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Novel Luminescent homo/heterometallic platinum(II) alkynyl complexes based on a Y-shaped pyridyl diphosphine

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Table of Contents

content	page
Cover page	**1**
Table of Contents	**2**
Characterizations (Fig. S1-S2)	**3-4**
Crystal Structures (Table S1-S4)	**5-8**
Photophysical Properties (Table S5-S6, Fig. S3-S7)	**9-15**
References	**16**

Characterizations

Additional IR Analysis

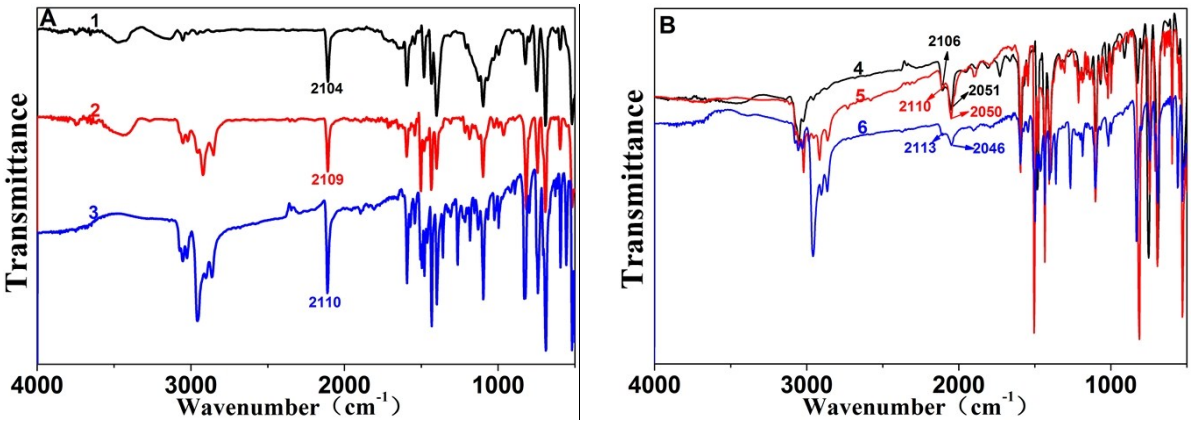

Fig. S1 FTIR spectra of complexes **1-3** (**A**) and **4-6** (**B**).

Characterizations

Additional $^{31}P\{^{1}H\}$ NMR Analysis

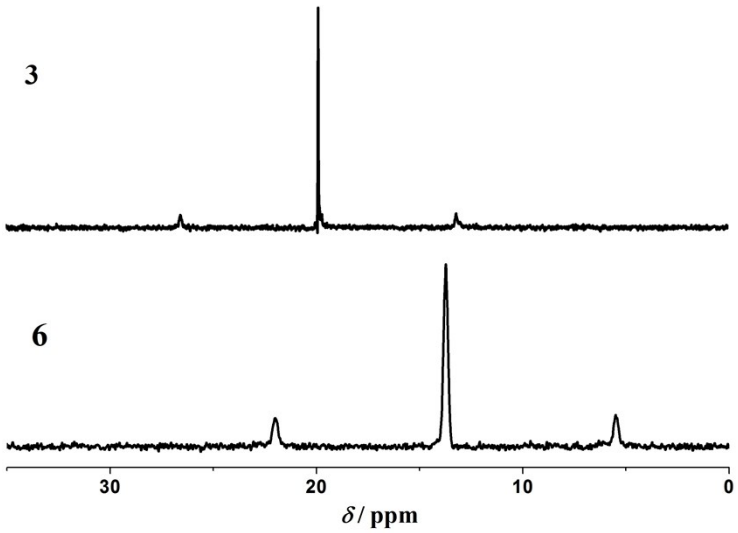

Fig. S2 $^{31}P\{^{1}H\}$ NMR spectra for complex **3** and **6 in $CDCl_3$ solution**.

Crystal Structures

Table S1. Crystal data and structure refinement for **1**·3/2CH_2Cl_2 and **3**·MeCN·CH_2Cl_2.

