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First NIR luminescent polymeric high-nuclearity Cd-Ln nanoclusters from a long-chain Schiff base ligand

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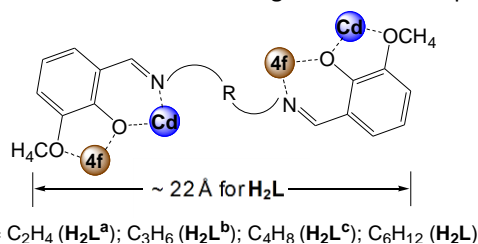
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Two classes of Cd-Ln nanoclusters [Ln₆Cd₂₂Cl₁₄(OH)₂L₁₀(OAc)₂₆]_n (Ln = La (1) and Nd (2)), and [Yb₆Cd₁₈Cl₆(OH)₂L₉(OAc)₂₈] (3) were prepared using a long-chain Schiff base ligand. 1 and 2 exhibit unusual 1-D coordination polymeric structures built by 28-metal drum-like units, while 3 has a 0-D 24-metal nano-drum-like architecture. Their NIR luminescence properties were investigated.

Metal nanoclusters with well-defined structures and interesting properties have emerged as a new class of nanomaterials for their potential applications in optoelectronics, magnetism, and as porous materials.^{1,2} High-nuclearity heterometallic nanoclusters (e.g., with more than twenty metal atoms) composed of d-block transition metals and lanthanide ions (Ln³⁺) are currently of interest due to the remarkable *physical* and *chemical* properties associated with this class of materials.^{3,4} Self-assembly by metal-ligand coordination is one of the most efficient processes that organize individual molecular components into nanosize species.^{5,6} Lanthanide ions tend to have relatively high coordination numbers (7-10) and exhibit variable coordination geometries. One important challenge for coordination chemists is the construction of coordination polymeric high-nuclearity d-f nanoclusters due to the difficulty in controlling the combination of the bulky lanthanide-based building blocks in the desired order. Although several large lanthanide-based clusters with nuclearities up to 136⁷ have been reported,^{8,9} there are only very few that have been recognized in polymeric networks.¹⁰⁻¹² Many reports have so far focused on high-nuclearity 3d-4f clusters, such as Cu/Ln,¹³ Mn/Ln¹⁴ and Ni/Ln¹⁵ cluster systems, in order to study their magnetic properties as single-molecule magnets. In contrast, high-nuclearity d-f systems with luminescence properties have received much less attention. Light-absorbing d-block metal chromophores (i.e. Pt^{II},¹⁶ Ru^{II},¹⁷ Zn^{II},¹⁸ Cr^{II}¹⁹ and Cd^{II}²⁰) can be

used as sensitizers for luminescence from Ln(III) centers following ligand→f and d→f energy-transfer.

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 clusters.²¹⁻²⁸ Schiff base ligands with flexible carbon-carbon backbones may provide more possibilities for the construction of unique frameworks because of their freedom of conformation. 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 (i.e. H₂L^{a-c}, Scheme 1).²¹⁻³¹ The structures of these lanthanide-based Schiff base complexes are often influenced by a variety of factors such as the ligand structure, the nature of metal ions, and pH value of environment. As part of our continuing studies focused on the construction of luminescent polynuclear lanthanide-based frameworks,^{32,33} we report here two classes of Cd-Ln nanoclusters [Ln₆Cd₂₂Cl₁₄(OH)₂L₁₀(OAc)₂₆]_n (Ln = La (1) and Nd (2)) and [Yb₆Cd₁₈Cl₆(OH)₂L₉(OAc)₂₈] (3), with a Schiff base ligand N,N'-bis(3-methoxysalicylidene)hexane-1,6-diamine (H₂L, Scheme 1). H₂L has a 6 carbon backbone. In a linear configuration, the length of H₂L is approximately 22 Å (Scheme 1). This appears to increase the flexibility of the ligand and seems to be a factor in the formation of larger metal clusters. Interestingly, 1 and 2 exhibit unusual 1-D polymeric structures in which 28-metal nano-drum-like Ln₆Cd₂₂ building units are linked by double Cl-bridges, while 3 has a 0-D 24-metal nano-drum-like architecture. Although a rich variety of coordination polymeric d-f frameworks with Schiff base ligands have been prepared,



Scheme 1 Flexible Schiff base ligands

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most of them are constructed using “single” metal ions or metal clusters with nuclearities less than five as building blocks.^{34–36} To the best of our knowledge, **1** and **2** are the first reported examples of 1-D polymeric high-nuclearity 4d–4f nanoclusters formed by flexible long-chain Schiff base ligands.

