Electronic Supplementary Material (ESI) for Analyst.

# Electronic Supplementary Information

## A highly selective chromogenic and fluorogenic chemodosimeter for dual detection of $Cu^{2+}$ based on a redox-active calix[4]arene with isoxazolyl-chloroanthracene

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***X-ray crystal data for compound* 1**: $C_{64}H_{44}Cl_2N_2O_6$, $M$ = 1007.91, triclinic, $a$ = 14.9128(2) Å, $b$ = 15.7951(2) Å, $c$ = 21.5622(3) Å, $\alpha$ = 90°, $\beta$ = 108.7995(6)°, $\gamma$ = 90°, $V$ = 4808.00(11) $Å^3$, space group $P2_1/n$, $Z$ = 4, calculated density 1.392 Mg $m^{-3}$, crystal dimensions ($mm^3$): 0.40 × 0.30 × 0.30, $T$ = 150(2) K, $\lambda$ (Mo $K_\alpha$) = 0.71073 Å, $\mu$ = Semi-empirical from equivalents, 46910 reflections collected, 11019 independent ($R_{int}$ = 0.0482), 680 parameter refined on $F^2$, $R_1$ = 0.0942, $wR2[F^2]$ = 0.2081 (all data), GOF on $F^2$ 1.043, $\Delta\rho_{max}$ = 0.487 $eÅ^{-3}$. Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 2184838.

***X-ray crystal data for $Cu(CH_3CN)_4(ClO_4)$***: $C_8H_{12}ClCuN_4O_4$, $M$ = 327.21, triclinic, $a$ = 8.34930(10) Å, $b$ = 20.4107(3) Å, $c$ = 23.8781(4) Å, $\alpha$ = 90°, $\beta$ = 90°, $\gamma$ = 90°, $V$ = 4069.19(10) $Å^3$, space group $P2_12_12_1$, $Z$ = 12, calculated density 1.602 Mg $m^{-3}$, crystal dimensions ($mm^3$): 0.45 × 0.15 × 0.12, $T$ = 150(2) K, $\lambda$ (Mo $K_\alpha$) = 0.71073 Å, $\mu$ = Semi-empirical from equivalents, 28578 reflections collected, 8960 independent ($R_{int}$ = 0.0549), 500 parameter refined on $F^2$, $R_1$ = 0.0956, $wR2[F^2]$ = 0.1413 (all data), GOF on $F^2$ 1.028, $\Delta\rho_{max}$ = 1.510 $eÅ^{-3}$. Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 2184839. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: data_request@ccdc.cam.ac.uk, or fax: +44-1223-336033].

*Synthesis of ligand **2***

A mixture of compound **6** (0.200 g, 0.342 mmol) and 10-chloroanthracene-9-hydroximoyl chloride (0.490 g, 1.69 mmol) in toluene (50 mL) was stirred. Then, $Et_3N$ (1.04 g, 10.3 mmol) was added dropwise and the mixture was refluxed for 24 h. The solvent was removed under vacuum, and the residue was dissolved in chloroform (30 mL), washed with water, and dried over $MgSO_4$. The residue obtained after evaporation of the solvent was subjected to a silica gel column chromatography using a gradient polarity (eluent: ethyl acetate/*n*-hexane, 1/14 to 1/6) to afford 0.0860 g (23%) of ligand **2** as a yellow solid; mp 168−171 $^{o}$C ($CHCl_3$/*n*-hexane); $R_f$ = 0.84 (ethyl acetate/*n*-hexane = 1:3); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.60 (d, $J$ = 8.7 Hz, 4H), 7.73 (d, $J$ = 8.7 Hz, 4H), 7.68−7.58 (m, 4H), 7.57−7.43 (m, 4H), 7.17 (d, $J$ = 7.3 Hz, 4H), 7.01 (t, $J$ = 7.3 Hz, 2H), 6.42-6.35 (m, 4H), 6.26 (d, $J$ = 7.1 Hz, 4H), 5.79 (s, 4H), 4.50 (d, $J$ = 13.6 Hz, 4H), 3.77 (t, $J$ = 7.1 Hz, 4H), 3.30 (d, $J$ = 13.6 Hz, 4H), 2.03−1.83 (m, 4H), 0.93 (t, $J$ = 7.4 Hz, 6H); $^{13}$C NMR (75 MHz) $\delta$ 169.4 ($C_q$), 160.4 ($C_q$), 155.5 ($C_q$), 155.1 ($C_q$), 137.5 ($C_q$), 133.0 ($C_q$), 131.1 ($C_q$), 131.0 ($C_q$), 129.1 (CH), 128.4 ($C_q$), 127.6 (CH), 126.8 (CH), 126.6 (CH), 126.1 (CH), 125.0 (CH), 123.3 (CH), 123.1 ($C_q$), 122.4 (CH), 108.6 (CH), 77.5 ($CH_2$), 64.2 ($CH_2$), 31.4 ($CH_2$), 23.3 ($CH_2$), 10.6 ($CH_3$); FAB-MS *m/z* 1092 ($M^+$); HRMS *m/z* calcd for $C_{70}H_{56}{}^{35}Cl_2N_2O_6$ 1090.3515, found 1090.3497.

*Synthesis of ligand **3***

A mixture of compound **7** (0.200 g, 1.25 mmol) and 10-chloroanthracene-9-hydroximoyl chloride (2.50 equiv) in toluene (50 mL) was stirred. Then $Et_3N$ (15.0 equiv) was added dropwise and mixture was refluxed for 24 h. The solvent was removed under vacuum, and the residue was dissolved in chloroform (30 mL), washed with water, and dried over $MgSO_4$. The solvents were removed under vacuum and the residue was purified by column chromatography with ethyl acetate/*n*-hexane (1:14) to give 0.295 g (57%) of ligand **3** as a yellowish green powder; mp 170−172 $^{o}$C ($CHCl_3$/*n*-hexane); $R_f$ = 0.86 (ethyl acetate/*n*-hexane = 1:3); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.61 (d, $J$ = 8.8 Hz, 2H), 7.86 (d, $J$ = 8.8 Hz, 2H), 7.68−7.59 (m, 2H), 7.57−7.47 (m, 2H), 7.13−6.97 (m, 3H), 6.60 (s, 1H), 5.15 (s, 2H), 2.40 (s, 6H); $^{13}$C NMR (75.4 MHz) $\delta$ 168.9 ($C_q$), 160.7 ($C_q$), 155.0 ($C_q$), 131.3 ($C_q$), 131.0 ($C_q$), 130.9 ($C_q$), 129.1 (CH), 128.5 ($C_q$), 126.8 (CH), 126.7 (CH), 126.0 (CH), 125.1 (CH), 124.7 (CH), 122.7 ($C_q$), 107.2 (CH), 64.5 ($CH_2$), 16.4 ($CH_3$); EI-MS *m/z* 413 ($M^+$); HRMS *m/z* calcd for $C_{26}H_{20}{}^{35}ClNO_2$ 413.1183, found 413.1181.

*Synthesis of compound **6***

A solution of compound **5** (0.200 g, 0.398 mmol), sodium hydride (0.190 g, 7.92 mmol) and 1-iodopropane (0.270 g, 1.60 mmol) in DMF (5 mL) was stirred at room temperature for 2 h. The mixture was diluted with water (100 mL) and extracted with chloroform (3 × 20 mL). The organic layer was dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by silica gel chromatography with ethyl acetate/*n*-hexane (1:6) to give 0.197 g (85%) of pure compound **6** as white powders; mp 170-172 $^{o}C$ ($CHCl_3$/*n*-hexane); $R_f$ = 0.84 (ethyl acetate/*n*-hexane = 1:3); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.14 (d, $J$ = 7.4 Hz, 4H), 6.98 (t, $J$ = 7.4 Hz, 2H), 6.32–6.18 (m, 6H), 4.99 (d, $J$ = 1.8 Hz, 4H), 4.56 (d, $J$ = 13.5 Hz, 4H), 3.71 (t, $J$ = 6.8 Hz, 4H), 3.19 (d, $J$ = 13.5 Hz, 4H), 2.38 (bt, 2H), 2.02-1.86 (m, 4H), 1.10 (t, $J$ = 7.4 Hz, 6H); $^{13}C$ NMR (75 MHz) $\delta$ 155.4 ($C_q$), 137.8 ($C_q$), 133.1 ($C_q$), 128.8 (CH), 127.4 (CH), 123.2 (CH), 122.2 (CH), 80.8 ($C_q$), 77.2 ($CH_2$), 74.6 (CH), 59.8 ($CH_2$), 31.3 ($CH_2$), 23.6 ($CH_2$), 10.9 ($CH_3$); FAB-MS *m/z* 584 ($M^+$); HRMS *m/z* calcd for $C_{40}H_{40}O_4$ 584.2927, found 584.2953.

*Synthesis of compound **8***

A solution of ligand **1** (30 mg, 0.03 mmol) and $Cu(ClO_4)_2$ (10 equiv) in 30 mL $CH_3CN/CHCl_3$ (v/v, 1:1) was stirred at room temperature for 12 h. The solvent was removed under vacuum, and the residue was dissolved in $CH_2Cl_2$ (30 mL), washed firstly with water, then with $NH_4Cl$, dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by silica gel chromatography with (ethyl acetate/*n*-hexane = 1:3) to give 17 mg (55%) of pure compound **8** as a yellow powder. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.59 (dt, $J$ = 8.8, 1.1 Hz, 4H), 7.76 (dt, $J$ = 8.7, 1.0 Hz, 4H), 7.65–7.58 (m, 4H), 7.54–7.48 (m, 4H), 6.83 (m, 4H), 6.74 (t, $J$ = 7.5 Hz, 2H), 6.68 (s, 4H), 6.48 (s, 2H), 5.18 (s, 4H), 4.05 (d, $J$ = 12.3 Hz, 4H), 3.32 (d, $J$ = 12.3 Hz, 4H); $^{13}C$ NMR (100 MHz) $\delta$ 187.8 ($C_q$), 185.7 ($C_q$), 167.8 ($C_q$), 160.8 ($C_q$), 154.6 ($C_q$), 147.9 ($C_q$), 132.5 (CH), 131.5 ($C_q$), 130.9 ($C_q$), 130.6 ($C_q$), 129.1 ($C_q$), 128.4 ($C_q$), 126.9 (CH), 125.8 (CH), 125.1 (CH), 124.4 (CH), 122.3 ($C_q$), 108.4 (CH), 65.6 ($CH_2$), 31.2 ($CH_2$); HRMS–FD (*m/z*) calcd for $C_{64}H_{40}Cl_2N_2O_8$, 1034.21672; found, 1034.21637. IR ($cm^{-1}$): 2921 (C-H stretch), 1655 (C=O stretch, quinone), 1608 (C=C stretch), 759 (C-Cl stretch).

