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Construction of Identical [2 + 2] Schiff-Base Macrocyclic Ligands by Ln^{III} and Zn^{II} Template Ions Including Efficient Yb^{III} Near-Infrared Sensitizers

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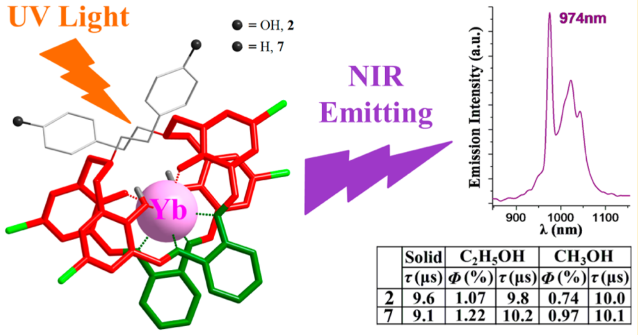
Supporting Information

ABSTRACT: Identical 34-membered [2 + 2] pendent-armed Schiff-base macrocyclic ligands (H_4L_a and H_4L_b) can be constructed via the condensation reactions between rigid *o*-phenylenediamine and extended dialdehydes (H_2hpdd/H_2pdd) in the presence of either Ln^{III} or Zn^{II} template with remarkable distinction on the ion radii and charge. X-ray single-crystal diffraction analyses reveal the formation of mononuclear Ln^{III} complexes (**1**−**4** and **7**) and dinuclear Zn^{II} complexes (**5** and **6**). It is noted that Ln^{III} macrocyclic complexes have eight-coordinate sandwich-like mononuclear structures fully surrounded by flexible and large-sized macrocyclic ligands. Photophysical studies have demonstrated that both H_4L_a and H_4L_b can serve as effective sensitizers for the Yb^{III} ion (**2** and **7**) exhibiting near-infrared emission at 974 nm with high quantum yields in solution (C_2H_5OH and CH_3OH, ∼1%). Moreover, the quantum yields of two Yb^{III} complexes **2** and **7** could be increased ∼15% in CH_3OH under weak alkaline condition (pH = 8−9), while no significant changes are observed in C_2H_5OH by contrast. We think the unique sandwich-like macrocyclic structures of Yb^{III} complexes **2** and **7** play important roles in simultaneously guaranteeing the effective match of the energy levels of Yb^{III} centers as well as shielding from the solvent molecules and counterions.



	Solid	C_2H_5OH		CH_3OH	
	τ (μs)	Φ (%)	τ (μs)	Φ (%)	τ (μs)
2	9.6	1.07	9.8	0.74	10.0
7	9.1	1.22	10.2	0.97	10.1

INTRODUCTION

Currently, there is a growing trend of investigations on near-infrared (NIR) luminescence of lanthanide complexes (Yb^{III}, Er^{III}, Nd^{III}) in the fields of light-emitting diodes,[1] solar cells,[2] fluoroimmunoassay,[3] bioimaging,[4] telecommunications,[5] energy conversion,[6] etc. When designing the NIR luminescent materials, researchers should first achieve the f−f transitions of lanthanide ions which are forbidden by Laporte's rule. It is proven that introduction of an organic sensitizer localized in the vicinity of the central metal ion (antenna effect) is an efficient strategy to achieve the indirect energy transfer and characteristic NIR emission bands.[7] To date, the reported organic sensitizers based on a triplet excited state sensitization process are mainly involved in diketones,[8] carboxylic acids,[9] 8-hydroxyquinolines,[10] polyenes,[11] calixarenes,[12] porphyrins,[13] and so on. However, there are still a few examples on Schiff-base macrocycles as successful NIR sensitizers.[14] In fact, it is difficult to find suitable macrocyclic ligands, at the same time, matching the energy levels of Ln^{III} ions as well as protecting the Ln^{III} centers from deactivation caused by the coupling with high-energy oscillators (C−H, O−H, N−H) in the solvents. Thus far, most of reported Schiff-base macrocyclic Yb^{III}, Er^{III}, and Nd^{III} complexes are related to 2,6-diformylpyridine dialdehyde-based macrocyclic ligands, but no NIR luminescent character has been reported.[14a,e,15]

In this work, we describe a new type of pendant-armed Schiff-base macrocyclic ligands containing rigid *o*-phenylenediamine and extended dialdehyde components, where identical and flexible [2 + 2] Schiff-base macrocyclic ligands (H_4L_a and H_4L_b) have been constructed via either Ln^{III} or Zn^{II} template forming mononuclear Ln^{III} complexes (**1**−**4** and **7**) or dinuclear Zn^{II} complexes (**5** and **6**), respectively (Scheme 1). More interestingly, effective NIR Yb^{III} luminescence (excited at 379 nm) has been achieved in the cases of two sandwich-like macrocyclic mononuclear complexes **2** and **7**, where the deactivation can be well controlled by the beneficial structures. The fully surrounded Yb^{III} centers, which are eight coordinated by Schiff-base macrocyclic ligands, prevent the fluorescence quenching from the competitive coordination of solvents, counterions, and other molecules.

