Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Novel Electrochemi- / Photo-Luminescence of Ag_3Cu_5 Heterometallic Alkynyl Clusters

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Experimental Section

Materials

All synthetic operations were performed under dry nitrogen atmosphere using Schlenk techniques and vacuum-line systems. The ligand 2,6-bis(diphenylphosphino)pyridine (dpppy) was purchased from Lude Fine Chemical Industry Co., Ltd., China. Phenylacetylene ($HC\equiv CC_6H_5$) and 4-methylphenylacetylene ($HC\equiv CC_6H_4CH_3$-4) were obtained from Acros Organics. All reagents were used as received and solvents were purified by standard methods. $(AgC\equiv CC_6H_4\text{-}R)_n$ (R=H, CH_3) [1] and $[Cu_2(\mu\text{-dpppy})_3](ClO_4)_2$ [2] were prepared according to the published methods.

Synthesis

$[Ag_3Cu_5(C\equiv CC_6H_5)_6(\mu\text{-dpppy})_3](ClO_4)_2$ (1). To 5 mL of a $CHCl_3/CH_3OH$ (4:1, v/v) solution of $[Cu_2(\mu\text{-dpppy})_3](ClO_4)_2$ (50.0 mg, 0.03 mmol) was added $[Ag(C\equiv CC_6H_5)]_n$ (19.0 mg, 0.09 mmol) with stirring at room temperature for 12 h to give a yellow solution. Diffusion of *n*-heptane onto the concentrated solution gave yellow crystals of **1**. Yield: 19.0 mg (57%). Elemental analysis (%) calcd for $C_{135}H_{99}N_3O_8P_6Cl_2Cu_5Ag_3$: C, 58.13; H, 3.58; N, 1.51; found: C, 57.98; H, 3.56; N, 1.55. ESI-MS [m/z (%)]: 1295.9 (100) $[M-(ClO_4)_2]^{2+}$. IR (KBr): $\nu = 2030$ (w, C≡C), 1096 (s，ClO_4^-) cm^{-1}. ^1H NMR (400.1 MHz, $CDCl_3$, TMS): $\delta = 8.12$ (t, $J = 8$ Hz , 3H), 7.59 (d, $J = 8$ Hz, 9H), 7.41 (d, $J = 8$ Hz, 3H), 7.35-7.24 (m, 12H), 7.20-7.14 (m, 9H), 7.07-7.02 (m, 12H), 6.92 (t, $J = 8$ Hz, 15H), 6.78 (t, $J = 8$ Hz, 12H), 6.58 (d, $J = 8$ Hz, 12H), 6.25 (d, $J = 8$ Hz, 12H) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): 4.94 ppm (d, $J_{Ag\text{-}P} = 376$ Hz, AgPPyPAg; $^2J_{P\text{-}P} = 27$ Hz, AgPPyPAg).

$[Ag_3Cu_5(C\equiv CC_6H_4CH_3\text{-}4)_6(\mu\text{-dpppy})_3](ClO_4)_2$ (2). To 5 mL of a $CH_2Cl_2/CH_3OH/ClCH_2CH_2Cl$ (4:0.5:0.5, v/v/v) solution of $[Cu_2(\mu\text{-dpppy})_3](ClO_4)_2$ (50.0 mg, 0.03 mmol) was added $[Ag(C\equiv CC_6H_4CH_3\text{-}4)]_n$ (20.0 mg, 0.09 mmol) with stirring at room temperature for 12 h to give a yellow-orange solution. Diffusion of n-hexane onto the concentrated solution gave orange crystals of **2**. Yield: 22.0 mg (64%). Elemental analysis (%) calcd for $C_{141}H_{111}N_3O_8P_6Cl_2Cu_5Ag_3$: C, 58.93; H, 3.89; N, 1.46; N,1.51; found: C, 58.17; H, 4.03; N,1.47. ESI-MS [m/z (%)]: 1336.6 (100) $[M-(ClO_4)_2]^{2+}$. IR (KBr): ν=2020 (w, C≡C), 1096 (s，$ClO4^-$) cm^{-1}. ^1H NMR (400.1 MHz, $CDCl_3$, TMS): $\delta = 8.12$ (t, $J = 8$ Hz, 3H), 7.59 (d, $J = 8$ Hz, 9H), 7.40 (d, $J = 8$ Hz, 3H), 7.35-7.24 (m, 6H), 7.20-7.14 (m, 9H), 7.07-7.02