Compound	**1**·3/2CH_2Cl_2	**3**·MeCN·CH_2Cl_2
Empirical formula	$C_{207}H_{154}Cl_6N_4P_8Pt_4$	$C_{123}H_{112}Cl_2N_4P_4Pt_2$
fw	3938.15	2231.13
Temperature (K)	193 (2)	193 (2)
radiation (λ, Å)	0.72000	0.72000
Crystal system	Orthorhombic	Monoclinic
Space group	*P*nna	*C*2/c
a (Å)	23.599 (5)	32.222 (6)
b (Å)	37.492 (7)	16.172 (3)
c (Å)	19.730 (4)	20.802 (4)
β (°)	90	92.77 (3)
V (Å^3)	17457 (6)	10827 (4)
Z	4	4
ρ_{calcd}, g/cm^3	1.498	1.369
μ, mm^{-1}	3.417	2.740
R1 (F_o)	0.0481	0.0375
wR2(F_o^2)	0.1362	0.1068
GOF	1.042	1.056

Crystal Structures

Table S2. Crystallographic data for compounds **[4]**$_\infty$·CH_2Cl_2·1/2EtOEt and **5**·CH_2Cl_2.

Compound	**[4]**$_\infty$·CH_2Cl_2·1/2EtOEt	**5**·CH_2Cl_2
Empirical formula	$C_{172}H_{128}Ag_4Cl_4N_2OP_4Pt_4$	$C_{179}H_{140}Ag_4Cl_2N_2P_4Pt_4$
fw	3716.28	3725.55
Temperature (K)	193.15	77(2)
radiation (λ, Å)	0.71073	0.72000
Crystal system	Orthorhombic	Monoclinic
Space group	*P*bca	*P*2(1)/c
a (Å)	24.901(5)	18.249(4)
b (Å)	24.480(5)	14.605(3)
c (Å)	26.342(5)	27.333(6)
β (°)	90	91.31(3)
V (Å^3)	16057(6)	7283(3)
Z	4	2
ρ_{calcd}, g/cm^3	1.537	1.699
μ, mm^{-1}	4.103	4.488
R1 (F_o)	0.0618	0.0484
wR2(F_o^2)	0.1657	0.1449
GOF	1.185	1.143

Crystal Structures

Table S3. Bond lengths and bond angles for **1**·3/2CH_2Cl_2 and **3**·MeCN·CH_2Cl_2.

	bond distance [Å]			
	1·3/2CH_2Cl_2		**3·MeCN·CH_2Cl_2**	
Pt–C	Pt(1)-C(44)#1 2.002(4) Pt(1)-C(44) 2.002(4) Pt(2)-C(4)#1 1.991(3)	Pt(2)-C(4) 1.991(3) Pt(3)-C(92) 1.999(4) Pt(3)-C(100) 2.002(4)	Pt(1)-C(1) 1.989(2)	Pt(1)-C(21) 1.988(2)
Pt–P	Pt(1)-P(1) 2.2883(10) Pt(1)-P(1)#1 2.2883(10) Pt(2)-P(2) 2.2822(11)	Pt(2)-P(2)#1 2.2823(11) Pt(3)-P(3) 2.2853(9) Pt(3)-P(4) 2.2832(10)	Pt(1)-P(1) 2.2908(7)	Pt(1)-P(2) 2.2845(7)
	bond angle [º]			
C–Pt–C	C(44)#1-Pt(1)-C(44) 179.19(19) C(4)-Pt(2)-C(4)#1 178.7(2) C(92)-Pt(3)-C(100) 178.00(16)		C(1)-Pt(1)-C(21) 173.29(10)	
P–Pt–P	P(1)-Pt(1)-P(1)#1 173.94(4) P(2)-Pt(2)-P(2)#1 176.17(4) P(4)-Pt(3)-P(3) 175.18(3)		P(2)-Pt(1)-P(1) 177.98(2)	
C–Pt–P	C(44)#1-Pt(1)-P(1) 93.45(11) C(44)-Pt(1)-P(1) 86.51(11) C(44)#1-Pt(1)-P(1)#1 86.51(11) C(44)-Pt(1)-P(1)#1 93.44(11) C(4)#1-Pt(2)-P(2) 87.16(12) C(4)-Pt(2)-P(2) 92.88(12) C(4)-Pt(2)-P(2)#1 87.16(12) C(4)#1-Pt(2)-P(2)#1 92.88(12) C(92)-Pt(3)-P(3) 93.42(13) C(92)-Pt(3)-P(4) 86.80(13) C(100)-Pt(3)-P(3) 84.69(10)		C(1)-Pt(1)-P(1) 87.68(7) C(1)-Pt(1)-P(2) 90.35(7) C(21)-Pt(1)-P(1) 93.80(7) C(21)-Pt(1)-P(2) 88.21(7)	

