Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Electronic Supporting Information

Sensitized Eu^{III} Luminescence through Energy Transfer from PtM_2 (M = Ag or Au) Alkynyl Chromophore in PtM_2Eu_2 Heteropentanuclear Complexes

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Table S1. Crystallographic Data for **1Eu**·2Et_2O and **2Eu**·4Et_2O.

	1Eu·2Et_2O	**2Eu**·4Et_2O
empirical formula	$C_{148}H_{112}Ag_2Cl_2Eu_2F_{36}N_6O_{22}P_6Pt$	$C_{156}H_{132}Au_2Cl_2Eu_2F_{36}N_6O_{24}P_6Pt$
formula weight	3981.91	4308.34
crystal system	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$
a,Å	15.030(4)	12.3652(1)
b,Å	15.677(4)	16.9603(2)
c,Å	19.167(4)	26.9859(2)
α, °	91.365(3)	106.747(7)
β,°	93.191(3)	95.282(12)
γ, °	106.915(3)	101.088(8)
V,Å^3	4310.2(17)	5252.32(4)
Z	1	1
r_{calcd} g/cm^{-3}	1.534	1.362
m,mm^{-1}	1.935	2.8
radiation (*l*, Å)	0.71073	0.71073
temp,(K)	293(2)	293(2)
R1(F_o)[a]	0.0592	0.057
wR2(F_o^2)[b]	0.1701	0.1509
GOF	1.064	1.006

[a] $R1 = \Sigma|F_o - F_c|/\Sigma F_o$ [b] $wR2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)]^{1/2}$

Table S2. Selected Bond Distances (Å) and Angles (°) of **1Eu**·2Et_2O and **2Eu**·4Et_2O.

1Eu·2Et_2O		**2Eu**·4Et_2O	
Pt1-C33	2.005(6)	Pt1-C32	2.035(7)
Pt1-P2	2.3260(19)	Pt1-P2	2.3097(16)
Pt1-Ag1	2.9291(8)	Pt1-Au1	2.9504(3)
Ag1-P1	2.409(2)	Au1-P1	2.3084(18)
Ag1-P3	2.402(2)	Au1-P3	2.3176(17)
Eu1-O1	2.452(6)	Eu1-O1	2.444(7)
Eu1-O2	2.489(6)	Eu1-O2	2.398(9)
Eu1-O3	2.396(6)	Eu1-O3	2.358(8)
Eu1-O4	2.381(6)	Eu1-O4	2.350(8)
Eu1-O5	2.449(6)	Eu1-O5	2.416(7)
Eu1-O6	2.390(7)	Eu1-O6	2.466(9)
Eu1-N1	2.574(7)	Eu1-N1	2.565(6)
Eu1-N2	2.564(5)	Eu1-N2	2.533(8)
Eu1-N3	2.540(8)	Eu1-N3	2.558(9)
P1-C1	1.837(7)	P1-C14	1.799(7)
P1-C3	1.804(7)	P1-C20	1.807(7)
P1-C9	1.801(8)	P1-C66	1.840(6)
P2-C1	1.827(7)	P2-C26	1.801(7)
P2-C2	1.831(7)	P2-C66	1.818(6)
P2-C15	1.821(8)	P2-C13A	1.828(6)
P3-C21	1.801(8)	P3-C1	1.810(7)
P3-C27	1.824(9)	P3-C7	1.782(8)
P3-C2A	1.842(7)	P3-C13	1.810(6)
C34-C33-Pt1	178.0(7)	C33-C32-Pt1	176.1(5)
C1-P2-Pt1	113.9(2)	C26-P2-Pt1	121.3(2)
C2-P2-Pt1	109.8(3)	C66-P2-Pt1	107.3(2)
C15-P2-Pt1	120.5(3)	C13A-P2-Pt1	113.2(2)
P1-Ag1-Pt1	95.37(5)	P1-Au1-Pt1	90.04(4)
P3-Ag1-Pt1	90.54(5)	P3-Au1-Pt1	94.43(4)
C33A-Pt1-C33	180.000(1)	C32A-Pt1-C32	180.000(2)
P2-Pt1-P2A	180.000(1)	P2-Pt1-P2A	180.000(2)
C33-Pt1-P2	85.8(2)	C32-Pt1-P2	84.52(17)
C33A-Pt1-P2	94.2(2)	C32-Pt1-P2A	95.48(17)
C33A-Pt1-Ag1	105.8(2)	C32A-Pt1-Au1	74.29(15)
C33-Pt1-Ag1	74.2(2)	C32-Pt1-Au1	105.71(15)
P2-Pt1-Ag1	87.10(5)	P2-Pt1-Au1	92.39(4)
P2A-Pt1-Ag1	92.90(5)	P2A-Pt1-Au1	87.61(4)
P3-Ag1-P1	172.26(7)	P1-Au1-P3	175.40(6)

