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Self-assembly of Luminescent 12-metal Zn-Ln Planar Nanoclusters with Sensing Properties towards Nitro Explosives

Dongmei Jiang,^a Xiaoping Yang,^{*,a} Xiaohui Zheng,^b Le Bo,^a Ting Zhu,^a Hongfen Chen,^a Lijie Zhang^a and Shaoming Huang^{*,a}

Two types of Zn-Ln nanoclusters $[Nd_2Zn_2L_2(L')_2(OAC)_2(NO_3)_2(H_2O)_2]$ (1) and $[Ln_6Zn_6L_2(L'')_2O_2(OAC)_{18}]$ (Ln = Nd (2) and Sm (3)) were prepared using one long Schiff base ligand (H₂L) with a naphthyl backbone and two short polydentate ligands (H₂L' and H₂L''). 1 and 2-3 show linear and planar structures with sizes of approximately 10 × 10 × 30 Å and 10 × 15 × 22 Å, respectively. The chromogenic Zn/Ligand components can act as efficient sensitizers for lanthanide luminescence, thus 1-3 show visible and NIR emissions. In these clusters, the Schiff base ligands display an "U-shaped" configuration, which is suitable to form $\pi \cdots \pi$ interactions and hydrogen bonds with nitro aromatic compounds. Interestingly, the Zn-Sm cluster 3 shows visible and NIR luminescent sensing of nitro explosives and exhibits high sensitivity to 1,4-DNB and TNT at ppb level.

Introduction

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Selective and sensitive detection of explosives such as nitroaromatics has been received extensive attention due to its potential application in national security and environmental protection.¹⁻³ For example, explosives such as nitrobenzene (NB), 1,4-dinitrobenzene (1,4-DNB), 2,4,6-trinitrotoluene (TNT) and cyclotrimethylene trinitramine (RDX) are common ingredients of industrial explosives (Scheme 1a). Recently, attention has focused on the fluorescence-based detection methods due to their high sensitivities, portability and short response times. A variety of fluorescent materials including conjugated polymers, nanoparticles and metal-organic frameworks (MOFs) have been extensively used for the sensing of explosives.⁴⁻⁶

Luminescent lanthanide-based complexes have been employed for the detection of various cations,^{7,8} anions ^{9,10} and small molecules,^{11,12} due to their specific luminescence properties such as large Stokes' shifts, high color purity and relatively long luminescence lifetimes.¹³ For example, many Eu(III)- and Tb(III)-based metal-organic frameworks with visible luminescence have been designed for this purpose.⁷⁻¹² In recent years, high-nuclearity heterometallic d-f nanoclusters have attracted considerable attention due to their unique *physical* and *chemical* properties.¹⁴⁻¹⁶ Many high-nuclearity CuLn,¹⁷ Mn-Ln¹⁸ and Ni-Ln¹⁹ clusters have been synthesized for the studies of magnetic properties (i. e. single-molecule magnets (SMM)). Zn²⁺ ion has saturated d¹⁰ electronic configuration, which prevents the quenching of lanthanide luminescence through d-d transitions (i.e. f→d energy transfer). The light-absorbing Zn(II) chromophores have been used as sensitizers for lanthanide emission in Zn-Ln complexes ("antenna effect").²⁰ Recently, Q.-F. Sun *et al.* reported the luminescent sensing properties toward nitro-aromatic explosives of a Eu₄ cluster in solution.²¹ To the best of our knowledge, there are no reports on the luminescent sensing of explosives based on high-nuclearity d-f nanoclusters.

An effective strategy towards the construction of luminescent polynuclear lanthanide complexes is the use of two kinds of chromogenic ligands with different sizes and coordination modes to meet the requirement of high coordination numbers of Ln3+ ions.22 Salen-type Schiff base ligands have been widely used in the synthesis of d-f complexes.²³⁻²⁸ As part of our continuing studies focused on the design of functional lanthanide-based materials,^{29,30} we report here two types of luminescent Zn-Ln nanoclusters with a specially designed Schiff base ligand N,N'-bis(3methoxysalicylidene)-1,5-naphthalenediamine (H₂L), which has an electron-rich naphthyl backbone (Scheme 1b). The new clusters are $[Nd_2Zn_2L_2(L')_2(OAc)_2(NO_3)_2(H_2O)_2]$ (1) and $[Ln_6Zn_6L_2(L'')_2O_2(OAc)_{18}]$ (Ln = Nd (2) and Sm (3)). Besides the long Schiff base ligand, aromatic bidentate ligand 1,3diphenylpropane-1,3-dione (H₂L') and tridentate ligand 3methoxy-benzene-1,2-diol (H₂L") are selected as secondary ligands for the formation of 1-3. The length of H_2L is approximately 20 Å, which is advantageous for the formation of large metal clusters. 1 and 2-3 show linear and planar structures with sizes of approximately 10 × 10 × 30 Å and 10 ×

^{a.} College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, China.; Zhejiang Key Laboratory of Carbon Materials, Wenzhou 325035, China.

