Anion-Dependent Self-Assembly of Near-Infrared Luminescent 24- and 32-Metal Cd–Ln Complexes with Drum-like Architectures

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Ⓢ *Supporting Information*

ABSTRACT: Two series of 4d−4f clusters $[Ln_8Cd_{24}L_{12}(OAc)_{48}]$ and $[Ln_6Cd_{18}L_9Cl_{8(10)}(OAc)_{28(26)}]$ (Ln = Nd, Gd, Er, and Yb) with novel drum-like structures were prepared using a flexible Schiff base ligand. Their NIR luminescence properties were determined.

The design and construction of high-nuclearity hetero-metallic d−f clusters has received extensive attention due to the remarkable physical and chemical properties associated with this class of materials.[1] Recently, research on polynuclear lanthanide complexes of Yb(III), Nd(III) and Er(III) with near-infrared (NIR) emission in the 900−1600 nm range has become a hot topic due to potential applications in bioassays and laser systems.[2] For example, light-absorbing d-block metal chromophores (i.e., Pt^{II},[3c,d] Ru^{II},[3e,f] Zn^{II},[3g,h] Cr^{II},[3i,j] and Cd^{II}[3k,l]) can be used as sensitizers for NIR luminescence from Ln(III) centers following ligand→f and d→f energy-transfers.[3] One of the challenges in this area is control over the stoichiometries and structures of high-nuclearity d−f complexes. This is due to the difficulty in controlling the variable coordination environment of the lanthanide ions. The majority of d−f clusters reported so far have employed simple polydentate rigid ligands, such as multicarboxylic acids, iminodiacetic acids, pyridine-carboxylate, and carbonyl ligands.[1,4]

Flexible ligands may provide more possibilities for the construction of unique frameworks because of their freedom of conformation. While flexible ligands featuring S, N, or O atom donors have been employed in the design of d-block transition metal frameworks,[5] relatively very few studies involving flexible ligands in the construction of high-nuclearity d−f clusters have been reported. Our recent studies have focused on the synthesis of polynuclear lanthanide complexes with different polydentate ligands.[6] For example, it has been found that the use of Schiff base ligands with flexible carbon−carbon backbones containing 3 and 4 methylene (CH₂) units resulted in various dinuclear,[6a] tetranuclear[6b] and hexanuclear[6c,d] d−f complexes. We were naturally curious as to the effect of increasing the $(CH_2)_n$ chain length. Complexes synthesized using the Schiff base ligand H₂L which has a 6 carbon backbone have remarkable and unprecedented molecular architectures. Thus, we report here two series of high nuclearity 4d−4f heterometallic clusters $[Ln_8Cd_{24}L_{12}(OAc)_{48}]$ and $[Ln_6Cd_{18}L_9Cl_8(OAc)_{28}]$ (or $[Ln_6Cd_{18}L_9Cl_{10}(OAc)_{26}]$) (H₂L = *N,N′*-bis(3-methoxy-salicylidene)hexane-1,6-diamine, Scheme 1). Both Ln(III) and

**Scheme 1. Flexible Ligand H₂L**
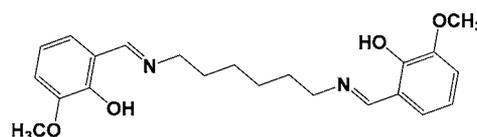
Cd(II) ions have the potential for high coordination numbers (6−8) with variable coordination geometries and this, combined with the use of the flexible ligand H₂L, appears to be the key to the self-assembly of these 24- and 32-metal Ln/Cd complexes. Although numerous polynuclear d−f complexes with varying structures have been prepared using Schiff base ligands, most of them have less than 10 metal atoms.[7] To the best of our knowledge, the 32-metal Cd−Ln complexes reported here are the highest nuclearity d−f complexes with Schiff base ligands thus far reported. More importantly, these complexes exhibit novel drum-like structures with the Ln(III) centers shielded within the nanoscale structures and protected from the outside solvent molecules which can quench lanthanide luminescence. This may help to improve their NIR luminescent properties.

