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Synthesis, Characterization, and Photophysical Properties of First Heterobinuclear Zn-Ln (Ln = La, Nd, Eu, Gd, Tb, Er, and Yb) Complexes Based on Asymmetric Schiff-Base Ligand

Dr. Shunsheng Zhao $^{\rm a}$, Xiangrong Liu $^{\rm b}$, Xingqiang Lü $^{\rm c}$ & Wai-kwok Wong $^{\rm c}$

^a College of Chemistry and Chemical Engineering, Xi'an University of Science and Technology, Xi'an, P. R. ChinaMinistry of Education Key Laboratory of Synthetic and Natural Functional Molecular Chemistry, Northwest University, Xiapos;an, P. R. China

^b College of Chemistry and Chemical Engineering, Xi'an University of Science and Technology, Xi'an, P. R. China

^c Department of Chemistry and Centre for Advanced Luminescent Materials, Hong Kong Baptist University, Waterloo Road, Kowloon Tong, Hong Kong, P. R. China Accepted author version posted online: 10 Jul 2012. Version of record first published: 23 Jan 2013.

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Synthesis, Characterization, and Photophysical Properties of First Heterobinuclear Zn-Ln (Ln = La, Nd, Eu, Gd, Tb, Er, and Yb) Complexes Based on Asymmetric Schiff-Base Ligand

Shunsheng Zhao¹, Xiangrong Liu², Xingqiang Lü³, and Wai-kwok Wong³

¹College of Chemistry and Chemical Engineering, Xi'an University of Science and Technology, Xi'an, P. R. China; and Ministry of Education Key Laboratory of Synthetic and Natural Functional Molecular Chemistry, Northwest University, Xi'an, P. R. China ²College of Chemistry and Chemical Engineering, Xi'an University of Science and Technology, Xi'an, P. R. China ³Department of Chemistry and Centre for Advanced Luminescent Materials, Hong Kong Baptist University, Waterloo Road, Kowloon Tong, Hong Kong, P. R. China

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Address correspondence to Dr. Shunsheng Zhao, College of Chemistry and Chemical Engineering, Xi'an University of Science and Technology, NO. 58 of Yanta Road, Xi'an 7100054, P. R. China. E-mail: shshzhao@xust.edu.cn **ABSTRACT** With a novel asymmetric Schiff-base zinc complex **ZnL**(H_2L = N-(3-methoxysalicylidene)-N'-(5-(4-cyanophenyl)-3-methoxysalicylidene) phenylene-1, 2-diamine), obtained from phenylene-1, 2-diamine, 3-methoxysalicylaldehyde, and 5-(4-cyanophenyl)-3-methoxysalicylaldehyde, as the precursor, a series of heterobinuclear Zn-Ln complexes [**ZnLnL**(NO₃)₃ (**CH**₃**CN**)] (Ln = La, 1; Ln = Nd, 2; Ln = Eu, 3; Ln = Gd, 4; Ln = Tb, 5; Ln = Er, 6; Ln = Yb, 7) were obtained by further reaction with Ln(NO₃)₃ · 6H₂O. Photophysical studies of these complexes show that the strong and characteristic NIR luminescence with emissive lifetimes in the microsecond range has been sensitized from the excited state of the asymmetric Schiff-base ligand due to effective intramolecular energy transfer.

KEYWORDS asymmetric Schiff base, near-infrared, sensitization and energy transfer

INTRODUCTION

The design and synthesis of luminescent lanthanide (Ln) complexes with long-lived and characteristic line-like emission bands (near UV to visible and NIR regions)^[1] has attracted much recent interest, due to their potential applications in bioassays, medicine, and materials science.^[2–4] For lanthanide ions, because the f–f transitions are parity forbidden, the absorption coefficients are normally very low, and the emissive rates are low, one way to overcome this drawback is by using organic ligand, with strong absorbing chromophores, to transfer energy to lanthanide (antenna effect).^[5] Thus, investigations in recent decades have focused on organic dyes^[6] and d-block metal complexes^[7] (i.e., Cr(III), Ru(II), Pt(II), Re(I), or Os(II)), which absorb light in the near-UV or visible ranges and have been demonstrated to effectively transfer energy to the lanthanide ions indirectly.