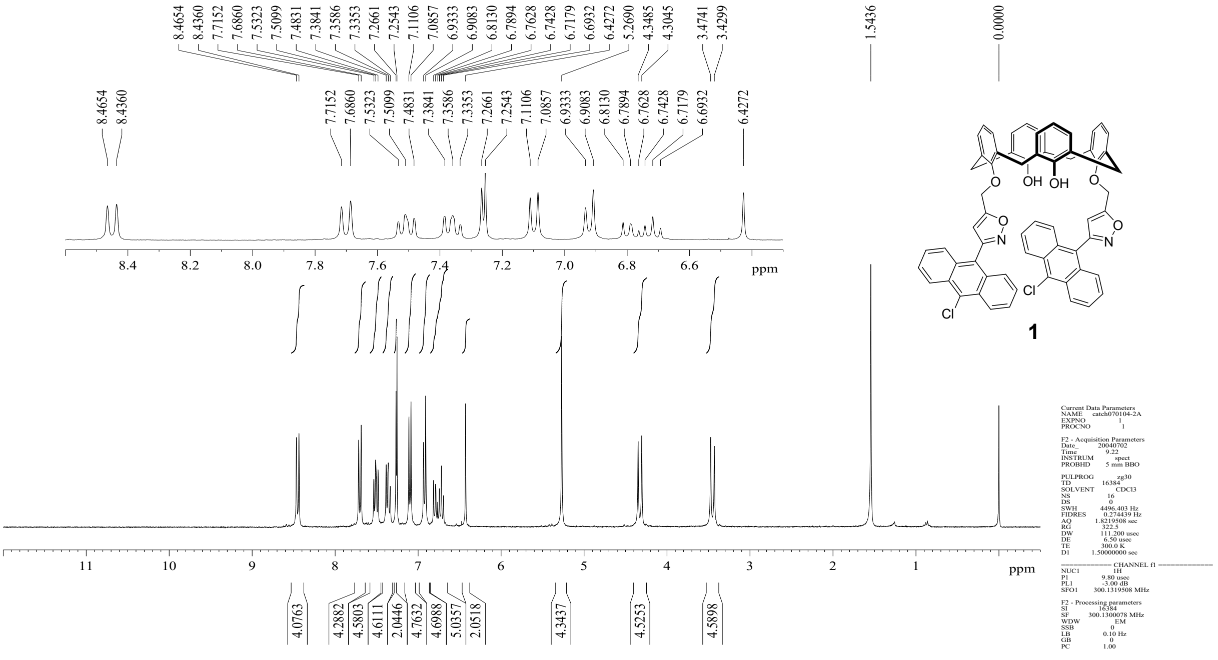

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**Fig. S1.** $^{1}H$ NMR (300 MHz, $CDCl_3$) spectrum of ligand **1**.

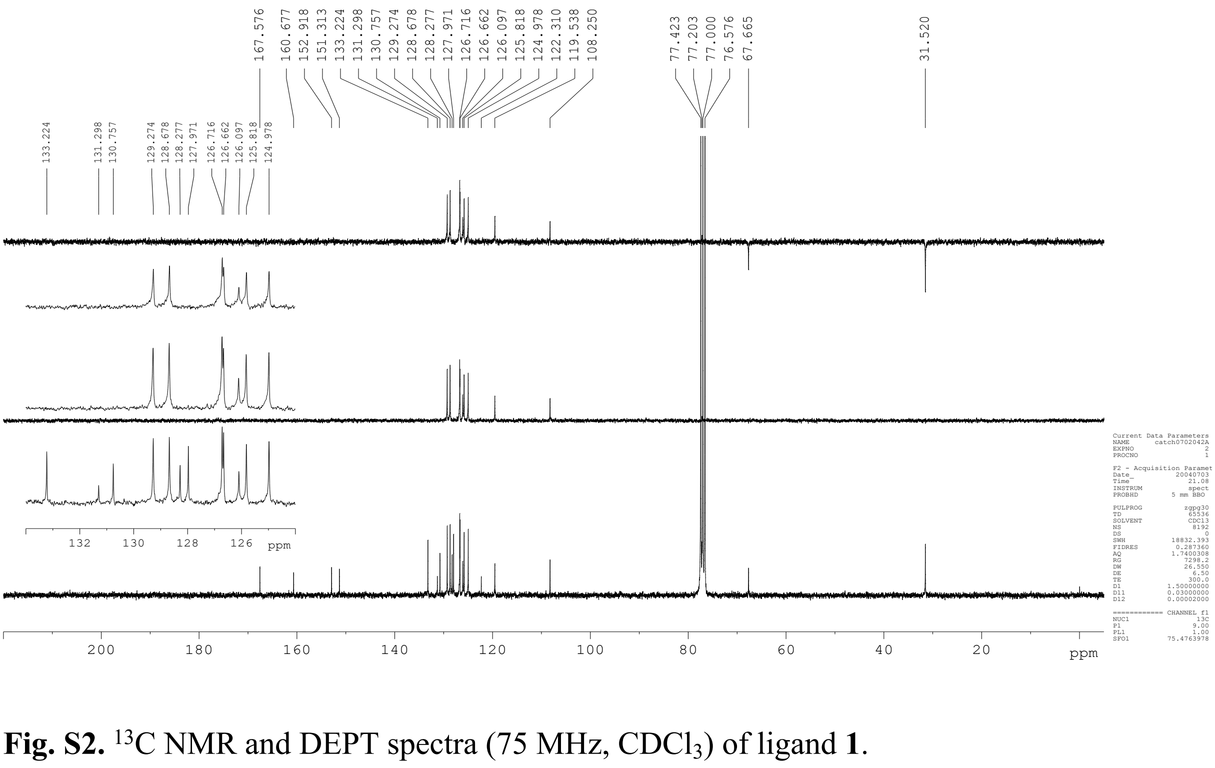

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**Fig. S2.** $^{13}C$ NMR and DEPT spectra (75 MHz, $CDCl_3$) of ligand **1**.