The Schiff-base ligand H₂L was prepared according to well-established procedures.³⁷ In the presence of NaOH (0.03 mol/L), reactions of H₂L with Cd(OAc)₂·4H₂O and LnCl₃·6H₂O (Ln = La and Nd) 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 similar 1-D polymeric structures containing 28-metal drum-like Ln₆Cd₂₂ building units. Hydroxide (OH⁻) anions are found in the structures of **1** and **2**, indicating that the basic environment favors the formation of these Cd–Ln clusters. Two views of the La₆Cd₂₂ structure of **1** are shown in Figure 1. The top view is essentially a side view, while the lower one is looking down onto the top of the drum. The drum dimensions are approximately 19 × 23 × 23 Å. The ends of the drum are created by two rings of 14 metals (3 La(III) and 11 Cd(II)) coordinated to half of the N, O binding groups of the 10 Schiff base ligands while the sides of the drum are formed by the -(CH₂)₆- linkers of the Schiff base ligands. Each La₃Cd₁₁ ring includes one OH⁻, seven Cl⁻ and thirteen OAc⁻ anions. For **1**, the internal sizes of the drum are approximately 7 × 9 × 9 Å, which are large enough to enclose small guest molecules such as

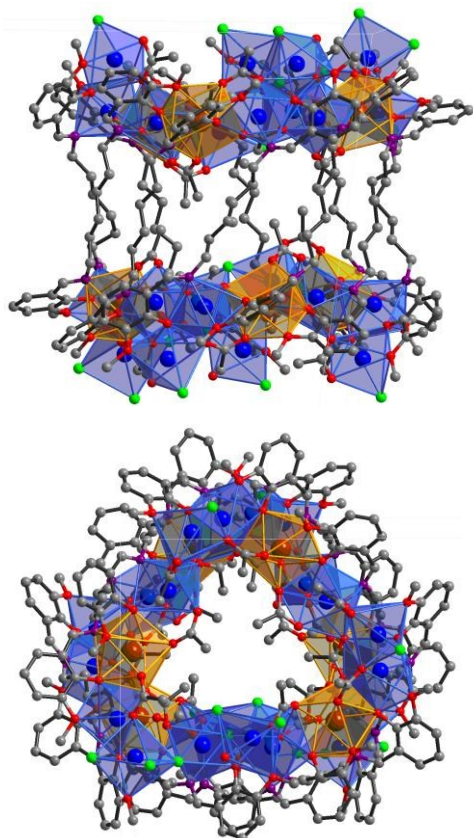


Figure 1 Two views of the drum-like La₆Cd₂₂ building unit in **1**: viewed along the *b*-axis (top) and *c*-axis (lower) (La³⁺: brown; Cd²⁺: blue; Cl⁻: green).

diethyl ether (Figure S1 in the ESI). A view of the 1-D polymeric chain-like structure of **1** is shown in Figure 2. The 1-D polymeric structure is formed by a zig-zag chain of alternating La₆Cd₂₂ units and double Cl⁻ anions which bridge between the metal clusters.

Different from the above reactions, the reaction of H₂L with Cd(OAc)₂·4H₂O and YbCl₃·6H₂O under the same experimental conditions produced 24-metal drum-like Cd–Yb cluster **3**. This maybe is due to the fact that the ion radius of Yb³⁺ is smaller than those of La³⁺ and Nd³⁺ (85.8 pm vs 106.1 pm and 99.5 pm). It is found that analogues of **3** with other lanthanide ions such as Tm³⁺ and Lu³⁺ can also be isolated under the same experimental conditions. A view of the crystal structure of **3** is shown in Figure 3. The ends of the drum are created by two rings of 12 metals (3 Yb(III) and 9 Cd(II)) coordinated to half of the N, O binding groups of the nine Schiff base ligands plus one OH⁻, three Cl⁻ and fourteen OAc⁻ ions, while the sides of the drum are formed by the -(CH₂)₆- linkers of the Schiff base ligands (Figure S2 in the ESI). In **1–3**, each Ln³⁺ ion and its closest two Cd²⁺ ions are linked by phenolic oxygen atoms of L ligand and OAc⁻ anions. The Cd–O and Cd–N bond lengths range from 2.211 Å to 2.648 Å and 2.242 Å to 2.334 Å, respectively. While the Ln–O and Ln–N bond lengths range from 2.301 Å to 2.682 Å and 2.476 Å to 2.638 Å, respectively.

