. Because of their porosity and various inherent properties from ligands and metal centers involved, these MOFs have found use in many areas, including gas storage^{1,2} and separation,^{2,3} sensing,4-8 and heterogeneous catalysis.9,10 While much effort has been put into the syntheses of MOFs for gas storage and separation, MOF sensors remain relatively underdeveloped. The known MOF sensors can be classified into two categories with respect to the guest interacting sites: (1) exposed metal centers and (2) exposed functional groups on the ligands. Generating unsaturated metal sites in MOF is more challenging and usually achieved by serendipity, because of the highly reactive nature of coordinately unsaturated metal centers. The second strategy can be utilized to rationally design MOF sensors, because a large variety of functional groups can be incorporated into the ligand via relatively simple organic synthesis. However, MOFs sensors in this category are still rare.4c

Lanthanide MOFs are attractive for sensing applications, because of not only the characteristic emissions but also the unique luminescence mechanism, ligand-to-metal energy transfer (LMET). The interactions between an analyte and functional groups of the ligands may facilitate or disrupt the LMET process, causing luminescence signal modulations as the reporting mechanism. With such a design in mind, our group is interested in preparing luminescent porous lanthanide MOFs with

This journal is © The Royal Society of Chemistry 2011

dangling functional groups in the pores or channels and exploring their potential applications as sensors. Although the porosity is not always predictable, there are some general rules to follow and adjustments to existing examples usually produce similar structures.^{11–13} Functional groups inside the pores/channels of the MOF serve as the binding site for guests, which can be incorporated either *via* ligand synthesis prior to MOF assembly^{4c,14} or post-synthetic modification.¹⁵

We design our functionalized MOFs based on two known unfunctionalized examples: [Tb₂(ADB)₃(DMSO)₄]·16DMSO (where ADB = 4.4'-azodibenzoate) by Yaghi and co-workers¹⁶ and $[Eu_2L_3(DMSO)_2(CH_3OH)_2] \cdot 2DMSO$ (where L = 4,4'ethyne-1,2-divldibenzoate) by our group.¹⁷ By replacing the N=N and C=C from the ligands in the known MOFs with a C=C linkage, different functional groups can be installed in the central region of the linear ligand. We envision that a similar skeleton could be anticipated when a functionalized ligand is used, *i.e.*, each bimetallic node is connected with 6 other nodes to form 3D porous frameworks with triangular channels along the body diagonal and functional groups dangling inside the channels (Scheme 1). It is worth noting that although stilbene dicarboxylate has been used in MOF synthesis with transition metals,18 neither stilbene dicarboxylate nor its derivatives have not been used in lanthanide MOFs. We chose thioether functional groups for two reasons: (1) the soft sulfur donors do not interfere with the assembly of lanthanide MOFs; (2) sulfur





Davenport Chemical Research Laboratories, Department of Chemistry, University of Toronto, 80 St George Street, Toronto, Ontario, Canada M5S 3H6. E-mail: dsong@chem.utoronto.ca; Fax: +1-416-978-7013; Tel: +1-416-978-7014

[†] Electronic supplementary information (ESI) available: Cif files for **2a-9**; TGA results of **6-9** and Na₂L_H; luminescence spectra of H₂L_H, H₂L_S, and compounds **6-9**; powder XRD patterns of **6-9**; TGA, FTIR and powder XRD spectra associated with the desolvation/resolvation cycle. CCDC reference numbers 791231–791239. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ce00750a.

donors may potentially bind with soft metal ions that might be able to enter the channels of the targeted MOFs, triggering luminescence signal change. In this paper, we reported the synthesis of the substituted stilbene dicarboxylic acid ligand with thioether side chains (H₂L_s, (*E*)-4,4'-(1,4-bis(methylthio)but-2ene-2,3-diyl)dibenzoic acid), the preparation and luminescent properties of the Eu(III) and Tb(III) MOFs of H₂L_s and H₂L_H ((*E*)-4,4'-stilbene dicarboxylic acid).

Experimental section

General Information

Elemental analyses were performed in our Chemistry Department on a PE 2400 C/H/N/S analyzer. Thermogravimetric analyses (TGA) were performed on a TA Instruments SDT Q600 instrument under a dinitrogen atmosphere with a heating rate of 10 °C per minute. NMR spectra were recorded on a Varian 400, or a Bruker Avance 400 spectrometer. Both ¹H and ¹³C NMR spectra were referenced and reported relative to the solvent's residual signals. Photoluminescence spectra were measured using a SPEX Fluorolog-3 spectrofluorometer (Jobin Yvon/SPEX, Edison, New Jersey). The powder XRD experiments were performed on an automated Siemens/Bruker D5000 diffractometer equipped with a high power line focus Cu-Ka source operating at 50 kV/35 mA. A solid-state Si/Li Kevex detector was used for removal of K^β lines. The diffraction patterns were collected on a $\theta/2 - \theta$ Bragg–Brentano reflection geometry with fixed slits. A step scan mode was used for data acquisition with a step size of $0.02^{\circ} 2-\theta$. Unless otherwise stated, all manipulations were performed in air and all reagents were purchased from commercial sources and used without further purification. McMurry coupling reaction was performed under an Ar atmosphere, but the work-up was carried out under ambient conditions. The THF solvent for McMurry coupling was purified by John Morris Scientific IT PureSolv PS-MD-6 system; Zn-Cu couple¹⁹ and methyl 4-acetylbenzoate²⁰ for the coupling reaction was prepared according to the literature procedures.

Synthesis of dimethyl 4,4'-(but-2-ene-2,3-diyl)dibenzoate (2a *trans*, 2b *cis*)

With vigorous stirring TiCl₄ (2.7 mL, 0.025 mol) was added slowly to a cold (0 °C) suspension of Zn-Cu couple (3.32 g) in THF (50 mL). The mixture was then refluxed for 1 h, cooled to ambient temperature, followed by the addition of a solution of methyl 4-acetylbenzoate (2.0 g, 0.011 mol) in THF (10 mL). The reaction mixture was further refluxed for 12 h. After cooling to ambient temperature, the reaction mixture was quenched with 10 mL of saturated K_2CO_3 (aq) and extracted with Et_2O . The organic layer was washed with brine, dried over MgSO₄. After MgSO₄ was filtered off, the solvents were removed to give the crude product, which was purified by silica gel column chromatography (eluted with CH₂Cl₂) to give a translcis mixture of compound 2 (1.0 g, 55% yield) as a light yellow oil. The two isomers can be separated through chromatography and isolated as white or light yellow solids, although it is not necessary for the next step. **2b**: ¹H NMR (CDCl₃, 400 MHz, 25 °C) δ 7.74 (d, J = 8.4 Hz, 4H), 7.00 (d, J = 8.4 Hz, 4H), 3.85 (s, 6H), 2.18(s, 6H); ¹³C NMR (CDCl₃, 400 MHz, 25 °C) δ 167.1, 149.3, 133.8, 129.3,

127.8, 52.2, 21.5. Anal. calcd for $C_{20}H_{20}O_4$: C, 74.06; H, 6.21. Found: C, 74.13; H, 6.24%. **2a**: ¹H NMR (CDCl₃, 400 MHz, 25 °C) δ 8.06 (d, J = 8.0 Hz, 4H), 7.34 (d, J = 8.0 Hz, 4H), 3.93 (s, 6H), 1.88(s, 6H); ¹³C NMR (CDCl₃, 100 MHz, 25 °C) δ 167.2, 149.2, 133.5, 129.9, 128.5, 52.3, 22.4.

