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Energy transfer pathways in the carbazole functionalized β-diketonate europium complexes†

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Two novel Eu^{3+} complexes $Eu(CDBM)_3 \cdot 2H_2O$ and $Eu(CCDBM)_3 \cdot 2H_2O$ have been synthesized (CDBM = 1-(4-(9-carbazol)phenyl)-3-phenyl-1,3-propanedione, CCDBM = 1-((4-(9-carbazol)methyl)phenyl)-3-phenyl-1,3-propanedione). $Eu(CDBM)_3 \cdot 2H_2O$ showed strong internal ligand charge transfer (ILCT) fluorescence and sensitized emission of Eu^{3+}. Due to the charge transfer character, the fluorescence band of CDBM shifted from 403 nm in cyclohexane to 559 nm in acetonitrile. Photophysical studies demonstrated that no energy was migrated from the ILCT excited state of the ligands to Eu^{3+}, and that Eu^{3+} was sensitized by the triplet state which was localized in the 1,3-diphenyl-1,3-propanedione (DBM) part. The quantum efficiencies of Eu^{3+} in the three complexes are in the order $Eu(DBM)_3 \cdot 2H_2O > Eu(CCDBM)_3 \cdot 2H_2O > Eu(CDBM)_3 \cdot 2H_2O$ in both solution and the solid state. The energy transfer pathways in the three Eu^{3+} complexes were discussed in detail. Based on the systematic photophysical studies, a new guideline for the organo-lanthanide light emitting materials has been proposed: ILCT should be avoided during molecular modification.

Introduction

Due to the forbidden character of the intra-4f transitions,[1] luminescent lanthanide ions exhibit long lifetime and high color purity emissions, which have made them ideally suited for various applications such as fluorescent probes,[2] optical signal amplifiers[3] and organic light-emitting diodes.[4,5] Unfortunately, for the same reason, the absorption coefficients of lanthanide ions are very low (less than 10 M^{-1} cm^{-1}).[6] To overcome this problem, organic chromophores which have much larger absorption coefficients ($\sim 10^4$ M^{-1} cm^{-1}) are usually coordinated to lanthanide ions to form lanthanide complexes. In this case, the sensitization process of the lanthanide ions generally consists of three steps: the excitation of the singlet excited state of the ligand, the subsequent intersystem crossing to its triplet state and energy transfer from the triplet state to the emission lanthanide ion.[1,6–8] On the other hand, direct energy transfer from the singlet excited state of the ligand to the lanthanide ion has also been observed.[9,10] Recently, sensitization of Eu^{3+} through charge transfer (CT) excited states of the ligand has also been reported.[11]

No matter which pathway the sensitization processes take, the energy absorbed by the ligand should be transferred to the lanthanide ions as much as possible to obtain a high quantum yield. However, this factor is sometimes ignored in the design of new organo-lanthanide materials. For instance, the carbazole functional group is usually incorporated into the β-diketonate ligands to improve the hole transfer mobility of lanthanide complexes.[12] Because the carbazole functional group is an electron donor and the carbonyl groups in β-diketonates can be regarded as electron acceptors, this modification may lead to the internal ligand charge transfer (ILCT) process. Unfortunately, most of the relevant papers did not investigate the energy transfer pathways in these modified complexes. Whether the energy can be transferred from the ILCT excited states to the lanthanide ion still remains an unsolved problem.

In order to investigate how these modifications influence the sensitization process in a lanthanide complex, we synthesized two new β-diketonate ligands by introducing a carbazole moiety into a classic 1,3-diphenyl-1,3-propanedione ligand (DBM) by different linkage (Scheme 1). In CDBM, the carbazole fragment was directly linked to DBM, while in CCDBM, the conjugation between carbazole fragment and the DBM part was interrupted by a $–CH_2–$ group to avoid the internal ligand charge transfer process. Europium complexes were prepared with these ligands because the triplet state energy level of DBM matched the receiving state of Eu^{3+} very well. Photophysical studies of these complexes in both solutions and the solid state revealed that Eu^{3+} could not be sensitized by the ILCT excited states of CDBM. The sensitization process still took the triplet pathway.

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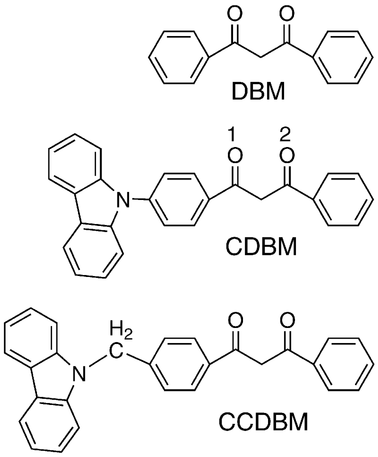


Scheme 1 Molecular structures of the three β-diketonate ligands.

Experimental

Synthesis of the ligands

DBM was purchased from ACROS and used as received. CDBM was synthesized according to our other paper.[13] The synthetic procedure of CCDBM was almost the same as that of CDBM except that 4-fluorobenzonitrile was replaced by 4-(bromomethyl)benzonitrile. See ESI† for the ^{1}H NMR data of CDBM and CCDBM.

