The effect of the conformation of flexible carboxylate ligands on the structures of metal–organic supramolecules†‡

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Three flexible bent dicarboxylate ligands, 2,2′-(2,3,5,6-tetramethyl-1,4-phenylene)-bis(methylene)bis(sulfanediyl)dibenzoic acid (H_2L^1), 2,2′-(1,4-phenylenebis(methylene))-bis(sulfanediyl)dibenzoic acid (H_2L^9) and 2,2′-(2,3,5,6-tetramethyl-1,4-phenylene)bis-(methylene)bis(oxy)dibenzoic acid (H_2L^{10}), have been designed and synthesized. The positions of the functional substituents are in 1,4-positions of the central benzene ring, and all the ligands can adopt *syn* and *anti* conformations. By applying these flexible ligands to assemble with thulium ions or zinc ions, three metal–organic supramolecules with metallamacrocycles or 1D chains have been isolated. L^1 adopts a *syn* conformation in complex **1**, leading to a 0D metallamacrocycle, L^9 in complex **2** adopts an *anti* conformation to form a 1D "rainbow-like" chain while L^{10} in complex **3** adopts both *syn* and *anti* conformations. L^{10} in a *syn* conformation connects $Zn_4(OH)_2(CO_2)_4$ SBU to form a 0D metallamacrocycle, which is further connected by the ligand in an *anti* conformation to generate a 1D coordination polymer.

Introduction

The rational design and synthesis of metal–organic frameworks (MOFs) with various configurations or multi-dimensional open frameworks has attracted much attention from chemists due to their interesting structural topologies and potential applications in catalysis, separation and gas storage, *etc*.[1–3] In general, the starting materials, such as in the conformation of the organic ligand, can determine the structure of the final product. Hence, it is possible to predict the final structure when some simple ligands are used, especially for rigid and small ligands.[4] In contrast to rigid ligands with single conformations, flexible ligands may adopt several kinds of conformation when they coordinate to metal ions, complicating the prediction of the final products.[5]

The difficulty of structural prediction has probably stimulated researchers' interests in the design and synthesis of MOFs employing flexible ligands to explore the relationships between the conformation of the ligand and the final structure.[6] On the other hand, flexible ligands in the construction of MOFs may generate novel complexes with interesting topologies and attractive properties. In particular, Allendorf *et al.*[7] have reported the design and synthesis of luminescent stilbene-based

MOFs. Tong *et al.*[8] have synthesized nanoscale cages based on conformationally-flexible cyclohexanehexacarboxylate. Zheng, Batten and Hong *et al.*[9] have reported new compounds built from long flexible multicarboxylate ligands and tested their physical properties, respectively. One of the hot topics is to study the effect of the conformation of flexible ligands, *syn* or *anti*, on structural topologies.[10,11]

Recently, we have designed a series of flexible bent dicarboxylate ligands[12] for the construction of discrete cages or cage-containing MOFs, in which the flexible bent dicarboxylate ligands are apt to adopt a *syn* conformation. Both *syn* and *anti* conformations co-existing in one complex are still rare in the reported work.

In this paper, we focus our attention on the construction of metal–organic supramolecules based on flexible dicarboxylate ligands and study the effect of their conformation on the final structures of the products. Three ditopic ligands possessing –CH_2–S– spacers or –CH_2–O– spacers, which endow flexibility to the whole ligand, have been applied in this work. By the self-assembly of these ligands with metal ions, three metal–organic supramolecules, $Tm_2(L^1)_2(dmf)_4(NO_3)_2$(**1**), $[Zn(L^9)(phen)]\cdot4H_2O$ (**2**) and $[Zn_4(L^{10})_3(\mu_3\text{-}OH)_2(H_2O)_2]\cdot2H_2O\cdot2EtOH$ (**3**) have been isolated, with the 0D metallamacrocycle of **1** based on a *syn*-L^1 ligand, the 1D "rainbow-like" zig-zag chain of **2** based on an *anti*-L^9 ligand and the 1D $Zn_4(OH)_2(CO_2)_4$-based chain of **3** based on both *syn*- and *anti*-L^{10} ligands (Scheme 1).