Symmetry transformations used to generate equivalent atoms: #1 -x+3/2,-y+1, z

Crystal Structures

Table S4. Bond lengths and bond angles for **[4]**$_\infty$·CH_2Cl_2·1/2EtOEt and **5**·CH_2Cl_2.

	bond distance [Å]			
	[4]$_\infty$·CH_2Cl_2·1/2EtOEt		**5**·CH_2Cl_2	
Pt–Ag	Pt(1)-Ag(1) 3.1807(10) Pt(1)-Ag(2) 2.9078(8)	Pt(2)-Ag(1) 2.9198(9) Pt(2)-Ag(2) 3.0122(9)	Pt(1)-Ag (1) 3.0831(9) Pt(1)-Ag(2) 3.0161(9)	Pt(2)-Ag(1) 3.0062(9) Pt(2)-Ag(2) 3.0317(6)
Pt–P	Pt(1)-P(2) 2.299(2)	Pt(2)-P(1) 2.307(2)	Pt(1)-P(2) 2.2994(11)	Pt(2)-P(1) 2.2933(10)
Pt–C	Pt(1)-C(1) 2.019(10) Pt(1)-C(11) 2.007(9) Pt(1)-C(21) 2.023(9)	Pt(2)-C(31) 2.030(10) Pt(2)-C(41) 2.008(10) Pt(2)-C(51) 1.998(10)	Pt(1)-C(1) 2.013(4) Pt(1)-C(21) 2.010(4) Pt(1)-C(51) 2.018(4)	Pt(2)-C(11) 2.021(4) Pt(2)-C(31) 2.008(4) Pt(2)-C(41) 1.999(4)
Ag–C	Ag(1)-C(1) 2.334(9) Ag(1)-C(21) 2.658(9) Ag(1)-C(41) 2.277(10) Ag(1)-C(2) 2.501(9) Ag(1)-C(42) 2.622(11)	Ag(2)-C(11) 2.696(9) Ag(2)-C(21) 2.604(10) Ag(2)-C(51) 2.473(9)	Ag(1)-C(11) 2.259(4) Ag(1)-C(21) 2.283(4) Ag(1)-C(12) 2.514(4) Ag(1)-C(22) 2.402(4)	Ag(2)-C(1) 2.490(4) Ag(2)-C(31) 2.291(4) Ag(2)-C(51) 2.413(4) Ag(2)-C(32) 2.545(4) Ag(2)-C(52) 2.626(4)
Ag–N		Ag(2)-N(1)#1 2.290(7)		
C–C	C(1)-C(2) 1.220(13) C(11)-C(12) 1.195(13) C(21)-C(22) 1.217(14)	C(31)-C(32) 1.164(13) C(41)-C(42) 1.216(15) C(51)-C(52) 1.210(13)	C(1)-C(2) 1.217(6) C(11)-C(12) 1.218(6) C(21)-C(22) 1.223(6)	C(31)-C(32) 1.225(6) C(41)-C(42) 1.211(6) C(51)-C(52) 1.214(6)
	bond angle [º]			
C–Pt–C	C(1)-Pt(1)-C(21) 88.3(4) C(11)-Pt(1)-C(21) 89.9(4) C(11)-Pt(1)-C(1) 177.0(4)	C(41)-Pt(2)-C(31) 86.9(4) C(51)-Pt(2)-C(31) 88.0(4) C(51)-Pt(2)-C(41) 170.4(4)	C(1)-Pt(1)-C(51) 87.48(17) C(21)-Pt(1)-C(1) 88.68(17) C(21)-Pt(1)-C(51) 172.27(16)	C(31)-Pt(2)-C(11) 90.75(16) C(41)-Pt(2)-C(11) 87.81(16) C(41)-Pt(2)-C(31) 174.84(16)
C–Pt–P	C(1)-Pt(1)-P(2) 88.3(3) C(11)-Pt(1)-P(2) 93.9(3) C(21)-Pt(1)-P(2) 172.4(3)	C(41)-Pt(2)-P(1) 93.6(3) C(51)-Pt(2)-P(1) 92.8(2) C(31)-Pt(2)-P(1) 170.4(3)	C(51)-Pt(1)-P(2) 89.15(13) C(21)-Pt(1)-P(2) 93.97(12) C(1)-Pt(1)-P(2) 173.32(12)	C(41)-Pt(2)-P(1) 87.17(11) C(31)-Pt(2)-P(1) 94.31(12) C(11)-Pt(2)-P(1) 174.94(12)
C–Ag–C	C(1)-Ag(1)-C(21) 68.3(3) C(21)-Ag(1)-C(41) 128.2(3) C(41)-Ag(1)-C(1) 155.1(3)	C(21)-Ag(2)-C(11) 64.9(3) C(51)-Ag(2)-C(11) 128.5(3) C(51)-Ag(2)-C(21) 137.2(3)	C(11)-Ag(1)- C(21)160.43(16) C(21)-Ag(1)-C(12) 146.22(15)	C(51)-Ag(2)-C(1) 69.26(14) C(31)-Ag(2)-C(1) 130.07(14) C(31)-Ag(2)-C(51) 155.0(1)
N–Ag–C		N(1)#1-Ag(2)-C(11) 92.4(3) N(1)#1-Ag(2)-C(21) 100.1(3) N(1)#1-Ag(2)-C(51) 117.3(3)		