Table S3. The Molecular Orbital Compositions (%) by SCPA Approach (C-squared Population Analysis Proposed by Ros and Schuit) and the Absorption and Emission Transitions for Complex **1** in CH_2Cl_2 Solution Calculated by TD-DFT Method at the PBE1PBE Level.

orbital	energy (eV)	MO contribution (%)			
		Pt (s/p/d)	Ag (s/p/d)	dpmp	C≡CC_6H_4tpy
LUMO+2	-1.82	3.55 (0/99/0)	7.89 (24/73/2)	27.51	61.05
LUMO+1	-1.94	2.92 (1/0/99)	3.45 (21/76/2)	7.92	85.71
LUMO	-2.73	16.86 (0/99/0)	11.10 (12/72/16)	36.03	36.01
HOMO	-6.52	19.08 (5/0/95)	4.51 (5/39/56)	5.09	71.31
HOMO-1	-6.92	0.77 (0/90/3)	12.41 (12/20/68)	16.45	70.37
HOMO-4	-7.22	26.95 (8/0/92)	28.53 (22/7/71)	41.83	2.68
HOMO-5	-7.4	19.31 (1/0/99)	1.71 (9/34/56)	27.13	51.85

states	*E*/nm (eV)	O.S.	component	CI coef.	assignment	measured (nm)
T_1	504.9 (2.46)	0.0000	HOMO→LUMO HOMO-1→LUMO+1	0.64820 0.25845	^{3}IL/^{3}LLCT/^{3}MC ^{1}IL/^{1}LLCT	516.5
S_1	408.5 (3.03)	0.9882	HOMO→LUMO	0.68132	^{1}IL/^{1}LLCT/^{1}MC	396.8
S_4	336.5 (3.68)	0.5527	HOMO-4→LUMO HOMO-5→LUMO	0.61100 -0.27952	^{1}IL/^{1}MC/^{1}MLCT ^{1}IL/^{1}MC/^{1}LLCT	318
S_9	305.3 (4.06)	1.2745	HOMO→LUMO+2 HOMO-1→LUMO+1	0.63319 0.21187	^{1}IL/^{1}MLCT/^{1}MC/^{1}LLCT ^{1}IL/^{1}LLCT	278.8

