Electronic Supplementary Information (ESI)

Unsymmetrical diarylethene derivatives as molecular keypad lock with tunable photochromism and fluorescence via Cu^{2+} and CN^- coordination

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Experimental section

Materials and instrumentations

$Cu(CH_3COO)_2 \cdot H_2O$, tetrabutylammonium cyanide (TBA^+CN^-) and n-butyl lithium (2.5 M solution in hexane) were purchased from Sigma–Aldrich and used without further purification. Other starting materials were commercially available and purified before use. All other reagents were of analytical purity and used without further treatment. The synthesis of 1-(5-chloro-2-methyl-3-thienyl)-2-(5-formyl- 2-methyl-3-thienyl) cyclopentene and 1-(5-formyl-2-methyl-3-thienyl)-2-(5-(naphthalen-1-yl) vinyl- 2-methyl-3-thienyl) cyclopentene (compounds **1** and **2** shown in Scheme S1) was based on the literature method.[1]

^1H NMR and ^{13}C NMR spectra in $CDCl_3$ were recorded on Brucker AM-400 spectrometers with tetramethylsilane (TMS) as the internal standard. Mass spectra (MS) were recorded on ESI mass spectroscopy. UV–vis absorption spectra were performed on a Varian Cray 500 spectrophotometer and fluorescence spectra were recorded on a Varian Cray Eclipse fluorescence spectrophotometer; both spectrophotometers were standardized.

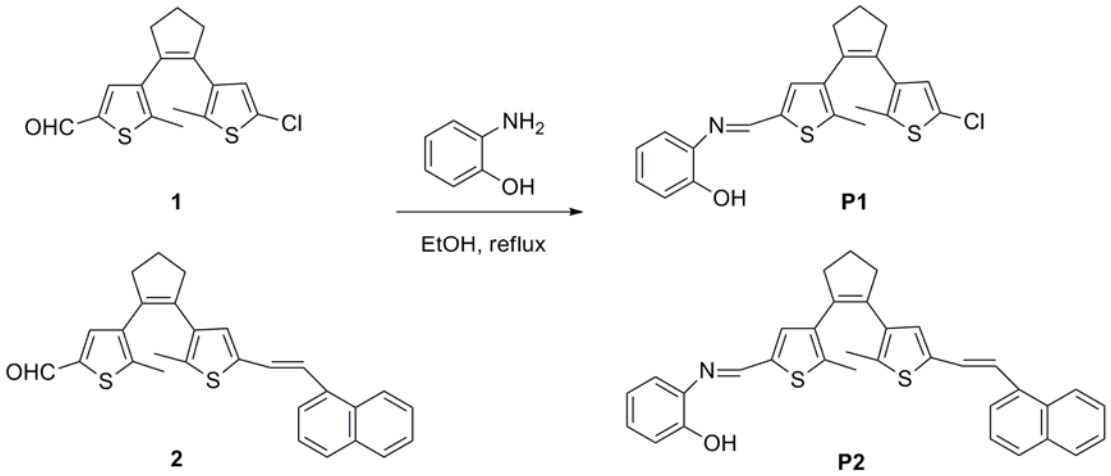
Synthesis of 1-(5- Chloro-2- methyl-3-thienyl)- 2- (5- 2-methyleneaminophenol-2-methyl- 3-thienyl)cyclopentene (**P1**)

A mixture of compound **1** (0.161 g, 0.5 mmol) with 2-aminophenol (0.273 g, 2.5 mmol) in ethanol (2.5 mL) was refluxed for 7 h until no compound **1** was detected by TLC silica gel plate. The solution was concentrated under vacuum. After cooling to room temperature, the solution of dichloromethane (6 mL) and n-hexane (6 mL) was added to the residue and a lot of gray solid precipitated from the solution. After filtration, the filtrate was concentrated under vacuum. The crude product was purified by recrystallization using dichloromethane and n-hexane to give the compound **P1** (0.166 g, 80.2%) as a red solid. ^1H NMR (400 MHz, $CDC1_3$, δ): 1.88 (s, 3H, $-CH_3$), 2.07 (m, 5H, $-CH_3$ and $-CH_2-$), 2.77 (m, 4H, $-CH_2-$), 6.61 (s, 1H, thiophene-H), 6.86 (m, 1H, benzene-H), 6.98 (d, 1H, *J* 8.0 Hz, benzene-H), 7.14 (m, 2H, benzene-H and thiophene-H), 7.23 (d, 1H, *J* 8.0 Hz, benzene-H), 8.60 (s, 1H, -CH=N-). ^{13}C NMR

(100 MHz, $CDCl_3$, δ): 14.2, 15.1, 22.9, 38.3, 38.4, 114.9, 115.7, 120.0, 125.4, 126.7, 128.5, 133.4, 133.9, 134.4, 134.7, 134.8, 135.2, 136.8, 138.8, 141.5, 149.5, 152.1. HRMS (ESI+, *m/z*): $[MH]^+$ calcd for $C_{22}H_{21}ClNOS_2$, 414.0753; found, 414.0754.

Synthesis of 1-(5- 2-methyleneaminophenol-2-methyl-3-thienyl)-2-(5-(naphthalen-1-yl) vinyl- 2-methyl-3-thienyl) cyclopentene (**P2**)

A mixture of compound **2** (0.104 g, 0.236 mmol) with 2-aminophenol (0.026 g, 0.236 mmol) in ethanol (2 mL) was refluxed for 3 h. After cooling to room temperature, the green precipitates were collected by filtration and washed with cold ethanol. The crude product was purified by recrystallization using ethanol to give the compound **P2** (0.073 g, 58.1%) as a green solid. ^1H NMR (400 MHz, $CDC1_3$, δ): 2.00 (s, 3H, $-CH_3$), 2.10 (m, 5H, $-CH_3$ and $-CH_2-$), 2.80 (t, 4H, *J* 7.6 Hz, $-CH_2-$), 6.81 (s, 1H, thiophene-H), 6.85 (m, 1H, benzene-H), 6.97 (d, 1H, *J* 8.0 Hz, -CH=CH-), 7.18 (m, 4H, benzene-H and thiophene-H), 7.49 (m, 4H, naphthalene-H), 7.69 (d, 1H, *J* 7.2 Hz, naphthalene-H), 7.76 (d, 1H, *J* 8.4 Hz, naphthalene-H), 7.85 (d, 1H, *J* 7.6 Hz, naphthalene-H), 8.17 (d, 1H, *J* 8.0 Hz, -CH=CH-), 8.62 (s, 1H, -CH=N-). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.7, 15.2, 23.0, 38.3, 38.5, 114.9, 115.7, 120.0, 123.2, 123.7, 124.2, 124.6, 125.7, 125.9, 126.1, 127.5, 127.9, 128.4, 128.6, 131.2, 133.7, 133.8, 134.2, 134.5, 135.3, 135.5, 135.9, 137.1, 138.6, 139.2, 141.6, 149.6, 152.1. HRMS (ESI+, *m/z*): $[MH]^+$ calcd for $C_{34}H_{30}NOS_2$, 532.1769; found, 532.1766.



Scheme S1 Synthetic routine of compounds **P1** and **P2**.

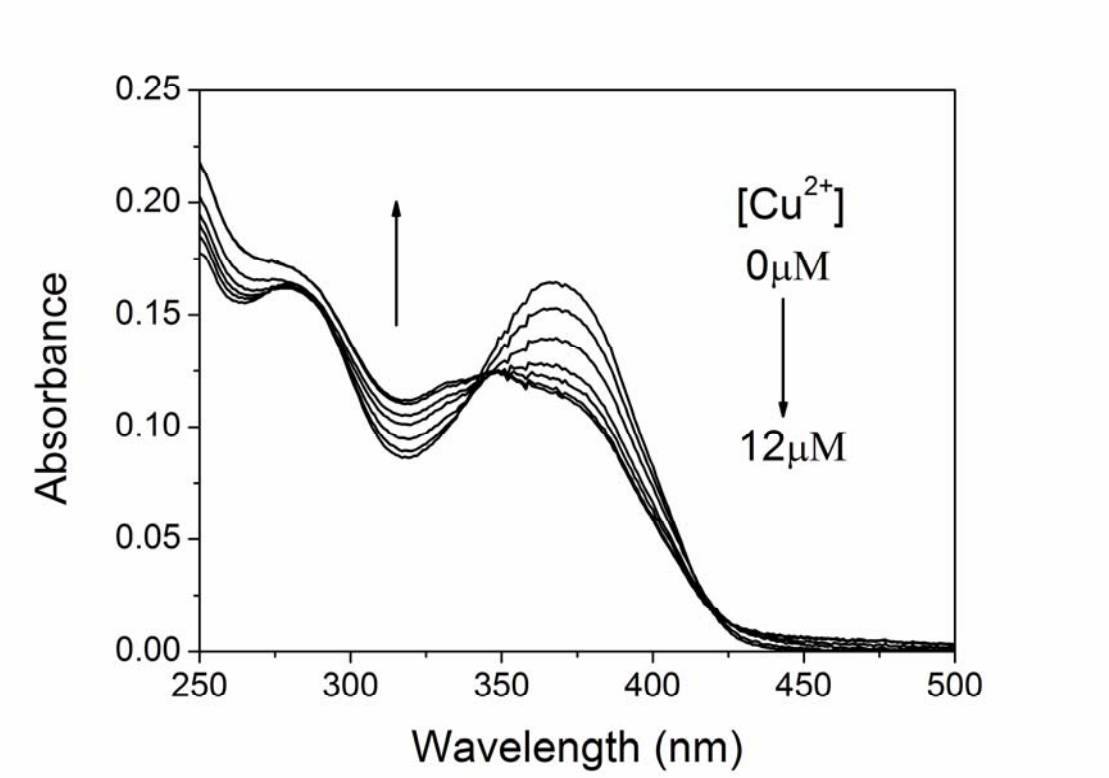


Fig. S1 UV−vis spectra of compound **P1** (1.0×10^{-5} M) and Cu^{2+} (0−1.2×10^{-5} M) in CH_3CN solution at 25 °C.

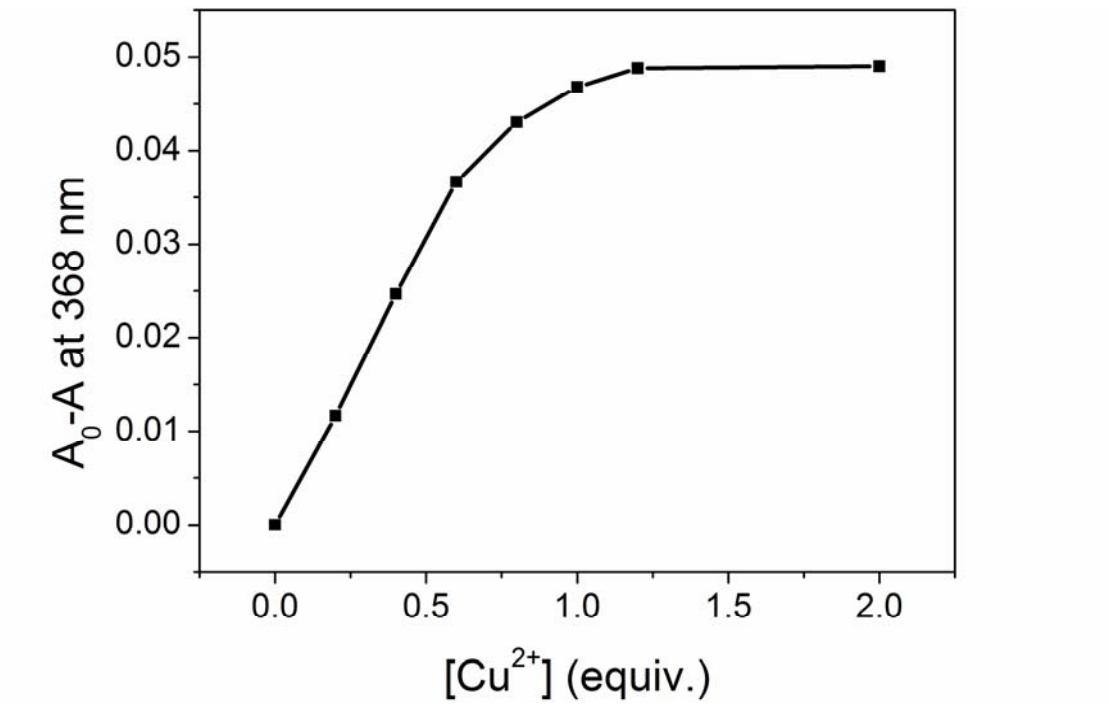


Fig. S2 UV−vis titration profile of compound **P1** at 368 nm upon addition of various amounts of Cu^{2+} in CH_3CN solution.

