Supplementary material

Novel Luminescent Iminephosphine Complex of Copper(I) with High Photochemical and Electrochemical Stability

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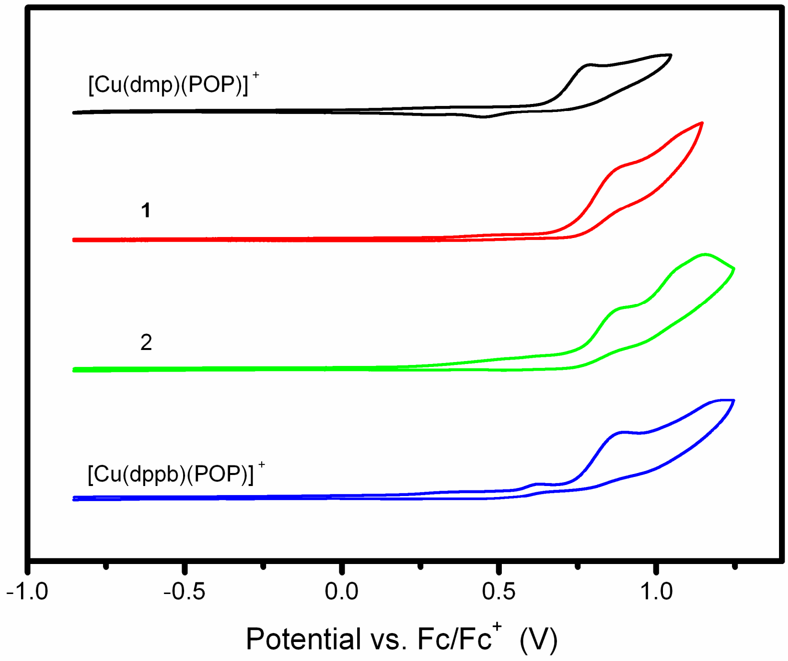

Figure S1. Oxidation waves of **1**, **2**, [Cu(dmp)(DPEphos)]$^+$ and [Cu(dppb)(DPEphos)]$^+$ in acetonitrile solution at room temperature. Scan rate 100 mVs^{-1} in 0.1 M TBAP.

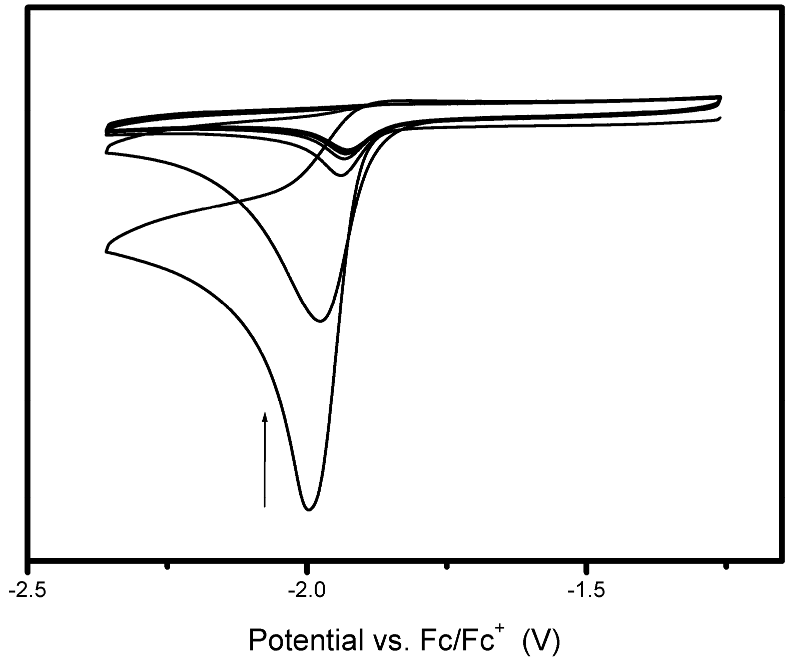

Figure S2. Multiple scan CVs for the reduction of **1** in acetonitrile solution at room temperature. Scan rate 100 mVs^{-1} in 0.1 M TBAP.