SCHEME 1 Controlled synthesis route of Zn-Ln heterobimetallic Schiff-base complexes. (color figure available online.)

Our past research^[8–12] has focused on the use of compartmental salen-type Schiff-base ligands to bind both 3d Zn(II) and 4f Nd(III), Er(III), or Yb(III) ions. These Schiff-base zinc complexes, as suitable chromophores, can act as antennae or sensitizers for NIR of visible lanthanide luminescence, and the π -conjugation of those salen-type Schiff-base ligands helps to enhance luminescent properties. Due to the energy transfer between antennae or sensitizers and lanthanides mostly through the triplet excited state of antennae to lanthanide ions, introduction of different substituents with different electronic properties (electron donor/electron acceptor) on the flanking phenyl rings of the Schiff-base ligands, which could increase the efficiency of intersystem crossing to improve the quantum yield of the triplet excited state of antennae, may consequently improve the NIR/ visible luminescent quantum efficiency of lanthanides. Cyan group, a strongly electron-withdrawing group, could potentially play an important role in changing the electronic properties of Schiff-base ligands and thus has been utilized in our study.

To the best of our knowledge, there was no literature available on the synthesis and luminescent properties of Zn-Ln heterobinuclear complexes based on asymmetric Schiff-base ligands, not even zinc complex of asymmetric Schiff-base **ZnL** (H₂L

= N-(3-methoxysalicylidene)-N'-(5-(4-cyanophenyl)-3-methoxysalicylidene) phenylene-1, 2-diamine). For the improvement of lanthanide ions' luminescence, we have therefore investigated the design, synthesis, and use of an asymmetric Schiff-base ligand to construct the Zn-Ln heterobinuclear complexes. Herein, a novel zinc complex of asymmetric Schiff-base **ZnL** ($H_2L = N$ -(3-methoxysalicylidene)-N'-(5-(4-cyanophenyl)-3-methoxysalicylidene) phenylene-1, 2-diamine), which has not been reported before, has been prepared under control of reaction time and ratio of starting reagents. With the **ZnL** as the precursor, a series of heterobinuclear Zn-Ln complexes $[ZnLnL(NO_3)_3(CH_3CN)]$ (Ln = La, 1; Nd, 2; Eu, 3; Gd, 4; Tb, 5; Er, 6; Yb, 7) are obtained respectively, as shown in Scheme 1. The photophysical properties of these complexes are reported, and the effective sensitization for the NIR luminescence of the Ln^{3+} ions is also discussed.

EXPERIMENTAL

Reagents and General Techniques

All chemicals for preparation were reagent grade purchased commercially and were used without further purification unless otherwise stated. Acetonitrile for photophysical measurement was dried with calcium hydride, distilled, and degassed by N₂ before use. 5-(4-Cyanophenyl)-3-methoxysalicylaldehyde was prepared from Suzuki coupling reaction of 4-cyanophenylboronic acid and 5bromo-3-methoxysalicylaldehyde under catalysis of Pd(PPh₃)₄. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. Infrared spectra were recorded on a Nicolet Nagna-IR 550 spectrophotometer in the region $4000-400 \,\mathrm{cm}^{-1}$ using KBr pellets. ¹H-NMR spectra were recorded on a JEOL EX-400 spectrometer with SiMe₄ as internal standard in CDCl₃ at room temperature. Electronic absorption spectra in the UV/Vis region were recorded with a Cary 300 UV spectrophotometer, steady-state visible fluorescence and PL excitation spectra on a Photon Technology International (PTI) Alphascan spectrofluorometer, and visible decay spectra on a pico-N₂ laser system (PTI Time Master). The quantum yield of the visible luminescence for each sample was determined by the relative comparison procedure, using a reference of a known quantum yield (quinine sulfate in 0.1 N H₂SO₄ solution, $\Phi_{\rm em} = 0.546$). NIR emission and excitation in solution were recorded by a PTI QM4 spectrofluorometer with a PTI QM4 Near-Infrared InGaAs detector.