Synthesis of dimethyl 4,4'-(1,4-dibromobut-2-ene-2,3diyl)dibenzoate (3a *trans*, 3b *cis*)

A mixture of 2a and 2b (648 mg, 2 mmol) as obtained above, Nbromosuccinimide (712 mg, 4 mmol) and benzoyl peroxide (97 mg, 0.4 mmol) were refluxed in cyclohexane (30 mL) for 5 h. The reaction mixture was cooled to ambient temperature and filtered. After the removal of solvent from the filtrate, the residual crude product was purified using silica gel column chromatography (eluted with 1:7 mixture of EtOAc: hexanes), affording colorless crystals of **3a** (460 mg, 48% yield) and **3b** (141 mg, 15% yield). **3a**: ¹H NMR (CDCl₃, 400 MHz, 25 °C) δ 8.15 (d, J = 8.4 Hz, 4H), 7.54 (d, J = 8.4 Hz, 4H), 4.00 (s, 4H), 3.96(s, 6H); ¹³C NMR (CDCl₃, 100 MHz, 25 °C) & 166.8, 142.6, 139.1, 130.2, 128.7, 52.5, 34.6. Anal. calcd for C₂₀H₁₈O₄Br₂: C, 49.82; H, 3.76. Found: C, 49.93; H, 3.95%. 3b: 1H NMR (CDCl₃, 400 MHz, 25 °C) δ 7.92 (d, J = 8.4 Hz, 4H), 7.14 (d, J = 8.4 Hz, 4H), 4.49 (s, 4H), 3.87(s, 6H); ¹³C NMR (CDCl₃, 100 MHz, 25 °C) δ 166.5, 143.8, 140.1, 129.5, 129.2, 52.2, 31.1. Anal. calcd. for C₂₀H₁₈O₄Br₂·0.75CH₂Cl₂: C, 45.66; H, 3.60. Found: C, 45.68; H, 3.52%.

Synthesis of (*E*)-dimethyl 4,4'-(1,4-bis(methylthio)but-2-ene-2,3diyl)dibenzoate (4)

Sodium methanethiolate (108 mg, 1.54 mmol) and **3a** (300 mg, 0.62 mmol) were refluxed in methanol (30 mL) under N₂ for 3 h. After the solvent was removed *in vacuo*, distilled water was added to dissolve the residual solid. The aqueous solution was acidified with excess 1 M HCl solution and extracted with EtOAc. The organic phase was then dried over MgSO₄. After filtration the solution was concentrated to dryness, affording **4** as a light yellow powder (231 mg, 95% yield). ¹H NMR (CDCl₃, 400 MHz, 25 °C) δ 8.10 (d, *J* = 8.4 Hz, 4H), 7.44 (d, *J* = 8.4 Hz, 4H), 3.94 (s, 6H), 3.29 (s, 4H), 1.83(s, 6H); ¹³C NMR (CDCl₃, 100 MHz, 25 °C) δ 166.8, 144.8, 137.0, 129.6, 129.3, 129.1, 52.2, 38.8, 16.0. Anal. calcd for C₂₂H₂₄O₄S₂: C, 63.43; H, 5.81. Found: C, 62.89; H, 5.83%.

Synthesis of (*E*)-4,4'-(1,4-bis(methylthio)but-2-ene-2,3diyl)dibenzoic acid (H_2L_S , 5)

Potassium hydroxide (1.1 g, 19 mmol) and **4** (500 mg, 1.2 mmol) were refluxed in methanol (60 mL) for 2 h. After removal of solvents *in vacuo*, distilled water was added to dissolve the residual solid. The aqueous solution was acidified with excess 1 M HCl to give a white suspension. The suspension was directly extracted with EtOAc. The organic phase was dried over MgSO₄ and concentrated to give 466 mg white powder of **5** in quantitative yield. ¹H NMR (CD₃OD, 400 MHz, 25 °C) δ 8.11 (d, *J* = 8.4 Hz, 4H), 7.58 (d, *J* = 8.4 Hz, 4H), 3.40 (s, 4H), 1.84(s, 6H); ¹³C NMR (DMSO-d₆, 100 MHz, 25 °C) δ 166.9, 144.2, 136.1, 129.6, 129.1, 129.0, 37.6, 14.6. Anal. calcd for C₂₀H₂₀O₄S₂: C, 61.83; H, 5.19. Found: C, 61.70; H, 5.34%.

Synthesis of [Tb(L_H)_{1.5}(DMSO)₂] · xDMSO (6)

A small vial containing a 2 mL DMSO solution of TbCl₃·6H₂O (8 mM) and H₂L_H (12 mM) was inserted into a large vial containing DMSO (8 mL) and triethylamine (0.024 mL, 0.17 mmol). The large vial was then sealed. The double-vial system was allowed to stand for 14 d at room temperature to afford **6** as colorless X-ray quality crystals. The crystals were collected by filtration and dried under vacuum for 1 h (7.6 mg, 46% yield). The synthesis of **6** has poor reproducibility. Anal. Calcd. for $C_{28}H_{27}O_8S_2Tb\cdot4DMSO$: C, 42.10; H, 5.00. Found: C, 42.44; H, 4.90%.

Synthesis of [Eu₂(L_H)₃(DMSO)₄]·xDMSO (7)

A small vial containing a 2 mL DMSO solution of EuCl₃·6H₂O (8 mM) and H₂L_H (12 mM) was inserted into a large vial containing DMSO (8 mL) and triethylamine (0.024 mL, 0.17 mmol). The large vial was then sealed. The double-vial system was allowed to stand for 14 d at room temperature to afford **7** as colorless X-ray quality crystals. The crystals were collected by filtration and dried under vacuum for 1 h (8.2 mg, 41% yield). Anal. calcd. for $C_{56}H_{54}O_{16}S_4Eu_2$ ·14DMSO: C, 40.21; H, 5.54. Found: C, 39.92; H, 5.17%.

Synthesis of $[Eu_2(L_S)_3(DMF)_2(H_2O)_2]$ (8)

Eu(NO₃)₃·6H₂O (17.8 mg, 0.040 mmol), H₂L_s (23.3 mg, 0.060 mmol), N,N'-dimethylformamide (4 mL) and distilled water (6 mL) were mixed and sealed in a 23 mL PTFE lined autoclave, then heated at 120 °C for 3 d. After cooling, yellow needle-shaped crystals of **8** were collected by filtration, washed with ethanol, and dried in air (26.5 mg, 80% yield). Anal. Calcd. for C₆₆H₇₂Eu₂N₂O₁₆S₆: C, 48.17; H, 4.41; N, 1.70. Found: C, 47.93; H, 4.17; N, 2.12%.