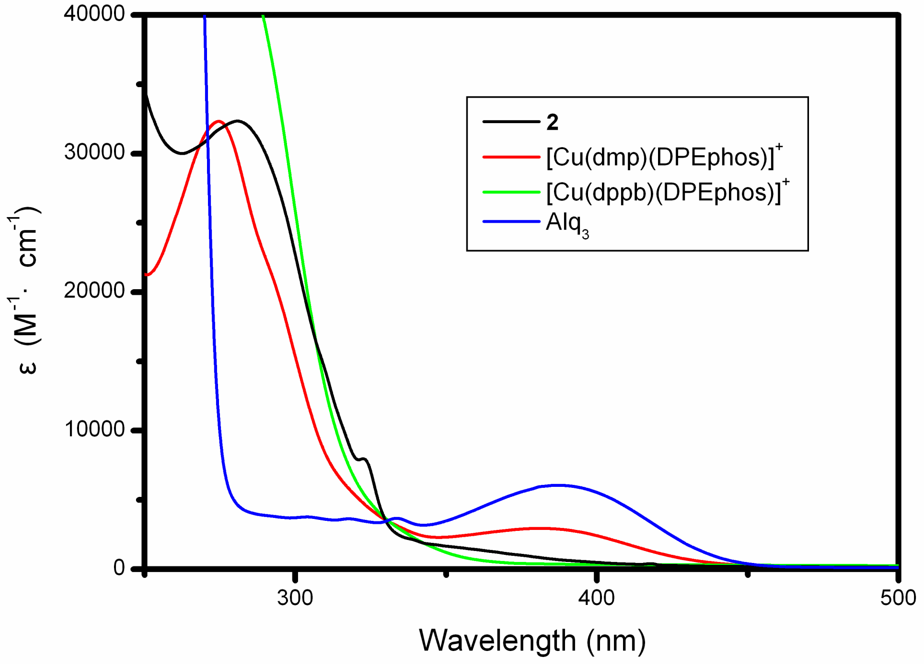

Figure S3. Absorption spectra of **2**, [Cu(dmp)(DPEphos)]$^+$, [Cu(dppb)(DPEphos)]$^+$ and Alq$_3$ in CH$_2$Cl$_2$ solutions.

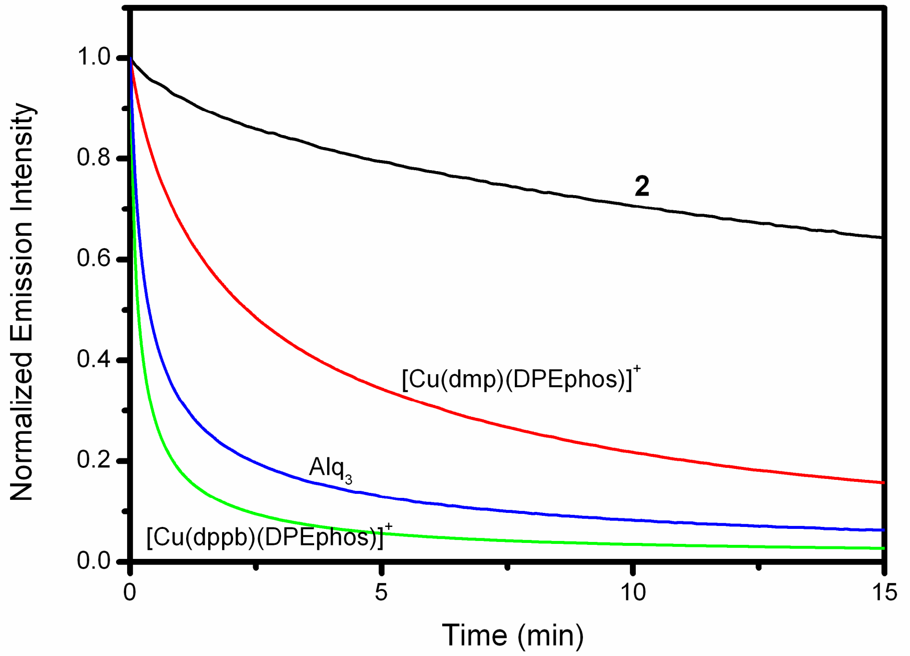

Figure S4. Photodegradation of **2**, [Cu(dmp)(DPEphos)]$^+$, [Cu(dppb)(DPEphos)]$^+$ and Alq$_3$ on the surface of silica-gel plates.