^{b.}Chemical Biology Research Center, School of Pharmaceutical Science, Wenzhou Medical University, Wenzhou 325035, China.

^{*}Email - xpyang@wzu.edu.cn

Electronic Supplementary Information (ESI) available: Experimental and characterization details, additional figures and tables. CCDC 1842949-1842951 for 1-3. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x.

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nitrobenzene (NB) 2-nitrotoluene (2-NT) 4-nitrotoluene (4-NT)



acetophenone (4-NBAP)

1,4-dinitrobenzene (1,4-DNB)



Scheme 1. (a) The structures of nitro explosives; (b) The coordination mode of Schiff base ligand H_2L in 1-3.

which may help to "capture" guest aromatic compounds such as nitro-aromatic explosives through π - π and electrostatic interactions. Among the Ln(III) ions, Sm(III) may show emission bands both in the visible (${}^{4}G_{5/2} \rightarrow {}^{6}H_{J}$) and in the NIR (${}^{4}G_{5/2} \rightarrow {}^{6}F_{J}$) ranges.³¹ Interestingly, the 12-metal Zn-Sm cluster **3** shows visible and NIR luminescent sensing of nitro explosives, and exhibits high sensitivity to nitro-aromatic 1,4-DNB and TNT at ppb level. To the best of our knowledge, **3** represents the first report of high-nuclearity d-f nanocluster for both visible and NIR luminescent sensing of nitro-aromatic explosives.

Results and discussion

Synthesis and structures

The Schiff base ligand H₂L was synthesized from the reaction of 2-hydroxy-3-methoxybenzaldehyde with 1,5naphthalenediamine in refluxing ethanol with a yield of 98%.³² The ¹H NMR spectrum of H₂L shows a signal for imino proton (-CH=N-) at 8.76 ppm (Figure S1 in the ESI), while the signal for the aldehyde proton (Ar-CHO) of the reactant at 10.0 ppm disappears. In the presence of Et₃N, reaction of H₂L and H₂L' with Zn(OAc)₂·2H₂O and Nd(NO₃)₃·6H₂O in refluxing methanol produced a yellow solution from which **1** was isolated as pale yellow crystalline solid. A view of the crystal structure of **1** is shown in Figure 1. The X-ray structure of **1** reveals a centrosymmetric core with two equivalent NdZnLL' moieties. In the NdZnLL' moiety, Nd³⁺ and Zn²⁺ ions are linked thy one OAc anion and phenolic oxveen atoms of Wo¹ Phenole Swith AGJ



Figure 1. A view of the crystal structure of 1 (Nd³⁺: blue; Zn²⁺: green)

separation of 3.487 Å. Nd³⁺ ion is nine-coordinate, surrounded by nine oxygen atoms from L and L' ligands, and NO₃⁻ and OAC⁻ anions. Zn²⁺ ion shows an octahedral geometry, coordinated with four oxygen and two nitrogen atoms from two L ligands, one OAC⁻ anion and one H₂O molecule. The Schiff base ligand is bound to all metal ions through its N and phenoxide and methoxy O atoms, while the L' ligand is only bound to one Nd³⁺ ion through its two O atoms. The metric dimensions of **1** measure approximately 10 × 10 × 30 Å. The Zn-O, Zn-N and Nd-O bond lengths range from 1.922 Å to 2.400 Å, 2.130 Å to 2.196 Å, and 2.285 Å to 2.536 Å, respectively.

