Supporting Information

Self-Assembly Synthesis, Structural Features, and Photophysical Properties of Dilanthanide Complexes Derived from a Novel Amide Type Ligand: Energy Transfer from Tb(III) to Eu(III) in a Heterodinuclear Derivative

Cunji Gao,[†] Alexander M. Kirillov,[‡] Wei Dou,[†] Xiaoliang Tang,[†] Liangliang Liu,[†] Xuhuan Yan,[†] Yujie Xie,[†] Peixian Zang,[†] Weisheng Liu,[†] Yu Tang*[†]

[†] Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000 P. R. China

‡ Centro de Quimica Estrutural, Complexo I, Instituto Superior Tecnico, The University of Lisbon, Av. Rovisco Pais, 1049-001, Lisbon, Portugal

Fax: (+86) 931-891-2582

E-mail: tangyu@lzu.edu.cn

Table S1. EDX analysis results for the complex [EuTb(μ_2-L)$_2$(NO$_3$)$_6$(EtOH)$_2$] (**4**)

Compound	Element	Wt %	Eu/Tb (EDX)
[EuTb(μ_2-L)$_2$(NO$_3$)$_6$(EtOH)$_2$]	Eu	48.15	0.93
	Tb	51.85	

Table S2. Hydrogen bonds in crystal packing [Å, °] of **1**, **2**, **3**, and **4**

Compounds	D-H…A	*d* (D-H)	*d*(H…A)	*d*(D…A)	∠DHA	Symmetry code
1	N(1)-H(1A)…O(3)	0.86	2.01	2.652(8)	130	
	N(3)-H(3A)…O(4)	0.86	1.99	2.648(8)	132	
	N(3)-H(3A)…O(11)	0.86	2.44	3.046(8)	128	1-x,-1/2+y,1/2-z
	O(16)-H(16)…O(15)	0.85	2.38	2.902(8)	120	
2	N(1)-H(1A)…O(3)	0.86	2.02	2.656(8)	130	
	N(3)-H(3A)…O(4)	0.86	1.97	2.642(7)	134	
	N(3)-H(3A)…O(11)	0.86	2.49	3.063(8)	125	1-x,-1/2+y,1/2-z
	O(16)-H(16)…O(15)	0.85	2.36	2.864(8)	118	
3	N(1)-H(1A) …O(3)	0.86	2.00	2.644(10)	131	
	N(3)-H(3A) …O(11)	0.86	2.47	3.050(11)	125	x,-1/2-y,-1/2+z
	N(3)-H(3A) …O(4)	0.86	1.97	2.633(10)	133	
	O(16)-H(16)…O(15)	0.85	2.38	2.872(10)	117	
4	O(16)-H(16)…O(15)	0.85	2.33	2.648(8)	131	1-x,-1/2+y,1/2-z
	N(1)-H(1A)…O(3)	0.86	2.01	2.648(8)	131	
	N3)-H(3A)…O(4)	0.86	1.98	2.646(8)	134	
	N(3)-H(3A)…O(11)	0.86	2.47	3.062(10)	126	x,-1/2-y,1/2+z

Table S3. Photophysical characterization of the compounds **1**, **2**, and **4**

Compounds	λ_{ex} (nm)	λ_{em} (nm)	Assignment	τ (ms)	Φ (%)
1	327	579	$^5D_0 \rightarrow {}^7F_0$		0.7
		591	$^5D_0 \rightarrow {}^7F_1$		
		617	$^5D_0 \rightarrow {}^7F_2$	0.314 ± 0.003	
		649	$^5D_0 \rightarrow {}^7F_3$		
		689	$^5D_0 \rightarrow {}^7F_4$		
		701	$^5D_0 \rightarrow {}^7F_4$		
2	327	489	$^5D_4 \rightarrow {}^7F_6$		52
		544	$^5D_4 \rightarrow {}^7F_5$	0.947 ± 0.002	
		584	$^5D_4 \rightarrow {}^7F_4$		
		622	$^5D_4 \rightarrow {}^7F_3$		
		649	$^5D_4 \rightarrow {}^7F_2$		
4	327	544	$^5D_4 \rightarrow {}^7F_5$	0.915 ± 0.002	2.5
		582	$^5D_0 \rightarrow {}^7F_0$	0.792 ± 0.004	
		592	$^5D_0 \rightarrow {}^7F_1$		
		617	$^5D_0 \rightarrow {}^7F_2$		
		653	$^5D_0 \rightarrow {}^7F_3$		
		689	$^5D_0 \rightarrow {}^7F_4$		
		701	$^5D_0 \rightarrow {}^7F_4$		