Experimental section

General. dppq, mdppq [1] and $[Cu(NCCH_3)_4](BF_4)$ [2] were prepared by the literature procedure, as were the comparative complexes $[Cu(dmp)(DPEphos)](BF_4)$ [3] and $[Cu(dppb)(DPEphos)](BF_4)$.[4] Other reagents and solvents employed were commercially available and were used without further purification. C, H, N elemental analyses were carried out on an Elementar Vario EL III elemental analyzer. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian-Unity INOVA-500.

Synthesis of Complexes. The complexes were synthesized according to the following general procedure: A mixture of $[Cu(NCCH_3)_4](BF_4)$ (0.314 g, 1.0 mmol) and DPEphos (0.538 g, 1.0 mmol) in CH_2Cl_2 (10 mL) was stirred for 10 min at room temperature and then added iminephosphine ligand (1.0 mmol). The reaction mixture was stirred for an additional 10 min and then the solution was concentrated for recrystallization to afford the product.

$[Cu(dppq)(DPEphos)]BF_4$ (1). Recrystallization from ethanol/ether, yield: 0.93 g, 93%. ^1H NMR ($CDCl_3$, 400MHz) [ppm]: δ 8.51 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 4.4 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 7.68 (t, J = 7.9 Hz, 1H), 7.48 (d t, J = 0.4 Hz, J = 6.8 Hz, 1H), 7.33-7.26 (m, 4H), 7.20-7.15 (m, 13H), 7.01-6.99 (m, 2H), 6.95-6.91 (m, 2H), 6.90-6.86 (m, 8H), 6.75-6.71 (m, 4H), 6.46-6.43 (m, 2H), 6.34-6.30 (m, 4H). ^{13}C NMR ($CDCl_3$, 100MHz) [ppm]: δ 157.71, 152.56, 139.70, 137.74, 134.66, 133.72, 132.51, 132.36, 132.32, 132.19, 132.06, 130.60, 130.56, 130.02, 129.82, 129.03, 128.87, 128.79, 128.70, 127.99, 125.29, 122.89, 120.14. Found: C, 68.02; H, 4.54; N, 1.40. Calc. for $C_{59}H_{50}BCuF_4NO_2P_3$: C, 67.60; H, 4.81; N, 1.34%.

$[Cu(mdppq)(DPEphos)]BF_4$ (2). Recrystallization from dichloromethane/ether, yield: 0.82 g, 81%. ^1H NMR($CDCl_3$, 400MHz) [ppm]: δ 8.52 (d, J = 8.4 Hz, 1H), 8.14 (d, J = 7.2 Hz, 1H), 7.60 (d t, J = 2.8 Hz, J = 7.6 Hz, 1H), 7.53 (t. J = 7.6 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.32-7.28 (m, 4H), 7.22-7.18 (m, 4H), 7.09-6.98 (m, 18H), 6.95-6.91 (m, 2H), 6.88-6.84 (m, 4H), 6.55-6.52 (m, 6H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 100MHz) [ppm]: δ 163.14, 157.82, 139.74, 137.40, 134.78, 133.58, 132.36, 132.26, 132.15, 132.01, 131.82, 131.59, 130.33, 130.18, 129.54, 128.79, 128.75, 128.66, 128.58, 126.89, 125.10, 124.72, 119.99, 27.70. Found: C, 64.28; H, 4.32; N, 1.30. Calc. for $C_{59}H_{48}BCl_2CuF_4NOP_3$: C, 64.35; H, 4.39; N, 1.27%.

Photophysical measurements. The solution samples for the luminescence studies were prepared by the freeze-pump-thaw technique. The samples of complexes in polymer film were prepared by spin-coating a mixture of the Cu^I complex (20 wt%) and poly(methyl methacrylate) (80 wt%) in CH_2Cl_2 onto a quartz glass slide. The samples for photodegradation studies were prepared in two ways: 1) 0.025 mmol complex and 1 g nanometer Al_2O_3 particles were mixed in 2 ml CH_2Cl_2, then removed the solution in vacuum and compacted the powder in a front face solid sample holder. 2) Drop the complex solution on the surface of a silica-gel plate, and then dry in air. UV-vis absorption and photoluminescence spectra were recorded by a