Reactions of H₂L with $Cd(OAc)_2 \cdot 2H_2O$ and $Ln(OAc)_3 \cdot 4H_2O$ in refluxing MeOH/EtOH produced yellow solutions from which the Cd−Ln complexes $[Ln_8Cd_{24}L_{12}(OAc)_{48}]$ (Ln = Nd (**1**), Gd (**2**), Er (**3**) and Yb (**4**)) were isolated as pale yellow crystalline solids. Complexes **1−4** are isomorphous, and possess 32-metal drum-like structures. Two views of the crystal structure of **1** are shown in Figure 1, and reveal *mm* symmetry. The top view is essentially a side-on view while the lower one is looking down into the top of the drum. The complex is of nanoscale proportions (19 × 26 × 26 Å). The ends of the drum are created by two rings of 16 metals (4 Nd(III) and 12 Cd(II)) coordinated to half of the N, O binding groups of the 12 Schiff base ligands plus 24 OAc⁻ anions. The sides of the drum are formed by the -(CH₂)₆- linkers of the Schiff base ligands. Thus each Schiff base ligand is coordinated to metals at both ends of the drum. In each 16-metal ring, four Nd ions are eight-coordinate. For the 12 Cd^{2+} ions, four of them have bipyramidal geometries, and the other eight Cd^{2+} ions are seven-coordinate (Supporting Information).
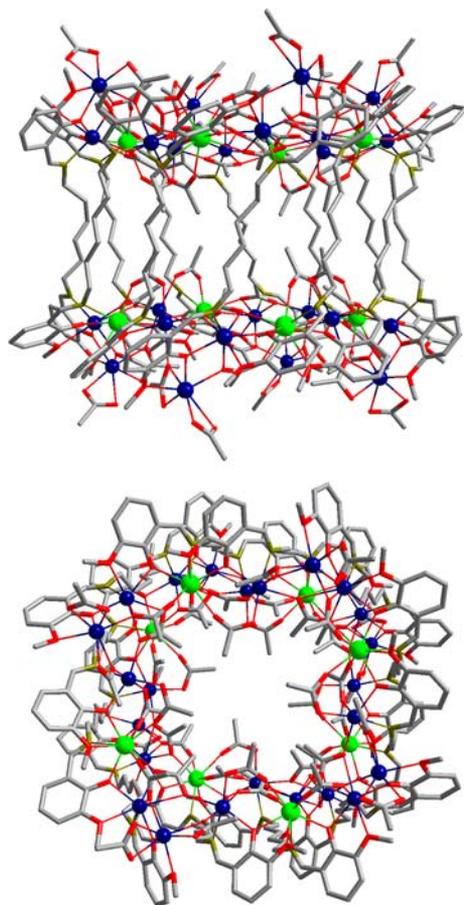
Figure 1. View of the crystal structure of **1**. Viewed along the *a*-axis (top) and *c*-axis (lower) (Nd³⁺, green; Cd³⁺, blue).
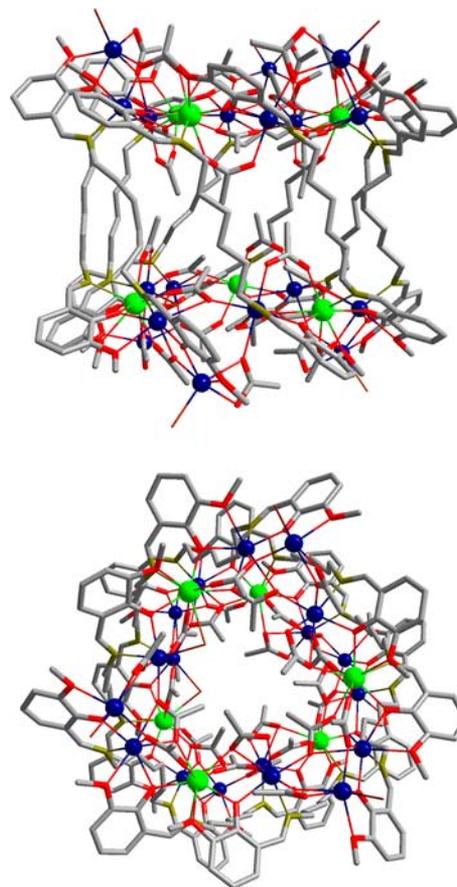

Figure 2. View of the crystal structure of **5**. Viewed along the *a*-axis (top) and *c*-axis (lower). (Nd³⁺, green; Cd³⁺, blue).