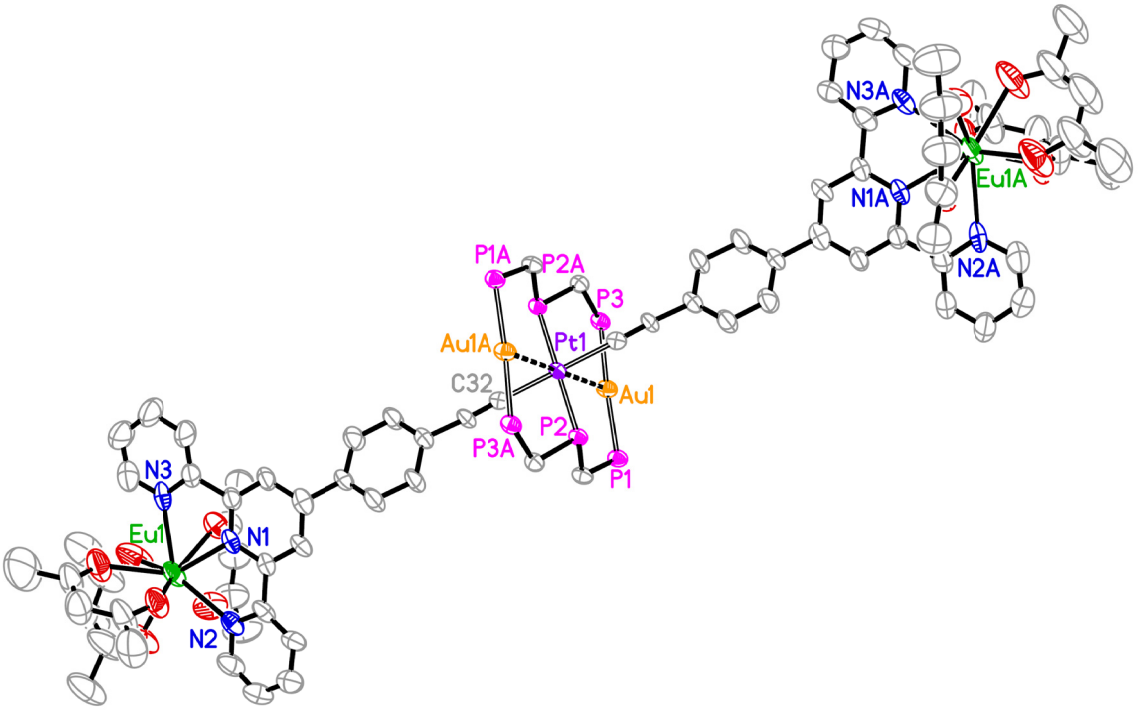


Figure S1. ORTEP drawing (30% thermal ellipsoid) of **2Eu**. The F atoms on the trifluoromethyl are omitted for clarity.

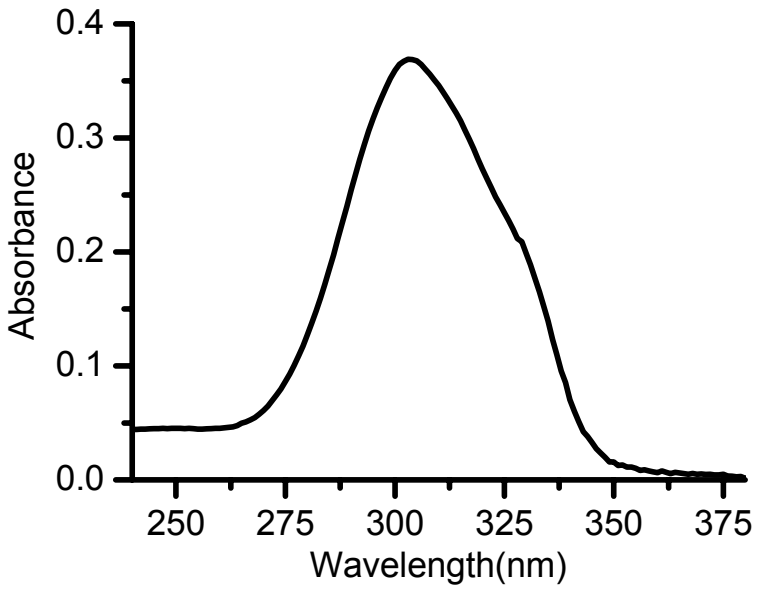


Figure S2. UV-vis electronic absorption spectrum of $Eu(hfac)_3(H_2O)_2$ in dichloromethane solution at 298 K.

