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Communication

Self-Assembly of NIR Luminescent 30-metal Drum-like and 12-metal Rectangular-like d-f Nanoclusters with Long-chain Schiff Base Ligands

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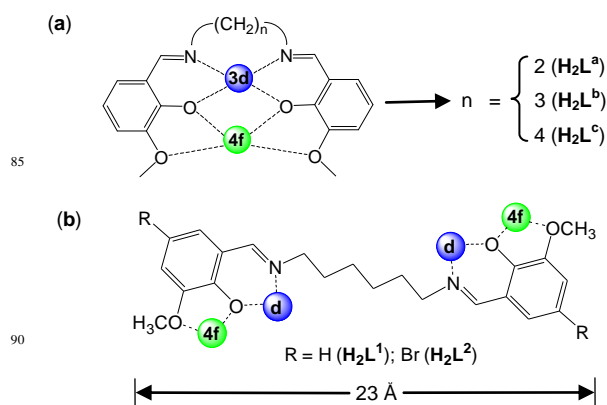
Two classes of heterobimetallic d-f nanoclusters $[\text{Ln}_6\text{Cd}_{24}(\text{L}^1)_{11}(\text{OAc})_{43}(\text{OH})]$ and $[\text{Ln}_4\text{Zn}_8(\text{L}^2)_2(\text{OAc})_{20}(\text{OH})_4]$ ($\text{Ln} = \text{Nd}$ and Yb) were prepared using flexible long-chain Schiff base ligands which have $(\text{CH}_2)_6$ backbones. Their NIR luminescence properties were determined.

Heterometallic nanoclusters comprised of d-block transition metals and lanthanide ions are currently of interest for their potential applications in optoelectronics, magnetism, and as porous materials.¹ For example, light-absorbing d-block metal chromophores (i.e. Pt^{II} ,^{2a,b} Ru^{II} ,^{2c,d} Zn^{II} ,^{2e,f} Cr^{II} ,^{2g,h} and Cd^{II} ,^{2i,j}) can be used as sensitizers for luminescence from $\text{Ln}(\text{III})$ centers following ligand $\rightarrow \text{f}$ and $\text{d} \rightarrow \text{f}$ energy-transfer. Self-assembly by metal-ligand coordination is one of the most efficient processes that organize individual molecular components into nanosize species.

Compartmental Schiff bases with two dissimilar metal-binding sites, one being specific for the d metal ion and another for the f metal ion, have been employed to synthesize d-f heteronuclear complexes.³ For example, in our previous studies, the use of Schiff base ligands $\text{H}_2\text{L}^{\text{a-c}}$ (Scheme 1a), which have flexible carbon-carbon backbones containing from 2 to 4 methylene (CH_2) units, resulted in a variety of binuclear,^{4a} trinuclear,^{4b} tetranuclear,^{4c} and hexanuclear^{4d,e} 3d-4f complexes ($3\text{d} = \text{Zn}, \text{Cu}$ and Ni). In these polynuclear complexes, the ligands exhibit classical "salen" type of coordination modes with the 3d-metal ions bound in the N_2O_2 cavities and the 4f-metal ions in the O_2O_2 cavities (Scheme 1a). It has been found that the $(\text{CH}_2)_n$ chain lengths of these flexible ligands may affect the structures of the d-f complexes. So far most flexible Schiff base ligands used in the construction of d-f polynuclear complexes have contained no more than 4 methylene units within the backbone.^{3,5} We were naturally interested in the influence of increasing the $(\text{CH}_2)_n$ chain length,⁶ and describe here results using two long-chain Schiff base ligands N,N' -bis(3-methoxysalicylidene)hexane-1,6-diamine (H_2L^1) and N,N' -bis(5-bromo-3-methoxysalicylidene)hexane-1,6-diamine (H_2L^2), which have flexible $(\text{CH}_2)_6$ backbones, respectively (Scheme 1b). In a linear configuration the lengths of $\text{H}_2\text{L}^{1,2}$ are approximately 23 Å. This appears to increase the flexibility of the ligands and seems to be a factor in the formation of larger metal clusters. The structures of d-f clusters are often influenced by a variety of factors such as the type of d-block metal ions and pH value of environment.³⁻⁵ Thus, two classes of d-f nanoclusters have been prepared from the reactions of $\text{H}_2\text{L}^{1,2}$ with $\text{M}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ($\text{M} = \text{Cd}^{2+}$ and Zn^{2+}) and $\text{Ln}(\text{OAc})_3 \cdot 4\text{H}_2\text{O}$ in the presence of added base (NaOH). They are