The construction of the Zn-Ln nanoclusters appears to be the secondary ligand dependant. Reactions of H₂L and H₂L" with $Zn(OAc)_2 \cdot 2H_2O$ and $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Nd and Sm) under the same experimental conditions as above produced yellow solutions from which isomorphous 2 and 3 were isolated as yellow crystalline solids. As shown in Figure 2, the X-ray structure of 2 reveals a centrosymmetric core with two equivalent Nd₃Zn₃LL''O(OAc)₉ moieties linked by two Schiff base ligands. In each Nd₃Zn₃LL"O(OAc)₉ moiety, the Nd³⁺ ions are 8-coordinate, surrounded by eight oxygen atoms from L and L" ligands, and OAc⁻ and O²⁻ anions. They are linked together by the L" ligand, one O²⁻ and four OAc⁻ anions with an average separation of 3.632 Å. Three Zn²⁺ ions have tetrahedral, square pyramidal and triangular bipyramidal geometries, respectively. Each Nd³⁺ ion and its closest two Zn²⁺ ions are linked by L and L'' ligands, and OAc⁻ and O²⁻ anions. The Zn(II)…Nd(III) distances range from 3.385 Å to 3.909 Å in 2. The Schiff base ligand is bound to two Zn²⁺ and two Nd³⁺ ions through its N and O atoms. The L" ligand is bound to two Zn²⁺ and three Nd³⁺ ions through its three O atoms. The metric dimensions of 2 measure approximately 10 × 15 × 22 Å. The Zn-O, Zn-N and Nd-O bond lengths range from 1.934 Å to 2.387 Å, 2.079 Å to 2.114 Å, and 2.216 Å to 2.603 Å respectively.

In the solid state, the structures of **2** and **3** have open 3D networks (Figure 3a), with guest molecules such as Et₂O, MeOH and H₂O accommodated within the channels. For example, in **3** intermolecular Ar-H···O(OAc⁻) and (OAc⁻)C-H···O(OAc⁻) hydrogen bonds (2.472 Å–2.669 Å) and (-OCH₃)C-H··· π interactions (2.932 Å–4.001 Å)^{33,34} between each molecule occur with eight of its closest neighbours, resulting in a network architecture with extended channels running along the *ac*-axes measuring approximately 7 × 7 Å (Figure 3a). In

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Figure 3b, a panoramic scanning electron microscopy (SEM) image shows the crystalline nature of **3**. Energy dispersive X-



Figure 2. Two views of the planar structure of **2**: viewed along the *bc*-axis (top) and *a*-axis (lower). (Nd³⁺: blue; Zn^{2+} : green)



Figure 3. Space filling view along the *ac*-axis (a), SEM image (b), and EDX spectrum (c) of 3.

ray spectroscopy (EDX) analysis of ${\bf 3}$ indicates that the molar ratio of Zn/Sm is 0.97 (Figure 3c), in agreement with the crystal structure.

Powder XRD patterns of **1-3** are similar to their simulated patterns generated from single crystal X-ray data (Figure S3). Thermogravimetric analyses show that on heating **1** and **2-3** undergo weight losses of about 2% and 5% before 100°C (Figure S4), respectively, assigned to the loss of uncoordinated solvent molecules such as Et₂O, MeOH and H₂O. Melting point measurements show that **1-3** are thermodynamically stable, starting to discompose from 172.4°C to 175.7°C (ESI).

Luminescence properties

The photophysical properties of 1-3 were studied in DME solution and the solid state. The free lighter and the solid state. absorption bands at 220, 274, 356 nm, which are red-shifted upon co-ordination to metal ions in 1-3 (Figure 4). For the free ligand H₂L, excitation at the absorption wavelength produces broad emission bands at 468, 482 and 499 nm (Figure S5). Upon excitation of the ligand-centered absorption bands, 1 and **2** exhibit typical NIR luminescence of Nd³⁺ (${}^{4}F_{3/2} \rightarrow {}^{4}I_{j/2}$ transitions, j = 9, 11 and 13) (Figure 5), while 3 shows visible and NIR emission spectra for Sm³⁺ (${}^{4}G_{5/2} \rightarrow {}^{6}H_{j/2}$ transitions, j = 5, 7, 9 and 11; ${}^{4}G_{5/2} \rightarrow {}^{6}F_{j/2}$ transitions, j = 1, 3, 5, 7 and 9) (Figure 6). 1-3 show two excitation bands from 277 nm to 411 nm, in agreement with their absorption spectra, confirming that the energy transfers from the chromogenic ligands to Ln³⁺ ions occur. For each Zn-Ln cluster, the luminescence spectrum in the solid state is similar to that in the solution. The excitation and emission wavelengths (λ_{ex} and λ_{em}), the absorption of excitation wavelengths (ϵ), quantum yields (Φ_{em}), emission lifetimes (τ) and energy transfer efficiencies (η_{sens}) of 1-3 in solution are given in Table 1.