Table S4. Selected bond lengths [Å] and angles [°] for the compounds **1**, **2**, **3**, and **4**

1					
Eu(1)—O(5)	2.318(5)	Eu(1)—O(7)	2.469(5)	Eu(1)—O(12)	2.506(5)
Eu(1)—O(2)	2.322(4)	Eu(1)—O(13)	2.473(5)	Eu(1)—O(10)	2.508(5)
Eu(1)—O(16)	2.353(5)	Eu(1)—O(9)	2.503(6)	Eu(1)—O(15)	2.559(5)
O(5)-Eu(1)-O(2)	79.47(18)	O(16)-Eu(1)-O(9)	74.3(2)	O(7)-Eu(1)-O(10)	74.45(18)
O(5)-Eu(1)-O(16)	87.5(2)	O(7)-Eu(1)-O(9)	50.00(19)	O(13)-Eu(1)-(10)	69.41(18)
O(2)-Eu(1)-O(16)	148.8(2)	O(13)-Eu(1)-O(9)	143.5(2)	O(9)-Eu(1)- O(10)	105.7(2)
O(5)-Eu(1)-O(7)	82.57(18)	O(5)-Eu(1)-O(12)	149.1(2)	O(12)-Eu(1)-O(10)	50.61(17)
O(2)-Eu(1)-O(7)	81.38(18)	O(2)-Eu(1)-O(12)	126.44(17)	O(5)-Eu(1)-O(15)	78.93(18)
O(16)-Eu(1)-O(7)	125.1(2)	O(16)-Eu(1)-O(12)	76.7(2)	O(2)-Eu(1)-O(15)	77.47(17)
O(5)-Eu(1)-O(13)	129.08(18)	O(7)-Eu(1)-O(12)	85.09(19)	O(16)-Eu(1)-O(15)	72.3(2)
O(2)-Eu(1)-O(13)	87.38(18)	O(13)-Eu(1)-O(12)	74.21(19)	O(7)-Eu(1)-O(15)	154.03(18)
O(16)-Eu(1)-O(13)	79.1(2)	O(9)-Eu(1)-O(12)	75.6(2)	O(13)-Eu(1)-O(15)	50.17(17)
O(7)-Eu(1)-O(13)	143.76(18)	O(5)-Eu(1)-O(10)	148.33(17)	O(9)-Eu(1)-O(15)	137.7(2)
O(5)-Eu(1)-O(9)	74.5(2)	O(2)-Eu(1)-O(10)	75.84(16)	O(12)-Eu(1)-O(15)	119.71(19)
O(2)-Eu(1)-O(9)	127.6(2)	O(16)-Eu(1)-O(10)	123.53(19)	O(10)-Eu(1)-O(15)	114.06(19)
2					
Tb(1)—O(2)	2.290(4)	Tb(1)—O(7)	2.447(5)	Tb(1)—O(10)	2.489(5)
Tb(1)—O(5)	2.295(5)	Tb(1)—O(13)	2.447(5)	Tb(1)—O(9)	2.492(6)
Tb(1)—O(16)	2.330(5)	Tb(1)—O(12)	2.479(5)	Tb(1)—O(15)	2.544(5)