Photophysical Properties

Electronic absorption spectra

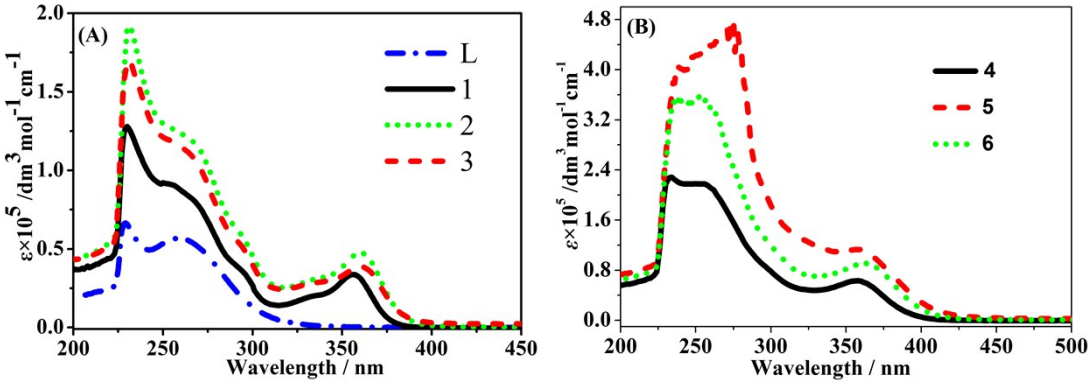

Fig. S3 The electronic absorption spectra of L ligand, **1-3** (A) and **4-6** (B) in CH_2Cl_2 solution at room temperature.

Photophysical Properties

Emission spectra

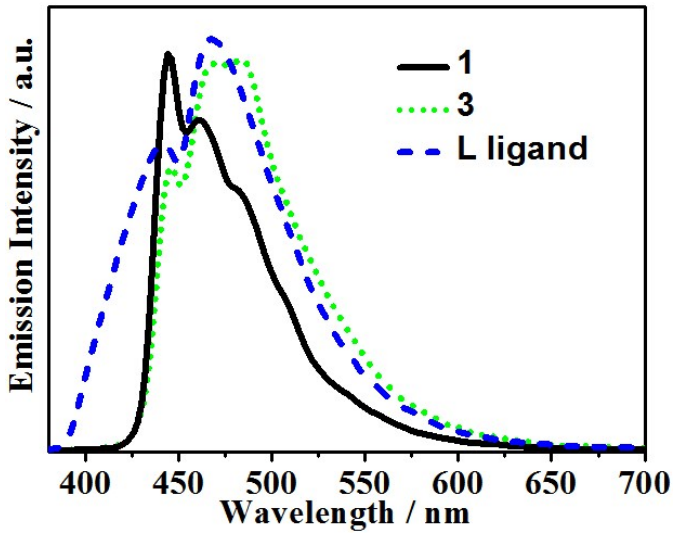

Fig. S4 Emission spectra of compounds **1**, **3** and L ligand in the solid state at 298 K.

Photophysical Properties

Emission spectra

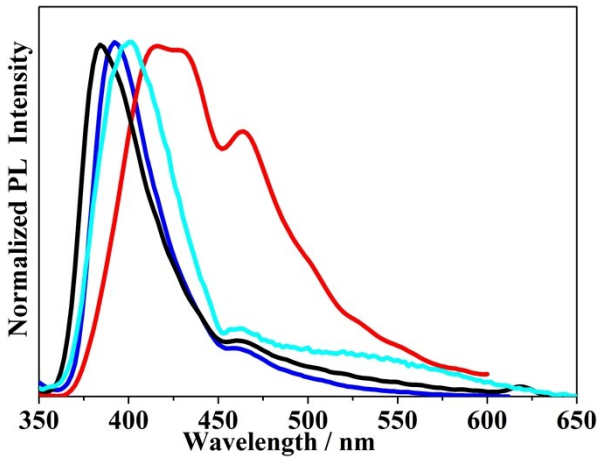

Fig. S5 Emission (λ_{ex} = 312 nm) spectra of compounds **1** (black line)**, 2** (red line)**, 3** (blue line) and L (cyan line) ligand in CH_2Cl_2 (298 K) with the concentration 1×10^{-4} M.