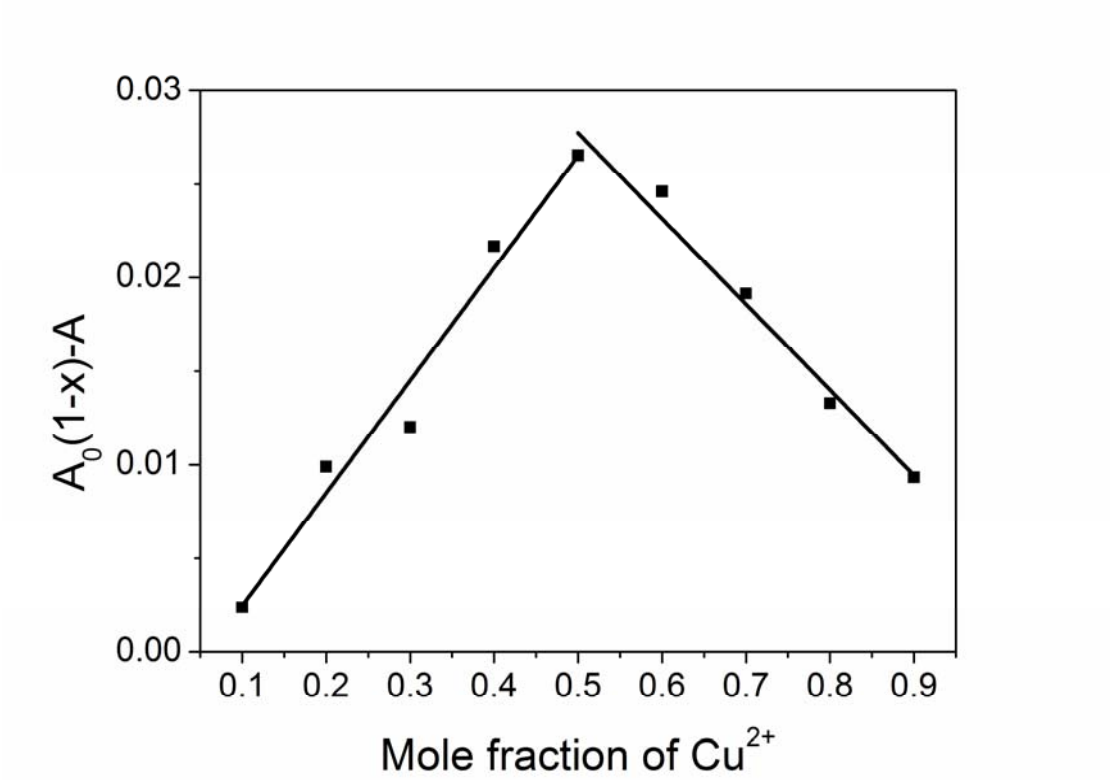


Fig.S3 Job's plot of compound **P1** and Cu^{2+}, A and A_0 are the absorbance value at 368 nm of compound **P1** in the presence and absence of Cu^{2+}, respectively; the total concentration of compound **P1** and Cu^{2+} is 1.0×10^{-5} M in CH_3CN solution at 25 °C.

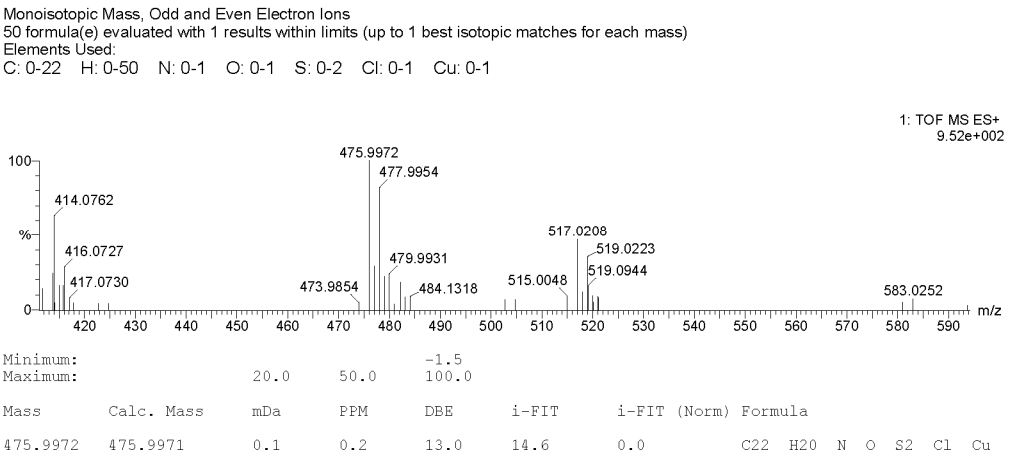


Fig. S4 HRMS (ESI+) spectrum of compound **P1** (10 μM) with Cu^{2+} (10 μM) in CH_3CN solution.

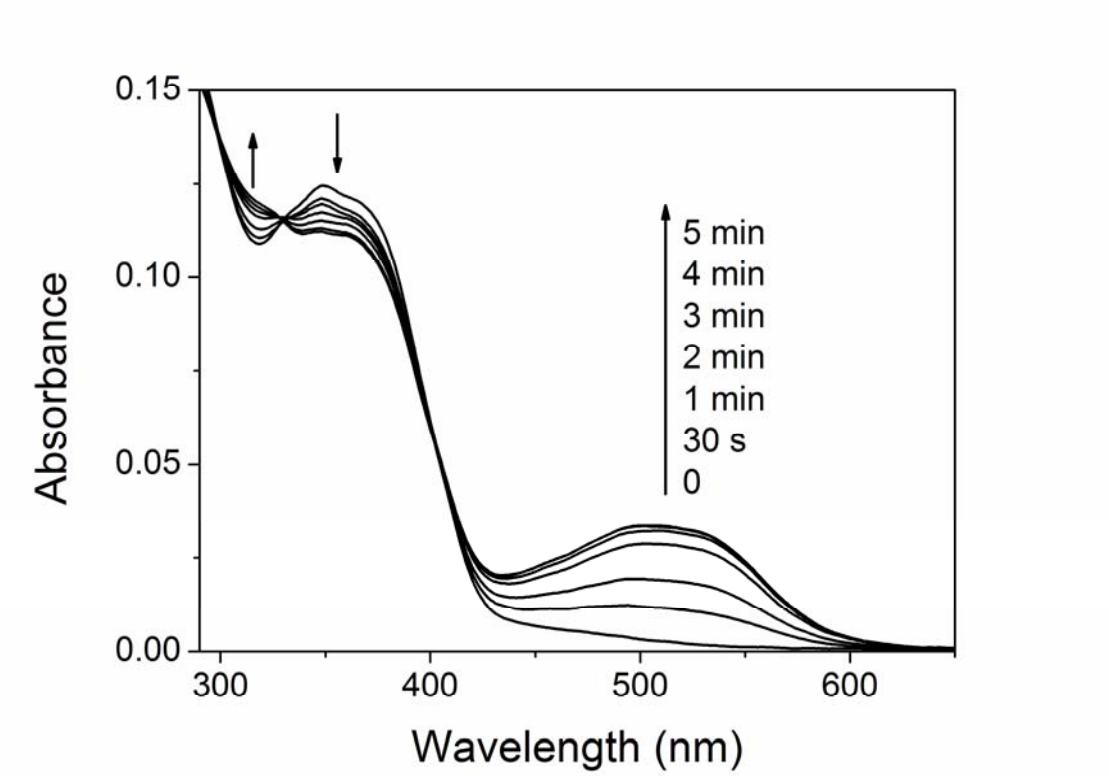


Fig.S5 Absorption spectral changes of complex **P1-Cu**$^{2+}$ in CH_3CN solution (1.0×10^{-5} M) upon irradiation with 365 nm light.

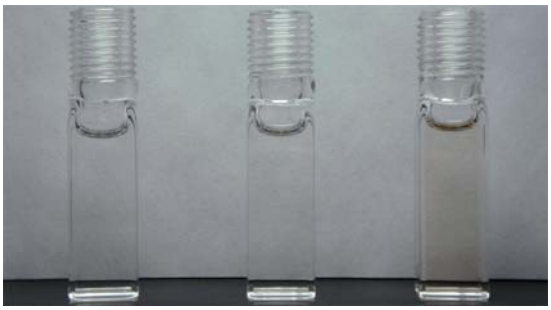


Fig. S6 Left to right: color images of compound **P1**, complex **P1-Cu**$^{2+}$, complex **P1-Cu**$^{2+}$ upon irradiation with 365 nm light in CH_3CN solution.

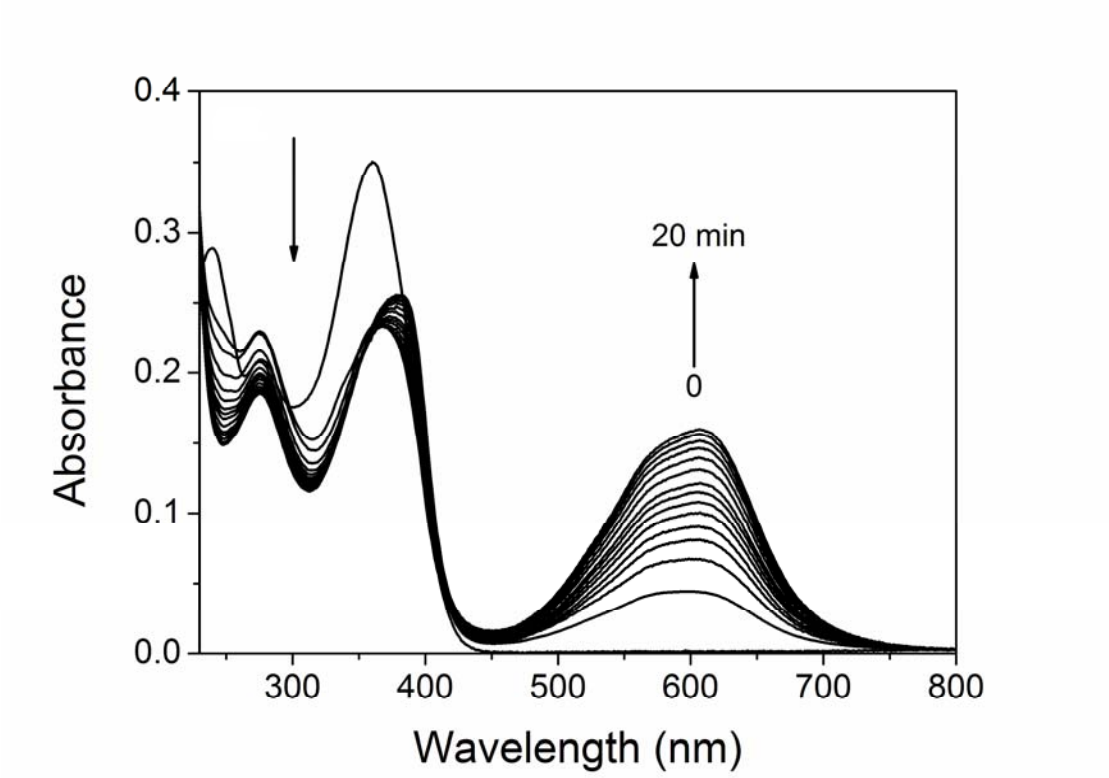


Fig. S7 Absorption spectral changes of compound **P2** in CH_3CN solution (1.0×10^{-5} M) upon irradiation with 365 nm light.

