J Chem Crystallogr (2008) 38:595–599
DOI 10.1007/s10870-008-9351-9

ORIGINAL PAPER

Structure and Fluorescence of Three New Homodinuclear Lanthanide (III)/Schiff-base Compounds $[\{Ln(clapi)\}_2] \cdot 2CH_3CN$ {Ln=La, Ce, Eu; H_3clapi = 2-(5-Chloride-2-hydroxyphenyl)-1,3-bis [4-(5-chloride-2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine}

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Received: 29 October 2006 / Accepted: 27 March 2008 / Published online: 9 April 2008

Abstract Three new homodinuclear lanthanide(III)/Schiff-base compounds $[\{Ln(clapi)\}_2] \cdot 2CH_3CN$ {Ln = La **1**, Ce **2**, and Eu **3**; H_3clapi = 2-(5-chloride-2-hydroxyphenyl)—1,3-bis [4-(5-chloride-2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine} have been prepared successfully by template procedure and characterized by elemental analysis, IR spectra, and the dinuclear cerium compound (**2**) selected as a representative was structurally characterized. The crystal system is triclinic with space group P-1, a = 10.588 Å, b = 11,521(2) Å, c = 13.979(3) Å, α = 109.66(3)°, β = 97.77(3)°, γ = 106.33(3)°, V = 1486.2(5) Å^3 and Z = 1. In compound **2**, each Ce atom is coordinated to four N and four O atoms from two clapi^{3-} ligands, forming a distorted square antiprism. Two phenol oxygen atoms from the middle arms of the two heptadentate ligands as μ_2-bridging connect the two Ce atoms. Compounds **1, 2** and **3** in CH_2Cl_2 exhibit strong blue fluorescence at room temperature, compound **3** has no typical red emission of Eu^{3+} at room temperature while exhibits strong red fluorescence at 77 K in CH_2Cl_2.

Keywords Crystal structure · Fluorescence · Homodinuclear compounds · Ln(III) · Schiff-base

Introduction

Schiff-base ligands with N, O donor sets are very attractive because of their versatile structures and remarkable ability to coordinate metal cations, and may be employed in the assembly of coordination architectures directed by lanthanide cations [1, 2] which can in reverse promote Schiff-base condensation and can give access to complexes of otherwise inaccessible ligands [3]. Schiff-base and lanthanide complexes are now extensively used as catalysts for RNA hydrolysis [4, 5], active agents in cancer radiotherapy [6], contrast agents for NMR imaging [7, 8], luminescent probes in visible and near IR domain [9, 10]. Among them, dinuclear lanthanide and Schiff-base complexes have been a hot topic and extensively reported because of their potential applications in biology and medicine [11–15], chemistry and technology [16]. For example, luminescent dinuclear lanthanides ions complexes of Schiff-base have been exploited to study metal–metal coupling processes and interactions, chemical environment of coordinated metal ions, the local site symmetry and fluxionality of the ligand frameworks [17, 18].

In the course of a program to synthesize dinuclear lanthanide Schiff-base complexes, we are interested in the formation of dinuclear lanthanide/N_4O_3 heptadentate Schiff-base complexes. It has been found that complexes formed by tripodal heptadentate N_4O_3-type Schiff-base coordinated to Ln^{3+} are normally highly unstable and very sensitive to moisture and metal ion-promoted hydrolysis of the imine C=N linkages [11, 12], therefore it is important to find a solution to get stable dinuclear lanthanide/N_4O_3 heptadentate Schiff-base complexes. In this respect, Orvig [11] and Kahwa [12] tried a template method using a new type of N_4O_3 Schiff-base containing imidazolidine and synthesized successfully stable homodinuclear lanthanide(III)/containing imidazolidine N_4O_3 Schiff-base complexes $[\{La(brapi)\}_2] \cdot 2CHCl_3$ and $[\{Sm(api)\}_2]$, respectively, while our efforts yielded a family of air-stable homodinuclear lanthanide(III)/Schiff-base complexes $[\{Ln(clapi)\}_2] \cdot 2CH_3CN$ {Ln=La **1**,

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Ce **2**, Eu **3**; H_3clapi = 2-(5-chloride-2-hydroxyphenyl)-1,3-bis [4-(5-chloride-2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine}.