Synthesis of HL^a and HL^b

N-(3-methoxysalicylidene)-phenylene-1, 2diamine HL^a. An ethanolic solution of 2-hydroxy-3methoxybenzaldehyde (1.52 g, 10 mmol) was added dropwise to a solution of phenylene-1,2-diamine (1.08 g, 10 mmol) in ethanol (100 mL) under room temperature. The mixture was heated to reflux and kept refluxing for another 4 hr under protection of nitrogen, then cooled down to room temperature and kept on standby for 1 week. An orange-red crystal was obtained and collected by filtration, washed with absolute ethanol, and dried under vacuum, yield 1.81 g (74.8%). ¹H-NMR: (400 MHz, CDCl₃) δ /ppm 13.54 (1H, -OH), 8.63 (1H, N=CH), 7.13-6.99 (4H, -Ph), 6.90 (1H, Ph), 6.80 (2H, -Ph), 4.02 (2H, -NH₂), 3.94 (3H, -OCH₃), MS (FAB, M⁺). Found: 243.2. Calculated for $C_{14}H_{14}N_2O_2$: 243.1.

N-(5-(4-cyanophenyl)-3-methoxysalicylidene)phenylene-1, 2-diamine HL^b. An ethanolic solution of 5-(4-cyanophenyl)-2-hydroxy-3methoxybenzaldehyde (1.26 g, 5 mmol) was added dropwise to a solution of o-phenylenediamine (0.54 g, 5 mmol) in ethanol (100 mL) under room temperature. The mixture was heated to reflux and kept for 4 hr under protection of nitrogen, then cooled down to room temperature and kept on standby for 1 week. Product was obtained and collected by filtration also as an orange-red crystal, washed with absolute ethanol, and dried under vacuum. Yield 1.12 g (68.3%). ¹H-NMR (400 MHz, CDCl₃): δ /ppm 13.85 (1H, -OH), 8.72 (1H, -CH=N), 7.74 (2H, -Ph), 7.68 (2H, Ph), 7.29 (1H, -Ph), 7.19 (1H, Ph), 7.16–7.09 (2H, Ph), 6.84–6.80 (2H, Ph), 4.13 (2H, -NH₂), 4.03 (3H, -OCH₃). MS (FAB,M⁺). Found: 344.3. Calculated for C₂₁H₁₇N₃O₂: 343.38.

Synthesis of ZnL

The asymmetric Schiff-base zinc complexes (**ZnL**) could be synthesized through two different procedures (Sch. 1).

Method A: HL^a (486 mg, 2.0 mmol) was added partially to a methanolic solution of Zn(OAc)₂·2H₂O (440 mg, 2.0 mmol) under room temperature. The clear solution obtained was stirred for 30 min. A solution of 5-(cyanophenyl)-3-methoxysalicylaldehyde (460 mg, 2.0 mmol) in methanol was added dropwise and the mixture was stirred for a further 24 hr under room temperature. The precipitate was collected by filtration; washed with methanol and diethyl ether, sequentially; and dried under vacuum. Yield 923 mg (85.5%). ¹H-NMR (400 MHz, DMSO-d₆): δ / ppm 9.17 (1H, -CH=N), 9.02 (s, 1H, -CH=N), 7.91-7.85 (m, 6H, -Ph), 7.62 (d, 1H, -Ph), 7.40 (t, 2H, -Ph), 7.28 (s, 1H, -Ph), 7.03 (d, 1H, -Ph), 6.87 (d, 1H, -Ph), 6.45 (t, 1H, -Ph), 3.88 (s, 3H, -OCH₃), 3.76 (3H, -OCH₃), MS (FAB, +ve). Found: 540.9. Calculated for $C_{29}H_{21}N_3O_4Zn$: 540.90.

Method B: **HL^b** (344 mg, 1.0 mmol) was added partially to a methanolic solution of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (244 mg, 1.2 mmol) under room temperature. The clear solution obtained was stirred for 30 min. A solution of 3-methoxysalicylaldehyde (231 mg, 1.0 mmol) in methanol was added dropwise and the mixture was stirred for a further 24 hr under room temperature. The precipitate was collected by filtration; washed with methanol and diethyl ether, sequentially; and dried under vacuum. Yield 462 mg (85.5%). ¹H-NMR and mass spectra are identical with that of the product from method A.