$[\text{Ln}_6\text{Cd}_{24}(\text{L}^1)_{11}(\text{OAc})_{43}(\text{OH})]$ ($\text{Ln} = \text{Nd}$ (**1**) and Yb (**2**)) and $[\text{Ln}_4\text{Zn}_8(\text{L}^2)_2(\text{OAc})_{20}(\text{OH})_4]$ ($\text{Ln} = \text{Nd}$ (**3**) and Yb (**4**)). Interestingly, Cd-Ln nanoclusters **1** and **2** exhibit 30-metal drum-like structures, while Zn-Ln nanoclusters **3** and **4** have 12-metal rectangular-like architectures. Hydroxide (OH^-) anions are found in the structures of **1-4**, indicating that the basic environment favors the formation of these nanoclusters. Differing from most other salen-type Schiff base ligands used in the synthesis of d-f complexes (i.e. $\text{H}_2\text{L}^{\text{a-c}}$, Scheme 1a), $\text{H}_2\text{L}^{1,2}$ exhibit "stretched" coordination modes with metal ions (Scheme 1b), resulting in large sizes of **1-4**. For example, the sizes of **1** and **2** are approximately $20 \times 24 \times 24$ Å, which allow their direct visualization using transmission electron microscopy (TEM). To the best of our knowledge, **3** and **4** represent the first report of rectangular-like d-f nanoclusters formed by the linking of Schiff base ligands.³⁻⁵

In the presence of NaOH (0.01 mol/L), reactions of H_2L^1 with $\text{Cd}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ln}(\text{OAc})_3 \cdot 4\text{H}_2\text{O}$ in refluxing methanol/ethanol produced yellow solutions from which **1** and **2** were isolated as pale yellow crystalline solids. **1** and **2** are isomorphous and have 30-metal drum-like structures. Two views of the crystal structure of **1** are shown in Figure 1a. The top view is essentially a side-on view while the lower one is looking down into the top of the drum. The ends of the drum are created by two rings of 15 metals (3 Nd(III) and 12 Cd(II)) coordinated to half of the N, O binding groups of the 11 Schiff base ligands while the sides of the drum are formed by the $-(\text{CH}_2)_6-$ linkers of the Schiff base ligands. For the two $\text{Nd}_3\text{Cd}_{12}$ rings, one includes one OH^- and twenty-one OAc^- anions and the other has twenty-two OAc^-



Scheme 1. "Bending" (a) and "stretching" (b) coordination modes of flexible Schiff base ligands $\text{H}_2\text{L}^{\text{a-c}}$ and $\text{H}_2\text{L}^{1,2}$.

anions to balance the charge of cluster. In **1**, the Cd-O and Cd-N bond lengths range from 2.108 Å to 2.614 Å and 2.218 Å to 2.322 Å, respectively. While the Nd-O and Nd-N bond lengths range from 2.281 Å to 2.600 Å and 2.544 Å to 2.605 Å, respectively. In **1** and **2**, each Ln³⁺ ion and its closest two Cd²⁺ ions are linked by phenolic oxygen atoms of L¹ ligand and OAc⁻ anions.