The carbon-carbon backbone of the H₂L ligand adopts an essentially “linear” configuration in **1–3**. Thus the height of each drum is strongly influenced by the length of H₂L. For example, the X-ray crystallographic data reveal that the molecular dimensions of **3** are approximately 17 × 19 × 19 Å. These dimensions have enabled us to obtain images of these molecular nanoparticles using transmission electron

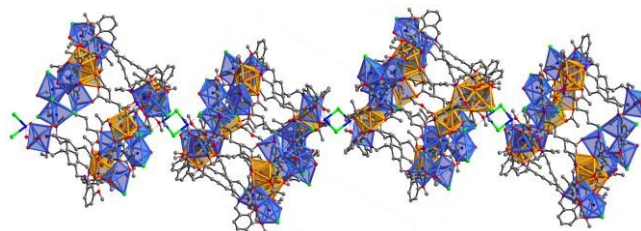


Figure 2 1-D polymeric chain-like structure of **1**.

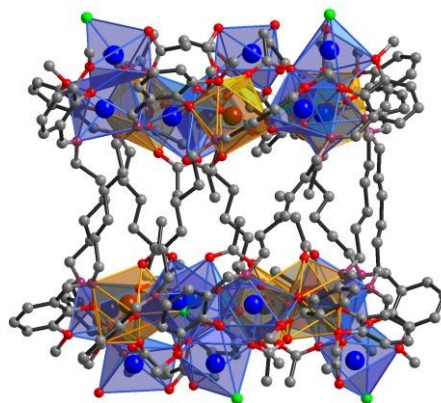


Figure 3 A view of the crystal structure of **3** along the *b*-axis (Yb³⁺: brown; Cd²⁺: blue; Cl⁻: green).

microscopy (TEM). Dilute solutions of **3** in MeCN were contacted with a Cu grid and the solvent carefully evaporated under vacuum. The TEM images obtained (Figure 4a) show uniform nanoparticles with diameters measuring approximately 1.92 nm which corresponds with the size of the 12-metal ring found in the crystal structure, indicating that the nanocluster retains its unique molecular structure in solution. In Figure 4b, a panoramic scanning electron microscopy (SEM) image shows the crystalline nature of **3**. Energy dispersive X-ray spectroscopy (EDX) analysis of **3** indicates that the Cd:Nd ratio is about 3:1, in agreement with the crystal structure (Figure 4c).

Powder XRD patterns of Cd-Ln clusters **1-3** are similar to their simulated patterns generated from single crystal X-ray data (Figure S3 in the ESI). ^1H NMR spectra of **2** and **3** in CDCl_3 contain multiple broad peaks ranging from -15 to $+17$ ppm and -70 to $+80$ ppm, respectively, while **1** shows a narrower range of $0.6 - 8.5$ ppm due to the diamagnetic La^{3+} ion. The ^1H NMR spectra of **1-3** remain unchanged for several weeks, indicating that the drum-like structures in **1-3** are stable in solution (Figures S4-S6 in the ESI).

The near-infrared (NIR) luminescence properties of **2** and **3** were studied in both solution and solid state. For **2** and **3**, the absorption bands in the UV-vis region are all red-shifted compared to those of the free ligand H_2L . As shown in Figure 5, the absorptions of **2** and **3** are about 10 times stronger than the free ligand, which enhances the ability of the ligand-center to absorb energy for sensitizing the lanthanide luminescence. The photophysical properties of Ln(III) ions depend markedly on their coordination environments.³⁸ It is noticeable that, in **2** and **3**, the Ln(III) centers are shielded within the drum-like structures and surrounded by chromogenic Cd(II) components (energy transfer donors), which may help to improve their luminescent properties.^{39,40} The excitation and emission spectra of **2** and **3** in CH_3CN are shown in Figure 6. Upon excitation of the ligand-centered absorption bands, **2** and **3** show typical NIR emission spectra for Nd^{3+} ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{j/2}$ transitions, $j = 9, 11$ and 13) and Yb^{3+} ($^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition),

