Nanoscale

Communication

Anion dependent self-assembly of 56-metal Cd-Ln nanoclusters with enhanced near-infrared luminescence properties

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Two series of Cd-Ln clusters: nano-drum [Ln₈Cd₂₄L₁₂(OAc)₄₈] and nano-double-drum [Ln₁₂Cd₄₄L₂₀Cl₃₀(OAc)₅₄] (Ln = Nd and Yb) were prepared using a flexible Schiff base ligand
10 **bearing two aryl-Br groups. Chloride (Cl⁻) ions, together with the interactions of Br with other electronegative atoms, play a key role in the formation of the nano-double-drums. The structures were studied by TEM and photophysical properties were determined.**

15 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] Self-assembly by metal-ligand coordination is one of the most efficient processes that organize individual 20 molecular components into nanosize species. High-nuclearty metal nanoclusters may show remarkable *physical* and *chemical* properties.[2] For example, for the magnetic properties, their large metal/ligand mass rations ensure high magnetic densities. A number of high-nuclearity 3d-4f nanoclusters based on Cu/Ln,[3a] 25 Mn/Ln[3b-d] and Ni/Ln[3e,f] systems have been constructed from simple polydentate rigid ligands, in order to study their magnetic properties as single-molecule magnets.

Light-absorbing d-metal chromophores (i.e. Pt^{II},[4a,b] Ru^{II},[4c,d] Zn^{II},[4e,f] Cr^{II}[4g,h] and Cd^{II}[4i,j]) can be used as sensitizers for near-30 infrared (NIR) luminescence from Ln(III) centers following ligand→f and d→f energy-transfers. 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 widely employed to synthesize d-f heteronuclear clusters. Recent studies 35 in our laboratories have focused on the construction of luminescent d-f clusters with flexible Schiff base ligands.[5] Flexible ligands may provide more possibilities for the construction of unique frameworks because of their freedom of conformation. For example, the use of Schiff base ligands H₂L^{a-c}, 40 which have flexible carbon-carbon backbones, resulted in a rich variety of tetranclear,[5b] hexanclear,[5c] twenty-four and thirty-two[5d] d-f clusters (d = Zn²⁺, Ni²⁺, Cu²⁺ and Cd²⁺). The structures of these metal clusters are often influenced by a variety of factors such as the ligand structure and the nature of the counter anions. 45 Compared with H₂L^c, N,N'-bis(5-bromo-3-methoxysalicylidene)hexane-1,6-diamine (H₂L, Scheme 1) has two bulky aryl-Br groups which may influence the formation processes of metal clusters via weak interactions of Br with other electronegative atoms (e. g. Br···Y; Y = H, N, O, S, F or Br).[6] As 50 part of our ongoing studies we have investigated the influence of this ligand structure and the type of anions present on the cluster

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R₁ = H: R₂ = C₃H₆ (**H₂Lᵃ**); C₄H₈ (**H₂Lᵇ**); C₆H₁₂ (**H₂Lᶜ**)

R₁= Br: R₂ = C₆H₁₂ (**H₂L**)
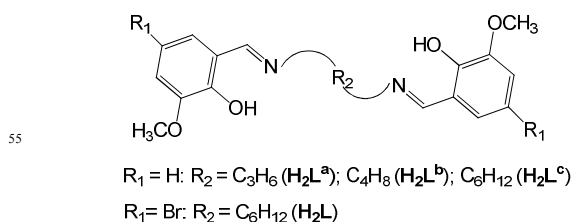
Scheme 1. Flexible ligands

60 architecture, we report here the first examples of Cd-Ln clusters in which two nano-drums are linked together via a common edge thus giving a nano-double-drum. Two classes of Cd-Ln nanoclusters can be prepared from the reactions of H₂L with Cd(OAc)₂·4H₂O and LnX₃·nH₂O (X = OAc ⁻ and Cl⁻). They are 65 [Ln₈Cd₂₄L₁₂(OAc)₄₈] (Ln = Nd (**1**) and Yb (**2**)) and [Ln₁₂Cd₄₄L₂₀Cl₃₀(OAc)₅₄] (Ln = Nd (**3**) and Yb (**4**)). Interestingly nano-double-drum 56-metal clusters **3** and **4** have enhanced NIR luminescence properties compared to the single nano-drums **1** and **2**. Although numerous polynuclear d-f 70 complexes with varying structures have been prepared using Schiff base ligands, most of them have less than ten metal atoms.[3,7] To the best of our knowledge, **3** and **4** are the highest nuclearity d-f clusters with Schiff base ligands thus far reported.