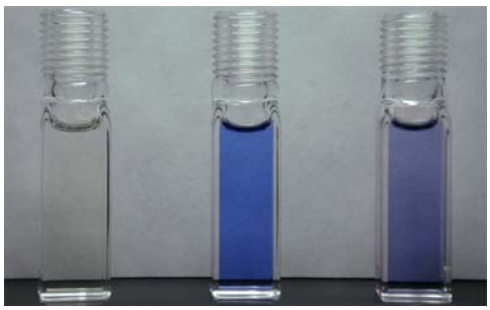


Fig. S8 Left to right: color images of compound **P2**, compound **P3**, complex **P3-Cu**$^{2+}$ in CH_3CN solution.

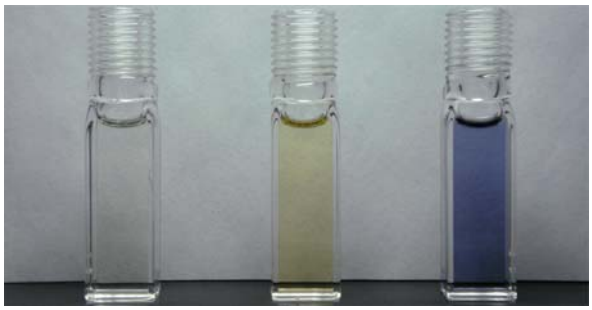


Fig. S9 Left to right: color images of compound **P2**, complex **P2-Cu**$^{2+}$, complex **P3-Cu**$^{2+}$ in CH_3CN solution.

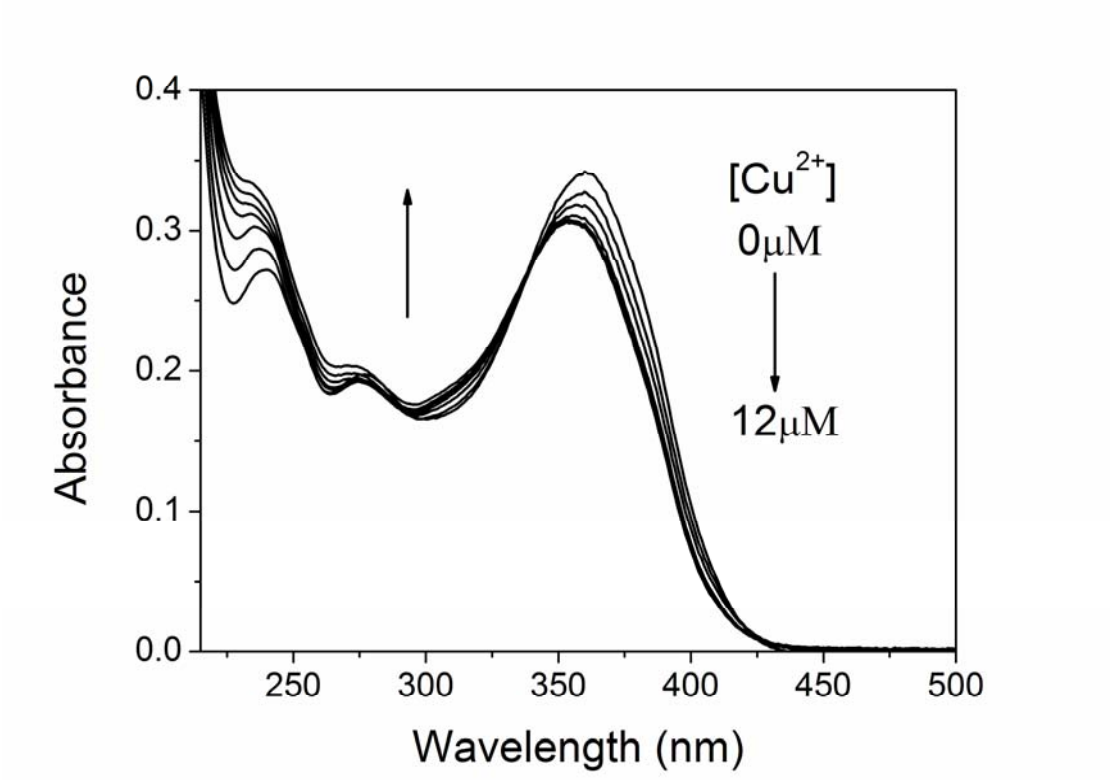


Fig. S10 UV−vis spectra of compound **P2** (1.0×10^{-5} M) and Cu^{2+} ($0-1.2 \times 10^{-5}$ M) in CH_3CN solution at 25 °C.

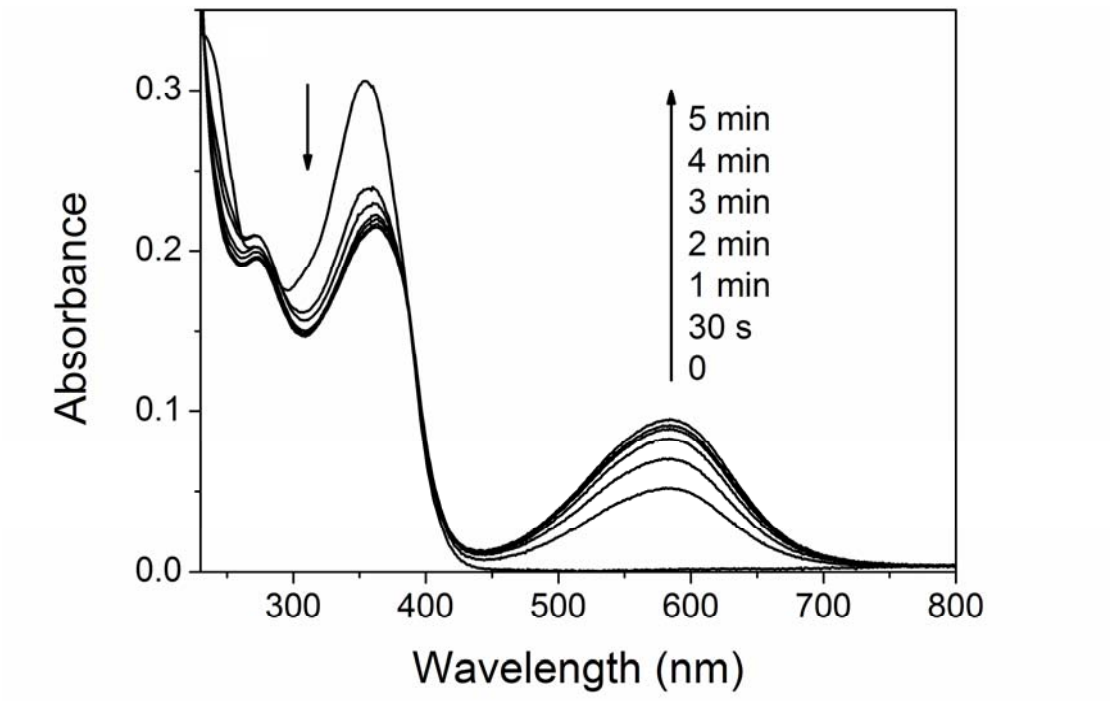


Fig. S11 Absorption spectral changes of complex **P2-Cu**$^{2+}$ in CH_3CN solution (1.0×10^{-5} M) upon irradiation with 365 nm light.

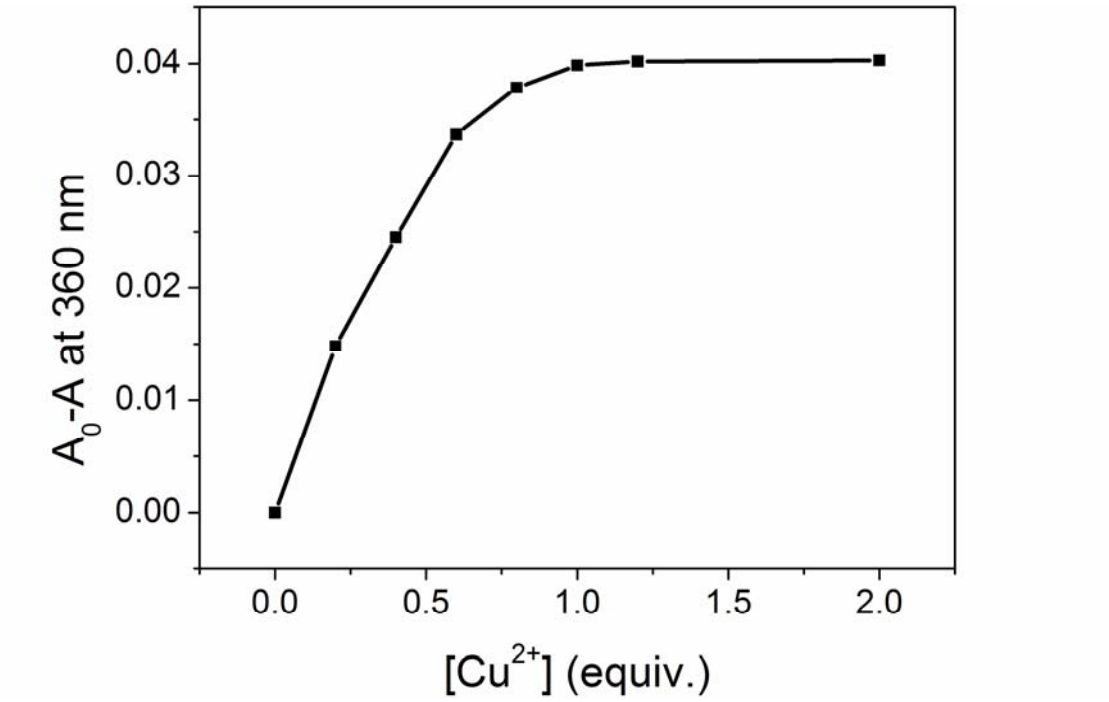


Fig. S12 UV−vis titration profile of compound **P2** at 360 nm upon addition of various amounts of Cu^{2+} in CH_3CN solution.