Perkin-Elmer Lambda 45 UV/VIS spectrophotometer and a HORIBA Jobin-Yvon FluoroMax-4 spectrometer, respectively. The solution photoluminescence quantum yield was measured by the literature method[5] with $[Ru(bpy)_3]^{2+}$ in degassed water as the standard ($\phi = 0.042$).[6] The film PL quantum yield were defined as the number of photons emitted per photon absorbed by the system and measured by FluoroMax-4 equipped with an integrating sphere. The luminescence decay measurements were performed by the time-correlated single-photon counting (TCSPC) upgrade on the FluoroMax-4 with a FluoroHub module. The lifetimes of solution samples were measured by TCSPC mode in conjunction with a nanoLED pulsed source (372 nm). The lifetimes of PMMA film samples were measured by multi-channel scaling (MCS) mode in conjunction with a spectraLED pulsed source (373 nm). Signals were collected using a FluoroHub module and analyse by the DAS6 Decay Analysis software (HORIBA Jobin-Yvon). Photodegradation studies were also performed at FluoroMax-4 in kinetics mode. All samples were irradiated at 330 nm using a 150 W Xe-lamp with 10 nm slit. The relative humidity of testing environment is 50%.

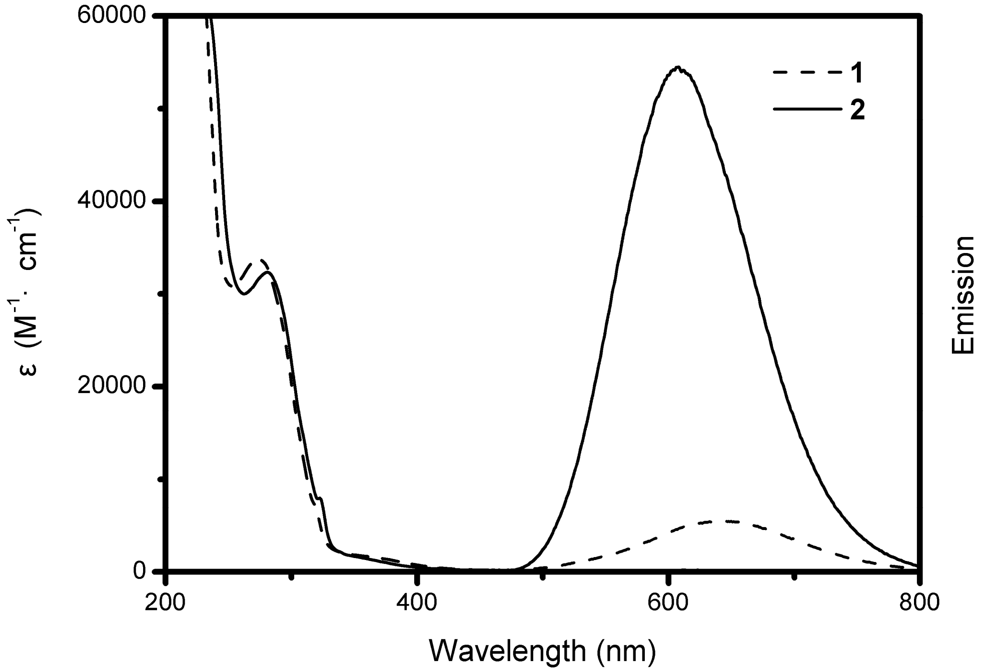

Figure S5. Absorption and emission spectra of **1** and **2** in CH_2Cl_2 at room temperature. Emission spectra excited at same conventions. Areas reflect the relative quantum yields.