O(2)-Tb(1)-O(5)	79.69(17)	O(16)-Tb(1)-O(13)	79.1(2)	O(5)-Tb(1)-O(10)	148.43(16)
O(2)-Tb(1)-O(16)	148.5(2)	O(7)-Tb(1)-O(13)	143.59(17)	O(16)-Tb(1)-O(10)	123.85(18)
O(5)-Tb(1)-O(16)	87.05(19)	O(2)-Tb(1)-O(12)	126.81(17)	O(7)-Tb(1)-O(10)	74.13(17)
O(2)-Tb(1)-O(7)	81.44(17)	O(5)-Tb(1)-O(12)	148.42(19)	O(13)-Tb(1)-O(10)	69.56(17)
O(5)-Tb(1)-O(7)	82.75(17)	O(16)-Tb(1)-O(12)	76.8(2)	O(12)-Tb(1)-O(10)	50.93(16)
O(16)-Tb(1)-O(7)	125.3(2)	O(7)-Tb(1)-O(12)	84.79(19)	O(2)-Tb(1)-O(9)	128.08(19)
O(2)-Tb(1)-O(13)	87.33(17)	O(13)-Tb(1)-O(12)	74.44(19)	O(5)-Tb(1)-O(9)	74.3(2)
O(5)-Tb(1)-O(13)	129.15(17)	O(2)-Tb(1)-O(10)	75.90(16)	O(16)-Tb(1)-O(9)	73.9(2)
O(13)-Tb(1)-O(15)	50.84(16)	O(2)-Tb(1)-O(15)	77.51(17)	O(7)-Tb(1)-O(9)	51.57(18)
O(12)-Tb(1)-O(15)	120.42(19)	O(5)-Tb(1)-O(15)	78.32(17)	O(13)-Tb(1)-O(9)	143.14(1)
O(10)-Tb(1)-O(15)	114.89(18)	O(16)-Tb(1)-O(15)	71.8(2)	O(12)-Tb(1)-O(9)	75.2(2)
O(9)-Tb(1)-O(15)	136.75(19)	O(7)-Tb(1)-O(15)	153.81(17)	O(10)-Tb(1)-O(9)	105.85(19)
3					
Gd(1)—O(2)	2.300(6)	Gd(1)—O(9)	2.493(7)	Gd(1)—O(12)	2.476(7)
Gd(1)—O(5)	2.296(6)	Gd(1)—O(13)	2.452(6)	Gd(1)—O(15)	2.537(7)
Gd(1)—O(16)	2.351(7)	Gd(1)—O(10)	2.489(6)	Gd(1)—O(7)	2.456(6)
O(2)-Gd(1)-O(5)	79.5(2)	O(5)-Gd(1)-O(10)	148.3(2)	O(5)-Gd(1)-O(15)	78.6(2)
O(2)-Gd(1)-O(16)	148.4(3)	O(16)-Gd(1)-O(10)	123.7(3)	O(16)-Gd(1)-O(15)	71.8(3)
O(5)-Gd(1)-O(16)	87.4(2)	O(9)-Gd(1)-O(10)	105.8(2)	O(9)-Gd(1)-O(15)	137.3(3)
O(2)-Gd(1)-O(9)	127.5(2)	O(13)-Gd(1)-O(10)	69.2(2)	O(13)-Gd(1)-O(15)	50.8(2)
O(5)-Gd(1)-O(9)	74.2(2)	O(2)-Gd(1)-O(12)	127.0(2)	O(10)-Gd(1)-O(15)	114.5(2)