Synthesis of the complexes

$Eu(DBM)_3 \cdot 2H_2O$: To a 50 ml round-bottomed flask, DBM (0.672 g, 3.0 mmol), NaOH (0.120 g, 3.0 mmol) were mixed in 10 ml ethanol and refluxed for 10 min, then it was added dropwise to 10 ml ethanol solution of $EuCl_3 \cdot 6H_2O$ (0.403 g, 1.1 mmol). The mixture was refluxed for 2 h and then poured into water. The crude product was obtained by filtration and purified by recrystallization in a mixture of THF–ethanol. All the other complexes were synthesized by the same procedure. The gadolinium complexes were synthesized to investigate the triplets of the ligands. All the complexes were characterized by element analysis (see ESI† for details).

Photophysical measurements

Absorption spectra were recorded with Shimadzu UV 3100 spectrophotometer, and steady state fluorescence spectra were taken with an Edinburgh Instruments FLS920 spectrometer. All the fluorescence spectra were corrected for the instrument response using a correction file provided by the manufacturer.

Lifetimes of Eu^{3+} were measured with Edinburgh Instruments FLS920 based on the time correlated single photon counting technology. A microsecond flash lamp was used as the excitation source and the signals were detected with a photomultiplier (Hamamatsu R955). Lifetimes of the ligands longer than 1 ns were detected with the same equipment using a hydrogen filled nanosecond flash lamp as the excitation source. A picosecond lifetime spectrometer Edinburgh Instruments Lifespec-Red was used to measure lifetimes shorter than 1 ns. In this equipment, a diode laser (operating at 372 nm, pulse duration 69 ps) controlled by a picosecond light pulser (Hamamatsu PLP-10) was used as excitation source. By processing the lifetime data with the F900 reconvolution software, a time resolution better than 1 ns for FLS920 and 20 ps for Lifespec-Red can be achieved.

Phosphorescence spectra of the gadolinium complexes were measured by mounting the samples into a cryostat (Oxford Instruments, Optistat DN) which had been cooled by liquid nitrogen to 77 K. A methanol–ethanol (1 : 4) mixture was chosen as the solvent to form a transparent glass at low temperatures.

The quantum yields of the complexes in solution were determined using quinine sulfate in 0.05 M H_2SO_4 as a standard (ϕ_f = 0.546 at 25 °C).[14,15] The quantum yields of the complexes in the solid state were measured with an integrating sphere[16,17] using a mercury lamp (365 nm) as the excitation source and a photodiode as the detector. The spectral response of the sphere and the photodiode were not calibrated, so the results can only be used in comparison.

Computational details

The calculations were carried out using the MOPAC6_RM1 package.[18] The geometry optimization of the three Eu^{3+} complexes have been done employing a semiempirical Sparkle/AM1 model.[19,20]

Results and discussion

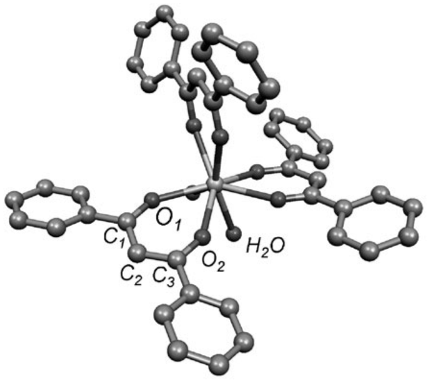
Molecular geometry

The optimized structures of the three Eu^{3+} complexes are shown in Fig. 1. Selected bond lengths around the central ion are tabulated in Table 1. It has been reported that the accuracy of the optimizations of the Eu^{3+} complexes using Sparkle/AM1 model is comparable with those using *ab initio* calculations.[21] Because the crystal structures of the three complexes are not available, we also optimized a $Eu(DBM)_3 \cdot phen$ complex,[22] in which the two water molecules are replaced by a neutral phenanthroline ligand. From Table 1 we can see that the discrepancies between the optimized and experimental structures of $Eu(DBM)_3 \cdot phen$ are within 0.03 Å, thus this model is accurate enough to describe our systems.

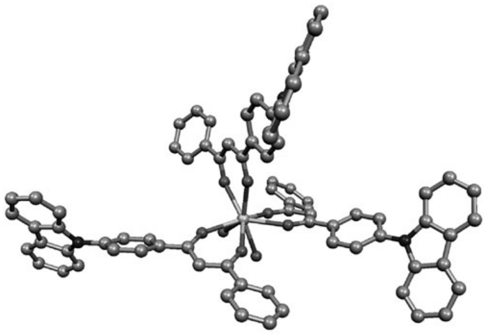
The coordination environments of the three complexes are all distorted square antiprisms. All the complexes belong to the C_1 point-group. From $Eu(DBM)_3 \cdot 2H_2O$ to $Eu(CDBM)_3 \cdot 2H_2O$ and $Eu(CCDBM)_3 \cdot 2H_2O$, the incorporation of the carbazole group does not change the coordination environment of Eu^{3+} significantly. The geometries of the first coordination sphere in the three complexes remain almost the same. This result indicates that the structure difference among the three Eu^{3+} complexes is not responsible for the big discrepancy of the Eu^{3+} emission (see the following text).

