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Tetranuclear NIR luminescent Schiff-base Zn–Nd complexes†

Xingqiang Lü,*[ab] Weiyu Bi,[a] Wenli Chai,[a] Jirong Song,[a] Jianxin Meng,[b] Wai-Yeung Wong,[b] Wai-Kwok Wong*[b] and Richard A. Jones[c]

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With the simple dinuclear Zn–Nd complex $[ZnNdL(H_2O)(NO_3)_3]$ (**1**) (**H_2L** = *N*,*N*′-bis-(3-methoxysalicylidene)ethylene-1,2-diamine) as the precursor, tetranuclear $[Zn_2Nd_2L_2\text{-}(4,4'\text{-bpy})(NO_3)_6]\cdot Et_2O$ (**2**) and $[Zn_2Nd_2L_2(4,4'\text{-bpe})]\cdot 2H_2O$ (**3**) (4,4′-bpy = 4,4′-bipyridine, 4,4′-bpe = *trans*-bis(4-pyridyl)ethylene) complexes are formed: suitable choice of bidentate linkers could construct multinuclear heterometallic 3d–4f Schiff-base complexes with improved luminescent properties, and the controlling of linker character shows a potentially effective way to the fine-tuning properties of NIR luminescence from Nd ions.

Introduction

Much recent effort has been devoted to luminescent lanthanide (Ln) complexes with long-lived and characteristic line like emission bands (near UV to visible and NIR regions),[1] because of their potential applications in bioassays,[2] medicine[3] and materials science.[4] The limit of low absorption coefficients due to the parity forbidden f–f transitions for these lanthanide ions,[5] has led to considerable exploration of suitable chromophores,[6] with intense and tunable absorption maxima in the visible region, to act as sensitizers of luminescence from lanthanides in complex systems. Several recent investigations have focused on organic dyes[7] and d-block metal complexes (*i.e.* Cr(III),[8] Ru(II),[9] Pt(II),[10] Re(I) or Os(II)[11]), which display absorption bands in the near-UV or visible ranges, and have been demonstrated to effectively transfer energy to the lanthanide ions indirectly.

Our past research[12] has focused on the use of compartmental salen-type Schiff-base ligands, to bind both 3d Zn(II) and 4f Nd(III), Yb(III) or Er(III) ions. These heterometallic systems, as suitable chromophores, can act as antennae or sensitizers for NIR lanthanide luminescence, and the π-conjugation of those salen-type Schiff-base ligands helps to enhance luminescent properties. In the view of fine-tuning of their NIR properties, three effective routes are adopted: (1) change of spacers or (2) electronic properties of the substituents on the flanking phenyl rings of the Schiff-base ligands to extend the conjugation of the complexes,[12g] and (3) of the functional bridge from OH to other anionic groups, to obtain multinuclear 3d–4f complexes.[12c] It is noticeable that in the above 3d–4f heterometallic complexes, the axial position of the 3d ions was occupied by anions (OAc^-, [12a,f] Cl^- [12c,e] or NO_3^- [12e,g]) or H_2O[12b,e,g] solvates from different reaction conditions, which may lead to partial luminescent quenching with OH solvates such as EtOH or H_2O around the 4f ions. If replaced by axial groups with rigid multidentate linkers of stronger coordination ability, polynuclear 3d–4f complexes should be obtained, which could effectively extend the electronic conjugation of the whole molecule, and endow multi-chromophores to increase the rate of the energy-transfer process, leading to better luminescent properties than that of the dinuclear complexes. Herein, with the simple dinuclear Zn–Nd complex $[ZnNdL(H_2O)(NO_3)_3]$ (**1**) as the precursor, we report the syntheses, structures and photophysical properties of two Zn–Nd tetranuclear complexes $[Zn_2Nd_2L_2(4,4'\text{-bpy})\text{-}(NO_3)_6]\cdot Et_2O$ (**2**) and $[Zn_2Nd_2L_2(4,4'\text{-bpe})]\cdot 2H_2O$ (**3**), which are formed from different bidentate (4,4′-bpy or 4,4′-bpe) linkers to connect with the two Zn–Nd salen-type Schiff-base architecture units on the axial positions of Zn ions; and their NIR luminescent characteristics can be effectively fine-tuned as a function of the linkage.

