

Syntheses, Structures and Photophysical Properties of New Heterodinuclear Cd–Ln Coordination Complexes (Ln = Sm, Eu, Tb, Nd, Ho, Er)

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Six novel heterodinuclear d–f coordination complexes [LnCd(C₈H₇O₃)₅(phen)(H₂O)] (Ln = Sm **1**, Eu **2**, Tb **3**, Nd **4**, Ho **5**, Er **6**; C₈H₇O₃ = 4-methoxybenzoate; phen = 1,10-phenanthroline) were synthesized by the hydrothermal method, and their structures were studied by single-crystal X-ray diffraction. The IR and UV/Vis/NIR absorption spectra and the luminescence spectra of the six complexes were determined at room temperature. They have the same molecular structure, and two neighboring molecules are connected by hydrogen bonds or by a Ln...O weak interaction to form dimer crystals. In the visible region, the emission spectra of complexes **1–3** show the intense characteristic bands of the corresponding Ln^{III} ions, which are mainly attributed to the ef-

ficient energy transfer from the d block to the f block, that is, to the good sensitization of the d block. Moreover, in the Cd–Ln coordination complexes, the Cd...Ln separation is very small, and the 4d orbitals of the Cd^{II} ion may influence the 4f orbitals of the Ln^{III} ion, which probably causes some of the f levels of the Ln^{III} ion to be adjusted, and this effect can be observed in the shifts or splittings of the absorption bands in the UV/Vis/NIR spectra of the complexes. Especially in complexes **4–6**, some energy levels of the Ln^{III} ions have shifts or splittings, hence the corresponding emission bands exhibit shifts or splittings in the NIR region.

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Introduction

Luminescent lanthanide(III) coordination complexes have attracted a great deal of attention for many years due to their potential applications in areas such as bimetal analysis and optical devices.^[1–3] Lanthanide ions can show linelike emission spectra with a narrow wavelength range and high color purity. In addition, the emission properties of this family of complexes are notable, and the emissions cover an exceptionally wide spectral range: near-infrared (Nd^{III}, Er^{III}, Yb^{III}), red (Eu^{III}, Pr^{III}, Sm^{III}), green (Er^{III}, Tb^{III}), and blue (Tm^{III}, Ce^{III}).^[4] Recently, much attention has been paid to the luminescence properties of lanthanide complexes in the near-infrared region. Lanthanide complexes that emit in the NIR region, a region where biological tissues and fluids are relatively transparent, have the potential for use in chemosensor and fluoroimmunoassay applications as well as optical amplification in lasers.^[5–7] However, the f→f transition of lanthanide ions is parity-forbidden. The absorption coefficients are very low, and the intensity of the luminescence is weak.^[8–10] To overcome this drawback, organic ligands with intense and broad absorption bands are introduced as energy donors into the system to sensitize the characteristic emissions of Ln^{III} ions; this is

named the “antenna effect”. Numerous ligands can serve as the “antenna”,^[11] for example β-diketones, flexible carboxylic acids, pyridine derivatives, aromatic carboxylic acids with highly conjugated and rigid structures, and so on.^[12–16] Currently, not only is the variety of ligands important, but also introducing transition-metal ions into the system to synthesize d–f heterometallic coordination complexes for enhancing the luminescence of the f block by sensitization of the d block. The absorption bands of the π→π* transitions of the ligands are usually located in the ultraviolet region, while the absorption bands (L→L* or L→M) of the d block probably lie in the blue region or the longer wavelength region, which will facilitate the energy transfer to the Ln^{III} ions (f block) and reduce the energy wasted. Thus the d block can sensitize the luminescence of the f block more efficiently. For example, in the Re–Ln and Pt–Ln complexes based on polypyridine bridging ligands and in the cyanide-bridged Ru–Ln coordination complexes, the d block sensitizes the luminescence of the f block efficiently.^[17] In addition, the selection of the central metal ions from the d block is extensive, for example, Os^{II}, Cr^{III}, Au^I, Zn^{II}, Cu^I, Ag^I, and so forth,^[18–23] but the reports on heterometallic Cd–Ln complexes are rare.^[24,25] We selected the Cd^{II} ion to synthesize Cd–Ln complexes. This choice has two main reasons. Firstly, cadmium(II) coordination complexes have excellent luminescence properties in the blue or the green region, which may approach the emissive states of Ln^{III} ions and probably serve the energy transfer. Secondly, the coordination number of the Cd^{II} ion is varied and is usually 6,

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7, or 8, which allows Cd^{II} ions to coordinate with organic ligands to form novel structures.^[26,27] The high coordination ability of Cd^{II} ions also prevents Ln^{III} ions from entering cadmium(II) complexes, which makes it difficult to synthesize heterometallic Cd–Ln complexes. However, we are very much interested in the excellent luminescence properties of cadmium(II) coordination complexes, so we continued to try various reaction conditions and obtained a series of Cd–Ln coordination complexes with luminescence properties.

In this paper, the syntheses, structures, and photophysical properties of six heterodinuclear Cd–Ln coordination complexes are reported. At the same time, in the six Cd–Ln complexes, the sensitization and the influence of the d block on the luminescence of the f block are discussed.

Results and Discussions

Crystal Structures of the Complexes

The formulas for the six complexes are identical with the exception of the lanthanide ion: [LnCd(C₈H₇O₃)₅(phen)(H₂O)] (Ln = Sm **1**, Eu **2**, Tb **3**, Nd **4**, Ho **5**, Er **6**). They are isomorphous and crystallize in the triclinic space group *P* $\bar{1}$. Therefore, only the structure of complex **1** is described in detail.

[SmCd(C₈H₇O₃)₅(phen)(H₂O)] (**1**) is a heterodinuclear d–f coordination complex, and each molecule of **1** contains one Sm^{III} ion, one Cd^{II} ion, five 4-methoxybenzoate groups, one phen molecule, and one coordinated water molecule (Figure 1).