Absorption

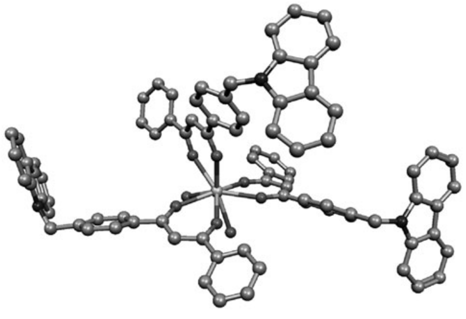
The absorption spectra of the complexes are very similar to that of the corresponding ligands, indicating that the singlet excited states of the ligands are not significantly affected by the complexation to the Eu^{3+} ion[6] (see Fig. S1 in ESI†). DBM shows a broad and structureless band centered at 350 nm. CDBM and CCDBM both have a sharp and structured band around 292 nm. We assigned this band to the locally excited



$Eu(DBM)_3·2H_2O$



$Eu(CDBM)_3·2H_2O$



$Eu(CCDBM)_3·2H_2O$

Fig. 1 Optimized geometries of the three Eu^{3+} complexes using the Sparkle/AM1 model. Hydrogen atoms are omitted for clarity.

state of carbazol moiety.[13] Compared with DBM, the broad and strong absorption band of CDBM is red shifted to 380 nm. Around 330 nm, CDBM shows a small and narrow shoulder. We assigned these two absorption bands to the charge transfer (CT) excited states corresponding to electron transfer from carbazole moiety to carbonyl group 2 and 1 (see Scheme 1), respectively.[13]

In the region from 300 to 400 nm, the absorption spectrum of CCDBM is very similar to that of DBM, except that a narrow and sharp band arises at 330 nm. Compared with CDBM, the disappearance of the broad band at 380 nm and the existence of the narrow band at 330 nm indicate that only the CT excited state related to carbonyl group 1 exists in CCDBM. One possible explanation for this phenomenon is that in CCDBM, the distance between carbazole fragment and carbonyl group 2 gets too long to form a CT excited state.

Excitation

The excitation spectra together with the absorption spectra of the three Eu^{3+} complexes are depicted in Fig. 2. The excitation spectra of $Eu(DBM)_3·2H_2O$ and $Eu(CCDBM)_3·2H_2O$ monitored at 611 nm (corresponding to $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}) closely resemble the corresponding absorption spectra (top and bottom panel in Fig. 2). In contrast, the excitation spectrum of $Eu(CDBM)_3·2H_2O$ monitored at 611 nm lost some features around 340 nm comparing with the absorption spectrum and the excitation spectrum monitored at the ILCT emission maximum (see the arrows in Fig. 2). This indicates that in $Eu(DBM)_3·2H_2O$ and $Eu(CCDBM)_3·2H_2O$, the Eu^{3+} ions are excited *via* the whole β-diketonate ligands, while the situation in $Eu(CDBM)_3·2H_2O$ is somewhat different due to the different conjugation system.

Sensitized Eu^{3+} emission

Upon excitation near the absorption maximum of the ligands, the three complexes all showed characteristic narrow band emissions of Eu^{3+} corresponding to the $^5D_0 \rightarrow {}^7F_J$ (J = 0–4) transitions (Fig. 3). The emission bands at 580 and 650 nm are very weak because their corresponding transitions $^5D_0 \rightarrow {}^7F_{0,3}$ are forbidden both in magnetic and electric dipole schemes.[23] The intensity of the emission band at 592 nm is relatively strong and independent of the coordination environment because the corresponding transition $^5D_0 \rightarrow {}^7F_1$ is a magnetic transition; on the contrary, the $^5D_0 \rightarrow {}^7F_2$ transition is an induced electric dipole transition and its corresponding intense emission at ~615 nm is very sensitive to the coordination environment.[23]

The energy transfer pathways

CDBM is highly fluorescent, DBM is non-fluorescent and CCDBM showed very weak fluorescence in all solvents (not shown). After coordinating with Eu^{3+}, the ligand fluorescence band shapes did not change very much.

At first glance to the fluorescence spectra of $Eu(CDBM)_3·2H_2O$, one may note that the intensity of the Eu^{3+} emission varies as the ligand emission band shifts

Table 1 Selected bond lengths (Å) around the central Eu^{3+} ion

	$Eu–O_1$[a]	$Eu–O_2$	$Eu–H_2O$	$C_1–O_1$	$C_3–O_2$	$C_1–C_2$	$C_2–C_3$
$Eu(DBM)_3·2H_2O$	2.377	2.375	2.399	1.290	1.291	1.410	1.409
$Eu(CDBM)_3·2H_2O$	2.377	2.376	2.398	1.290	1.291	1.409	1.410
$Eu(CCDBM)_3·2H_2O$	2.380	2.380	2.398	1.291	1.290	1.407	1.410
$Eu(DBM)_3·phen$	2.380	2.385	—	1.288	1.289	1.409	1.409
$Eu(DBM)_3·phen$[b]	2.351	2.383	—	1.267	1.271	1.407	1.401

[a] See Fig. 1 for atom numbering. [b] Crystal structure from ref. 22.