O(16)-Gd(1)-O(9)	74.6(3)	O(5)-Gd(1)-O(12)	148.4(2)	O(12)-Gd(1)-O(15)	120.3(3)
O(2)-Gd(1)-O(13)	87.3(2)	O(16)-Gd(1)-O(12)	76.6(3)	O(2)-Gd(1)-O(7)	81.5(2)
O(5)-Gd(1)-O(13)	129.4(2)	O(9)-Gd(1)-O(12)	75.3(2)	O(5)-Gd(1)-O(7)	82.5(2)
O(16)-Gd(1)-O(13)	79.0(3)	O(13)-Gd(1)-O(12)	74.5(2)	O(16)-Gd(1)-O(7)	125.4(3)
O(9)-Gd(1)-O(13)	143.6(3)	O(10)-Gd(1)-O(12)	51.2(2)	O(9)-Gd(1)-O(7)	51.0(2)
O(2)-Gd(1)-O(10)	75.9(2)	O(2)-Gd(1)-O(15)	77.4(3)	O(13)-Gd(1)-O(7)	143.6(2)
O(10)-Gd(1)-O(7)	74.4(2)	O(12)-Gd(1)-O(7)	84.9(2)	O(15)-Gd(1)-O(7)	153.8(2)
4					
Eu(1)—O(2)	2.380(12)	Eu(1)—O(12)	2.362(10)	Eu(1)—O(10)	2.408(13)
Eu(1)—O(5)	2.417(11)	Eu(1)—O(7)	2.427(15)	Eu(1)—O(15)	2.627(13)
Eu(1)—O(16)	2.335(14)	Eu(1)—O(13)	2.443(15)	Eu(1)—O(9)	2.462(14)
Tb(1)—O(5)	2.198(11)	Tb(1)—O(15)	2.470(13)	Tb(1)—O(9)	2.532(14)
Tb(1)—O(16)	2.359(14)	Tb(1)—O(13)	2.489(14)	Tb(1)—O(10)	2.589(12)
Tb(1)—O(2)	2.250(12)	Tb(1)—O(7)	2.485(14)	Tb(1)—O(12)	2.616(9)
O(2)-Eu(1)-O(5)	76.0(3)	O(16)-Eu(1)-O(13)	79.9(5)	O(12)-Eu(1)-O(15)	121.9(6)
O(2)-Eu(1)-O(16)	144.0(5)	O(12)-Eu(1)-O(13)	76.9(4)	O(7)-Eu(1)-O(15)	148.6(4)
O(5)-Eu(1)-O(16)	85.1(5)	O(7)-Eu(1)-O(13)	147.1(6)	O(13)-Eu(1)-O(15)	50.1(3)
O(2)-Eu(1)-O(12)	129.8(6)	O(2)-Eu(1)-O(10)	76.6(4)	O(10)-Eu(1)-O(15)	114.9(6)
O(5)-Eu(1)-O(12)	150.4(6)	O(5)-Eu(1)-O(10)	147.0(6)	O(2)-Eu(1)-O(9)	125.8(6)
O(16)-Eu(1)-O(12)	78.9(4)	O(16)-Eu(1)-O(10)	127.9(5)	O(5)-Eu(1)-O(9)	72.94)
O(2)-Eu(1)-O(7)	80.5(4)	O(12)-Eu(1)-O(10)	53.3(3)	O(16)-Eu(1)-O(7)	126.8(6)
O(5)-Eu(1)-O(7)	81.1(4)	O(7)-Eu(1)-O(10)	76.6(4)	O(12)-Eu(1)-O(7)	88.8(4)
O(16)-Eu(1)-O(9)	74.9(4)	O(13)-Eu(1)-O(10)	71.1(4)	O(7)-Eu(1)-O(9)	51.9(3)