Synthesis of [ZnLnL(NO₃)₃(CH₃CN)] (Ln = La, 1; Nd, 2; Eu, 3; Gd, 4; Tb, 5; Er, 6; Yb, 7)

General procedure: Asymmetric Schiff-base zinc complex **ZnL** (54.1 mg, 0.1 mmol) was suspended in CH_3CN (20 mL) and heated to reflux. Lanthanide nitrate (45 mg, 0.1 mmol) was added and the suspension became clear and was kept reflux for 30 min. The clear solution was cooled down to room temperature and filtrated. The filtrate was allowed to evaporate the solvent slowly to give the target complex. The product was collected by filtration, washed with CH_3CN , and dried under vacuum.

[ZnLaL(NO₃)₃(CH₃CN)] 1: ZnL and La(NO₃)₃ · $6H_2O$ were used, yield 63.1%. Element analysis: calculated for $C_{29}H_{21}LaN_6O_{13}Zn$: C 40.23, H 2.44, N 9.71; found: C 41.06, H 2.67, N 10.81; MS (FAB, +ve). Found: 801.9. Calculated for [M-(CH₃CN)-(NO₃)]⁺: 801.96. FT-IR (KBr, cm⁻¹): 2223, 1613, 1584, 1551, 1462, 1384, 1303, 1266, 1230, 1190, 1094, 1075, 1031, 965, 834, 811, 762, 741, 695, 659, 633, 577, 551, 508, 440.

[ZnNdL(NO₃)₃(CH₃CN)] 2: ZnL and Nd(NO₃)₃. 6H₂O were used, yield 48.9%. Element analysis: calculated for C₂₉H₂₁N₆NdO₁₃Zn: C 39.98, H 2.43, N 9.65; found: C 40.82, H 2.65, N 10.75; MS (FAB, +ve). Found: 809.1. Calculated for [M-CH₃₋ CN-(NO₃)]⁺: 809.15. FT-IR (KBr, cm⁻¹): 2240, 1613, 1584, 1552, 1463.2, 1384.4, 1303.4, 1270.7, 1234, 1193, 1097, 1077, 1033, 967, 835.8, 815, 758, 744, 694, 661, 635, 584, 558, 517, 443.

[ZnEuL(NO₃)₃(CH₃CN)] 3: ZnL and Eu(NO₃)₃. 6H₂O were used, yield 55.81%. Element analysis: calculated for $C_{29}H_{21}EuN_6O_{13}Zn$: C 39.63, H 2.41, N 9.56; found: C 40.48, H 2.63, N 10.66; MS(FAB, +ve). Found: 816.8. Calculated for [M-(CH₃CN)-(NO₃)]⁺: 816.88. FT-IR (KBr, cm⁻¹): 2223, 1612, 1584, 1551, 1462, 1384, 1303, 1266, 1230, 1190, 1094, 1075, 1031, 965, 834, 811, 762, 741, 695, 659, 633, 577, 551, 508, 440.

[ZnGdL(NO₃)₃(CH₃CN)] 4: ZnL and Gd(NO₃)₃. 6H₂O were used, yield 56.4%. Element analysis: calculated for C₂₉H₂₁GdN₆O₁₃Zn: C 39.40, H 2.39; N 9.51; found: C 40.24, H 2.61, N 10.60; MS (FAB, +ve). Found: 822.1. Calculated for [M-(CH₃-CN)-(NO₃)]⁺: 822.16. FT-IR (KBr, cm⁻¹): 2225, 1618, 1589, 1550, 1467, 1384, 1328, 1273, 1235, 1194, 1098, 1075, 1041, 965, 834, 766, 783, 743, 694, 633, 552, 509, 439. **[ZnTbL(NO₃)₃(CH₃CN)] 5:** ZnL and Tb(NO₃)₃. 6H₂O were used, yield 65.2%. Element analysis: calculated for C₂₉H₂₁N₆O₁₃TbZn: C 39.32, H 2.39, N 9.49; found: C 40.17, H 2.61, N 10.58; MS (FAB, +ve). Found: 823.4. Calculated for [M-(CH₃₋ CN)-(NO₃)]⁺: 823.84. FT-IR (KBr, cm⁻¹): 2221, 1617, 1584, 1549, 1465, 1384, 1328, 1271, 1230, 1193, 1099, 1076, 1041, 960, 833, 760, 783, 743, 696, 630, 551, 507, 435.