In this paper, we present the synthesis, structural characterization and fluorescence of the new complexes. The crystal structure and fluorescence of the stable homodinuclear cerium(III)/Schiff-base complex [{Ce(clapi)}$_2$]· 2CH_3CN (**2**) was reported here for the first time. Importantly, [{Eu(clapi)}$_2$] · 2CH_3CN (**3**) exhibits very strong red fluorescence from Eu^{3+} at 77 K, but very weak at room temperature.

Experimental

Materials

$Eu(NO_3)_3 \cdot 6H_2O$ was prepared by neutralization of 99.9% Eu_2O_3 with HNO_3 acid. All the other chemicals are of reagent grade. H_3clapi was prepared by condensation of stoichiometric 5-chloride-salicylaldehyde and triethylenetetramine.

General and Physical Measurements

Infrared spectra were recorded on a Nicolet 170SX RT-IR spectrophotometer, elemental analysis was performed on a Perkin-Elmer 240C analytical instrument and fluorescence spectra on an Aminco Bowman Series 2 luminescence spectrometer.

Single Crystal X-ray Crystallography of **2**

The data for compound **2** were collected by ω/scan on a CAD4SDP4 four-circle single crystal X-ray diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293(2) K. Empirical absorption corrections were made from ψ-scan data using the program SHELXTL-93 at the data reduction stage. The structure was solved by direct methods and refined by Full-matrix least square on F^2 (SHELXTL V5.1). Anisotropic thermal factors were assigned to all the non-hydrogen atoms. Relevant details of the structure determination are presented in Table 1. The selected bond distances and angles are presented in Table 2. Crystallographic data in CIF format have been deposited at the Cambridge Crystallographic Data Centre with CCDC No. 153094.

Table 1 Crystal data and structure refinement for **2**

Empirical formula	$C_{58}H_{54}N_{10}Ce_2Cl_6O_6$
Formula weight	1480.05
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
a = 10.558(2) Å	α = 109.66(3)°
b = 11.521(2) Å	β = 97.77(3)°
c = 13.979(3) Å	γ = 106.33(3)°
Volume	1486.2(5) $Å^3$
Z	1
Density (calculated)	1.654 Mg/m^3
Absorption coefficient	1.841 mm^{-1}
F(000)	738
Crystal size	0.3 × 0.2 × 0.2 mm^3
Theta range for data collection	1.60–25.00°
Index ranges	$0 \le h \le 12, -13 \le k \le 13, -16 \le l \le 16$
Reflections collected	5538
Independent reflections	5226 [R(int) = 0.0531]
Completeness to theta = 25.00	99.8%
Absorption correction	Psi-scan
Max. and min. transmission	0.67 and 0.45
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5226/0/355
Goodness-of-fit on F^2	1.138
Final R indices [I>2sigma(I)]	R1 = 0.0621, wR2 = 0.1620
R indices (all data)	R1 = 0.0917, wR2 = 0.1862
Largest diff. peak and hole	2.377 and −2.216 e $Å^{-3}$

Preparation of [{Ln(clapi)}$_2$] · 2CH_3CN (**1**, **2** and **3**)

In a typical procedure, the title compounds were prepared by the following template method: To a solution of 0.4695 g (3 mmol) 5-chloride-salicylaldehyde in methanol (100 mL) was added 1 mmol $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = La, Ce, or Eu) in methanol (20 mL) and then the resulting solution was refluxed for 1 h. Excess triethylenetetramine (4 mmol) was added and the solution was allowed to reflux for two days. The initial yellow solution turned slowly into a deep yellow or red color on addition of triethylenetetramine. Crude yellow precipitates of **1** and **3** or red precipitate of **2** were collected (30–40% yield) and dried in vacuum. Air-stable single crystals were obtained by re-crystallization of the corresponding crude products in CH_3CN/CH_2Cl_2. (Found: C, 47.22; H, 3.69; N, 9.52; La, 19.13%. Calc. for $C_{58}H_{54}N_{10}La_2Cl_6O_6$ **1**: C, 47.12; H, 3.66; N, 9.48; La, 18.82%; Found: C, 47.21; H, 3.72; N, 9.39; Ce, 19.05%. Calc. for $C_{58}H_{54}N_{10}Ce_2Cl_6O_6$ **2**: C, 47.06; H, 3.65; N, 9.47; Ce, 18.93%; Found: C, 46.53; H, 3.65; N, 9.36; Eu, 19.95%. Calc. for $C_{58}H_{54}N_{10}Eu_2Cl_6O_6$ **3**: C, 46.24; H, 3.58; N, 9.30; Eu, 20.33%.)