The Cd(II) ion tends to have relatively high coordination numbers (6-8) and exhibits variable coordination geometries, somewhat similar to Ln(III). This may favor the formation of high-nuclearity Cd-Ln clusters **1** and **2**. Compared with Cd(II), the Zn(II) ion tends to have lower coordination numbers (4-6) and exhibits some common coordination geometries such as square-planar, tetragonal pyramid and octahedral. Thus, reactions of H₂L² with Zn(OAc)₂·4H₂O and Ln(OAc)₃·4H₂O under the same experimental conditions as above produced 14-metal Zn-Ln

(a)

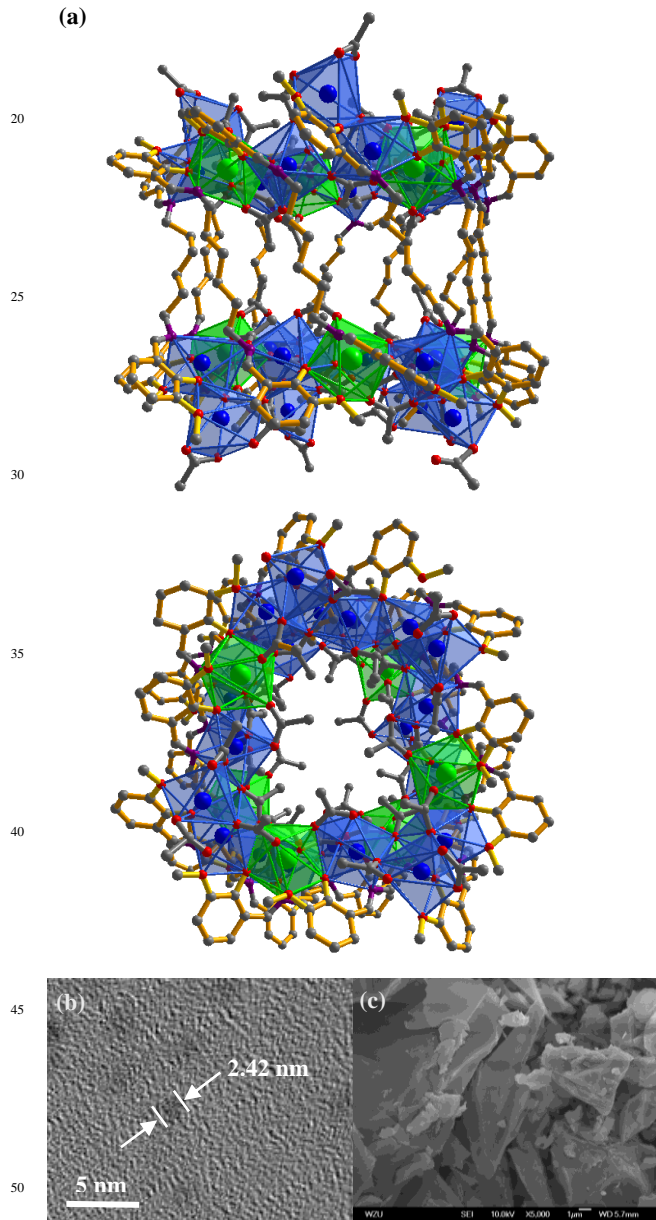


Figure 1. (a) Two views of the drum-like structure of **1**: viewed along the *c*-axis (top) and *ab*-axis (lower) (Nd³⁺: green; Zn²⁺: blue); (b, c) TEM and SEM images of **1**.

clusters **3** and **4**. They are isomorphous and have rectangular-like structures. Two views of the crystal structure of **3** are shown in Figure 2. The left view is looking right in front of the rectangle while the right one is essentially a side-on view. The X-ray structure of **3** reveals a centrosymmetric core with two equivalent Nd₂Zn₄(OAc)₁₀(OH)₂ moieties linked by two Schiff base ligands. Interestingly, the rectangular form of **3** is like a vertical strip cut from the drum-like structure of **1**. In each Nd₂Zn₄(OAc)₁₀(OH)₂ moiety, two Nd³⁺ ions have similar coordination environments, surrounded by nine oxygen atoms from one L² ligand, two OH⁻ and five OAc⁻ ions. They are bridged by two OH⁻ groups with a separation of 4.191 Å. All four Zn²⁺ ions have tetrahedral geometries. In **3** and **4**, each Ln³⁺ ion and its closest three Zn²⁺ ions are linked by phenolic oxygen atoms of the L² ligand, OAc⁻ anions and/or OH⁻ anions. The distances between Ln³⁺ and Zn²⁺ ions range from 3.648 Å to 3.800 Å. The average distances for the Zn-O (phenolic) (1.970 Å **3**, 1.963 Å **4**), Zn-N (1.994 Å **3**, 1.993 Å **4**) and Ln-O (phenolic) (2.529 Å **3**, 2.521 Å **4**) bonds are comparable to those found in the literature.³⁻⁵