[ZnErL(NO₃)₃(CH₃CN)] 6: ZnL and $Er(NO_3)_3$. 6H₂O were used, yield 65.2%. Element analysis: calculated for C₂₉H₂₁ErN₆O₁₃Zn: C 38.95, H 2.37, N 9.40; found: C, 39.81; H 2.59, N 10.48; MS (FAB, +ve). Found: 832.1. Calculated for [M-(CH₃₋ CN)-(NO₃)]⁺: 832.17. FT-IR (KBr, cm⁻¹): 2223, 1616, 1585, 1549, 1466, 1384, 1328, 1272, 1232, 1193, 1099, 1076, 1041, 966, 833, 762, 785, 743, 693, 633, 552, 507, 437.

[ZnYbL(NO₃)₃(CH₃CN)] 7: ZnL and Yb(NO₃)₃. 6H₂O were used, yield 65.5%, Element analysis: calculated for C₂₉H₂₁N₆O₁₃YbZn: C 38.70, H 2.35, N 9.34; found: C 39.57, H 2.57, N 10.42; MS (FAB, +ve). Found: 836.7. Calculated for [M-(CH₃₋ CN)-(NO₃)]⁺: 837.00. FT-IR (KBr, cm⁻¹): 2220, 1613, 1584, 1552, 1465, 1384, 1303, 1274, 1233, 1191, 1092, 1071, 1026, 964, 837, 812, 757, 747, 694, 662, 638, 587, 554, 507, 448.

RESULTS AND DISCUSSION

Synthesis and Spectra Analysis

As shown in Scheme 1, reaction of 2-hydroxy-3methoxybenzaldehyde and phenylene-1, 2-diamine, in the molar ratio of 1:1 in ethanol under reflux for 4 hr, after several days' standby and being cooled down to room temperature, affords an orange needle-like crystal. The ¹H-NMR spectrum shows signals corresponding to phenyl groups (δ 6.78–7.13, 7H), phenolic hydroxyl group (δ 13.54, 1H), methoxyl group (δ 3.91, 3H), methylene (δ 8.63, 1H), and nonreacted amino group (δ 4.02, 2H). The FAB-MS spectrum exhibits one peak at m/z 243.2, which corresponds to its molecular ion of the compound **HL**^a. Selected NMR and mass spectra data are listed in Table 1.

By reaction of 5-(4-cyanophenyl)-3methoxysalicyaldehyde and phenylene-1,2-diamine, with the similar procedure used above,

TABLE 1 Selected NMR, Mass, and FT-IR Spectra of HL^a, HL^b, and ZnL

	¹ H-NMF	R (ppm)		
Compound	C <i>H</i> =N	OCH ₃	MS (FAB, m/z)	FT-IR (KBr), cm ⁻¹
HL ^a	8.63	3.94	243.2	1616 C=N
HL ^b	8.72	4.03	344.3	1617 C=N
ZnL	9.17,	3.88,	540	1627 C=N
	9.02	3.76	$[M+H]^+$	

N-(5-(4-cyanophenyl)-3-methoxysalicylidene)-phenylene-1, 2-diamine (HL^b) could be obtained and has been characterized by ¹H-NMR and mass spectra. The ¹H-NMR spectrum of **HL^b** shows signals corresponding to phenyl groups (δ 6.80–7.74, 10H), phenolic hydroxyl group (δ 13.85, 1H), methoxyl group $(\delta 4.03, 3H)$, methylene $(\delta 8.72, 1H)$, and nonreacted amino group (δ 4.13, 2H). The FAB-MS spectrum exhibits one peak at m/z 344.3, which corresponds to its molecular ion of the compound **HL^b**. Selected NMR and mass spectra data are also listed in Table 1.