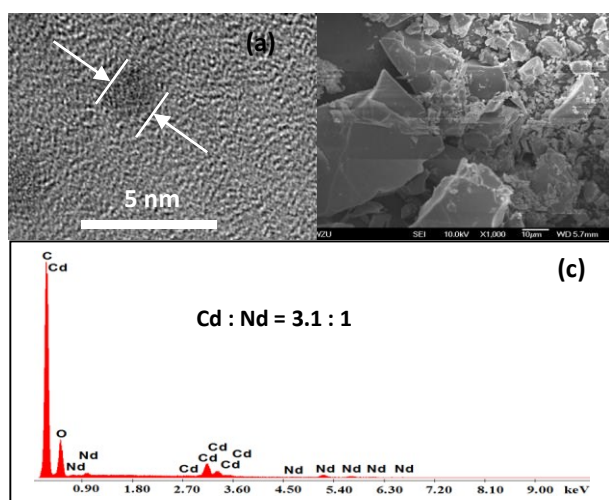


Figure 4 TEM (a) and SEM (b) images, and EDX (c) spectrum of **3**.

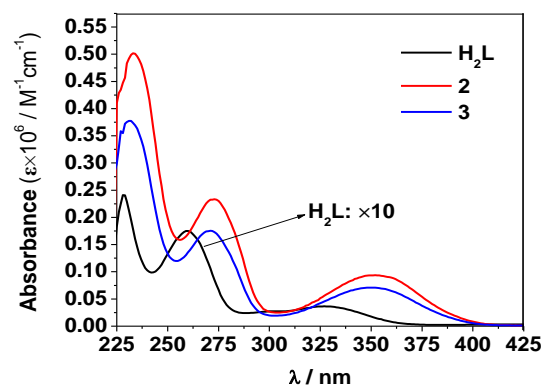


Figure 5 UV-Vis spectra of the free H_2L and Cd-Ln clusters **2** and **3** in CH_3CN . ($C = 10^{-8}$ – 10^{-7} M).

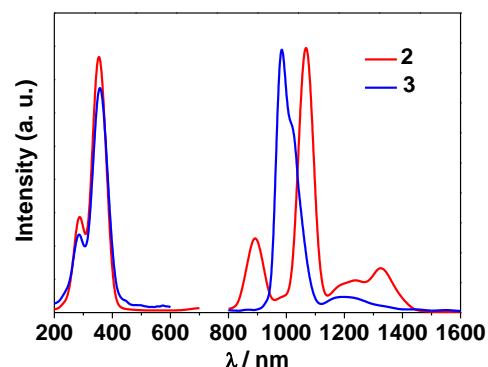
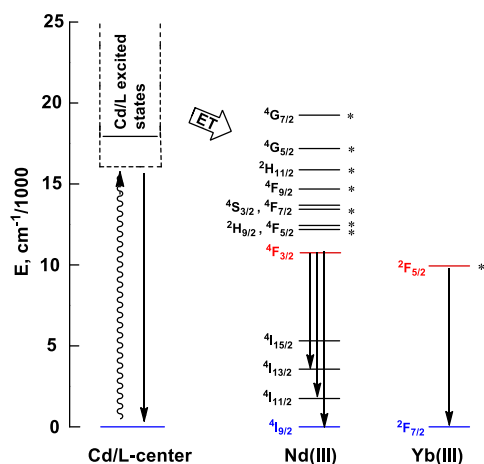


Figure 6 NIR emission spectra of **2** and **3** in CH_3CN .

respectively. **2** and **3** show two excitation bands at approximately 280 nm and 350 nm (Figure 6), in agreement with their absorption spectra, confirming that the energy transfers from the Cd/L centers to Ln^{3+} ions occur. As shown in Scheme 2, the energy transfer in **2** is favorable since the Nd^{3+} ion has many possible energy-accepting levels lying above the NIR luminescent level ($^4\text{F}_{3/2}$).^{41,42} In **3** the Yb^{3+} ion has only a single excited state $^2\text{F}_{5/2}$ at $10,200 \text{ cm}^{-1}$. The energy-transfer process in **3** may perhaps be described as electron transfer mechanism and/or phonon-assisted energy transfer mechanisms.^{43,44} The emission lifetimes (τ) of **2** and **3** are $2.7 \mu\text{s}$ and $8.9 \mu\text{s}$, respectively. The NIR luminescence of lanthanide ions may be quenched by C-H vibrations from the ligands, and the quenching efficiency increases as the distance $\text{Ln}^{3+} \cdots \text{C-H}$ decreases.⁴⁵ The emission lifetimes of **2** and **3** are shorter than those lanthanide-based clusters formed by ligands without C-H groups (i.e. C-H bonds are replaced by C-F bonds in ligating molecules).^{46,47} The intrinsic quantum yields (Φ_{Ln}) of Nd^{3+} emission in **2** and Yb^{3+} emission in **3** are calculated as 1.08 % and 0.45 %, respectively, using $\Phi_{\text{Ln}} = \tau/\tau_0$ ($\tau_0 = 250 \mu\text{s}$ and $2000 \mu\text{s}$, the natural lifetimes of Nd^{3+} and Yb^{3+} , respectively).^{48,49} For either **2** or **3**, the NIR luminescence spectrum in the solid state is similar to that in the solution (Figures S7 and S8 in the ESI).