Reactions of H₂L with Cd(OAc)₂·4H₂O and Ln(OAc)₃·4H₂O 75 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 32-metal single-drum-like structures. Two views of the crystal structure of **1** are shown in Fig. 1a. The top view is essentially a side-on view while the 80 lower one is looking down into the top of the drum. 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⁻ ions while the sides of the drum are formed by the -(CH₂)₆- linkers of the Schiff base ligands. The 85 X-ray crystallographic data reveal that the molecular dimensions of **1** are approximately 22 × 27 × 27 Å. It is also possible to obtain images of these molecular nanoparticles using transmission electron microscopy (TEM). Dilute solutions of **1** in MeCN were contacted with a Cu grid and the solvent carefully 90 evaporated under vacuum. The TEM images obtained (Fig. 1b) show uniform nanoparticles with diameters measuring approximately 2.72 nm which corresponds well with the diameter of the 16-metal ring end of the nano-drum found in the crystal structure. In Fig. 1c a panoramic scanning electron microscopy 95 (SEM) image shows the crystalline nature of **1**.
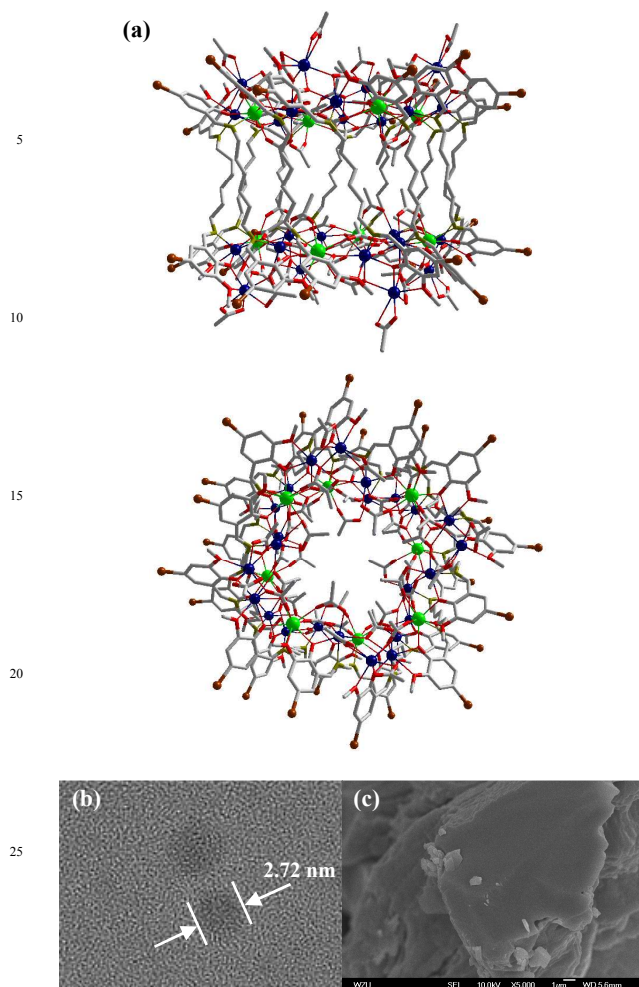
Fig. 1 (a) Two views of the nano-drum-like structure of **1**: viewed along the *b*-axis (top) and *a*-axis (lower) (Nd^{3+}: green; Cd^{2+}: blue; Br: brown); (b, c) TEM and SEM images of **1**.

The self-assembly process of nano-drum-like structures appears to be anion dependent. Thus, if Cl^- anions are introduced into the reactions with the use of $LnCl_3 \cdot 6H_2O$, unprecedented 56-metal clusters **3** and **4** are produced which have linked nano-double-drum-like architectures. Two views of the crystal structure of **3** are shown in Fig. 2a. The X-ray structure of **3** reveals a centrosymmetric core with two equivalent 28-metal single-drum $Nd_6Cd_{22}L_{10}Cl_{15}(OAc)_{27}$ moieties linked by four Cl^- anions. In each 28-metal moiety, two rings of 14 metals (3 Nd(III) and 11 Cd(II)) are linked by 10 Schiff base ligands. In **3**, each Ln^{3+} ion and its closest two Cd^{2+} ions are linked by phenolic oxygen atoms of L^{2-}, OAc^- anions and/or Cl^- anions. The distances between Ln^{3+} and Cd^{2+} ions range from 3.645 Å to 3.907 Å. The molecular dimensions of **3** (ca. 44 × 27 × 27 Å) are, of course, significantly larger than those of **1** or **2**. A TEM image of **3** (Fig. 2b) shows 4.45 nm sized nanoparticles, in agreement with the dimensions found in the crystal structure. An SEM image of **3** is shown in Fig. 2c.