 HL^{a} and HL^{b} have good solubility in $CH_{2}Cl_{2}$ and CHCl₃ but slightly dissolve in methanol or ethanol. However, HL^a dissolves immediately when added to a methanolic solution containing equivalent $Zn(OAc)_2$, indicating that the reaction between HL^a and Zn(OAc)₂ takes place and forms a reaction intermediate. The condensation between the amino group and aldehyde group occurred upon the addition of 5-bromo-2-hydroxy-3-methoxybenzaldehyde into the intermediate, which gave the asymmetric Schiff-base zinc complex (ZnL). The zinc complex has poor solubility in dichloromethane, chloroform, methanol, or ethanol and, contrarily, good solubility in DMSO. The ¹H-NMR spectrum of ZnL in DMSO-d₆ suggests the asymmetric Schiff-base structure. Compared to the NMR spectrum of HL^a (Table 1), signals with the chemical shift at 13.85 (phenolic hydroxy) and 4.13 (amino) disappeared, and the integral of the peak area suggests two different protons from the CH=N group and 13 protons from the phenyl group. The FAB-MS spectrum of **ZnL** shows only its molecular ion at m/z 519, which also proves the asymmetric Schiff-base zinc complex structure. ZnL could also be prepared according to the route of method B, which allowed **HL^b** to react with Zn(OAc)₂ first, followed by the addition of 2-hydroxy-3-methoxybenzaldehyde.

Complexes

Addition of corresponding lanthanide nitrate to a refluxing suspension of ZnL in fresh distilled dry acetonitrile gives a clear solution, which gives the corresponding heterobimetalic Zn-Ln Schiff-base complexes after being cooled down to room temperature and kept on standby for several days. FT-IR (Table 2) spectra of these bimetallic complexes 1-7, in which the characteristic absorptions of the ν (C=N) vibration are at 1612–1618 cm⁻¹, similar to that for the precursor **ZnL**, are slightly red-shifted by $9-15 \text{ cm}^{-1}$ relative to those of **ZnL** (1627 cm⁻¹) upon coordination of the lanthanide metal ions. Characteristic absorptions of the ν (N-O) vibration at 1462– 1467 cm^{-1} and 1384 cm^{-1} should be attributed to the coordinated nitrate anion. Characteristic absorptions of the ν (-C=N) vibration at 2220–2245 cm⁻¹ could be found in these complexes. The FAB-MS spectra of the seven complexes (1-7) exhibit one peak at m/z 801.9 (1), 809.1 (2), 816.8 (3), 822.1 (4), 823.4 (5), 832.1 (6), or 836.7 (7), corresponding to the major species $[ZnLaL(NO_3)_2]^+$ for **1**, $[ZnNdL(NO_3)_2]^+$ for **2**, $[ZnEuL(NO_3)_2]^+$ for **3**, $[ZnGdL(NO_3)_2]^+$ for **4**, $[ZnTbL(NO_3)_2]^+$ for 5, $[ZnErL(NO_3)_2]^+$ for 6, or $[ZnYbL(NO_3)_2]^+$ for 7, further indicating the discrete ZnLnL (Ln = La, Nd, Eu, Gd Tb, Er, or Yb) molecule structure of the complexes. **Photophysical Properties of the Complexes**

> The photophysical properties of the complexes 1-7 have been examined in dilute MeCN solution at

asymmetric

TABLE 2 Selected FT-IR and Mass Spectra of Heterobimetallic

	IR (cm $^{-1}$)	MS (FAB-MS m/z)
1 ZnLaL	2223 (−C≡N), 1614 (C=N),	802
	1462 (N-O), 1384 (N-O)	$[M-CH_3CN-NO_3]^+$
2 ZnNdL	2240 (−C≡N), 1614 (C=N),	809
	1463 (N-O), 1384 (N-O)	$[M-CH_3CN-NO_3]^+$
3 ZnEuL	2223 (−C≡N), 1613 (C=N),	817
	1462 (N-O), 1385 (N-O)	$[M-CH_3CN-NO_3]^+$
4 ZnGdL	2225 (−C≡N), 1617 (C=N),	822
	1466 (N-O), 1384 (N-O)	$[M-CH_3CN-NO_3]^+$
5 ZnTbL	2221 (−C≡N), 1613 (C=N),	823
	1460 (N-O), 1384 (N-O)	$[M-CH_3CN-NO_3]^+$
6 ZnErL	2223 (−C≡N), 1617 (C=N),	832
	1461 (N-O), 1384 (N-O)	$[M-CH_3CN-NO_3]^+$
7 ZnYbL	2220 (−C≡N), 1614 (C=N),	837
	1451 (N-O), 1384 (N-O)	$[M-CH_3CN-NO_3]^+$