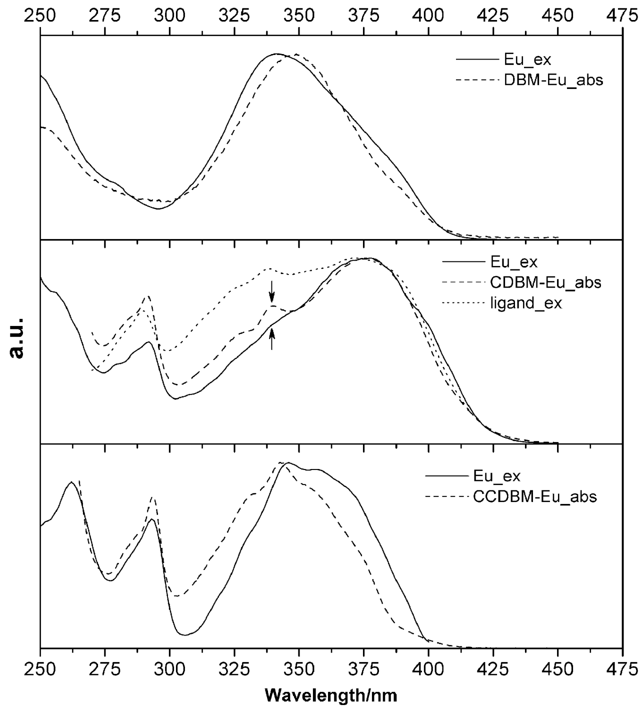


Fig. 2 The excitation and absorption spectra of the three complexes in CH_2Cl_2. The solid lines are the excitation spectra monitored at 611 nm; The dotted line in the middle panel is the excitation spectrum monitored at 511 nm, which is the emission maximum of CDBM in CH_2Cl_2.

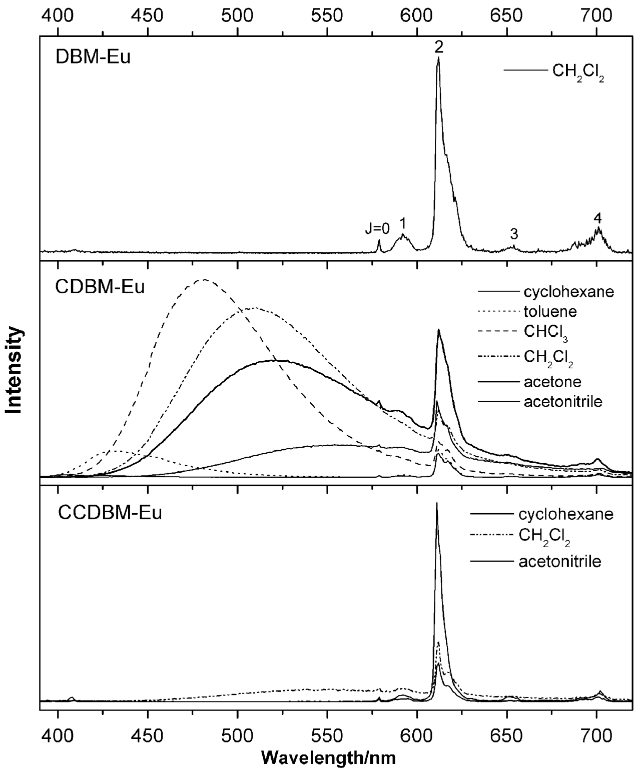


Fig. 3 The corrected emission spectra of the three complexes recorded in solution. Upper panel: emission spectrum of 10^{-5} M $Eu(DBM)_3 \cdot 2H_2O$ in CH_2Cl_2; middle panel: emission spectra of 10^{-5} M $Eu(CDBM)_3 \cdot 2H_2O$ in various solvents; bottom panel: emission spectra of 10^{-5} M $Eu(CCDBM)_3 \cdot 2H_2O$ in cyclohexane, CH_2Cl_2 and acetonitrile.

(Fig. 3, middle panel). Since sensitization of lanthanide ion through the singlet pathway has been proposed theoretically[24] and observed experimentally,[9,10] it is reasonable to assume that the ILCT excited state of CDBM may be involved in the sensitization process of Eu^{3+}. Generally speaking, two mechanisms are invoked in the sensitization process of Ln^{3+} ion: Dexter (exchange) mechanism[25] and Förster (dipole–dipole) mechanism.[1,26] According to these two mechanisms, the energy-transfer rate is proportional to the overlap of the ligand emission spectrum and the lanthanide absorption spectrum.[1,24] It is very probable that in some solvents, the energy level of the ILCT excited state of CDBM may perfectly match the receiving states of Eu^{3+} and efficient energy transfer may occur. In order to expose the energy transfer pathways, we studied the photophysical properties of $Eu(CDBM)_3 \cdot 2H_2O$ and $Gd(CDBM)_3 \cdot 2H_2O$ in several solvents. The results are listed in Table 2. The fluorescence properties of the free ligand are also presented to study the heavy atom effect of the lanthanide ions. Gd^{3+} can not receive energy from most organic ligands because the energy level of its lowest excited state is too high (about 32 000 cm^{-1}).[7,9] Thus Gd^{3+} complex can be used as a model to study the ligand fluorescence in the presence of heavy atom effect but in the absence of energy transfer. If energy transferred from the ILCT excited states of CDBM to Eu^{3+} in certain solvents, quantum yield reduction and lifetime shortening should be observed for CDBM in the Eu^{3+} complex compared with those in the Gd^{3+} complex. However, both quantum yields and lifetimes of CDBM are almost the same in both complexes in all solvents (Table 2).