(m, 12H), 6.92 (t, J = 8 Hz, 15H), 6.78 (t, J = 8 Hz, 12H), 6.58 (d, J = 8 Hz, 12H), 6.25 (d, J = 8 Hz, 12H), 2.29 (s, 18H, CH_3). ppm. $^{31}P\{1H\}$ NMR (162 MHz, $CDCl_3$): 4.77 ppm (d, $J_{Ag\text{-}P}$ = 372 Hz, AgPPyPAg; $^2J_{P\text{-}P}$ = 28 Hz, AgPPyPAg)

Apparatus

Positive-ion ESI-MS spectra were performed on a Thermo Finnigan DECAX-3000 LCQ mass spectrometer using dichloromethane/methanol or acetonitrile/methanol as the mobile phase at the Fujian Institute of Research on the Structure of Matter, the Chinese Academy of Sciences. Elemental analyses (C, H, N) were carried out on a Perkin-Elmer model 240C automatic instrument. IR spectra were recorded on a Nicolet 6700 FT-IR spectrophotometer with KBr pellets. ^1H NMR spectra, with chemical shifts reported relative to tetramethylsilane, and $^{31}P\{^1H\}$ NMR spectra with chemical shifts relative to 85% H_3PO_4 external reference were recorded on a Bruker AVANCE 400 MHz spectrometer. UV-Vis absorption spectra were recorded at 298K on a Perkin-Elmer Lambda 25 UV-Vis spectrometer. Steady-state excitation and emission spectra at room temperature were determined on an Edinburgh Analytical Instrument (FLS920 fluorescence spectrometer). Emission lifetimes were determined on an Edinburgh Analytical Instrument (FLS920 fluorescence spectrometer) with a light-emitting diode lamp (405 nm) and analyzed by the use of a program for exponential fits. The luminescence quantum yield of the sample was determined according to

$$\Phi_s = \Phi_r (B_r / B_s) (n_s / n_r)^2 (D_s / D_r) \qquad (1)$$

where the subscripts s and r refer to the sample and reference solutions, respectively, $B = 1–10^{-AL}$. A is the absorbance at the excitation wavelength, L is the path length, n is the refractive index of the solvent, and D is the integrated emission intensity. A degassed acetonitrile solution of $[Ru(bpy)_3](PF_6)_2$ (Φ_{em}= 0.062) [3] were used as the reference.

Crystal Structural Determination

The Crystals **1** and **2** coated with epoxy resin were measured on a Mar CCD 165 nm diffractometer by the oscillation scan technique at 193K using the Beijing Synchrotron Radiation Facility with a 3W1A beam (λ = 0.71000 Å). The cell refinement and data reduction were computed using the *HKL2000* software.[4] The structure was solved by direct method or the heavy atoms were located from

E-map. The remaining non-hydrogen atoms were determined from successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically except those mentioned otherwise. The structure was refined on F^2 by full-matrix least-squares methods using the *SHELXTL-97* program package. [5] The crystallographic parameters and details for data collections and refinements of crystals **1** and **2** are summarized in Table S1. Selected bond distances and angles for complexes **1** and **2** are listed in Table S2.

Crystal Structures

Table S1. Crystallographic data for compounds **1** and **2**.