It is found that analogs of **1-4** with other lanthanide ions such as Pr³⁺, Sm³⁺, Ho³⁺ and Lu³⁺ can also be isolated under the same experimental conditions, indicating that these nanoclusters are easy to be repeatedly synthesized. It is noticeable that, the Schiff base ligands exhibit a “stretched” coordination mode with metal ions in **1-4**. This may be due to the fact that, compared with those Schiff base ligands with shorter carbon-carbon backbones such as H₂L^{a-c}, there is less of a chelating or templating effect with the long-chain backbones of H₂L^{1,2}. Thus the heights of drum-like and rectangular-like structures are mainly decided by the lengths of Schiff base ligands, resulting in the formation of nanoscale clusters. The molecular dimensions of **1** and **2** are bigger than those of **3** and **4** (i. e. 20 × 24 × 24 Å for **1** vs 8 × 19 × 24 Å for **3**). It is also possible to obtain images of these Cd-Ln molecular nanoparticles using transmission electron microscopy (TEM). Dilute solutions of **1** in CH₃CN were contacted with a Cu grid and the solvent carefully evaporated under vacuum. The TEM images obtained (Figure 1b) show uniform nanoparticles with diameters measuring approximately 2.42 nm which corresponds well with the diameter of the 15-metal ring end of the drum found in the crystal structure, indicating that the nanocluster retains its unique molecular structure in solution. Energy dispersive X-ray spectroscopy (EDX) analysis of **1** indicates that the Cd:Nd ratio is about 4:1, in agreement with the crystal structure (Figure S1). In Figure 1c a panoramic scanning electron microscopy (SEM) image shows the crystalline nature of **1**.

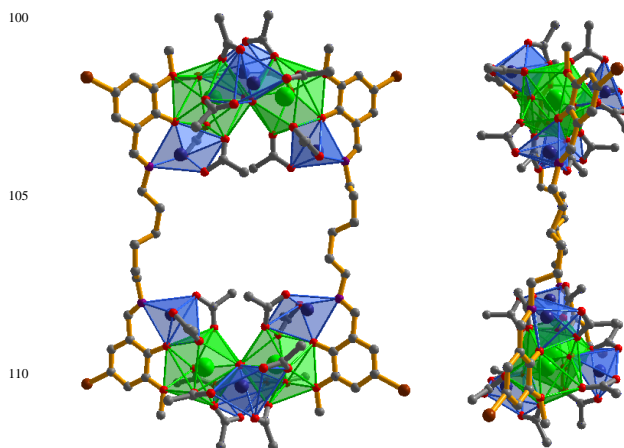


Figure 2. Two views of the square-like structure of **3**: viewed along the *b*-axis (left) and *ac*-axis (right). (Nd³⁺: green; Zn²⁺: blue)

The ^1H NMR spectrum of **1** in CDCl_3 contains multiple broad peaks ranging from -15 to $+17$, due to the diamagnetic Nd^{3+} ion. They remain unchanged for several weeks, indicating that this Cd-Ln cluster with drum-like structure is stable in solution (Figure S2). Powder XRD patterns of **3** and **4** are similar to their simulated patterns generated from single crystal X-ray data (Figure S3). Molar conductivity studies of **1-4** in CH_3CN confirm that these molecular nanoparticles are neutral in solution, in accordance with the solid state structures. These nanoclusters are easy to decompose when heated. For example, the thermogravimetric analysis of **1** shows that it starts to decompose from 195°C (Figure S4).