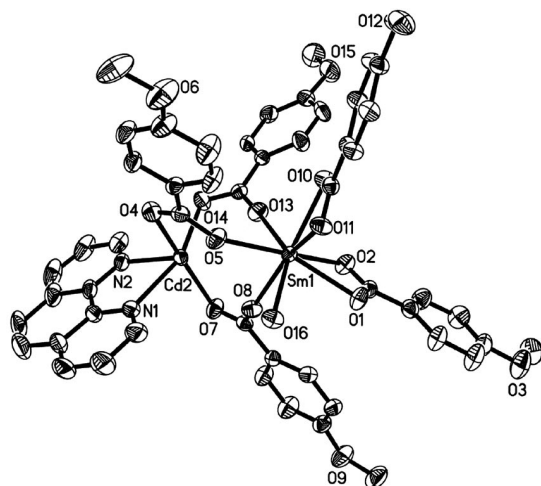


Figure 1. The molecular structure of complex **1**.

Three 4-methoxybenzoato ligands bridge the Sm^{III} and Cd^{II} ions and the other two 4-methoxybenzoato ligands chelate the Sm^{III} ion with one coordinated water molecule, which makes the Sm^{III} ion eight-coordinate. The five-coordinate Cd^{II} ion is coordinated to two N atoms from one phen molecule and three carboxyl oxygen atoms from three 4-methoxybenzoato ligands. As shown in Figure 2, in the crystal two neighboring molecules are connected through

hydrogen bonds coming from the coordinated water molecule and one carboxyl oxygen atom (O16A–H···O1B, O16B–H···O1A, 2.720 Å) to form the dimer structure. In the other complexes, the hydrogen bonds used to form the dimers are O16–H···O8 (2.717 Å) for **3**, O16–H···O7 (2.719 Å) for **5**, and O3–H···O14 (2.705 Å) for **6**. However in the crystal of [EuCd(C₈H₇O₃)₅(phen)(H₂O)] (**2**) (Figure 3), the molecular arrangement is a little different from that of complex **1**, that is, the dimers are connected by Eu···O weak interactions (Eu1···O1, 4.246 Å) except for the hydrogen bonds coming from the coordinated water and the carboxyl oxygen atom [O1–H···O15, 2.713(4) Å] (Figure 4).

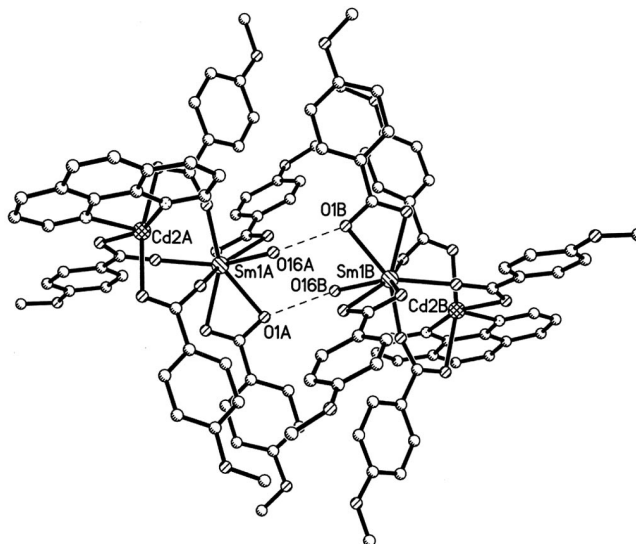


Figure 2. The dimer structure of complex **1**.

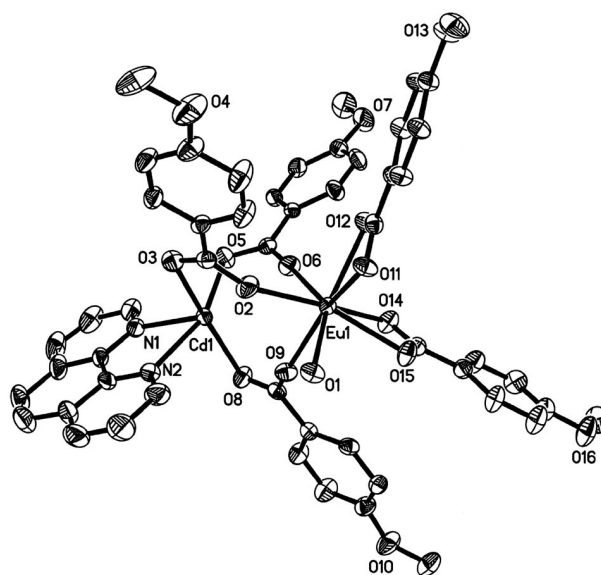


Figure 3. The molecular structure of complex **2**.

Because the crystal quality of complex **4** is not good, its crystal structure can not be completely solved by the data from the single-crystal X-ray diffraction analysis. However, in comparison with the other five complexes, complex **4** has

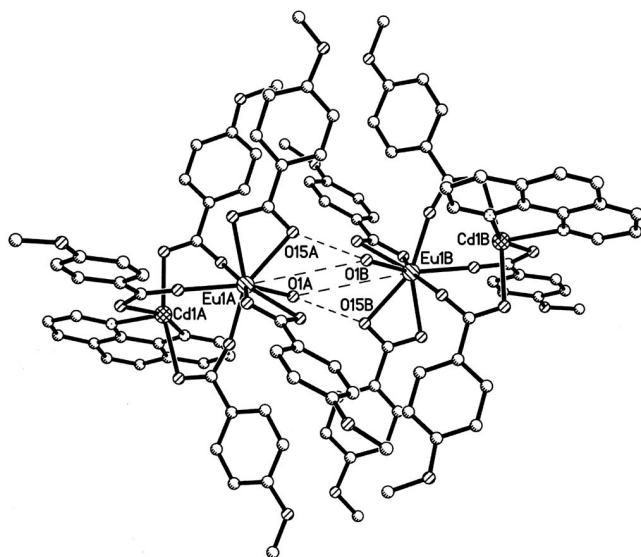


Figure 4. The dimer structure of complex 2.

the same crystal system and space group, similar crystal cell structure, and a similar IR spectrum; meanwhile, its elemental analysis results approximate its predicted molecular formula. We deduce that its molecular structure is similar to that of the other five complexes. However, we can not exclude other structural modes.