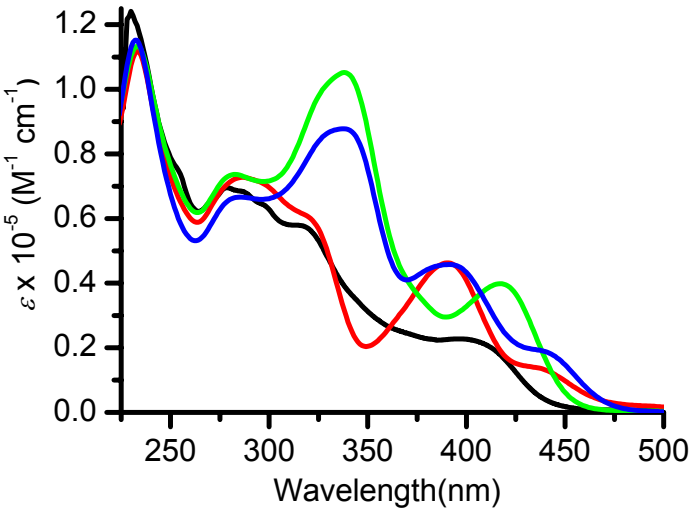


Figure S3. UV-vis electronic absorption spectra of complexes **1** (black), **2** (red), **3** (green) and **4** (blue) in dichloromethane solutions at 298K.