Synthesis of $[Tb_2(L_S)_3(DMF)_2(H_2O)_2]$ (9)

The synthesis of **9** is similar to that of **8**, but with $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ (14.9 mg, 0.040 mmol). Yellow needle-shaped crystals of **9** were collected by filtration, washed with ethanol, and dried in air (22.6 mg, 68% yield). Anal. calcd for $\text{C}_{66}\text{H}_{72}\text{N}_2\text{O}_{16}\text{S}_6\text{Tb}_2$: C, 47.77; H, 4.37. Found: C, 47.87; H, 4.47%.

X-Ray crystallographic analysis

X-Ray quality single crystals of **6–9** were obtained as described in the sections above; those of **2a**, **2b**, **3a**, **3b** and **4** were obtained from slow evaporation of the solvent from the corresponding CH₂Cl₂ solutions. All crystals were mounted on the tip of a MiTeGen MicroMount. All single-crystal X-ray diffraction data were collected on a Bruker Kappa Apex II diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) operating at 50 kV and 30 mA, at 120 K or 150 K controlled by an Oxford Cryostream 700 series low temperature system. The data integration and absorption correction were performed with the Bruker Apex 2 software package.²¹ All structures were solved by the direct methods except for compound **9** which was solved by Patterson method. All structure solution and refinements were performed using SHELXTL V6.14.²² A disordered phenyl ring of the ligand in **7** and the thioether side chains in **8** and **9** have been modeled successfully. The residual diffuse electron density of unidentified solvent molecules in the lattices of **6** and **7** was removed with the SQUEEZE function of PLATON program²³ and their contributions were not included in the formula, although elemental analysis results suggest that the removed electron density may originate at least partially from several DMSO molecules. All non-hydrogen atoms except for the atoms involved in the disordered portions were refined anisotropically. The positions of the hydrogen atoms were calculated using the riding model. Selected crystallographic data of the MOFs and synthesis intermediates are summarized in Table 1, while selected bond lengths and angles of **6–9** are listed in Table 2.

Results and discussion

Ligand synthesis

As shown in Scheme 2, ligand H_2L_S can be synthesized in 5 steps in a 19% overall yield. Compound 1 was synthesized from carboxylation of 4-iodo-acetophenone under CO in 80% yield.10 McMurry coupling¹⁹ reaction of 1 produces a mixture of *trans* (2a) and cis (2b) isomers of 2, in about 1 : 4 ratio according to the ¹H NMR spectrum of the crude product. Although the *cis* isomer **2b** is the major product, the subsequent bromination of **2b** using NBS causes the isomerization of the double bond to give 3a as the major product. Therefore, the mixture of 2a and 2b resulting from the McMurry coupling step can be used directly for the bromination reaction and the *trans*(3a)/*cis*(3b) isomers of 3 can be separated after the bromination step using column chromatography. The treatment of the trans compound 3a with NaSCH₃ affords 4, which can then be hydrolyzed to produce H_2L_S , 5. The geometry at the C=C linkage of 2a, 2b, 3a, 3b and 4 has been confirmed by X-ray crystallography (see Fig. S1, ESI[†]). According to the crystal structures, the two phenyl rings and the C=C linkage of 2a, 3a and 4 are no longer co-planar due to the steric effect imparted by the substituents.

MOF preparation and structure description

The ligand (*E*)-4,4'-(ethene-1,2-diyl)dibenzoic acid, H_2L_H , is commercially available. The MOFs 6 and 7 can be prepared in crystalline form in moderate yields by slow diffusion of triethylamine vapor into the mixed solution of H_2L_H and $MCl_3 \cdot 6H_2O$ (M = Tb in 6 and Eu in 7) at ambient temperature. Some unidentified amorphous precipitates were also observed during the preparation of 6 and 7. These amorphous precipitates have lower density compared to the crystals of 6 and 7 and therefore, can be flushed away with DMSO. The crystals of 6 and 7 collapse into powders quickly upon contact with acetone and chloroform; they also lose solvents and become opaque rapidly upon standing in air. Compounds 6 and 7 are insoluble in common solvents, suggesting the polymeric nature of their structures.

Because of the structural similarity between L_{H}^{2-} and 4,4'azodibenzoate (ADB) used by Yaghi,¹⁶ the corresponding Tb(III) MOFs, **6** and [Tb₂(ADB)₃(DMSO)₄]·*x*DMSO, show almost identical structures, *e.g.*, same space group, similar unit cell parameters and topology. Compound **6** crystallized in the monoclinic space group *C*2/*c*. As shown in Fig. 1a, each Tb(III) center adopts distorted tricapped trigonal prismatic coordination Downloaded by Purdue University on 12 March 2013 Published on 08 December 2010 on http://pubs.rsc.org | doi:10.1039/C0CE00750A

Table 1 Crystallographic data

		,
$\begin{array}{cccc} C_{38}H_{57}O_{13}S_{7}Tb & C_{82}H_{132}O_{29}S_{17}\\ 1105.18 & 2430.82 \\ 120(2) & 150(2) & 150(2) \\ C2/c & P2_{12}I_{1} \\ 27.6859(5) & 16.5736(7) \\ 16.9435(4) & 21.7897(8) \\ 28.0346(6) & 35.1329(14) \\ 90 & 000 & 90 \\ 101.6030(10) & 90 \\ 101.6030(10) & 90 \\ 101.6030(10) & 90 \\ 101.6030(10) & 90 \\ 101.6030(10) & 90 \\ 101.6030(10) & 90 \\ 101.6030(10) & 90 \\ 101.6030(10) & 90 \\ 101.6030(10) & 90 \\ 12882.2(5) & 12687.4(9) \\ 8 & 4 \\ 1.140 & 1.273 \\ 1.318 \\ 1.318 \\ 1.3367 & 1.2687.4(9) \\ 1.338 \\ 1.367 & 1.2687.4(9) \\ 1.338 \\ 1.367 & 1.273 \\ 1.346 & 1.273 \\ 1.346 & 1.273 \\ 1.346 & 1.273 \\ 1.346 & 1.273 \\ 1.346 & 1.273 \\ 1.346 & 1.238 \\ 1.346 & 1.238 \\ 1.346 & 1.238 \\ 1.346 & 1.238 \\ 1.346 & 1.343 \\ 1.440 & 1.358 \\ 1.440 & 1.358 \\ 1.440 & 1.348 \\ 1.440 & 1.440 \\ 1.440 & 1.440 \\ 1.440 & 1.440 \\ 1.440 & 1.440 \\ 1.440 & 1.440 \\ 1.440 & 1.440 \\ 1.440 & 1.440 \\ 1.440 & 1.440 \\ 1.440 & 1.440 \\ 1.440 & 1.440 \\ 1.440 & 1.440 \\ 1.440 & 1.440 \\ 1.440 & 1.440 \\ 1.440 & 1.440 \\ 1.440 & 1.440 \\ 1.440 & 1.440 \\ 1.440 & 1.440 \\ 1.440 & 1.440 \\ 1.440 $	$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{l} C_{33}H_{36}NO_8S_5Tb\\ 829,73\\ 150(2)\\ P\bar{l}\\ 8.6455(12)\\ 14.142(2)\\ 14.142(2)\\ 14.142(2)\\ 14.142(2)\\ 11.3.240(9)\\ 94.36(10)\\ 113.240(9)\\ 94.36(10)\\ 113.240(9)\\ 94.36(10)\\ 113.240(9)\\ 94.36(10)\\ 113.240(9)\\ 94.36(10)\\ 113.240(9)\\ 94.36(10)\\ 113.240(9)\\ 94.36(10)\\ 113.240(9)\\ 94.36(10)\\ 113.240(9)\\ 94.36(10)\\ 113.240(9)\\ 94.36(10)\\ 113.240(9)\\ 113.240(9)\\ 94.36(10)\\ 113.240(9)\\ 113$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		91.028(2) 94.463(2) 1805.42(11) 2 1.513 1.538 1.538 31341 6985 1.029 $R_1 = 0.0589$ $R_2 = 0.1475$ $R_1 = 0.0774$ $WR_2 = 0.1621$

