Design and synthesis of a near infra-red luminescent hexanuclear Zn–Nd prism†

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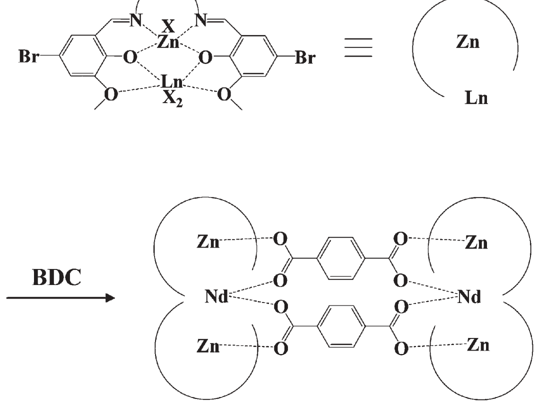
The use of the Schiff-base ligand *N*,*N*′-bis(5-bromo-3-methoxysalicylidene)propylene-1,3-diamine (H_2L) and 1,4-benzenedicarboxylate (BDC) enables the construction of the hexanuclear luminescent Zn–Nd complex $[Zn_4Nd_2L_4(1,4\text{-}BDC)_2]\cdot[Nd(NO_3)_5(H_2O)]\cdot Et_2O\cdot 2EtOH\cdot 3H_2O$.

Self-assembly processes involving metal–ligand coordination with organic ligands are often used for the construction of d-block transition metal based macrocycles, cages, polyhedra and metal–organic framework (MOF) materials.[1] Many new compounds have been realized using this approach which employs nitrogen-containing heteroaryls, cyano-substituted aromatic ligands, *o*-catecholamides, hydroxamates and phosphorus-containing ligands.[2] Recent interest has also focused on the development of heteropolynuclear systems containing both d-block metals as well as lanthanide(III) ions because of their potential application in catalysis, magnetism and novel molecular devices.[3] However, control over the stoichiometries and structures of higher nuclearity lanthanide complexes is synthetically challenging due to the difficulty in controlling the variable coordination environment of the ions.[4] Relatively far fewer d–f cluster compounds have been prepared using carboxylates, amino acetates, betaines, and 2-pyridones as ligands.[5]

Our recent studies have focused on the use of a variety of "salen" style Schiff-base ligand with two dissimilar metal-binding sites for the synthesis of heterometallic 3d–4f complexes (Scheme 1).[6] For bimetallic 3d–4f complexes the metals are located in a roughly planar ligand set. An interesting feature in these complexes is the presence of a uninegative ligand which frequently occupies an axial site on the 3d metal giving it a distorted square-based pyramidal configuration. In the case of acetate (OAc^-) we have found that this ligand can often span both 3d and 4f metals. These factors suggested that complexes of higher nuclearity could be designed with the use of a combination of suitable Schiff base ligands and carefully chosen multidentate ligands which can occupy these bridging/axial sites of each 3d–4f moiety. We report here the successful application of this strategy with the synthesis, structure and photochemistry of $[Zn_4Nd_2L_4(1,4\text{-}BDC)_2]\cdot[Nd(NO_3)_5(H_2O)]\cdot Et_2O\cdot 2EtOH\cdot 3H_2O$ **1** (1,4-BDC = 1,4-benzenedicarboxylate). We chose the BDC group as a convenient bidentate linker since it is readily available and has been used for the construction of transition metal coordination polymers but less so for lanthanide based systems.[7] Although many 3d–4f salen-type complexes have been described in the past two decades, most of them are composed of relatively simple dinuclear cores.[8] To the best of our knowledge, **1** represents the first report of a polynuclear 3d–4f architecture obtained by linking two 3d–4f salen moieties with BDC groups.

Reaction of equimolar amounts of H_2L, $Zn(OAc)_2\cdot 2H_2O$, $Nd(NO_3)_3\cdot 6H_2O$ and 1,4-BDC in ethanol afforded **1** in 55% yield.‡ The complex crystallizes as the dication $[Zn_4Nd_2L_4(1,4\text{-}BDC)_2]^{2+}$ along with $[Nd(NO_3)_5(H_2O)]^{2-}$ acting as the counter anion. The crystal structure of the cation is shown in Fig. 1.§ There are two independent dimers in **1** and both of them lie about inversion centres. There are several interesting structural features that should be noted. The use of the 1,4-BDC ligand results in the stabilization of two *trimetallic* Zn_2NdL_2 fragments instead of simple bimetallic 3d–4f units (Fig. 2). The Zn ions are bound in the O_2N_2 cavities of each L group while the Nd ion is bound by the outer O_2O_2 sets of both L groups. Two BDC groups bridge the Zn_2Nd moieties such that each carboxylate group spans a Zn–Nd set. Each Nd(III) ion is ten-coordinated and surrounded by ten oxygen atoms of L and 1,4-BCD ligands. The resulting complex cation has an interesting internal elongated prism-like cavity which



Scheme 1 Controlled design of multinuclear heterometallic 3d–4f complex.