The self-assembly process of the drum-like structures appears to be anion dependent. Thus, if Cl⁻ anions are introduced into the reactions with the use of LnCl₃·6H₂O, 24-metal drum-like complexes $[Ln_6Cd_{18}L_9Cl_8(OAc)_{28}]$ (Ln = Nd (**5**) and Gd (**6**)) and $[Ln_6Cd_{18}L_9Cl_{10}(OAc)_{26}]$ (Ln = Er (**7**) and Yb (**8**)) are produced. Complexes **5** and **6** are isomorphous. As shown in Figure 2, the drum-like architecture of **5** is formed by two 12-metal rings $(Er_3Cd_9Cl_4(OAc)_{14})$ linked by nine L²⁻ ligands. The molecular dimensions of **5** (16 × 21 × 21 Å) are smaller than those of **1**. Complexes 7 and 8 are also isomorphous. The slight difference between **5**–**6** vs **7**–**8** is that in **7**–**8** two bridging Cl⁻ anions replace two tridentate OAc⁻ anions (Figure S1, Supporting Information).

In **1**–**8**, each Ln³⁺ ion and its closest two Cd²⁺ ions are linked by phenolic oxygen atoms of L²⁻, OAc⁻ anions and/or Cl⁻ anions. The distances between Ln³⁺ and Cd²⁺ ions range from 3.595 to 3.964 Å while the Ln−Ln distances lie in a narrow range of 10.099−10.402 Å for **1**–**4** and 9.303−9.647 Å for **5**–**8**. The ionic radius differences among the 4f ions do not result in significant changes in the structures of complexes and we have also isolated analogs of these compounds with Ce³⁺, Eu³⁺, Tb³⁺, Dy³⁺, Tm³⁺ and Lu³⁺.

The d-block metal ions introduced into lanthanide complexes may conceivably play two different roles in the luminescence properties of Ln³⁺ ions. They may enhance the luminescence via d→f energy transfer,[3] or they may quench the luminescence via f→d energy transfer.[8] For example, chromogenic Cd components have been used as sensitizers
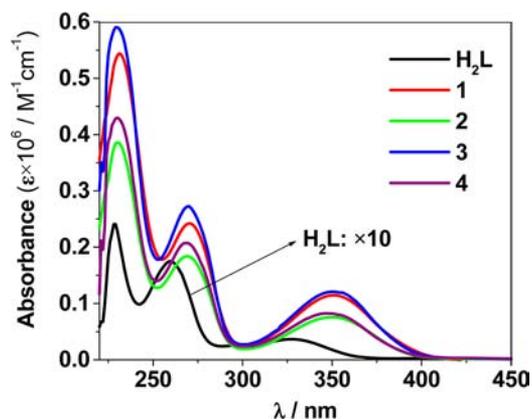
for lanthanide luminescence following ligand→f and d→f energy-transfers (i.e., via LMCT excited states).[3k,l,9]

The photophysical properties of **1**–**8** were studied in CH₃CN. Molar conductivity studies in CH₃CN confirm that these complexes are neutral, in accordance with the solid state structures. The free ligand H₂L exhibits absorption bands at 226, 260, and 327 nm which are all red-shifted upon coordination to metal ions in **1**–**8** (Figure 3 and Figure S2, Supporting Information).