Results and discussion

NMR

As shown in Scheme 1, reaction of an equimolar amount of **H_2L**, $Zn(OAc)_2\cdot 2H_2O$ and $Nd(NO_3)_3\cdot 6H_2O$ in absolute ethanol afforded dinuclear precursor **1** in a good yield of *ca.* 80%. Further reaction of **1** with the second 4,4′-bipyridyl ligand 4,4′-bpy or 4,4′-bpe in 2 : 1 ratio in DMF–EtOH resulted in the formation of tetranuclear **2** or **3**, respectively.

Unchanged NMR spectroscopic results (as shown in ESI,† Fig. 1s) reveals that complexes **1–3** are stable in CD_3OD solution at room temperature for up to one month. The ^1H NMR spectra of **2** or **3** show large shifts (δ from 14.22 to −6.70 ppm for **2**, 14.31 to −7.87 ppm for **3**) of the resonances to high fields in the neodymium compounds due to the lanthanide-induced shift. Two down-field signals (δ 14.22 and 13.25 ppm for **2**; δ 14.31 and 13.27 ppm for **3**) are assigned

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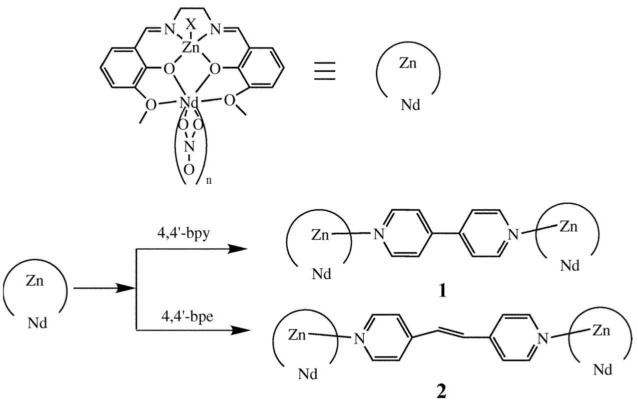
[a] *Department of Chemical Engineering, Shaanxi Key Laboratory of Physico-inorganic Chemistry, Northwest University, Xi'an 710069 Shaanxi, China. E-mail: lvxq@nwu.edu.cn*
[b] *Department of Chemistry, Hong Kong Baptist University, Waterloo Road, Kowloon Tong, Hong Kong, China. E-mail: wkwong@hkbu.edu.hk*
[c] *Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A5300, Austin, 78712-0165, TXUSA*

† Electronic supplementary information (ESI) available: Table 1s: Interatomic distances (Å) and bond angles (°) with esds for complexes **2** and **3**. Fig. 1s: ^1H NMR spectra of complexes **1–3** in CD_3OD at room temperature. Fig. 2s: View of the stacking of **2**. Fig. 3s: View of the stacking of **3**. See DOI: 10.1039/b710204f



Scheme 1 Controlled design of tetranuclear heterometallic 3d–4f complexes.

to the pyridyl protons of complexed linkers, shifted down-field relatively compared with free 4,4′-bpy (δ 7.82 and 8.69 ppm) or 4,4′-bpe (δ 7.48, 7.73 and 8.74 ppm). The signals of the coordinated ligand (δ from 11.77 to −5.36 ppm for **2** and δ from 11.77 to −5.17 ppm for **3**) are significantly spread relative to those of the free $\mathbf{H_2L}$ Schiff base (δ from 8.42 to 3.82 ppm) and in diamagnetic **1** (δ from 11.72 to −5.07 ppm).