Results and discussion

Syntheses

As mentioned above, the conformation of the organic ligand plays important roles in the final architecture. We have studied

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† This article is part of a themed issue on Coordination polymers: structure and function.
‡ Electronic supplementary information (ESI) available: Structural figures and TGA data for complexes **1–3**. CCDC 775311–775313. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0nj00328j
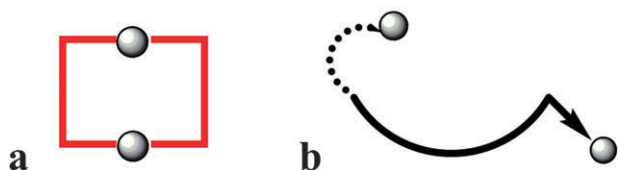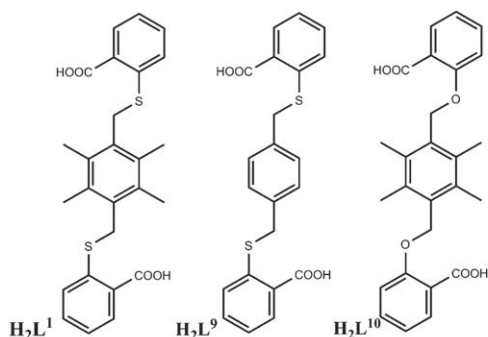
Scheme 1 The flexible carboxylate ligands used in this work and the subunits (a, b) formed by flexible ligands with a *syn*-conformation (red) and an *anti*-conformation (black).

the relationships between the conformation of the ligand and the structure of the final product when the positions of the functional substituents are changed from 1,2- and 1,3- to the 1,4-positions of the central benzene ring, providing different geometries of the carboxylate ligands.[12b] In this work, we focus our attention on introducing functional groups into the 1,4-positions due to its minimal steric hindrance. The organic ligands were synthesized according to the literature.[13] In different conditions, a 1,4-substituted ligand coordinating with appropriate coordination geometry metal ions will give plentiful frameworks, such as 0D discrete molecules or 1D supramolecular chains by adopting *syn*- or *anti*-conformations (Scheme 2). By the self-assembly of flexible dicarboxylate ligands with thulium ions or zinc ions, three metal–organic supramolecules have been synthesized.

Metallamacrocycle of complex 1. Single-crystal X-ray diffraction reveals that complex **1** is a rectangular macrocycle made up of two L^1 ligands and two thulium ions. The asymmetric unit of **1** consists of one thulium ion, one L^1 ligand, two coordinated dmf molecules and one coordinated nitrate ion. There is only half a complex in the asymmetry unit, the other part is generated by an inversion centre. The central Tm ion, which lies about an inversion centre, is eight-coordinated by four oxygen atoms from two L^1 ligands, four oxygen atoms
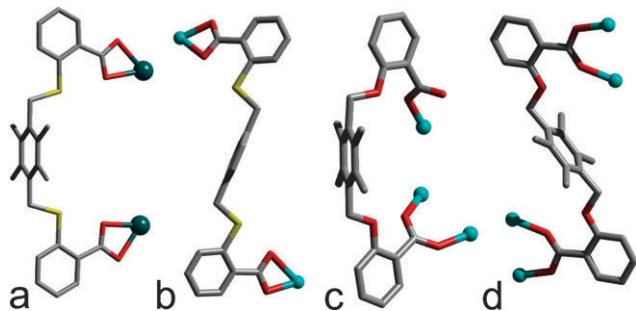
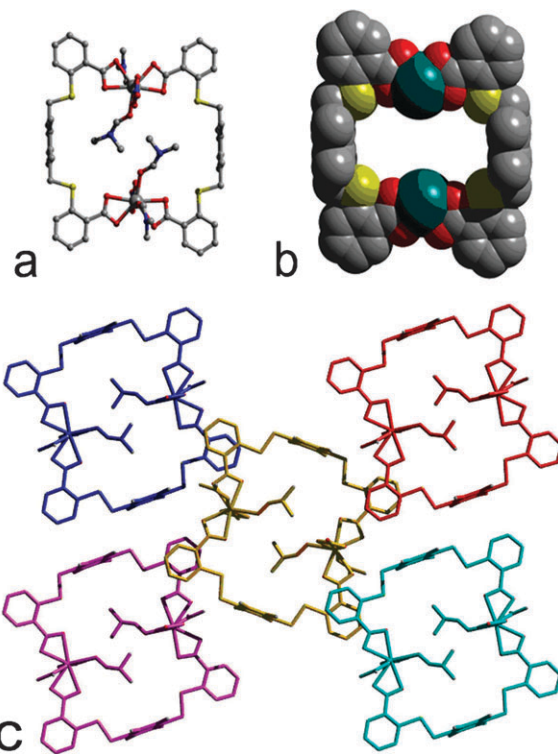
Scheme 2 The *syn* and *anti* conformations of ligands **1–3**.

