Promoting near-infrared emission of neodymium complexes by tuning the singlet and triplet energy levels of β-diketonates

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A series of neodymium complexes with various modified β-diketonates and their corresponding gadolinium complexes have been synthesized and characterized. The singlet and triplet energy levels of the coordinated ligands were measured and compared. These complexes emit characteristic Nd^{3+} light at about 880, 1060, 1330 nm with long-lived lifetimes. The relationship between the structure and photophysical properties has been discussed and the energy transfer process in these complexes has been studied.

Introduction

Lanthanide ions have attracted considerable attentions due to their intense, line-like and long-lived emissions, which cover a spectral range from the near-UV to the visible and even the near-infrared (NIR) region. The NIR, especially 800–1700 nm, luminescence from lanthanide ions such as Pr^{III}, Nd^{III}, Er^{III} and Yb^{III} is of particular interest due to its electronic and optical applications, especially for optical communications, biological and sensor applications.[1] For fundamental purposes, research efforts are often focused on the following areas: (1) design of ligands with large steric hindrance or other methods to avoid relaxation of energy through resonance vibration;[2] (2) adjustment of the triplet energy level of the ligand to match the lowest unoccupied orbital of the central ion;[3] (3) improvement of the energy transfer by synthesis of heterobimetallic compounds or introducing a functional group into the emitting molecule or combining the electronic conductive material directly with the emitting material, such as conductive polymers *etc.*, to promote the transport of the electrons and holes.[4] However for the near-infrared ions, their lowest excited states and their ground states are very close in energy, therefore the emission often occurs in the infrared region and their intensities are weaker by several orders of magnitude ($\varphi_{\mathrm{pl}} \approx 10^{-4}$–$10^{-6}$) compared to that of visible emission based on europium and terbium complexes. Furthermore, their deactivation process often occurs easily through a non-radiative transition and energy transfer problems exist between the ligand and the central ion. Therefore, to choose appropriate ligands for sensitization the near-infrared ion is important.

β-Diketones are popular ligands for lanthanide ions,[5] which have the following advantages: (1) the diketone ligand has strong absorption within a large wavelength range for its π–π* transition and consequently has been targeted for its ability to sensitize the luminescence of the Ln^{3+} ions; (2) the ability of the diketonate and lanthanide ions to form an adduct is strong. (3) the β-diketonate lanthanide complexes are stable enough for practical usage.

In this study, a series of neodymium β-diketonate complexes formed by various modification of the β-diketonate ligands have been synthesized and characterized. The singlet and triplet energy levels of the ligands have been determined. The relationship between the structure and the photophysical properties has been compared and the energy transfer process in the complexes has been discussed.

Experimental

Materials and reagents

All the materials and reagents were used as purchased without further purification except otherwise stated. Dibenzoylmethane (HDBM) was purchased from Merck Company. Phenanthroline (phen), 4,7-diphenyl-1,10-phenanthroline (bath), naphthyle, naphthyl acetate and 4-*tert*-butylbenzoyl chloride were purchased from Acros Chemical Co. Dinaphthoylmethane (HDNM) was synthesized by Claisen condensation between naphthyl acetate and 2-acetylnaphthalene. The reagents were dried using appropriate methods before use.

Instrument

Corrected visible (400–800 nm) and near-IR (800–1600 nm) photoluminescence spectra were measured on an Edinburgh Instrument (EI) FLS 920 spectrometer. For the latter, a liquid-nitrogen cooled Ge detector with a standard lock-in technique was used. Decay curve measurements in the visible region were carried out using an EI Life-Spec-red instrument, while the NIR region ones were performed on an EI FL920 time-resolved spectrometer by monitoring at about 1060 nm luminescence decay after excitation with a 100 ps pulse of a PDL 800-B laser. The phosphorescence spectra of Gd complexes were measured on an EI FLS 920 spectrometer at 77 K and