Photophysical Properties

Computational Details

All the calculations were carried out by using the Gaussian 09 program package[1] to get insight into the photophysical properties of $[4]_{\infty}$. The initial structure was extracted from the crystallographically determined geometry. To analyze the emission properties of the cluster, one hundred triplet excited states were calculated by the time-dependent DFT (TD-DFT)[2, 3] method at the gradient corrected correlation functional PBE1PBE[4] level on the basis of the ground state geometry structure. In these calculations, the Hay–Wadt double-ζ with a Los Alamos relativistic effect basis set (LANL2DZ)[5, 6]consisting of the effective core potentials (ECP) was employed for the Ag and Pt atoms, and 6-31G* basis set for the remaining non-metal atoms. Visualization of the frontier molecular orbitals was performed by GaussView software[7]. In the Multiwfn[8] program package, Ros-Schuit method[9] (C-squared population analysis method, SCPA) was supported to analyze the partition orbital composition.

Photophysical Properties

Table S5. Partial molecular orbital compositions (%) in the triplet excited state for the simplified model of **[4]**$_\infty$ in solid state by TD-DFT method at the PBE1PBE level.

orbital	energy (eV)	MO contribution (%)			
		Ag	Pt	C≡CR	L
LUMO+9	-0.027	32.72	10.31	33.30	23.67
LUMO+8	-0.136	51.42	6.80	14.96	26.82
LUMO+1	-2.721	2.01	2.27	1.17	94.55
HOMO	-4.054	45.36	4.32	21.11	29.21
HOMO-4	-6.041	13.91	35.51	50.55	0.03

Table S6 The excitation transitions for the simplified model of **[4]**$_\infty$ in solid state by TD-DFT method at the PBE1PBE level.

states	*E*, nm (eV)	O.S.	transition	contrib.	assignment
T_1	434 (2.85)	0.0026	HOMO-4→LUMO+1	91.42%	^{3}MMLCT/^{3}LLCT
T_2	354 (3.50)	0.2015	HOMO→LUMO+9	70.11%	^{3}MMLCT/^{3}LMMCT/^{3}IL/^{3}LLCT
			HOMO→LUMO+8	26.52%	^{3}MMLCT/^{3}LMMCT/^{3}IL/^{3}LLCT