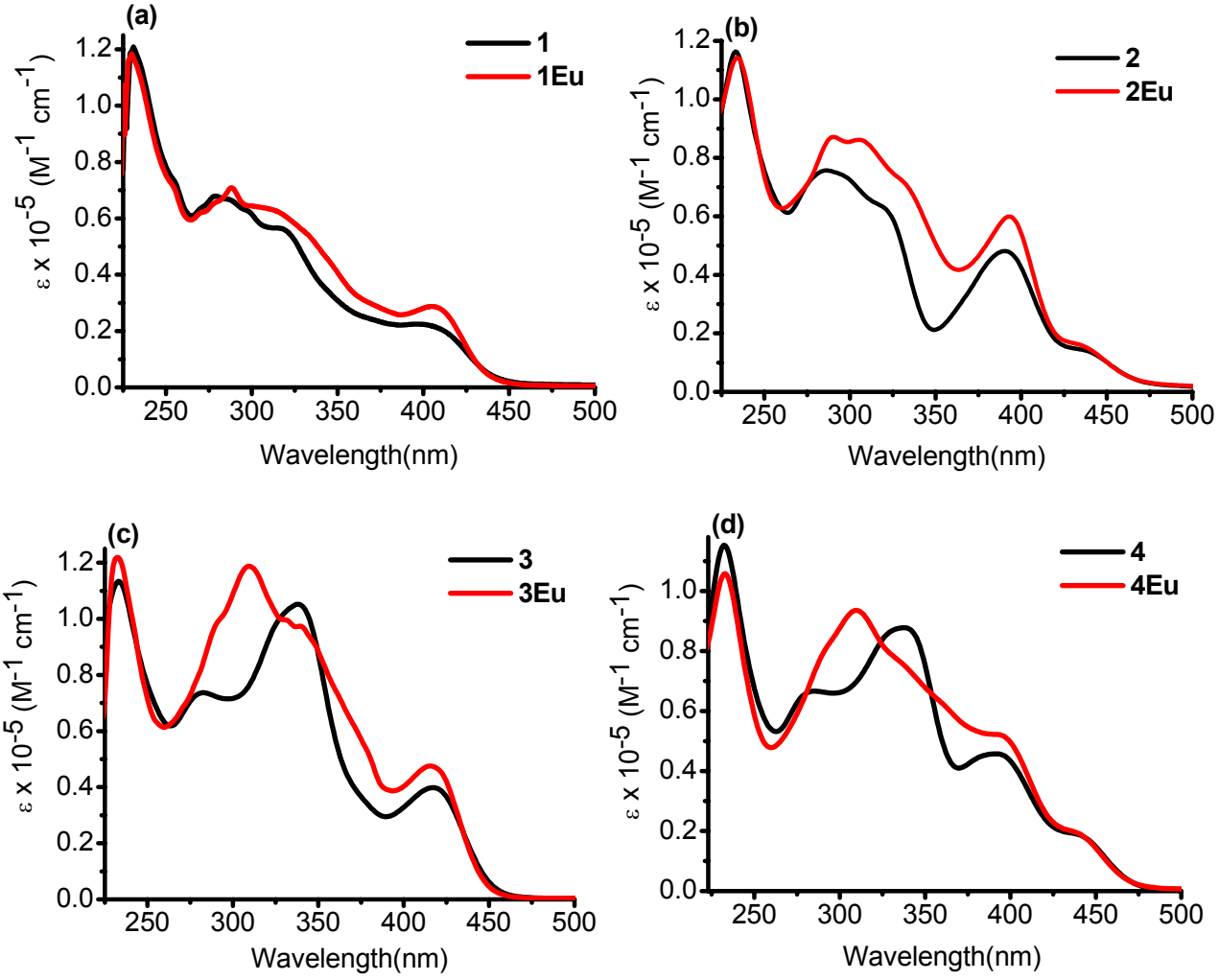


Figure S4. UV-vis electronic absorption spectra of complexes **1** and **1Eu** (a), **2** and **2Eu** (b), **3** and **3Eu** (c), and **4** and **4Eu** (d).

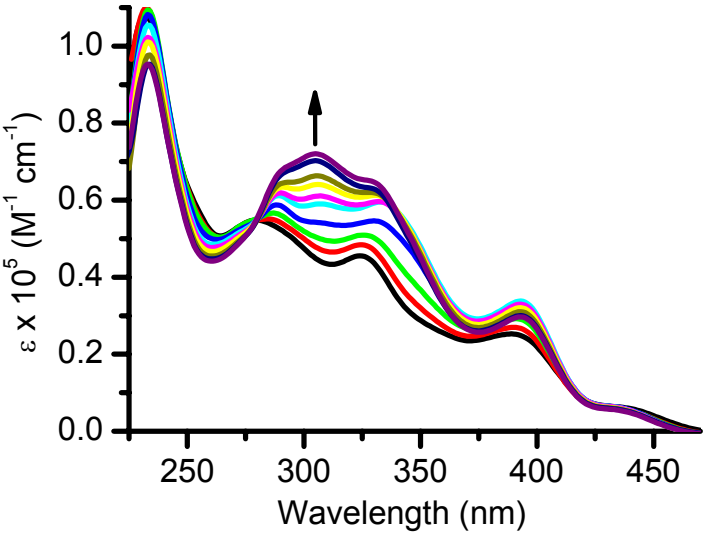


Figure S5. Changes in the UV-vis absorption spectra by titration of 1×10^{-5} M **2** with $Eu(hfac)_3(H_2O)_2$ in dichloromethane solution at 298 K.

