Energy Transfer Pathways in the Carbazole Functionalized

β-Diketonate Europium Complexes

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Electronic Supplementary Information

1. ^{1}H NMR Data of CDBM and CCDBM.

CDBM: ^{1}H NMR (CDCl$_3$, TMS): δ(ppm) 6.95 (s, 1H), 7.32 (t, 2H, J=7.14, 7.21Hz), 7.44 (t, 2H, J=8.03, 7.17Hz), 7.52 (t, 4H, J=9.33, 8.12Hz), 7.59 (t, 1H, J=7.23, 7.32Hz), 7.73 (d, 2H, J=8.47Hz), 8.03 (d, 2H, J=7.19Hz), 8.15 (d, 2H, J=7.72Hz), 8.23 (d, 2H, J=8.54Hz), 16.93 (s, 1H).

CCDBM: ^{1}H NMR (CDCl$_3$, TMS): δ(ppm) 5.59 (s, 2H), 6.76 (s, 1H), 7.24 (d, 2H, J=10.58Hz), 7.28 (d, 2H, J=7.21Hz), 7.34 (d, 2H, J=8.18Hz), 7.45 (m, 4H, J=8.28, 7.02, 7.76Hz), 7.54 (t, 1H, J=6.01, 8.53Hz), 7.88 (d, 2H, 6.64Hz), 7.93 (d, 2H, J=7.11Hz), 8.14 (d, 2H, J=8.64Hz), 17.05 (s, 1H).

2. Absorption spectra of the three ligands and the corresponding Eu3+ complexs recorded in dichloromethane.
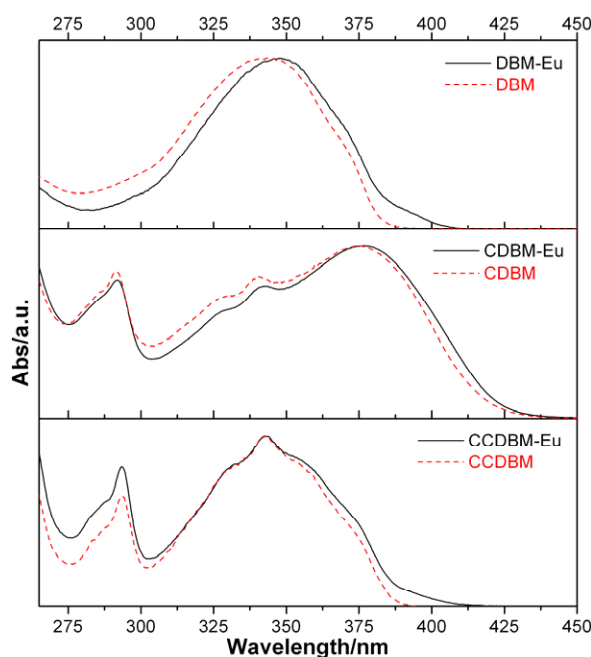

Fig. S1. Absorption spectra of the three ligands and the corresponding Eu^{3+} complexes recorded in

dichloromethane. Red dashed line: free ligands; Black solid line: complexes.

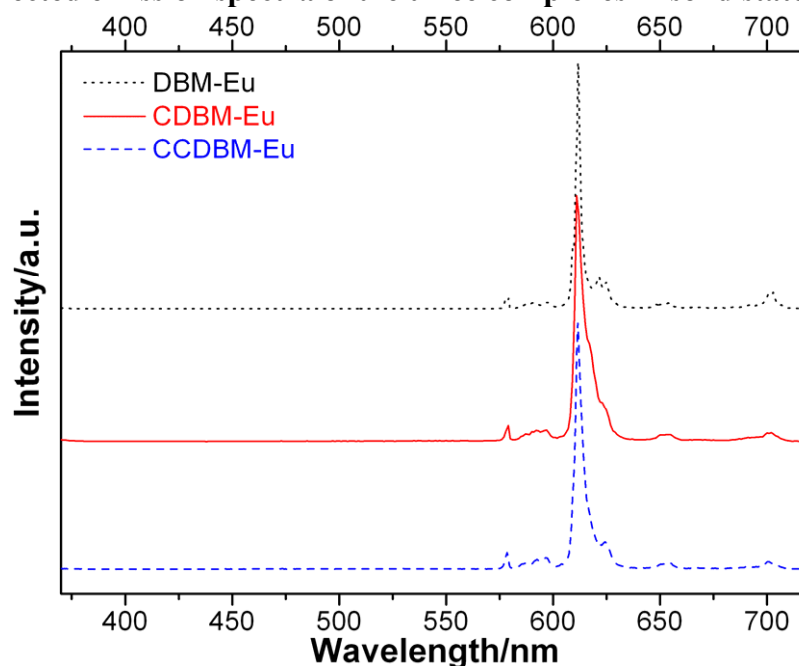## 3. The corrected emission spectra of the three complexes in solid state.