Table 2 Photophysical properties of CDBM as a free ligand and in Gd^{3+}, Eu^{3+} complexes in various solvents

		τ/ns			Q_s		
Solvent	Band position /1000 cm^{-1}	Free ligand	Gd	Eu	Free ligand	Gd	Eu
Acetonitrile	17.89	3.88[a]	3.89	3.93	0.036[b]	0.014	0.013
Acetone	19.19	5.21	5.22	5.33	0.073	0.043	0.041
CH_2Cl_2	19.65	5.54	5.49	5.55	0.154	0.069	0.062
$CHCl_3$	20.70	3.19	3.17	3.13	0.131	0.094	0.094
THF	21.23	2.04	1.95	1.89	0.074	0.051	0.054
Diethyl ether	22.83	0.18	0.17	0.17	0.015	0.007	0.006
Toluene	23.26	0.13	0.14	0.12	0.013	0.010	0.009
Cyclohexane	24.81	0.04	0.03	0.03	0.001	0.0006	0.0008

[a] Error ±2%. [b] Error ±5%.

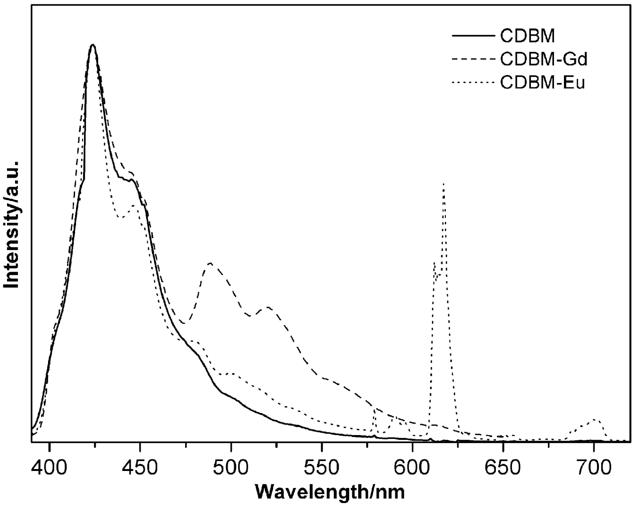


Fig. 4 The emission spectra of CDBM (solid line), Gd(CDBM)$_3 \cdot 2H_2O$ (dashed line) and Eu(CDBM)$_3 \cdot 2H_2O$ (dotted line) at 77 K in methanol–ethanol (1 : 4) glass.

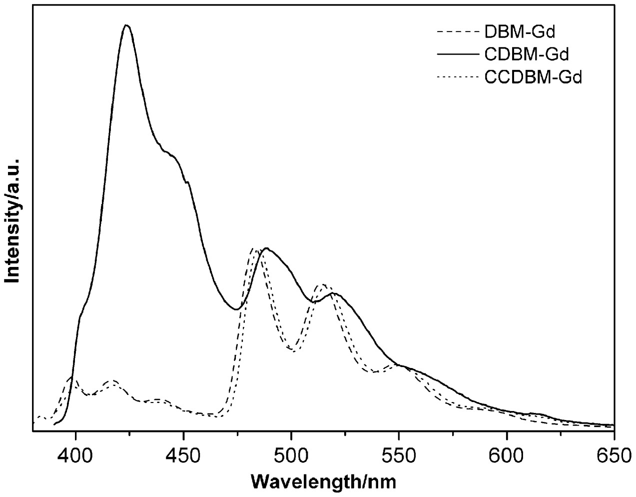


Fig. 5 Phosphorescence spectra of Gd(DBM)$_3 \cdot 2H_2O$ (dashed line), Gd(CDBM)$_3 \cdot 2H_2O$ (solid line) and Gd(CCDBM)$_3 \cdot 2H_2O$ (dotted line).

These data imply that Eu^{3+} can not be sensitized by the ILCT excited state of CDBM. Another striking result is that the lifetimes of the free ligand remained all the same upon coordination with Gd^{3+} and Eu^{3+}. That is to say, there is no detectable heavy atom effect for the ILCT excited state of CDBM.

It is also noteworthy that the ILCT fluorescence quantum yields of CDBM decreased dramatically after coordination with Gd^{3+} and Eu^{3+} (Table 2). We will explain this confusing phenomenon in the following text.