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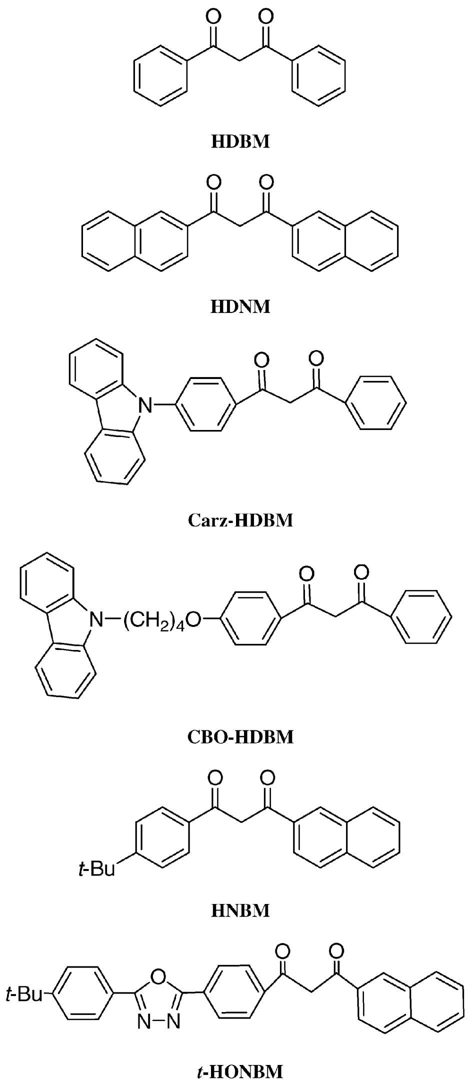


Scheme 1 The chemical structures of the β-diketone ligands used in this paper.

their lifetimes were determined simultaneously using a microsecond lamp as the excitation source.

^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer. Mass spectra were taken on a ZAB-HS Micromass instrument (UK). Elemental analyses were performed on an Elementar Vario EL instrument (Germany). FT-IR spectra were taken on a Nicolet MAGNA-IR 750 spectrometer.

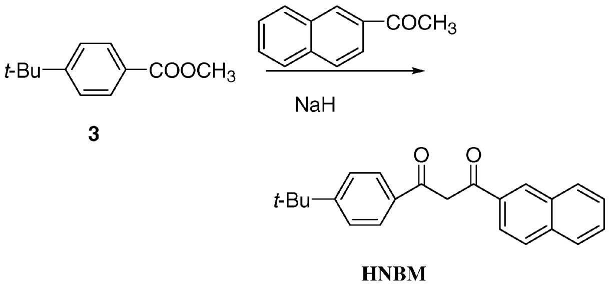
Synthesis

Previously, we have synthesized the carbazole-modified HDBMs, *i.e.* Carz-HDBM and CBO-HDBM respectively for coordinating with Eu^{III} ions.[6] In this paper, we have synthesized the neodymium complexes with these ligands and other newly synthesized ligands. Nd(DBM)$_3$(phen), Nd(DBM)$_3$(bath) and Nd(DNM)$_3$(bath) were also synthesized and characterized for comparison. The chemical structures of the β-diketone ligands used in this paper are shown in Scheme 1.

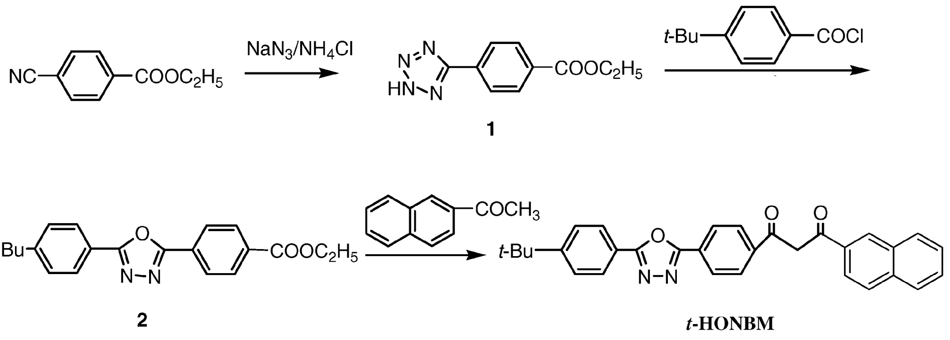
The oxadiazole-modified β-diketone ligand *t*-HONBM was synthesized through a multi-step method as shown in Scheme 2, and another *tert*-butyl modified β-diketone ligand HNBM was synthesized by the Claisen condensation method as shown in Scheme 3.

Synthesis of ethyl 4-(2*H*-tetrazol-5-yl)benzoate (1). Ethyl 4-cyanobenzoate (5.2 g, 30 mmol), NaN$_3$ (2.93 g, 45 mmol) and NH$_4$Cl (2.4 g, 45 mmol) were dissolved in 30 mL DMF, and the mixture was refluxed below 100 °C for 24 h. After cooling to room temperature, it was poured into 400 mL distilled water and carefully acidified with dilute HCl and then filtered. The white powder obtained was dried and weighed (yield 72%). ^{1}H NMR (CDCl$_3$), δ (ppm): 8.26–8.24 (d, 2H), 8.22–8.20 (d, 2H), 4.47–4.41 (q, 2H), 1.45–1.42 (t, 3H).