As shown in Figure 5, both 1 and 2 display NIR emission bands of Nd³⁺ at about 873, 1066 and 1335 nm. The emission lifetimes (τ) of 1 and 2 in DMF are 6.08 µs and 6.10 µs, respectively (Figure S6). The intrinsic quantum yields (Φ_{Ln}) of Nd³⁺ emission in 1 and 2 are calculated as 2.43% and 2.44%, respectively, using $\Phi_{Ln} = \tau/\tau_0$ ($\tau_0 = 250 \ \mu s$,³⁵ the natural lifetime of Nd³⁺). The emission quantum yields (Φ_{em}) of 1 and 2 are 0.75% and 0.95%, respectively. Thus, the efficiencies (η_{sens}) of the energy transfer from Zn/Ligand-center to Nd³⁺ 1 and 2 are calculated as 30.86% and 38.93%, respectively, using $\eta_{sens} = \Phi_{em}/\Phi_{Ln}$.³⁶ This indicates that the chromogenic ligands in 2 has higher energy transfer efficiency than in 1. It is found that there is one coordinated H₂O molecule near the Nd³⁺ ion in 1,







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Figure 5. Excitation	and emission spe	ectra of 1 and 2 in	n DMF.

Figure 7. The visible emission lifetime of 3 in DMF.

Table 1. The excitation and emission wavelengths (λ_{ex} and λ_{em}), the absorption of excitation wavelengths (ϵ), quantum yields (Φ_{em}), emission lifetimes (τ) and energy transfer efficiencies (η_{sens}) of **1-3** in solution. (^a The addition of 30 μ M 1,4-DNB)

Clusters	λ_{ex} (nm) / ϵ (× 10 ⁵ M ⁻¹ cm ⁻¹)	λ_{em} (nm)	τ (μs)	Φ_{em} (%)	η _{sens} (%)
1	311/0.07, 411/0.03	872, 1067, 1334	6.08	0.75	30.86
2	300/0.17, 404/0.09	874, 1065, 1335	6.10	0.95	38.93
3	Vis. 277/0.33, 364/0.29	562, 598, 645, 706	24.75 (21.01 ª)	0.32 (0.09 ª)	38.55
	NIR 279/0.34, 360/0.28	912, 953, 1030, 1178	23.15	0.29	_

which may efficiently quench the luminescence of lanthanide ions through non-radiative exchange of electronic energy of Ln³⁺ to the high vibrational modes of OH-groups.³⁷

For the visible emission spectrum of **3**, the ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$ (598 nm) and ${}^4G_{5/2}$ \rightarrow ${}^6H_{9/2}$ (645 nm) transitions are hypersensitive transitions and responsible for the most intense lines of Sm(III) emission (Figure 6). The visible emission lifetime (τ) of **3** is 24.75 µs in DMF (Figure 7), which is comparable to values reported for other Sm(III) complexes.^{38,39} The intrinsic quantum yield (Φ_{Ln}) of Sm³⁺ emission in **3** is calculated as 0.83%, using $\Phi_{Ln} = \tau/\tau_0$ ($\tau_0 = 3.0 \text{ ms}$,⁴⁰ the natural lifetime of Sm³⁺). The visible emission quantum yield (Φ_{em}) of **3** is 0.32%. The efficiency (η_{sens}) of the energy transfer from the Zn/Ligandcenter to Sm³⁺ is calculated as 38.55%, using $\eta_{sens} = \Phi_{em}/\Phi_{Ln}$.³⁶ For 3, the main line in the NIR area is at 953 nm due to the $^4G_{5/2} \rightarrow {}^6F_{5/2}$ transition, and a long NIR emission lifetime (τ), up to 23.15 μ s was recorded in DMF (Figure S6). The NIR emission quantum yield (Φ_{em}) of **3** is 0.29%.



Figure 6. Excitation and emission spectra of 3 in DMF.



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Luminescent sensing of explosives

In the planar structure of 2 and 3, two Schiff base ligands exhibit an outward "U-shaped" configuration with two benzene rings turning to the same side of H₂L and almost perpendicular to the middle naphthalene ring (Figures 1, 2 and S7a). The sensing ability of 3 for nitro explosives such as nitrobenzene (NB), 2-nitrotoluene (2-NT), 4-nitrotoluene (4-4-nitrobenzene acetophenone (4-NBAP), NT). 2.4.6trinitrotoluene (TNT), 1,4-dinitrobenzene (1,4-DNB), cyclotrimethylene trinitramine (RDX) and cyclotetramethylene tetranitramine (HMX) has been investigated in DMF (Scheme 1b). The intensities of the visible emission at 645 nm (${}^{4}G_{5/2} \rightarrow$ $^{6}H_{9/2}$) and NIR emission at 953 nm ($^{4}G_{5/2} \rightarrow {}^{6}F_{5/2}$) of **3** were recorded as the explosives were added with different concentrations. The luminescence intensities at 645 nm of the Sm³⁺ ions are gradually decreased as the concentrations of explosives increase (Figures 8 and S8). Interestingly, the visible lanthanide luminescence was found to be quenched rapidly upon the addition of 1,4-DNB and TNT. For example, the visible emission intensities are decreased about 50% when the concentrations of added 1,4-DNB and TNT solutions are 7.5 and 21 µM, respectively. However, the concentrations of other nitro explosives added should be more than 1000 µM to reduce the visible emission intensities of 3 by half (Figure S8). As shown in Figure 9, the luminescence quenching percentages of 3 towards 1,4-DNB and TNT are 70% and 51%, respectively. While, all of the other nitro explosives have minor effects on the luminescence intensity of **3** at low content (< 30 μ M), with the quenching efficiencies less than 10%. This indicates that 3 has high sensitivity towards 1,4-DNB and TNT over other nitro explosives.