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† Electronic Supplementary Information (ESI) available: Experimental details, 2D-COSY spectrum of **1** and crystal structure of **2**. See 10.1039/b518128c

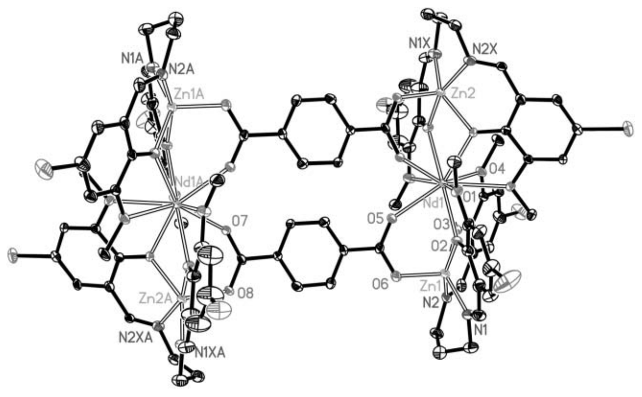

Fig. 1 X-Ray structure of **1**. The complex resides around a crystallographic inversion center at 0, 0, ½. Atoms whose labels are appended by an A are related by −*x*, −*y*, 1 − *z*. Thermal ellipsoids are drawn at the 25% probability level.

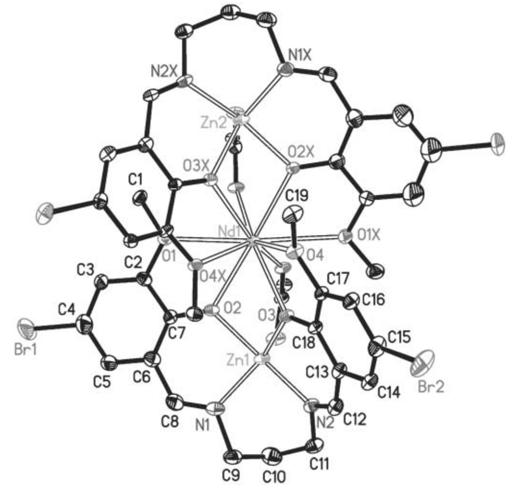

Fig. 2 View of the structure of one Zn_2NdL_2 moiety of **1**. Thermal ellipsoids are drawn at the 25% probability level.

measures approximately 10 Å × 5 Å, although the aryl groups of each BCD units are not perfectly eclipsed.

NMR spectroscopic studies show that **1** is stable in CD_3OD solution for up to one month at 298 K. As shown in Fig. 3, the ^{1}H NMR spectrum contains 14 signals corresponding to four equivalent L groups plus two equivalent 1,4-BDC anions, in agreement with the solid state structure. A 2D-COSY analysis allowed assignment of the signals (see Figure S1, ESI†). The complexed 1,4-BDC anion displays two signals for 4 benzyl protons at δ 12.95 and 14.33 ppm, respectively, which shift to lower field than those of free 1,4-BDC.

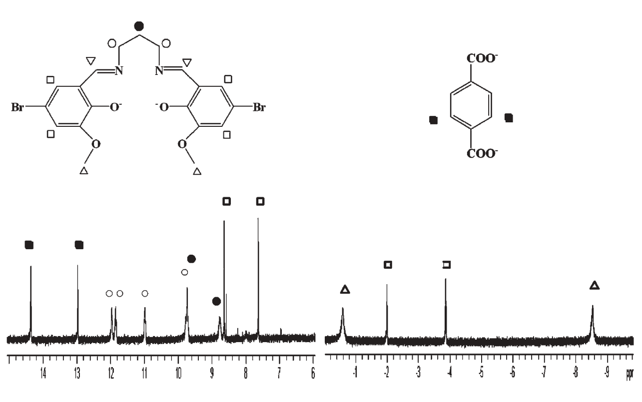

Fig. 3 ^{1}H NMR spectrum of **1** in CD_3OD. The peaks of solvent, Et_2O and EtOH, together with two signals (2.022 ppm and 3.339 ppm) of N=CH protons, have been omitted for clarity.

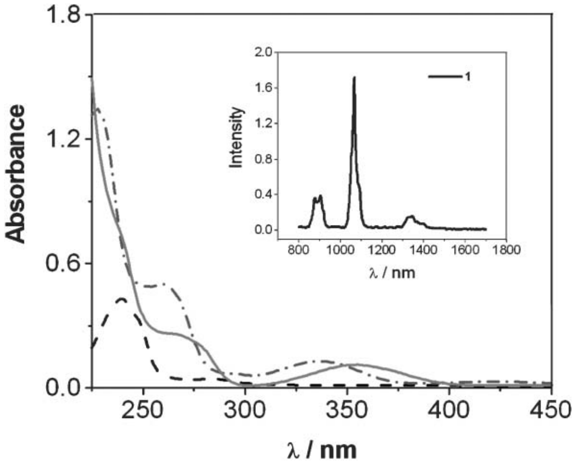

Fig. 4 Absorption spectra of free ligands BDC (---) and H_2L (-··-), and **1** (—) in CH_3OH. (Insert: NIR luminescence of **1** in CH_3OH (2.5×10^{-6} M) at room temperature).