Fig. S2. The corrected emission spectra of the three complexes in solid state.

4. The Element Analysis of the Complexes

Table S1. Element Analysis Results of the Complexes

		C%	H%	N%
Eu(DBM)$_3$·2H$_2$O	Calc.	63.01	4.35	
	Found	63.10	4.39	
Gd(DBM)$_3$·2H$_2$O	Calc.	62.63	4.32	
	Found	62.71	4.30	
Eu(CDBM)$_3$·2H$_2$O	Calc.	71.89	4.32	3.10
	Found	71.46	4.22	2.84
Gd(CDBM)$_3$·2H$_2$O	Calc.	71.61	4.30	3.09
	Found	71.77	4.26	2.90
Eu(CCDBM)$_3$·2H$_2$O	Calc.	72.30	4.62	3.01
	Found	72.30	4.46	3.17
Gd(CCDBM)$_3$·2H$_2$O	Calc.	72.03	4.61	3.00
	Found	72.05	4.58	3.19

5. The Calculations of the Rate Constants in Fig. 7.

5.1. k$_{flu}$. k$_{flu}$ is calculated according to Equation S1:

$$k_{flu} = \frac{\varphi_f}{\tau_f} \tag{S1}$$

The calculation results are summarized in Table S2.

Table S2. The Fluorescence Rate Constants k_{flu} of CDBM in Eu(CDBM)$_3$·2H$_2$O Complex

solvents	φ_f	τ_f/ns	$k_{flu}/10^7$
acetonitrile	0.013	3.93	0.3
acetone	0.041	5.33	0.8
CH$_2$Cl$_2$	0.062	5.55	1.1
CHCl$_3$	0.094	3.13	3.0
THF	0.054	1.89	2.9
aether	0.006	0.17	3.5
toluene	0.009	0.12	7.5
cyclohexane	0.0008	0.03	2.7

5.2. k_T. k_T is determined from the phosphorescence lifetime of Gd(CDBM)$_3$·2H$_2$O at 77K. This is just an approximation to the real k_T value with the assumption that all the non-radiative decays have been suppressed at 77K and that temperature effect is not significant for k_T. With equation S2 we can get $k_T \approx 600$

$$k_T \approx \frac{1}{\tau_p} = \frac{1}{1.6 \times 10^{-3}} = 625 \tag{S2}$$

5.3. k_{et}. Because the Eu^{3+} ion is sensitized through the triplet pathway in Eu(CDBM)$_3$·2H$_2$O, oxygen may compete with the sensitization process. However, deoxygenation of the Eu(CDBM)$_3$·2H$_2$O solutions did not intensify the Eu^{3+} luminescence intensity. This result indicates that k_{et} exceeds 10^7 s^{-1}.[1]

5.4. k_{obs}. k_{obs} is calculated according to equation S3.

$$k_{obs} = \frac{1}{\tau_{Ln}} \tag{S3}$$

τ_{Ln} is the observed lifetime of Eu^{3+} emission (Table 4 in the manuscript).

6. The Failure of Obtaining Single Crystals of the Complexes.

On referee asked why we failed to obtain the single crystal structures of the complexes. We want to clarify that we have tried all methods we knew to grow single crystals of the complexes. Unfortunately, for the well known reason (it is hard to grow single crystal for lanthanide complexes), we failed. However, because we only used the qualitative results obtained by the theoretical modeling in the discussion of energy transfer pathways, the theoretical modeling results are sufficient enough.

References

(1)   Klink, S. I.; Grave, L.; Reinhoudt, D. N.; van Veggel, F. C. J. M.; Werts, M. H. V.; Geurts, F.

A. J.; Hofstraat, J. W. *J. Phys. Chem. A.* **2000**, *104*, 5457.