The absorptions of the complexes are significantly stronger than the free ligand, which is advantageous for the ligand-center

Figure 3. UV−vis spectra of H₂L and complexes **1**–**4** in CH₃CN (C = 10^{-7}–10^{-6} M).

to absorb energy for sensitizing the lanthanide luminescence. For the free ligand H_2L, excitation of the absorption band at 295 or 410 nm produces a broad emission band at $\lambda_{max} = 515$ nm (Figure S3, Supporting Information). Upon excitation of the ligand-centered absorption bands, complexes **1** and **5** show the NIR luminescence of Nd^{3+} ($^4F_{3/2} \rightarrow {}^4I_{j/2}$ transitions, $j = 9, 11$ and 13)), and complexes **4** and **8** show that of Yb^{3+} ($^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition) (Figure 4). The excitation spectra of
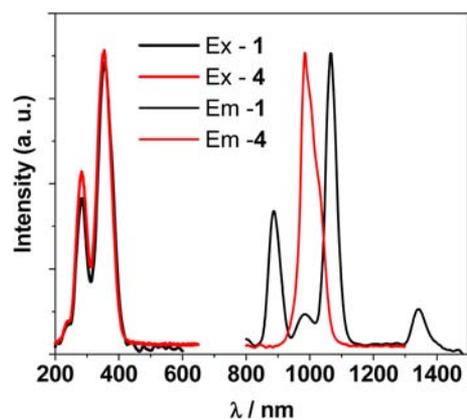

Figure 4. NIR excitation and emission spectra of complexes **1** and **4** in CH_3CN.

Nd(III) and Yb(III) complexes show two bands at approximately 285 and 355 nm (Figure 4), in agreement with their absorption spectra, confirming that energy transfer from the Cd/L centers to Ln^{3+} ions occurs. In Nd(III) complexes, the energy transfer is favorable since the Nd^{3+} ion has many possible energy-accepting levels lying above the emissive $^4F_{3/2}$ state at 11 300 cm^{-1} (Scheme 2).[10] The emission lifetimes (τ)

Scheme 2. Energy Levels in Lanthanide Complexes[a]
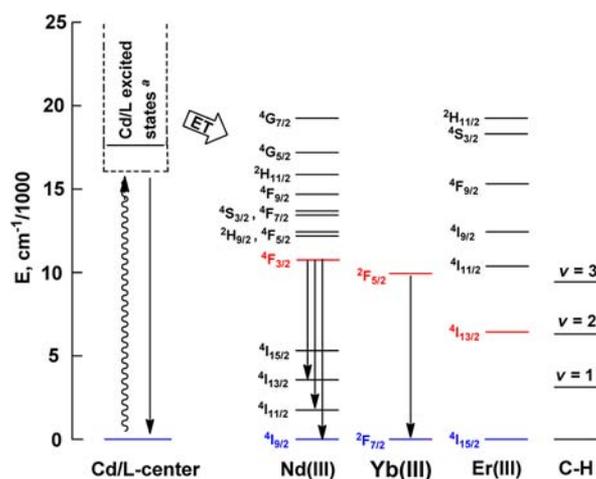
[a]Approximate energy level: estimated from the visible emission of lanthanide complexes, which may come from the intraligand transition mixing with the LMCT transition).[3l,9]

of **1** and **5** are 2.9 and 1.4 μs, respectively. The intrinsic quantum yields (Φ_{Ln}) of Nd^{3+} emission in **1** and **5** are calculated as 1.16 and 0.56%, respectively, using $\Phi_{Ln} = \tau/\tau_0$ (τ_0 = 250 μs, the natural lifetime of Nd^{3+}). In contrast, the Yb^{3+} ion has only a single excited state $^2F_{5/2}$ at 10 200 cm^{-1} which is much lower than those of the Cd/L center. The energy-transfer

process in these Yb(III) complexes may perhaps be described as electron transfer mechanism and/or phonon-assisted energy-transfer mechanisms.[11] The former mechanism is based on the fact that among the lanthanides, Yb(III) does not possess a very negative reduction potential (−1.05 V vs the NHE) and can be transiently reduced to Yb(II) when the sensitizer acts as an electron donor in its excited state. The emission lifetimes of **4** and **8** are 9.7 and 10.9 μs, respectively. So the intrinsic quantum yields of Yb^{3+} emission in **4** and **8** are calculated as 0.49 and 0.55%, respectively.