Crystallography

The X-ray crystal structure analysis unambiguously revealed the tetranuclear 3d–4f structures for complexes **2** and **3**. Fig. 1 and 2 show the molecular structure of **2** or **3** in the asymmetric unit: two independent dimers lie about the inversion center, and one 4,4′-bipyridyl linker (4,4′-bpy for **2**, 4,4′-bpe for **3**) bridges the two Zn ions. Each Zn(II) ion lies in a five-coordinate environment and adopts a distorted square pyramidal geometry, where the inner N_2O_2 core from the Schiff-base $\mathbf{H_2L}$ ligand comprises the basal plane, and one N atom from the 4,4′-bipyridyl ligand occupies the apical position. Each Nd(III) ion is ten-coordinated, composed of the outer O_2O_2 cavity of the Schiff-base $\mathbf{H_2L}$ ligand and six O atoms from three bidentate nitrate anions. The average length of Zn–O (phenolic), Nd–O (phenolic, methoxy or nitrate) or Zn–N bonds (as shown in ESI,† Table 1s) is in the normal range and comparable to those of other dinuclear Zn–Nd Schiff-base complexes.[12a,g] The Zn–Nd distances of each dimer in **2** and **3** are 3.544(2) and 3.581(2) Å, respectively, slightly longer than those of previous Zn–Nd Schiff-base complexes,[12] in which the apical position of Zn ions was occupied by O atoms from solvates (H_2O) or anions (OAc^- or NO_3^-), instead of N atoms from the 4,4′-bipyridyl ligands in complexes **2** and **3**.

The change of 4,4′-bipyridyl linker length from 4,4′-bpy to 4,4′-bpe leads to a significant change of the conjugation extension in the two tetranuclear complexes. In **2**, the Zn···Zn separation from bridged 4,4′-bpy is 11.221(2) Å, and as shown in ESI,† Fig. 2s, no appreciable aromatic π–π stacking interactions are present, though various complementary intermolecular C–H···O (C11–H11···O13 and C20–H20···O8) hydrogen bonds were generated to lead to the formation of a multi-dimensional hydrogen bonded framework. For **3**, The existence of C=C of 4,4′-bpe endows extended electronic conjugation of the tetranuclear molecule system, and increases the distance of the Zn···Zn separation (13.295(2) Å). A detailed examination of the crystal packing of **3** revealed weak aromatic π–π stacking (3.751(5) Å), which together with complementary intermolecular C–H···O (C11–H11···O7) hydrogen bonds (as shown in ESI,† Fig. 3s), cause the close stacking of the multi-dimensional network. The solvate molecules of **2** and **3** are not bound to the framework and they exhibit no observable interactions with the host structure.

Photophysical properties

The UV-Vis absorption spectra of complexes **1–3** in MeOH solution at room temperature are shown in Fig. 3. Similar ligand-centered solution absorption spectra (204, 228, 271 and 348 nm) are observed, red-shifted upon coordination to the metal ions compared with that (226, 248 and 337 nm) of the free Schiff-base ligand $\mathbf{H_2L}$. The smaller molar absorption coefficients of complex **2** in the same condition (solvent and concentration), should be attributed to the larger π-system of complex **3**. At room temperature in MeOH solution, the emission spectra of complexes **1–3** are shown in Fig. 4: the typical NIR emission bands of Nd^{3+} ($4F_{3/2} \rightarrow 4I_{J/2}$, $J = 9, 11, 13$), show no shifts but obvious differences of relative intensity. The emissions at 863 nm must be assigned to the $4F_{3/2} \rightarrow 4I_{9/2}$, 1060 nm to $4F_{3/2} \rightarrow 4I_{11/2}$ and 1328 nm to