For Zn^{2+} and Cd^{2+} ions, their saturated d^{10} electronic configuration prevents the quenching of lanthanide luminescence through a d-d transition ($f \rightarrow d$ energy transfer),⁷ which favors the using of light-absorbing Zn(II) and Cd(II) chromophores as sensitizers for lanthanide luminescence. The photophysical properties of **1-4** were studied in both solution and the solid state. For these d-f clusters, their absorption bands in the UV-vis region are all red-shifted compared to those of the free ligands $\text{H}_2\text{L}^{1,2}$ (Figure 3). It is noticeable that the absorptions of **1-4** are much stronger than the free ligands $\text{H}_2\text{L}^{1,2}$, which enhances the ability of the ligand-center to absorb energy for sensitizing the lanthanide luminescence. For the free ligands $\text{H}_2\text{L}^{1,2}$, excitations of the absorption bands produce broad emission bands at $\lambda_{\text{max}} = 515$ nm and 509 nm, respectively (Figure S5). The emission and excitation spectra of **1-4** in CH_3CN are shown in Figures 4 and S6. Upon excitation of the ligand-centered absorption bands, **1** and **3** show the NIR luminescence of Nd^{3+} ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{1/2}$ transitions, $j = 9$, 11 and 13), and **2** and **4** show that of Yb^{3+} ($^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition).

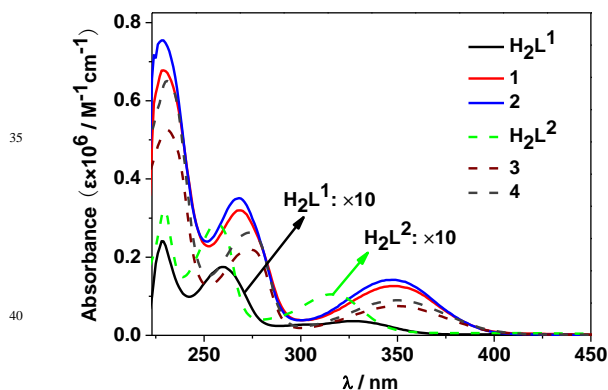


Figure 3. UV-Vis spectra of free $\text{H}_2\text{L}^{1,2}$ and **1-4** in CH_3CN at 298 K. ($C = 10^{-7} - 10^{-6}$ M)

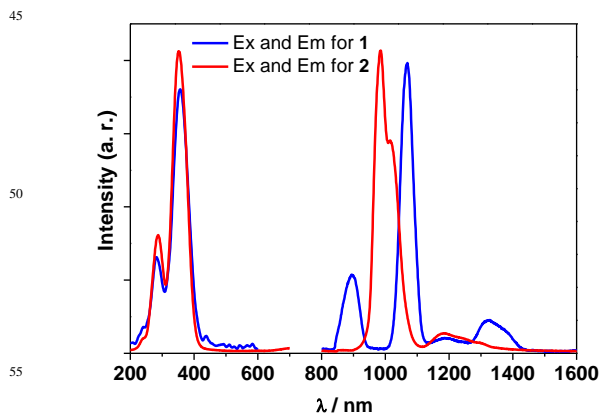


Figure 4. The NIR spectra of **1** and **2** in CH_3CN at 298 K.