RESULTS AND DISCUSSION

Syntheses of 34-Membered [2 + 2] Pendant-Armed Schiff-Base Macrocyclic Complexes in the Presence of Ln^{III} and Zn^{II} Ion Templates. Our synthetic strategy is based upon the Schiff-base condensation between *o*-phenylenedi-

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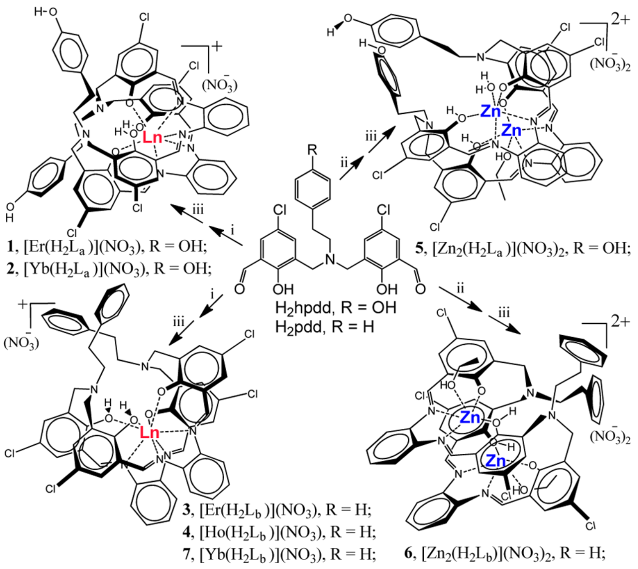
Scheme 1. Synthetic Procedure of Macrocyclic Complexes Under Ln^{III} or Zn^{II} Template[a]



[a] Conditions: (i) $Ln(NO_3)_3 \cdot nH_2O/CH_3OH$, reflux, 10 min; (ii) $Zn(NO_3)_2 \cdot 6H_2O/C_2H_5OH$, reflux, 10 min; (iii) *o*-phenylenediamine/C_2H_5OH, reflux, 2 h.

amine and two extended dialdehydes with different pendant arms (H_2hpdd and H_2pdd)[16] in the presence of certain template ions. The experimental results reveal that Ln^{III} (Ln = Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb) and Zn^{II} ions could act as effective template ions to build 34-membered [2 + 2] folded macrocyclic mononuclear Ln^{III} and dinuclear Zn^{II} complexes, respectively. Commonly, different macrocyclic ligands will be yielded when different template ions with distinguishable ion radii and charge (such as Ln^{III} and Zn^{II}) are used in the process of synthesizing Schiff-base macrocyclic complexes.[14] To the best of our knowledge, this is the first series of Robson-type macrocyclic Ln^{III} complexes based on rigid diamines, because the coordination geometry of a Ln^{III} center is very difficult to be met for previously reported rigid and planar Robson-type macrocyclic ligands. Thus, the selection of our extended dialdehydes to produce flexible and large-sized macrocyclic ligands is believed to be a suitable strategy for preparing Robson-type macrocyclic Ln^{III} complexes even with rigid diamines such as *o*-phenylenediamine. The single crystals of Ln^{III} (Ln = Ho, Er, Yb) and Zn^{II} macrocyclic complexes **1**–**6** were successfully obtained from the acetonitrile/methanol mixture by slow evaporation in air at room temperature.

Spectral Characterizations and Crystal Structures of Macrocyclic Ln^{III} and Zn^{II} Complexes 1–7. In the ESI-MS spectra, the formation of [2 + 2] macrocyclic mononuclear complexes for every lanthanide ion (Ln = Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb) can be clearly verified by a positive peak at m/z = 1234.50–1264.30 (Figure 1). This peak can be assigned as the species of $[M + H]^+$, which is in good agreement with the theoretic simulations. Similarly, the formation of dinuclear Zn^{II} complexes **5** and **6** based on identical [2 + 2] Schiff-base macrocyclic ligands can also be assigned and simulated successfully in their mass spectra, as shown in Figures S1 and S2, Supporting Information. In addition, a strong FT-IR absorption peak is found at 1611–1614 cm^{-1} in all Zn^{II} and Ln^{III} complexes (Figures S3–9, Supporting Information), indicating the transformation from the aldehyde groups (1660 and 1664 cm^{-1}) to the Schiff-base C═N units.