Synthesis of ethyl 4-(5-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-2-yl)benzoate (2). Under N$_2$ protection, 11 mL (0.055 mol) 4-*tert*-butylbenzoyl chloride was added dropwise to 50 mL pyridine containing 10.9 g (0.05 mol) of compound **1**. The



Scheme 3 Synthetic route to HNBM.



Scheme 2 Synthetic route to *t*-HONBM.

mixture was allowed to react for 10 h at 80–90 °C. After most of the solvent was removed by rotary evaporation, the mixture was poured into 400 mL distilled water and a brown precipitate was obtained. This was filtered off, dried and weighed (yield: 97%).

Synthesis of 1-(4-(5-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-2-yl) phenyl)-3-(naphthalen-2-yl)propane-1,3-dione (*t*-HONBM). This compound was prepared by Claisen condensation with equimolar quantities of compound **2** (14 g, 0.04 mol) and 1-(naphthalen-2-yl)ethanone (6.8 g, 0.04 mol) in the presence of NaH. The reaction was allowed to proceed in dry dimethylbenzene for 24 h at room temperature then for 72 h at 40 °C. After that it was poured into 400 mL water and HCl was added dropwise to it until pH = 2–3. Then the mixture was extracted with $CHCl_3$ and the product recrystallized from absolute alcohol. The yellow powder obtained was dried in a vacuum oven at 60 °C (yield: 23%). ^1H NMR ($CDCl_3$), δ (ppm): 16.91 (s, 1H), 8.58 (s, 1H), 8.29–8.27 (d, 2H), 8.20–8.18 (d, 2H), 8.11–8.09 (d, 2H), 8.06–8.04 (m, 1H), 8.02–8.00 (d, 1H), 7.96–7.94 (d, 1H), 7.91–7.89 (d, 1H), 7.64–7.57 (m, 4H), 7.07 (s, 1H), 1.39 (s, 9H). m/z: 474. FT-IR (cm^{-1}): 3057w, 2962m, 2903w, 2868w, 1934vw, 1613s, 1602s, 1579s, 1557vs, 1528s, 1492vs, 1462m, 1431w, 1417w, 1389w, 1366w, 1299w, 1271w, 1253vw, 1213w, 1195w, 1161vw, 1122w, 1098w, 1071w, 1014w, 995vw, 964w, 953vw, 921vw, 858w, 841w, 826w, 792s, 756m, 714m, 688w. Elemental analysis (%): Calcd. for $C_{31}H_{26}N_2O_3$ (M = 474.55), C: 78.46, H: 5.52, N, 5.90; Found: C: 77.92, H: 5.57, N: 5.93%.

Synthesis of 1-(4-*tert*-butylphenyl)-3-(naphthalen-2-yl)propane-1,3-dione (HNBM). This compound was synthesized by reacted methyl 4-*tert*-butylbenzoate with 1-(naphthalen-2-yl)ethanone in the dry dimethylbenzene using NaH as the activator at room temperature for more than 72 h, the procedure was similar to the one above. ^1H NMR ($CDCl_3$), (δ ppm): 17.0 (s, 1H), 8.55 (s, 1H), 8.04–7.89 (m, 6H), 7.60–7.57 (m, 2H), 7.56–7.52 (d, 2H), 7.00 (s, 1H), 1.38 (s, 9H). m/z: 330. FT-IR (cm^{-1}): 1628w, 1599s, 1580s, 1524vs, 1503vs, 1463m, 1431w, 1387vw, 1367w, 1299w, 1267w, 1251vw, 1212w, 1193m, 1126w, 1111w, 1061vw, 1015w, 949vw, 911vw, 866vw, 846w, 822w, 794m, 757w, 696w. Elemental analysis (%): Calcd. for $C_{23}H_{22}O_2$ (M = 330.42), C: 83.60, H: 6.71; Found: C: 83.41, H: 6.66%.