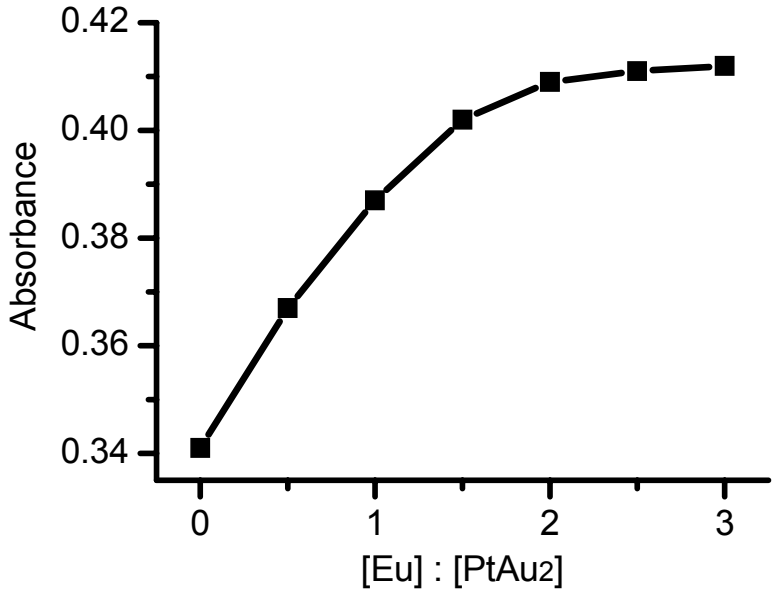


Figure S6. Changes of the absorbance at 380 nm versus the ratio of Eu to $PtAu_2$ moiety by the titration of 0.74×10^{-5} M **4** with $Eu(hfac)_3(H_2O)_2$ in dichloromethane at 298 K due to the formation of complex **4Eu**.

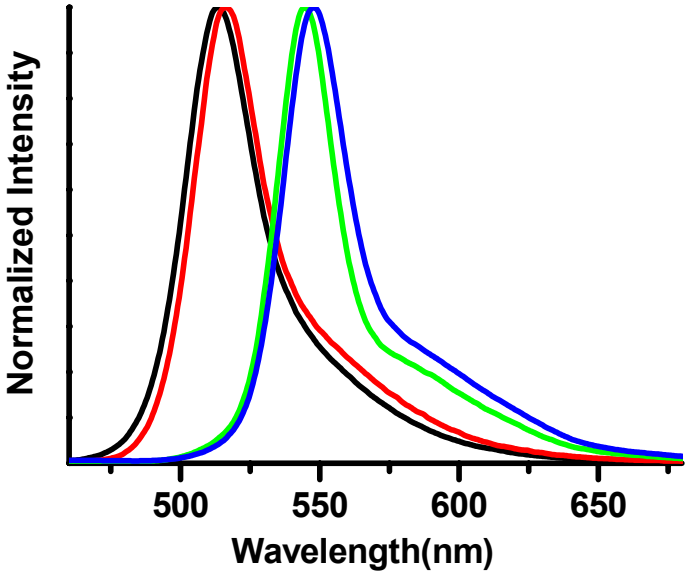


Figure S7. Emission spectra of **1** (black), **2** (red), **3** (green), and **4** (blue) in dichloromethane solutions at 298 K.