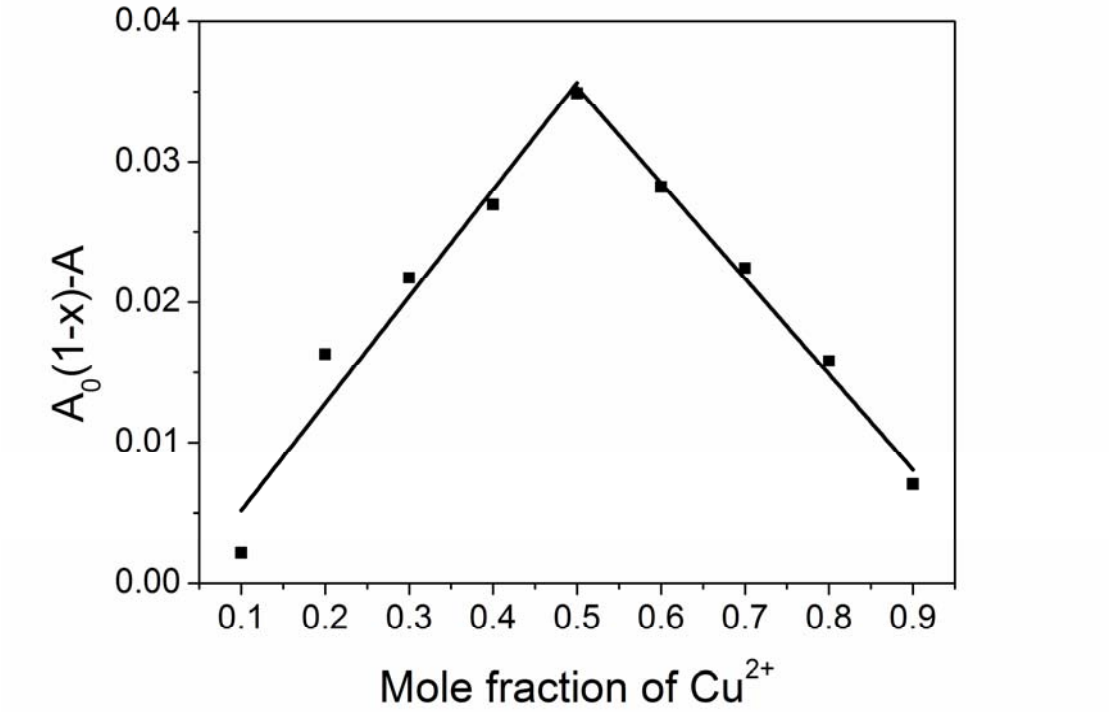


Fig. S13 Job's plot of compound **P2** and Cu^{2+}, A and A_0 are the absorbance value at 360 nm of compound **P2** in the presence and absence of Cu^{2+}, respectively; the total

concentration of compound **P2** and Cu^{2+} is 1.0×10^{-5} M in CH_3CN solution at 25 °C.

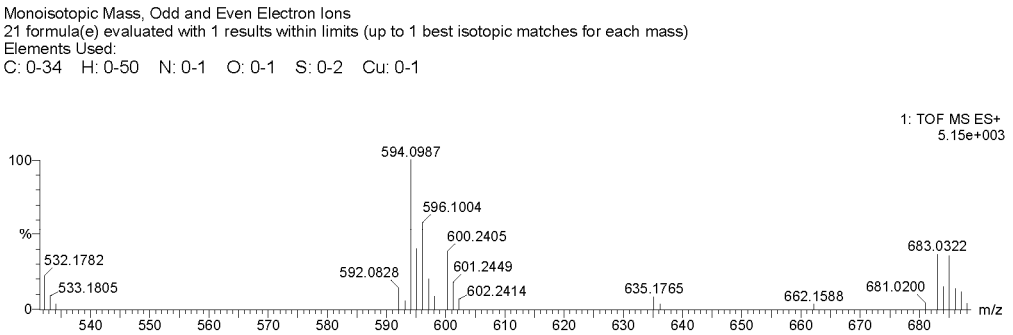


Fig. S14 HRMS (ESI+) spectrum of compound **P2** (10 μM) with Cu^{2+} (10 μM) in CH_3CN solution.

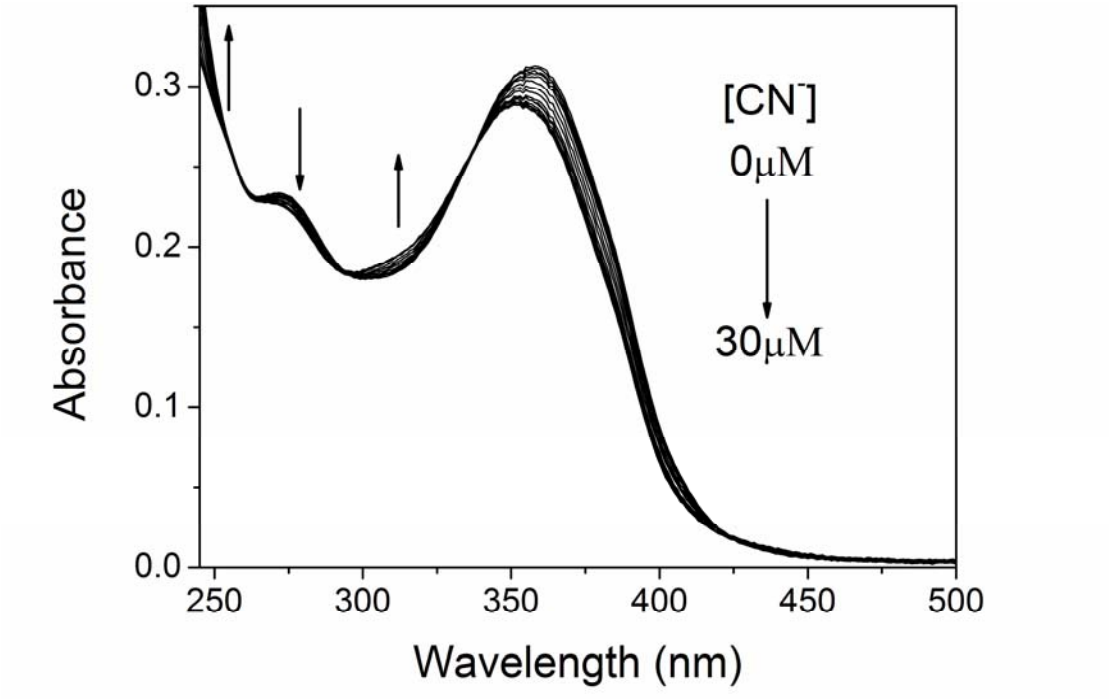


Fig. S15 UV−vis spectra of complex **P2-Cu^{2+}** (1.0×10^{-5} M) and CN^- ($0-3.0\times10^{-5}$ M) in CH_3CN solution at 25 °C.

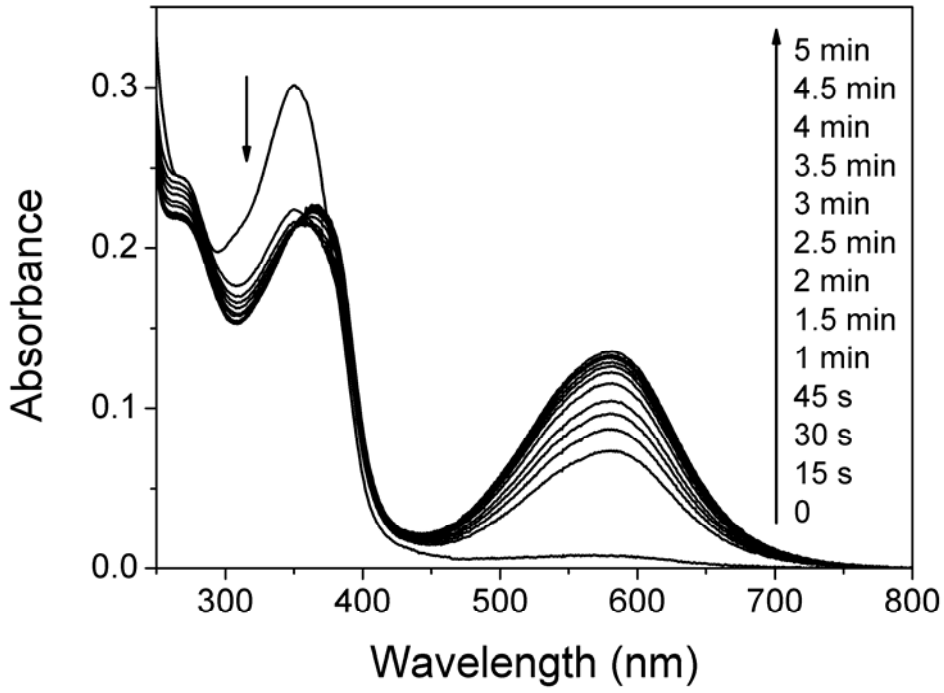


Fig. S16 Absorption spectral changes of complex **P2-Cu^{2+}-CN^{-}** in CH_3CN solution (1.0×10^{-5} M) upon irradiation with 365 nm light.

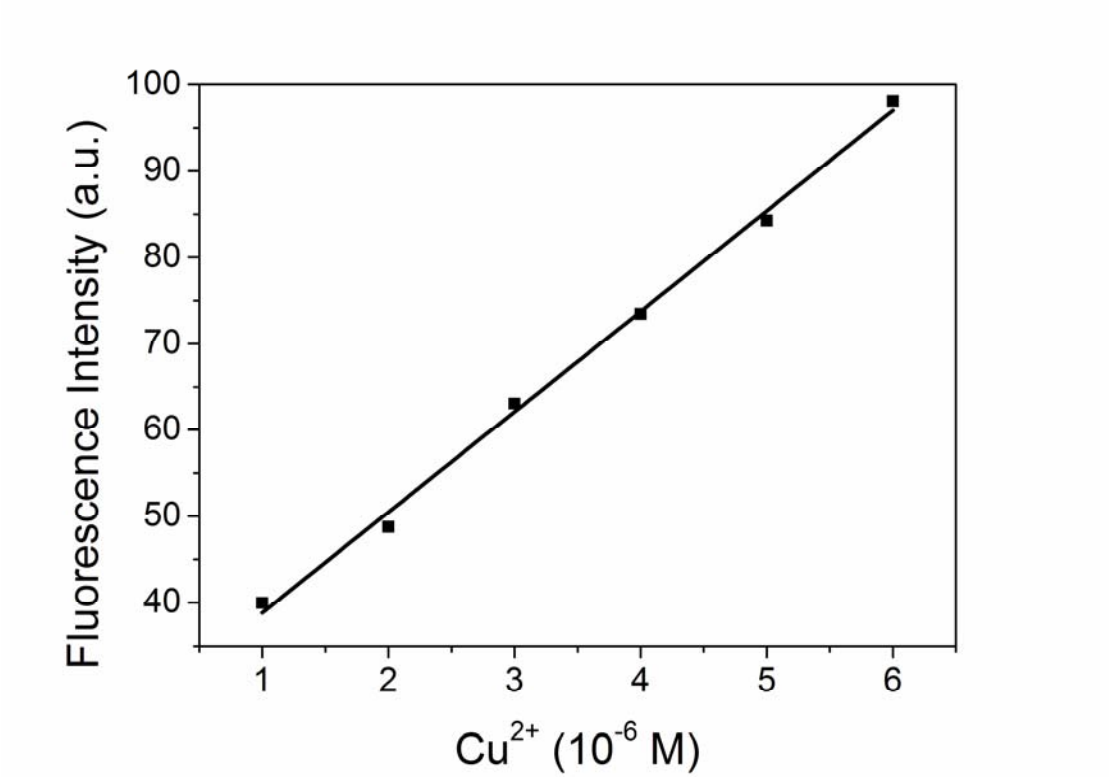


Fig. S17 Plot of fluorescence intensity at 445 nm change of compound **P2** (10 μM) against varied concentrations of Cu^{2+} from 1.0 to 6.0 μM in CH_3CN solution (λ_{ex}

=360 nm, slit: 10 nm/10 nm, PMT Volts: 600.). R= 0.996, k= 2.72×10^{7} au/M

The Standard Deviation (σ= 0.826) was obtained by fluorescence responses (10-times of consecutive scanning on the Cary Eclipse fluorescence spectrophotometer). Therefore, the detection limit was calculated by the formula (3σ/k) and gave a result as 9.11×10^{-8} M.