General procedures for the preparation of Nd^{III} and Gd^{III} complexes. Nd complexes were synthesized according to the conventional method, described as follows:

A mixture of β-diketone (3.0 mmol), bath or phen (1.00 mmol) and NaOH (3.00 mmol) in 30 mL of THF was slowly added to 10 mL of $NdCl_3 \cdot 6H_2O$ (0.389 g, 1.00 mmol) ethanol solution under stirring. After being refluxed for 3 h, a yellow precipitate formed. It was filtered and recrystallized from 30 mL of THF and EtOH (1 : 1, v/v). The yields are about 85%.

$Nd(Carz\text{-}DBM)_3$(bath) Calcd. for $C_{105}H_{70}N_5O_6Nd \cdot 3\text{-}C_2H_5OH$ (M = 1780.191), C: 74.89, H: 4.30, N: 3.93, Found: C: 74.62, H: 4.62, N: 3.96%. FT-IR (cm^{-1}): 1597m, 1548m, 1502s, 1480s, 1451vs, 1421m, 1396m, 1362w, 1335w, 1314w, 1228w, 1228w, 1170w, 1120w, 1104w, 1071w, 1058w, 1026w, 1016w, 1001vw, 970vw, 916vw, 852vw, 832vw, 804vw, 804vw, 791vw, 767w, 749w, 723w, 701, 673w.

$Nd(CBO\text{-}DBM)_3$(bath) Calcd. for $C_{117}H_{94}N_5O_9Nd \cdot \text{-}C_2H_5OH$ (M = 1904.374), C: 75.05, H: 5.29, N: 3.68; Found: C: 74.96, H: 5.02, N: 3.54%. FT-IR (cm^{-1}): 3054w, 2940w, 2875w, 1592vs, 1548vs, 1522s, 1498vs, 1483vs, 1452vs, 1423s, 1398vs, 1348w, 1326w, 1304w, 1252m, 1218m, 1172m, 1154w, 1129vw, 1121vw, 1109vw, 1090vw, 1070w, 1058w, 1025w, 1001w, 969vw, 938vw, 926vw, 844w, 803w, 768m, 750m, 723m, 702w, 665vw.

$Nd(NBM)_3$(bath): Calcd. for $C_{93}H_{82}N_2O_6Nd$ (M = 1464.903), C: 76.25, H: 5.44, N: 1.91; Found: C: 76.79, H: 5.27, N: 2.24%. FT-IR (cm^{-1}): 1599m, 1587s, 1547s, 1521vs, 1496s, 1463w, 1440m, 1418vs, 1393m, 1363w, 1344w, 1309w, 1297w, 1269w, 1235vw, 1193w, 1121w, 1091vw, 1063vw, 1015w, 961vw, 933vw, 851w, 832w, 788m, 763w, 741w, 702w, 686w.

$Nd(t\text{-}ONBM)_3$(bath): Calcd. for $C_{119}H_{91}N_8O_9Nd \cdot 2.5\text{-}C_2H_5OH$ (M = 2036.4965), C: 73.13, H: 5.25, N: 5.50; Found: C: 72.77, H: 4.92, N: 5.81%. FT-IR (cm^{-1}): 3056w, 2963w, 2903w, 2868w, 1599s, 1590s, 1561s, 1517vs, 1486vs, 1462m, 1441s, 1422s, 1396s, 1344w, 1296w, 1271w, 1235vw, 1194w, 1153w, 1117w, 1096w, 1068w, 1015w, 962w, 859w, 843w, 789w, 759w, 741w, 717w, 703w, 677w.

Synthesis of the Gd complexes. For measurement of the triplet energy level of the ligand, gadolinium complexes were synthesized accordingly. The procedures were as follows:

To a 50 mL ethanol solution containing 1 mmol of $GdCl_3 \cdot 6H_2O$, a solution of 3 mmol β-diketone in THF and 1.0 mol L^{-1} NaOH (aq) was added dropwise under stirring. Then it was refluxed for 5 h and rotary evaporated. The obtained solid was washed with water several times. Finally it was recrystallized from THF–ethanol and the precipitate was filtered and dried.

$Gd(DBM)_3(H_2O)_2$: Calcd. for $C_{45}H_{37}O_8Gd$ (M = 863.033), C: 62.63, H: 4.32; Found: C: 61.91, H: 3.83%.

$Gd(DNM)_3(H_2O)_2$: Calcd. for $C_{69}H_{49}O_8Gd$ (M = 1163.393), C: 71.24, H: 4.25; Found: C: 71.24, H: 4.00%.