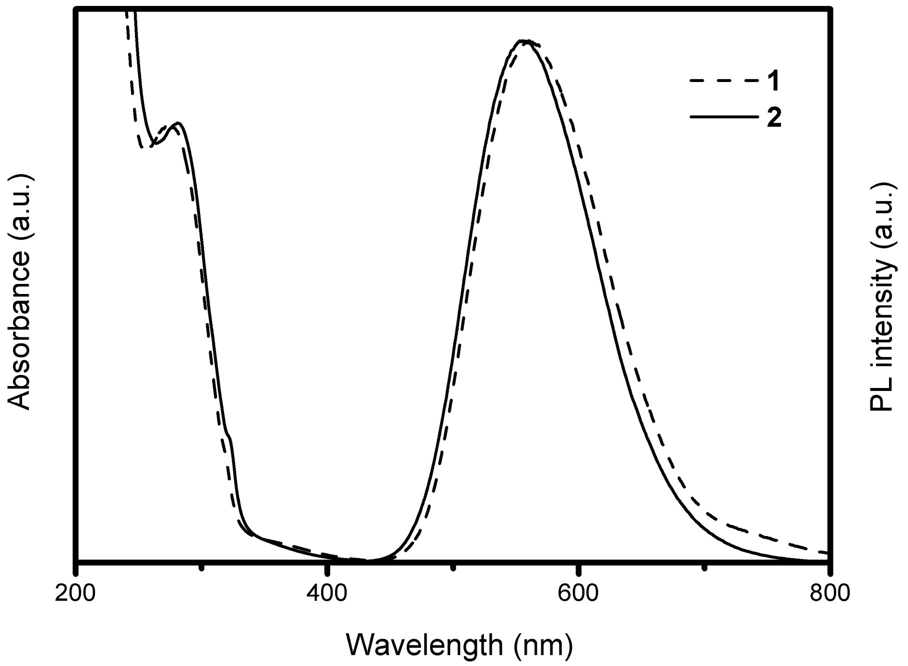

Figure S6. Absorption and emission spectra of 20 wt% **1** and 20 wt% **2** in PMMA films at room temperature.

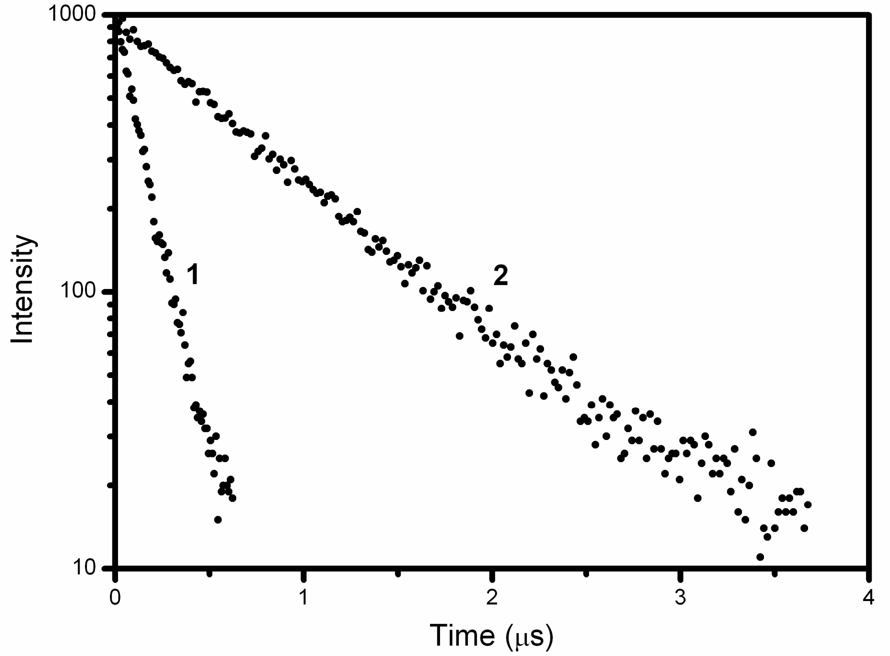

Figure S7. Emission decay of complexes **1** (at 642 nm) and **2** (at 608 nm) in CH_2Cl_2 at room temperature following pulsed excitation (λ_{ex} = 372 nm).