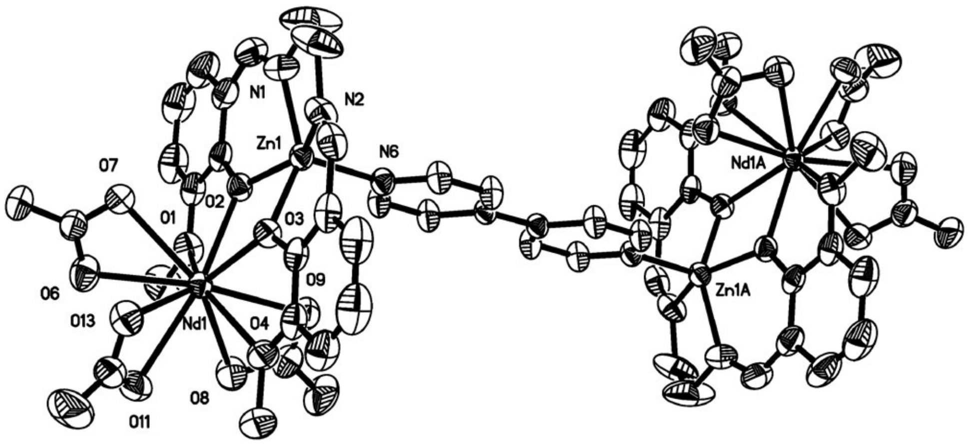


Fig. 1 Perspective drawing of compound **2**; H atoms and solvates are omitted for clarity.

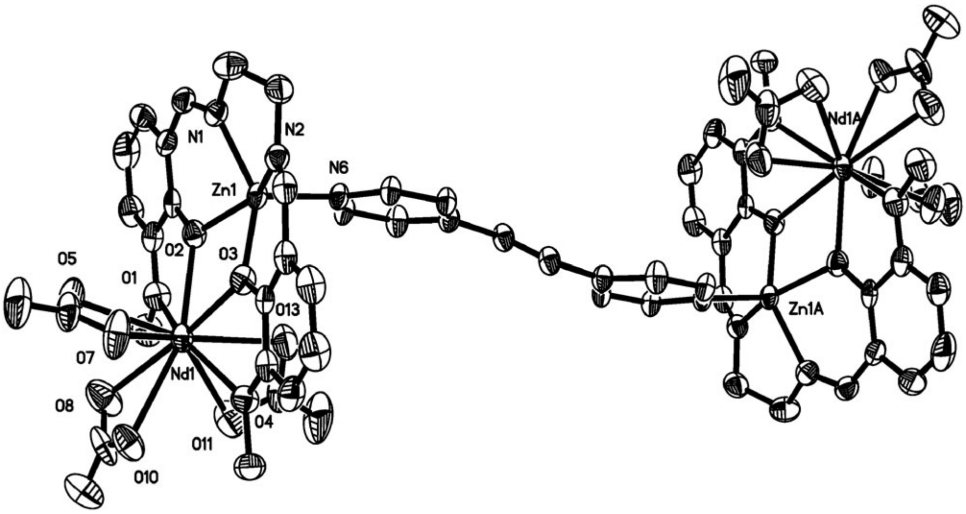


Fig. 2 Perspective drawing of compound **3**; H atoms and solvates are omitted for clarity.

$4F_{3/2} \rightarrow 4I_{13/2}$ transition of Nd^{3+}. Due to the limitation of our equipment, the excitation spectra and the NIR luminescent lifetime could not be measured. The free **H_2L^1** ligand, 4,4′-bipyridyl linkers and Nd(NO$_3$)$_3$ do not exhibit NIR luminescence under the same conditions, and the ligand-centered fluorescence of complexes **1–3** in the visible region is almost quenched in solution at room temperature, which suggests that the energy transfer from the antenna (3d Zn complexes) to lanthanide ions takes place efficiently.[13]

It is noteworthy that the relative intensities of the three compound transitions are structured, both in dilute MeOH solution and in the solid state. In solution, almost identical NIR emission spectra were obtained, and the relative emission intensities of complexes **2** or **3** at 1060 nm were *ca.* 1.6 or 2.6 times to that of the dinuclear Zn–Nd precursor **1**, and *ca.* 1.3 or 1.7 times to that of the pyridine adduct of **1**, when compared the relative intensity using solutions with their concentrations adjusted to give the same absorbance values at 337 nm, which indicates that the emission should result from the Zn–Nd bimetallic species, and higher nuclearity species (Zn$_2$Nd$_2$) with two chromophores could effectively increase the luminescent properties of their complexes. Moreover, the route to multinuclear formation, completely avoids luminescent quenching from OH-containing bridges or solvents.[12c] Especially for the superior luminescent complexes **2** and **3**, the function of the linkers at the axial position of Zn ions endows the adjustment of whole conjugation extension to some extent, which should be due to the larger size of spectral overlap[14] between the same broad ligand-centered emission spectra (donor) and the Nd-centered narrow line absorption spectrum (acceptor), and may be a new way to make better use of fine-tuning sensitizers to lanthanide ions. With respect to their luminescent properties in the solid state, similar NIR emission spectra are observed, and well resemble their characteristics in dilute solution. Differences of relative intensities of complexes **1–3** in the solid state from those in solution, further demonstrates that the directional close stacking of crystal molecules has a significant effect on their luminescence besides high nuclearity.