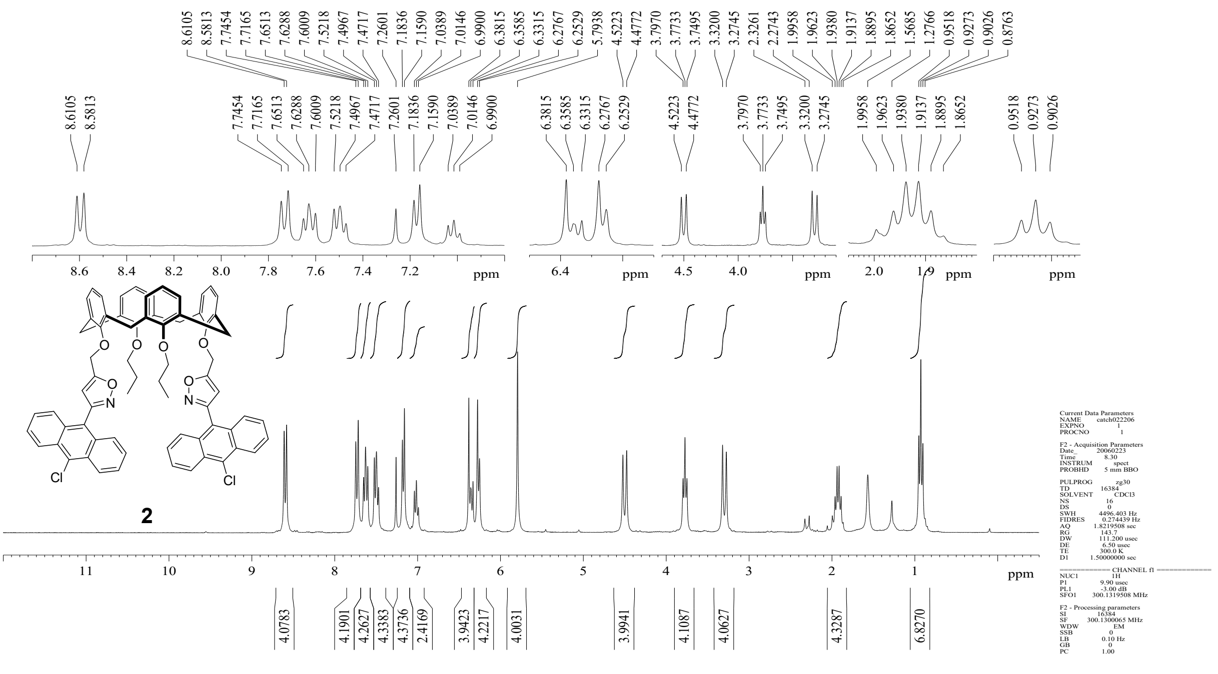


**Fig. S3.** $^1$H NMR (300 MHz, $CDCl_3$) spectrum of ligand **2**.

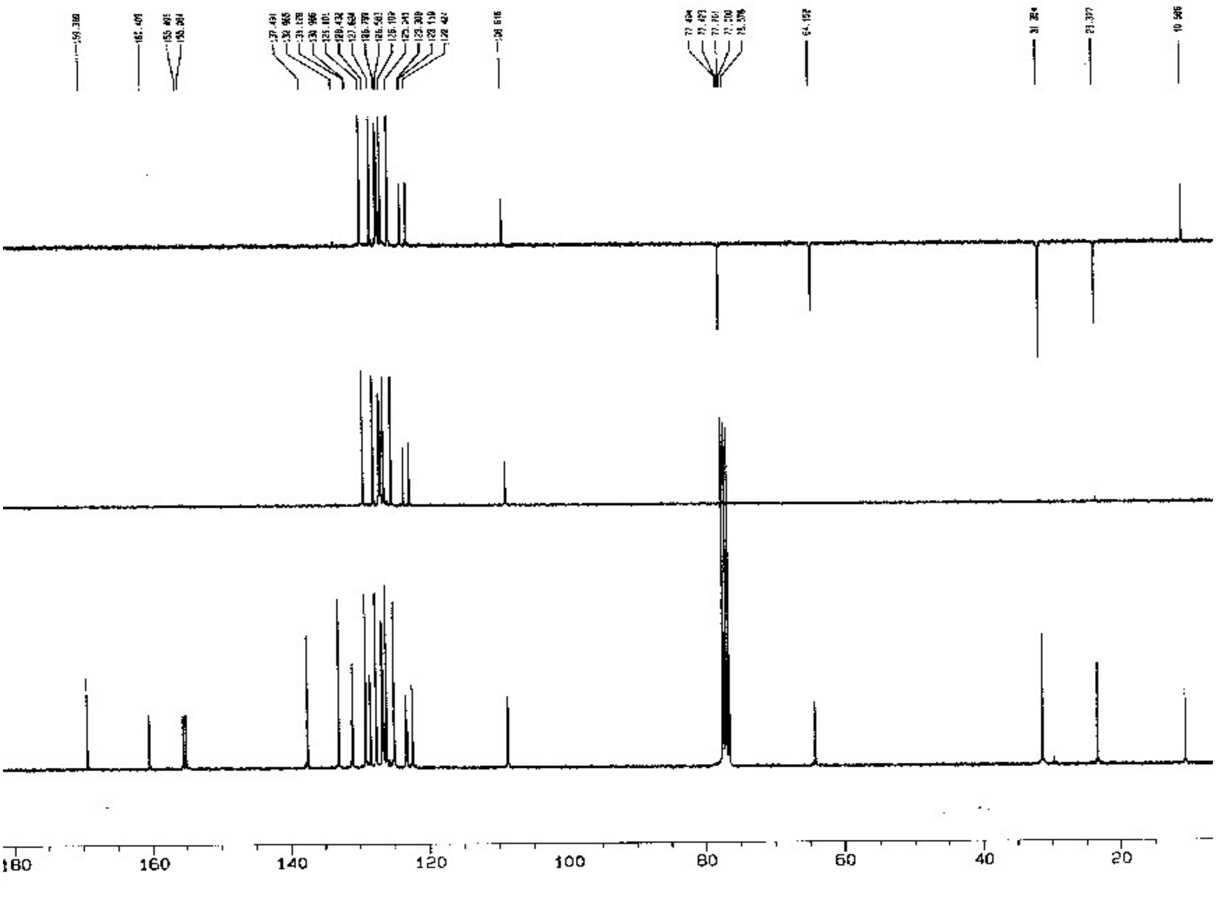


**Fig. S4.** $^{13}$C NMR and DEPT spectra (75 MHz, $CDCl_3$) of ligand **2**.

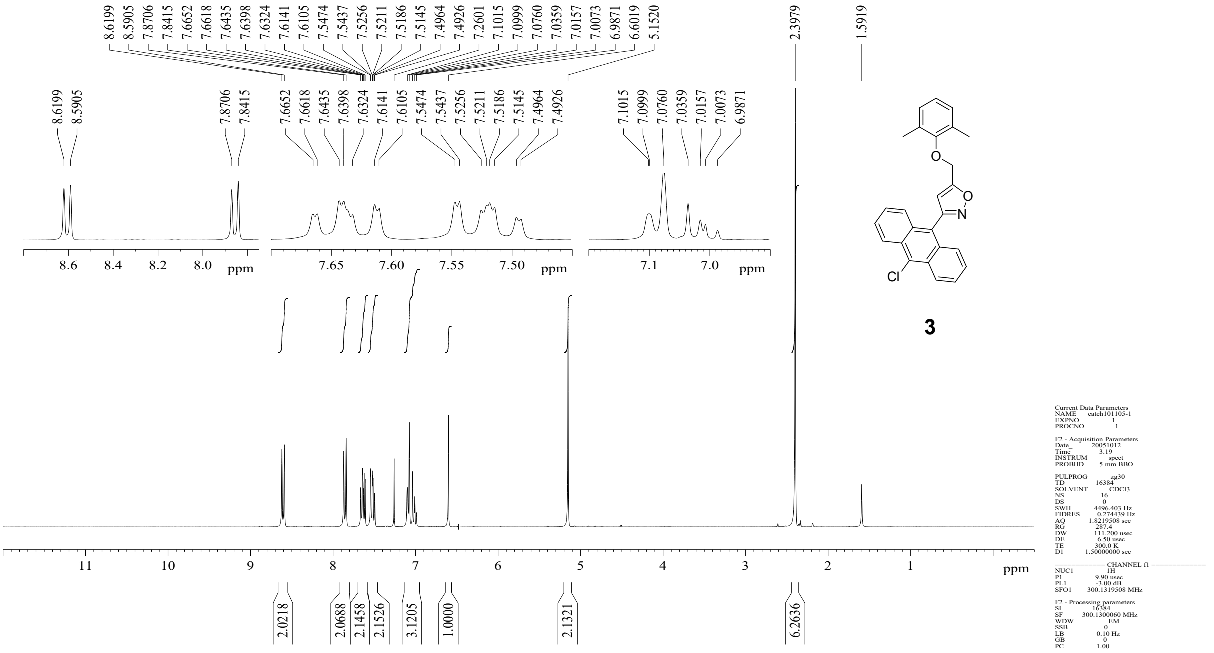


**Fig. S5.** $^1$H NMR (300 MHz, CDCl$_3$) spectrum of ligand **3**.

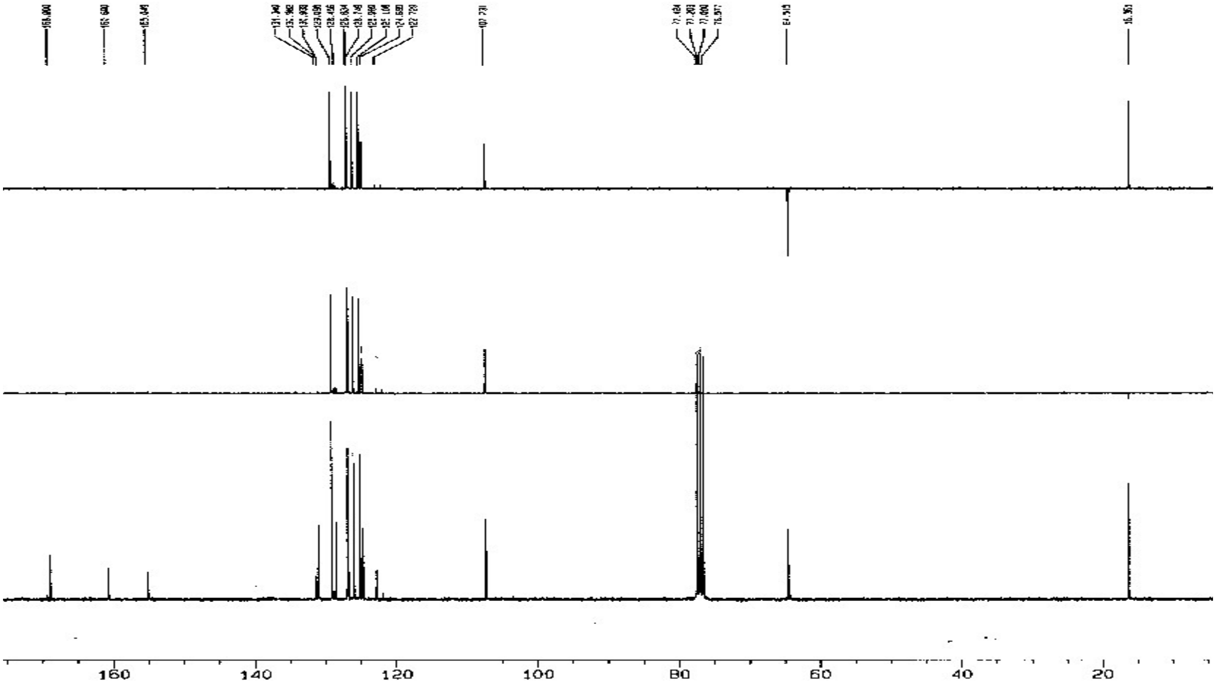


**Fig. S6.** $^{13}$C NMR and DEPT spectra (75 MHz, CDCl$_3$) of ligand **3**.

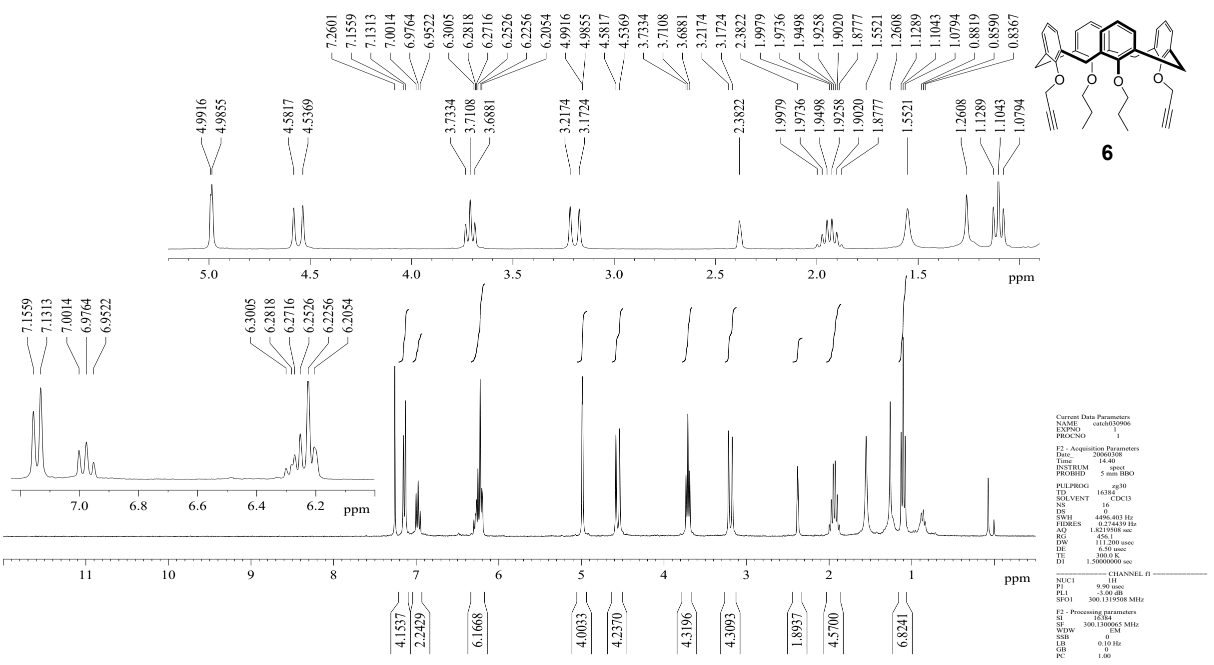


**Fig. S7.** $^1$H NMR (300 MHz, $CDCl_3$) spectrum of compound **6**.

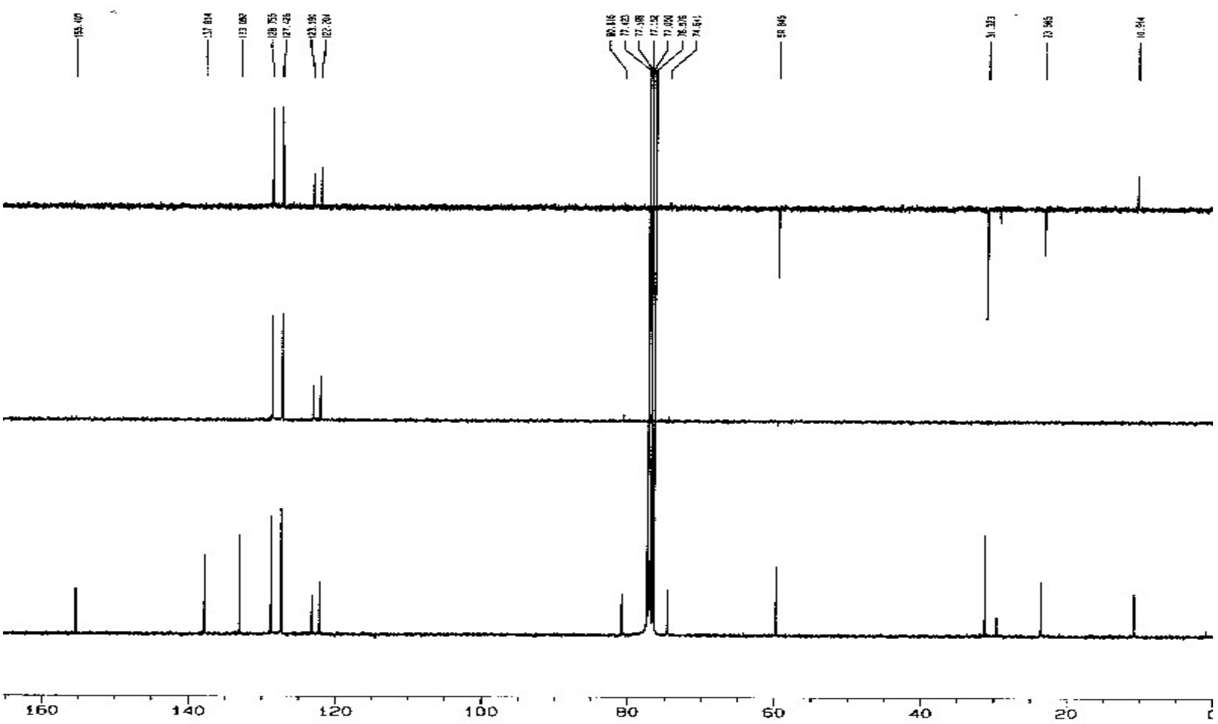