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Figure 8. Decrease in visible luminescence intensity of 3 (λ_{ex} = 364 nm) in DMF (15 μ M) upon the addition of different concentrations of 1,4-DNB.



Figure 9. The visible luminescence quenching efficiencies of 3 (λ_{ex} = 364 nm) (15 μ M) towards explosives (30 μ M).

The luminescence quenching constants (K_{SV}) can be calculated by the Stern-Volmer (SV) equation,⁴¹ $I_0/I = K_{SV}[A] + 1$, where I_0 and I are the emission intensities before and after the addition of the explosive, respectively, and [A] is the molar concentration of the explosive. As shown in Figure 10, the K_{SV} values for the response of **3** to 1,4-DNB and TNT are calculated as 75350 M⁻¹ and 40910 M⁻¹, respectively, which are among the highest values of known fluorescent complexes for the detection of nitro explosives.^{5,6,42,43} While the K_{SV} values to other explosives are only from 179 M⁻¹ to 1010 M⁻¹. The detection limit can be calculated by the $3\sigma/K_{SV}$ equation, where σ is the standard deviation. The visible luminescence detection limits of **3** to 1,4-DNB and TNT are 0.08 μ M and 0.15 μ M, respectively, demonstrating the extremely high sensitivity of **3** towards the detection of these two explosives at the ppb level.

For the NIR luminescence of 3, the additional of explosives leads to varying degrees of weakening of the emission intensities (Figures 11, S8 and S9). For example, when the concentration of added 1,4-DNB solution is 11 µM, the emission intensity is decreased about 50%. As shown in Figure 12, the K_{SV} values for the response of **3** to nitro-aromatic explosives are higher than those to nitro-aliphatic explosives such as RDX and HMX. It is noticeable that, the K_{SV} value to 1,4-DNB (104.97 \times 10³ M⁻¹) is much greater than others (3.47 \times 10^3 M^{-1} - 28.17 × 10³ M⁻¹), indicating that **3** exhibits higher sensibility to 1,4-DNB. The NIR luminescence detection limit of 3 to 1,4-DNB is calculated as 2.86 µM. The reusability of 3 was investigated using the powder XRD. The powder XRD pattern of the recycled sample of 3 after treated with 1,4-DNB is still similar to its simulated pattern generated from single crystal Xray data (Figure S3d), indicating that the cluster is reusable in the sensing of nitro explosives.

The selectivity of **3** towards 1,4-DNB in the presence of other explosives was investigated. The initial luminescence spectrum of **3** (15 μ M) in DMF was recorded. As shown in Figure 13, at first very few luminescence quenching was observed when another explosive was added twice (the increase in concentration of explosive was 5 μ M each time). However, the addition of equal amount of 1,4-DNB to this





Figure 10. The visible luminescence quenching constants (K_{SV}) of **3** towards explosives.



Figure 11. Decrease in NIR luminescence intensity of 3 (λ_{ex} = 360 nm) in DMF (15 μ M) upon the addition of different concentrations of 1,4-DNB.



Figure 12. The NIR luminescence quenching constants (K_{SV}) of **3** towards explosives.

effect on luminescence intensity, but the further addition of 1,4-DNB gave significant luminescence quenching again. The stepwise decrease in luminescence intensities demonstrates the high selectivity of **3** for 1,4-DNB even in the presence of other nitro explosives.

Photoinduced electron transfer (PET) and resonance energy transfer (RET) mechanisms have been widely used to explain the high sensitivity of fluorescence-quenching-based

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sensors towards nitroaromatic explosives.⁴⁴ For the PET process, usually, the conduction band (CB) of the chemosensor lies higher than the LUMO energies of the nitro analytes



Figure 13. The decrease in luminescence intensities of **3** upon the addition of various nitro explosives followed by 1,4-DNB in DMF.