from two coordinated dmf molecules and one coordinated nitrate ion with an average Tm–O distance of 2.326 Å. Both carboxylate groups of the L^1 ligand adopt a chelating mode to connect one Tm ion. The average dihedral angle between the side benzene ring and the central benzene ring is 89.8°.

Thus, two Tm ions are connected by two L^1 ligands to generate a rectangular metallamacrocycle with dimensions of 13.40 × 8.61 Å (Fig. 1a and b). The remaining coordination sites of the Tm ion are occupied by coordinated solvates and the NO_3^- anion to prevent further extension. The metallamacrocycles are further connected to one another through π···π interactions between the side benzene rings of L^1 ligands in different molecules to generate a 2D layer (Fig. 1c). Each metallamacrocycle connects four adjacent metallamacrocycles through π···π interactions. If the metallamacrocycles are considered as nodes and the π···π interactions between the two benzene rings are considered as linkers, then the 2D layer possesses a (4, 4) net.

In complex **1**, the flexible L^1 ligand adopts a *syn* conformation to coordinate the metal ions (Scheme 2a), providing a rectangular metallamacrocycle. However, if the flexible ligand adopted an *anti* conformation or a mixture of *syn* and *anti* conformations, what kind of structure would result?

Fortunately, when we used other analogous ligands to assemble with transition metal ions, compounds containing an *anti* conformation or both *syn* and *anti* conformations of the ligands were isolated.

1D "rainbow-like" zigzag chain (2). Single-crystal X-ray diffraction measurements reveal that complex **2** crystallizes in the monoclinic $P2_1/c$ space group. The asymmetric unit of **2**
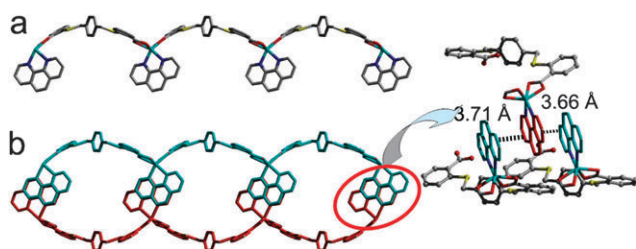

Fig. 1 (a) and (b): The rectangular metallamacrocycle of **1**. (c): The 2D layer formed by π···π interactions.

Fig. 2 (a) The 1D "rainbow-like" chain of complex **2** along the *a* axis; (b) the 2D supramolecular layer formed by π···π interactions between chains.

consists of one zinc ion, one L^9 ligand and one phen molecule. The central zinc ion in **2** is six-coordinated by four oxygen atoms from two different L^9 ligands and two nitrogen atoms from one chelating phen molecule. Both carboxylate groups of L^9 are deprotonated during the reaction and adopt a bidentate chelating mode to chelate one zinc ion.