$Gd(CBO\text{-}DBM)_3(H_2O)_2$: Calcd. for $C_{93}H_{82}N_3O_{11}Gd$ (M = 1574.66), C: 70.93, H: 5.25, N: 2.67; Found: C: 71.27, H: 5.15, N: 2.67%.

$Gd(NBM)_3(H_2O)_2$: Calcd. for $C_{69}H_{67}O_8Gd$ (M = 1181.52), C: 70.14, H: 5.72; Found: C: 70.01, H: 5.86%.

$Gd(Carz\text{-}DBM)_3(H_2O)_2$: Calcd. for $C_{81}H_{58}N_3O_8Gd$ (M = 1358.59), C: 71.61, H: 4.30, N: 3.09; Found: C: 71.32, H: 4.53, N: 3.11%.

$Gd(t\text{-}ONBM)_3(H_2O)_2$: Calcd. for $C_{93}H_{79}N_6O_{11}Gd$ (M = 1613.91), C: 69.21, H: 4.93, N: 5.21; Found: C: 69.02, H: 5.10, N: 5.14%.

Results and discussion

UV-Vis and photoluminescent (PL) spectra of the free ligands and corresponding neodymium complexes

The UV-Vis absorption spectra of the free ligands in 1,2-dichloromethane are shown in Fig. 1(a). The maximum absorptions as well as their molar absorption coefficients are summarized in Table 1. It can be seen that the free ligands

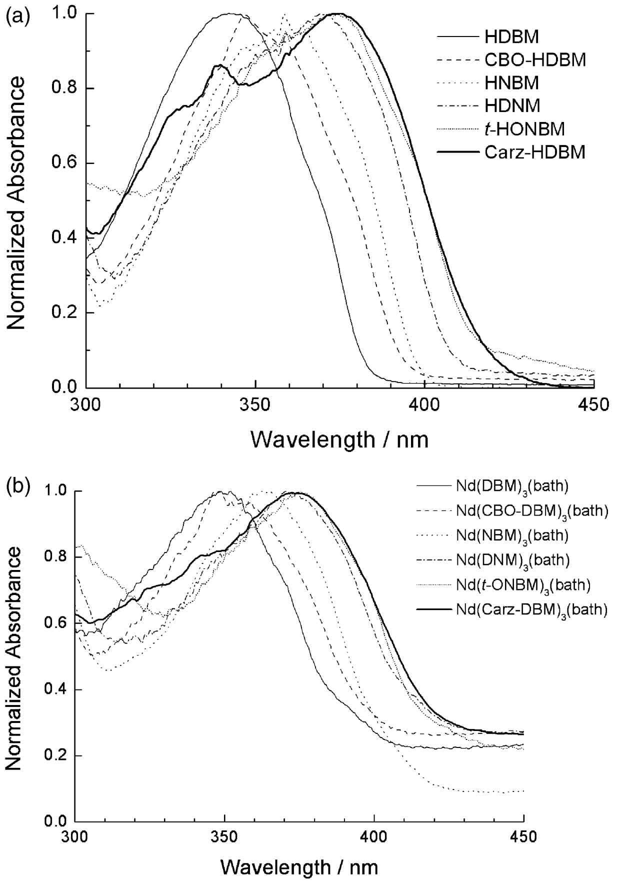


Fig. 1 UV-Vis absorption of the free ligands (a) and corresponding neodymium(III) complexes (b) in 1,2-dichloromethane.

have strong absorptions between 300–400 nm with extinction coefficients of the order of 10^4 $M^{-1}cm^{-1}$ magnitude, which mainly arise from the intramolecular π–π* transition. The absorptions of the new ligands Carz-HDBM and *t*-HONBM have the longest wavelengths (about 375 nm, *ca.* 26 700 cm^{-1}), which are red-shifted about 33 nm compared to HDBM due to the extended conjugation system. The UV-Vis absorption spectra of the Nd^{III} complexes were also obtained in 1,2-dichloromethane, and these are illustrated in Fig. 1(b). It is found that these complexes can also absorb strongly in the UV-Vis region with extinction coefficients of the same order as the free ligands. Comparing Fig. 1(a) with Fig. 1(b), it is clear that the shapes of the absorption spectra of the free ligands and those of their corresponding complexes are similar, suggesting that the coordination of the Nd^{3+} does not have a significant influence on the $^1\pi\pi^*$ state energy (0–0 transition).[7]

Table 1 Photophysical data of the free ligands

Ligand	λ_{max}/nm (ε/$M^{-1}cm^{-1}$)	λ_{max}^{em}/nm	Singlet energy/cm^{-1}	τ^a/ns
HDBM	342 (2.35×10^4)	434	~23 041	1.20
CBO-HDBM	347 (3.32×10^4)	433	~21 413	4.76
HDNM	371 (3.28×10^4)	467	~20 284	6.50
HNBM	359 (2.71×10^4)	493	~23 095	2.83
Carz-HDBM	375 (2.06×10^4)	485	~20 619	6.94
t-HONBM	375 (3.85×10^4)	507	~19 724	5.26

[a] τ: lifetime.