(Scheme 2), 45,46 and the electrons can be transferred from the electron rich chemosensor (i.e. H₂L) to electron-deficient nitro analytes, resulting in fluorescence quenching (Scheme S1). The luminescence of 3 results from the antenna effect in which the Zn/L moieties absorb the energy and transfer it to Sm³⁺ ions. Thus, in 3 when the excitation energy absorbed by Zn/L moieties is consumed through the PET process, the lanthanide luminescence intensity is decreased. Since charge transfer is generally considered to be a short range interaction, the configuration of the Schiff base ligands in 3 may play a significant role in the sensing selectivity to nitro explosives. As shown in Figure S7a, the "U-shaped" configuration of the Schiff base ligands is found to be more suitable to form $\pi \cdots \pi$ interactions and -CH…O(NO₂-Ar) hydrogen bonds with 1,4-DNB and TNT, which have more than one nitro groups, than other explosives, resulting in the high sensitivity to these two explosives. For 1,4-DNB and TNT, the intensities of their interactions with the Schiff base ligand may be different. As shown in Figure S7b, when -CH…O(NO2-Ar) hydrogen bonds are formed between 3 and explosives, 1,4-DNB has more overlap with the naphthyl ring of L than TNT, resulting in a stronger interaction between 1,4-DNB and L. Thus, 3 shows a higher quenching constant (K_{SV}) towards 1,4-DNB. The formation of a ground-state charge-transfer (CT) complex between the π -electron-rich Schiff base ligands of **3** and the electron-poor 1,4-DNB was investigated by UV-vis titration and lifetime measurements.²¹ The addition of 1,4-DNB caused a significant blue-shift and increase in the absorbance intensity at 288 nm (Figure S10). Meanwhile, the lifetime of 3 decreases obviously from 24.75 μ s to 21.01 μ s when the concentration of added 1,4-DNB is 30 μ M (Table 1).

Energy transfer is considered to be a long range process. When the emission band of the fluorophore has an effective overlap with the absorption band of the analyte, the resonance energy transfer (RET) can occur, resulting in the quenching of fluorescence. As shown in Figure 14, the absorption spectrum of TNT has a large overlap with the emission spectrum of **3**, resulting in the highly selective





Scheme 2. HOMO and LUMO energies for the selected explosives.



Figure 14. Spectral overlap between normalized absorbance spectra of explosives and the normalized emission spectra of **3** (λ_{ex} = 364 nm) in DMF.

wavelength (364 nm) than other explosives (i.e. $\varepsilon = 0.10 \times 10^5$ $M^{-1}cm^{-1}$ and 0.20 × 10⁵ $M^{-1}cm^{-1}$ for 1,4-DNB and TNT, respectively). This means 1,4-DNB and TNT can compete with the Zn/Ligand moieties for the light energy, thus decreasing the probability of energy transfer from Zn/Ligand moieties to subsequently quenching Sm³⁺ and the lanthanide luminescence.43 Compared with 1,4-DNB, TNT has higher absorption at the excitation wavelength and its absorption spectrum has a larger overlap with the emission spectrum of 3. Thus, for PET and RET mechanisms, the greater K_{SV} value of **3** towards 1,4-DNB indicates that the PET mechanism is dominant in the luminescence quenching process of 3.

Experimental

Materials and methods

The Schiff-base ligand H_2L was prepared according to wellestablished procedures.²⁹ Physical measurements: NMR: AVANCE III AV500. 500 spectrometer (¹H, 500 MHz) at 298 K; IR: Nicolet IS10 spectrometer; Elemental analyses (C, H, N) of compounds were carried out on a EURO EA3000 elemental analysis after dried in an oven at 100°C for 2 hours. Melting points were obtained in sealed glass capillaries under

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dinitrogen and are uncorrected. The thermogravimetric analyses were carried out on a TA Instruments Q600. The UVvisible absorption spectra were recorded at RT using an UV-3600 spectrophotometer. Field emission scanning electron microscopy (FESEM) images were recorded on a Nova NanoSEM 200 scanning electron microscope.