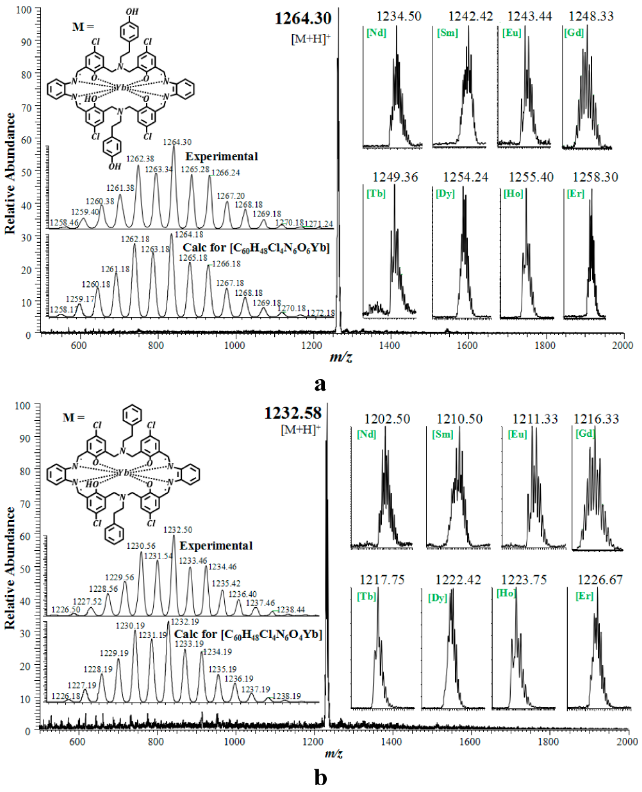


Figure 1. ESI-MS (positive) of [2 + 2] macrocyclic mononuclear Ln^{III} complexes based on H_2hpdd (a) and H_2pdd (b), together with the experimental and calculated peaks of isotopic distribution of Yb^{III} complexes **2** and **7** corresponding to the peak at 100% abundance for comparison.

The molecular structures of Ln^{III} and Zn^{II} complexes **1**–**6** with the atom-numbering scheme are shown in Figure 2. They all have an identical 34-membered [2 + 2] folded macrocyclic skeleton (H_2L_a or H_2L_b). However, the folded macrocyclic ligands in **1**–**6** display a distinguishable conformation where the two types of functional pendant arms ($-CH_2CH_2C_6H_4OH$ or $-CH_2CH_2C_6H_5$) orientate toward the different directions. Moreover, one-half of the four coordinated phenolic protons are retained, which can be verified by the electroneutrality principle for the whole molecules. In four mononuclear Ln^{III} complexes (**1**–**4**), they have the same sandwich-like configuration for the main cationic structures. Every Ln^{III} center is bound by two N_2O_2 cores from two Salen parts of H_2L_a or H_2L_b, resulting in eight-coordinate geometry. As for two dinuclear Zn^{II} complexes (**5** and **6**), the coordination configuration for each Zn^{II} center is five-coordinated pyramidal (τ = 0.245/0.277 for Zn1/Zn2 in **5** and 0.245 for Zn1 in **6**).[17] The basal coordination atoms of each Zn^{II} ion are still composed of the N_2O_2 core from one Salen part of the macrocyclic ligand (H_2L_a or H_2L_b), and the apical position is occupied by one oxygen atom from the solvent molecule (water or ethanol). It is noted that no μ_2-bridging unit is found between the two zinc centers, which is different from most of the reported Robson-type macrocyclic complexes. Actually, the structures of two Zn^{II} complexes are further stabilized by intramolecular π–π stacking interactions which are observed between two pairs of facing 4-chlorophenol rings in the macrocyclic ligands (Figures S22 and S23, Supporting