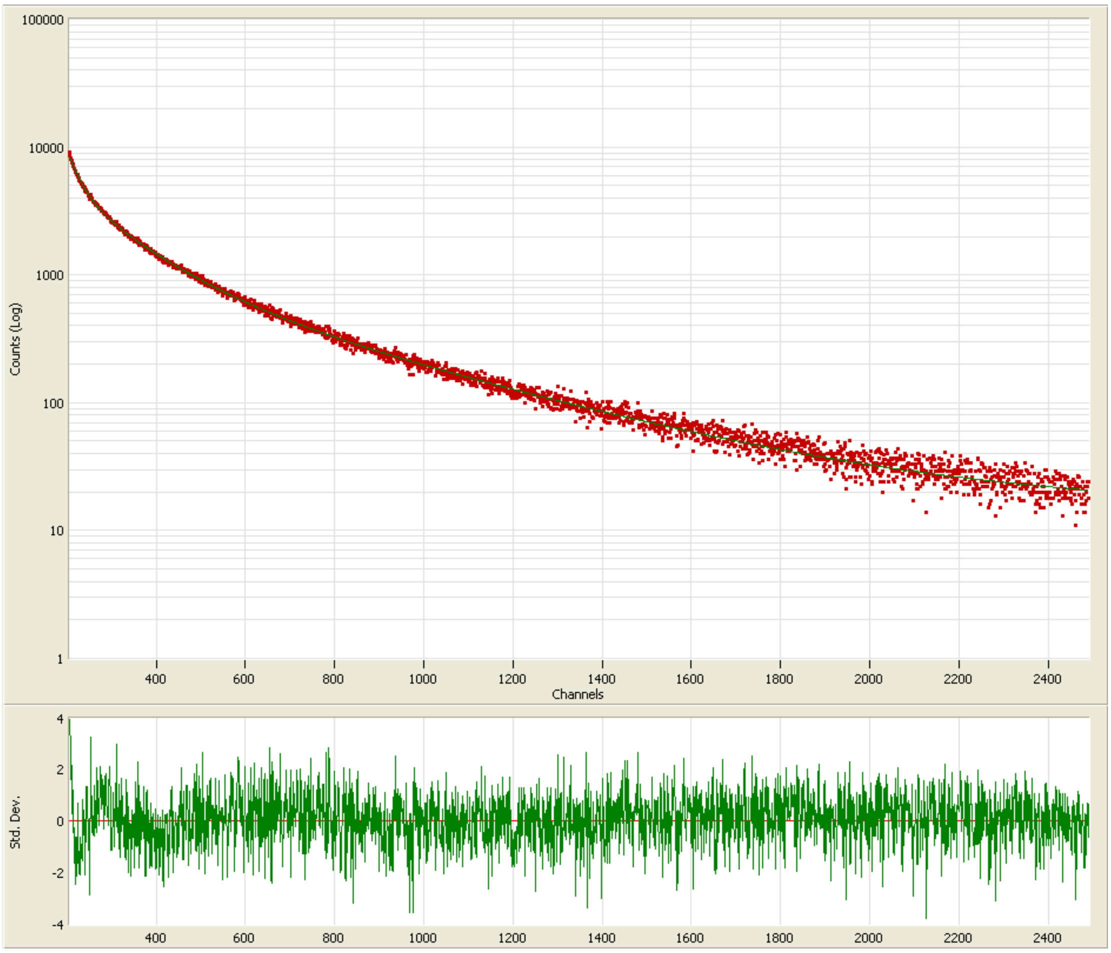

Figure S8. Emission decay of complex **1** (at 560 nm) in PMMA film at room temperature following pulsed excitation (λ_{ex} = 373 nm). Time calibration: 0.50 μs/ch. The emission decay was fitted by the following three-exponential kinetic traces: $I(t)$ = 3327 exp(-t/64.7) + 1081 exp(-t/218.1) + 3765 exp(-t/13.7).