O(12)-Eu(1)-O(9)	79.0(4)	O(2)-Eu(1)-O(15)	74.6(3)	O(13)-Eu(1)-O(9)	147.7(5)
O(2)-Eu(1)-O(13)	86.3(5)	O(5)-Eu(1)-O(15)	74.6(3)	O(10)-Eu(1)-O(9)	110.1(5)
O(5)-Eu(1)-O(13)	124.6(5)	O(16)-Eu(1)-O(15)	70.9(4)	O(15)-Eu(1)-O(9)	134.1(6)
O(5)-Tb(1)-O(16)	89.6(5)	O(2)-Tb(1)-O(7)	81.8(4)	O(15)-Tb(1)-O(10)	114.1(5)
O(5)-Tb(1)-O(2)	83.2(4)	O(15)-Tb(1)-O(7)	158.3(5)	O(13)-Tb(1)-O(10)	67.4(3)
O(16)-Tb(1)-O(2)	153.3(6)	O(13)-Tb(1)-O(7)	139.8(5)	O(7)-Tb(1)-O(10)	72.4(4)
O(5)-Tb(1)-O(15)	81.7(4)	O(5)-Tb(1)-O(9)	75.2(4)	O(9)-Tb(1)-O(10)	102.4(4)
O(16)-Tb(1)-O(15)	73.4(4)	O(16)-Tb(1)-O(9)	73.1(4)	O(5)-Tb(1)-O(12)	147.3(6)
O(2)-Tb(1)-O(15)	80.1(4)	O(2)-Tb(1)-O(9)	128.7(6)	O(16)-Tb(1)-O(12)	73.5(3)
O(5)-Tb(1)-O(13)	133.1(5)	O(15)-Tb(1)-O(9)	139.1(6)	O(2)-Tb(1)-O(12)	123.8(5)
O(16)-Tb(1)-O(13)	78.3(4)	O(13)-Tb(1)-O(9)	139.5(4)	O(15)-Tb(1)-O(12)	118.2(5)
O(2)-Tb(1)-O(13)	88.1(3)	O(7)-Tb(1)-O(9)	50.5(3)	O(13)-Tb(1)-O(12)	71.6(3)
O(15)-Tb(1)-O(13)	51.5(3)	O(5)-Tb(1)-O(10)	150.0(6)	O(7)-Tb(1)-O(12)	82.1(3)
O(5)-Tb(1)-O(7)	84.3(5)	O(16)-Tb(1)-O(10)	118.8(4)	O(9)-Tb(1)-O(12)	73.2(3)
O(16)-Tb(1)-O(7)	123.0(5)	O(2)-Tb(1)-O(10)	75.3(4)	O(10)-Tb(1)-O(12)	48.5(2)