It seems reasonable to assume that the bridging effect of Cl^- anions plays a key role in the formation of the double-drum-like structures of **3** and **4**. Meanwhile, the phenolic Br groups introduced into the H_2L may also contribute to the self-assembly of the double-drum-like structures. In **3** and **4**, intermolecular
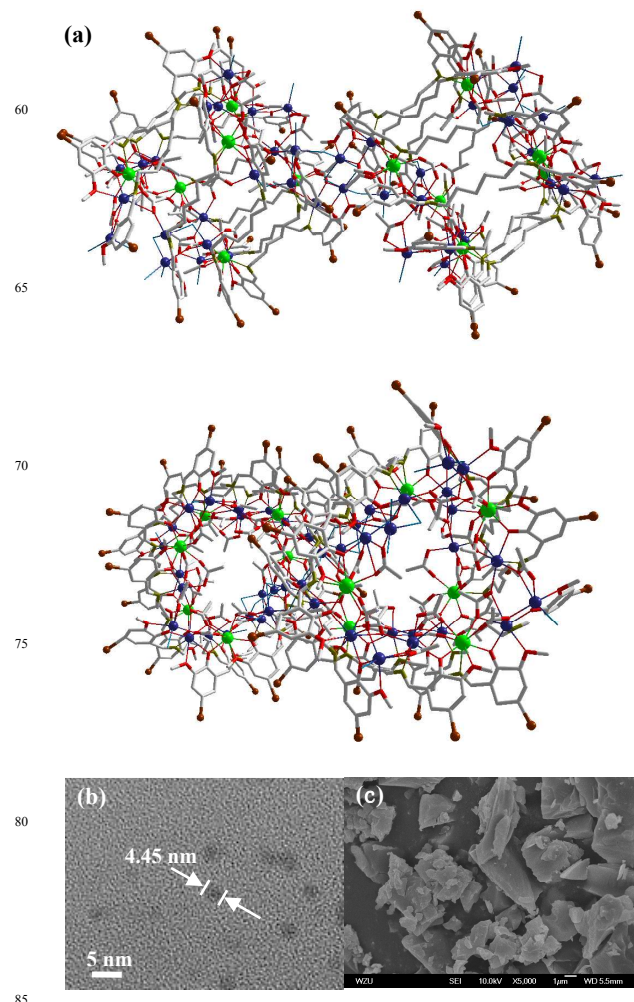
Fig. 2 (a) Two views of the nano-double-drum structure of **3**: viewed along the *b*-axis (top) and *a*-axis (lower) (Nd^{3+}: green; Cd^{2+}: blue; Br: brown); (b, c) TEM and SEM images of **3**.

$Br \cdots H\text{-}C$ interactions between aromatic Br atoms and hydrogen atoms of salen methoxy groups and coordinated OAc^- anions (i.e. $Br(17)\cdots C(176)$ 4.014 Å, $Br\cdots H$ 3.219 Å **3**) and $Br\cdots Br$ interactions (i.e. $Br(17)\cdots Br(20)$ 3.616 Å **3**)[8] are formed between the 16-metal rings of two face-to-face closed molecules (Fig. S1). Intermolecular $Cl\cdots H\text{-}C$ interactions between coordinated Cl^- atoms and hydrogen atoms of salen methoxy groups (i.e. $Cl(22)\cdots C(132)$ 3.340 Å, $Cl\cdots H$ 2.723 Å **3**) are also found between the 16-metal rings. These intermolecular interactions favor the close approach of two metal-cluster moieties, which may facilitate linking via Cl bridges.

Powder XRD patterns of **1-4** are similar to their simulated patterns generated from single crystal X-ray data (Fig. S2). Molar conductivity studies in CH_3CN confirm that these molecular nanoparticles are neutral in solution, in accordance with the solid state structures. ^1H NMR spectra of **3** and **4** in $CDCl_3$ contain multiple broad peaks ranging from −18 to +17 ppm and −60 to +40 ppm, respectively. They remain unchanged for several weeks, indicating that materials with nano-double-drum-like structures are stable in solution (Figs. S3, S4). The TEM images obtained for **1** and **3** also provide convincing evidence that the compounds retain their unique molecular structures in solution (Figs. 1, 2).