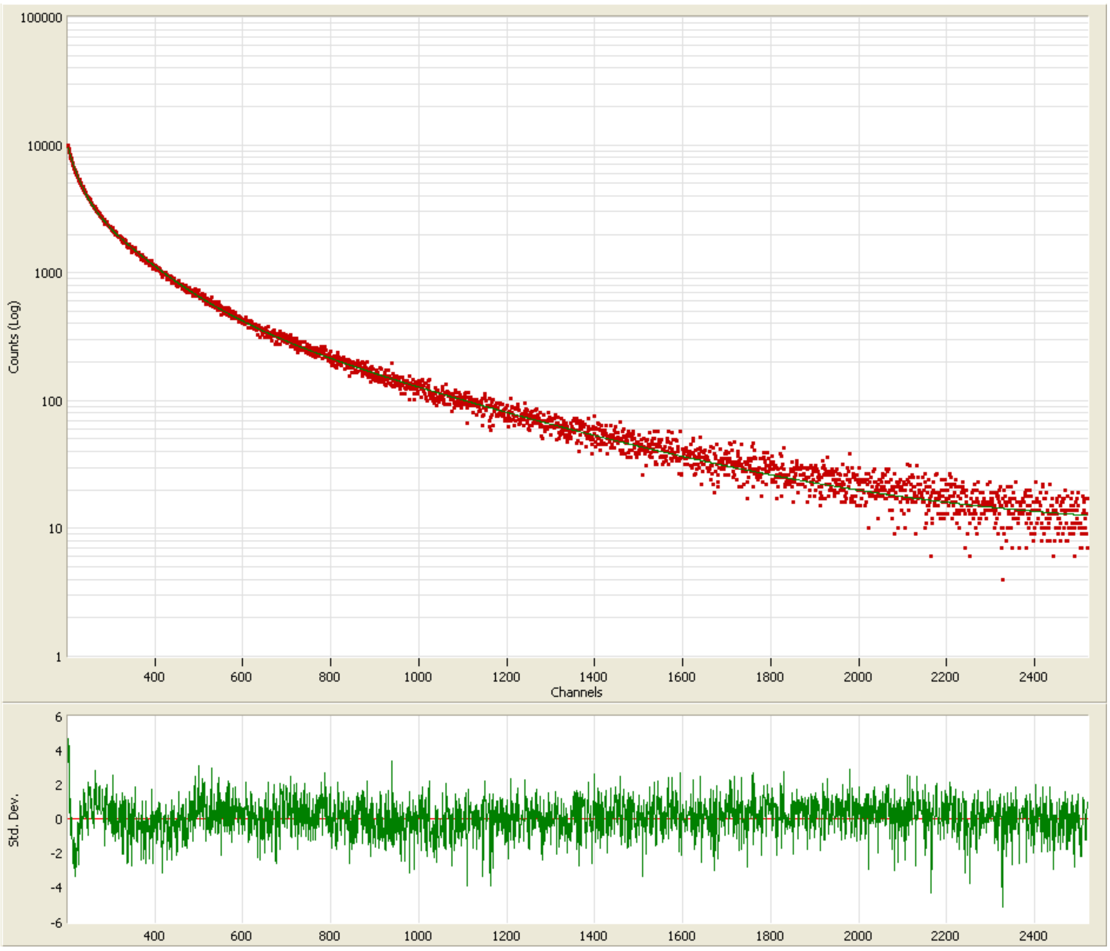

Figure S9. Emission decay of complex **2** (at 555 nm) in PMMA film at room temperature following pulsed excitation (λ_{ex} = 373 nm). Time calibration: 0.50 μs/ch. The emission decay was fitted by the following three-exponential kinetic traces: $I(t)$ = 3552 exp(-t/56.7) + 791 exp(-t/206.4) + 5153 exp(-t/11.8).

Electrochemical measurements. Cyclic voltammetry were performed in a gas-tight single-compartment three-electrode cell with a BAS Epsilon Electrochemical Analyzer at room temperature. A glassy carbon disk and a platinum wire were used as the working and auxiliary electrodes, respectively. The reference electrode was Ag/$AgNO_3$ in CH_3CN. The ferrocene couple Fc^+/Fc was selected as the external reference. The CV measurements were carried out in dried CH_3CN solutions with 0.1 M *n*-tetrabutylammonium perchlorate (TBAP) and 2.0 mM Cu^I complexes. The solution was bubbled with argon for 10 min before measurements, and kept under a positive argon pressure during the measurements.

Quantum chemical calculations. The ground-state geometric parameters were obtained from X-ray single-crystal structures, and the calculation was performed with Gaussian 03 software package.[7] “Double- ξ ” quality basis sets were employed for the C, H, N, P and O (6-311++G**) and Cu (LANL2DZ). The electron density diagrams of molecular orbitals were generated using GaussView program.