For **1-3**, a broad Cd/L centered emission can be detected at about 528 nm upon excitation of the ligand-centered absorption bands (Figure 7). For **1**, the La^{3+} ion cannot accept



Scheme 2 The energy levels in Cd-Ln nanoclusters **2** and **3**. Those marked with * can act as energy acceptors by either Förster or Dexter mechanism (the former requiring $|\Delta J| = 2, 4,$ or 6 at the lanthanide, and the latter requiring $|\Delta J| = 0$ or 1 with the exception of $|\Delta J| = |\Delta J'| = 0$, which is forbidden.^{50,51}

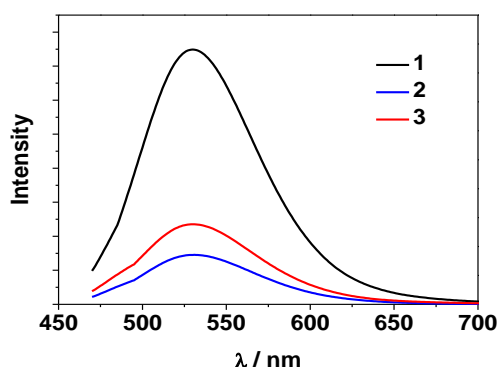


Figure 7 Visible emission spectra of **1-3** with the same absorbance value at $\lambda_{\text{ex}} = 350$ nm in CH_3CN .

any energy from the sensitizer. With the same absorbance value at the excitation wavelength (350 nm), the Cd/L centered emissions of **2** and **3** are much weaker than that of La(III) cluster **1**, due to the energy transfers to Nd^{3+} and Yb^{3+} ions, respectively. Although **2** and **3** show different types of structures (1-D polymeric structure vs 0-D structure), their Cd/L centered emissions still can be compared when they have the same absorbance value at the excitation wavelength (350 nm). As shown in Figure 7, the Cd/L centered emission of **3** is stronger than that of **2**, indicating that the energy transfer to Nd^{3+} ion in **2** is more efficient than that to Yb^{3+} ion in **3**.

Conclusions

We have successfully demonstrated the construction of two polymeric Cd-Ln clusters (**1** and **2**) with 28-metal drum-like $\text{Ln}_6\text{Cd}_{18}\text{L}_9$ ($\text{Ln} = \text{La}$ and Nd) building units. The self-assembly process of the polymeric structures appears to be ion radius dependent. Thus, when the smaller lanthanide ion Yb^{3+} is

employed in the reaction, a 24-metal drum-like cluster **3** is produced. To the best of our knowledge, **1** and **2** represent the first report of 1-D polymeric high-nuclearity 4d-4f nanoclusters formed by flexible long-chain Schiff base ligands. With the Ln(III) centers enclosed within the drum-like structures, **2** and **3** show interesting NIR luminescence properties. The results provide new insights into the construction of luminescent polymeric metal nanoclusters with high-nuclearity d-f building units and offer a promising foundation for the development of new functional materials. Further studies focused on this synthetic methodology to construct polymeric high-nuclearity d-f nanoclusters bearing flexible chain-like ligands with even longer carbon backbones and different d-metal ions are in progress.

Acknowledgements

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Notes and references

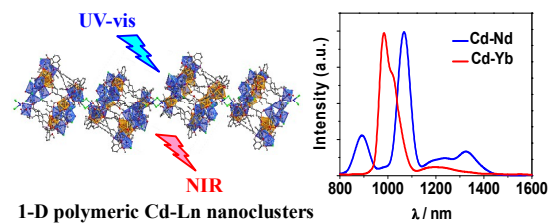
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First NIR luminescent polymeric high-nuclearity Cd-Ln nanoclusters from a long-chain Schiff base ligand

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Two novel 1-D polymeric Cd-Ln (Ln = La and Nd) nanoclusters with 28-metal drum-like building units were prepared using a long-chain Schiff base ligand.