Photophysical Properties of the Complexes

UV/Vis/NIR Spectra of the Complexes

The assignments for the UV/Vis/NIR spectra of the six complexes and the two ligands are listed in Table 1. The free ligands (4-methoxybenzoic acid and phen) exhibit the $\pi \rightarrow \pi^*$ transition bands, which are not shifted perceptibly in the spectra of the complexes, indicating that the conjugation of the planar ligands changes little after coordinating with the Ln^{III} and the Cd^{II} ions.^[28] Meanwhile, the spectra of complexes 1, 4, 5, and 6 exhibit the characteristic absorption bands of the corresponding Ln^{III} ions, while the spectra of complexes 2 and 3 do not show those characteristics, because their $f \rightarrow f$ transitions are forbidden. The UV/Vis/NIR spectra of all the complexes are given in the Supporting Information (Figures S1–S6). In the following discussion, the relationship between the absorption spectra and the emission spectra will be mentioned.

Luminescence Properties of the Complexes in the Visible Region

We studied the room-temperature luminescence properties of the six complexes in the solid state. The assignments of the emission bands are summarized in Table 2.

Complexes 1–3 show emissions only in the visible region. In Figure 5, with $\lambda_{\text{Ex.}} = 345$ nm, complex 1 exhibits a broad and strong emission band at 360–500 nm, which should be assigned to a ligand-to-metal charge transfer (LMCT) of

Table 1. Assignments of absorption bands for the UV/Vis/NIR spectra of the complexes and the ligands.

Complex	λ [nm] (Assignment)
1	250, 336 ($\pi \rightarrow \pi^*$); 404 ($^6\text{H}_{5/2} \rightarrow ^4\text{F}_{7/2}$); 472 ($^6\text{H}_{5/2} \rightarrow ^4\text{F}_{5/2}$); 520 ($^6\text{H}_{5/2} \rightarrow ^4\text{F}_{3/2}$); 654 ($^6\text{H}_{5/2} \rightarrow ^4\text{G}_{5/2}$); 940 ($^6\text{H}_{5/2} \rightarrow ^6\text{F}_{11/2}$); 1080 ($^6\text{H}_{5/2} \rightarrow ^6\text{F}_{9/2}$); 1236 ($^6\text{H}_{5/2} \rightarrow ^6\text{F}_{7/2}$); 1382 ($^6\text{H}_{5/2} \rightarrow ^6\text{F}_{5/2}$); 1492 ($^6\text{H}_{5/2} \rightarrow ^6\text{F}_{3/2}$); 1662 ($^6\text{H}_{5/2} \rightarrow ^6\text{F}_{1/2}$)
2	254, 336 ($\pi \rightarrow \pi^*$)
3	252, 374 ($\pi \rightarrow \pi^*$)
4	248, 342 ($\pi \rightarrow \pi^*$); 472 ($^4\text{I}_{9/2} \rightarrow ^4\text{G}_{11/2}$); 514 ($^4\text{I}_{9/2} \rightarrow ^4\text{G}_{9/2}$); 524 ($^4\text{I}_{9/2} \rightarrow ^4\text{G}_{7/2}$); 580 ($^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}$); 682 ($^4\text{I}_{9/2} \rightarrow ^4\text{F}_{9/2}$); 744 ($^4\text{I}_{9/2} \rightarrow ^4\text{F}_{7/2}$); 800 ($^4\text{I}_{9/2} \rightarrow ^4\text{F}_{5/2}$); 864 ($^4\text{I}_{9/2} \rightarrow ^4\text{F}_{3/2}$)
5	248, 348 ($\pi \rightarrow \pi^*$); 420 ($^5\text{I}_8 \rightarrow ^5\text{G}_5$); 452 ($^5\text{I}_8 \rightarrow ^5\text{F}_1$); 480 ($^5\text{I}_8 \rightarrow ^5\text{F}_3$); 540 ($^5\text{I}_8 \rightarrow ^5\text{F}_4$); 646 ($^5\text{I}_8 \rightarrow ^5\text{F}_5$); 884 ($^5\text{I}_8 \rightarrow ^5\text{I}_5$); 1144, 1180 ($^5\text{I}_8 \rightarrow ^5\text{I}_6$)
6	248, 350 ($\pi \rightarrow \pi^*$); 402 ($^4\text{I}_{15/2} \rightarrow ^4\text{F}_{9/2}$); 448 ($^4\text{I}_{15/2} \rightarrow ^4\text{F}_{5/2}$); 488 ($^4\text{I}_{15/2} \rightarrow ^4\text{F}_{7/2}$); 522 ($^4\text{I}_{15/2} \rightarrow ^4\text{S}_{3/2}$); 654 ($^4\text{I}_{15/2} \rightarrow ^4\text{F}_{9/2}$); 798 ($^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$); 968 ($^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$); 1514, 1488, 1416, 1376 ($^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$)
4-methoxybenzoic acid	254, 294 ($\pi \rightarrow \pi^*$)
phen	254, 340 ($\pi \rightarrow \pi^*$)

Table 2. Assignments of the emission bands in the visible region of the complexes and the ligands.