1 and **2** show two excitation bands at approximately 285 nm and 355 nm, while **3** and **4** have one at approximately 370 nm, in agreement with their absorption spectra, confirming that the energy transfers from the d/L centers to Ln^{3+} ions occur (Scheme S1). For each Cd-Ln or Zn-Ln nanocluster the NIR luminescence spectrum in the solid state is similar to that in the solution. In Nd(III) clusters, the energy transfer is favorable since the Nd^{3+} ion has many possible energy-accepting levels lying above the NIR luminescent level ($^4\text{F}_{3/2}$, Scheme S1).⁸ The emission lifetimes (τ) of **1** and **3** are $2.2 \mu\text{s}$ and $1.2 \mu\text{s}$, respectively. The intrinsic quantum yields (Φ_{Ln}) of Nd^{3+} emission in **1** and **3** are calculated as 0.88% and 0.48%, respectively, using $\Phi_{\text{Ln}} = \tau/\tau_0$ ($\tau_0 = 250 \mu\text{s}$, the natural lifetime of Nd^{3+}).⁹ In Yb(III) clusters, the Yb^{3+} ion has only a single excited state $^2\text{F}_{5/2}$ at $10,200 \text{ cm}^{-1}$ (Scheme S1). The energy-transfer process in **2** and **4** may perhaps be described as electron transfer mechanism and/or phonon-assisted energy-transfer mechanisms.¹⁰ The emission lifetimes of **2** and **4** are $9.2 \mu\text{s}$ and $8.1 \mu\text{s}$, respectively. So the intrinsic quantum yields of Yb^{3+} emission in **2** and **4** are calculated as 0.46% and 0.41%, respectively ($\tau_0 = 2000 \mu\text{s}$ for Yb^{3+}).⁹ With “open” rectangular-like structures, **3** and **4** have similar emission lifetimes as other Zn-Ln Schiff-base complexes reported.^{5, 11}

In conclusion, we have successfully demonstrated the construction of 30-metal Cd-Ln and 12-metal Zn-Ln nanoclusters **1-4** from two flexible Schiff base ligands which have long $(\text{CH}_2)_6$ chain backbones. Upon excitation of the ligand-centered absorption bands, **1-4** show interesting NIR luminescence properties. The long-chain Schiff base ligands show “stretched” coordination modes with metal ions in **1-4**, resulting in the formation of drum-like Cd-Ln and rectangular-like Zn-Ln architectures with large dimensions. The results suggest that even larger metal clusters with flexible Schiff base ligands should be possible by increasing the length of the ligands. Further studies focused on the construction of d-f nanoclusters bearing flexible chain-like ligands with even longer carbon backbones and different d-metal ions are in progress.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Full experimental and characterization details for **1-4** are included in the Supporting Information. CCDC 1023236, 1023237, 983620 and 1011985 for **1-4** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

- 1 (a) B. Wang, Z. Zang, H. Wang, W. Dou, X. Tang, W. Liu, Y. Shao, J. Ma, Y. Li and J. Zhou, *Angew. Chem., Int. Ed.*, 2013, **52**, 3756-3759; (b) J.-B. Peng, Q.-C. Zhang, X.-J. Kong, Y.-Z. Zheng, Y.-P. Ren, L.-S. Long, R.-B. Huang, L.-S. Zheng and Z. Zheng, *J. Am. Chem. Soc.*, 2012, **134**, 3314-3317; (c) E. G. Mednikov, M. C. Jewell and L. F. Dahl, *J. Am. Chem. Soc.*, 2007, **129**, 11619-11630; (d) V. M. Mereacre, A. M. Ako, R. Clerac, W. Wernsdorfer, G. Filoti, J. Bartolome, C. E. Anson and A. K. Powell, *J. Am. Chem. Soc.*, 2007,