geometry with seven oxygen donor atoms from the carboxylic groups of $L_{H^{2-}}$ ligands and two oxygen donor atoms from terminal DMSO ligands occupying the nine coordination sites. The trigonal prism is defined by O2, O3, O4, O5, O6, and O8; the three rectangular faces are capped by O1, O4A, and O7, respectively. The three capping atoms and Tb1 are roughly coplanar, as indicated by that the sum of the three relevant bond angles is 355.4(1)°, close to 360°. As shown in Fig. 1b, two adjacent Tb(III) centers are bridged by four carboxylate groups to form a bimetallic node with the Tb-Tb distance of 4.0866(4) Å, comparable to the literature values.¹⁶ There is a crystallographically imposed center of inversion at the centroid of each di-Tb node. Because of unsymmetrical bridging, the Tb1-O4A bond length is 2.851(3) Å, while all the remaining Tb-O bond lengths are within the range of 2.293(3)-2.480(4) Å. As shown in Fig. 2a, each di-Tb node is connected to six neighboring nodes via stilbene linkers to form a 3D infinite framework. Similar to Yaghi's $[Tb_2(ADB)_3(DMSO)_4] \cdot xDMSO$, a 2-fold interpenetration has been observed in the crystal lattice of 6 (Fig. 2b), as a result of the long linker group employed in the organic ligand.

Although switching from Tb(III) to Eu(III) usually produces isostructural analogues, the Eu(III) MOF of $L_{H^{2-}}$, 7, crystallized in a different space group $(P2_12_12_1)$ compared to 6. Similar to the Tb(III) centers in 6, each Eu(III) center adopts distorted tricapped trigonal prismatic coordination geometry with seven oxygen donor atoms from the carboxylic groups of L_H²⁻ ligands and two oxygen donor atoms from terminal DMSO ligands occupying the nine coordination sites (Fig. 3a). The trigonal prism is defined by O1, O4, O6, O8, O9, and O13; the three rectangular faces are capped by O7, O10, and O14, respectively. The three capping atoms and Eu1 are roughly coplanar, as indicated by that the sum of the three relevant bond angles is $355.6(2)^\circ$, close to 360° . As shown in Fig. 3b, two adjacent Eu(III) centers are bridged by four carboxylate groups to form a bimetallic node with the Eu-Eu distance of 4.0743(6) Å, comparable to the literature values.^{17,23} In contrast to the di-Tb nodes in 6, there is no crystallographically imposed center of inversion at the centroid of the di-Eu nodes in 7, as a result of the chiral space group in which 7 crystallized. Because of unsymmetrical bridging by O7 and O4, Eu1–O7 and Eu2–O4 bond lengths are 2.802(6) and 2.813(6) Å, respectively, while all the remaining Eu-O bond lengths are within the range of 2.346(6)–2.511(3) Å. As shown in Fig. 4a, each bimetallic node is connected to six neighboring nodes via stilbene linkers to form a 3D infinite framework. Because of the large spacing generated by the long linker, 2-fold interpenetration has been observed in the crystal lattice of 7 (Fig. 4b).

Similar to the carboxylates in $[Eu_2L_3(DMSO)_2(CH_3OH)_2]$ · 2DMSO (L = 4,4'-ethyne-1,2-diyldibenzoate),¹⁷ three coordination modes have been observed for the carboxylates in the lattices of **6** and **7** (Scheme 3): chelation mode, bridging mode, and chelate-bridging mode. In the lattice of $[Eu_2L_3(DMSO)_2-(CH_3OH)_2]$ ·2DMSO, the two carboxylates within each L^{2-} ligand can adopt different coordination modes. In contrast, the two carboxylate ligands within each L_H^{2-} ligand always adopt the same coordination mode in the lattices of **6** and **7**.

MOF **8** and **9** can be prepared as light yellow needle-shaped crystals in good yields from $M(NO_3)_3 \cdot 6H_2O$ (M = Eu in **8** and Tb in **9**) and H_2L_S solution under solvothermal conditions in DMF/H₂O. These two isostructural 3D coordination polymers

Published on 08 December 2010 on http://pubs.rsc.org | doi:10.1039/C0CE00750A Downloaded by Purdue University on 12 March 2013