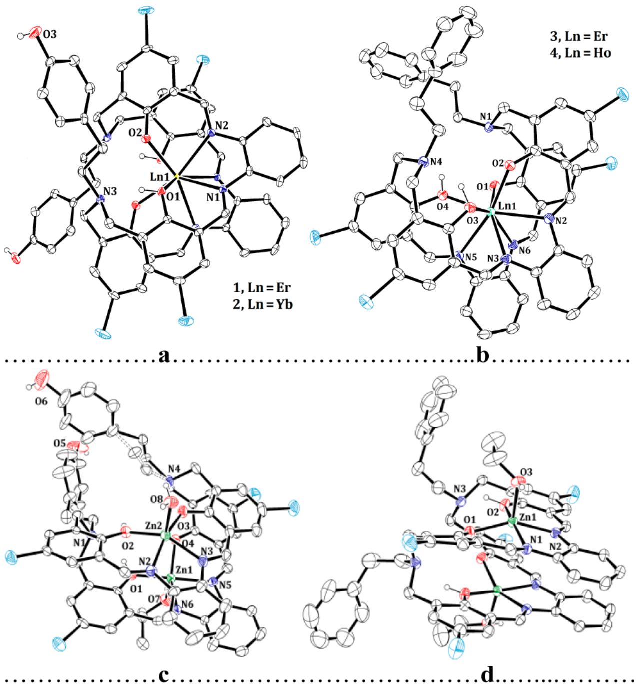


Figure 2. ORTEP drawings of cationic structures of [2 + 2] macrocyclic Ln^{III} and Zn^{II} complexes with atom-numbering scheme: (a) **1** and **2** (Ln = Er, Yb), (b) **3** and **4** (Ln = Er, Ho), (c) **5**, and (d) **6**. Displacement ellipsoids are drawn at the 30% probability level, and the phenolic hydrogen atoms are shown as small spheres of arbitrary radii.

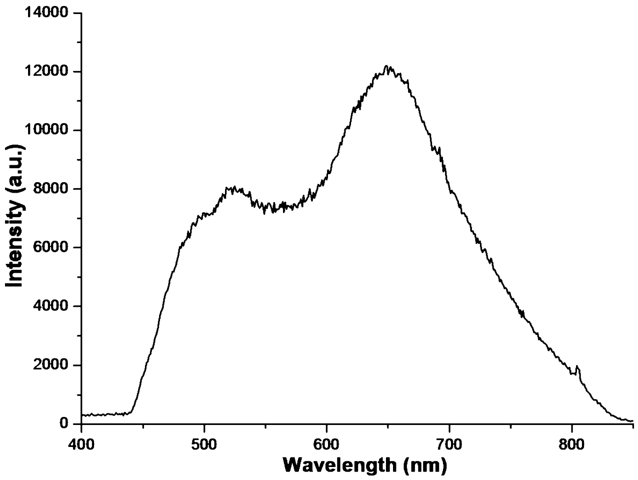


Figure 3. Phosphorescence emission of the Gd^{III} complexes based on the [2 + 2] macrocyclic Schiff-base ligands in the solid state at 77 K.

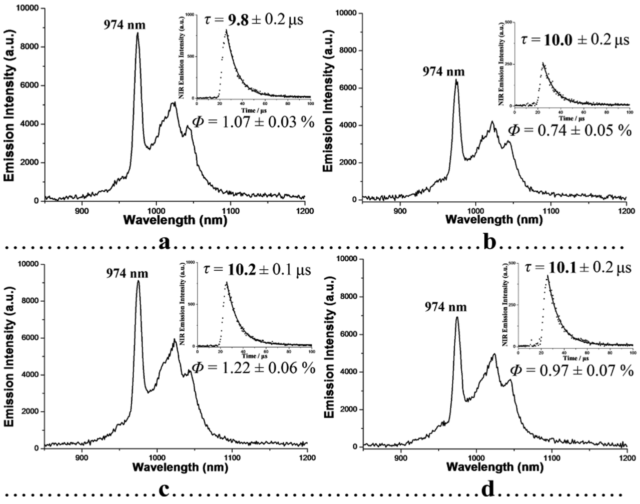


Figure 4. Fluorescence emission spectra of Yb^{III} complex **2** in (a) C_2H_5OH and (b) CH_3OH together with complex **7** in (c) C_2H_5OH and (d) CH_3OH upon excitation at λ_{ex} = 379 nm. (Inset) Lifetimes of fluorescence upon excitation at λ_{em} = 974 nm ([M] = 2 μM).

Information). The centroid-to-centroid separations between them are 3.620(6) and 3.642(6) Å in **5** and 3.635(4) and 3.643(4) Å in **6**, resulting in short $Zn^{II}\cdots Zn^{II}$ separations of 4.186(4) and 3.926(2) Å, respectively.

It is suggested that the two Schiff-base macrocyclic ligands H_4L_a and H_4L_b show their potential to (i) work as antenna chromophores which could sensitize certain lanthanide ions by efficient intramolecular energy transfer, (ii) provide suitable coordinated atoms and charges to saturate the coordination number of the central lanthanide ions when forming charge-neutral complexes, (iii) form stable complexes to protect the central lanthanide ions from further coordination by undesired quenchers, and (iv) enhance the ligand-to-metal sensitization efficiency by four chloric substitutions. Indeed, our experimental results demonstrate that both of the two Schiff-base macrocyclic ligands serve as octadentate ligands and efficient Yb^{III} NIR sensitizers by forming unique sandwich-like macrocyclic complexes.