The L^9 ligand adopts an *anti* conformation with dihedral angles between the central benzene ring and the side benzene rings of 59.5 and 69.5°; the dihedral angle between the two side benzene rings is 52.46°. Thus, the whole ligand acts as a bridging linker to connect zinc ions from opposite sides into 1D "rainbow-like" zig-zag chains (Fig. 2a), in which all the zinc ions are in exactly a linear arrangement with the phen molecules hanging in the same side of the line.

The strong π···π interactions between the coordinated phen molecules in different chains further connects the 1D zig-zag chains to form a 2D layer containing large 1D channels (Fig. 2b). The dimensions of the 1D channels are 10.8×8.8 Å, in which the uncoordinated water molecules reside, as shown in Fig. 3.

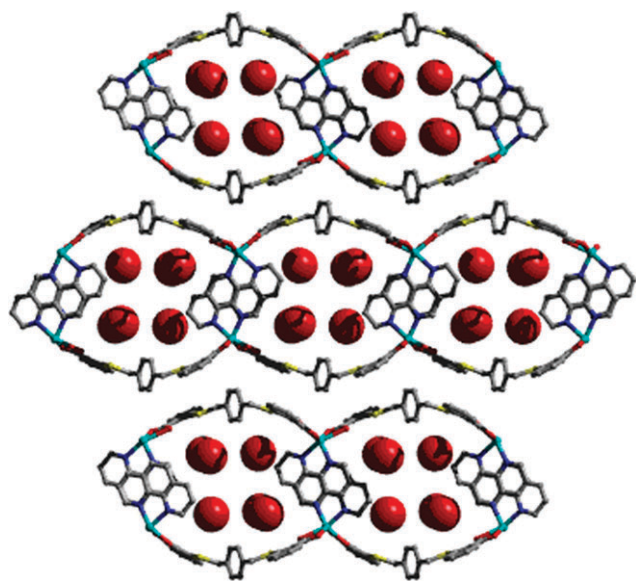**1D chain based on tetranuclear SBU (3).** X-Ray diffraction reveals that **3** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit possesses two crystallographically-independent zinc ions (Zn1 and Zn2), one and a half L^{10} carboxylate ligands, one μ_3-OH and one coordinated water molecule. The half L^{10} ligand in the asymmetric unit lies about an inversion centre. Zn1 is coordinated by three carboxyl oxygen atoms and one bridging OH$^-$ group in a tetrahedral geometry with an average Zn–O distance of 1.935(7) Å. Zn2 is coordinated by two carboxyl oxygen atoms, one terminal water molecule and two bridging OH$^-$ groups in a triangle bipyramidal geometry, giving an average Zn–O distance of 2.041(6) Å.

Different from complexes **1** and **2** mentioned above, there are two kinds of conformation of the L^{10} ligand in complex **3**. The two carboxylate groups of the *syn*-L^{10} ligand possess different coordination modes: one adopts a bidentate bridging mode to connect two zinc ions, while the other adopts a monodentate coordination mode to link one zinc ion (Scheme 2c). Both carboxylate groups of the *anti*-L^{10} ligand adopt a bidentate bridging mode to link two zinc ions, as shown in Scheme 2d. Thus, Zn1 and Zn2 are engaged by two bridging OH$^-$ groups and four carboxylate groups (two from *syn*-L^{10} and two from *anti*-L^{10}) to form a tetranuclear planar SBU, $Zn_4(OH)_2(CO_2)_4$ (Fig. 4a) that is quite different from the $Zn_4O(CO_2)_6$ cluster[14] but is similar to the reported $Cu_4(OH)_2(CO_2)_4$ SBU.[15] The tetranuclear SBUs are further connected by *anti*-L^{10} along the *b* axis to generate a 1D chain with the nearest Zn–Zn distance in different SBUs being 10.23 Å.

The *syn*- and *anti*-L^{10} ligands play different roles in the formation of the 1D chain structure: the *syn*-L^{10} ligands only connect zinc ions to form the tetranuclear SBU, while the *anti*-L^{10} ligands not only take part in the formation of the SBU, but also further link the SBU to form 1D chains.