Photophysical Properties

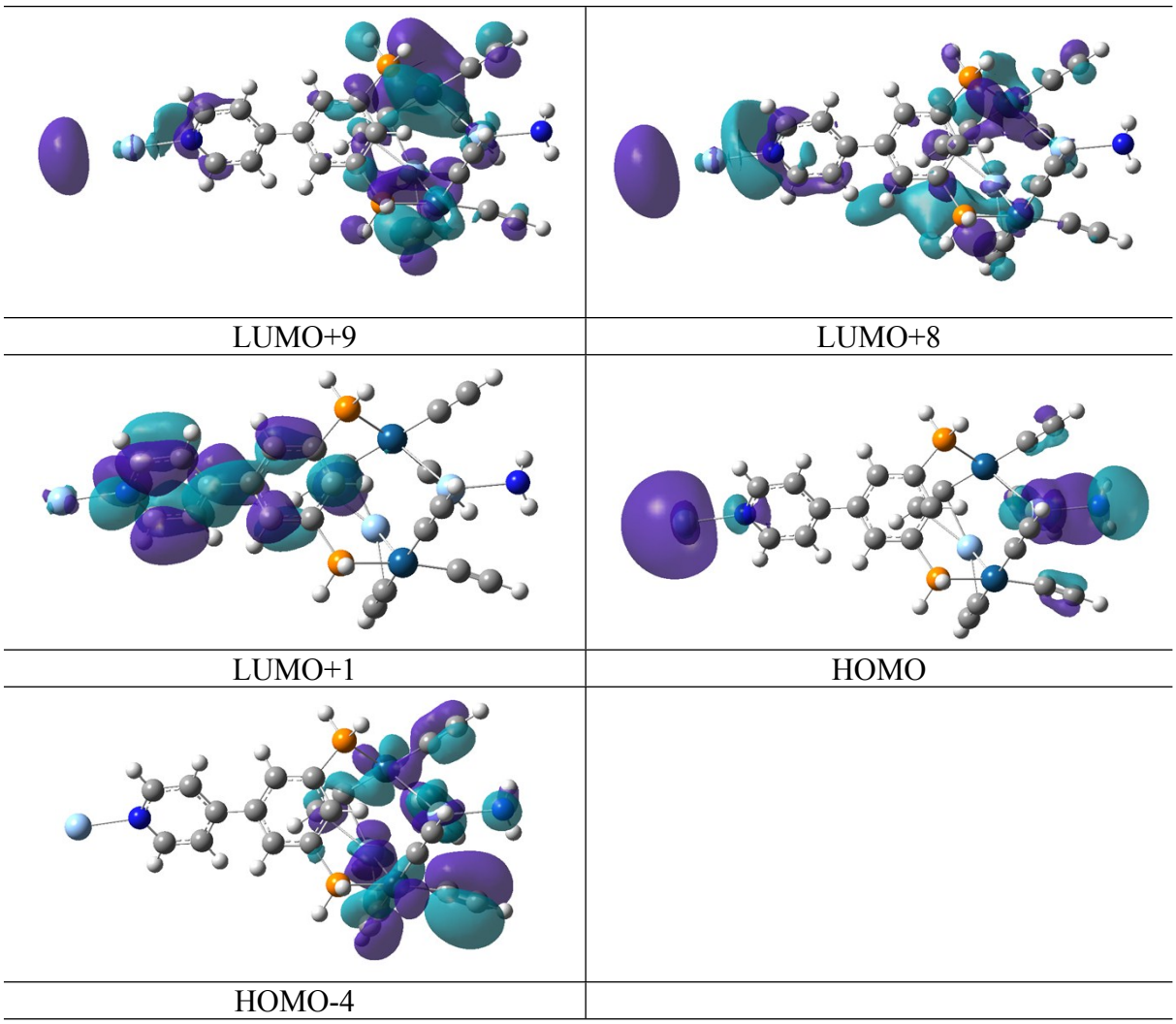

Fig. S6. Plots of the frontier molecular orbitals involved in the excitation transitions of the simplified model of **[4]**$_\infty$ in solid state by TD-DFT method at the PBE1PBE level. The cyan, royalblue, orange, blue, gray, and white spheres represent the silver, platium, phosphorus, nitrogen, carbon, and hydrogen atoms, respectively.

Photophysical Properties

Emission spectra

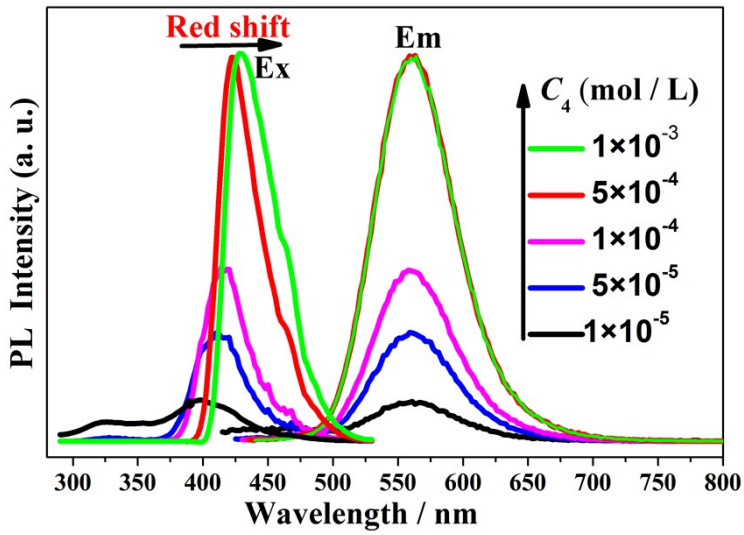

Fig. S7 Variation of the excitation (left, λ_{em} = 560 nm) and emission (right, independent of the λ_{ex} used) spectra of **4** in $ClCH_2CH_2Cl$ (298 K) with the concentration 1×10^{-5} M (black), 5×10^{-5} M (blue), 1×10^{-4} M (maganta), 5×10^{-4} M (red), and 1×10^{-3} M (green).

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