For Er(III) complexes **3** and **7** no obvious or very weak NIR emission attributable to the Er^{3+} ion was observed under the experimental conditions. Although the Er^{3+} ion has several electronically excited states that would be energetically appropriate for accepting energy from a sensitizer, its NIR emission may be quenched by C−H vibrations from the ligand (Scheme 2). In **3** and **7**, the resonance energy transfer (RET) from the emitting Er^{3+} ion to the oscillating C−H group is more efficient than those in Nd(III) and Yb(III) complexes, since the energy gap of the radiative (f−f) transition for the Er^{3+} ion ($^4I_{13/2} \rightarrow {}^4I_{15/2}$: ~6500 cm^{-1}) is smaller than those of Nd^{3+} ($^4F_{3/2} \rightarrow {}^4I_{j/2}$: ~7400 ($j = 13$), ~9400 ($j = 11$), ~11 000 ($j = 9$)) and Yb^{3+} ($^2F_{5/2} \rightarrow {}^2F_{7/2}$: ~10 000 cm^{-1}) and matches better the energy of the vibrational overtone(s) of C−H groups with low vibrational quanta (ν).[12]

For complexes **1−8**, a broad Cd/L centered emission can be detected at about 540 nm upon excitation of the ligand-centered absorption bands. For Gd(III) complexes **2** and **6**, the Gd^{3+} ion possesses no energy levels below 32 000 cm^{-1} and therefore cannot accept any energy from the sensitizer. As shown in Figure 5, the Cd/L centered emissions of **1**, **3**, and **4**
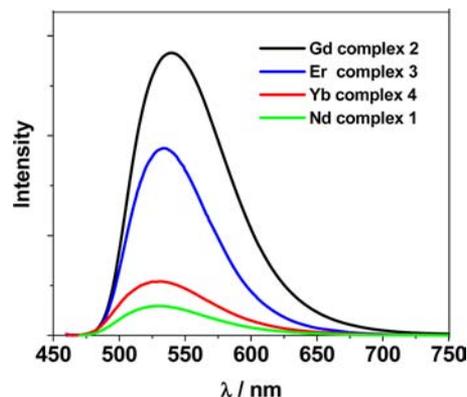

Figure 5. Visible emission spectra of complexes **1−4** with the same absorbance value at $\lambda_{ex} = 350$ nm in CH_3CN.

are weaker than that of Gd(III) complex **2**, due to the energy transfers to Nd^{3+}, Er^{3+} and Yb^{3+} ions, respectively. With the same absorbance value at the excitation wavelength (350 nm), the Cd/L centered emissions in **3** are 7.9 and 3.5 times as strong as those in **1** and **4**, respectively, indicating that the energy transfer to lanthanide ion in **3** is less efficient than those in **1** and **4**. The energy transfer difference between **1** and **3** may be due to the fact that the Nd^{3+} ion has more appropriate energy-accepting levels than the Er^{3+} ion in the range 15 000−20 000 cm^{-1} (Scheme 2),[10] in which the accepted energy is transferred to the NIR luminescent levels of the lanthanide ions through internal conversion. This is also observed in complexes **5−8** (Figure S4, Supporting Information).

In conclusion, we have successfully demonstrated a new route for the anion-dependent self-assembly of high-nuclearity d−f metal clusters with unusual drum-like architectures using flexible Schiff base ligands. With the Ln(III) centers shielded within the structures, these clusters display interesting NIR luminescence properties. The results provide new insights into the construction of novel high-nuclearity clusters and offer a promising foundation for the development of new functional materials. Further studies focused on this synthetic methodology and exploration of complexes of even higher nuclearity using more flexible Schiff base ligands are in progress.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Experimental procedures and crystal structure determination details; X-ray crystallographic data for **1**−**8** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Müller, A. *Nature* **2007**, *447*, 1034−1035. (b) Müller, A.; Kögerler, P.; Dress, A. W. M. *Coord. Chem. Rev.* **2001**, *222*, 193−218. (c) Mednikov, E. G.; Jewell, M. C.; Dahl, L. F. *J. Am. Chem. Soc.* **2007**, *129*, 11619−11630.

(2) (a) Bünzli, J.-C. G. *Chem. Rev.* **2010**, *110*, 2729−2755. (b) Binnemans, K. *Chem. Rev.* **2009**, *109*, 4283−4374. (c) Frangioni, J. V. *Curr. Opin. Chem. Biol.* **2003**, *7*, 626−634.