Synthetic procedures

H₂**L**. Hydroxy-3-methoxybenzaldehyde (20.0 mmol, 3.0430 g) was dissolved in 15 mL EtOH, and a solution of 1,5naphthalenediamine (10.0 mmol, 1.5808 g) in 20 mL EtOH was then added drop by drop. The resulting solution was stirred and heated under reflux for 2.5 hours. It was allowed to cool and was then filtered. The solid was washed with EtOH (3 × 5 ml) and then dried in the air at room temperature to give yellow product. Yield (based on 1,5-naphthalenediamine): 4.1793 g (98%). Elemental analysis: Found: C, 73.44; H, 5.66; N, 6.55%; Calc. for C₂₆H₂₂N₂O₄: C, 73.23; H, 5.20; N, 6.57%. IR (CH₃CN, cm⁻¹): 1600 (s), 1507 (m), 1460 (s), 1410 (m), 1250 (s), 1080 (m), 965 (s), 781 (s), 685 (m). ¹H NMR δ H (500 MHz, CDCl₃) 8.76 (2H, s), 8.26 (2H, d), 7.56 (2H, m), 7.29 (2H, d), 7.26 (4H, s), 7.11 (2H, d), 7.06 (2H, d), 6.95 (2H, t), 3.99 (6H, s).

 $[Nd_2Zn_2(L)_2(L')_2(OAc)_2(NO_3)_2(H_2O)_2]$ (1). $Zn(OAc)_2 \cdot 2H_2O$ (0.40 mmol, 0.0876 g), Nd(NO₃)₃·6H₂O (0.30 mmol, 0.1315 g), H₂L (0.30 mmol, 0.1333 g) and H₂L' (0.35 mmol, 0.0785 g) were dissolved in MeOH (50 mL) at room temperature, and a solution of triethylamine in EtOH (1.00 mol/L, 1 ml) was then added. The resulting solution was stirred and heated under reflux for 30 mins. It was allowed to cool and was then filtered. Diethyl ether was allowed to diffuse slowly into the filtrate at room temperature and pale yellow crystals were obtained after one month. The crystals were filtered off, washed with MeOH (5 ml) and dried in the air for one week. Yield (based on $Nd(NO_3)_3 \cdot 6H_2O$: 0.1400 g (47 %). m. p. > 172.4°C (dec.). Elemental analysis: Found: C, 51.85; H, 3.77; N, 4.15%. Calc. For C₈₆H₇₂N₆Nd₂O₂₄Zn₂: C, 51.81; H, 3.69; N, 4.22%. IR (CH₃CN, cm⁻¹): 1610 (s), 1460 (s), 1390 (s), 1210 (s), 975 (m), 786 (s), 741 (s), 684 (m).

 $[Nd_6Zn_6L_2(L'')_2O_2(OAc)_{18}] (2). The procedure was the same as that for 1 using Zn(OAc)_2·2H_2O (0.40 mmol, 0.0876 g), Nd(NO_3)_3·6H_2O (0.35 mmol, 0.1534 g), H_2L (0.40 mmol, 0.1705 g) and H_2L'' (0.40 mmol, 0.0561 g). Pale yellow single crystals of 2 were formed after one month. Yield (based on Nd(NO_3)_3·6H_2O): 0.0882g (39%). m. p. > 174.6°C (dec.). Elemental analysis: Found: C, 35.76; H, 3.80; N, 1.49%. Calc. for C_{118}H_{158}N_4O_{63}Nd_6Zn_6: C, 36.34; H, 4.13; N, 1.44%. IR (CH_3CN, cm⁻¹): 1610 (s), 1550 (s), 1390 (s), 1210 (s), 975 (w), 792 (m), 743 (m), 686 (w).$

 cm⁻¹): 1610 (s), 1550 (s), 1460 (s), 1390 (s), 1210 (m)_A,974 (w),

 786 (w), 747 (w), 689 (w).

Photophysical Studies

Visible and NIR luminescence spectra were recorded on a FLS 980 fluorimeter. The light source for the spectra was a 450 W xenon arc lamp with continuous spectral distribution from 190 to 2600 nm. Liquid nitrogen cooled Ge PIN diode detector was used to detect the NIR emissions from 800 nm to 1700 nm. The temporal decay curves of the fluorescence signals were stored by using the attached storage digital oscilloscope. The quantum yields (Φ_{em}) were obtained by using an integrating sphere, according to eqn $\Phi_{em} = N_{em} / N_{abs}$, where N_{em} and N_{abs} are the numbers of emitted and absorbed photons, respectively. Systematic errors have been deducted through the standard instrument corrections. All the measurements were carried out at room temperature.