Compound	**$2(1)\cdot 5CHCl_3\cdot 2H_2O$**	**$2(2)\cdot CH_2Cl_2$**
Empirical formula	$C_{275}H_{211}Ag_6Cl_{19}Cu_{10}N_6O_{18}P_{12}$	$C_{283}H_{226}Ag_6Cl_6Cu_{10}N_6O_{16}\ P_{12}$
fw	6215.31	5833.66
Temperature (K)	193(2)	193(2)
radiation (λ, Å)	0.71000	0.71000
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/n$	$C2/c$
a (Å)	18.820 (4)	29.400 (6)
b (Å)	27.340 (6)	17.068 (3)
c (Å)	25.240 (5)	48.669 (10)
β (°)	96.94(3)	92.25(3)
V (Å^3)	12892(5)	24403(8)
Z	2	4
ρ_{calcd}, g/cm^3	1.601	1.588
μ, mm^{-1}	1.585	1.526
R1 (F_o)	0.0811	0.0903
wR2(F_o^2)	0.2224	0.3118
GOF	1.126	1.104

Crystal Structures

Table S2. Selected bond distances (Å) and angles (º) for complexes **1** and **2**.

	$\mathbf{2(1)\cdot 5CHCl_3\cdot 2H_2O}$		$\mathbf{2(2)\cdot CH_2Cl_2}$	
Ag – Cu	Ag(1)-Cu(1) 2.659(2) Ag(1)-Cu(3) 2.641(2) Ag(1)-Cu(5) 3.216(2) Ag(2)-Cu(1) 2.632(2) Ag(2)-Cu(2) 2.645(2) Ag(2)-Cu(5) 3.160(2)	Ag(3)-Cu(2) 2.615(2) Ag(3)-Cu(3) 2.648(2) Ag(3)-Cu(5) 3.170(2)	Ag(1)-Cu(1) 2.6453(12) Ag(1)-Cu(3) 2.6525(14) Ag(1)-Cu(4) 3.1717(13) Ag(2)-Cu(1) 2.6682(13) Ag(2)-Cu(2) 2.6591(13) Ag(2)-Cu(4) 3.1552(14)	Ag(3)-Cu(3) 2.6432(13) Ag(3)-Cu(2) 2.6738(13) Ag(3)-Cu(4) 3.1844(13)
Cu – Cu	Cu(1)-Cu(5) 2.531(2) Cu(1)-Cu(4) 2.561(3) Cu(2)-Cu(5) 2.548(3) Cu(2)-Cu(4) 2.561(2)	Cu(3)-Cu(4) 2.574(3) Cu(3)-Cu(5) 2.604(2) Cu(4)-Cu(5) 2.684(2)	Cu(1)-Cu(4) 2.5393(15) Cu(1)-Cu(5) 2.6628(15) Cu(2)-Cu(4) 2.6003(15) Cu(2)-Cu(5) 2.6262(14)	Cu(3)-Cu(5) 2.6178(15) Cu(3)-Cu(4) 2.6191(16) Cu(4)-Cu(5) 2.7403(16)
Ag – C	Ag(1)-C(21) 2.519(15) Ag(1)-C(41) 2.644(15)	Ag(2)-C(1) 2.515(16) Ag(3)-C(11) 2.609(15)	Ag(1)-C(41) 2.562(9) Ag(1)-C(61) 2.594(9) Ag(2)-C(21) 2.505(9)	Ag(3)-C(31) 2.490(9) Ag(3)-C(71) 2.689(10)