Near-Infrared Luminescence of Macrocyclic Yb^{III} Complexes 2 and 7. The triplet ($^3\pi\pi^*$) excited state energy levels of two macrocyclic ligands (H_4L_a and H_4L_b) were determined from corresponding Gd^{III} complexes in the solid state at 77 K, and they were found to be the same as 19 120 cm^{-1} (Figure 3). Thus, the energy difference between the $^3\pi\pi^*$ state of the macrocyclic ligands and the lowest $^2F_{5/2}$ excited state of the Yb^{III} ion is calculated to be 8916 cm^{-1},[18a] indicative of the possibility of efficient Yb^{III} NIR sensitization.[18b,c] Further quantitative luminescence measurements for Yb^{III} complexes **2** or **7** in the solid state or solution (2 μM) indicate that the two Schiff-base macrocyclic ligands are able to efficiently sensitize the Yb^{III} ion emission in the NIR domain. One strong characteristic emission band was observed at 974 nm for both of them when excited at 379 nm (Figure 4), which is assigned as the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition and is split into three bands because of the crystal-field effects.[18d,e] Control experiments for other mononuclear lanthanide (Ln = Nd, Sm, Eu, Tb, Dy, Ho, Er) macrocyclic complexes reveal that no characteristic emission bonds could be observed. Meanwhile, the absence of significant residual emission of the macrocyclic ligands also indicates the efficient energy transfer from the ligands to Yb^{III} ion in complexes **2** and **7**.

The lifetimes (τ) of Yb^{III} complexes **2** and **7** were further recorded in the solid state and in solution, as shown in the insets of Figure 3 and Table 1. The little differences of lifetimes for both of them demonstrate that the fully surrounded Yb^{III} structures are stable both in the solid state and in solution. This means that no solvent molecules and counterions could be bound to the central Yb^{III} ion in these two cases. To quantify the intramolecular ligand-to-lanthanide energy transfer as well as the quenching processes that take place in Yb^{III} complexes **2** or **7**, luminescence quantum yields upon macrocyclic ligand sensitizers (H_4L_a and H_4L_b) were measured in methanol or ethanol, respectively (Table 2). By using one reported Yb^{III} complex of tropolone as the standard,[11b] the fluorescence

Table 1. Crystal Data and Structural Refinements for Compounds 1·2CH$_3$OH, 2·2CH$_3$OH, 3, 4·CH$_3$CN, 5, and 6

	1·2CH$_3$OH	2·2CH$_3$OH	3	4·CH$_3$CN	5	6
empirical formula	$C_{62}H_{56}Cl_4N_7O_{11}Er$	$C_{62}H_{56}Cl_4N_7O_{11}Yb$	$C_{60}H_{48}Cl_4N_7O_7Er$	$C_{62}H_{51}Cl_4N_8O_7Ho$	$C_{62}H_{56}Cl_4N_8O_{14}Zn_2$	$C_{64}H_{60}Cl_4N_8O_{12}Zn_2$
fw	1384.20	1389.98	1288.11	1326.84	1409.73	1405.74
temp (K)	291(2)	291(2)	291(2)	291(2)	291(2)	291(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst size (mm)	0.15 × 0.12 × 0.10	0.16 × 0.13 × 0.08	0.16 × 0.12 × 0.11	0.18 × 0.14 × 0.14	0.19 × 0.15 × 0.12	0.16 × 0.13 × 0.12
cryst system	orthorhombic	orthorhombic	monoclinic	monoclinic	triclinic	orthorhombic
space group	*Aba*2	*Aba*2	$P2_1/c$	$P2_1/c$	$P\bar{1}$	*Pbcn*
a (Å)	18.705(3)	18.705(3)	18.881(3)	19.030(4)	13.254(5)	20.580(2)
b (Å)	14.048(2)	14.048(2)	21.899(4)	21.908(5)	14.856(6)	21.589(2)
c (Å)	23.527(4)	23.527(4)	13.895(2)	13.942(3)	16.855(7)	13.637(1)
α (deg)	90	90	90	90	67.948(7)	90
β (deg)	90	90	104.524(3)	104.955(4)	78.837(7)	90
γ (deg)	90	90	90	90	76.295(6)	90
V (Å^3)	6182.3(18)	6182.3(18)	5561.7(16)	5616(2)	2968(2)	6058.7(10)
Z/D_{calcd} (g/cm^3)	4/1.487	4/1.493	4/1.538	4/1.569	2/1.577	4/1.541
$F(000)$	2804	2812	2596	2680	1448	2896
μ (mm^{-1})	1.595	1.751	1.762	1.662	1.064	1.040
h_{min}/h_{max}	−21/24	−24/24	−10/22	−22/22	−15/15	−24/23
k_{min}/k_{max}	−18/12	−13/18	−26/25	−26/23	−17/17	−25/25
l_{min}/l_{max}	−30/30	−30/30	−15/16	−16/16	−18/20	−14/16
data/params	7134/386	6948/387	9719/712	9889/740	10357/833	5339/407
R_1, wR_2 [$I > 2\sigma(I)$]^a	R_1 = 0.0407	R_1 = 0.0338	R_1 = 0.0568	R_1 = 0.0346	R_1 = 0.0657	R_1 = 0.0406
	wR_2 = 0.0754	wR_2 = 0.0923	wR_2 = 0.1448	wR_2 = 0.0852	wR_2 = 0.1152	wR_2 = 0.1118
R_1, wR_2 (all data)^a	R_1 = 0.0845	R_1 = 0.0439	R_1 = 0.0976	R_1 = 0.0516	R_1 = 0.1549	R_1 = 0.0526
	wR_2 = 0.0886	wR_2 = 0.1115	wR_2 = 0.1591	wR_2 = 0.0911	wR_2 = 0.1347	wR_2 = 0.1183
Flack parameter	−0.021(12)	0.018(13)				
S	0.96	1.13	1.02	1.03	1.00	1.05
max/min $\Delta\rho$ (e Å^{-3})	0.98/−0.76	1.48/−1.33	1.74/−1.05	1.32/−0.71	1.12/−0.76	0.60/−0.58