(3) (a) Ward, M. D. *Coord. Chem. Rev.* **2010**, *254*, 2634−2642. (b) Vigato, R. A.; Peruzzo, V.; Tamburini, S. *Coord. Chem. Rev.* **2009**, *253*, 1099−1201. (c) Li, X.-L.; Shi, L.-X.; Zhang, L.-Y.; Wen, H. M.; Chen, Z. N. *Inorg. Chem.* **2007**, *46*, 10892−10900. (d) Xu, H.-B.; Shi, L.-X.; Ma, E.; Zhang, L.-Y.; Wei, Q.-H.; Chen, Z.-N. *Chem. Commun.* **2006**, 1601−1603. (e) Baca, S. G.; Adams, H.; Grange, C. S.; Smith, A. P.; Sazanovich, I.; Ward, M. D. *Inorg. Chem.* **2007**, *46*, 9779−9789. (f) Davies, G. M.; Pope, S. J. A.; Adams, H.; Faulkner, S.; Ward, M. D. *Inorg. Chem.* **2005**, *44*, 4656−4665. (g) Yin, M.; Lei, X.; Li, M.; Yuan, L.; Sun, J. *J. Phys. Chem. Solids* **2006**, *67*, 1372−1378. (h) Xu, H.-B.; Wen, H.-M.; Chen, Z.-H.; Li, J.; Shi, L.-X.; Chen, Z.-N. *J. Chem. Soc., Dalton Trans.* **2010**, *39*, 1948−1953. (i) Torelli, S.; Imbert, D.; Cantuel, M.; Bernardinelli, G.; Delahaye, S.; Hauser, A.; Bünzli, J.-C. G.; Piguet, C. *Chem.—Eur. J.* **2005**, *11*, 3228−3242. (j) Piguet, C.; Bünzli, J.-C. G.; Bernardinelli, G.; Hopfgartner, G.; Petoud, S.; Schaad, O. *J. Am. Chem. Soc.* **1996**, *118*, 6681−6682. (k) Chi, Y.-X.; Niu, S.-Y.; Jin, J.; Wang, R.; Li, Y. *J. Chem. Soc., Dalton Trans.* **2009**, *47*, 7653−7659. (l) Chi, Y.-X.; Niu, S.-Y.; Wang, Z.-L.; Jin, J. *Eur. J. Inorg. Chem.* **2008**, 2336−2343.

(4) (a) Xiang, S.-C.; Hu, S.-M.; Sheng, T.-L.; Fu, R.-B.; Wu, X.-T.; Zhang, X.-D. *J. Am. Chem. Soc.* **2007**, *129*, 15144−15146. (b) Zaleski, C. M.; Depperman, E. C.; Kampf, J. W.; Kirk, M. L.; Pecoraro, V. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 3912−3914. (c) Mishra, A.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *J. Am. Chem. Soc.* **2004**, *126*, 15648−15649.

(5) (a) Robin, A. Y.; Fromm, K. M. *Coord. Chem. Rev.* **2006**, *250*, 2127−2157. (b) Xie, Y.-B.; Zhang, C.; Li, J.-R.; Bu, X.-H. *J. Chem. Soc., Dalton Trans.* **2004**, 562−569.

(6) (a) Yang, X.-P.; Lam, D.; Chan, C.; Stanley, J. M.; Jones, R. A.; Holliday, B. J.; Wong, W.-K. *J. Chem. Soc., Dalton Trans.* **2011**, *40*, 9795−9801. (b) Yang, X.-P.; Jones, R. A.; Lynch, V.; Oye, M. M.; Holmes, A. L. *J. Chem. Soc., Dalton Trans.* **2005**, *5*, 849−851. (c) Yang, X.-P.; Jones, R. A.; Wong, W.-K.; Lynch, V.; Oye, M. M.; Holmes, A. L. *Chem. Commun.* **2006**, 1836−1838. (d) Yang, X.-P.; Chan, C.; Lam, D.; Schipper, D.; Stanley, J. M.; Chen, X.; Jones, R. A.; Holliday, B. J.; Wong, W.-K.; Chen, S.-C.; Chen, Q. *J. Chem. Soc., Dalton Trans.* **2012**, *41*, 11449−11453.