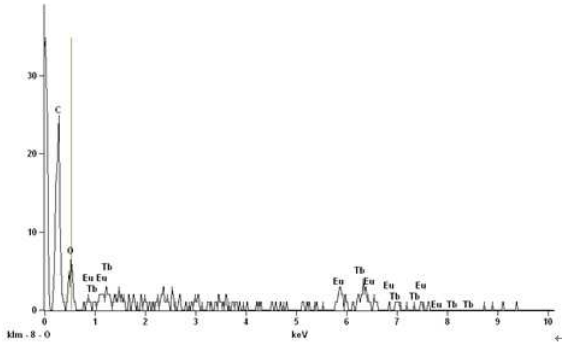


Figure S1 EDX spectrum of [EuTb(μ_2-L)$_2$(NO$_3$)$_6$(EtOH)$_2$] (**4**).

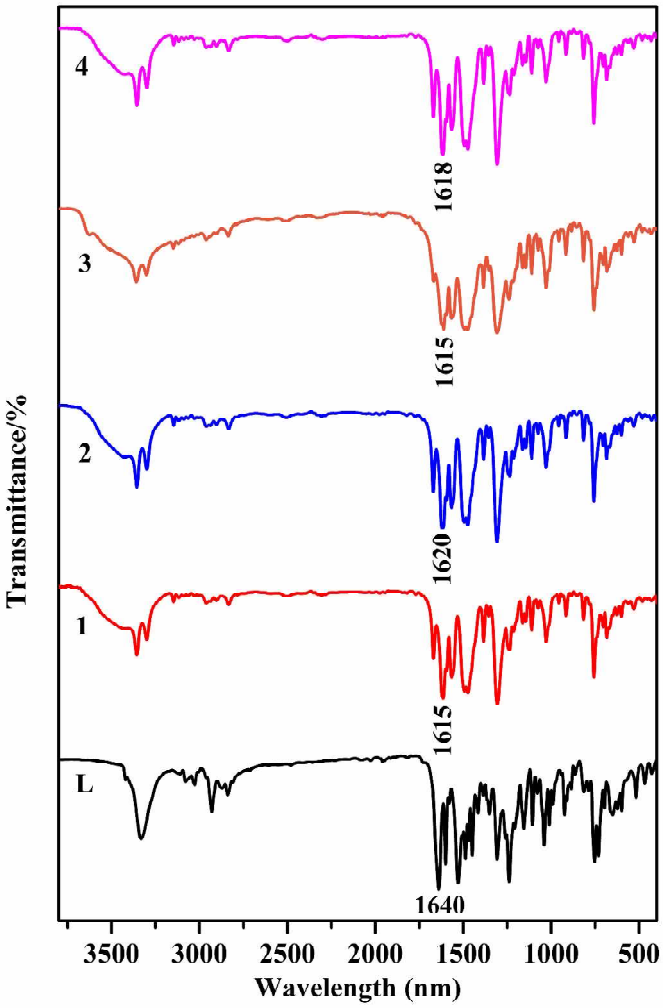


Figure S2. FTIR spectra of the free ligand **L** and complexes **1**–**4**.

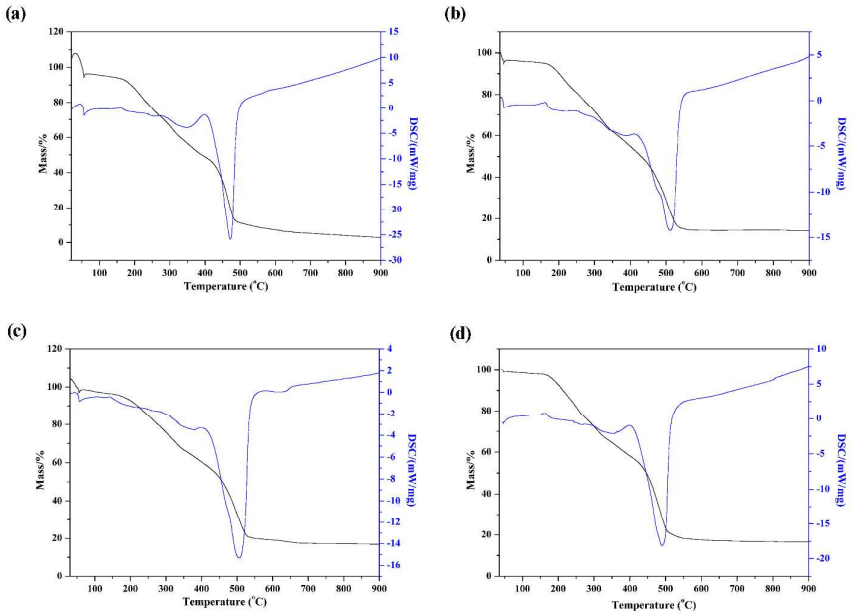


Figure S3. (a) The TGA-DSC curves of **1** (a), **2** (b), **3** (c), and **4** (d).

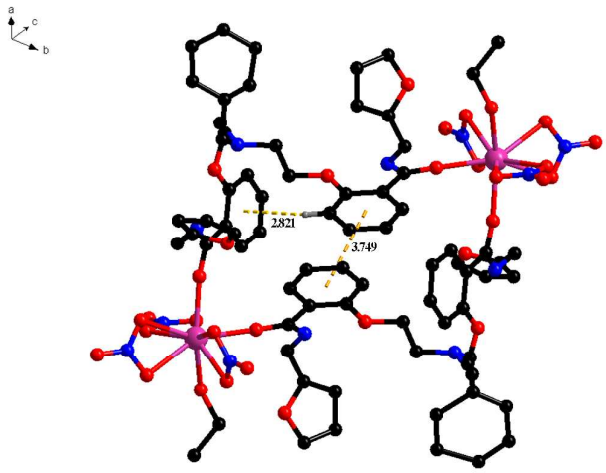


Figure S4. The intramolecular π–π and C-H…π stacking interactions in the complex **1**.