Complex	$\lambda_{\text{Ex.}}$ [nm] (Bandwidth Ex., Bandwidth Em.)	$\lambda_{\text{Em.}}$ [nm] (Assignment)
1	345 (3 nm, 3 nm)	360–500 (LMCT), 562 ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$), 598 ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$), 644 ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$)
2	358 (3 nm, 1 nm)	580 ($^5\text{D}_0 \rightarrow ^7\text{F}_0$), 592 ($^5\text{D}_0 \rightarrow ^7\text{F}_1$), 617 ($^5\text{D}_0 \rightarrow ^7\text{F}_2$), 655 ($^5\text{D}_0 \rightarrow ^7\text{F}_3$), 703 ($^5\text{D}_0 \rightarrow ^7\text{F}_4$)
3	347 (1 nm, 1 nm)	490 ($^5\text{D}_4 \rightarrow ^7\text{F}_6$), 547 ($^5\text{D}_4 \rightarrow ^7\text{F}_5$), 585 ($^5\text{D}_4 \rightarrow ^7\text{F}_4$), 623 ($^5\text{D}_4 \rightarrow ^7\text{F}_3$)
4	392 (3 nm, 3 nm)	400–500 (LMCT)
5	356 (3 nm, 3 nm)	370–450 (LMCT)
6	354 (3 nm, 3 nm)	370–500 (LMCT)
4-methoxybenzoic acid	297 (3 nm, 1 nm)	328 (LLCT)
phen	344 (3 nm, 3 nm)	363, 381, 407 (LLCT)

the d block (Cd–L section),^[29,30] because the emission band is different from that of the free ligands (4-methoxybenzoic acid and phen) in shape and position; moreover, the emissions of the ligands have been quenched. In the emission spectrum of complex **1** (Figure 5), the other three peaks at 562, 598 and 644 nm are weaker and correspond to $^4G_{5/2} \rightarrow ^6H_{5/2}$, $^4G_{5/2} \rightarrow ^6H_{7/2}$, and $^4G_{5/2} \rightarrow ^6H_{9/2}$ transitions of the Sm^{III} ion,^[14,31] which indicates that the energy transfer from the d block to the f block is incomplete and most of the energy is used for luminescence from the d block itself.

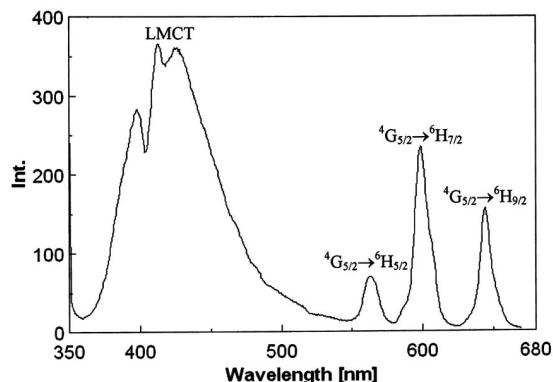


Figure 5. The emission spectrum of complex **1** ($\lambda_{\text{ex.}} = 345$ nm, Bandwidth Ex.: 3 nm, Bandwidth Em.: 3 nm).

In the emission spectra of complexes **2** and **3** (Figures 6 and 7), only the characteristic emission bands of Eu^{III} and Tb^{III} appear, while the luminescence of the d block is quenched completely. The emission spectrum of complex **2**, excited at 358 nm, exhibits the five characteristic emissions of the Eu^{III} ion. Two intense peaks at 592 and 617 nm are assigned to $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions, and three weak peaks at 580, 655, and 703 nm correspond to $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_3$, and $^5D_0 \rightarrow ^7F_4$, respectively.^[28,32] The intensity of the $^5D_0 \rightarrow ^7F_2$ transition (electric dipole) is stronger than that of the $^5D_0 \rightarrow ^7F_1$ transition (magnetic dipole), and this indicates that the coordination environment of the Eu^{III} ion is asymmetric, which is confirmed by the crystallographic analysis.^[3] In the spectrum of complex **3**, excited at 347 nm, the intense emission bands of the Tb^{III} ion are observed: $^5D_4 \rightarrow ^7F_6$ (490 nm), $^5D_4 \rightarrow ^7F_5$ (547 nm),

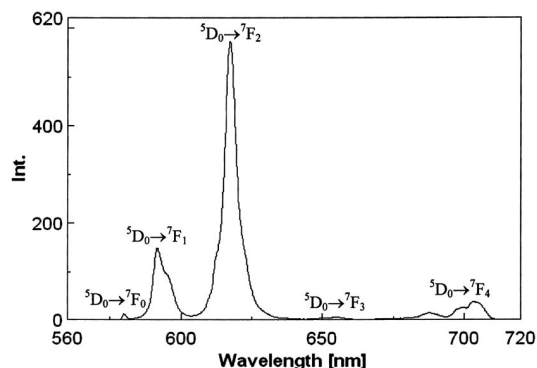


Figure 6. The emission spectrum of complex **2** ($\lambda_{\text{ex.}} = 358$ nm, Bandwidth Ex.: 3 nm, Bandwidth Em.: 1 nm).

$^5D_4 \rightarrow ^7F_4$ (585 nm), and $^5D_4 \rightarrow ^7F_3$ (624 nm).^[33,34] The luminescence of the d block is quenched in the two complexes, and the characteristic emissions of the Ln^{III} ions are enhanced by the better sensitization of the d block.