Cu – C	Cu(1)-C(41) 1.927(15) Cu(1)-C(1) 1.936(15) Cu(2)-C(11) 1.927(15) Cu(2)-C(31) 1.967(15) Cu(3)-C(21) 1.918(16)	Cu(3)-C(51) 1.945(17) Cu(4)-C(31) 2.053(14) Cu(4)-C(41) 2.060(15) Cu(4)-C(51) 2.089(14) Cu(5)-C(1) 2.061(15) Cu(5)-C(11) 2.034(15)	Cu(1)-C(61) 1.924(9) Cu(1)-C(21) 1.976(9) Cu(2)-C(51) 1.931(10) Cu(2)-C(31) 1.963(9) Cu(3)-C(71) 1.931(10) Cu(3)-C(41) 1.935(9)	Cu(4)-C(21) 2.037(10) Cu(4)-C(41) 2.062(9) Cu(4)-C(31) 2.061(9) Cu(5)-C(51) 2.124(10) Cu(5)-C(71) 2.132(11) Cu(5)-C(61) 2.135(12)
Cu– N	Cu(1)-N(1) 2.057(12) Cu(2)-N(2) 2.049(12)	Cu(3)-N(3) 2.060(12)	Cu(1)-N(1) 2.088(7) Cu(2)-N(2) 2.071(7)	Cu(3)-N(3) 2.066(7)
P – Ag – P	P(1)-Ag(1)-P(6) 115.44(15) P(3)-Ag(2)-P(2) 118.11(14)	P(5)-Ag(3)-P(4) 120.70(14)	P(1)-Ag(1)-P(6) 117.97(8) P(3)-Ag(2)-P(2) 119.73(8)	P(5)-Ag(3)-P(4) 118.35(8)
P – Ag – C	P(1)-Ag(1)-C(21) 122.9(4) P(6)-Ag(1)-C(21) 91.5(3) P(3)-Ag(2)-C(1) 125.1(3)	P(2)-Ag(2)-C(1) 90.9(3) P(5)-Ag(3)-C(11) 124.7(3) P(4)-Ag(3)-C(11) 90.6(4)	P(1)-Ag(1)-C(41) 120.5(2) P(6)-Ag(1)-C(41) 87.6(2) P(3)-Ag(2)-C(21) 123.9(2)	C(21)-Ag(2)-P(2) 89.9(2) C(31)-Ag(3)-P(5) 122.6(2) C(31)-Ag(3)-P(4) 90.1(2)
C – Cu – C	C(41)-Cu(1)-C(1) 162.2(6) C(11)-Cu(2)-C(31)163.5(6) C(21)-Cu(3)-C(51)160.2(6) C(41)-Cu(4)-C(31)120.1(6) C(41)-Cu(4)-C(51)111.4(6)	C(31)-Cu(4)-C(51)113.4(6) C(21)-Cu(5)-C(1) 116.5(6) C(21)-Cu(5)-C(11)117.0(5) C(1)-Cu(5)-C(11) 112.6(6)	C(61)-Cu(1)-C(21)162.4(5) C(51)-Cu(2)-C(31)161.6(5) C(71)-Cu(3)-C(41)162.5(4) C(21)-Cu(4)-C(41)117.2(4) C(21)-Cu(4)-C(31)114.4(3)	C(41)-Cu(4)-C(31)113.1(3) C(51)-Cu(5)-C(61)116.2(4) C(51)-Cu(5)-C(71)117.4(4) C(61)-Cu(5)-C(71)118.4(4)
C – Cu – N	C(41)-Cu(1)-N(1) 97.1(5) C(1)-Cu(1)-N(1) 99.7(6) C(11)-Cu(2)-N(2) 100.9(5)	C(31)-Cu(2)-N(2) 95.6(5) C(21)-Cu(3)-N(3) 99.0(6) C(51)-Cu(3)-N(3) 100.7(5)	C(61)-Cu(1)-N(1) 104.6(4) C(21)-Cu(1)-N(1) 92.9(3) C(51)-Cu(2)-N(2) 104.8(4)	C(31)-Cu(2)-N(2) 93.5(3) C(71)-Cu(3)-N(3) 106.7(4) C(41)-Cu(3)-N(3) 90.7(3)