The photophysical properties of **1-4** were studied in CH_3CN

and the solid state. For **1-4**, the absorption bands in the UV-vis region are all red-shifted compared to those of the free ligand H$_2$L. As shown in Fig. 3, the absorptions of **1-4** 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. It is noticeable that the absorptions of **3** and **4** are stronger than **1** and **2**. For the free ligand H$_2$L, excitation of the absorption bands at 298 nm or 415 nm produces a broad emission band at λ_{max} = 509 nm (Fig. S5). For these Cd-Ln nanoclusters, upon excitation of the ligand-centered absorption bands, **1** and **3** show typical NIR emission spectra for Nd^{3+} ($^4F_{3/2} \rightarrow {}^4I_{j/2}$ transitions, j = 9, 11 and 13), and **2** and **4** show those for Yb^{3+} ($^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition) in both solution and the solid state (Fig. 4). The excitation spectra of **1-4** show two bands at approximately 290 nm and 380 nm (Fig. 4), in agreement with their absorption spectra. We were naturally interested in the influence of structural differences in the Cd-Ln nanoclusters on their photophysical properties. The relative emission intensities of **3** *vs.* **1** and **4** *vs.* **2** were determined under the same experimental conditions in CH$_3$CN with the same absorbance value at 380 nm, respectively. The relative NIR emission intensities were estimated to be 3.3 and 2.5 for **3**:**1** (measured at 1068 nm) and **4**:**2** (measured at 979 nm), respectively, indicating that nanoclusters with double-drum-like structures have superior luminescence properties compared to those with single-drum-like structures (Figs. S6 and S7). This can also be confirmed by comparing their luminescence lifetimes. The emission lifetimes (τ) of **1** and **3** are 2.6 μs and 3.8 μs, respectively. The intrinsic quantum yields (Φ_{Ln}) of Nd^{3+} emission in **1** and **3** are calculated as 1.04 % and 1.52 %, respectively, using $\Phi_{Ln} = \tau/\tau_0$ (τ_0 = 250 μs, the natural lifetime of Nd^{3+}).[9] The
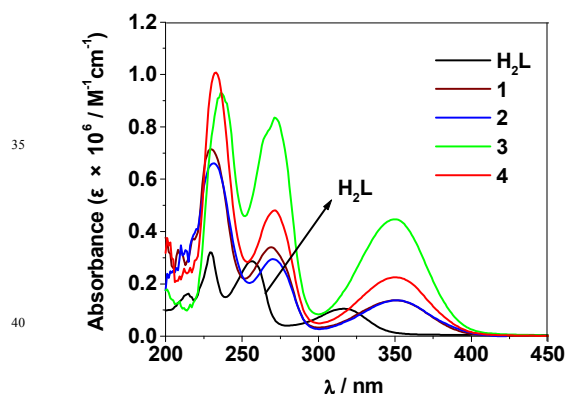

**Fig. 3** UV-Vis spectra of the free H$_2$L and **1-4** in CH$_3$CN at 298K.
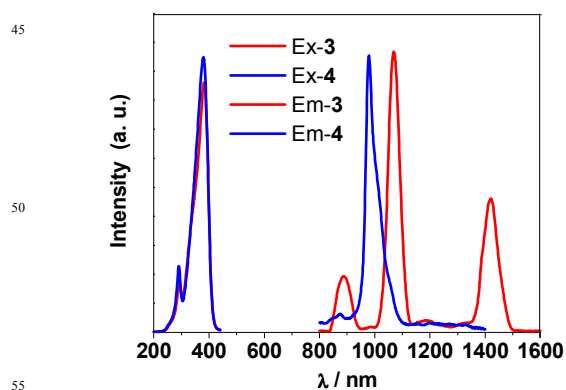
Fig. 4 The excitation and NIR emission spectra of **3** and **4** in CH$_3$CN at 298K.

emission lifetimes of **2** and **4** are 9.5 μs and 12.3 μs, respectively. So the intrinsic quantum yields of Yb^{3+} emission in **2** and **4** are calculated as 0.48% and 0.62%, respectively. (τ_0 = 2000 μs for the natural lifetime of Yb^{3+})