> Selected bond lengths (Å) and angles (deg) of MOFs Table 2

2.395(5) 2.421(5) 2.421(5) 2.421(5) 2.421(5) 2.452(5) 2.452(5) 7.6.12(18) 76.12(18) 78.99(16) 78.99(16) 77.903(18) 77.903(18) 77.903(18) 73.52(17) 144.60(16) 73.52(17) 143.52(17) 143.52(17) 143.52(17) 143.52(17) 143.52(17) 143.52(17) 143.52(17) 143.52(17) 143.52(17) 143.52(17) 143.52(17) 143.52(17) 143.52(17) 143.52(17) 143.52(17) 143.52(17) 110.64(18) 75.59(18) 110.64(18) 75.53(17) 110.64(18) 75.53(17) 110.64(18) 75.53(17) 110.64(18) 75.53(17) 110.64(18) 75.53(17) 110.64(18) 75.53(17) 110.64(18) 75.53(17) 110.64(18) 75.53(17) 110.64(18) 75.53(17) 110.64(18) 75.53(17) 110.64(18) 75.53(17) 110.64(18) 75.53(17) 110.64(18) 75.53(17) 110.64(18) 75.53(17) 110.64(18) 75.53(17) 110.64(18) 75.53(17) 110.64(18) 75.53(17) 110.64(18) 75.53(17) 110.64(18) 75.53(18) 75 68.07(17) 51.04(16) 76.05(15) 76.05(15) 121.80(16) 127.17(16) 17.25(17) 2.371(5) 2.391(5) $\begin{array}{c} Tb(1)-O(7)\\ Tb(1)-O(8)\\ Tb(1)-O(8)\\ Tb(1)-O(4)\\ Tb(1)-O(6)\\ Tb(1)-O(6)\\ Tb(1)-O(1)\\ Tb(1)-O(1)\\ Tb(1)-O(3)\\ O(7)-Tb(1)-O(3)\\ O(7)-Tb(1)-O(3)\\ O(7)-Tb(1)-O(3)\\ O(7)-Tb(1)-O(3)\\ O(7)-Tb(1)-O(4)\\ O(7)-Tb(1)-Tb(1)-Tb(1)\\ O(7)-Tb(1)-Tb(1)-Tb(1)\\ O(7)-Tb(1)-Tb(1)-Tb(1)\\ O(7)-Tb(1)-Tb(1)-Tb(1)\\ O(7)-Tb(1)-Tb(1)-Tb(1)-Tb(1)\\ O(7)-Tb(1)-Tb(1)-Tb(1)\\ O(7)-Tb(1)-Tb$ $\begin{array}{c} 0(3, \mathbf{A}) - \mathrm{Tb}(1) - 0(4)\\ 0(7) - \mathrm{Tb}(1) - 0(6)\\ 0(8) - \mathrm{Tb}(1) - 0(6)\\ 0(3, \mathbf{A}) - \mathrm{Tb}(1) - 0(6)\\ 0(3, \mathbf{A}) - \mathrm{Tb}(1) - 0(6)\\ 0(7) - \mathrm{Tb}(1) - 0(1)\\ 0(3, \mathbf{A}) - \mathrm{Tb}(1) - 0(1)\\ 0(3, \mathbf{A}) - \mathrm{Tb}(1) - 0(1)\\ 0(3, \mathbf{A}) - \mathrm{Tb}(1) - 0(1)\\ 0(4) - \mathrm{Tb}(1) - 0(1)\\ 0(3, \mathbf{A}) - \mathrm{Tb}(1) - 0(1)\\ 0(3, \mathbf{A}) - \mathrm{Tb}(1) - 0(1)\\ 0(4) - \mathrm{Tb}(1) - 0(5)\\ 0(4) - \mathrm{Tb}(1) - 0(5)\\ 0(3, \mathbf{A}) - \mathrm{Tb}(1) - 0(5)\\ 0(4) - \mathrm{Tb}(1) - 0(5)\\ 0(4) - \mathrm{Tb}(1) - 0(5)\\ 0(4) - \mathrm{Tb}(1) - 0(5)\\ 0(3, \mathbf{A}) - \mathrm{Tb}(1) - 0(2)\\ 0(3, \mathbf{A}) - \mathrm{Tb}(1) -$ 0(3A)-Tb(1)-0(3) 0(4)-Tb(1)-0(3) 0(6)-Tb(1)-0(3) 0(6)-Tb(1)-0(3) 0(1)-Tb(1)-0(3) 0(5)-Tb(1)-0(3) 0(2)-Tb(1)-0(3) 6 $\begin{array}{c} 2.424(5)\\ 2.448(5)\\ 2.448(5)\\ 2.448(5)\\ 2.480(5)\\ 2.480(5)\\ 2.480(5)\\ 2.480(5)\\ 2.480(5)\\ 79.51(19)\\ 79.51(19)\\ 79.17(17)\\ 76.26(19)\\ 77.31(19)\\ 146.26(17)\\ 146.26(17)\\ 146.26(17)\\ 146.26(17)\\ 136.12(17)\\ 75.8(2)\\ 77.36(17)\\ 135.12(19)\\ 135.12(17)\\ 75.8(2)\\ 75.8(2)\\ 77.36(17)\\ 135.12(17)\\ 75.8(2)\\ 77.36(17)\\ 135.12(17)\\ 75.8(2)\\ 135.12(17)\\ 75.8(2)\\ 135.12(17)\\ 75.8(2)\\ 135.12(17)\\ 75.8(2)\\ 135.12(17)\\ 75.8(2)\\ 135.12(17)\\ 75.8(2)\\ 135.12(17)\\ 75.8(2)\\ 135.12(17)$ 99.3(2) 72.50(18) 2.418(5)2.424(5)2.390(5) O(4)-Eu(1)-O(6) O(3A)-Eu(1)-O(6) O(8)-Eu(1)-O(6) O(6)-Eu(1)-O(1) O(7)-Eu(1)-O(2) O(4)-Eu(1)-O(2) O(3A)-Eu(1)-O(2) O(4)-Eu(1)-O(1) O(3A)-Eu(1)-O(1) O(8)-Eu(1)-O(1) O(3A)-Eu(1)-O(8) O(7)-Eu(1)-O(6) O(7)-Eu(1)-O(3A) O(4)-Eu(1)-O(3A) O(7)-Eu(1)-O(8) O(4)-Eu(1)-O(8) O(7)-Eu(1)-O(1)Eu(1)-O(3) O(7)-Eu(1)-O(4) O(6)-Eu(1)-O(2)O(8)-Eu(1)-O(2) D(1)-Eu(1)-O(2) O(7)-Eu(1)-O(5)O(4)-Eu(1)-O(5)Eu(1)-O(7) Eu(1)-O(4) Eu(1)-O(3A) Eu(1)-O(6) Eu(1)-O(1) Eu(1)-O(2) Eu(1)-O(2) Eu(1)-O(5) Eu(1)-O(8)× 69.5(2) 71.0(2) 151.9(2) 82.21(18) 132.7(2) 73.4(2) 69.1(2) 69.1(2) 67.98(19) 67.98(19) $\begin{array}{c} 75.79(19) \\ 67.75(19) \\ 66.6(2) \\ 140.1(2) \\ 49.23(18) \\ 115.6(2) \end{array}$ $\begin{array}{c} 115.0(2) \\ 75.1(2) \\ 131.59(19) \end{array}$ 84.4(2) 78.0(2) 78.0(2) 73.7(2) 142.1(2) 1142.1(2) 1142.1(2) 1142.1(2) 1142.1(2) 1142.1(2) 1133.8(2) 1133.8(2) 72.5(2) 77.5(2) 77.1(2) 37.63(18) 66.11(18) 50.18(17) 139.4(2)118.0(2)38.69(17) 125.0(2) 116.8(2) $\begin{array}{c} 0(14) - Eu(1) - 0(7) \\ 0(10) - Eu(2) - 0(7) \\ 0(7) - Eu(2) - 0(2) \\ 0(7) - Eu(2) - 0(3) \\ 0(7) - Eu(2) - 0(3) \\ 0(7) - Eu(2) - 0(13) \\ 0(7) - Eu(2) - 0(15) \\ 0(7) - Eu(2) - 0(15) \\ 0(7) - Eu(2) - 0(12) \\ 0(7) - Eu(2) - 0(11) \\ 0(15) - Eu(2) - 0(1$ 0(2)-Eu(2)-0(4) 0(3)-Eu(2)-0(4) 0(15)-Eu(2)-0(4) 0(12)-Eu(2)-0(4) O(16)-Eu(2)-O(4) O(11)-Eu(2)-O(4) O(13) - Eu(1) - O(7)O(8)_Eu(1)_O(7) O(9)_Eu(1)_O(7) O(4)-Eu(1)-O(7) O(6)-Eu(1)-O(7) O(1)-Eu(1)-O(7) $\begin{array}{c} 2.424(6)\\ 2.455(6)\\ 2.455(6)\\ 2.455(6)\\ 2.455(6)\\ 2.2355(6)\\ 2.3355(6)\\ 2.3355(6)\\ 2.3355(6)\\ 2.3355(6)\\ 7.45(2)\\$ 86.24(19) 70.4(2) 70.9(2) 53.2(2) 01.9(2) 399(7) O(6)-Eu(1)-O(9) O(1)-Eu(1)-O(9) O(13)-Eu(1)-O(9) O(13)-Eu(1)-O(9) O(8)-Eu(1)-O(9) O(4)-Eu(1)-O(14) O(6)-Eu(1)-O(14) O(1)-Eu(1)-O(14) O(4)-Eu(1)-O(13) O(6)-Eu(1)-O(13) O(1)-Eu(1)-O(13) O(4)-Eu(1)-O(8) O(4)-Eu(1)-O(8) O(6)-Eu(1)-O(8) O(1)-Eu(1)-O(8) O(13)-Eu(1)-O(8) O(13)-Eu(1)-O(14) O(13)-Eu(1)-O(10) Eu(2)-O(16) Eu(2)-O(16) Eu(2)-O(11) Eu(2)-O(4) O(4)-Eu(1)-O(6) O(4)-Eu(1)-O(1) O(6)-Eu(1)-O(1) O(8)-Eu(1)-O(14) D(9)-Eu(1)-O(14) D(4)-Eu(1)-O(10) O(14) - Eu(1) - O(10)O(6)-Eu(1)-O(10) O(1)-Eu(1)-O(10) O(8)-Eu(1)-O(10) O(9)-Eu(1)-O(10) O(4)-Eu(1)-O(9) Eu(1)-O(10) Eu(1)-O(7) Eu(2)-O(15) Eu(2)-O(12) Eu(1)-O(13) Eu(1)-O(8) Eu(1)-O(14)Eu(2)-O(7) Eu(2)-O(5) Eu(2)-O(2) Eu(2)-O(3) Eu(1)-O(9) $\begin{array}{c} 123.63(12)\\ 79.12(13)\\ 80.96(14)\\ 79.39(13)\\ 76.19(15)\\ 138.19(15)\end{array}$ 143.64(15) 74.96(14) 136.09(13) 69.29(15) 146.46(13) 79.48(13) 79.48(13) 73.28(12) 73.28(12) 77.37(14) 100.09(14) $\begin{array}{c} 154.10(12)\\ 129.15(13)\\ 85.95(13)\\ 71.77(12)\\ 101.42(14) \end{array}$ 70.41(13) 52.84(13) 75.32(13) 64.90(12) 2.307(3) 2.322(3) 2.322(3) 2.325(4) 2.416(4) 2.416(4) 2.433(4) 2.450(4) 2.480(4) 2.851(3) 76.48(12) 77.23(12) 140.61(13) 86.13(13) 14.58(12) 16.19(12) 48.31(10) 37.35(12) 67.33(12) 40.68(12) 2.293(3) 0(4)-Tb(1)-0(3) 0(5)-Tb(1)-0(3) 0(6)-Tb(1)-0(3) 0(4)-Tb(1)-0(8) 0(5)-Tb(1)-0(8) 0(5)-Tb(1)-0(8) 0(3)-Tb(1)-0(8) 0(3)-Tb(1)-0(7) 0(3)-Tb(1)-0(7) 0(3)-Tb(1)-0(7) 0(3)-Tb(1)-0(1) 0(4)-Tb(1)-0(1) 0(4)-Tb(1)-0(1) 0(3)-Tb(1)-0(1) 0(3)-Tb(1)-0(1) 0(3)-Tb(1)-0(1) 0(3)-Tb(1)-0(1) 0(3)-Tb(1)-0(2) 0(3)-Tb(1)-0(2) 0(3)-Tb(1)-0(2) 0(4)-Tb(1)-0(2) 0(4)-Tb(1)-0(2 0(5)-Tb(1)-0(4A) 0(6)-Tb(1)-0(4A) 0(3)-Tb(1)-0(4A) D(8)-Tb(1)-O(4A) D(7)-Tb(1)-O(4A) 0(1)-Tb(1)-0(4A) 0(2)-Tb(1)-0(4A) Tb(1)-0(5) O(4)-Tb(1)-O(6) O(5)-Tb(1)-O(6) Tb(1)-O(4A) O(4)-Tb(1)-O Tb(1)-O(1) Tb(1)-O(2) Tb(1)-O(4) Tb(1)-O(5) [b(1)-0(7) [b(1)-0(3) $\Gamma b(1) - O(8)$ [b(1)-O(6)