(7) (a) Andruh, M. *Chem. Commun.* **2011**, *47*, 3025−3042. (b) Sakamoto, M.; Manseki, K.; Okawa, H. *Coord. Chem. Rev.* **2001**, *219*, 379. (c) Winpenny, R. E. *Chem. Soc. Rev.* **1998**, *27*, 447.

(8) (a) Wen, V.; Zhao, Y.; Wang, L.; Zhang, M.; Gao, D. *J. Rare Earths* **2007**, *25*, 679−683. (b) Brayshaw, P. A.; Bünzli, J.-C. G.; Froidevaux, P.; Harrowfield, J. M.; Kim, Y.; Sobolev, A. N. *Inorg. Chem.* **1995**, *34*, 2068−2076. (c) Cantuel, M.; Bernardinelli, G.; Imbert, D.; Bünzli, J.-C. G.; Hopfgartner, G.; Piguet, C. *J. Chem. Soc., Dalton Trans.* **2002**, 1929−1940. (d) Metcalf, D. H.; Bolender, J. P.; Driver, M. S.; Richardson, F. S. *J. Phys. Chem.* **1993**, *97*, 553−564.

(9) (a) Chen, Q.-Y.; Luo, Q.-H.; Hu, X.-L.; Shen, M.-C.; Chen, J.-T. *Chem.—Eur. J.* **2002**, *8*, 3984−3990. (b) Wei, K.-J.; Xie, Y.-S.; Ni, J.; Zhang, M.; Liu, Q.-L. *Cryst. Growth Des.* **2006**, *6*, 1341−1350.

(10) (a) Ward, M. D. *Coord. Chem. Rev.* **2007**, *251*, 1663−1677. (b) Bünzli, J.-C. G.; Piguet, C. *Chem. Soc. Rev.* **2005**, *34*, 1048−1077. (c) Shavaleev, N. M.; Accorsi, G.; Virgili, D.; Bell, D. R.; Lazarides, T.; Calogero, G.; Armaroli, N.; Ward, M. D. *Inorg. Chem.* **2005**, *44*, 61−72. (d) Davies, G. M.; Pope, S. J. A.; Adams, H.; Faulkner, S.; Ward, M. D. *Inorg. Chem.* **2005**, *44*, 4656−4665.

(11) (a) Horrocks, W. D.; Bolender, J. P.; Smith, W. D.; Supkowski, R. M. *J. Am. Chem. Soc.* **1997**, *119*, 5972−5973. (b) Reinhard, C.; Gudel, H. U. *Inorg. Chem.* **2002**, *41*, 1048−1055.

(12) (a) Artizzu, F.; Mercuri, M. L.; Serpe, A.; Deplano, P. *Coord. Chem. Rev.* **2011**, *255*, 2514−2529. (b) Wada, Y.; Okubo, T.; Ryo, M.; Nakazawa, T.; Hasegawa, Y.; Yanagida, S. *J. Am. Chem. Soc.* **2000**, *122*, 8583−8584. (c) Ermolaev, V. L.; Sveshnikova, E. B. *Russ. Chem. Rev.* **1994**, *63*, 905−922. (d) Hernandez, I.; Tan, R. H. C.; Pearson, J. M.; Wyatt, P. B.; Gillin, W. P. *J. Phys. Chem. B* **2009**, *113*, 7474−7481. (e) Hernandez, I.; Zheng, Y.-X.; Motevalli, M.; Tan, R. H. C.; Gillin, W. P.; Wyatt, P. B. *Chem. Commun.* **2013**, *49*, 1933−1935. (f) Monguzzi, A.; Tubino, R.; Meinardi, F.; Biroli, A. O.; Pizzotti, M.; Demartin, F.; Quochi, F.; Cordella, F.; Loi, M. A. *Chem. Mater.* **2009**, *21*, 128−135. (g) Doffek, C.; Alzakhem, N.; Bischof, C.; Wahsner, J.; Guden-Silber, T.; Lugger, J.; Platas-Iglesias, C.; Seitz, M. *J. Am. Chem. Soc.* **2012**, *134*, 16413−16423.

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