Table 2 Selected bond lengths [Å] and angles [°] for **2**

Ce(1)–O(1)	2.324(7)	Ce(1)–N(2)#1	2.584(7)
Ce(1)–O(2)#1	2.333(6)	Ce(1)–N(4)#1	2.849(7)
Ce(1)–O(3)	2.433(5)	N(4)–Ce(1)#1	2.849(7)
Ce(1)–O(3)#1	2.449(5)	Ce(1)–N(3)	2.852(7)
Ce(1)–N(1)	2.574(8)	Ce(1)–Ce(1)#1	4.0245(15)
O(1)–Ce(1)–O(2)#1	127.9(2)	O(1)–Ce(1)–O(3)	83.3(2)
O(2)#1–Ce(1)–N(2)#1	69.5(2)	O(2)#1–Ce(1)–O(3)	146.5(2)
O(3)–Ce(1)–N(2)#1	140.3(2)	O(1)–Ce(1)–O(3)#1	143.9(2)
O(3)#1–Ce(1)–N(2)#1	114.2(2)	O(2)#1–Ce(1)–O(3)#1	85.6(2)
N(1)–Ce(1)–N(2)#1	89.2(2)	O(3)–Ce(1)–O(3)#1	69.0(2)
O(1)–Ce(1)–N(4)#1	84.3(2)	O(1)–Ce(1)–N(1)	70.1(2)
O(2)#1–Ce(1)–N(4)#1	109.8(2)	O(2)#1–Ce(1)–N(1)	74.1(3)
O(3)–Ce(1)–N(4)#1	82.23(19)	O(3)–Ce(1)–N(1)	112.6(2)
O(3)#1–Ce(1)–N(4)#1	69.78(19)	O(3)#1–Ce(1)–N(1)	141.5(2)
N(1)–Ce(1)–N(4)#1	147.9(2)	O(1)–Ce(1)–N(2)#1	73.3(2)
N(2)#1–Ce(1)–N(4)#1	64.3(2)	O(3)#1–Ce(1)–N(3)	82.5(2)
O(1)–Ce(1)–N(3)	109.1(2)	N(1)–Ce(1)–N(3)	64.4(2)
O(2)#1–Ce(1)–N(3)	87.1(2)	N(2)#1–Ce(1)–N(3)	149.1(2)
O(3)–Ce(1)–N(3)	68.79(19)	N(4)#1–Ce(1)–N(3)	145.67(19)

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 2, -z$

Results and Discussion

IR Spectra of the Title Compounds

The IR spectra of the title compounds show that the peak due to O–H···N stretching vibration from 3300 to 2100 cm^{-1} in H_3clapi is disappeared in compound **1**, **2** and **3**, and the peak due to C=N stretching vibration in H_3clapi shifts from 1632 to 1623 cm^{-1} in compound **1**, **2** and **3**. The loss of intramolecular hydrogen bonds and the formation of the new compounds **1**, **2** and **3** is the main reason for the latter shift.