If the sensitization process does not take the singlet pathway, it must have taken the triplet pathway. Low-temperature spectra of free CDBM, Gd(CDBM)$_3 \cdot 2H_2O$ and Eu (CDBM)$_3 \cdot 2H_2O$ have been measured to prove this point of view. The results are shown in Fig. 4. The three profiles all showed strong emission bands at ~423 nm, which was confirmed to be a fluorescence band by lifetime measurements (about 2 ns). In the spectrum of Gd(CDBM)$_3 \cdot 2H_2O$, a moderately strong emission band emerged at ~489 nm. Lifetime measurements proved it to be a phosphorescent band (lifetime 1.6 ms). In the case of Eu(CDBM)$_3 \cdot 2H_2O$, this phosphorescence band almost completely disappeared and the characteristic narrow emission bands of Eu^{3+} appeared (Fig. 4). This result demonstrated that the sensitization process of Eu^{3+} still took the triplet pathway. As a consequence, the Dexter type energy transfer should be the dominant mechanism in the sensitization process of Eu^{3+}.[24,27]

However, there is still one confusing problem left: where does the phosphorescence band come from? In the first part of this section, we have already concluded that the coordinating lanthanide ions have little heavy atom effects on the ILCT excited states of CDBM. Obviously the ILCT excited state is not the origin of the phosphorescence band. We noticed that the triplet state energy level of CDBM (20 450 cm^{-1}) lies very close to that of DBM (20 520 cm^{-1}).[28] It is very likely that the triplet excited state of CDBM still localizes in the DBM fragment. To confirm this assumption, we recorded the phosphorescence spectra of Gd(DBM)$_3 \cdot 2H_2O$ and Gd(CCDBM)$_3 \cdot 2H_2O$, the results together with that of Gd(CDBM)$_3 \cdot 2H_2O$ are illustrated in Fig. 5. One can find from Fig. 5 that Gd(DBM)$_3 \cdot 2H_2O$ displays weak fluorescence band around 420 nm (lifetime 1 ns) and strong phosphorescence band around 500 nm (1.8 ms). Both bands show fine structures and closely resembled each other in band shape. The triplet state energy level of Gd(DBM)$_3 \cdot 2H_2O$ was determined to be 20 700 cm^{-1} from the 0–0 transition of the phosphorescence band. This result agrees well with that reported in literature.[28] In the spectrum of Gd(CDBM)$_3 \cdot 2H_2O$, the ILCT fluorescence becomes dominate and the intensity of the phosphorescence band gets relatively weak. However, despite the dissimilarity in relative intensity, the phosphorescence band shape and the 0–0 transition band position of Gd(CDBM)$_3 \cdot 2H_2O$ (20 450 cm^{-1}) are almost the same as that of Gd(DBM)$_3 \cdot 2H_2O$. This result suggests that the incorporation of the carbazole functional group into DBM only causes the ILCT fluorescence. It does not affect the triplet energy level of DBM at all. In fact, the population of the triplet states gets smaller because most of the energy has been released in the form of ILCT fluorescence. Generally speaking, the triplet state energy level of the ligands will decrease if the conjugation system is enlarged. This result indicates that the conjugation system of CDBM only has been slightly enlarged compared with that of DBM. The optimized molecular structure of Eu(CDBM)$_3 \cdot 2H_2O$ also supported this conclusion. As can be seen from Fig. 1, the carbazole moiety and the DBM part are not coplanar. The carbazole fragment is twisted about 50° with respect to the phenyl ring. As a result, the conjugation system of CDBM remains almost the same as that of DBM.

Since the D–π–A system has been interrupted by a –CH$_2$– group, the ILCT fluorescence of CCDBM has been greatly suppressed and the phosphorescence spectrum closely resembles that of DBM (Fig. 5). This result further supports our conclusion.

As already discussed above, the introducing of carbazole functional group to DBM depopulates the triplet excited states, through which the Eu^{3+} is sensitized. Based on this

Table 3 The overall quantum yields Q_s (%) of Eu^{3+} in the three complexes in various solvents

Solvents	DBM–Eu	CDBM–Eu	CCDBM–Eu
Acetonitrile	0.63	0.10	0.47
CH_2Cl_2	0.31	0.08	0.15
Cyclohexane	1.94	0.07	0.29

conclusion, we further supposed that the ILCT fluorescence which was caused by incorporation of carbazole group into DBM impaired the sensitization efficiency of Eu^{3+} in the $Eu(CDBM)_3 \cdot 2H_2O$ system. The overall quantum yields of Eu^{3+} in the three complexes are listed in Table 3. We can see from Table 3 that the overall quantum efficiency of Eu^{3+} are in the order $Eu(DBM)_3 \cdot 2H_2O > Eu(CCDBM)_3 \cdot 2H_2O > Eu(CDBM)_3 \cdot 2H_2O$ in all solvents.

Now it is clear that the introducing of carbazole functional group impaired the whole sensitization process of Eu^{3+} in the $Eu(CDBM)_3 \cdot 2H_2O$ system, but we still do not know exactly which steps are disturbed in the overall process. The overall efficiency of the lanthanide emission depends on three factors:

$$\Phi = \Phi_{isc}\Phi_{et}\Phi_{Ln} \qquad (1)$$

where Φ_{isc} is the singlet to triplet intersystem crossing efficiency, Φ_{et} is the energy transfer quantum yield and Φ_{Ln} is the intrinsic luminescence quantum yield.[7,29] The intrinsic luminescence quantum yield of Eu^{3+} (Φ_{Ln}) can be determined by eqn (2):