For **1-4**, a broad Cd/L centered emission can be detected at about 530 nm upon excitation of the ligand-centered absorption bands. With the same absorbance value at the excitation wavelength (380 nm), the Cd/L centered emissions of Nd(III) nanoclusters **1** and **3** are weaker than those of Yb(III) nanoclusters **2** and **4**, indicating that the energy transfers to lanthanide ions in the former are more efficient than those in the later (Fig. 5). The energy transfer difference between Nd(III) nanoclusters and Yb(III) nanoclusters may be due to the fact that the Nd^{3+} ion has many appropriate energy-accepting levels in the range of 15,000-20,000 cm^{-1}, in which the accepted energy is transferred to the NIR luminescent levels of the lanthanide ions through internal conversion. As shown in Scheme 2, according to either of selection rules for Förster and Dexter energy transfers (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),[10] those energy levels that can act as energy acceptors are marked with an asterisk (*). The Yb^{3+} ion has only a single excited state $^2F_{5/2}$ at 10,200 cm^{-1}. The energy-transfer process in the Yb(III) nanoclusters may perhaps be described as electron transfer mechanism and/or phonon-assisted energy-transfer mechanisms.[11]
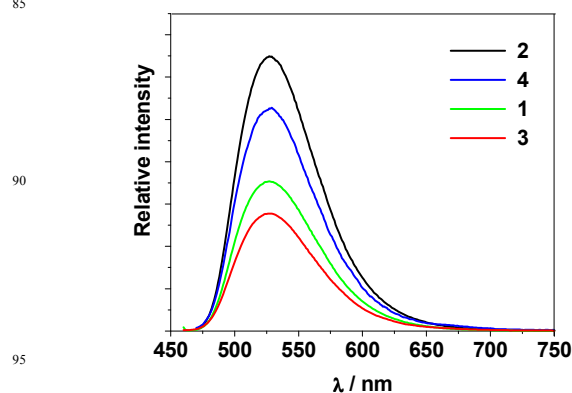
Fig. 5 The visible emission spectra of **1-4** in CH$_3$CN at 298K.
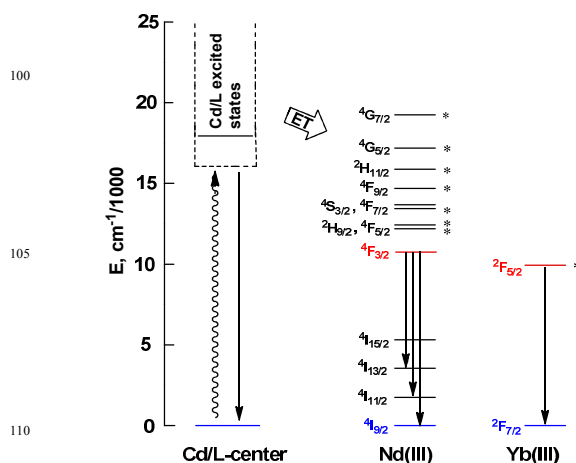
Scheme 2 The energy levels in Cd-Ln nanoclusters **1-4** (Those marked with ***** can act as energy acceptors by either Förster or Dexter mechanism).

Conclusions

In conclusion, we have successfully demonstrated the anion dependent construction of two 56-metal Cd-Ln nanoclusters from a specifically designed flexible Schiff base ligand which bears two aryl-Br groups. They show unusual nano-double-drum-like architectures, and exhibit better NIR luminescence properties compared to the corresponding 32-metal single-nano-drums. The Cl^- ions from the lanthanide salts, as well as aryl-Br groups introduced into the Schiff base ligands, play a key role in the self-assembly process of the double-nano-drums. To the best of our knowledge, these two 56-metal Cd-Ln nanoclusters are the highest nuclearity d-f Schiff base clusters thus far reported. The results provide new insights into the construction of higher nuclearity molecular nanoparticles and offer a promising foundation for the development of new functional materials. Further studies focused on this synthetic methodology to construct d-f clusters of even higher nuclearity are in progress.

Acknowledgements

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 972369-972372 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.

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Synopsis TOC

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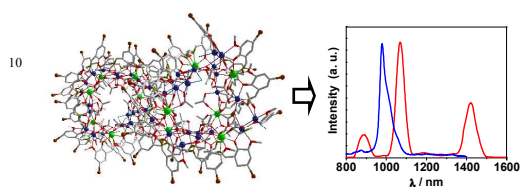
20 Two luminescent 56-metal Cd-Ln nanoclusters with unusual nano-double-drum-like structures were prepared using a flexible Schiff base ligand which contains two aryl-Br groups.

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