Scheme 2 Synthesis of ligand H_2L_S (5).



Fig. 1 ORTEP drawings of **6**: (a) the coordination sphere of a Tb(III) center showing the tricapped trigonal prismatic coordination geometry; (b) the structure of a dinuclear node $[Tb_2L_{H3}(DMSO)_4]$ with the stilbene linkers reduced to the *ipso* carbons. The thermal ellipsoids are plotted at 50% probabilities. All hydrogen atoms are omitted for clarity.

both crystallized in the triclinic space group $P\overline{1}$. Compound 8 will be used as an example for structure descriptions below. Each Eu(III) center adopts a highly irregular coordination geometry with seven oxygen donor atoms from L_S^{2-} ligands, one oxygen donor atom from a DMF molecule, and one oxygen donor atom from a H₂O molecule occupying the nine coordination sites. Each Eu(III) center is linked with an adjacent Eu(III) center by two bridging oxygen atoms from two carboxylates, forming a di-Eu node as shown in Fig. 5. A similar di-Tb node found in 9 is shown in Fig. 5. There is a crystallographically imposed center of inversion at the centroid of each bimetallic node. Unlike the carboxylates in 6 and 7 which show three types of coordination



Fig. 2 The extended structure of 6: (a) a drawing of one set of 3D framework, projection along the *b* axis; (b) a space filling drawing showing the two interpenetrating frameworks, one in red and the other in blue. Hydrogen atoms and lattice solvent molecules are omitted for clarity.

modes, the carboxylates in 8 and 9 only show two types of coordination modes: the chelating mode (for 2/3 of the L_S^{2-} ligands) and the chelate-bridging mode (for 1/3 of the L_S^{2-} ligands). The bridging mode is not observed in 8 or 9. Most Eu-O and Tb-O bond lengths are in the ranges of 2.390(5)-2.480(5) Å and 2.371(5)-2.463(5) Å, respectively, except for those of Eu1-O3 and Tb1–O3 which are 2.648(5) and 2.653(5) Å, respectively, due to the unsymmetrical bridging of O3 in each case. In the crystal lattice, each bimetallic node is connected with six adjacent nodes via six organic linkers to form an infinite 3D framework (Fig. 6a). Compared to the $L_{H^{2-}}$ ligand, the $L_{S^{2-}}$ ligand has bulkier thioether substituents on the central CC double bond. Because MOFs 6 and 7 assembled with L_{H}^{2-} ligands display a 2-fold interpenetration, we expect no more than 2-fold of interpenetration in MOFs 8 and 9. To our surprise, 3-fold interpenetrating frameworks without any non-coordinating guest molecules were observed in both 8 and 9 (Fig. 6b). Calculation via PLATON program²³ shows no solvent accessible space, indicating that the addition framework has taken up all



Fig. 3 ORTEP drawings of 7: (a) the coordination sphere of a Eu(III) center showing the tricapped trigonal prismatic coordination geometry; (b) the structure of a dinuclear node $[Eu_2(L_H)_3(DMSO)_4]$. The thermal ellipsoids are plotted at 50% probabilities. All hydrogen atoms are omitted for clarity.

the space that is occupied by solvent molecules in MOFs 6 and 7. It appears that the introduction of the thioether side chains makes the inter-framework interactions stronger than the framework–solvent interactions.