Fig. 3 (a) The 3D packing structure of complex **2** along the *c* axis showing the uncoordinated water molecules locating in the 1D channels.
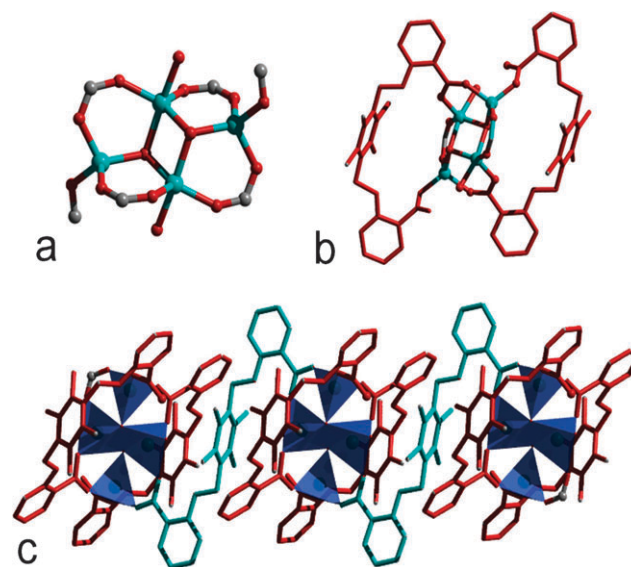

Fig. 4 (a) The $Zn_4(OH)_2(CO_2)_4$ SBU in complex **3**; (b) the *syn*-conformational L^{10} ligand in the SBU; (c) the 1D chain structure formed by the *anti*-conformational L^{10} ligand (blue) connecting the tetranuclear SBU.

Thermogravimetric analysis

Thermogravimetric analyses have been undertaken for complexes **1–3**. A TGA study on an as-isolated crystalline sample of **1** showed a 17.74% weight loss from 50 to 300 °C, corresponding to the loss of two coordinated dmf molecules (calc.: 17.8%). The second gradual weight loss of 6.85% from 300 to 355 °C corresponded to the loss of one coordinated NO_3^- ion (calc.: 7.6%). After 355 °C, **1** started to decompose. For complex **2**, there was a slow weight loss of 9.92% from 50 to 170 °C, in accordance with the loss of four uncoordinated water molecules (calc.: 9.84%). After that, **2** started to decompose. For complex **3**, there was a slow weight loss of 5.89% from 100 to 155 °C, corresponding to the loss of one uncoordinated EtOH molecule (calc.: 5.1%). The complex was stable up to 220 °C, after which it started to decompose.

Conclusion

By employing 1,4-substituted flexible dicarboxylate ligands to assemble with thulium ions and zinc ions, three metal–organic supramolecules were constructed. In complex **1**, the **L**[1] ligand adopts a *syn* conformation, which is the key to forming a 0D metallamacrocycle. The *anti* conformation of the **L**[9] ligand in complex **2** results in the formation of a 1D "rainbow-like" chain structure. The mixed conformations (*syn* and *anti*) of the **L**[10] ligands play an important role in the formation of the tetranuclear SBU and 1D chain in complex **3**. Our research further indicates that the conformation (*syn* and *anti*) of the ligands has a significant effect on the structure of the complexes (Scheme 3). The difference between the conformations is that *syn* is convergent and *anti* is divergent, so the former produces closed systems, while the latter leads to polymerisation. The *syn*-**L** ligand is apt to generate zero-dimensional structures, such as the metallamacrocycle in complex **1**, while the *anti*-**L** ligand is apt to forming extending frameworks, such as the 1D chain structures in complexes **2** and **3**. Further studies will focus on the design and synthesis of novel frameworks by controlling the conformation of the flexible carboxylate ligands.
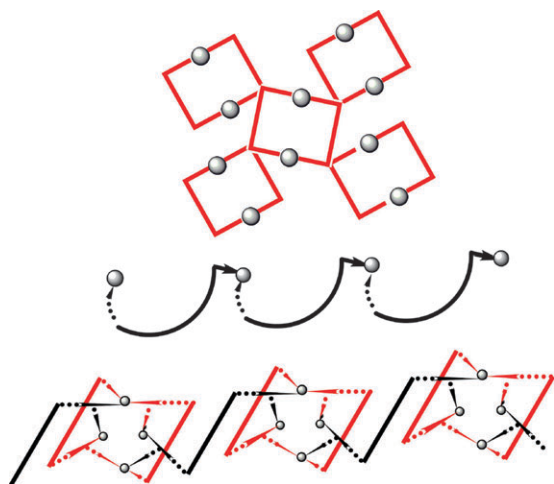
Scheme 3 Schematic representations of metallamacrocycle, "rainbow" chain and 1D chain based on tetranuclear clusters.