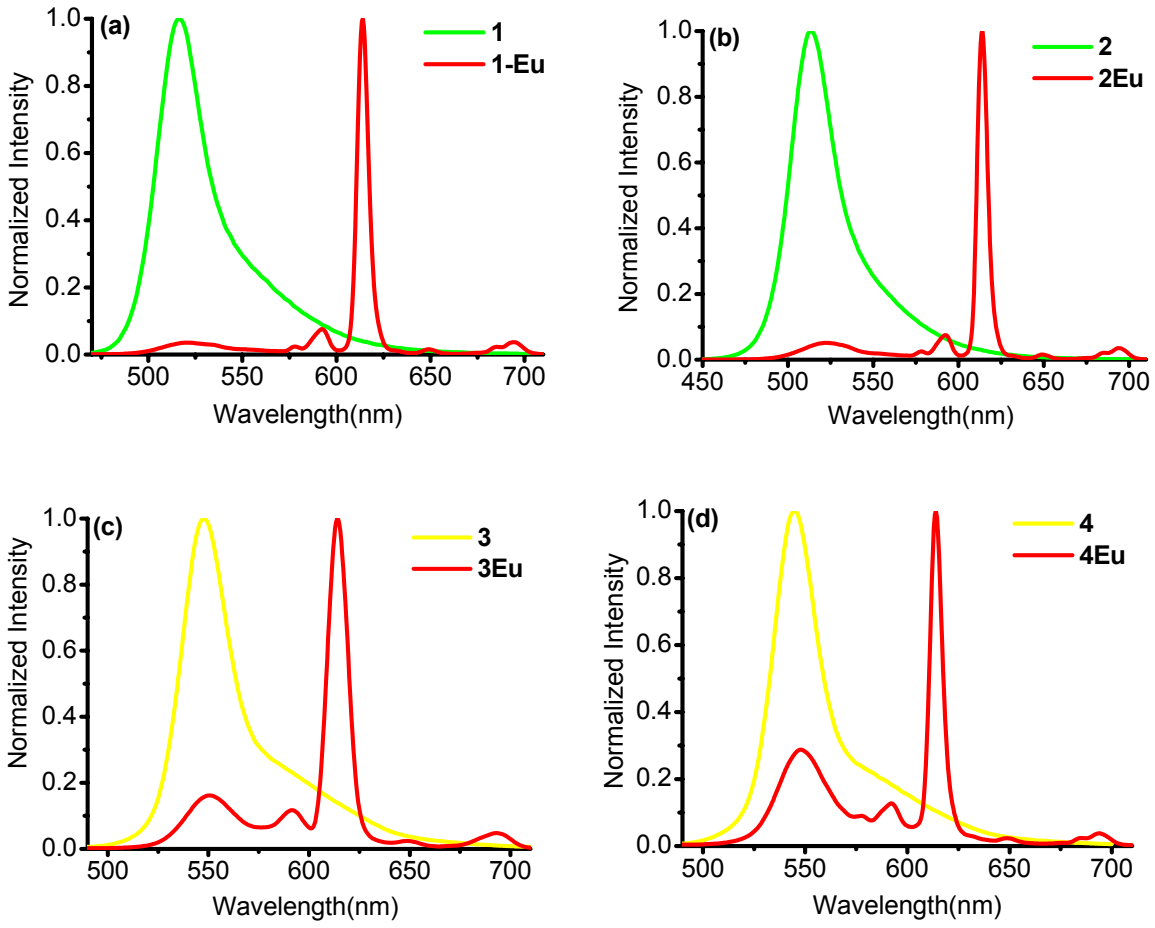


Figure S8. Emission spectra of complexes **1** and **1Eu** (a); **2** and **2Eu** (b); **3** and **3Eu** (c), and **4** and **4Eu** (d).