**Fig. S8.** $^{13}$C NMR and DEPT spectra (75 MHz, $CDCl_3$) of compound **6**.

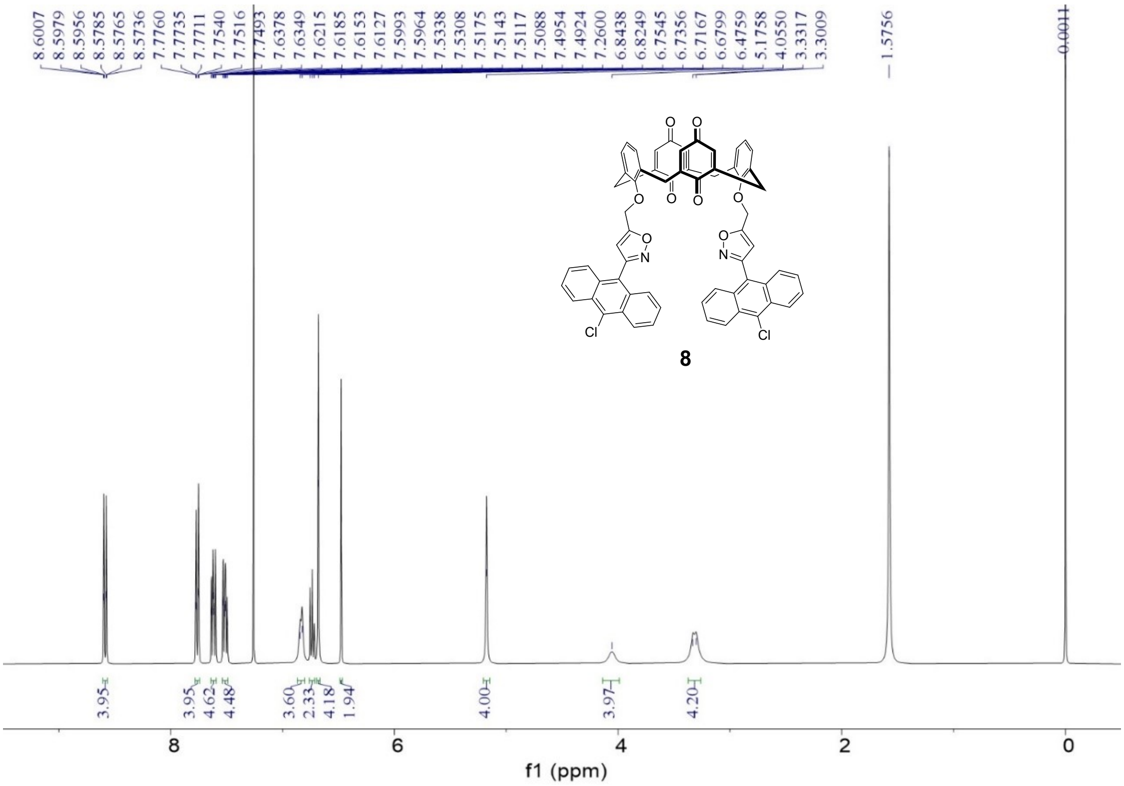


**Fig. S9.** $^1$H NMR (400 MHz, $CDCl_3$) spectrum of compound **8**.

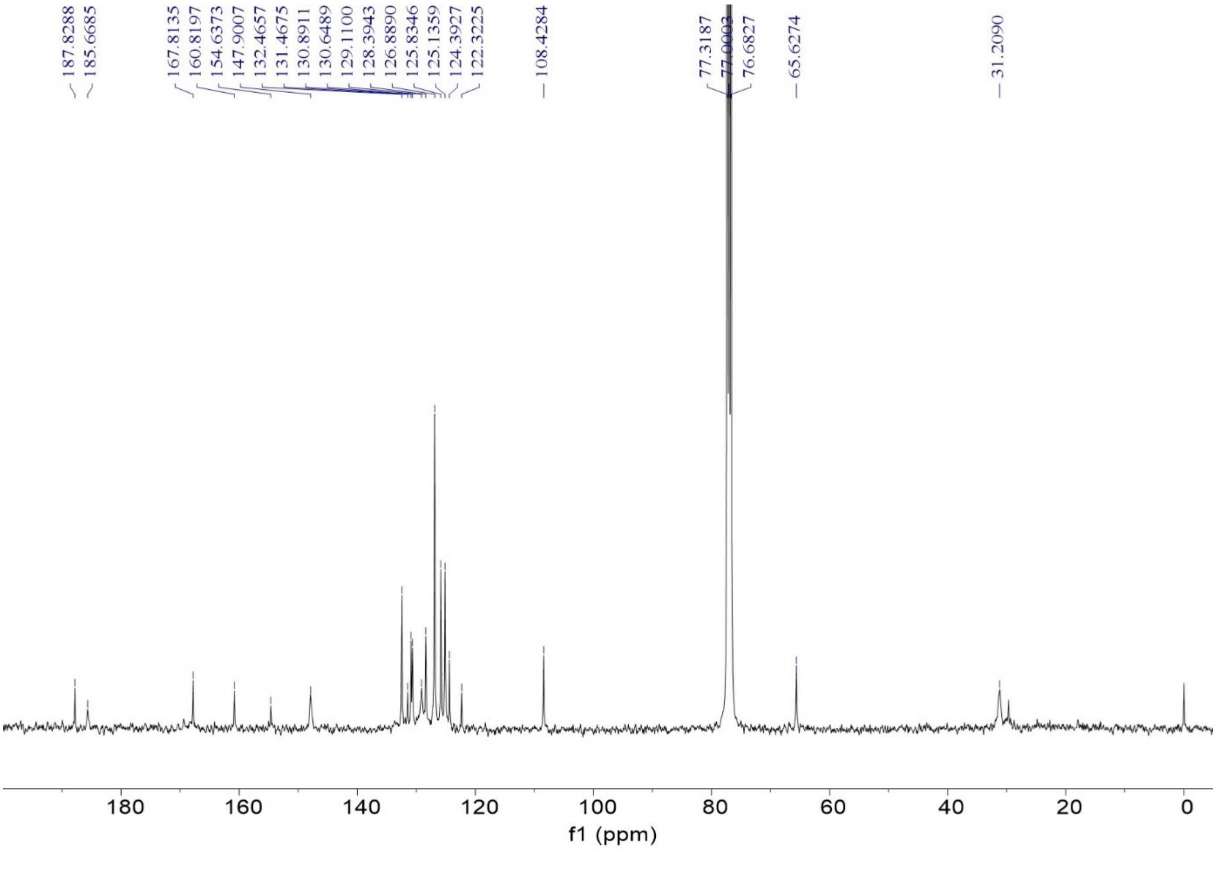
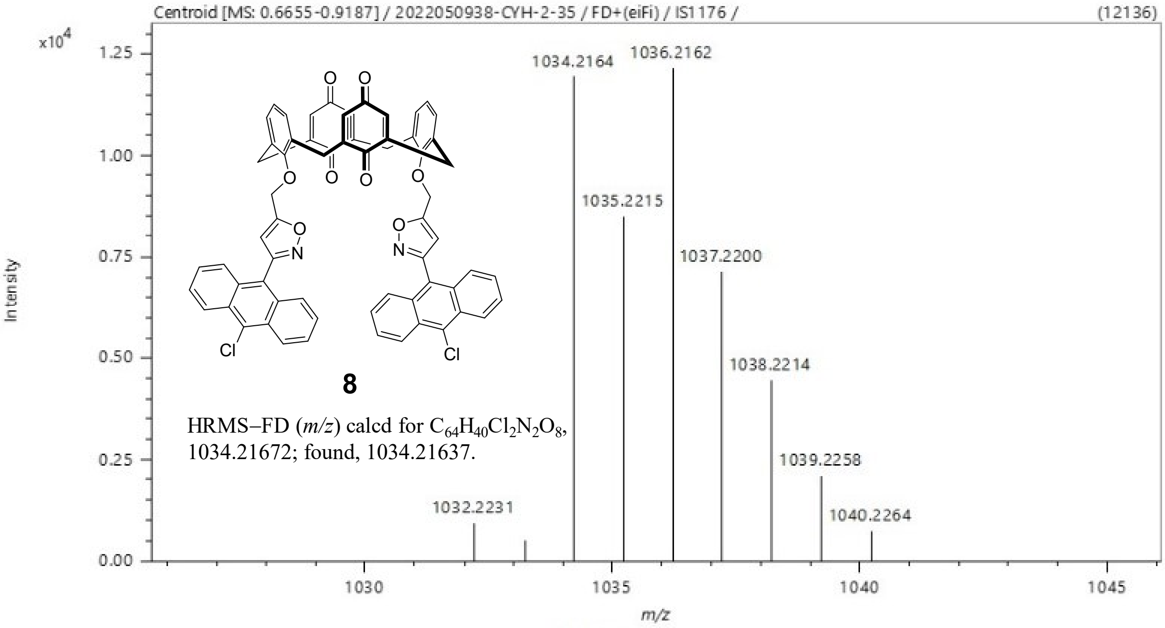
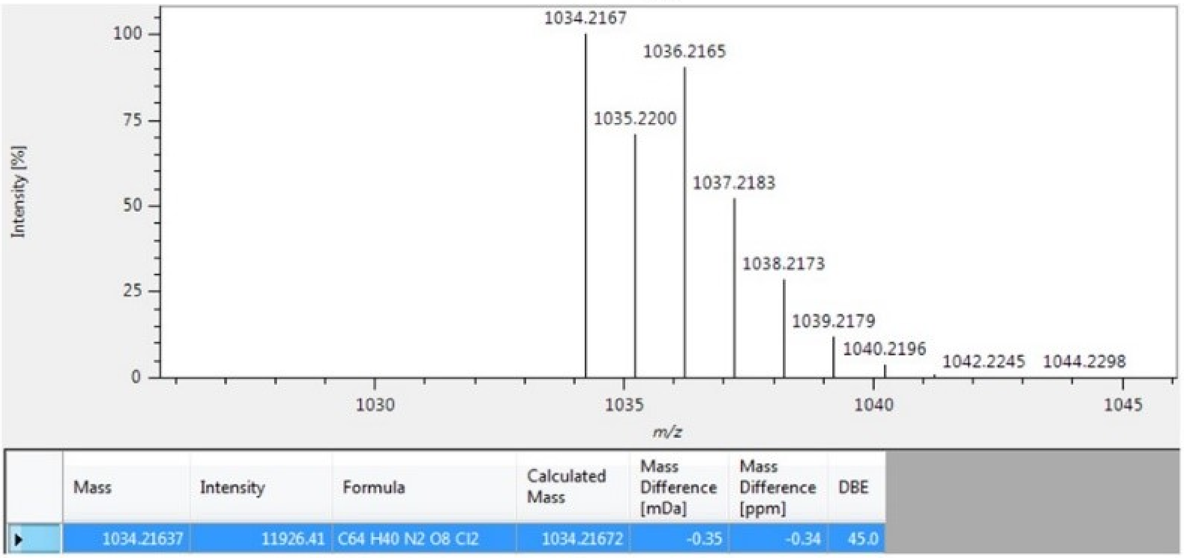


**Fig. S10.** $^{13}$C NMR and DEPT spectra (100 MHz, $CDCl_3$) of compound **8**.



**8**

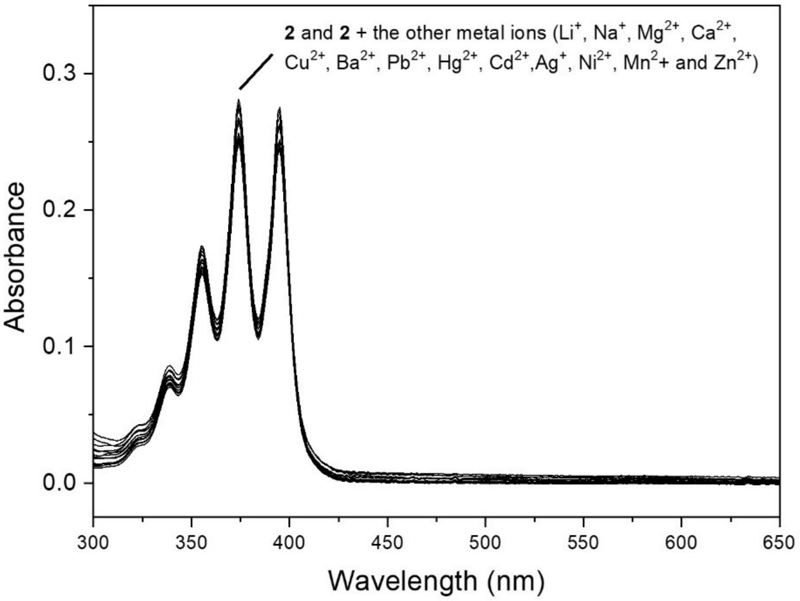
HRMS–FD (*m/z*) calcd for $C_{64}H_{40}Cl_2N_2O_8$, 1034.21672; found, 1034.21637.