The PL spectra of the free ligands were measured using thin films on quartz at room temperature. All of them exhibit intense, short-lived fluorescence. The emissions are due to the deactivation of the lowest electronic singlet states. The maximum emissions of the six free ligands are in the order of CBO-HDBM ≈ HDBM < HDNM < Carz-HDBM < HNBM < *t*-HONBM, and range from 433 nm (CBO-HDBM) to 507 nm (*t*-HONBM), showing that the singlet energy level of the ligand can be lowered by extending the conjugation of the ligand or by the introduction of an electron donor or acceptor group. The maximum emission of CBO-HDBM is close to that of HDBM, which can be attributed to the fact that introduction of a donor group (carbazole) to HDBM through a flexible chain does not have an important influence on the π system of the molecule. The red shifted PL wavelengths of the other free ligands can be ascribed to the enlarged π system. The emissions of the complexes in the UV-Vis region were also measured using thin films on quartz at 298 K. It was found that the complexes can emit broad weak bands in the visible region. By comparing the emission intensities of the complexes to those of their corresponding free ligands, it was found that the ligand luminescence is greatly suppressed, showing that ligand-to-metal energy transfer takes place.[8] The PL spectra of free ligands and corresponding complexes are given in Fig. 2.

Lifetime of the free ligands

Lifetime experiments show that the decay curves of the free ligands can be fitted to a biexponential decay, except for that of *t*-HONBM (which can be fitted to a monoexponential decay format). The average lifetimes of them are in the nanosecond timescale within the range of 1.0–7.0 ns (Table 1). This indicates that the main energy transfer process in the present complexes may be through the triplet state of the ligands.

Triplet energy level of the coordinated ligands

Since the band gap between the ground state and the first excited state of gadolinium is very large due to its half-full electronic configuration, the energy absorbed by the ligand can

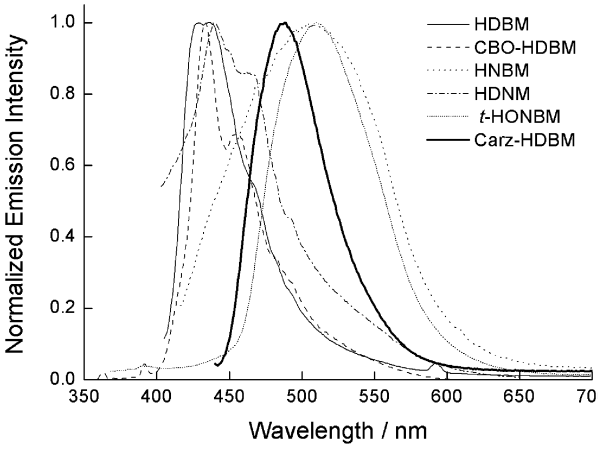


Fig. 2 PL spectra of the free ligands.

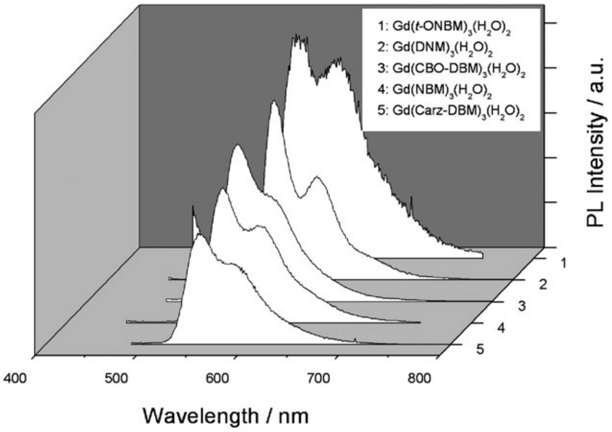


Fig. 3 PL spectra of Gd complexes in the solid state at 77 K.