Crystal Structures

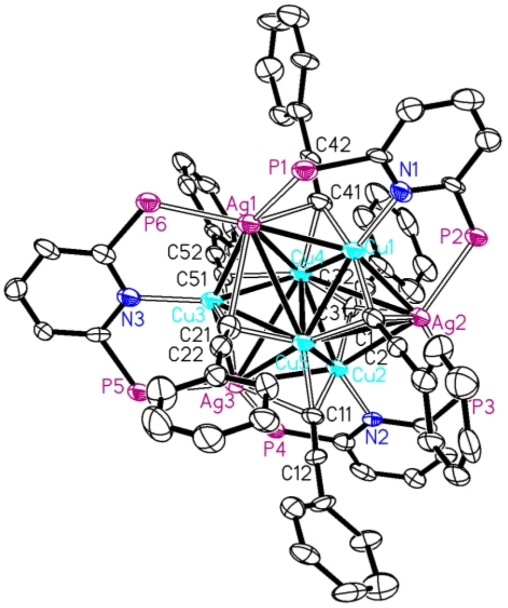

Fig. S1. ORTEP drawing of the cation of complex **1** with atom labelling scheme showing 30% thermal ellipsoids. Phenyl rings on the phosphorus atoms and hydrogen atoms are omitted for clarity.

Photophysical Properties

Table S3. Photophysical data for **1** and **2** at room temperature.

Compound	Medium	λ_{abs}/nm ($\varepsilon \times 10^{-5}$ / dm^3 mol^{-1} cm^{-1})	λ_{em}/nm (τ_{em}/μs) [a]	Φ_{em} [b]
1	solid		590 (0.71)	
	CH_2Cl_2	235 (1.90), 246 (1.67), 273 (0.88), 417 (0.05)	595 (0.20)	0.015
	CH_3CN	206 (2.40), 234 (1.39), 270 (0.69), 417 (0.05)	602 (0.10)	0.004
	CH_3CN/H_2O (10:90,v/v)	234 (1.40), 244 (1.24), 272 (0.89), 425 (0.15)	592 (0.18)	0.062
2	solid		594 (0.79)	
	CH_2Cl_2	264 (2.05), 251 (1.87), 276 (0.96), 427 (0.05)	604 (0.23)	0.013
	CH_3CN	207 (3.22), 237 (1.45), 272 (0.82), 427 (0.04)	609 (0.10)	0.007
	CH_3CN/H_2O (10:90,v/v)	233 (1.61), 244 (1.42), 276 (1.03), 436 (0.16)	604 (0.10)	0.058

[a] The excitation wavelength in the lifetime measurements are at 405 nm. [b] The quantum yields were measured using $[Ru(bpy)_3](PF_6)_2$ as a standard. [3]

Photophysical Properties

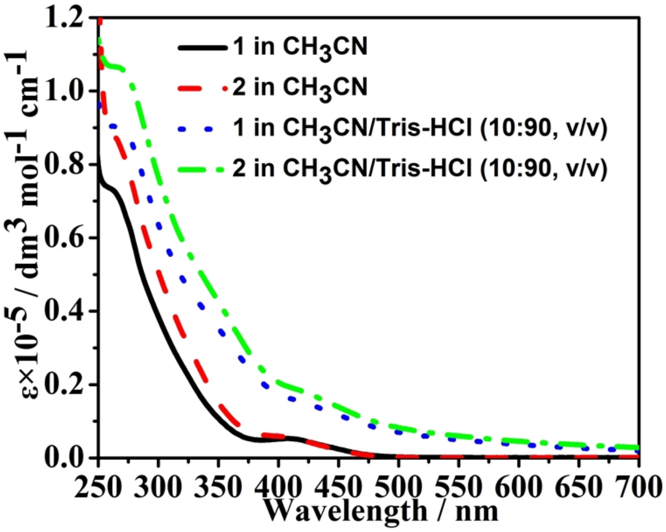

Fig. S2. UV–Vis spectra of complexes **1** and **2** in CH_3CN solution and CH_3CN/Tris-HCl (10:90, v/v, pH 9.0) mixture.