| | Mass | Intensity | Formula | Calculated Mass | Mass Difference [mDa] | Mass Difference [ppm] | DBE |
|---|---|---|---|---|---|---|---|
| ▶ | 1034.21637 | 11926.41 | C64 H40 N2 O8 Cl2 | 1034.21672 | -0.35 | -0.34 | 45.0 |

**Fig. S11.** HRMS of compound **8**.

(a)



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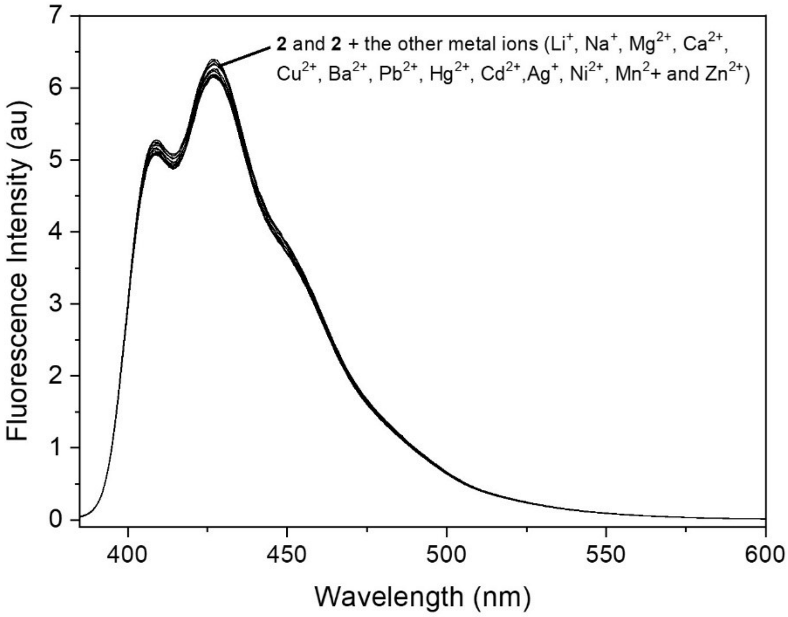
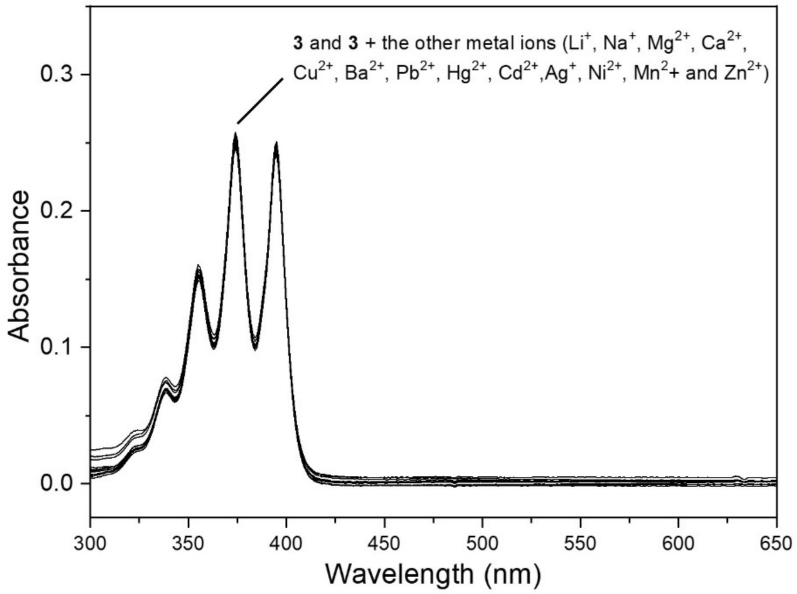


**Fig. S12.** (a) UV-vis and (b) fluorescent spectra ($\lambda_{ex}$ = 375 nm) of ligand **2** (20 μM) in the absence and presence of 10 equiv of 13 metal perchlorates in $CH_3CN/CHCl_3$ (v/v, 1:1) at 298 K.