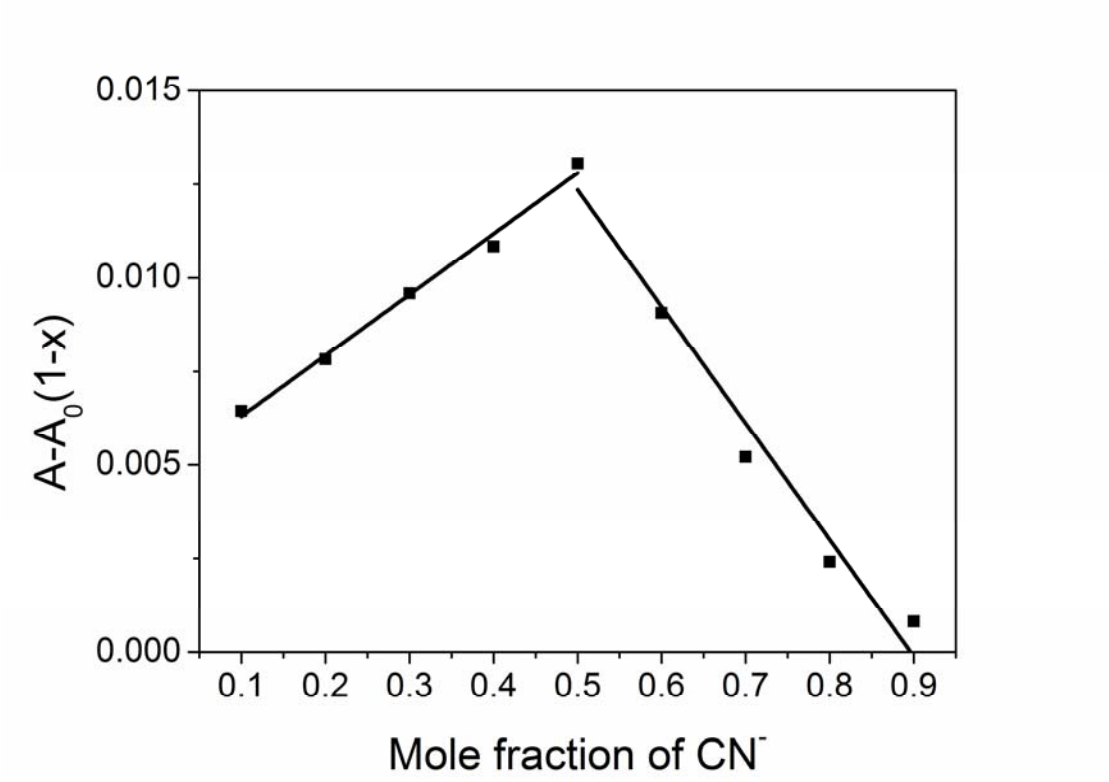


Fig. S18 Job's plot of complex **P2-Cu**$^{2+}$ and CN^-, A and A_0 are the absorbance value at 355 nm of complex **P2-Cu**$^{2+}$ in the presence and absence of CN^-, respectively; the total concentration of complex **P2-Cu**$^{2+}$ and CN^- is 1.0×10^{-5} M in CH_3CN solution at 25 °C.

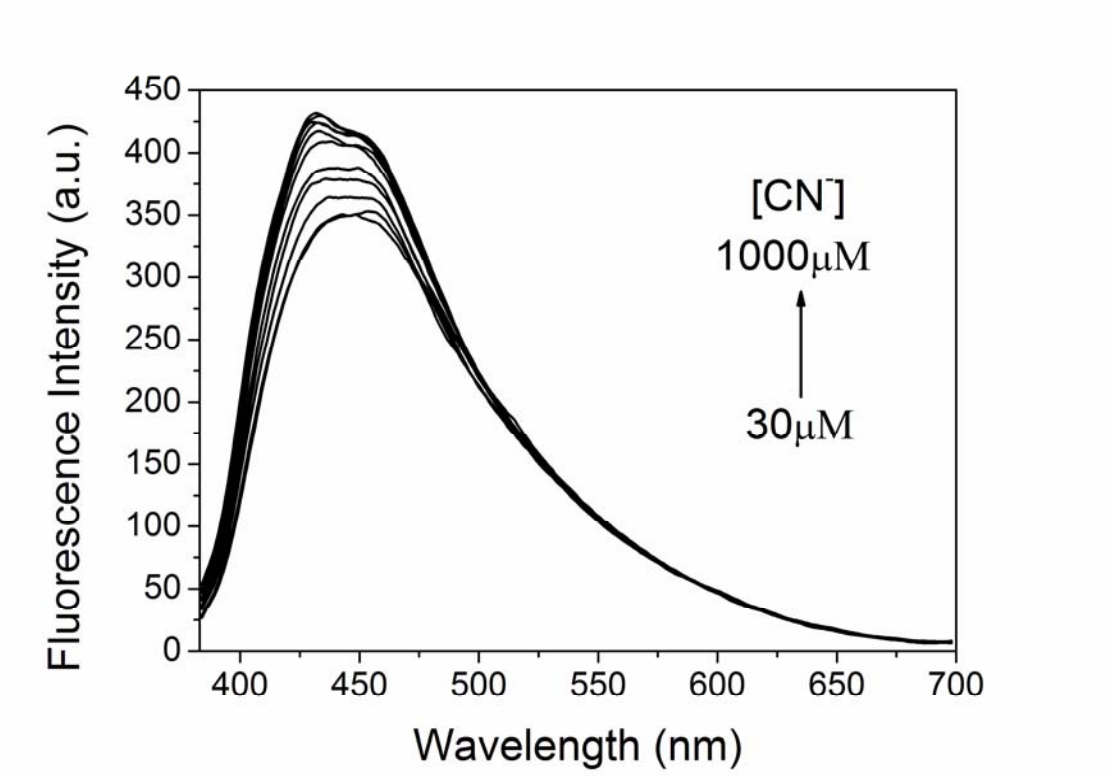


Fig. S19 Fluorescence spectral changes of compound **P2-Cu**$^{2+}$ (1.0×10^{-5} M) with CN^- (3.0×10^{-5} M−1.0×10^{-3} M) in CH_3CN solution at 25 °C, λ_{ex}= 360 nm.

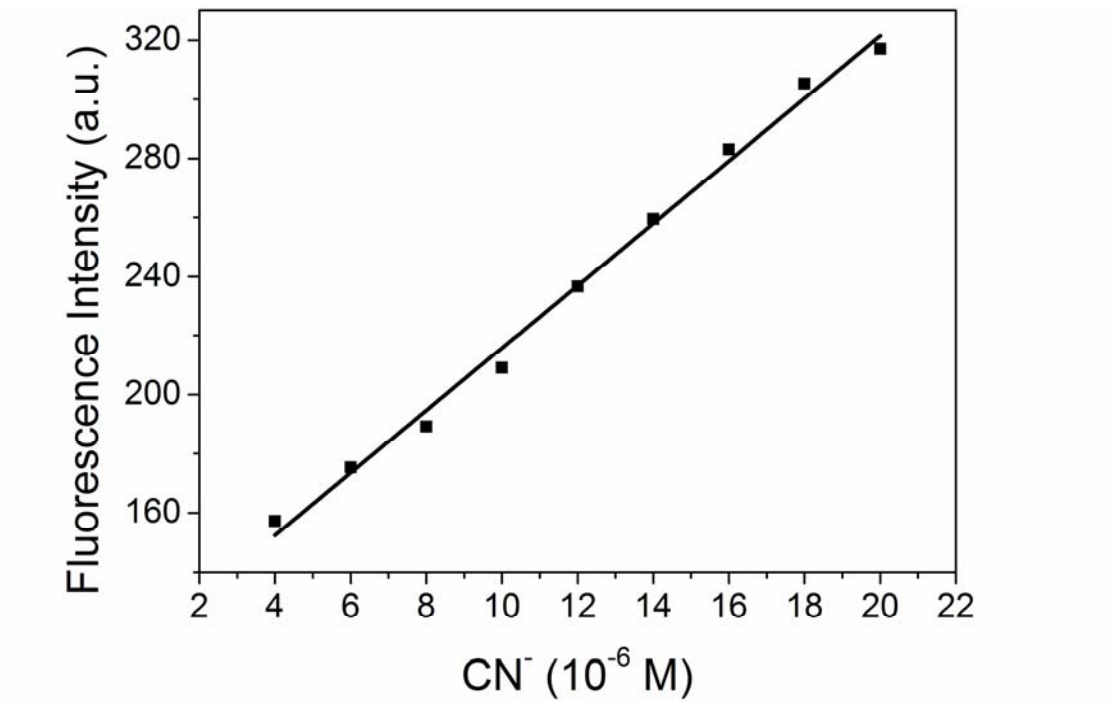


Fig. S20 Plot of fluorescence intensity at 448 nm change of complex **P2-Cu**$^{2+}$ (10 μM) against varied concentrations of CN^- from 4.0 to 20.0 μM in CH_3CN solution (λ_{ex}

=360 nm, slit: 10 nm/10 nm, PMT Volts: 600.). R= 0.993, k= 1.1×10^{8} au/M

The Standard Deviation (σ= 0.826) was obtained by fluorescence responses (10-times of consecutive scanning on the Cary Eclipse fluorescence spectrophotometer). Therefore, the detection limit was calculated by the formula (3σ/k) and gave a result as 2.25×10^{-8} M.

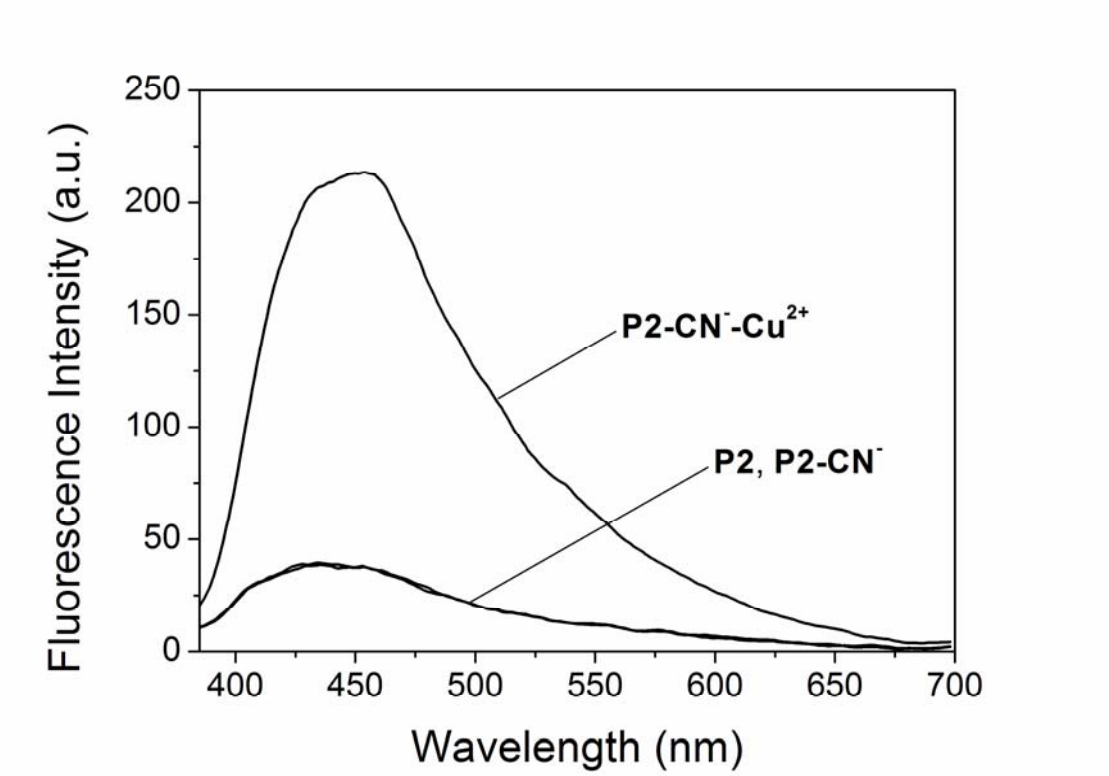


Fig. S21 Fluorescence spectra of compound **P2**, **P2-CN$^-$** and complex **P2-CN$^-$-Cu^{2+}** in CH_3CN solution (1.0×10^{-5} M) upon irradiation with 365 nm light, λ_{ex}= 360 nm.