Solvent inclusion and porosity

In MOFs **6–9**, the organic spacers and the bimetallic nodes assemble into approximately orthogonal skeletons. Each set of framework can also be viewed as an infinite assembly of 'cubes' defined by twelve organic spacers and eight bimetallic nodes. If the frameworks are viewed along the body diagonal direction of the 'cubes', triangular shaped channels can be seen (Fig. 7a). MOFs **6** and **7** have similar triangular shaped channels in which the lattice solvent molecules reside. Gas adsorption/desorption experiments on MOFs **6** and **7** show no porosity, presumably because the removal of solvents causes the structure to collapse. As shown in Fig. 7b, in the lattice of MOF **8** (**9** is similar to **8**) the thioether side chains fills the 'trigonal prismatic' space (along the *a* direction) defined by the stilbene skeletons completely. In addition, the 3-fold interpenetration makes the formation of



Fig. 4 The extended structure of 7: (a) a drawing of one set of 3D framework, projection along the c axis; (b) a space filling drawing showing the two interpenetrating frameworks, one in red and the other in blue. Hydrogen atoms and lattice solvent molecules are omitted for clarity.

channels perpendicular to the *a* direction impossible, leading to the non-porous structures (see Fig. S2, ESI^{\dagger}).

Although there is no solvent accessible space in MOF **8**, we envision that the removal of the coordinating solvents may create solvent accessible void space. The solvent removal can be achieved by heating the as-synthesized sample of **8** at 140 °C for 4 h. The resulting de-solvated sample displays little weight loss at 130–165 °C (Fig. S12b, ESI[†]) compared to as-synthesized **8** (Fig. S12a, ESI[†]), suggesting the removal of a significant amount



Scheme 3 Different coordination modes of carboxylate ligands.



Fig. 5 ORTEP drawings. M = Eu(8) or Tb (9). Thermal ellipsoids are plotted at 50% probabilities. All L_S^{2-} ligands are reduced to the carboxylic groups and an *ipso* carbon from the phenyl ring and all hydrogen atoms are omitted for clarity.

of solvents. Accordingly, the IR spectrum of the de-solvated **8** shows a significant decrease in intensities of the signals at 1661 cm⁻¹ (coordinating DMF molecules)^{24,25} and 3300 cm⁻¹ (broad peak from H₂O), compared to the as-synthesized **8** (Fig. S13, ESI†). When the de-solvated **8** is soaked in the mixture of DMF/



Fig. 6 Extended structures of **8** (or **9**): (a) one set of framework; (b) space filling drawing of three interpenetrating frameworks coated with different colors.



Fig. 7 Diagrams showing: (a) MOF 6, space filling model, projection down the a + b direction; lattice solvent molecules are omitted for clarity. (b) MOF 8, space filling model for the skeleton and stick model for the thioether functional groups, projection down the *a* direction.

H₂O ($\nu/\nu = 1 : 1$) overnight and then washed with ethanol and airdried, the resulting re-solvated **8** shows a weight loss at 120–165 °C in TGA (Fig. S12c, ESI[†]), similar to as-synthesized **8**. Correspondingly, the IR spectrum of the re-solvated **8** shows the recovery of the intensities of the signals at 1661 and 3300 cm⁻¹ (Fig. S13c, ESI[†]). Powder XRD experiments show that compound **8** remains crystalline after the solvent removal and reentry processes (Fig. S14, ESI[†]). Note that the crystals are insoluble in a DMF/H₂O mixture even at 120 °C and therefore the dissolution/recrystallization possibility during the soaking process at room temperature can be ruled out.

Thermogravimetric analysis

Thermal gravimetric analysis (TGA) of MOFs **6** and **7** (Fig. S3, ESI†) shows that the loss of coordinating and lattice DMSO solvent molecules starts at ambient temperature and reaches completion at around 250 °C. The plateau between 130 and 200 °C is calculated to be $[M_2(L_H)_3(DMSO)_2]$, partially de-solvated MOFs. After the complete removal of solvent molecules, the remaining solid are stable up to 550 °C without weight loss. At 550–600 °C, the weight loss can be attributed to the decomposition of the ligand, which is supported by the identical

decomposition temperature displayed by Na₂L_H (Fig. S5, ESI†). According to TGA, the compositions of sample **6** and **7** were calculated to be $[Tb_2(L_H)_3(DMSO)_4] \cdot 8DMSO$ and $[Eu_2(L_H)_3(DMSO)_4] \cdot 14DMSO$ respectively, which correspond well with the elementary analysis results.

TGA of MOF 8 and 9 (Fig. S4, ESI[†]) showed a first weight loss of ~11% at 130–165 °C, which is attributed to the complete removal of coordinating H₂O and DMF molecules. After that, the loss of the ligand proceeds in a stepwise fashion as the temperature rises slowly.

Luminescence properties

The photoluminescence excitation and emission spectra of MOFs **6–9** are shown in Fig. S15 (ESI[†]). Both **6** and **7** show broad ligand-based emission between 420 and 490 nm with the emission maximum at 447 nm (Fig. S15a and b, ESI[†]), which are similar to the luminescence spectrum of the free ligand H_2L_H (Fig. S6, ESI[†]).

The emission of compound 8 (Fig. S15c, ESI[†]) consists of both the ligand-based and metal-based luminescence. The sharp lines at 393, 464 and 535 nm in the excitation spectrum can be assigned to the metal-centered transitions ${}^{7}F_{0,1} \rightarrow {}^{5}L_{6}$, ${}^{7}F_{0,1} \rightarrow {}^{5}D_{2}$, ${}^{7}F_{0,1}$ \rightarrow ⁵D₁, respectively. The weak broad band centered at \sim 370 nm in the excitation spectrum can be attributed to the ligand-based excitation. The sharp emission peaks at 579, 591, 615, and 696 nm in the emission spectrum are characteristic Eu-centered transitions ${}^{5}D_{0}-{}^{7}F_{0}$, ${}^{5}D_{0}-{}^{7}F_{1}$, ${}^{5}D_{0}-{}^{7}F_{2}$, and ${}^{5}D_{0}-{}^{7}F_{4}$ respectively. When 393 nm is used as the excitation wavelength, at which an intense metal-centered excitation and a weak ligand-centered excitation co-exist, the ligand-based emission can be observed as a weak broad band centered at around 490 nm, along with intense Eu-based emissions. To examine whether LMET contributes to the Eu-based emissions, a second emission spectrum (emission (ii) in Fig. S15c, ESI[†]) was recorded with 350 nm excitation wavelength, at which only ligand-based absorption occurs. The resulting emission spectrum shows not only the ligand-based emission, but also the characteristic Eu emissions with relatively low intensity compared to the ligand-based emission, indicating the occurrence of LMET at low efficiency. Compound 9 (Fig. S15d, ESI[†]) shows broad ligand-based excitation and emission at 350-450 nm, 475-600 nm respectively, while the direct f-f transition of Tb³⁺ happens under 487 nm excitation (${}^{7}F_{6}-{}^{5}D_{4}$) and the emission peaks at 542 nm, 584 nm, 620 nm on emission (ii) can be assigned to ${}^{5}D_{4}-{}^{7}F_{5}$, ${}^{5}D_{4}-{}^{7}F_{4}$, ⁵D₄-⁷F₃, respectively. Preliminary luminescent response tests were carried out by measuring the luminescence spectrum of desolvated compound 8 soaked in HgCl₂ solution in THF and CdCl₂ aqueous solution. No significant luminescence signal change has been observed.