(a)



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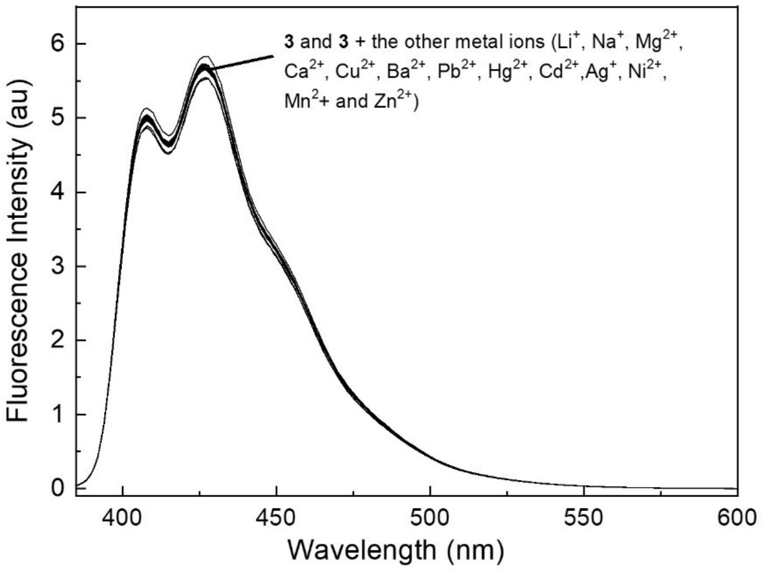
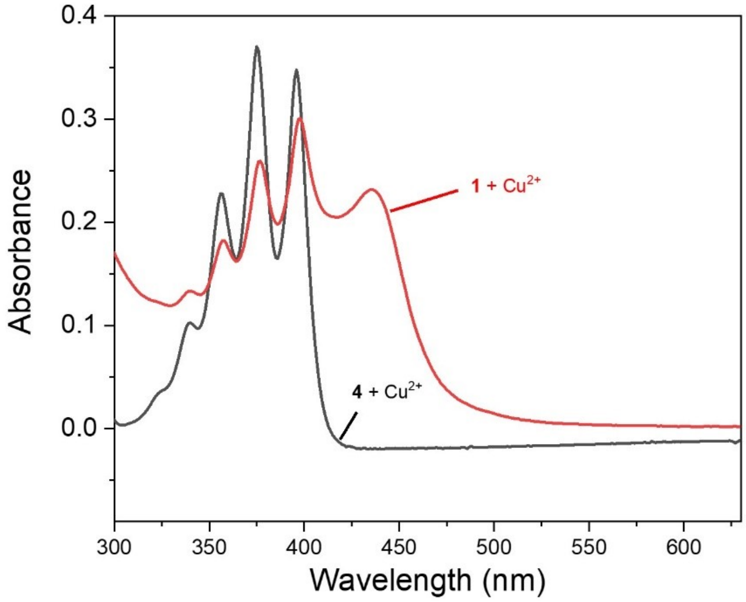


**Fig. S13.** (a) UV-vis and (b) fluorescent spectra ($\lambda_{ex}$ = 375 nm) of ligand **3** (20 μM) in the absence and presence of 10 equiv of 13 metal perchlorates in $CH_3CN/CHCl_3$ (v/v, 1:1) at 298 K.

(a)



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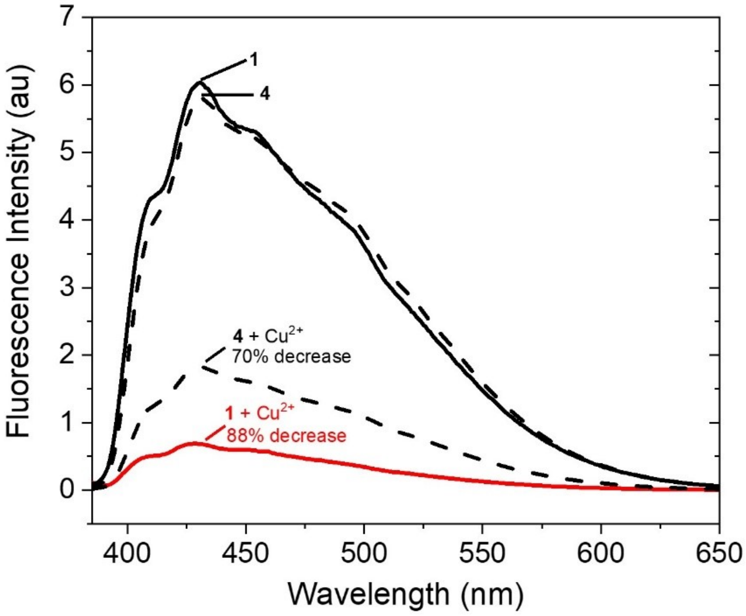


**Fig. S14.** (a) UV-vis and (b) fluorescent spectra ($\lambda_{ex}$ = 375 nm) of ligands **1** and **4** (20 μM) in the absence and presence of 10 equiv of $Cu(ClO_4)_2$ in $CH_3CN/CHCl_3$ (v/v, 1:1) at 298 K, respectively.

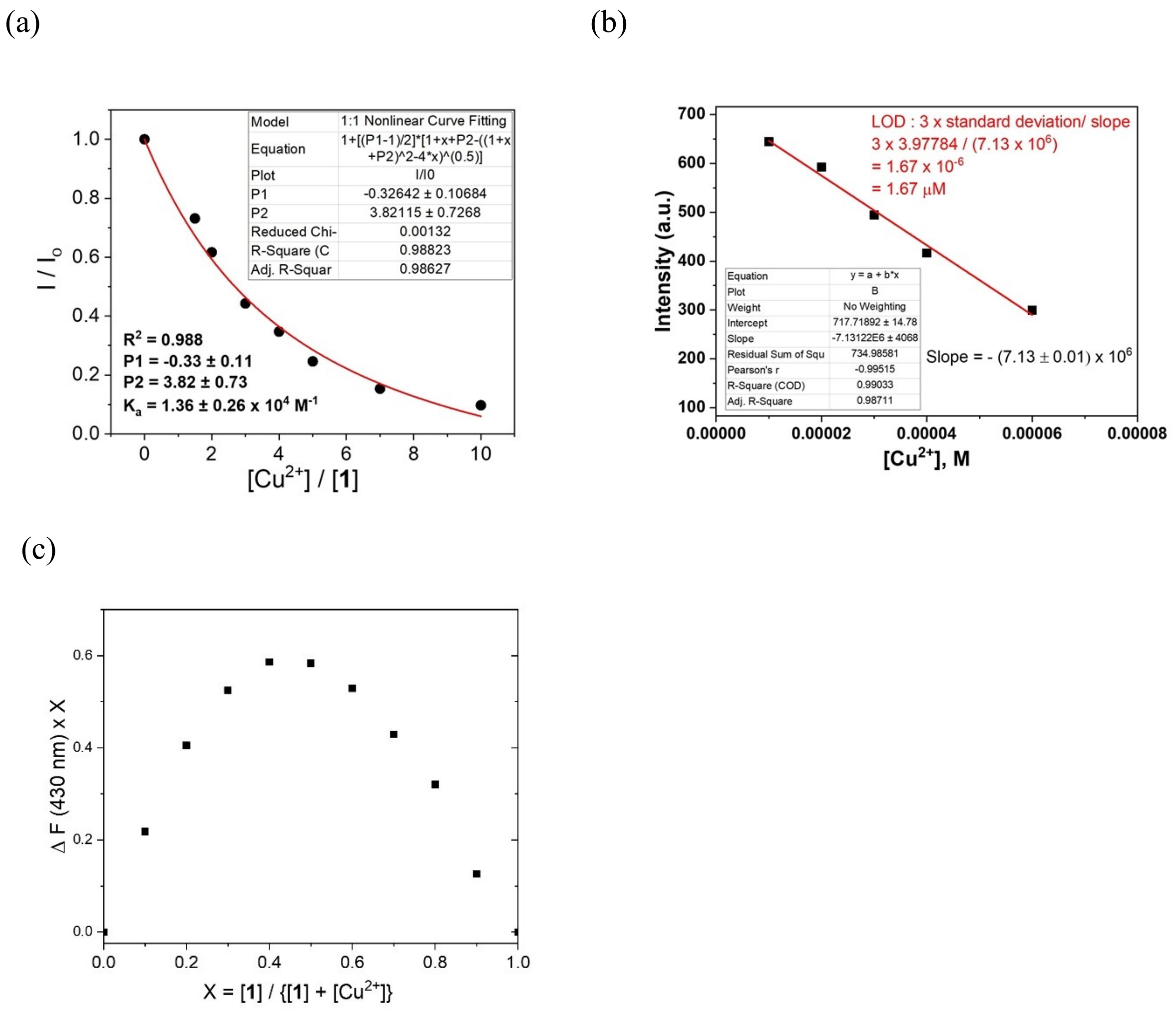


**Fig. S15.** Binding constant of ligand **1** (20 μM) with $Cu(ClO_4)_2$ by (a) nonlinear least-square curve-fitting plot; (b) the limits of detection (LOD): changes in the fluorescence intensity of compound **1** (20 μM) upon the addition of various concentration of $Cu^{2+}$ in $CH_3CN/CHCl_3$ (v/v, 1:1) at 298 K. The fluorescence intensity of compound **1** at 430 nm decreases linearly with the concentration of $Cu^{2+}$ in the range of 0 ~ 60 μM. The limit of detection (LOD) was determined to be 3 × 3.98/(7.13 × $10^6$) M = 1.674 μM, in which ten experiments were performed for the determination of standard deviation. (c) Job plot of ligand **1** with $Cu^{2+}$ in $CH_3CN/CHCl_3$ (v/v, 1:1).