not be transferred to the central ion. In this case, the phosphorescence observed should be belonged to the coordinated ligand and consequently the triplet energy of the coordinated ligand can be estimated.[9] The phosphorescent spectra of the Gd complexes from thin films on quartz at 77 K show strong emissions composed of two distinct bands (Fig. 3), corresponding to the emission from the lowest two triplet states of β-diketonate ligand molecules.[7] The long lifetime values measured (typically > 70 μs) are consistent with emission from a characteristic triplet state.[10] To estimate the triplet energy level, we take 0–0 transition as a measurement. From the energy vibration feature of the phosphorescence bands of the Gd^{3+} complexes, the triplet energy state of the ligands has been estimated to be in the range of 20 410–18 520 cm^{-1} (Table 2). According to Dexter's theory,[11] the suitability of the energy difference $\Delta E = E_L - E_{Ln}$ between the first excited energy level of the Ln^{3+} ion E_{Ln}(11 500 cm^{-1} for Nd^{+3} $^4F_{3/2}$) and the triplet state energy level of the ligand E_L is a critical factor for efficient energy transfer. If the triplet state energy level of the ligand is too high, then the energy transfer rate constant will decrease due to the diminishing in the overlap between the donor and the acceptor. On the other hand, if the energy level of the ligand is too low, energy back transfer from the central ion to the ligand will take place.

In the case of these complexes, energy transfer takes place from the triplet excited state, because the singlet state of the ligands is depopulated very fast to the triplet state and Dexter-type energy transfer is the dominant mechanism.[12] Applying these considerations to the β-diketonates, it can be expected that *t*-HONBM will be the best ligand for sensitizing Nd^{3+} emission.

Table 2 Triplet energy levels of the coordinated ligands

Complex	λ_{em}/nm	T_1/cm^{-1}	ΔE^a/cm^{-1}
$Gd(DBM)_3(H_2O)_2$	535	20 410	8910
$Gd(CBO\text{-}DBM)_3(H_2O)_2$	548, 585	19 080	7580
$Gd(DNM)_3(H_2O)_2$	564, 606	18 280	6780
$Gd(NBM)_3(H_2O)_2$	554, 589	18 870	7370
$Gd(Carz\text{-}DBM)_3(H_2O)_2$	550, 589	18 980	7480
$Gd(t\text{-}ONBM)_3(H_2O)_2$	570, 609	18 520	7020

[a] $\Delta E = T_1 - 11\,500(^4F_{3/2})$.

Sensitized NIR emission

Fig. 4 illustrates emissions in the NIR region from the complexes upon excitation of the antenna chromophore. All of the synthesized complexes show the characteristic emission bands of the Nd^{3+} ion in the NIR region, which are assigned to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ (880 nm), $^4F_{3/2} \rightarrow {}^4I_{11/2}$ (1060 nm) and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ (1330 nm) transitions, respectively. Among them, the band at 1060 nm is dominant and is most important because it is potentially applicable to laser emission. The unsymmetrical multiple components and the different relative intensities of three characteristic bands may be ascribed to the various coordination environments of Nd^{3+} in amorphous solid matrices[13] and the unsymmetrical nature of the ligands.[14]

Decay curves of these complexes could be fitted biexponentially by monitoring at about 1060 nm in the powder form with a domain lifetime of the order of μs, as shown in Table 3. The shortest lifetime corresponds most probably to a hydrated species (the complexes are quite hygroscopic). Therefore only the longer lifetime has been taken into consideration. It can be seen from Table 3 that $Nd(CBO\text{-}DBM)_3(bath)$ has the shortest lifetime (14.0 μs) while $Nd(t\text{-}ONBM)_3(bath)$ has the longest one (24.9 μs), the latter are almost twice that of the former. By comparing our results with the terphenyl[15] or polydentate terphenylene-functionalized[14] Nd^{III} complex in both the DMSO (1.2 μs for the former and 1.4 μs for the latter) and DMSO-d_6 (both are 2.5 μs) media, it can be concluded that by direct coordination of the antenna chromophore to the lanthanide ion, the lifetime can be greatly improved. The longer lifetimes are beneficial in the optical amplification process. Since the observed rate constant k is the sum of the natural radiative rate constant (k_0) and the non-radiative rate constant k_{nr}, and as the k_0 for Nd^{3+} is 4000 s^{-1}, it is obvious that for the near-IR emitting ions, k is dominated by non-radiative deactivation of the luminescent state. It can be inferred that the non-radiative deactivation rate constant of the complexes are in the order: $Nd(CBO\text{-}DBM)_3(bath) > Nd(DBM)_3(bath) > Nd(DBM)_3(phen) > Nd(Carz\text{-}DBM)_3(bath) > Nd(DNM)_3(bath) > Nd(t\text{-}ONBM)_3(bath)$.