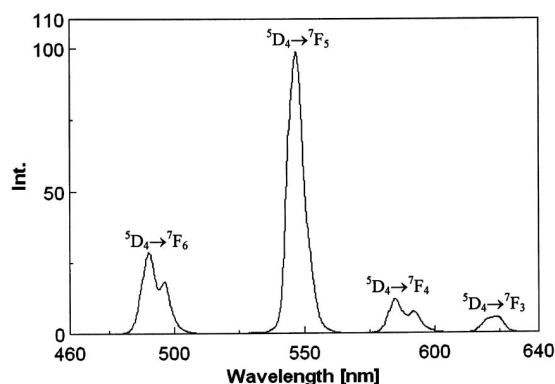


Figure 7. The emission spectrum of complex **3** ($\lambda_{\text{ex.}} = 347$ nm, Bandwidth Ex.: 1 nm, Bandwidth Em.: 1 nm).

Comparing the emission spectra of complexes **1–3**, we can find that the characteristic emission intensity of the Sm^{III} ion in complex **1** is much weaker than that of the Eu^{III} ion in **2** and the Tb^{III} ion in **3**, because in complex **1**, the luminescence of the d block is not quenched completely, that is, the energy transfer from the d block (Cd–L section) to the f block (Sm–L section) is incomplete. We think that, the efficiency with which the luminescence of the Ln^{III} ion can be sensitized depends on the matching between the energy levels of the Ln^{III} ions and the ligand (4-methoxybenzoic acid) or the d block. According to “a theory of sensitized luminescence in solids” by Dexter^[35] and the statement that the region in which organic ligands can be sensitized most effectively is $\Delta E = 2100\text{--}3200\text{ cm}^{-1}$ by Sato et al. and others,^[36] the 4-methoxybenzoic acid ligand, having its $\pi \rightarrow \pi^*$ transition band at 294 nm (34014 cm^{-1}), can transfer the energy to the excited states of the Ln^{III} ion in the $30814\text{--}31914\text{ cm}^{-1}$ range (Figure 8). However, the energy gap between the states in this range and the emissive states ($^4G_{5/2}$, Sm^{III} **1**; 5D_0 , Eu^{III} **2**; 5D_4 , Tb^{III} **3**) of the Ln^{III} ions

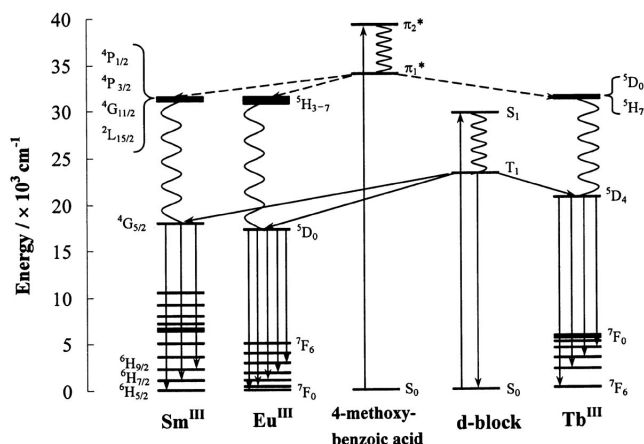


Figure 8. Diagram of the energy levels of complexes **1** (Sm^{III}), **2** (Eu^{III}), **3** (Tb^{III}), 4-methoxybenzoic acid, and the d block.

Table 3. The elemental analysis results and the IR spectral band assignments for the complexes.

Elemental Analysis: calcd. for C ₅₂ H ₄₅ N ₂ CdLnO ₁₆ (found)						
	1	2	3	4	5	6
C	51.03 (51.33)	51.06 (51.26)	50.66 (50.97)	51.32 (51.59)	50.44 (50.72)	50.21 (50.63)
H	3.75 (3.73)	3.75 (3.72)	3.73 (3.70)	3.78 (3.75)	3.71 (3.68)	3.72 (3.68)
N	2.33 (2.30)	2.34 (2.30)	2.34 (2.29)	2.36 (2.32)	2.32 (2.28)	2.29 (2.27)
Cd	9.39 (9.24)	9.40 (9.23)	9.28 (9.17)	9.36 (9.28)	9.24 (9.13)	9.21 (9.11)
Ln	12.76 (12.36)	12.81 (12.48)	13.16 (12.97)	12.31 (11.91)	13.48 (13.39)	13.88 (13.56)
IR (KBr) [cm ⁻¹]	1	2	3	4	5	6
$\nu(\text{OH})$	3428	3434	3426	3433	3443	3433
$\nu(\text{Ar-H})$	3073, 3003	3073, 3004	3073, 3004	3075, 3004	3006	3071, 3006
$\nu(\text{CH}_3)$	2935, 2836	2937, 2837	2935, 2836	2935, 2837	2933, 2838	2932, 2837
$\nu(\text{C}=\text{C})$	1532, 1513	1552, 1529, 1514	1559, 1530, 1512	1529, 1514	1533, 1514	1535, 1510
$\nu(\text{asCOO-})$	1605	1605	1605	1606	1606	1606
$\nu(\text{sCOO-})$	1416	1418	1418	1418	1423	1422
$\nu(\text{Ar-O})$	1256	1259	1258	1258	1258	1257
$\nu(\text{C-C})$	1172	1173	1173	1172	1174	1173
$\nu(\text{C-N})$	1103	1103	1103	1103	1104	1104
$\nu(\text{C-O})$	1030	1029	1029	1030	1030	1030
$\delta(\text{C-H, Ar})$	1311	1312	1312	1311	1312	1312
$\delta(\text{Ar-H})$	862, 786, 728	861, 786, 727	863, 786, 727	860, 786, 727	858, 785, 727	857, 786, 728
$\nu(\text{Cd-N})$	545	539	540	540	541	543
$\nu(\text{Cd-O})$	511	508	511	511	511	513
$\nu(\text{Ln-O})$	420, 379	419, 378	420, 379	420, 377	419, 379	419, 382

is large, so most of the energy from the ligand will be wasted in the nonradiative intersystem crossing, and it is too hard to sensitize the luminescence of the Ln^{III} ion. However, Figure 8 shows that the energy gap between the emissive state (T_1 , 23500 cm⁻¹) of the d block and the emissive state of the Ln^{III} ions presents more feasibility for energy transfer and sensitization. So the d block dominates the role of sensitizing the luminescence of the Ln^{III} ion in the complexes.