- **Nonlinear least-square curve-fitting plot**

$$I/I_0 = 1 + \frac{I_{lim}/I_0 - 1}{2}\left[1 + \frac{C_M}{C_H} + \frac{1}{K_a C_H} - \sqrt{\left(1 + \frac{C_M}{C_H} + \frac{1}{K_a C_H}\right)^2 - 4\frac{C_M}{C_H}}\right]$$

where I is fluorescent intensity of **1** in presence of $Cu^{2+}$ ion, $I_0$ is fluorescent intensity of **1** without $Cu^{2+}$ ion, $I_{lim}$ is fluorescent intensity reaching a limitation by adding excessive $Cu^{2+}$

ion, $C_M$ is the concentraton of $Cu^{2+}$ ion added and $C_H$ is the concentration of **1**. By allowing $I_{lim}/I_0$ and **1**/$K_aC_H$ to be floating parameters (P1 and P2), the $K_a$ value was obtained by a nonlinear least-squares analysis of $I/I_0$ versus $[Cu^{2+}]/[\mathbf{1}]$.

**References for nonlinear least-square curve-fitting plot**

1. L. Fang, W.-H. Chan, Y.-B. He, D. W. J. Kwong and A. W. M. Lee, *J. Org. Chem.* 2005, **70**, 7640–7646.
2. B. Valeur, J. Pouget and J. Bouson, *Journal of Physical Chemistry,* 1992, **96**, 6545–6549.

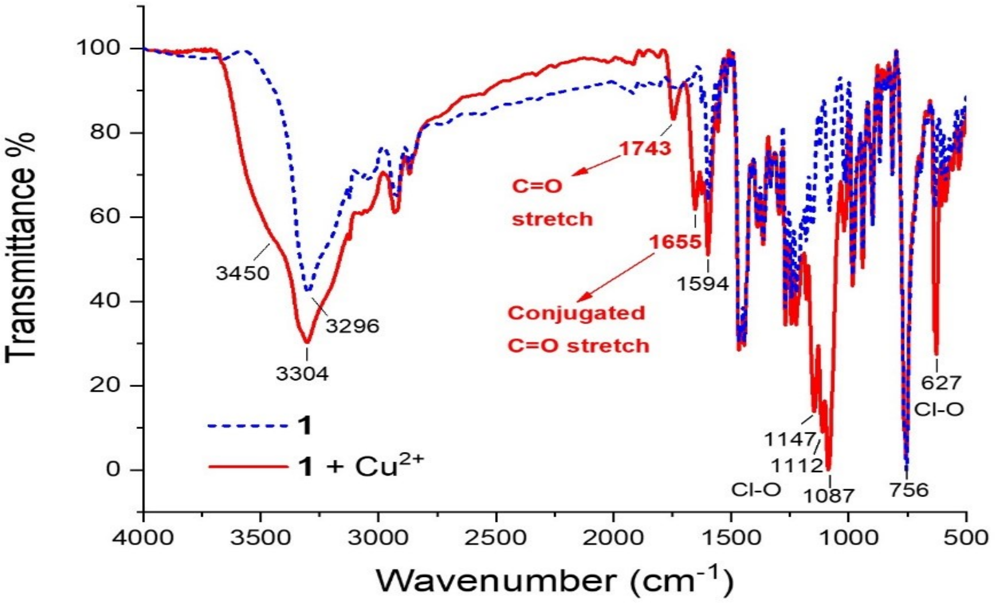
- **The limit of Detection (LOD)**

LOD = 3 × standard deviation/slope

**References for LOD.**

1. G. L. Long and J. D. Winefordner, *Analytical Chemistry*, 1983, **55**, 712A–724A.
2. V. Thomsen, D. Schatzlein and D. Mercuro, *Spectroscopy*, 2003, **18**, 112–114.
3. H. J. Kim, J. H. Lee and J.-I. Hong, *Tetrahedron*, 2011, **52**, 4944–4946.

(a)



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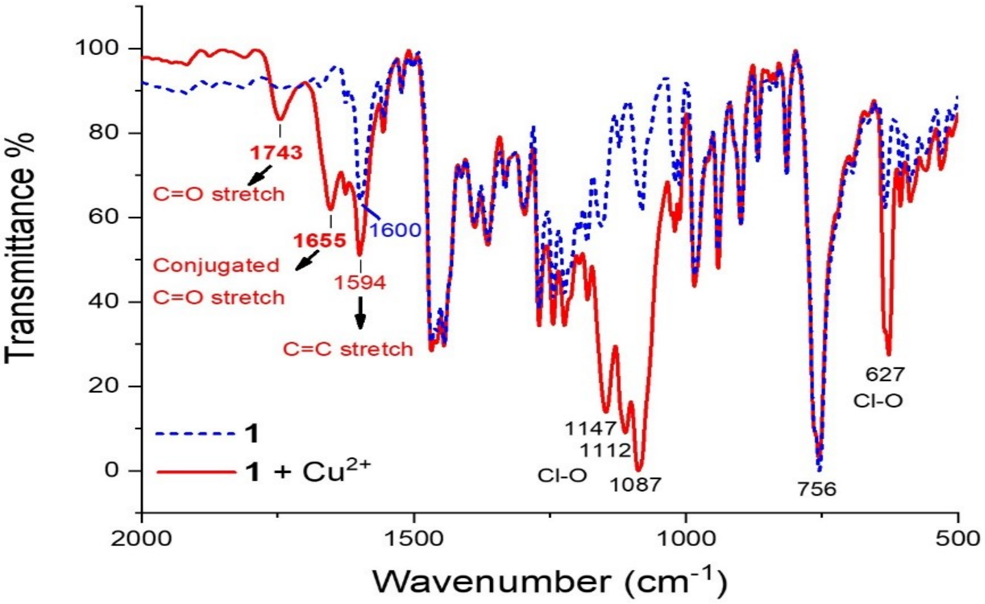
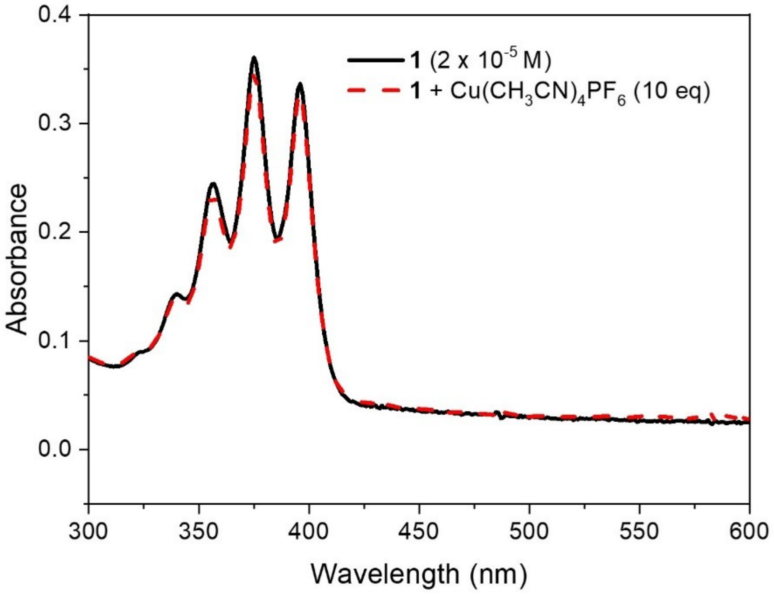


**Fig. S16.** FTIR (KBr) spectra of ligand **1** and its complexation with $Cu(ClO_4)_2$. (a) Full region in 500–4000 cm$^{-1}$; (b) the expansion of (a) in the 500–2000 cm$^{-1}$ region.

(a)



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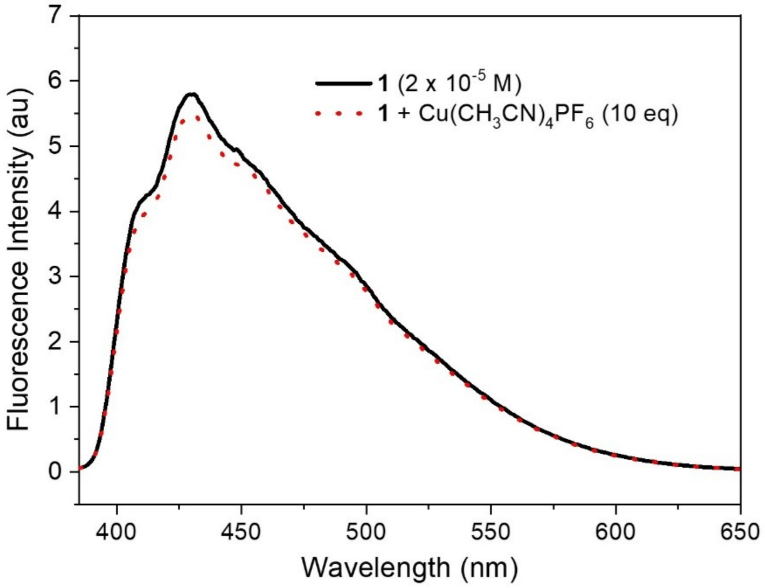
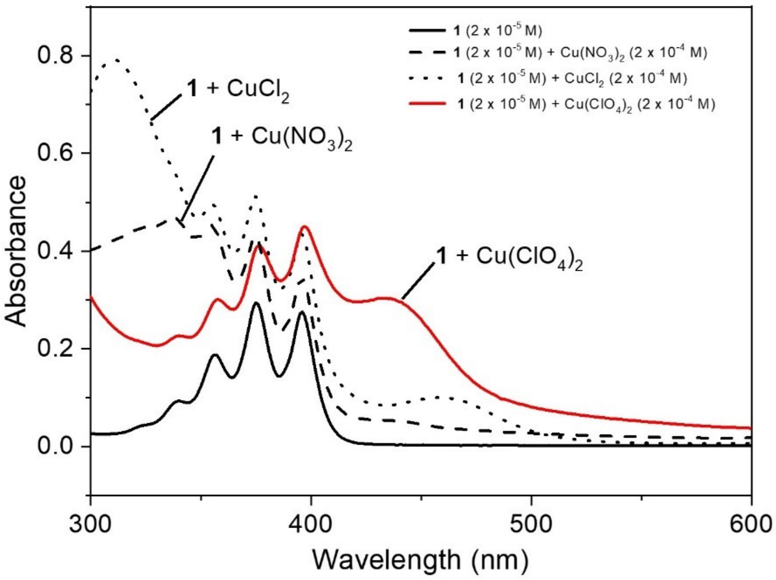