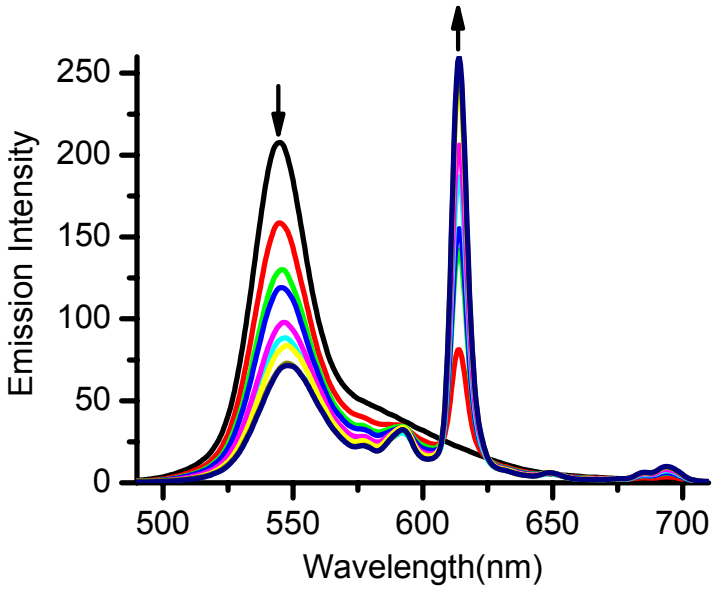
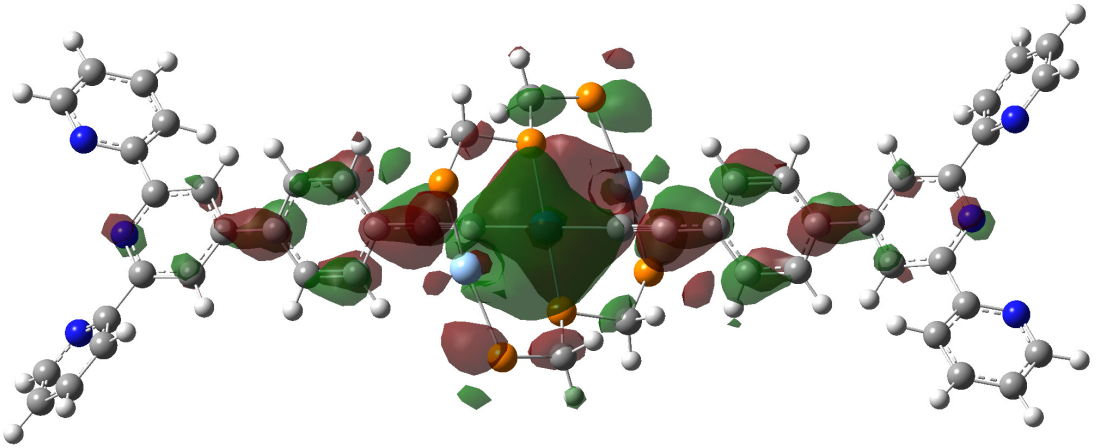
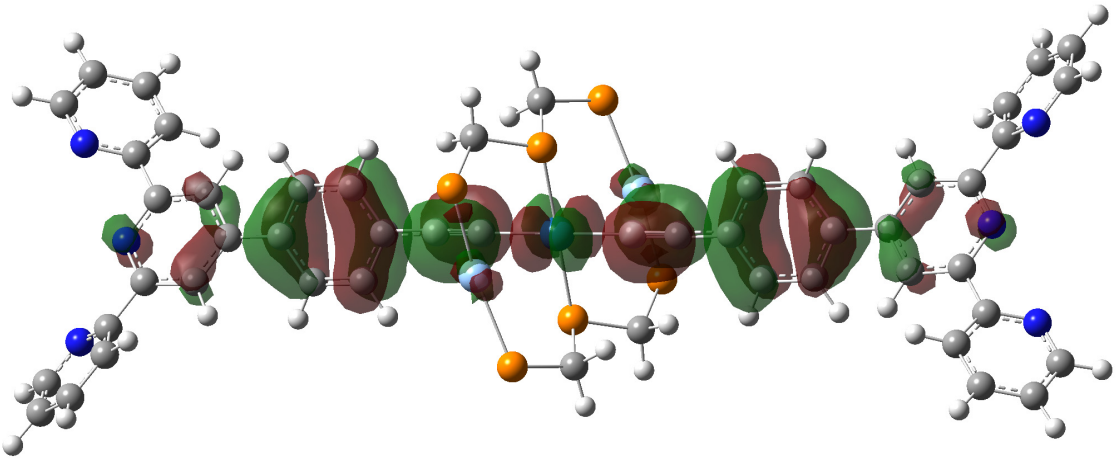


Figure S9. Titration of 0.74×10^{-5} M **4** with $Eu(hfac)_3(H_2O)_2$ in dichloromethane solution at 298 K upon excitation at 413 nm, showing the quenching of the $PtAu_2$-based emission.



LUMO



HOMO

Figure S10. Plots of the HOMO and LUMO of complex **1** calculated by TD-DFT method at the PBE1PBE level (isovalue = 0.02). For clarity, the phenyl rings in dpmp are omitted.