- 129, 9248-9249; (e) S.-C. Xiang, S.-M. Hu, T.-L. Sheng, R.-B. Fu, X.-T. Wu and X.-D. Zhang, *J. Am. Chem. Soc.*, 2007, **129**, 15144-15146; (f) C. Papatiantafyllopoulou, T. C. Stamatatos, C. G. Efthymiou, C.-S. Luis, F. A. A. Paz, S. P. Perlepes and G. Christou, *Inorg. Chem.*, 2010, **49**, 9743-9745.
- 2 (a) X.-L. Li, L.-X. Shi, L.-Y. Zhang, H. M. Wen, Z. N. Chen, *Inorg. Chem.*, 2007, **46**, 10892-10900; (b) H.-B. Xu, L.-X. Shi, E. Ma, L.-Y. Zhang, Q.-H. Wei and Z.-N. Chen, *Chem. Commun.*, 2006, 1601-1603; (c) H.-M. Wen, Y. Yang, X.-S. Zhou, J.-Y. Liu, D.-B. Zhang, Z.-B. Chen, J.-Y. Wang, Z.-N. Chen and Z.-Q. Tian, *Chem. Sci.*, 2013, **4**, 2471-2477; (d) S. G. Baca, H. Adams, C. S. Grange, A. P. Smith, I. Sazanovich and M. D. Ward, *Inorg. Chem.*, 2007, **46**, 9779-9789; (e) M. Yin, X. Lei, M. Li, L. Yuan and J. Sun, *J. Phys. Chem. Solids*, 2006, **67**, 1372-1378; (f) H.-B. Xu, H.-M. Wen, Z.-H. Chen, J. Li, L.-X. Shi and Z.-N. Chen, *J. Chem. Soc., Dalton Trans.*, 2010, **39**, 1948-1953; (g) S. Torelli, D. Imbert, M. Cantuel, G. Bernardinelli, S. Delahaye, A. Hauser, J.-C. G. Bünzli and C. Piguet, *Chem. Eur. J.*, 2005, **11**, 3228-3242; (h) C. Piguet, J.-C. G. Bünzli, G. Bernardinelli, G. Hopfgartner, S. Petoud and O. Schaad, *J. Am. Chem. Soc.*, 1996, **118**, 6681-6682; (i) Y.-X. Chi, S.-Y. Niu, J. Jin, R. Wang, Y. Li, *J. Chem. Soc., Dalton Trans.*, 2009, **47**, 7653-7659; (j) Y.-X. Chi, S.-Y. Niu, Z.-L. Wang, J. Jin, *Eur. J. Inorg. Chem.*, 2008, 2336-2343.
- 3 (a) M. Sakamoto, K. Manseki and H. Okawa, *Coord. Chem. Rev.*, 2001, **219**, 379-414; (b) R. E. P. Winpenny, *Chem. Soc. Rev.*, 1998, **27**, 447-452; (c) C. Camp, V. Guidal, B. Biswas, J. Pecaut, L. Dubois and M. Mazzanti, *Chem. Sci.*, 2012, **3**, 2433-2448.
- 4 (a) W.-K. Lo, W.-K. Wong, W.-Y. Wong, J. Guo, K.-T. Yeung, Y.-K. Cheng, X.-P. Yang and R. A. Jones, *Inorg. Chem.*, 2006, 9315-9325; (b) X.-P. Yang, S. Desmond, A. Liao, J. M. Stanley, R. A. Jones and B. J. Holliday, *Polyhedron*, 2013, **52**, 165-168; (c) X.-P. Yang, R. A. Jones, V. Lynch, M. M. Oye and A. L. Holmes, *J. Chem. Soc., Dalton Trans.*, 2005, **5**, 849-851; (d) X.-P. Yang, R. A. Jones, W.-K. Wong, V. Lynch, M. M. Oye and A. L. Holmes, *Chem. Commun.*, 2006, 1836-1838; (e) X.-P. Yang, C. Chan, D. Lam, D. Schipper, J. M. Stanley, X. Chen, R. A. Jones, B. J. Holliday, W.-K. Wong, S.-C. Chen and Q. Chen, *J. Chem. Soc., Dalton Trans.*, 2012, **41**, 11449-11453.
- 5 (a) M. Andruh, *Chem. Commun.*, 2011, **47**, 3025-3042; (b) X. Feng, W. Zhou, Y. Li, H. Ke, J. Tang, R. Clerac, Y. Wang, Z. Su and E. Wang, *Inorg. Chem.*, 2012, **51**, 2722-2724; (c) T. Yamaguchi, J.-P. Costes, Y. Kishima, M. Kojima, Y. Sunatsuki, N. Brefuel, J.-P. Tuchagues, L. Vendier and W. Wernsdorfer, *Inorg. Chem.*, 2010, **49**, 9125-9135; (d) C. E. Burrow, T. J. Burchell, P.-H. Lin, F. Habib, W. Wernsdorfer, R. Clerac and M. Murugesu, *Inorg. Chem.*, 2009, **48**, 8051-8053; (e) G. Novitchi, S. Shova, A. Caneschi, J.-P. Costes, M. Gdaniec and N. Stanica, *J. Chem. Soc., Dalton Trans.*, 2004, 1194-1200.