In the following, we will further discuss the sensitization by the d block with a look at the relationship between the UV/Vis/NIR absorption spectra and the emission spectra of the complexes. In the absorption spectrum of complex **1** (Table 3, Figure S1), the $^6\text{H}_{5/2} \rightarrow ^4\text{G}_{5/2}$ transition band of the Sm^{III} ion is the weakest, while in the absorption spectra of complexes **2** and **3** (Table 3, Figures S2 and S3), the $^7\text{F}_0 \rightarrow ^5\text{D}_0$ transition of the Eu^{III} ion is forbidden, as is the $^7\text{F}_6 \rightarrow ^5\text{D}_4$ transition of the Tb^{III} ion. However, after the heterodinuclear Cd–Ln complexes are formed, the d block can sensitize the luminescence of the Ln^{III} ions, that is, the energy can be transferred from the emissive state (T_1) of the d block to the emissive states ($^4\text{G}_{5/2}$, Sm^{III} **1**; $^5\text{D}_0$, Eu^{III} **2**; $^5\text{D}_4$, Tb^{III} **3**) of the Ln^{III} ions. When these excited electrons return to the ground states from the emissive states of the Ln^{III} ions, the energy being released by radiation, complexes **1–3** will show the corresponding characteristic emissions of the Ln^{III} ions. If the d block does not sensitize the f block, the emissions of the Ln^{III} ions, but only those depending on electronic transitions of the Ln^{III} ions themselves, will not appear in the spectra of complexes **1–3**. So, the characteristic emissions of the f block mainly profit from the sensitization of the d block in complexes **1–3**. In addition, as it is shown in Figure 8, the energy gap between the emissive state (T_1) of the d block and the $^5\text{D}_4$ state of

the Tb^{III} ion is the smallest, and the wasted energy is less in the intersystem crossing, so the characteristic emission bands of Tb^{III} in complex **3** are stronger than those of Sm^{III} in **1** and Eu^{III} in **2**. Meanwhile, Figure 8 shows that there are six $^6\text{F}_J$ ($J = 1/2–11/2$) states between the emissive state ($^4\text{G}_{5/2}$) and the ground states ($^6\text{H}_J$) of the Sm^{III} ion. When these excited electrons in the emissive $^4\text{G}_{5/2}$ state return to the ground states, they must pass the $^6\text{F}_J$ states. This process must cause part of the energy to be wasted, and the energy transfer from the d block to the f block will be affected, so the luminescence of the Sm^{III} ion is weaker and the luminescence of the d block still exists in complex **1**.

Complexes **4–6** mainly show luminescence in the NIR region, while in the visible region they only show weak emissions (LMCT) of the d block (Figures S7–S9 in the Supporting Information).

Luminescence Properties in the NIR Region

At room temperature, the NIR emission spectra of complexes **4–6** in the solid state were measured by an FLS 920 combined time-resolved and steady-state fluorescence spectrometer with a Ge detector. The emission spectrum of complex **4** presents two emission bands at 913 nm and 992 nm ($\lambda_{\text{Ex.}} = 657$ nm) (Figure 9), which can be assigned to $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ and $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ transitions of the Nd^{III} ion, respectively. The two emission bands of complex **4** show shifts relative to the bands of the reported Nd complexes^[37,38] and the theoretical values.^[39] The absorption bands of the Nd^{III} ion in complex **4** (Figure S4 in the Supporting Information) also present shifts relative to those of the isolated Nd^{III} ion, for which the shift of the $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{3/2}$ transition corresponding to 864 nm is known (the theoretical value is 899 nm) to have a broad band (840–920 nm). This indicates that the $^4\text{F}_{3/2}$ state of the Nd^{III} ion

generates the shift and splittings, so the emission bands (992 and 913 nm) also present shifts in complex **4**. This is caused by the formation of the heterometallic d–f coordination complex.

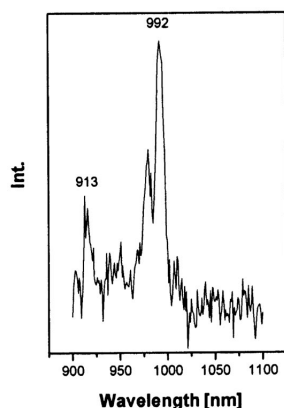


Figure 9. The NIR emission spectrum of complex **4** ($\lambda_{\text{Ex.}} = 657$ nm).

For complex **5** with $\lambda_{\text{Ex.}} = 985$ nm, the emission at 1001 nm can be assigned to the $^5F_5 \rightarrow ^5I_7$ transition of the Ho^{III} ion, while both emission bands at 1378 and 1513 nm can be assigned to the $^5F_5 \rightarrow ^5I_6$ transition,^[40] which is attributed to the splittings of the 5I_6 state. This can be illustrated by the absorption spectrum of complex **5** (Figure S5): the absorption band corresponding to the $^5I_8 \rightarrow ^5I_6$ transition is broad (1100–1200 nm), and the strongest peak lies at 1144 nm with a shoulder at 1180 nm, indicating that the 5I_6 state of the Ho^{III} in complex **5** generates splittings. So both of the two observed emissions at 1378 and 1513 nm are assigned to the $^5F_5 \rightarrow ^5I_6$ transition (Figure 10).