$$\Phi_{Ln} = \tau_{obs}/\tau_r \qquad (2)$$

in which τ_{obs} is the observed lifetime of Eu^{3+} and τ_r stands for the radiative lifetime of Eu^{3+}. The radiative lifetime τ_r of $^5D_0$ state can be calculate according to the procedures in literature.[30,31] The calculated τ_r and Φ_{Ln} of Eu^{3+} in various solvents are listed in Table 4. It can be seen from Table 4 that the differences between the intrinsic quantum yields are relatively small. This can not be responsible for the big discrepancy in the overall quantum yields. According to the Dexter mechanism, the energy transfer quantum yield Φ_{et} is determined by two factors: one is the distance between the ligand and the lanthanide ion; the other one is the spectra overlap of the ligand phosphorescence spectrum and the absorption spectrum of the lanthanide ion. As discussed above, the geometry of the central $Eu(DBM)_3 \cdot 2H_2O$ part in the three complexes remains almost the same. Therefore, the distances between the ligands and the lanthanide ions can be regarded as the same because the outer carbazole moieties are not involved in the sensitization process. On the other hand, the phosphorescence spectra are very similar, thus the spectra overlaps are nearly identical, too. For these two reasons, Φ_{et} are also excluded for the possible explanation. In the case of $Eu(DBM)_3 \cdot 2H_2O$, the Φ_{isc} should be close to unity because the phosphorescence is dominant in the low-temperature emission spectrum of $Gd(DBM)_3 \cdot 2H_2O$ (Fig. 5).[33] However, the Φ_{isc} of $Eu(CDBM)_3 \cdot 2H_2O$ is far from unity because the intersystem crossing efficiency for the ILCT excited state is very low. This can be clearly seen from the low-temperature emission spectrum of $Gd(CDBM)_3 \cdot 2H_2O$, in which the ILCT fluorescence dominates (Fig. 5). Thus, we concluded that the incorporation of the carbazole group reduced the Φ_{isc} of CDBM and further impaired the whole sensitization process of Eu^{3+} in the $Eu(CDBM)_3 \cdot 2H_2O$ system. Although the phosphorescence spectrum of $Gd(CCDBM)_3 \cdot 2H_2O$ is very close to that of $Gd(DBM)_3 \cdot 2H_2O$, the overall quantum efficiency of Eu^{3+} in $Eu(CCDBM)_3 \cdot 2H_2O$ is still lower than that in $Eu(DBM)_3 \cdot 2H_2O$ (Table 3). This relatively small decrease of sensitization efficiency may be due to the weak ILCT fluorescence of CCDBM and the locally excited states of carbazole moiety (around 350 nm, not shown in Fig. 5).

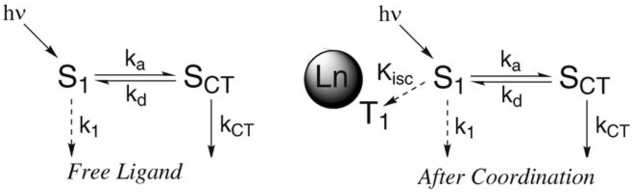
Table 4 The observed lifetime τ_{obs} (in ms), radiative lifetime τ_r (in ms) and the intrinsic quantum yields of Eu^{3+} in various solvents

		DBM–Eu			CDBM–Eu			CCDBM–Eu		
Solvent	$n_D^{20\,a}$	τ_{obs}	τ_r	Φ_{Ln}	τ_{obs}	τ_r	Φ_{Ln}	τ_{obs}	τ_r	Φ_{Ln}
Acetonitrile	1.3441	0.20	1.50	0.13	0.17	1.23	0.14	0.16	1.52	0.11
CH_2Cl_2	1.4242	0.21	2.10	0.10	0.16	1.41	0.11	0.20	1.48	0.14
Cyclohexane	1.4262	0.24	2.12	0.11	0.16	1.65	0.10	0.20	2.09	0.10

[a] Refractive index at 20 °C, taken from ref. 32.

Now we are able to discuss the unsolved problem in the third paragraph of this sub-section: why does the ILCT fluorescence of CDBM decrease after coordinating with Gd^{3+} and Eu^{3+}? Because CDBM is a typical Donor–π–Acceptor molecule containing a carbazole moiety, the ILCT fluorescence of CDBM can be described with a "twisted intramolecular charge transfer (TICT)" model.[34] According to this model, the locally excited state S_1 (non-CT character) was formed immediately after excitation (Scheme 2, left side). Then the molecule undergoes a charge transfer reaction (k_a) to form a TICT state (S_{CT}), in which the carbazole moiety is perpendicular to the benzene ring. The two states can establish equilibrium and decay to the ground state independently (Scheme 2, left side).[35,36] However, after coordinating with the lanthanide ions, the intersystem crossing rate (k_{isc}) of S_1 has been greatly enhanced due to the heavy atom effect. As a result, k_a not only has to compete with k_1, but also has to compete with k_{isc} (Scheme 2, right side). That is to say, the heavy atom effect of the lanthanide ions indirectly reduced the quantum yield of the ILCT fluorescence.