**Fig. S17.** (a) UV-vis and (b) fluorescent spectra ($\lambda_{ex}$ = 375 nm) of ligand **1** (20 μM) in the absence and presence of 10 equiv of $Cu(CH_3CN)_4PF_6$ in $CH_3CN/CHCl_3$ (v/v, 1:1) at 298 K, respectively.

(a)



(b)

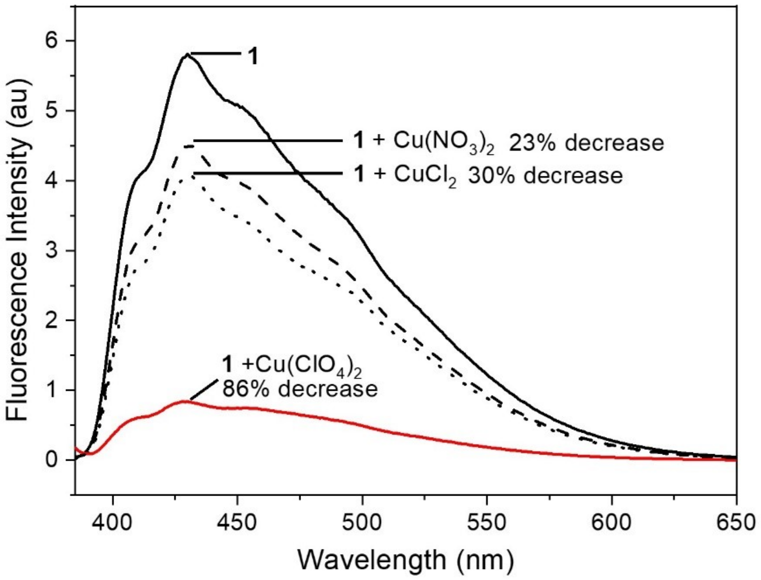


**Fig. S18.** (a) UV-vis and (b) fluorescent spectra ($\lambda_{ex}$ = 375 nm) of ligand **1** (20 μM) in different $Cu^{2+}$ salts (10 equiv) in $CH_3CN/CHCl_3$ (v/v, 1:1) at 298 K, respectively.

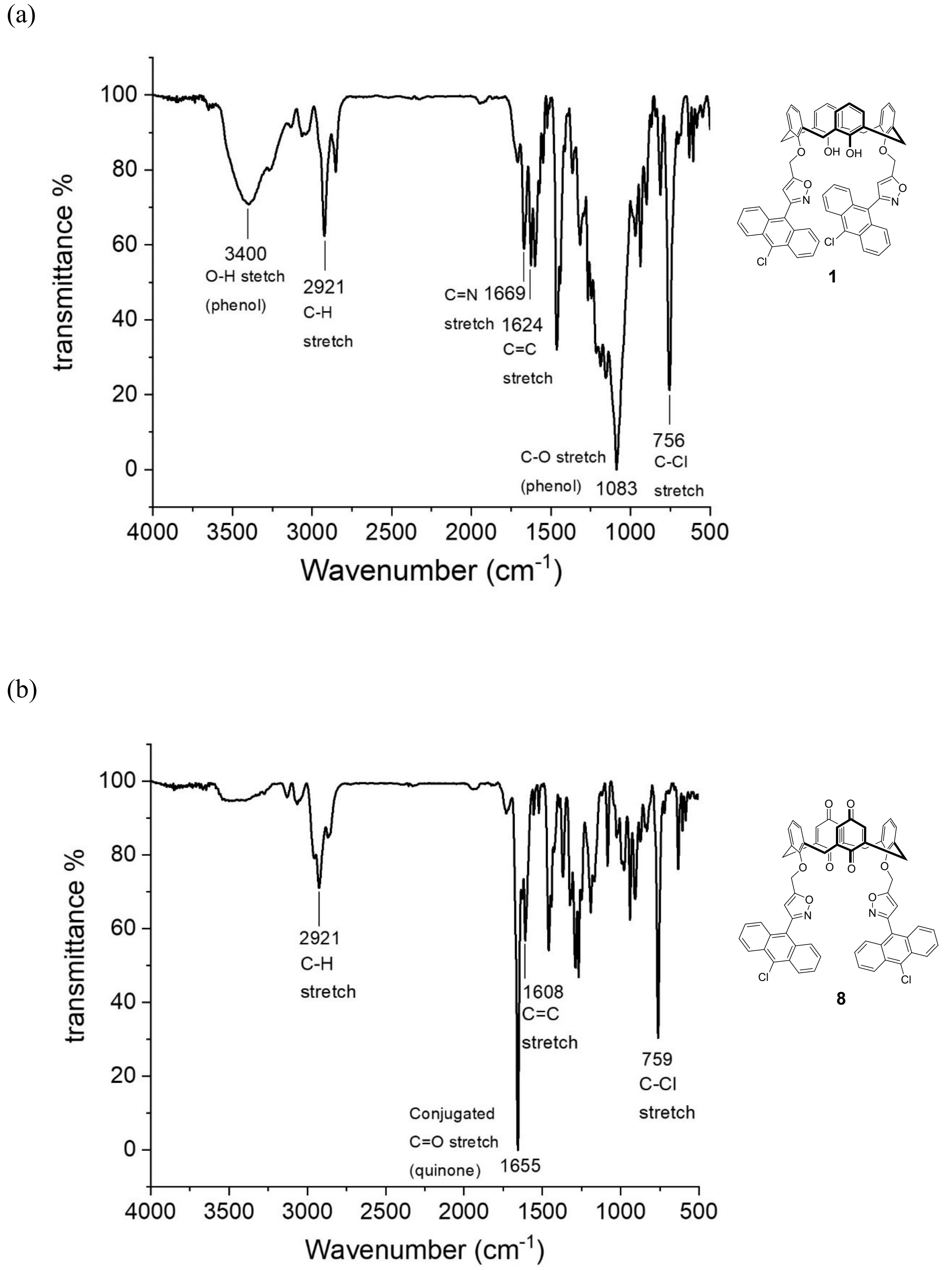


**Fig. S19.** FTIR (KBr) spectra of (a) ligand **1** and (b) compound **8** in the 500–4000 cm$^{-1}$ region.

## Quantum yields ($\Phi_F$)

The relative fluorescent quantum yields ($\Phi_F$) of 9,10-diphenylanthrance (DPA) and ligand **1** in $CH_3CN/CHCl_3$ (v/v, 1:1) at 298 K were determined using 9,10-diphenylanthrance as a standard ($\Phi_F$ of 9,10-diphenylanthrance in cyclohexane = 0.97 was used) based on eqn 1. $\Phi_F = (F/F_o) \times (A_o/A) \times (n/n_o)^2 \times \Phi_F{}^o$ (eqn 1), where $A$ and $A_o$ are the absorbance of the sample and the standard at the excitation wavelength, respectively; $F$ and $F_o$ are the integrated fluorescence emissions of the sample and the standard, respectively; and $n$ and $n_o$ are solvent refractive indexes of the sample and the standard, respectively. The results are summarized in Tables S1 and S2. References for quantum yields ($\Phi_F$): (a) A. M. Brouwer, Standards for photoluminescence quantum yield measurements in solution (IUPAC Technical Report), *Pure Appl. Chem.*, 2011, **83**, 2213–2228; (b) W. R. Dawson and M. W. Windsor, Fluorescence yields of aromatic compounds, *J. Phys. Chem.,* 1968, **72**, 3251–3260; (c) N. J. Turro, Modern molecular photochemistry, Benjamin Cummings, Menlo Park, 1978.

**Table S1.** The data for the quantum yield measurement of 9,10-diphenylanthrance in cyclohexane or $CH_3CN/CHCl_3$ (v/v, 1:1) at 298 K ($\lambda_{ex}$ = 355 nm).

| | $A_{(355\ nm)}$ | F | $F/F_o$ | $A_o/A$ | $n/n_o$ | Quantum yield |
|---|---|---|---|---|---|---|
| DPA[1] | 0.068 | 51260704 | 1.00 | 1.00 | 1.00 | 0.97 |
| DPA | 0.085 | 63411498 | 1.24 | 0.80 | 0.98 | 0.94 |

[1] The data of 9,10-diphenylanthrance (DPA) was measured in cyclohexane.

**Table S2.** The data for the quantum yield measurement of ligand **1** in $CH_3CN/CHCl_3$ (v/v, 1:1) at 298 K using 9,10-diphenylanthrance (DPA) as the standard ($\lambda_{ex}$ = 355 nm).

| | $A_{(355\ nm)}$ | F | $F/F_o$ | $A_o/A$ | $n/n_o$ | Quantum yield |
|---|---|---|---|---|---|---|
| **1** | 0.049 | 4709391 | 0.074 | 1.73 | 1.00 | 0.12 |
| DPA | 0.085 | 63411498 | 1.00 | 1.00 | 1.00 | 0.94 |