Experimental

Synthesis of H₂L¹

Sodium methoxide (1.62 g, 30 mmol) was dissolved in absolute methanol (200 mL) and cooled to room temperature. 2-Metcaptobenzoic acid (4.63 g, 30 mmol) was then added with stirring, and the stirring was continued for 10 min. To the resulting suspension was added 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene (3.2 g, 10 mmol) and the reaction mixture was stirred under reflux for 6 h. The solid was filtered while still hot, dissolved in water and filtered to remove any undissolved substance. The filtrate was acidified with dilute hydrochloric acid, and the precipitates were filtered, washed with water and hot methanol. Yield: (2.09 g, 45%). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.23 (s, 12 H), 4.66 (s, 4 H), 6.98–7.10 (m, 4 H), 7.18–7.23 (m, 4 H).

Synthesis of H₂L⁹

H_2L^9 was prepared by a similar route to H_2L^1 using 1,4-bis(bromomethyl)benzene (2.64 g, 10 mmol) instead. Yield: (2.46 g, 60%). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 4.19 (s, 2 H), 7.2–7.9 (m, 4 H), 13.05(s, 1 H).

Synthesis of H₂L¹⁰. A mixture of 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene (3.2 g, 10 mmol), methyl salicylate (3.08 g, 22.0 mmol) and K_2CO_3 (3.04 g, 22 mmol) in 40 mL acetone was reflux for 6 h. The reaction mixture was filtered while it was still hot, then cooled to room temperature and a white precipitate formed. The white solid and an NaOH aqueous solution (20 mL, 2 mol L^{-1}) were mixed in 30 mL of methanol and stirred for 8 h under reflux. After cooling to room temperature, the clear solution was acidified to pH 2 by diluted hydrochloric acid. The resulting white precipitate was washed with water and dried in the air to give H_2L^{10}, yield: (1.3 g, 30%). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.25 (s, 6 H), 5.14 (s, 2 H), 7.04 (t, 1 H), 7.38 (d, 1 H), 7.52 (m, 2 H), 12.50 (s, 1 H).

Preparation of Tm₂(L¹)2(dmf)₄(NO₃)₂ (1)

$Tm(NO_3)_2 \cdot 6H_2O$ (0.01 g), H_2L^1 (0.01 g, 0.0214 mmol) and perchloric acid (01 d) in 1 mL mixed solvents of DMF, EtOH and H_2O (v/v = 5 : 2 : 1) were dissolved and heated in a sealed tube at 90 °C for 2 d. Crystals of **1** were obtained (yield: 0.023 g, 65% based on H_2L^1). Elemental anal. calc. for **1**: C, 45.71; H, 4.436; N, 4.998%; Found: C, 45.64; H, 4.641; N, 4.627%.