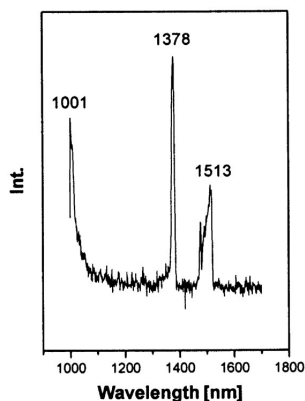


Figure 10. The NIR emission spectrum of complex **5** ($\lambda_{\text{Ex.}} = 985$ nm).

In some papers, Er^{III} complexes usually only exhibit one emission band at about 1535 nm corresponding to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition,^[1,41] whereas complex **6** exhibits two emission bands at 1343 and 1515 nm ($\lambda_{\text{Ex.}} = 985$ nm) (Figure 11). We think that both of the emission bands should be assigned to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition, because the $^4I_{13/2}$ state of the Er^{III} ion in complex **6** is split. By observ-

ing the UV/Vis/NIR absorption spectrum of complex **6** (Figure S6), we can find that the absorption band corresponding to the $^4I_{15/2} \rightarrow ^4I_{13/2}$ transition is broad and includes two split peaks: the strong peak (split into 1488 and 1514 nm) and the weak shoulder peak (split into 1376 and 1416 nm). So when the excited electrons return to the ground state ($^4I_{15/2}$) from the split state ($^4I_{13/2}$), complex **6** shows two emission bands both of which are split (Figure 11). In complex **6**, the observed emission spectrum is consistent with the absorption spectrum, which further proves the reliability of the assignments for the emission spectrum of complex **6**.

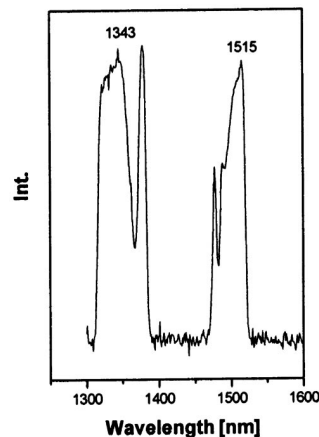


Figure 11. The NIR emission spectrum of complex **6** ($\lambda_{\text{Ex.}} = 985$ nm).

In comparison with the results in some relevant papers, the NIR emission spectra of complexes **4–6** present splittings or shifts,^[42,43] which are mainly attributed to the formation of the heterodinuclear Cd–Ln coordination complexes. From the crystal structures of the complexes, the Cd...Ln separation of the molecule is very small (in the 3.66–3.72 Å region), thus the 4d orbitals of the Cd^{II} ion may influence the 4f orbitals of the Ln^{III} ion, which probably causes part of the f levels of the Ln^{III} ion to be adjusted.

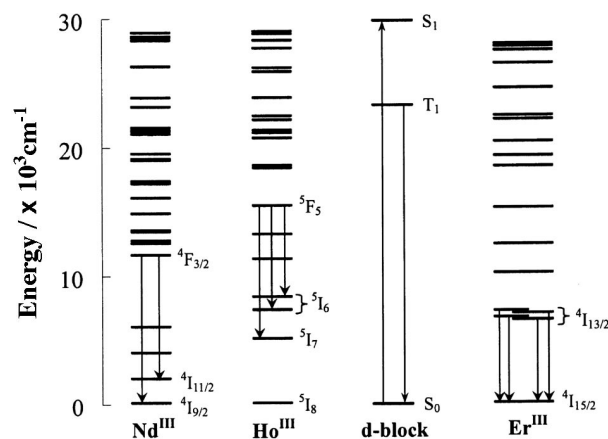


Figure 12. Diagram of the NIR luminescence processes of complexes **4**, **5**, and **6**.

As a result, some of the levels of the Ln^{III} ions in complexes **4–6** present splittings and shifts that are clearly visible in the UV/Vis/NIR spectra. So the corresponding emission bands of complexes **4–6** exhibit shifts or splittings in the NIR region. Figure 12 gives an illustration of the possible emission processes of complexes **4–6**.

Conclusions

Six new heterodinuclear coordination complexes (Cd–Ln where Ln = Sm, Eu, Tb, Nd, Ho, Er) were synthesized by the hydrothermal method, and their structures were determined by single-crystal X-ray diffraction (except for complex **4**). They have the same molecular structure and two neighboring molecules are connected by hydrogen bonds or weak interactions to form dimer crystals. The study of the photophysical properties indicates that the d block influences the f block in two aspects: (i) In these complexes, the d block can sensitize the luminescence of the f block. Especially, complexes **1–3** have intense characteristic emissions in the visible region, owing to efficient sensitization of the f block by the d block. (ii) In these heterodinuclear Cd–Ln complexes, the Cd $\cdots$ Ln separation is smaller, so the 4d orbitals of the Cd $^{\text{II}}$ ion may influence the 4f orbitals of the Ln^{III} ion, which probably causes the intramolecular levels to be adjusted. So some of the f levels of the Ln^{III} ion are adjusted, and this is reflected in the UV/Vis/NIR spectra of the complexes. Especially in complexes **4–6**, some absorption bands show shifts or splittings relative to those of the isolated Ln^{III} ion. So the corresponding emission bands of complexes **4–6** present shifts or splittings relative to those of some reported Ln complexes.

Experimental Section

Materials and Methods: $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ were prepared by dissolving the corresponding lanthanide oxide (99.99%) in an excess of nitric acid. $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, phen, and 4-methoxybenzoic acid were AR and used as purchased. The elemental analyses were carried out with a PE-240C elemental analyzer and PLASMA-II ICP, and the structures of the complexes were determined with a Bruker SMART APEX II X-diffractometer. The IR spectra were recorded with a JASCO FT/IR-480 spectrometer with pressed KBr and the UV/Vis/NIR spectra (diffuse reflectance) were determined with a JASCO V-570 spectrometer. The excitation and emission spectra were measured with a JASCO FP-6500 fluorescence spectrometer, and the NIR spectra were determined with a FLS 920 combined time-resolved and steady-state fluorescence spectrometer with a Xe lamp as the light source and a Ge detector.