Recent attention has focused on the near infrared (NIR) emissive properties of lanthanide complexes of Yb(III), Nd(III) and Er(III) with organic dyes and 3d-transition metal complexes as sensitizers for luminescence.[6,9] The UV–visible spectra of H_2L, 1,4-BDC, and **1** in CH_3OH solution are shown in Fig. 4. The free ligand H_2L exhibits absorption bands at 228, 260 and 336 nm, and 1,4-BDC at 240 nm, which are red-shifted upon coordination to the metal ions in **1**. **1** shows typical NIR emission bands of Nd^{3+} assigned to the $^4F_{3/2} \rightarrow {}^4I_{j/2}$ (j = 9, 11, 13) transition upon excitation of the ligand centered absorption band either at 275 or 330–360 nm. The emissions at 876 and 905 nm can be assigned to $^4F_{3/2} \rightarrow {}^4I_{9/2}$, 1068 nm to $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and 1352 nm to $^4F_{3/2} \rightarrow {}^4I_{13/2}$ transitions of Nd^{3+}. The free ligands H_2L and 1,4-BDC, and $Nd(NO_3)_3{\cdot}6H_2O$ do not exhibit NIR luminescence in CH_3OH under similar conditions. A similar NIR luminescence is observed for **1** in the solid state. These observations are consistent with the NIR luminescence of **1** in solution stemming from the hexametallic Zn_4Nd_2 core with a structure similar to that found in the solid state. We were naturally interested in comparing the photophysical properties of **1** with related Nd(III) complexes. The relative emission intensities of **1** and the related simple dinuclear Zn–Nd complex $[ZnNdL(OAc)(NO_3)_2]$ (**2**) (see Figure S2, ESI†) were determined under the same experimental conditions. With the same absorbance value at 275 nm, the relative emission intensity at 1068 nm was estimated to be 5.5 for 1 : 2 in CH_3OH, indicating that with the central metal ion encapsulated by four chromophoric ligands and shielded from solvent interactions, **1** has superior luminescence properties compared to **2**.

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Notes and references

‡ *Experimental procedure* for **1**: A mixture of H_2L (0.050 g, 0.10 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (0.022 g, 0.10 mmol) in 10 ml of EtOH was stirred and refluxed for 15 min.[10] A solution of $Nd(NO_3)_3{\cdot}6H_2O$ (0.044 g, 0.10 mmol) in 5 ml EtOH was added and the mixture was refluxed for 15 min. A solution of 1,4-BDC (0.017 g, 0.10 mmol) in ethanol (5 mL) was added and the resulting mixture was refluxed for 30 min and filtered. Diethyl ether was allowed to diffuse slowly into this solution at room temperature and pale yellow single crystals were obtained in three weeks. Yield 0.049 g (55%, based on H_2L). ESI-MS (CH_3CN) *m*/*z*: 1435 $[Zn_4Nd_2L_4(1{,}4\text{-BDC})_2]^{2+}$. ^1H NMR (400 MHz, CD_3OD): δ (ppm) −8.552 (3H), −3.892 (1H), −2.014 (1H), −0.615 (3H), 2.022 (1H), 3.339 (1H), 7.605 (1H), 8.607 (1H), 8.737 (1H), 9.709 (1H), 9.781 (1H), 10.958 (1H), 11.826 (1H), 11.943 (1H), 12.952 (1H), 14.333 (1H). IR (CH_3OH, cm^{-1}): 3420.1, 1683.8, 1652.7, 1635.4, 1558.5, 1539.9, 1506.4, 1456.7, 1395.0, 1362.1, 1235.2, 1032.9, 667.9. Photoluminescence measurements were made at room temperature with a 1 m SPEX 1704 spectrometer and a liquid-nitrogen cooled Ge detector. The excitation was provided by an argon ion laser using either the UV multiline optics (333.6–363.8 nm range) or the 275.4 nm laser line.

§ *Crystal data* for **1**: $C_{92}H_{82}Br_8N_{13}O_{40}Nd_3Zn_4$, M = 3343.19, triclinic, space group $P\bar{1}$, a = 18.754(4), b = 21.528(4), c = 21.625(4) Å, α = 60.63(3)°, γ = 74.65(3)°, β = 72.93(3)°, V = 7197(2) $Å^3$, Z = 2, D_c = 1.543 g cm^{-3}, μ(Mo-Kα) = 4.008 mm^{-1}, F(000) = 3250, T = 153 K. R_1 = 0.0651, wR_2 = 0.1615 for 25125 independent reflections with a goodness-of-fit of 0.957. All data were collected on a Nonius Kappa CCD diffractometer and structures solved using the program SHELXL-97. CCDC reference number 290932. See http://www.rsc.org/suppdata/cc/ for crystallographic data in CIF format.

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