X-ray Crystallography. Crystallographic data were collected on a Rigaku Mercury CCD diffractometer equipped with graphite-monochromated Mo*Kα* radiation (λ = 0.71073 Å) at T = 293(2) K. Absorption corrections were applied by using the SADABS program.[8] The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using SHELX-97 program package.[9,10] Complex **1** crystallizes in space groups $P\bar{1}$, while complex **2** crystallizes in the monoclinic space groups $P2_1/c$. Solvent molecules were crystallized in the crystal lattice for all of the complexes. For **1**, each molecule cocrystallizes with one ethanol solvent molecules. For **2**, each molecule cocrystallizes with one CH_2Cl_2 solvent molecules. The $BF4^-$ anions in the complexes were refined successfully (The $BF4^-$ anions are not disordered). All nonhydrogen atoms were refined anisotropically. The positions of the hydrogen atoms attached to carbon atoms were fixed at their ideal positions.

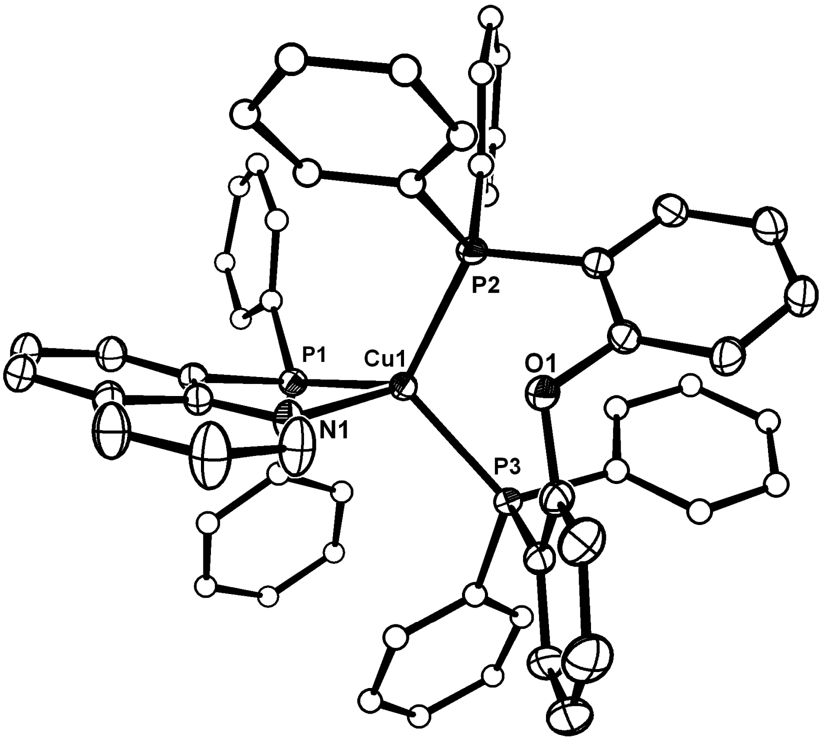

Figure S10. ORTEP diagram of the complex cation in **1**.

Table S1. Crystal data and structure refinement for **1** and **2**.

	1	**2**
Formula	$C_{59}H_{50}BCuF_4NO_2P_3$	$C_{59}H_{48}BCl_2CuF_4NOP_3$
Fw	1048.27	1101.15
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	11.023(3)	18.361(5)
b (Å)	14.753(4)	12.831(4)
c (Å)	16.362(4)	24.921(7)
α (deg)	92.285(4)	90.00
β (deg)	91.635(5)	103.232(5)
γ (deg)	96.309(3)	90.00
V (Å^3)	2641.2(12)	5715(3)
Z	2	4
D_c (g cm^{-3})	1.318	1.280
μ (mm^{-1})	0.562	0.612
Crystal size (mm)	0.39×0.37×0.17	0.19×0.16×0.12
$\theta_{\min}$, $\theta_{\max}$ (°)	2.19, 27.45	2.98, 25.00
F(000)	1084	2264
Goodness-of-fit on F^2	1.047	1.095
$w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$	a=0.1190, b=0.2767	a=0.1277, b=2.1234
Collected reflcns	20583	34854
Unique reflcns	11808	10007
Observed reflcns [$I > 2\sigma(I)$]	9206	7747
R_{int}	0.0208	0.0426
Refined parameters	642	677
$R_1{}^a/wR_2{}^b$ [$I > 2\sigma(I)$]	0.0545/0.1584	0.0710/0.2020
$R_1{}^a/wR_2{}^b$ (all data)	0.0673/0.1771	0.0886/0.2216

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