$^a R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Fluorescence Quantum Yields (Φ) and Lifetimes (τ) for Yb^{III} Complexes 2 and 7, Together with Their Relative Sodium Phenolate in the Solid State and Solution^a

	solid	C$_2$H$_5$OH		CH$_3$OH	
	τ (μs)	Φ (%)^b	τ (μs)	Φ (%)^b	τ (μs)
2	9.6 ± 0.1	1.07 ± 0.03	9.8 ± 0.2	0.74 ± 0.05	10.0 ± 0.2
7	9.1 ± 0.1	1.22 ± 0.06	10.2 ± 0.1	0.97 ± 0.07	10.1 ± 0.2
2 + NaOH^c		1.03 ± 0.04	10.6 ± 0.2	0.85 ± 0.04	10.4 ± 0.1
7 + NaOH^c		1.18 ± 0.10	9.7 ± 0.2	1.12 ± 0.06	9.0 ± 0.1

$^a \lambda_{ex}$ = 379 nm was used for quantum yield determinations. ^{b}Quantum yields were measured using a Yb^{III} complex of tropolone as the standard. ^{c}The pH of the solution was controlled about 8−9 ([M] = 2 μM).

quantum yields of **2** and **7** were determined to be 1.07 ± 0.03% and 1.22 ± 0.06% at λ_{ex} = 379 nm in C$_2$H$_5$OH, while they are 0.74 ± 0.05% and 0.97 ± 0.07% in CH$_3$OH, respectively. In comparison with previously reported Yb^{III} NIR sensitizers,[10a,18] our macrocyclic Yb^{III} complexes **2** and **7** are suggested to display relatively high fluorescence quantum yields even in the protonic solvents.

The obvious differences measured in ethanol and methanol suggest a stronger nonradiative deactivation process in the latter, where the Yb^{III} ion might be better protected by the Schiff-base macrocyclic ligands. Considering the deactivation of the high-energy vibrations, we tried to exclude the O−H oscillators of phenolic hydroxyl by adding NaOH. Corresponding measurements for two Yb^{III} complexes on their fluorescence emission, quantum yields, and lifetimes reveal that the characteristic emission bands for two sodium phenolates are still at 974 nm in ethanol and methanol (Figures S10 and S11, Supporting Information). However, their molar absorption coeffcients are increased by contrast, as can be seen in Figures S13 and S14, Supporting Information. It is noted that the quantum yields of sodium phenolates are almost the same as their relative Yb^{III} complexes in ethanol, while they increase ~15% in methanol (Table 2). Our results manifest the intramolecular energy transfer of macrocyclic Yb^{III} complexes **2** and **7** could be influenced by the solvent and deprotonation process, where the Yb^{III} ion could be more efficiently protected by the macrocyclic ligands in ethanol with stronger intramolecular ligand-to-ytterbium energy transfer.

■ CONCLUSION

In summary, we demonstrated that identical [2 + 2] pendant-armed Schiff-base macrocyclic ligands (H$_4$L$_a$ and H$_4$L$_b$) can be constructed via either Ln^{III} or Zn^{II} template with remarkable distinction on the ion radii and charge, and corresponding mononuclear Ln^{III} complexes (**1**−**4** and **7**) and dinuclear Zn^{II} complexes (**5** and **6**) are obtained. The use of the flexible and

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large-sized macrocyclic ligands, which contain rigid *o*-phenylenediamine and extended dialdehyde components, makes possible the formation of unique eight-coordinate sandwich-like mononuclear Ln^{III} macrocyclic complexes. Furthermore, the above-mentioned macrocyclic ligands can serve as effective sensitizers for the Yb^{III} ion (**2** and **7**), exhibiting near-infrared emission with high quantum yields. It is concluded that the formation of the unique sandwich-like macrocyclic complexes simultaneously guarantees the effective match of the energy levels of Yb^{III} centers and shield from the solvent molecules and counterions.