room temperature and are summarized in Table 3 and Figs. 1-3. As shown in Figure 1, the similar ligand-centered solution absorption spectra (range 200-485 nm, peaks at about 305-310 nm) of complexes 1-7 in the UV-visible region are observed, which could be attributed to π - π transaction of the asymmetric Schiff-base ligand. For complexes 1-7, the similar residual visible emission bands (ca. 510 nm and $\tau < 1$ ns, almost undetectable) and low quantum yields ($\Phi_{em} < 10^{-5}$) in dilute absolute MeCN solution at room temperature are observed (Fig. 2). Photoexcitation of the antennae in the range of 200–485 nm ($\lambda_{ex} = 394$ nm for **2**, 388 nm for **6**, or 390 nm for 7), as shown in Fig. 3, gives rise to the characteristic emissions of the Nd³⁺ ion (${}^4F_{3/2} \rightarrow$ ${}^{4}I_{I/2}, J=9, 11, 13$), the Yb³⁺ ion (${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$), and the Er^{3+} ion (${}^{4}\text{I}_{13/2} \rightarrow {}^{4}\text{I}_{15/2}$) in the NIR region. For complex 2, the emissions at 872, 1066, and 1333 nm can be assigned to ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$, ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$, and ${}^4F_{3/2} \rightarrow$ ${}^{4}I_{13/2}$ transitions of the Nd³⁺ ion, respectively. For complexes **6** and **7**, the emissions at 1535 and 976 cm^{-1} can be attributed to the ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition of the Er³⁺ ion and the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition of the Yb³⁺ ion, respectively. The complexes 1, 3, 4, and 5 don't exhibit NIR luminescence under the same condition, but have the relatively stronger (506 nm for 1, 509 nm for 4, 510 nm for 5) or weakened (511 nm for 3) luminescence of the Schiff-base ligand in the visible region, as shown in Table 3. For **1**, it is because the La^{3+} ion has no f-electron so that there is no f-f transition in complex 1 and no NIR emission observed. For 4, it is because the Gd^{3+} ion has no energy levels below $32,000 \,\mathrm{cm}^{-1}$, and therefore cannot accept any energy from the antennae excited state.^[13] For **5**, the energy

TABLE 3 Selected Photophysical Data for Complexes 1–7

	Absorption $\lambda_{max}/nm [log(\epsilon/dm^3mol^{-1}cm^{-1})]$	Excitation λ_{exc}/nm	Emission $\lambda_{ m em}/ m nm(\Phi_{Zn-L} imes 10^4, au)$
1 ZnLaL	307 (4.51)	397	506 (1.47 ns)
2 ZnNdL	304 (4.59)	394	511 (0.91 ns),
			872 (1187 ns),
			1066, 1333
3 ZnEuL	304 (4.72)	399	511(0.93 ns), 1535
4 ZnGdL	307 (4.68)	395	509 (1.30 ns)
5 ZnTbL	308 (4.70)	396	510 (1.81 ns)
6 ZnErL	305 (4.62)	388	507 (1.10 ns), 1535
7 ZnYbL	307 (4.58)	390	536 (1.01 ns), 976 (10,826 ns)



FIGURE 1 Absorption spectra of complex 1–7 in acetonitrile at room temperature (c = $2\times 10^{-5}\,\text{M}).$

level of the excited state is lower than the energy lever of Tb^{3+} so that it cannot transfer energy to the Tb^{3+} .^[14] It is special for **3**. The energy level is higher than that of Eu³⁺; however, no characteristic emission of Eu³⁺ was detected. One explanation is that there may be a deactivation pathway that involves a charge-transfer from the **ZnL** excited state to the Eu³⁺ ion.