Structure of **2**

Compound **2** crystallized in triclinic space group P–1, $a = 10.588$ Å, $b = 11{,}521(2)$ Å, $c = 13.979(3)$ Å, $\alpha = 109.66(3)°$, $\beta = 97.77(3)°$, $\gamma = 106.33(3)°$, $V = 1486.2(5)$ Å^3 and $Z = 1$. The asymmetric unit of **2**, presented in Fig. 1, contains 41 non-hydrogen atoms. There are one Ce, three O, three Cl, twenty-nine C and five N atoms, which are crystallographically independent. Each Ce atom is coordinated to four N and four O atoms with Ce–O distances in the range of 2.324(7)–2.449(5) Å (av. Ce–O = 2.385 Å) and Ce–N distances from 2.574(8) to 2.852(7) Å (av. Ce–N = 2.715 Å). The O–Ce–O bond angles are distributed in the range 69.0(2)–146.5(2)° (av. O-Ce–O = 109.4°), O–Ce–N bond angles in the range 68.79(19)–141.5(2)° (av. O–Ce–N = 93.1°), N–Ce–N bond angles in the range 64.3(2)–149.1(2)°(av. N–Ce–N = 110.1°), thus each Ce^{3+} centre has an approximate square antiprismatic geometry, and two such coordination polyhedra of Ce edge-share through O(3)···O(3a) (2.764 Å), as shown in Figs. 2 and 3, with an intramolecular Ce······Ce distance of 4.024 Å. Of the four oxygen atoms connected to Ce atom, two are from terminal phenols and the other two, as μ_2-bridging, from the middle arms of the two heptadentate ligands. Of the four nitrogen atoms, two are from imidazolidine parts and the other two from imines (see Fig. 3). The average Ce–N (N atoms from imidazolidine) bond lengths (2.851 Å) are significantly longer than that of Ce–N (N atoms from imine) (2.573 Å) and the average Ce–O (O atoms from the middle arms of the two heptadentate ligands) bond lengths (2.441 Å) are longer than that of Ce–O (O atoms from the terminal phenols) bond

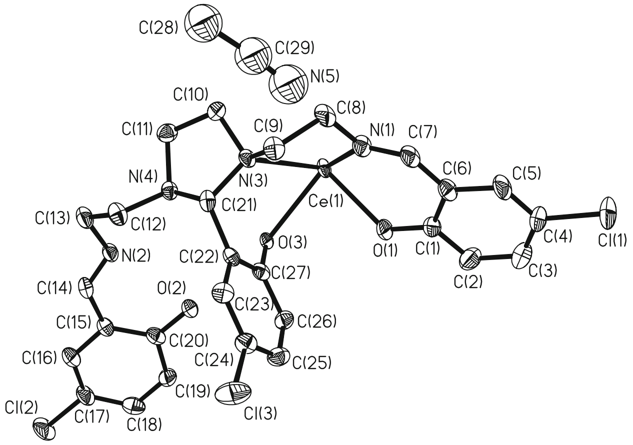

Fig. 1 ORTEP view of the asymmetric unit in compound **2**, showing the atom-labeling scheme with 30% probability ellipsoids (all hydrogen atoms are omitted for clarity)

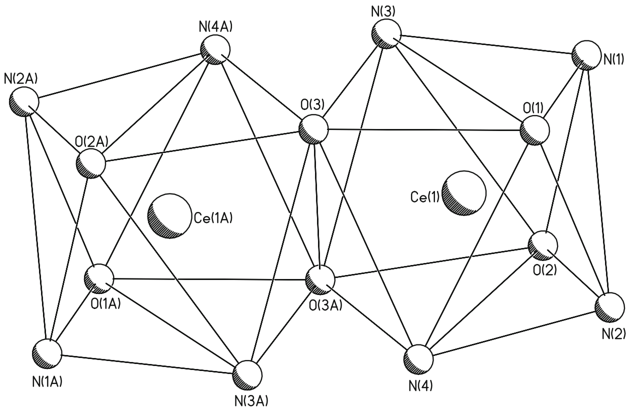

Fig. 2 The approximate square antiprismatic geometry around each Ce^{3+} ion in **2**

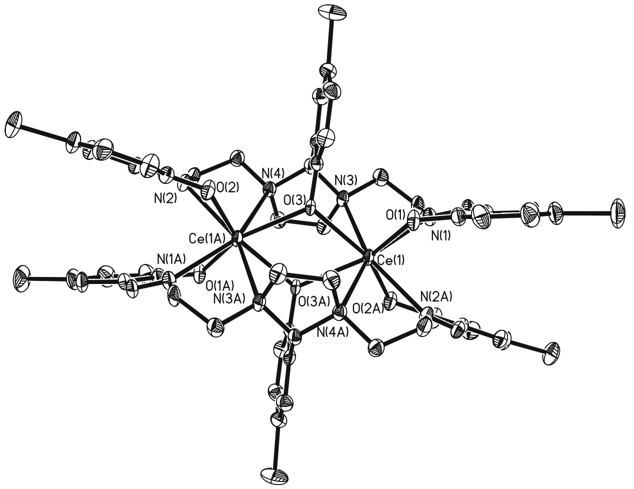

Fig. 3 ORTEP view of the sandwich dimmer in **2**, showing the atom-labeling scheme with 30% probability ellipsoids (hydrogen atoms and CH_3CN was omitted for clarity)