It is instructive to compare our results with that of Kim *et al.*, who have observed a different phenomenon in their experiments.[11] The authors concluded that the Eu^{3+} ion could be sensitized by the CT excited states of the 4-naphthalen-1-ylbenzoic acid (NAC-1) and 4-[4-(4-methoxyphenyl)-naphthalen-1-yl]benzoic acid (NAC-2) ligands. The discrepancy between their observation and ours might be due to the following facts: (i) the charge transfer character of NAC-1 and NAC-2 is not as strong as CDBM. When the solvent was



Scheme 2

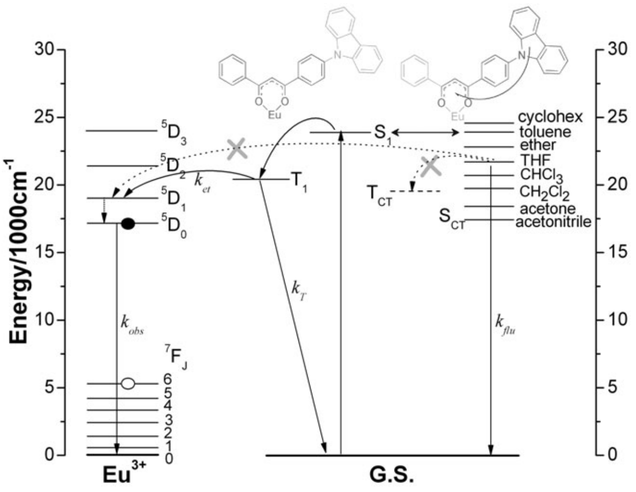


Fig. 6 Schematic representation of the energy transfer pathways in the $Eu(CDBM)_3 \cdot 2H_2O$ system: $k_{flu} \approx 10^7\ s^{-1}$, $k_T \approx 600\ s^{-1}$, $k_{et} > 10^7\ s^{-1}$, $k_{obs} = 6.3 \times 10^3\ s^{-1}$. See ESI† for the calculation details of the rate constants.

changed from cyclohexane to acetonitrile, NAC-1 and NAC-2 showed a red shift of 30 and 40 nm, respectively, whereas CDBM showed a red shift of 156 nm. (ii) NAC-1 and NAC-2 are benzoic acids and CDBM is a β-diketone. These two kinds of ligands are very different in acidity, formation constants and so on. We also want to emphasize that our conclusion is suitable for the β-diketonate system which has strong CT character.

To sum up, the ILCT excited states in $Eu(CDBM)_3 \cdot 2H_2O$ can neither be transformed into triplet excited states nor sensitize Eu^{3+} ion directly. However, the energy of the ILCT states can be partially transferred to the Eu^{3+} indirectly. The Eu^{3+} ion is still sensitized through the triplet excited state which localizes in the DBM part. The energy transfer processes in $Eu(CDBM)_3 \cdot 2H_2O$ are schematically represented in Fig. 6.

Solid state

How the chemical modifications of the ligands affect the sensitization process of lanthanide complexes in the solid state is an essential issue in many practical applications (*e.g.* OLEDs). In this regard, we measured the emission spectra and the quantum yields of the three Eu^{3+} complexes in the solid state.

A distinct difference of the emission spectra between the solid state (Fig. S2 in ESI†) and solution (Fig. 3) is that there is no observable ligand emission in the solid state emission spectra. It is possible that the ILCT emission energy may have been transferred to the Eu^{3+} ion or that the ILCT fluorescence may be quenched due to the intermolecular interactions (π–π stacking, hydrogen bonds, *etc.*) in the solid state. If it is the energy transfer that lead to the disappearance of the strong ILCT emission bands in $Eu(CDBM)_3 \cdot 2H_2O$, we should be able to observe ILCT fluorescence for $Gd(CDBM)_3 \cdot 2H_2O$. However, no fluorescence can be detected for the three Gd^{3+} complexes in the solid state. This leads to the conclusion that the ILCT fluorescence must have been quenched in the solid state. Because the ILCT excited states are not involved in the sensitization process both in the solid state and solutions, it is expected that the quantum efficiency of the three Eu^{3+} complexes in the solid state should present the same trend as that in solutions. We measured the quantum efficiencies of the three Eu^{3+} complexes in the solid state and the results are 0.30, 0.09 and 0.18% for $Eu(DBM)_3 \cdot 2H_2O$, $Eu(CDBM)_3 \cdot 2H_2O$ and $Eu(CCDBM)_3 \cdot 2H_2O$, respectively. These data agree very well with those obtained in solutions (especially that in CH_2Cl_2). This result strongly suggests that the sensitization process of the three Eu^{3+} complexes in the solid state should be similar to that in solution.

Conclusions

Photophysical properties of the β-diketonate–europium complex $Eu(CDBM)_3 \cdot 2H_2O$ have been thoroughly studied in several solvents. It is revealed that the ILCT fluorescence of the ligand CDBM is not involved in the sensitization process of Eu^{3+} in this complex. The Eu^{3+} ion is still sensitized through the triplet excited state which localizes in the DBM part. In another europium complex $Eu(CCDBM)_3 \cdot 2H_2O$, in which the conjugation system between the carbazole moiety and the DBM part has been interrupted, decreased ILCT fluorescence and increased Eu^{3+} emissions have been observed. This supported our conclusion in another way. The quantum efficiencies of the three Eu^{3+} complexes in the solid state have been observed to show the same trend as that in solutions. This proved that our conclusion is still valid in the solid state. All these observations give an important implication for the design of organic–lanthanide light-emitting materials. That is, one should avoid ILCT fluorescence when one applies chemical modifications to the ligand to get better performances of the materials.

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