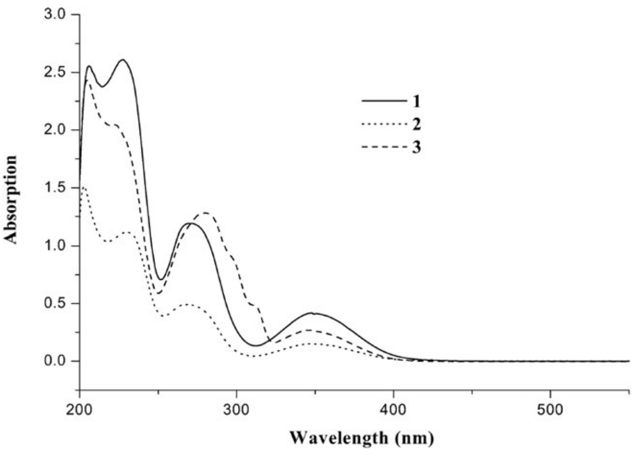


Fig. 3 UV-Vis spectra of **1** (solid line), **2** (dotted line) and **3** (dashed line) in MeOH solution at 2 × 10^{-5} M at room temperature.

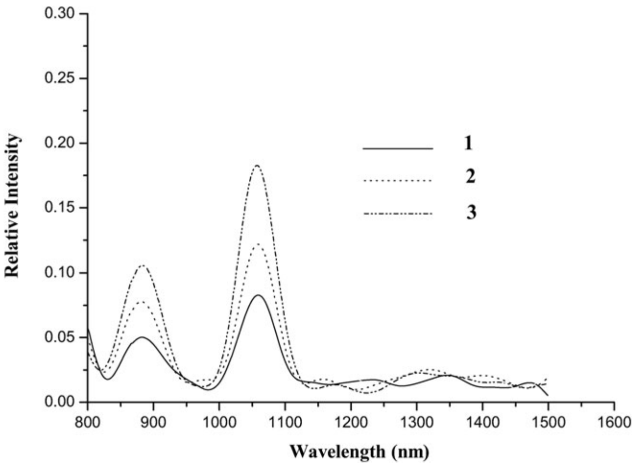


Fig. 4 NIR emission spectra of **1** (solid line), **2** (dotted line) and **3** (dash-dot-dot line) in MeOH solution at 2 × 10^{-5} M at room temperature.

Conclusion

In conclusion, suitable choice of 4,4′-bipyridyl linkers replacing axial bound H_2O solvates of 3d Zn^{2+} ions from the dinuclear precursor could construct tetranuclear heterometallic Zn–Nd complexes, with extended molecular conjugation, and more chromophores, leading to better luminescent properties than those of dinuclear complexes. The controlling of function from the linkage shows a potentially effective way to the fine-tuning of luminescent properties in 3d–4f Schiff-base coordination complexes in the future.

Experimental

All chemicals were commercial products of reagent grade and were used without further purification. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. Infrared spectra were recorded on a Nicolet Nagna-IR 550 spectrophotometer in the region 4000–400 cm^{-1} using KBr pellets. ^1H NMR spectra were recorded on a JEOL EX270 spectrometer in CD_3OD at room temperature. Electronic absorption spectra in the UV/Vis region were recorded with a Hewlett Packard 8453 UV/Vis spectrophotometer, and steady-state visible fluorescence on a pico-N2 laser system (PLT Time Master) with λ_{ex} = 337 nm. NIR emission was detected by a liquid-nitrogen cooled INSb IR detector (EG & G) with a preamplifier and recorded by a lock-in amplifier system. The third harmonic, 355 nm line of a Nd-YAG laser (Quantel Brilliant B), was used as the excitation light source.