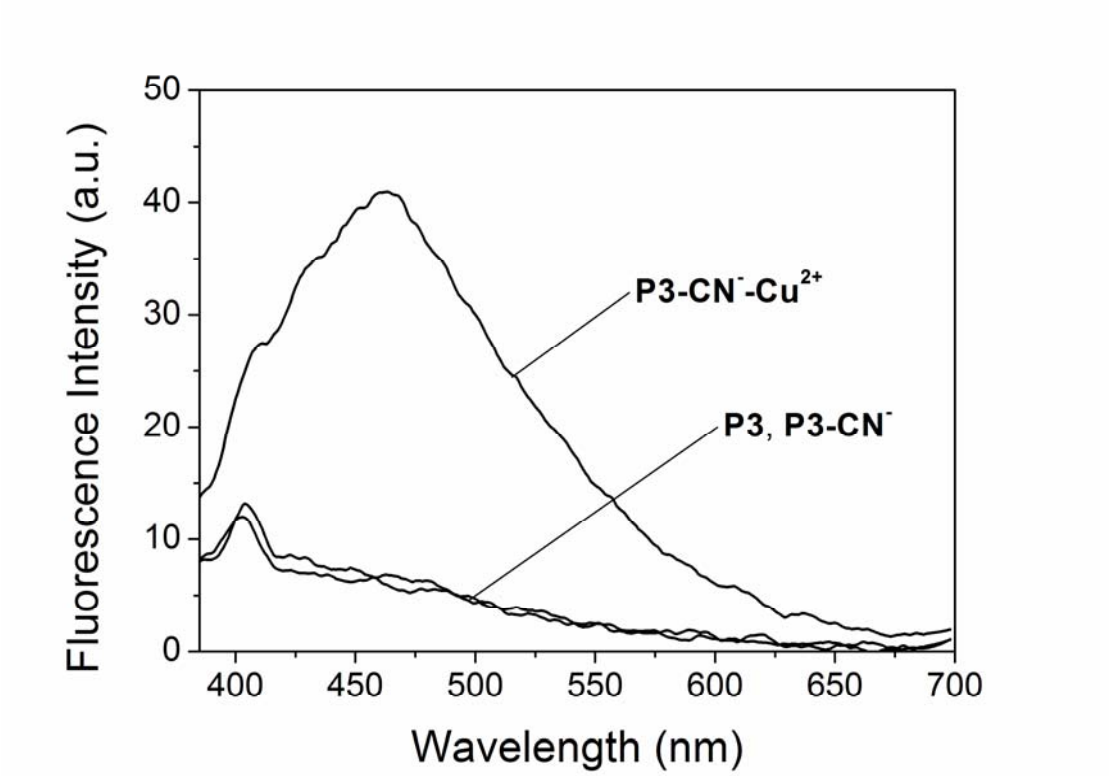


Fig. S22 Fluorescence spectra of compound **P3**, **P3-CN**$^-$ and complex **P3-CN**$^-$**-Cu**$^{2+}$ in CH_3CN solution (1.0×10^{-5} M) upon irradiation with 365 nm light, λ_{ex}= 360 nm.

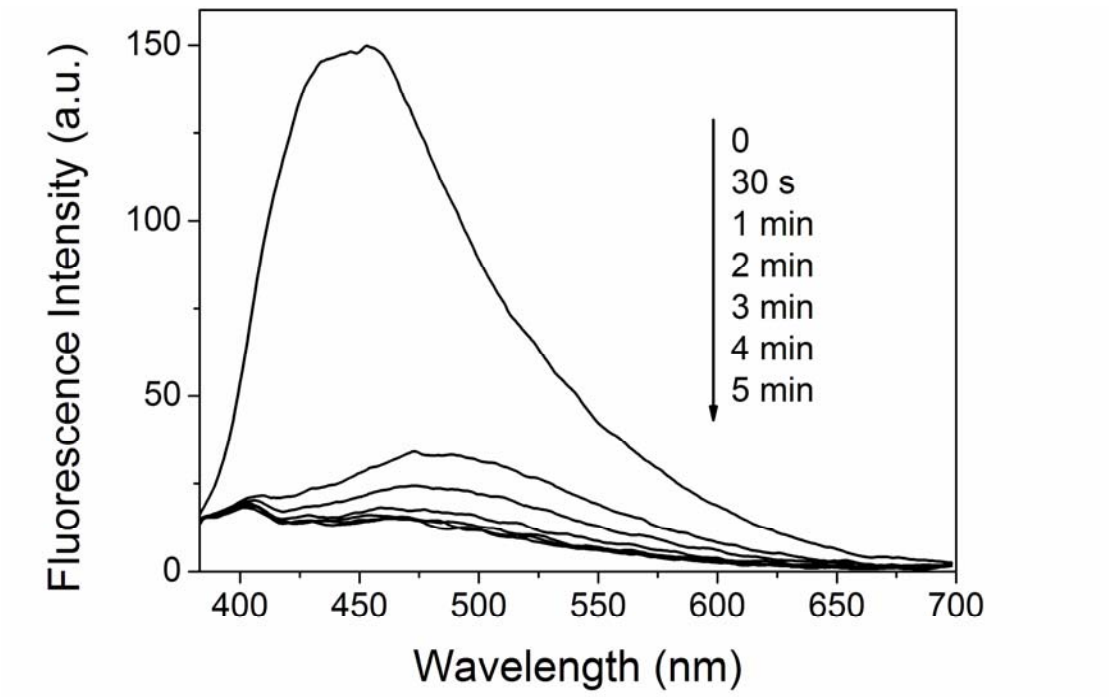


Fig. S23 Fluorescence changes of complex **P2-Cu**$^{2+}$ in CH_3CN solution (1.0×10^{-5} M) upon irradiation with 365 nm light, λ_{ex}= 360 nm.

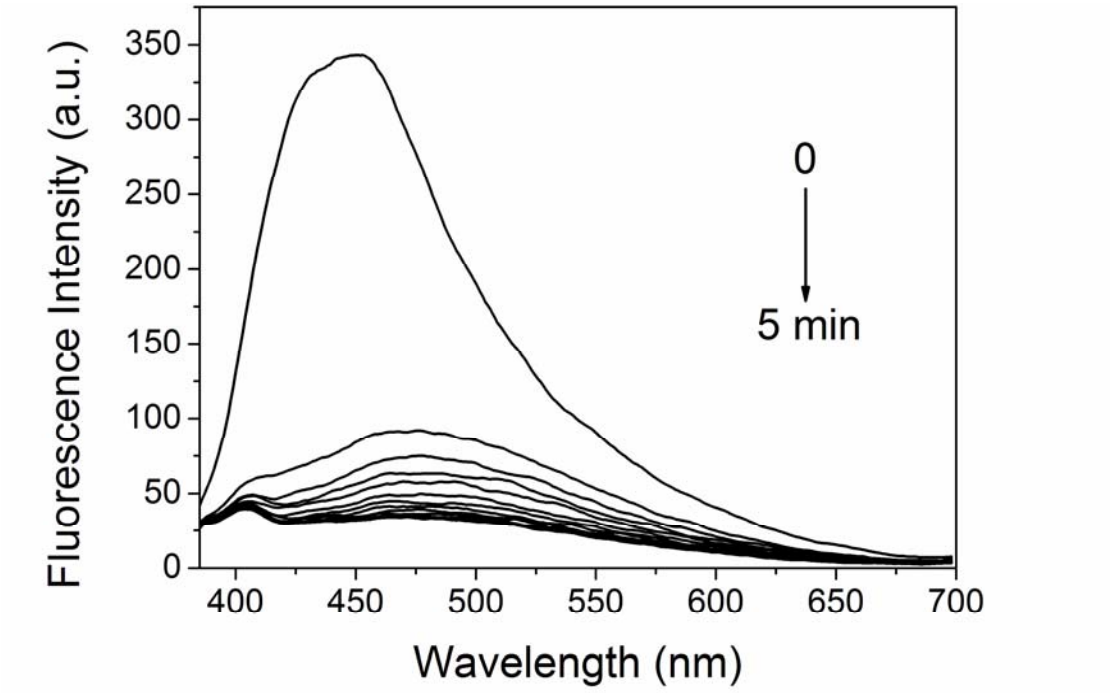


Fig. S24 Fluorescence changes of complex **P2-Cu^{2+}-CN^{-}** in CH_3CN solution (1.0×10^{-5} M) upon irradiation with 365 nm light, λ_{ex}= 360 nm.

Table S1. Truth table for the monomolecular circuit

Entry	Input-1 UV	Input-2 Cu^{2+}	Input-3 CN^{-}	Output-1 I≤100	Output-2 100<I≤150	Output-3 I>150
1	0	0	0	1	0	0
2	0	0	1	1	0	0
3	0	1	0	0	1	0
4	1	0	0	1	0	0
5	0	1	1	0	0	1
6	1	0	1	1	0	0
7	1	1	0	1	0	0
8	1	1	1	1	0	0

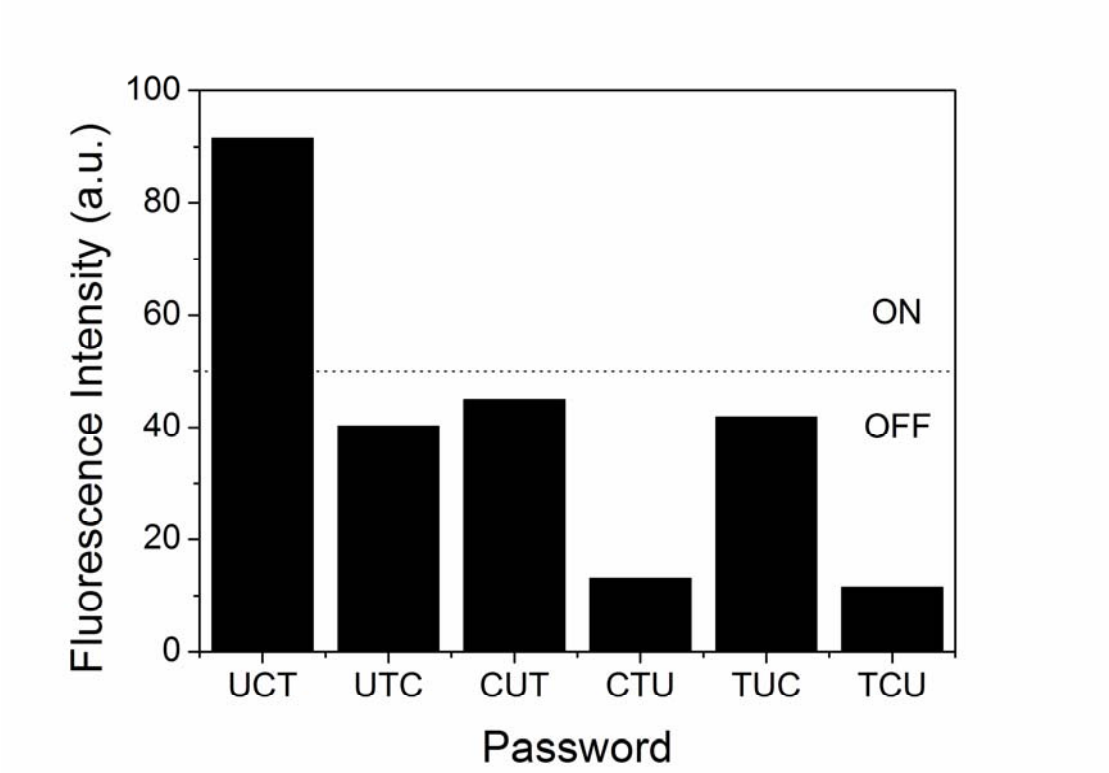


Fig. S25 Fluorescence emission output of compound **P2** corresponding to six possible input combinations at 448 nm.