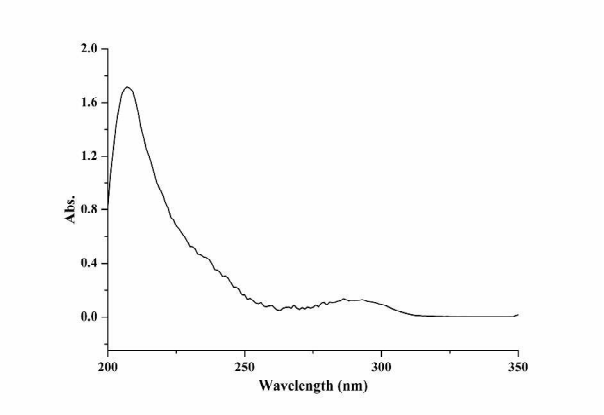


Figure S5. Absorption spectrum of the complex **3** in CH_3OH solution.

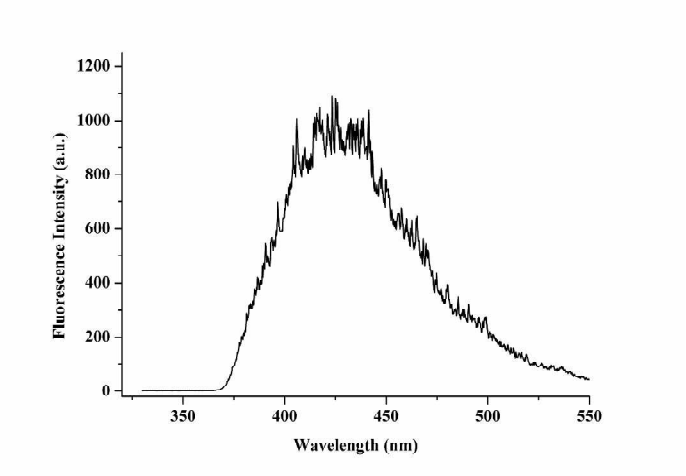


Figure S6. Phosphorescence spectrum of the compound **3** in a 1:1 methanol-ethanol mixed solution.

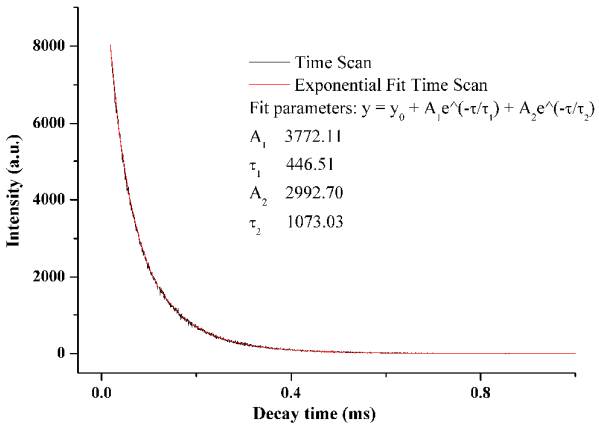


Figure S7. Low-temperature luminescence decay profiles for complex **1**. The average lifetime $< \tau_{obs} >$ is 858 ± 5 μs calculated according to the eq $< \tau > = (\sum A_i\tau_i^2)/(\sum A_i\tau_i)$.[1]