lengths (2.328 Å). The four nitrogen atoms of each ligand are coplanar within max. deviation of 0.0098 Å and the middle phenolate rings inclined 90.3° to this plane, while the two terminal phenolate rings are inclined to the four nitrogen coplanar by ca.13.4°, which is smaller than 25° reported in reference 13, the change probably reflects the influence of the presence of chloride atoms in the phenol ring.

Fluorescence of the Title Compounds

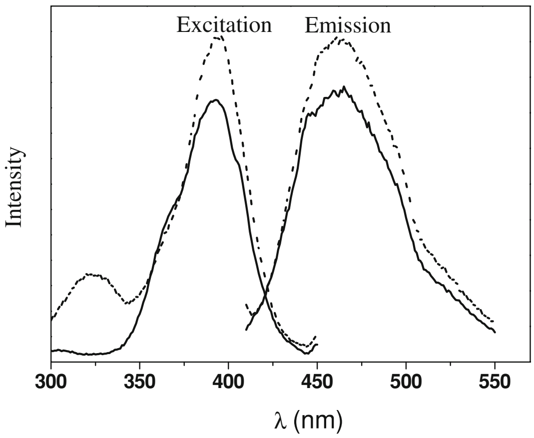

Fig. 4 The room temperature excitation and emission spectra of **2** ($\lambda_{em} = 462$ nm, $\lambda_{exc} = 394$ nm) (*short dash line*) and H_3clapi ($\lambda_{em} = 463$ nm, $\lambda_{exc} = 393$ nm) (*solid line*) at a concentration of 5×10^{-5} M in CH_2Cl_2, respectively

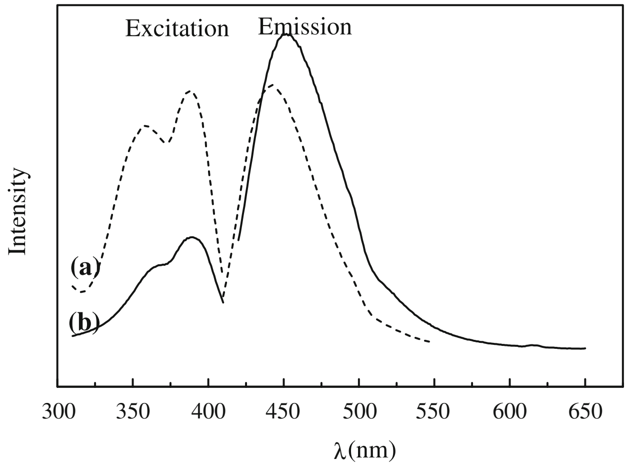

Fig. 5 The excitation and emission spectra of **1** and **3** at room temperature (**a**) The excitation and emission spectra of **1** (5×10^{-5} M) in CH_2Cl_2 ($\lambda_{em} = 462$ nm, $\lambda_{ex} = 394$ nm); (**b**) The excitation and emission spectra of **3** (5×10^{-5} M) in CH_2Cl_2 ($\lambda_{em} = 462$ nm, $\lambda_{ex} = 394$ nm)

Figure 4 shows the fluorescent spectra of compound **2** and H_3clapi (5×10^{-5} M) in CH_2Cl_2 at room temperature. The band at 394 nm observed for the compound in both excitation spectra for the ligand and compound **2** is presumably from the electronic states of ligand [12], and the new band at 320 nm for compound **2** is mainly ascribed to spin allowed transition from 4f to 5d of Ce^{3+} ion [19]. Under 394 nm excitation for **2**, an intensive band recorded at 462 nm, which is also observed in the free ligand under 394 nm excitation. The indication of intensive band at 462 nm is also found in spectrum for either compounds **1** or **3** (Fig. 5) in CH_2Cl_2 at room temperature except for lack of the peak at 320 nm in the excitation spectrum of **2**. Unfortunately, no typical red emission of Eu^{3+} is observed at room temperature in compound **3**. However, at 77 K the emission at 618 nm (Fig. 6) which is the typical transition of $^5D_0 \rightarrow ^7F_2$ for Eu^{3+} ion is inspected by excitation of light in the range 325–400 nm ($\lambda_{max} = 360$ nm). Meanwhile it also shows a broad poorly resolved peak in the range 400–500 nm in the emission spectrum of compound **3**. Additionally, no splitting peak at 580 nm for the forbidden $^5D_0 \rightarrow ^7F_0$ transition indicates that there is only one site for