Syntheses

H_2L: *N*,*N*′-bis(3-methoxysalicylidene)ethylene-1,2-diamine. Schiff base **H_2L** was obtained from *o*-vanilin (6.3 g, 40 mmol) and 1,2-diaminoethane (1.4 ml, 20 mmol) according to a well-established procedure from the literature.[15] Yield: 5.0 g, 76%. Calc. for $C_{18}H_{20}O_4N_2$: C, 65.84; H, 6.14; N, 8.53%. Found: C, 65.58; H, 6.06; N, 8.63%. ^1H NMR (270 MHz, CD_3OD): δ (ppm) 8.42 (2H), 6.91 (4H), 6.71 (2H), 3.96 (4H), 3.82 (6H).

$[ZnNdL(H_2O)(NO_3)_3]$ (1). To a stirred suspension of **H_2L** (0.033 g, 0.10 mmol) in absolute ethanol (5 ml), $Zn(OAc)_2 \cdot 2H_2O$ (0.022 g, 0.10 mmol) was added and heated under reflux for 5 h. A solution of $Nd(NO_3)_3 \cdot 6H_2O$ (0.044 g, 0.10 mmol) in absolute ethanol (2 ml) was then added and the mixture was refluxed for another 3 h. The clear yellow solution was then cooled to room temperature and volatile materials were removed under reduced pressure to give the product in *ca.* 77% yield. Calc. for $C_{18}H_{20}O_{14}N_5ZnNd$: C, 29.22; H, 2.72; N, 9.46%. Found: C, 28.38; H, 2.66; N, 9.33%. ^1H NMR (270 MHz, CD_3OD): δ (ppm) 11.72 (1H), 9.41 (1H), 8.35 (1H), 8.02 (1H), 7.91 (1H), 7.70 (1H), 3.85 (1H), 3.64 (1H), 2.99 (1H), 2.85 (1H), 1.15 (3H), 0.29 (1H), −3.45 (1H), −5.17 (3H). IR (KBr, cm^{-1}): 3422 (br), 2933 (w), 1635 (s), 1607 (m), 1457 (vs), 1386 (m), 1344 (s), 1281 (vs), 1220 (m), 1074 (m), 1030 (m), 966 (m), 855 (w), 785 (w), 737 (m), 639 (w).

$[Zn_2L_2Nd_2(4,4'\text{-bpy})(NO_3)_6] \cdot Et_2O$ (2). To a solution of **1** (74 mg, 0.10 mmol) in absolute ethanol (4 ml) was added 4,4′-bpy (7.8 mg, 0.05 mmol) and the mixture was refluxed for 2 h. Then 2 ml absolute DMF was added to give a clear yellow solution. Diethyl ether was allowed to diffuse slowly into this solution at room temperature and pale yellow single crystals were obtained in three weeks. Yield: 46 mg (55%). Calc. for $C_{50}H_{49}N_{12}O_{27}Zn_2Nd_2$: C, 35.98; H, 2.96; N, 10.07%. Found: C, 38.13; H, 3.05; N, 9.96%. ^1H NMR (270 MHz, CD_3OD): δ (ppm) 14.22 (1H), 13.25 (1H), 11.77 (1H), 10.60 (1H), 8.91 (1H), 8.23 (1H), 8.01 (1H), 7.96 (1H), 7.90 (1H), 4.64 (1H), 3.61 (1H), 3.35 (1H) 2.99 (1H), 2.85 (1H), 2.71 (1H), 1.19 (3H), 0.20 (1H), −0.42 (1H), −1.40 (1H), −3.56 (1H), −5.36 (3H), −6.70 (1H). IR (KBr, cm^{-1}): 3435 (w), 2939 (w), 1638 (s), 1610 (m), 1461 (vs), 1392 (m), 1318 (s), 1277 (vs), 1218 (s), 1074 (m), 1030 (m), 958 (w), 849 (w), 820 (w), 737 (m), 639 (w).