Conclusions

We have designed and synthesized a new ligand with thioether side chain, and successfully assembled both non-functionalized L_{H}^{2-} and functionalized L_{S}^{2-} ligand into luminescent 3D MOFs **6–9** with lanthanide metal ions. MOFs **6**, **7**, and **9** display ligandbased luminescence, while MOF **8** showed both ligand-based and Eu-centered luminescence. The structures of MOFs **6** and **7** closely resemble Yaghi's [Tb2(ADB)3(DMSO)4] · 16DMSO (where ADB = 4,4'-azodibenzoate). The skeletons of MOFs 8 and 9 define similar trigonal prismatic space as seen in 6 and 7. However, the thioether functional groups fill the space completely and the 3-fold interpenetration prevents the formation of channels along other directions, making the as-synthesized 8 and 9 non-porous. The coordiating DMF and H_2O solvents in 8 and 9 can be removed by heating. Such solvent removal can be reversed by soaking the desolvated crystals in a DMF and H₂O mixture. The desolvated crystals of 8 show no significant luminescent property change upon exposure to heavy metal ions. The formation of the 3-fold interpenetration in 8 and 9 are likely for thermal dynamic reasons, *i.e.*, the interframework interactions are stronger than framework-solvent interactions. By changing the size, number, or nature of the functional groups on the ligands and solvents, we may potentially create some extra space in the resulting MOFs. Finally, the installation of thioether side chains enables the LMET and thus enhances Eu-based luminescence. This effect could be attributed at least partly to the steric bulk provided by the side chains, which prevents the ligand from being coplanar and in turn, alters the ligand energy levels.

Acknowledgements

This research is supported by grants to D.S. from the Natural Science and Engineering Research Council (NSERC) of Canada, the Ontario Ministry of Research and Innovation. We thank Winnik group for sharing instruments and Meng Zhang for the assistance on photoluminescence measurements.

References

- 1 L. J. Murray, M. Dincă and J. R. Long, *Chem. Soc. Rev.*, 2009, 38, 1294–1314.
- 2 R. Zou, A. I. Abdel-Fattah, H. Xu, Y. Zhao and D. D. Hickmott, *CrystEngComm*, 2010, **12**, 1337–1353.
- 3 J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477–1504.
- 4 (a) B. Chen, Y. Yang, F. Zapata, G. Lin, G. Qian and E. B. Lobkovsky, Adv. Mater., 2007, **19**, 1693–1696; (b) Y. Xiao, Y. Cui, Q. Zheng, S. Xiang, G. Qian and B. Chen, Chem. Commun., 2010, **46**, 5503–5505; (c) B. Chen, L. Wang, Y. Xiao, F. R. Fronczek, M. Xue, Y. Cui and G. Qian, Angew. Chem., Int. Ed., 2009, **48**, 500–503; (d) B. Chen, L. Wang, F. Zapata, G. Gian and E. B. Lobkovsky, J. Am. Chem. Soc., 2008, **130**, 6718–6719; (e) B. Chen, S. Xiang and G. Qian, Acc. Chem. Res., 2010, **43**, 1115–1124.
- 5 B. V. Harbuzaru, A. Corma, F. Rey, J. L. Jordá, D. Ananias, L. D. Carlos and J. Rocha, *Angew. Chem.*, *Int. Ed.*, 2009, **48**, 6476– 6479.
- 6 B. Zhao, X.-Y. Chen, P. Cheng, D.-Z. Liao, S.-P. Yan and Z.-H. Jiang, J. Am. Chem. Soc., 2004, **126**, 15394–15395.
- 7 W.-G. Lu, L. Jiang, X.-L. Feng and T.-B. Lu, *Inorg. Chem.*, 2009, 48, 6997–6999.
- 8 Z. Xie, L. Ma, K. E. deKrafft, A. Jin and W. Lin, J. Am. Chem. Soc., 2010, 132, 922–923.
- 9 J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450–1459.
- L. Ma, C. Abney and W. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248–1256.
 O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi
- and J. Kim, *Nature*, 2003, **423**, 705–714.
 12 J. J. Perry IV, J. A. Perman and M. J. Zaworotko, *Chem. Soc. Rev.*, 2009, **38**, 1400–1417.
- 13 D. J. Tranchemontagne, J. L. Mendoza-Cortés, M. O'Keeffe and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, 38, 1257–1283.

- (a) H. Deng, C. J. Doonan, H. Furukawa, R. B. Ferreira, J. Towne, C. B. Knobler, B. Wang and O. M. Yaghi, *Science*, 2010, 327, 846– 850; (b) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, 404, 982–986; (c) S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita and S. Kitagawa, *J. Am. Chem. Soc.*, 2007, 129, 2607–2614; (d) S. Horike, S. Bureekaew and S. Kitagawa, *Chem. Commun.*, 2008, 471–473.
- 15 Z. Wang and S. M. Cohen, *Chem. Soc. Rev.*, 2009, **38**, 1315–1329. 16 T. M. Reineke, M. Eddaoudi, D. Moler, M. O'Keeffe and
- O. M. Yaghi, J. Am. Chem. Soc., 2000, 122, 4843–4844.
 17 B. T. Nguyen Pham, L. M. Lund and D. Song, Inorg. Chem., 2008, 47,
- 6329–6335.
 18 (a) C. A. Bauer, T. V. Timofeeva, T. B. Settersten, B. D. Patterson, V. H. Liu, B. A. Simmons and M. D. Allendorf, J. Am. Chem. Soc., 2007, 129, 7136–7144; (b) J. Yang, J.-F. Ma, S. R. Batten and Z.-M. Su, Chem. Commun., 2008, 2233–2235; (c) F. P. Doty, C. A. Bauer, A. J. Skulan, P. G. Grant and M. D. Allenforf, Adv.

Mater., 2009, **21**, 95–101; (*d*) J. Yang, J.-F. Ma, Y.-Y. Liu and S. R. Batten, *CrystEngComm*, 2009, **11**, 151–159; (*e*) L. Zhang, Y.-L. Yao, Y.-X. Che and J.-M. Zheng, *Cryst. Growth Des.*, 2010, **10**, 528–533.

- 19 J. E. McMurry, M. P. Fleming, K. L. Kees and L. R. Krepski, J. Org. Chem., 1978, 43, 3255–3266.
- 20 J. Liu, J. Chen and C. Xia, J. Catal., 2008, 253, 50-56.
- 21 Apex 2 Software Package; Bruker AXS inc., 2008.
- 22 G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112–122.
- 23 (a) A. L. Spek, *Acta Crystallogr.*, 1990, **A46**, C34; (b) A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2000.
- 24 S. Viswanathan and A. de Bettencourt-Dias, *Inorg. Chem.*, 2006, 45, 10138–10146.
- 25 D. C. Wilson, S. Liu, X. Chen, E. A. Meyers, X. Bao, A. V. Prosvirin, K. R. Dunbar, C. M. Hadad and S. G. Shore, *Inorg. Chem.*, 2009, 48, 5725–5735.