Photophysical Properties

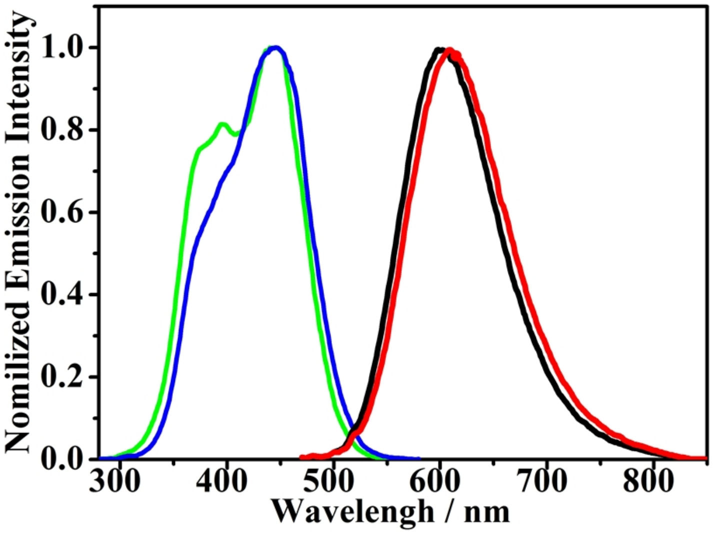

Fig. S3. Excitations and emissions of 0.1 mM **1** (green and black line, respectively) and **2** (blue and red line, respectively) in CH_3CN solution, λ_{ex} =450 nm.

Electrochemistry

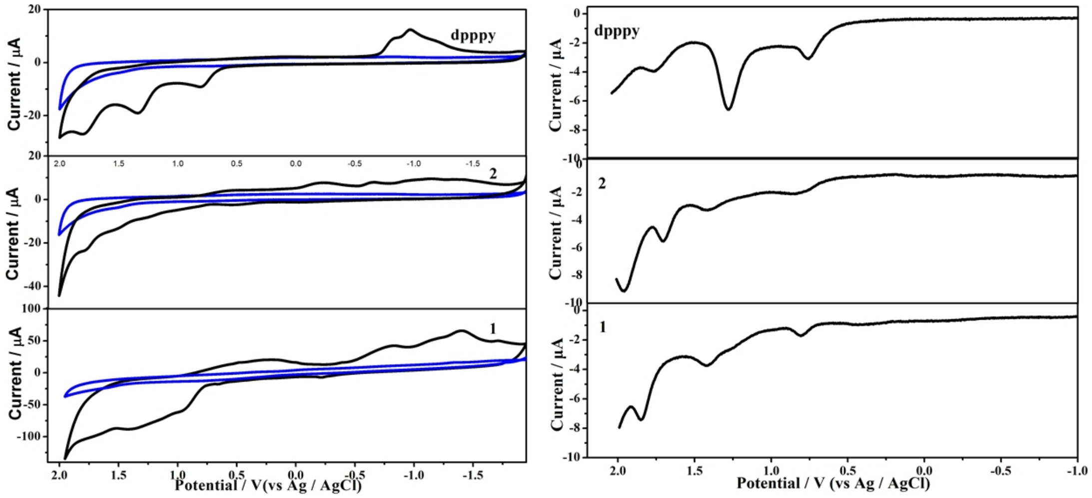

Fig. S4. CVs (left) and DPV (right) of 0.1 mM **1**, **2** and 1.0 mM dpppy ligand in deaerated CH_3CN (0.1 M TBAP) at GCE. Scan rate, 100 mv s^{-1}. The blue lines represent the CVs in the blank solution under the same experimental conditions.