Calculation

Theoretical studies were carried out by using the Gaussian 03 program package.[2] The ground state geometries of the compounds were optimized by using density functional theory (DFT). The hybrid B3LYP functional[3] and the 6-31G* basis set[4] were used, and the solvent effect of CH_3CN was taken into account by the polarizable continuum model (PCM).[5]

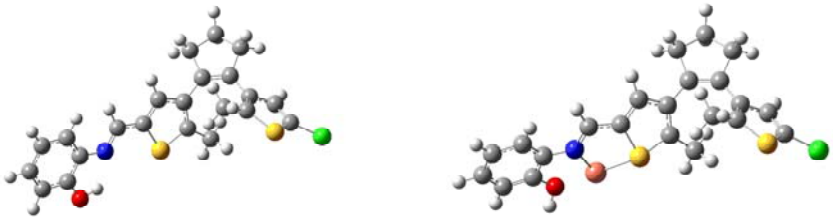


Fig. S26 Left to right: the proposed conformations of compound **P1** (C-C = 3.69 Å) and **P1-Cu^{2+}** complex (C-C = 3.60 Å).

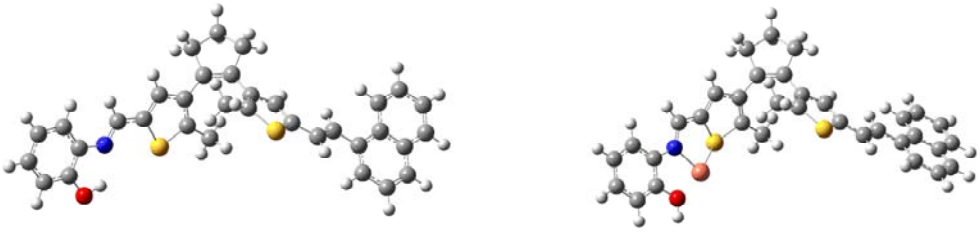


Fig. S27 Left to right: the proposed conformations of compound **P2** (C-C = 3.67 Å) and **P2-Cu^{2+}** complex (C-C = 3.67 Å)

In order to study the excited states of the compounds, time-dependent DFT (TDDFT) studies were carried out by using the hybrid PBE0 functional[6] and the 6-31G* basis set,[4] with the solvent effect of CH_3CN taken into account by the conductor-like polarizable continuum model (C-PCM).[7]

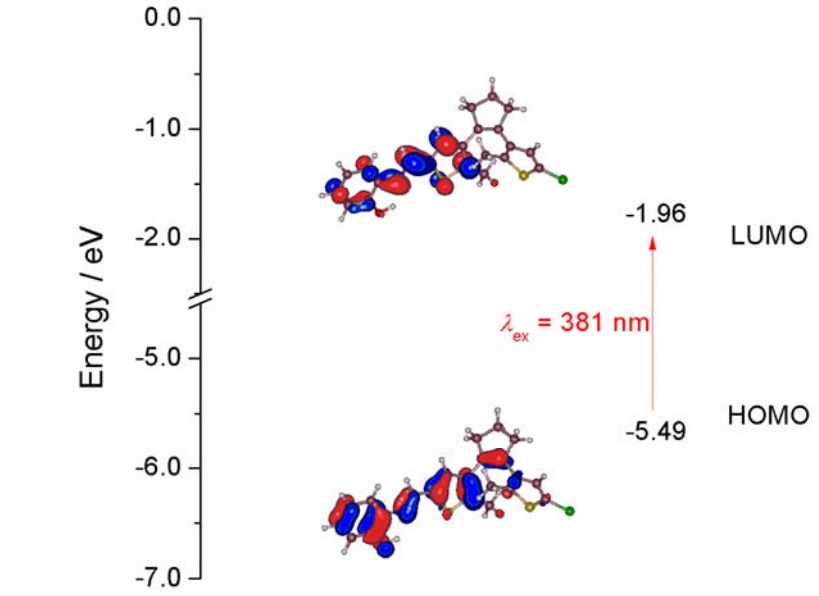


Fig. S28 Excitation of compound **P1**.

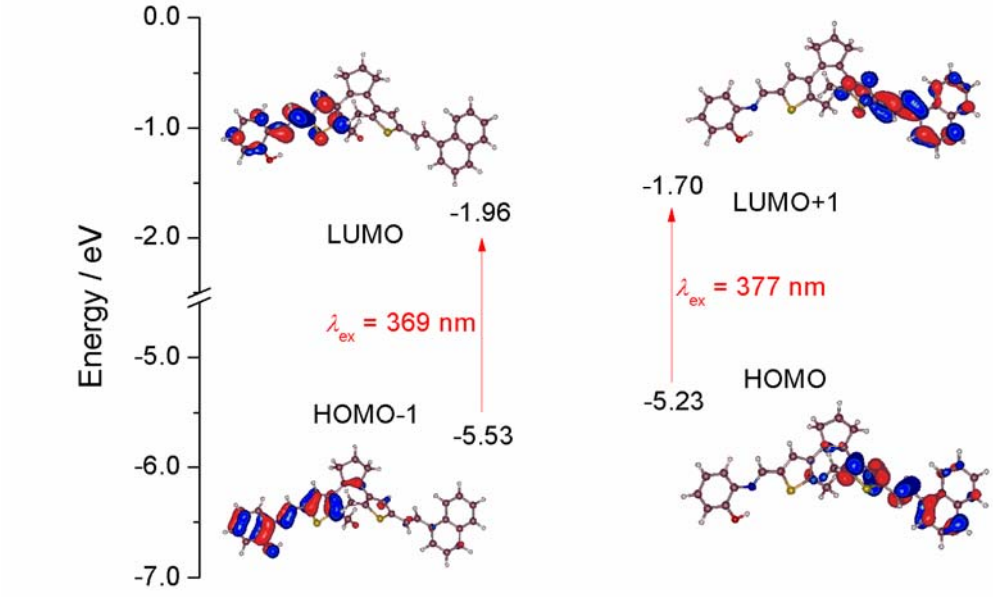


Fig. S29 Excitation of compound **P2**.

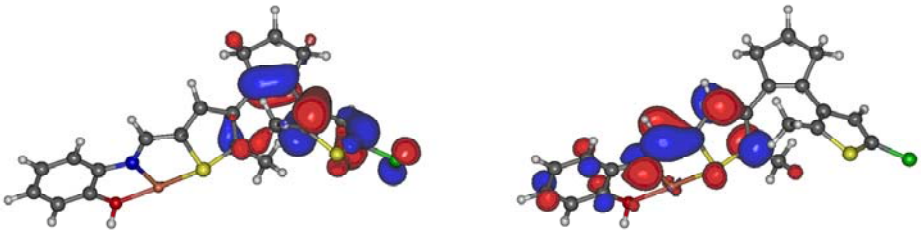


Fig. S30 HOMO (left) and LUMO (right) of **P1-Cu**$^{2+}$ complex.

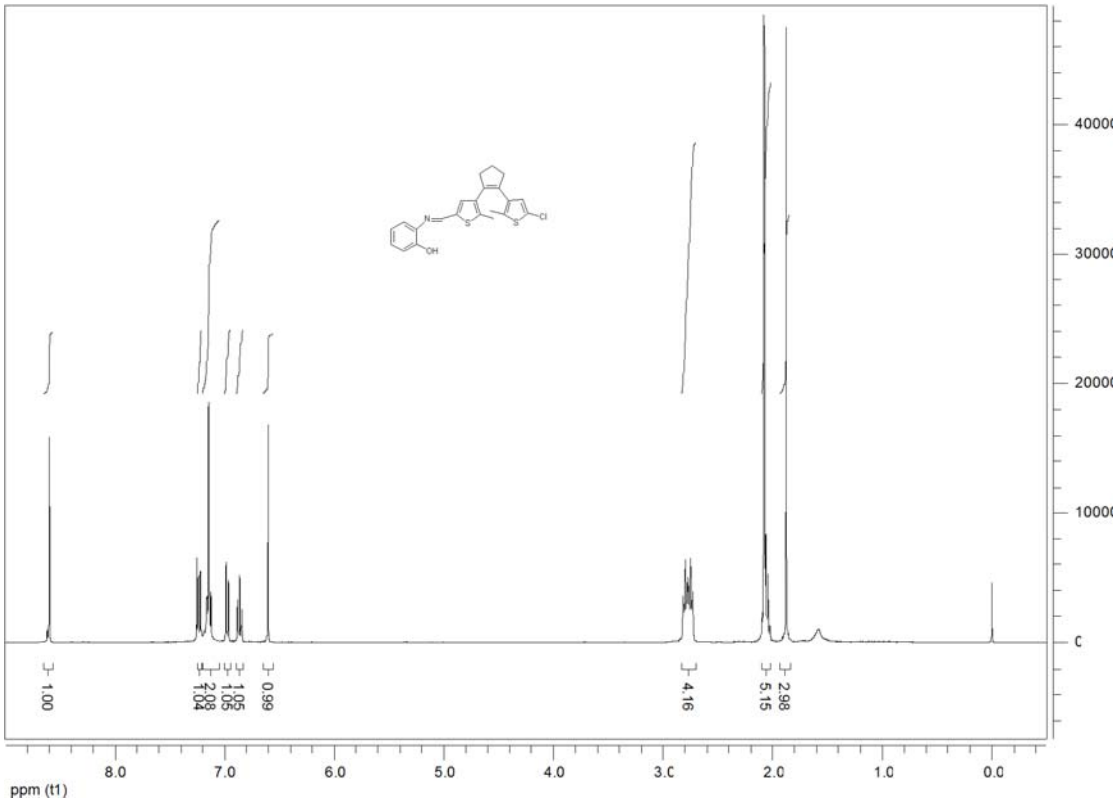


Fig. S31 ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **P1**.