Syntheses of the Complexes

Synthesis of $\text{SmCd}(\text{C}_8\text{H}_7\text{O}_3)_5(\text{phen})(\text{H}_2\text{O})$ (1**):** A solution of 4-methoxybenzoic acid (0.14 g, 1 mmol) in MeOH (8 mL) and H_2O (5 mL) was adjusted to pH = 6 with NaOH (1 mol L $^{-1}$) and HAc. A solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.08 g, 0.25 mmol) and $\text{Sm}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ (0.12 g, 0.25 mmol) in H_2O (8 mL) was added to the above solution while stirring and heating, but there was a white precipitate, which was dissolved by adding HAc. After the solution of phen (0.05 g, 0.25 mmol) in EtOH (5 mL) was added to the above mixed solution, the final solution was sealed in a Teflon-lined autoclave and heated at 90 °C for 140 h. After cooling to ambient temperature, the reaction solution was filtered, and yellow crystals were obtained, washed out with the mother liquor and air-dried.

The preparation methods of complexes **2–6** are similar to that of complex **1**, except that the corresponding $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ were used instead of $\text{Sm}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$, and the time of reaction and crystallization was different. The results of elemental analyses and the assignments for the IR spectra of all six complexes are listed in

Table 4. Crystal data and structure refinement for the complexes.

Complex	1	2	3	4	5	6
Empirical formula	$\text{C}_{52}\text{H}_{45}\text{N}_2\text{O}_{16}\text{CdSm}$	$\text{C}_{52}\text{H}_{45}\text{N}_2\text{O}_{16}\text{CdEu}$	$\text{C}_{52}\text{H}_{45}\text{N}_2\text{O}_{16}\text{CdTb}$	$\text{C}_{52}\text{H}_{45}\text{N}_2\text{O}_{16}\text{CdNd}$	$\text{C}_{52}\text{H}_{45}\text{N}_2\text{O}_{16}\text{CdHo}$	$\text{C}_{52}\text{H}_{45}\text{N}_2\text{O}_{16}\text{CdEr}$
Formula mass	1216.65	1218.26	1225.22	1210.5	1231.23	1233.6
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
T [K]	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
a [Å]	12.380(2)	12.3489(16)	12.3443(19)	12.323(3)	12.3358(12)	12.334(2)
b [Å]	13.899(2)	13.9651(18)	13.945(2)	13.950(3)	13.9507(13)	13.941(2)
c [Å]	16.804(4)	16.776(2)	16.752(4)	16.030(3)	16.696(2)	16.652(4)
α [°]	108.446(3)	108.7080(10)	108.548(2)	84.41(3)	108.5700(10)	108.530(3)
β [°]	104.769(3)	104.4330(10)	104.561(2)	67.96(3)	104.499(2)	104.539(3)
γ [°]	104.394(2)	104.313(2)	104.370(2)	75.47(3)	104.3450(10)	104.338(2)
V [Å 3]	2475.4(9)	2479.2(6)	2471.0(8)	2472.5(9)	2463.3(5)	2455.0(9)
Z	2	2	2	2	2	2
D_{calcd} [g cm $^{-3}$]	1.632	1.632	1.647	1.660	1.666	1.666
μ [mm $^{-1}$]	1.678	1.756	1.924	2.100	2.205	2.205
$F(000)$	1218	1220	1224	1228	1226	1226
θ range [°]	1.97 to 29.17	1.82 to 29.05	1.83 to 29.09	1.83 to 29.04	1.83 to 29.05	1.83 to 29.05
Reflns. collected	15555	15569	15452	15459	15348	15348
Ind. Reflns. (R_{int})	11438 (0.0161)	11418 (0.0192)	11372 (0.0213)	11362 (0.0146)	11276 (0.0162)	11276 (0.0162)
Data/restraints/parameters	11438/2/657	11418/2/761	11372/0/693	11362/2/657	11276/0/721	11276/0/721
GOF on F^2	1.018	1.015	1.030	1.018	1.030	1.030
R_1 [$I > 2\sigma(I)$]	0.0329	0.0356	0.0349	0.0286	0.0306	0.0306
wR_2 [$I > 2\sigma(I)$]	0.0722	0.0753	0.0835	0.0639	0.0688	0.0688
R_1 [all data]	0.0446	0.0500	0.0452	0.0363	0.0397	0.0397
wR_2 [all data]	0.0790	0.0824	0.0901	0.0682	0.0736	0.0736

Table 3. IR spectra are given in Figures S10–S15 in the Supporting Information.

Determination of Crystal Structures: Suitable single crystals of the six complexes were selected, and data were collected with a Bruker SMART APEX II X-diffractometer with graphite-monochromated Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. All data were corrected for the Lorentz polarization factor and empirical absorption. The structures were solved with direct methods and refined by a full-matrix least-squares analysis on F^2 by using the SHELXTL-97 program.^[44] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found by mixed methods. Crystal parameters and refinement data are summarized in Table 4. Because the crystal quality of complex **4** was not good, its crystal structure could not be completely solved by using the data from the single-crystal X-ray diffraction analysis. So the crystal data for complex **4** in Table 4 is incomplete. Selected bond lengths and angles of complexes **1**, **2**, **3**, **5**, and **6** are listed in Tables S1–S5 in the Supporting Information.

CCDC-669392 (for **1**), -669393 (for **2**), -669394 (for **3**), -669395 (for **5**) and -669396 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): UV/Vis/NIR and IR spectra of the six complexes, emission spectra in the visible region of complexes **4–6**, and selected bond lengths and angles of complexes **1**, **2**, **3**, **5**, and **6**.

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