It is worth noting that for complex **2**, **6**, or **7**, the similar excitation spectrum ($\lambda_{ex} = 387 \text{ nm}$ for **2**, 379 nm for **6**, or 385 nm for **7**) was monitored at the respective NIR emission peak (1066 nm for **2**, 1535 nm for **6**, or 976 nm for **7**) or the residual visible emission peak (510 nm) of complex **2** or **7**, clearly showing that both the visible and NIR emissions are originated from the same π - π * transitions of the **H₂L** Schiff-base ligand for complexes **2**, **6**, and **7**,



FIGURE 2 UV-visible ranged excitation and emission spectra of complex 1, 2, 4, 5, and 6 in acetonitrile at room temperature ($c = 2 \times 10^{-5}$ M).



FIGURE 3 Near-infrared excitation spectra (monitored at 1066 nm for 2, 1535 nm for 6, and 976 nm for 7) and NIR emission spectra of complex 2, 6, and 7 in acetonitrile at room temperature ($c = 2 \times 10^{-5}$ M).

which suggests that the energy transfer from the antenna to the Ln³⁺ ions takes place efficiently.^[13] Moreover, for complexes 2 and 7, the respective luminescent decay curves obtained from timeresolved luminescent experiments can be fitted mono-exponentially with a time constant of microseconds (1.19 μ s for 2 at 872 nm and 10.83 μ s for 7 at 976 nm), and the intrinsic quantum yield Φ_{Ln} $(0.476\% \text{ for } 2 \text{ or } 0.542\% \text{ for } 7) \text{ of the } \text{Ln}^{3+} \text{ emission}$ may be estimated by $\Phi_{Ln} = \tau_{obs}/\tau_0$, where τ_{obs} is the observed emission lifetime and τ_0 is the "neutral lifetime," viz 0.25 ms and 2.0 ms for the Nd³⁺ and Yb³⁺ ions, respectively,^[15] which indicates the presence of a single emitting center for both 2 and 7 in dilute MeCN solution.^[16] Due to the limitation of our instrument, we were unable to determine the τ_{obs} value for the Er^{3+} ion and thus could not estimate the Φ_{Ln} value for the Er^{3+} ion, though the NIR emission of the Er^{3+} ion is observed for complex 6. The quantum efficiencies of both 2 and 7 are a little higher than those of binuclear ZnLn from the symmetric salen-type Schiff-base ligands,^[17] which should result from increasing efficiency of intersystem crossing of the asymmetric ligand, thus enhancing the sensitization process. From the viewpoint of the energy level match, though the energy gap (${}^{4}F_{3/2}$, 11,062 cm⁻¹) of the Nd³⁺ ion in complex **2** is smaller than that $({}^{2}F_{5/2},$ 9931 cm^{-1}) of the Yb³⁺ ion in complex 7, a higher quantum efficiency of 7 is shown than that of 2, possibly because the excited state of the Nd^{3+} ion is more sensitive to being quenched by the distant C-H oscillators of the Schiff-base ligand H_2L , besides the fewer opportunities of nonradiative migration from the single emitting transition (${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$) of the Yb³⁺ ion in complex 7.^[18]

CONCLUSION

In conclusion, with the phenylene-1,2-diamine, 3-methoxysalicylaldhyde, and 5-(4-cyanophenyl)-3-methoxysalicylaldehyde as starting materials, novel asymmetric Schiff-base zinc complex ZnL and Zn-Ln heterobinuclear complexes [ZnLnL(NO₃)₃(CH₃CN)] (1-7) are obtained. The results of their photophysical studies show that the strong and characteristic NIR luminescence with emissive lifetimes in the microsecond range has been sensitized from the excited state of the ligand due to the effective intramolecular energy transfer. Although the asymmetric Schiff-base ligand used has not significantly enhanced the NIR luminescent efficiency of lanthanide ions compared to that of symmetric ligands, this work affords a method for specific design and preparation of heterometallic complexes from the asymmetric Schiff-base ligands appended with different functional groups for fine tuning of NIR/visible luminescent properties of lanthanide complexes.

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