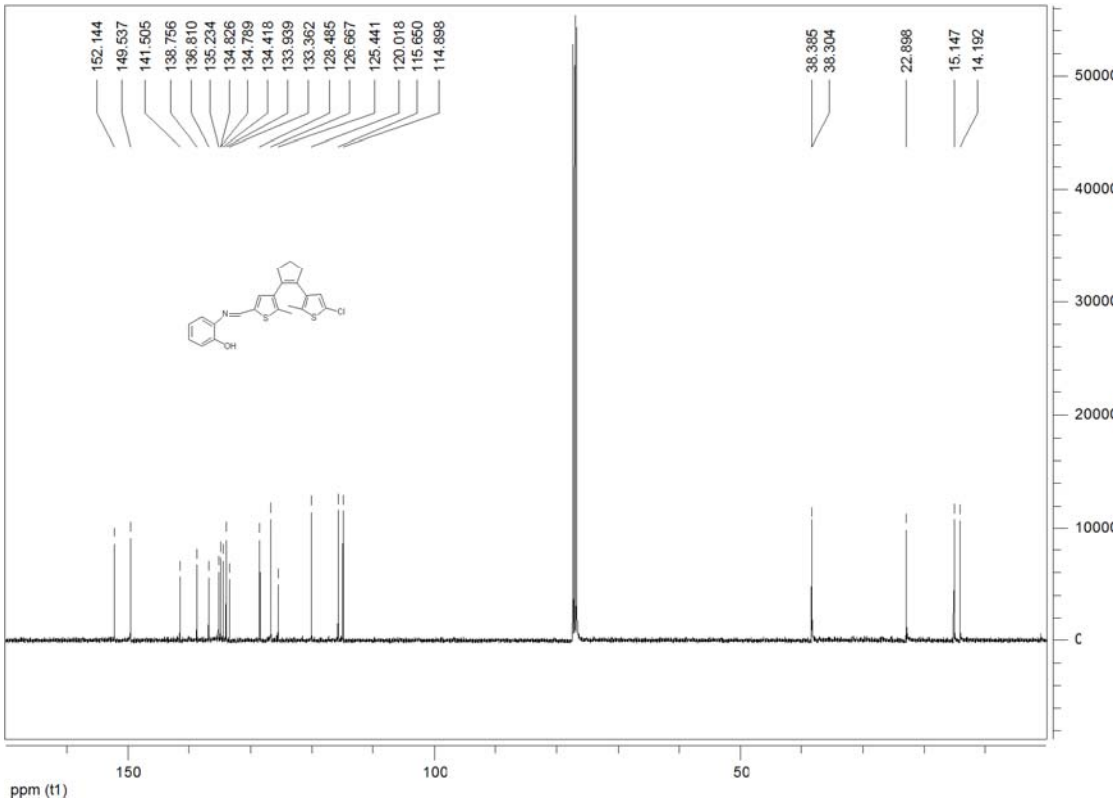
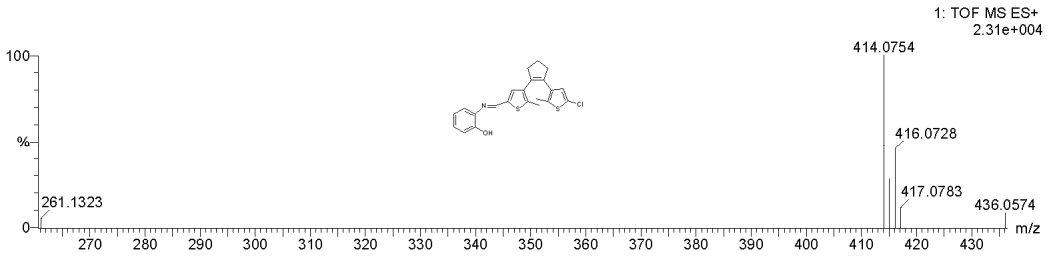


Fig. S32 ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of compound **P1**.

Monoisotopic Mass, Even Electron Ions
4851 formula(e) evaluated with 24 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-22 H: 0-50 N: 0-6 O: 0-20 S: 0-3 Cl: 0-3



Minimum:				-1.5			
Maximum:		3.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
414.0754	414.0753	0.1	0.2	12.5	9.6	0.0	C22 H21 N O S2 Cl

Fig. S33 HRMS (ESI+) spectrum of compound **P1**.

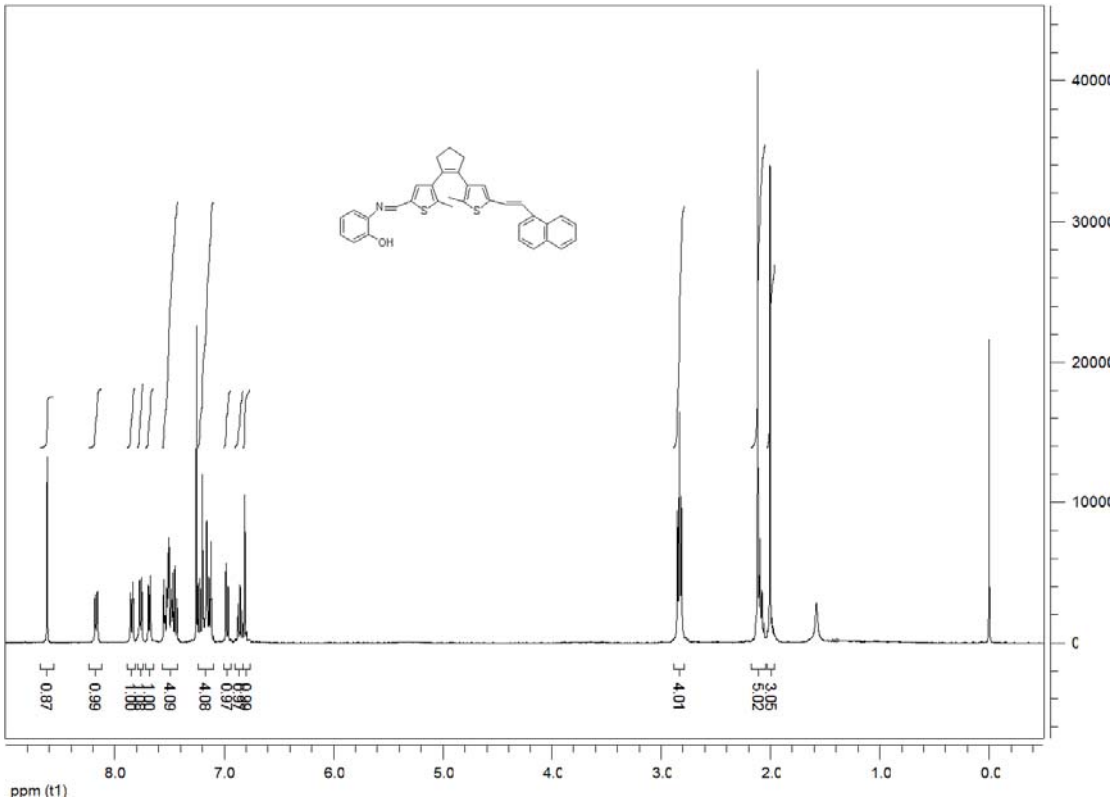


Fig. S34 ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **P2**.

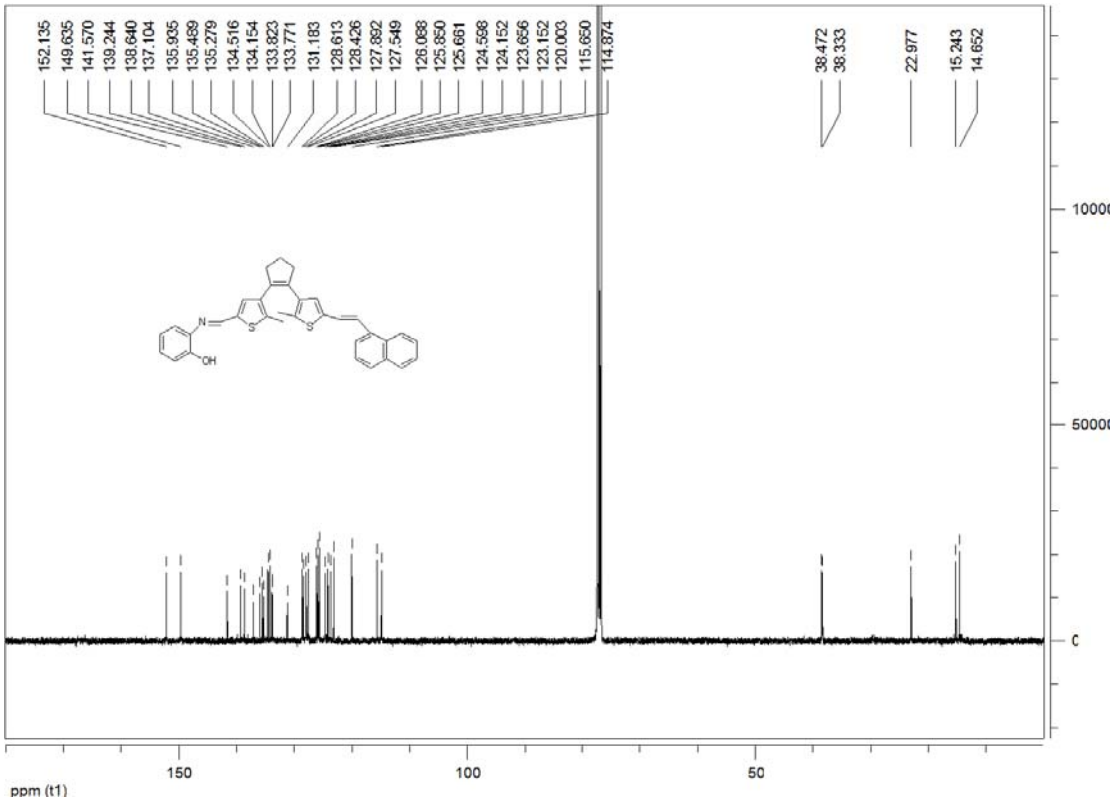
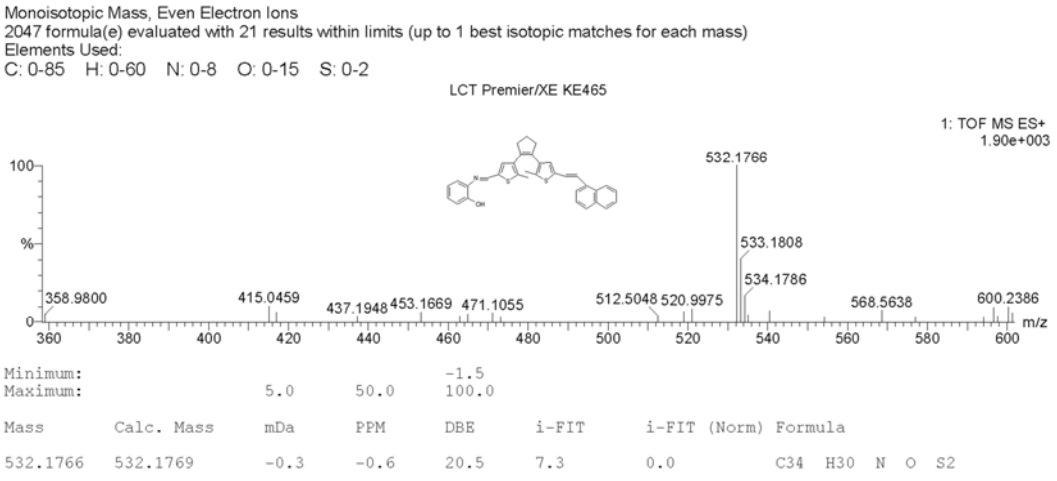


Fig. S35 ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of compound **P2**.



Minimum:				-1.5			
Maximum:		5.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
532.1766	532.1769	-0.3	-0.6	20.5	7.3	0.0	C34 H30 N O S2

Fig. S36 HRMS (ESI+) spectrum of compound **P2**.

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