■ EXPERIMENTAL SECTION

Materials and Methods. Unless otherwise specified, solvents of analytical grade were purchased directly from commercial sources and used without any further purification. Dialdehydes H_2hpdd and H_2pdd were synthesized following our previously reported procedure.[16]

^{1}H NMR spectroscopic measurements were performed on a Bruker AM 500 NMR spectrometer using TMS ($SiMe_4$) as an internal reference at room temperature. Elemental analyses were measured with a PerkinElmer 1400C analyzer. Infrared spectra (4000−400 cm^{-1}) were collected on a Nicolet FT-IR 170X spectrophotometer at 25 °C using KBr plates. UV−vis spectra were recorded with a Shimadzu UV-3150 double-beam spectrophotometer using a quartz glass cell with a path length of 10 mm. Near-infrared emission fluorescence and phosphorescence properties were determined on a Edinberge FLS920 fluorometer. Electrospray ionization mass spectra (ESI-MS) were recorded on a ThermoFisher Scientific LCQ Fleet mass spectrometer within the range 100−2000 amu.

Synthesis of 1. $Er(NO_3)_3·6H_2O$ (0.045 g, 0.10 mmol) was dissolved in methanol (10 mL) and added to a solution of H_2hpdd (0.047 g, 0.10 mmol) in methanol (20 mL). The mixture was refluxed for 10 min, and then a methanol (10 mL) solution of *o*-phenylenediamine (0.012 g, 0.11 mmol) was added. The orange yellow solution was refluxed for an additional 2 h, cooled to room temperature, and filtered. The filtrate was concentrated to give complex **1** in a yield of 86% (0.057 g). Anal. Calcd for $C_{62}H_{56}Cl_4N_7O_{11}Er$: C, 53.80; H, 4.08; N, 7.08. Found: C, 53.71; H, 4.02; N, 7.01. ESI-MS (positive mode, *m*/*z*): 1258.30, {[Er(HL$_a$)] + H}$^+$ (100%). Main FT-IR absorptions (KBr pellets, cm^{-1}): 3433, 1614 (s, CH═N), 1543, 1441, 1381, 753. Orange yellow single crystals of complex **1**·$2CH_3OH$ were grown from a mixture of methanol/acetonitrile (v/v = 4:1) by slow evaporation in air at room temperature for 2 weeks.

Synthesis of 2. The synthetic process of **2** is the same as that of **1** except that $Yb(NO_3)_3·5H_2O$ (0.045 g, 0.10 mmol) was used. Yield: 82% (0.054 g). Anal. Calcd for $C_{62}H_{56}Cl_4N_7O_{11}Yb$: C, 53.57; H, 4.06; N, 7.05. Found: C, 53.50; H, 4.01; N, 7.00. ESI-MS (positive mode, *m*/*z*): 1264.30, {[Yb(HL$_a$)] + H}$^+$ (100%). Main FT-IR absorptions (KBr pellets, cm^{-1}): 3420, 1614 (s, CH═N), 1543, 1448, 1375, 1250, 1196, 753. Orange yellow crystals of solvent complex **2**·$2CH_3OH$ were obtained by slow evaporation of a mixture of methanol/acetonitrile solution (v/v = 3:1) for 2 weeks.

Synthesis of 3. The synthetic process of **3** is the same as that of **1** except that H_2pdd (0.046 g, 0.10 mmol) was used. Yield: 85% (0.055 g). Anal. Calcd for $C_{60}H_{48}Cl_4N_7O_7Er$: C, 55.94; H, 3.76; N, 7.61. Found: C, 55.89; H, 3.71; N, 7.55. ESI-MS (positive mode, *m*/*z*): 1226.60, {[Er(HL$_b$)] + H}$^+$ (100%). Main FT-IR absorptions (KBr pellets, cm^{-1}): 3429, 3027, 1612 (s, CH═N), 1542, 1446, 1382, 1321, 1197, 869, 750. Orange yellow crystals of complex **3** were obtained by slow evaporation of a mixture of methanol/acetonitrile solution (v/v = 4:1) for 2 weeks.