Electrochemiluminescence

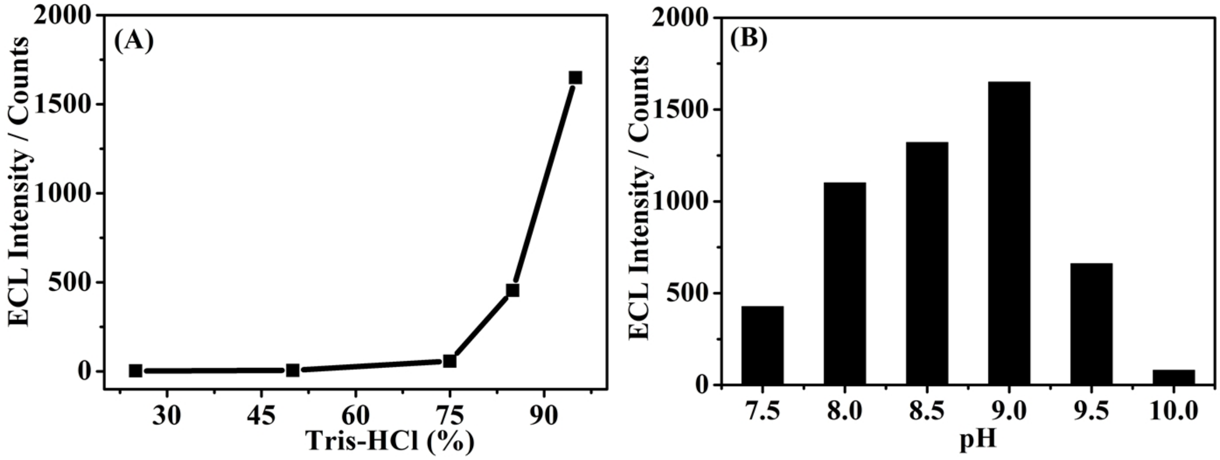

Fig. S5. The ECL responses of 10 μM **1** in a solution containing (A) 0.05 M pH 9.0 Tris-HCl / CH_3CN solution with different ratio of Tris-HCl buffer solutions, and (B) 0.05 M Tris-HCl (95%) and CH_3CN (5%) at various pH on GC working electrode. Scan rate, 100 mv s^{-1}.

Electrochemiluminescence

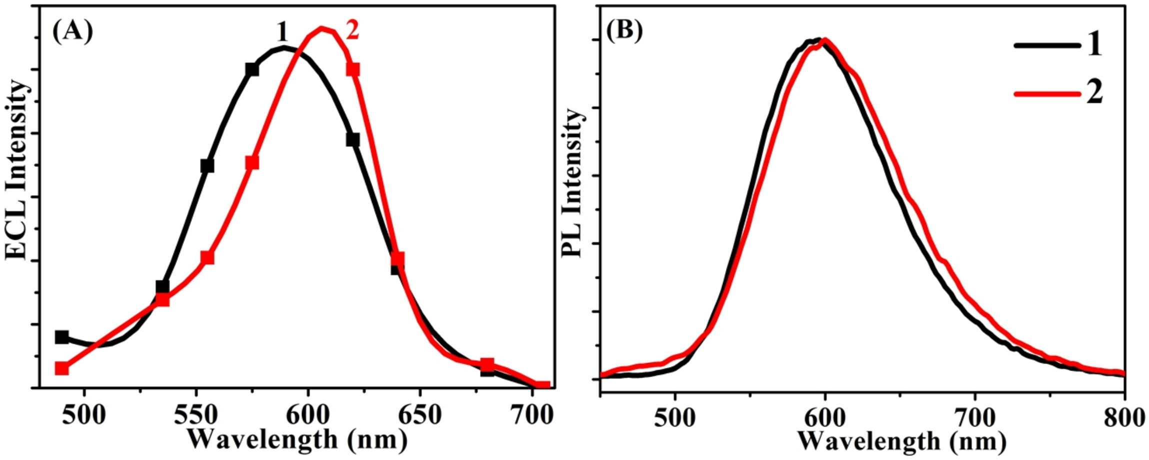

Fig. S6. ECL (A) and PL spectra (B) of **1** and **2** in a solution containing 0.05 M pH 9.0 Tris-HCl (95%) and CH_3CN (5%) solution.

References

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