As many papers have suggested, the intrinsic quantum yield (φ_{int}) can be estimated from eqn (1),[16] in which τ is the

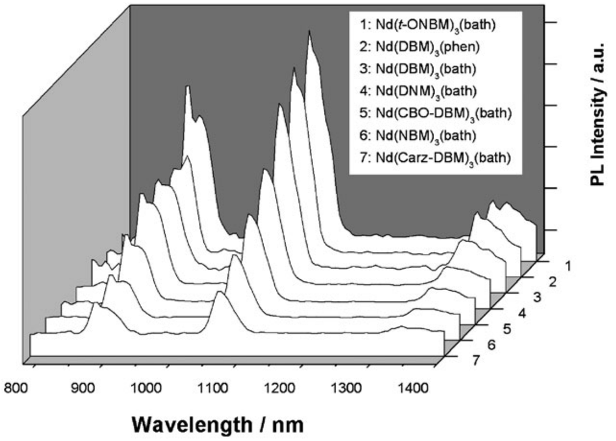


Fig. 4 NIR photoluminescence of synthesized complexes in the solid state.

Table 3 Lifetime and intrinsic quantum efficiency data of the complexes

Complex	τ/μs (at 1060 nm)	$\varphi_{\mathrm{int}}{}^{a}/10^{-2}$	$k/10^4\ \mathrm{s}^{-1}$
Nd(DBM)$_3$(phen)	0.707 ± 0.002 (62.9%) 21.5 ± 0.6 (37.1%)	8.6 ± 0.2	4.7 ± 0.1
Nd(DBM)$_3$(bath)	0.670 ± 0.003 (52.3%) 20.2 ± 0.4 (47.7%)	8.1 ± 0.1	4.94 ± 0.09
Nd(CBO-DBM)$_3$(bath)	0.803 ± 0.004 (28.6%) 14.0 ± 0.1 (71.4%)	5.60 ± 0.03	7.14 ± 0.04
Nd(DNM)$_3$(bath)	0.845 ± 0.005 (11.6%) 24.5 ± 0.2 (88.4%)	9.81 ± 0.09	4.08 ± 0.04
Nd(NBM)$_3$(bath)	—	—	—
Nd(Carz-DBM)$_3$ (bath)	0.864 ± 0.005 (7.8%) 24.2 ± 0.2 (92.2%)	9.69 ± 0.09	4.13 ± 0.04
Nd(*t*-ONBM)$_3$ (bath)	0.994 ± 0.008 (6.7%) 24.9 ± 0.2 (93.3%)	9.95 ± 0.07	4.02 ± 0.03

[a] φ_{int}: intrinsic quantum yield $= \tau/\tau_0$, $\tau_0 = 0.25$ ms.

observed emission lifetime and τ_0 is the radiative or natural lifetime (0.25 ms from the literature), but this refers only to the quantum yield of the lanthanide-based emission process and takes no account of the factors such as intersystem crossing and energy-transfer process.

$$\varphi_{\mathrm{int}} = \tau/\tau_0 \tag{1}$$

The intrinsic quantum yields of the title complexes are listed in Table 3, and are in the reverse order to that of the non-radiative deactivation rate constants of the complexes. Obviously, Nd(*t*-ONBM)$_3$(bath) has achieved the lowest non-radiative deactivation rate constant and the highest intrinsic QE.

Conclusion

We have synthesized a series of neodymium complexes consisting of electron-donating or withdrawing moieties. The PL spectra of these complexes show characteristic emission in the NIR region with unsymmetrical profiles and different relative intensities. The singlet energy levels as well as the triplet levels of the ligands have been estimated. The new complexes have lifetimes on the μs timescale and Nd(*t*-ONBM)$_3$(bath) complex has the longest lifetime and thus the highest intrinsic efficiency. It may be related to the fact that the lowest triplet energy level of the *t*-HONBM ligand is closer to $^4F_{3/2}$ of the Nd^{3+} ion compared to the other ligands, therefore it can have good energy transfer to the central ion. This fact indicates the near infrared emission of neodymium complexes can be promoted by modifying the ligand and consequently tuning the singlet and triplet energy levels.

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