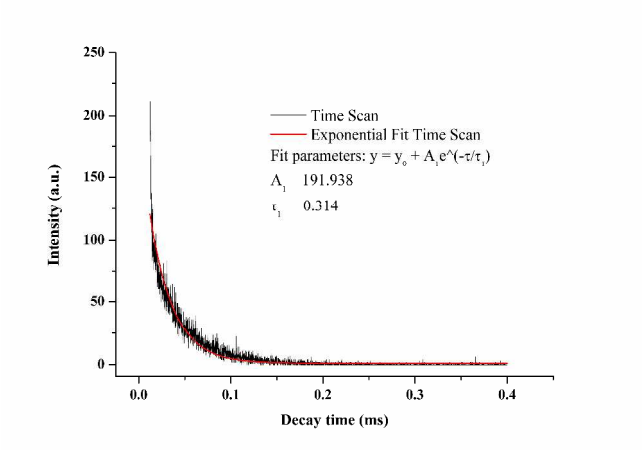


Figure S8. Luminescence decay curve of the $^5D_0$ energy level of the compound **1** at room temperature.

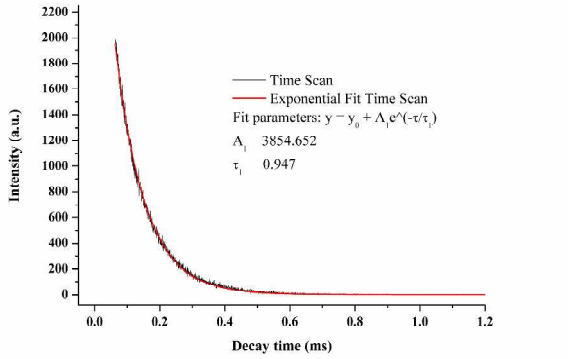


Figure S9. Luminescence decay curve of the $^5D_4$ energy level of the compound **2** at room temperature.

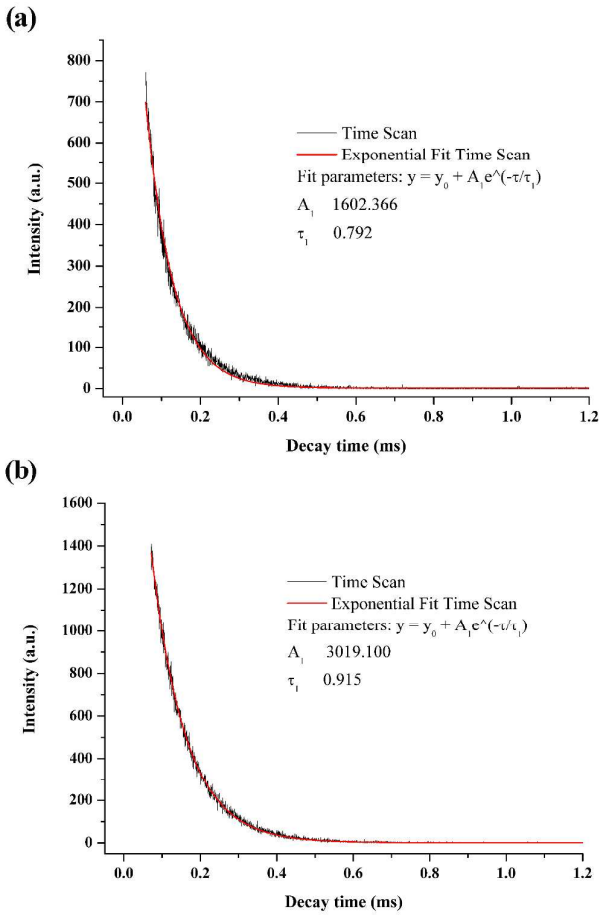


Figure S10. (a) Luminescence decay curve of the $^5D_0$ energy level of the compound **4** at room temperature; (b) Luminescence decay curve of the $^5D_4$ energy level of the compound **4**.

REFERENCES

(1) (a) Martínez, V. M.; Arbeloa, F. L.; Prieto, J. B.; Arbeloa I. L. *J. Phys. Chem. B* **2005,** *109,* 7443. (b) Ma, Y. F.; Wang, H. P.; Liu, W. S.; Wang, Q.; Xu, J. Tang, Y. *J. Phys. Chem. B* **2009**, *113,* 14139.