Synthesis of 4. The synthetic process of **4** is the same as that of **3** except that $Ho(NO_3)_3·5H_2O$ (0.045 g, 0.10 mmol) was used. Yield: 89% (0.057 g). Anal. Calcd for $C_{62}H_{51}Cl_4N_8O_7Ho$: C, 56.12; H, 3.87; N, 8.44. Found: C, 56.03; H, 3.80; N, 8.37. ESI-MS (positive mode, *m*/*z*): 1223.60, {[Ho(HL$_a$)] + H}$^+$ (100%). Main FT-IR absorptions (KBr pellets, cm^{-1}): 3431, 3028, 1611 (s, CH═N), 1546, 1445, 1379, 1322, 1195, 872, 750. Orange yellow crystals of solvent complex **4**·CH_3CN were obtained by slow evaporation of a mixture of methanol/acetonitrile solution (v/v = 4:1) for 2 weeks.

Synthesis of 5. $Zn(NO_3)_2·6H_2O$ (0.032 g, 0.11 mmol) was dissolved in ethanol (10 mL) and added to a solution of H_2hpdd (0.047 g, 0.10 mmol) in ethanol (20 mL). The mixture was refluxed for 10 min, and then an ethanol (10 mL) solution of *o*-phenylenediamine (0.012 g, 0.11 mmol) was added. The orange yellow solution was refluxed for an additional 2 h, cooled to room temperature, and filtered. The filtrate was concentrated to give complex **5** in a yield of 90% (0.063 g). ^{1}H NMR (500 MHz, CD_3OD) δ: 8.50 (s, 4H), 7.62 (s, 4H), 7.50 (dd, *J* = 7.1, 3.7 Hz, 4H), 7.32 (s, 4H), 7.01 (s, 8H), 6.71 (s, 4H). Anal. Calcd for $C_{62}H_{56}Cl_4N_8O_{14}Zn_2$: C, 52.82; H, 4.00; N, 7.95. Found: C, 52.75; H, 3.93; N, 7.90. ESI-MS (positive mode, *m*/*z*): 1381.52, {[Zn$_2$(L$_a$)] + 5CH_3OH + H}$^+$; 1419.08, {[Zn$_2$(L$_a$)] + 2H_2O + 5CH_3OH + H}$^+$ (100%); 1430.92, {[Zn$_2$(L$_a$)] + 6CH_3OH + H_2O}$^+$; 1454.92, {[Zn$_2$(L$_a$)] + 4H_2O + 5CH_3OH + H}$^+$. Main FT-IR absorptions (KBr pellets, cm^{-1}): 3420, 1614 (s, CH═N), 1537, 1441, 1381, 1321, 1196, 1046, 748. Orange yellow single crystals of complex **5** were grown from a mixture of ethanol/acetonitrile (v/v = 2:1) by slow evaporation in air at room temperature for 3 weeks.

Synthesis of 6. The synthetic process of **6** is the same as that of **5** except that H_2pdd (0.046 g, 0.10 mmol) was used. Yield: 93% (0.065 g). ^{1}H NMR (500 MHz, CD_3OD) δ: 8.49 (s, 4H), 7.61 (s, 4H), 7.51 (dd, *J* = 6.3, 3.3 Hz, 4H), 7.31 (s, 10H), 7.21 (d, *J* = 6.4 Hz, 4H), 6.99 (s, 4H), 3.36 (s, 8H). Anal. Calcd for $C_{64}H_{60}Cl_4N_8O_{12}Zn_2$: C, 54.68; H, 4.30; N, 7.97. Found: C, 54.60; H, 4.21; N, 7.92. ESI-MS (positive mode, *m*/*z*): 1221.42 {[Zn$_2$(L$_a$)]+2H_2O}$^+$ (100%). Main FT-IR absorptions (KBr pellets, cm^{-1}): 3433, 1614 (s, CH═N), 1537, 1441, 1381, 1310, 1196, 1046, 748. Orange yellow crystals of solvent complex **6** were obtained by slow evaporation of a mixture of ethanol/acetonitrile solution (v/v = 2:1) for 3 weeks.

Synthesis of 7. The synthetic process of **7** is the same as that of **2** except that H_2pdd (0.046 g, 0.10 mmol) was used. Yield: 85%, (0.055 g). Anal. Calcd for $C_{60}H_{48}Cl_4N_7O_7Yb$: C, 55.69; H, 3.74; N, 7.58. Found: C, 55.61; H, 3.70; N, 7.52. ESI-MS (positive mode, *m*/*z*): 1232.50, {[Yb(HL$_a$)]+H}$^+$ (100%). Main FT-IR absorptions (KBr pellets, cm^{-1}): 3396, 3061, 1613 (s, CH═N), 1545, 1455, 1304, 1032, 750.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables of selected bond distances and angles, hydrogen-bonding parameters, UV−vis, FT-IR, ESI-MS, ^{1}H NMR, fluorescence spectra, perspective view of the packing structures for related complexes, and X-ray crystallographic data in CIF format (CCDC nos. 1044864−1044869). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00283.

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Notes

The authors declare no competing financial interest.

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