Crystallography

Data were collected on a Smart APEX CCD diffractometer with graphite monochromated Mo-K α radiation (λ = 0.71073 Å) at 190 K. The data set was corrected for absorption based on multiple scans and reduced using standard methods. Data reduction was performed using DENZO-SMN.⁴⁷ The structures were solved by direct methods and refined anisotropically using full-matrix least-squares methods with the SHELX 97 program package.48 Coordinates of the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in the calculation isotropically but not refined. Neutral atom scattering factors were taken from Cromer and Waber.⁴⁹ Crystallographic data for 1-3 have been deposited with the Cambridge Crystallographic Data (CCDC reference numbers 1842949-1842951). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. Selected bond lengths of 1-3 are given in Tables S1-S3 (Supporting Information).

1: $C_{86}H_{72}N_6O_{24}Zn_2Nd_2$, orthorhombic, space group Pbca, *a* = 15.923(3), *b* = 20.416(4), *c* = 24.500(5) Å, α = 90°, β = 90°, γ = 90°, *V* = 7965(3) Å³, *Z* = 4, *Dc* = 1.662 g cm⁻³, μ (Mo-K α) = 1.961 mm⁻¹, *F*(000) = 4008, *T* = 190 K. *R*₁ = 0.0781, *wR*₂ = 0.2313 for 6779 independent reflections with a goodness-of-fit of 1.086.

2: $C_{118}H_{158}N_4O_{63}Zn_6Nd_6$, monoclinic, space group P2(1)/n, a = 18.0116(4), b = 22.1288(5), c = 19.8728(3) Å, $\alpha = 90^{\circ}$, $\beta = 114.9620(10)^{\circ}$, $\gamma = 90^{\circ}$, V = 7180.9(3) Å³, Z = 2, Dc = 1.803 g cm⁻³, μ (Mo-K α) = 3.201 mm⁻¹, F(000) = 3876, T = 190 K. $R_1 = 0.0953$, $wR_2 = 0.2705$ for 7678 independent reflections with a goodness-of-fit of 1.083.

3: $C_{103}H_{110}N_4O_{58}Zn_6Sm_6$, monoclinic, space group P2(1)/n, a = 18.465(7), b = 22.557(8), c = 20.143(7) Å, $\alpha = 90^\circ$, $\beta = 115.879(6)^\circ$, $\gamma = 90^\circ$, V = 7549(5) Å³, Z = 2, Dc = 1.592 g cm⁻³, μ (Mo-K α) = 3.306 mm⁻¹, F(000) = 3536, T = 190 K. $R_1 = 0.0994$, $wR_2 = 0.2647$ for 12887 independent reflections with a goodness-of-fit of 1.021.

Conclusions

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In conclusion we have successfully demonstrated the application of a "two-ligand" approach to the construction of two types of Zn-Ln nanoclusters 1-3 with one long Schiff base ligand (H₂L) featuring a electron-rich naphthyl backbone and two short polydentate ligands (H₂L' and H₂L''). The 4-metal Zn-Nd cluster 1 and 12-metal Zn-Nd/Sm clusters 2-3 show linear and planar structures with sizes of approximately $10 \times 10 \times 30$ Å and $10 \times 15 \times 22$ Å, respectively. In the solid state, both 2 and ${\bf 3}$ structures have open 3D networks with extended channels (i.e. 7 × 7 Å for 3). All 1-3 exhibit typical luminescence of lanthanide ions. For the Zn-Nd clusters, 2 shows better luminescence properties than 1. In these clusters, the Schiff base ligands exhibit an "U-shaped" configuration. The Zn-Sm cluster 3 shows visible and NIR luminescent sensing of nitro explosives and exhibits high selectivity and sensitivity to 1,4-DNB and TNT. To the best of our knowledge, 3 represents the first report of high-nuclearity d-f nanocluster for both visible and NIR luminescent sensing of nitro explosives. Further studies focused on this synthetic methodology and improvement in the selectivity and sensitivity of nitro explosives by the construction of novel luminescent highnuclearity lanthanide-based nanoclusters are in progress.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Journal of Materials Chemistry C Accepted Manuscript

Table of Contents

Self-assembly of Luminescent 12-metal Zn-Ln Planar Nanoclusters with Sensing Properties towards Nitro Explosives

Dongmei Jiang, Xiaoping Yang, Xiaohui Zheng, Le Bo, Ting Zhu, Hongfen Chen, Lijie Zhang and Shaoming Huang

Two types of 4- and 12-metal Zn-Ln nanoclusters (Ln = Nd and Sm) were constructed using one long Schiff base ligand with a naphthyl backbone and two short polydentate ligands, and the 12-metal Zn-Sm cluster shows interesting visible and NIR luminescent sensing of nitro explosives with high sensitivity to 1,4-DNB and TNT at ppb level.