Table 1 Crystal data and refinement for complexes **2** and **3**

Compound	**2**	**3**
Empirical formula	$C_{50}H_{49}N_{12}Nd_2O_{27}Zn_2$	$C_{48}H_{50}N_{12}Nd_2O_{28}Zn_2$
M	1669.23	1662.22
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	9.5651(5)	9.1671(14)
b/Å	10.5104(6)	10.4152(16)
c/Å	16.2462(9)	16.667(3)
α/°	77.6550(10)	92.882(3)
β/°	80.6800(10)	100.841(3)
γ/°	74.2530(10)	104.315(3)
$V/Å^3$	1527.92(15)	1506.5(4)
Z	1	1
$D_c/g\ cm^{-3}$	1.814	1.832
Crystal size/mm	0.31 × 0.25 × 0.21	0.35 × 0.31 × 0.23
μ(Mo-Kα)/mm^{-1}	2.542	2.579
T/K	293(2)	293(2)
Data/restraints/parameters	6658/0/422	6121/0/415
Quality-of-fit indicator	1.028	0.948
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0256$ $wR_2 = 0.0680$	$R_1 = 0.0595$ $wR_2 = 0.1322$
R indices (all data)	$R_1 = 0.0281$ $wR_2 = 0.0690$	$R_1 = 0.1145$ $wR_2 = 0.1600$

[$Zn_2L_2Nd_2$(4,4′-bpe)$(NO_3)_6$]·$2H_2O$ (3). To a solution of **1** (74 mg, 0.10 mmol) in absolute ethanol (4 ml) was added 4,4′-bpe (9.2 mg, 0.05 mmol) and the mixture was refluxed for 2 h. Then 2 ml absolute DMF was added to give a clear yellow solution. Diethyl ether was allowed to diffuse slowly into this solution at room temperature and pale yellow single crystals were obtained in two weeks. Yield: 51 mg (61%). Calc. for $C_{48}H_{50}N_{12}O_{28}Zn_2Nd_2$: C, 34.68; H, 3.03; N, 10.11%. Found: C, 34.76; H, 3.07; N, 10.24%. ^{1}H NMR (270 MHz, CD_3OD): δ (ppm) 14.31 (1H), 13.27 (1H), 11.77 (1H), 8.65 (1H), 8.26 (1H), 8.01 (1H), 7.94 (1H), 7.68 (1H), 7.53 (1H), 5.20 (1H), 4.78 (1H), 3.65 (1H), 3.54 (1H), 3.11 (1H), 3.01 (1H), 2.79 (1H), 1.28 (3H), 0.31 (1H), −0.50 (1H), −2.69 (1H), −3.46 (1H), −5.17 (3H), −6.71 (1H), −7.87 (1H). IR (KBr, cm^{-1}): 3463 (br), 2936 (w), 1666 (s), 1616 (vs), 1582 (m), 1550 (m), 1458 (vs), 1389 (s), 1303 (vs), 1232 (s), 1194 (s), 1096 (w), 1073 (w), 1082 (w), 965 (m), 846 (w), 734 (m), 510 (w).

Crystal structure determination. Single crystals of **2** and **3** of suitable dimensions were mounted onto thin glass fibers. All the intensity data were collected at 298 K on a Bruker SMART CCD diffractometer (Mo-Kα radiation, λ = 0.71073 Å) in Φ and ω scan modes. Structures were solved by Patterson methods followed by difference Fourier syntheses, and then refined by full-matrix least-squares techniques against F^2 using SHELXTL.[16a] All other non-hydrogen atoms were refined with anisotropic thermal parameters. Absorption corrections were applied using SADABS.[16b] All hydrogen atoms were placed in calculated positions and refined isotropically using a riding model. Crystallographic data and refinement parameters for the complexes are presented in Table 1. Relevant atomic distances and bond angles are collected in ESI,† Table 1s.

CCDC reference number 652822 (for **2**) and 652823 (for **3**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b710204f

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