Preparation of [Zn(L⁹)(phen)]·4H₂O (2)

$Zn(NO_3)_2 \cdot 6H_2O$ (0.01 g, 0.034 mmol), H_2L^9 (0.01 g, 0.0243 mmol) and phen (0.01 g, 0.055 mmol) were dissolved in a 10 mL mixture of DMF, EtOH and H_2O (v/v = 5 : 2 : 1) and heated in a sealed tube at 90 °C for 33 h. The resulting colourless crystals were collected in 60% yield (0.01 g) on the basis of H_2L^9. Elemental anal. calc. for **2**: C, 56.54; H, 3.90; N, 3.88%; Found: C, 56.85; H, 4.08 N, 3.55%.

Preparation of [Zn₄(L¹⁰)₃(OH)₂(H₂O)₂]·2H₂O·2EtOH (3)

$Zn(NO_3)_2 \cdot 6H_2O$ (0.01 g, 0.034 mmol), H_2L^{10} (0.01 g, 0.023 mmol) and NEt_3 (1 d) in a 10 mL mixture of DMF,

EtOH and H_2O (v/v = 5 : 2 : 1) was placed in a test tube at room temperature. Colourless crystals of **3** suitable for X-ray analysis were obtained at the bottom of the tube after a few days (yield: 0.0149 g, 35% based on H_2L^{10}). Elemental anal. calc. for **3**: C, 56.24; H, 5.065%. Found: C, 55.59; H, 4.914%.

Crystal structure determinations

Crystallographic data for **1**–**3** were collected on a Bruker Smart APEXII CCD diffractometer with Mo-K$_\alpha$ radiation (λ = 0.71073 Å) at room temperature. All structures were solved by the direct method using the SHELXS program of the SHELXTL package and refined by the full-matrix least-squares method with SHELXL.[16] The metal atoms in each complex were located from the E-maps, and other non-hydrogen atoms located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. The organic hydrogen atoms were generated geometrically (C–H 0.96 Å). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center: 775311 for **1**, 775312 for **2** and 775313 for **3**.‡

Crystal data for **1**: $C_{64}H_{76}N_6O_{18}S_4Tm_2$, M = 1683.41, monoclinic, space group $P2_1/n$, a = 9.0709(7), b = 17.7102(13), c = 21.7080(16) Å, β = 100.6210(10), U = 3427.6(4) Å^3, Z = 2, D_c = 1.631 Mg m^{-3}, μ(Mo-K$_\alpha$) = 0.71073 mm^{-1}, T = 298 K, 19 610 reflections collected. Refinement of 7659 reflections (488 parameters) with $I > 2\sigma(I)$ converged at final R_1 = 0.0339 (R1 all data = 0.0663), wR_2 = 0.0730 (w$R2$ all data = 0.0853), gof = 1.009.

Crystal data for **2**: $C_{34}H_{28}N_2O_6S_2Zn$, M = 694.04, monoclinic, space group $P2_1/c$, a = 7.8023(6), b = 31.614(2), c = 15.2690(12) Å, β = 103.204(2), U = 3666.7(5) Å^3, Z = 4, D_c = 1.243 Mg m^{-3}, μ(Mo-K$_\alpha$) = 0.71073 mm^{-1}, T = 298 K, 15 623 reflections collected. Refinement of 5253 reflections (426 parameters) with $I > 2\sigma(I)$ converged at final R_1 = 0.0758 (R1 all data = 0.1088), wR_2 = 0.2053 (w$R2$ all data = 0.2316), gof = 1.031.

Crystal data for **3**: $C_{39}H_{41}O_{12}Zn_2$, M = 832.46, triclinic, space group $P\bar{1}$, a = 12.2854(19), b = 13.199(2), c = 14.514(2) Å, α = 66.739(2), β = 65.433(3), γ = 63.684(2), U = 1853.5(5) Å^3, Z = 2, D_c = 1.492 Mg m^{-3}, μ(Mo-K$_\alpha$) = 0.71073 mm^{-1}, T = 298 K, 11 030 reflections collected. Refinement of 8032 reflections (498 parameters) with $I > 2\sigma(I)$ converged at final R_1 = 0.00548 (R1 all data = 0.1180), wR_2 = 0.1036 (w$R2$ all data = 0.1293), gof = 0.988.

Acknowledgements

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