- 6 X.-P. Yang, D. Schipper, R. A. Jones, L. A. Lytwak, B. J. Holliday and S.-M. Huang, *J. Am. Chem. Soc.*, 2013, **135**, 8468.
- 50 7 (a) M. Cantuel, G. Bernardinelli, D. Imbert, J.-C. G. Bünzli, G. Hopfgartner and C. Piguet, *J. Chem. Soc., Dalton Trans.*, 2002, 1929-1940; (b) D. H. Metcalf, J. P. Bolender, M. S. Driver and F. S. Richardson, *J. Phys. Chem.*, 1993, **97**, 553-564; (c) V. Wen, Y. Zhao, L. Wang, M. Zhang and D. Gao, *J. Rare Earths*, 2007, **25**, 679-683; (d) J. Jankolovits, C. M. Andolina, J. W. Kampf, K. N. Raymond and V. L. Pecoraro, *Angew. Chem., Int. Ed.*, 2011, **50**, 9660-9664; (e) P. A. Brayshaw, J.-C. G. Bünzli, P. Froidevaux, J. M. Harrowfield, Y. Kim and A. N. Sobolev, *Inorg. Chem.*, 1995, **34**, 2068-2076.
- 8 (a) S. G. Baca, H. Adams, D. Sykes, S. Faulkner and M. D. Ward, *Dalton Trans.*, 2007, 2419-2430; (b) G. M. Davies, S. J. A. Pope, H. Adams, S. Faulkner and M. D. Ward, *Inorg. Chem.*, 2005, **44**, 4656-4665; (c) G. F. de Sá, O. L. Malta, C. de Mello Donegá, A. M. Simas, R. L. Longo, P. A. Santa-Cruz and E. F. da Silva Jr, *Coord. Chem. Rev.*, 2000, **196**, 165-195; (d) J.-C. G. Bünzli and C. Piguet, *Chem. Soc. Rev.*, 2005, **34**, 1048-1077; (e) N. M. Shavaleev, G. Accorsi, D. Virgili, D. R. Bell, T. Lazarides, G. Calogero, N. Armaroli and M. D. Ward, *Inorg. Chem.*, 2005, **44**, 61-72.
- 9 (a) S. B. Meshkova, Z. M. Topilova, D. V. Bolshoy, S. V. Beltyukova, M. P. Tsvirko, V. Y. Venchikov and V. Ya, *Acta Phys. Pol. A*, 1999, **95**, 983-990; (b) S. I. Klink, L. Grave, D. N. Reinhoudt and F. C. J. M. v. Veggel, *J. Phys. Chem. A*, 2000, **104**, 5457-5468.
- 10 (a) W. D. Horrocks, J. P. Bolender, W. D. Smith and R. M. Supkowski, *J. Am. Chem. Soc.*, 1997, **119**, 5972-5973; (b) C. Reinhard and H. U. Gudel, *Inorg. Chem.*, 2002, **41**, 1048-1055.
- 75 11 (a) W.-K. Wong, H. Liang, W.-Y. Wong, Z. Cai, K.-F. Li and K.-W. Cheah, *New J. Chem.*, 2002, **26**, 275-278; (b) W.-K. Wong, A. Hou, J. Guo, H. He, L. Zhang, W.-Y. Wong, K.-F. Li, K.-W. Cheah, F. Xu and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 2001, 3092-3098. (c) X. Lü, W. Bi, W. Chai, J. Song, J. Meng, W.-Y. Wong, W.-K. Wong and R. A. Jones, *New J. Chem.*, 2008, **32**, 127-131; (d) W.-K. Lo, W.-K. Wong, J. Guo, W.-Y. Wong, K.-F. Li and K.-W. Cheah, *Inorg. Chim. Acta*, 2004, **357**, 4510-4521. (e) W. Bi, T. Wei, X. Lü, Y. Hui, J. Song, S. Zhao, W.-K. Wong and R. A. Jones, *New J. Chem.*, 2009, **33**, 2326-2334.