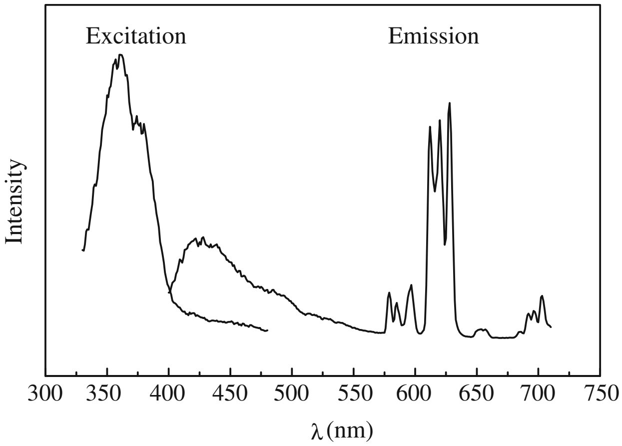

Fig. 6 The excitation and emission spectra of **3** at 77 K. (λ_{em} = 618 nm, λ_{ex} = 360 nm

Eu^{3+} ion. It is noted that $^5D_0 \rightarrow {}^7F_0$ transition can only be detected in those C_1, C_s, C_n and C_{nv} groups in total 32 point groups, revealing that the local symmetry of Eu^{3+} ion of 3 in triclinic system may be C_1 group after excited [20]. The electric dipole transition $^5D_0 \rightarrow {}^7F_2$ which is forbidden for Eu^{3+} ion in compounds **3** according to the coordination polyhedral of Eu^{3+} ion with D_{4d} symmetry [21, 22] is more intensive than the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ reflecting the actual crystal electric field symmetry at Eu^{3+} ion centre is lower than the ca. D_{4d} adopted by the coordination polyhedral or trigger the hypersensitive behavior of the $^5D_0 \rightarrow {}^7F_2$ transition [12]. This is probably due to the aromatic electronic clouds [22] and polarization effects [23]. Three stronger bands at 691, 695 and 703 nm are assigned to $^5D_0 \rightarrow {}^7F_4$ transition of Eu^{3+} ion. A peak at 652 nm attributed to $^5D_0 \rightarrow {}^7F_3$ transition of Eu^{3+} ion is so low that it can be taken as forbidden.

Conclusions

It is clear that the cooperative assembly of lanthanide ions and N_4O_3-type heptadentate Schiff-base offer a rich chemistry as exemplified by the isolation of the title compounds which broaden the present understanding and provide insights toward the synthesis of novel structures of dinuclear lanthanide/N_4O_3 heptadentate Schiff-base complexes with designed functional groups and consequently desired properties, for example, compounds **1**, **2** and **3** in CH_2Cl_2 exhibit strong blue fluorescence at room temperature, while compound **3** has no typical red emission of Eu^{3+} ion at room temperature, but compound **3** in CH_2Cl_2 exhibits strong red fluorescence at 77 K. It is highly likely that similar dinuclear lanthanide/N_4O_3 heptadentate Schiff-base complexes can also be prepared and can be extended to (1) a variety of Schiff-base ligands, (2) different trivalent lanthanide cations, including mixed metals and (3) different solvent molecules like CH_3CN which significantly affect properties as the compounds because, for example, solvation may affect the lanthanide(III) ion site symmetry while O–H and C–H stretching vibrations can quench Ln^{3+} emission. Work on this theme is currently underway.

Acknowledgements Many thanks to professor Xiaozeng You of Coordination Chemistry Institute, Nanjing University, P.R. China for his kind help.

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