Electronic Supplementary Information

A Cu^{2+}-selective colorimetric-fluorometric sensor based on an anthracenyl-modified oxacalix[4]arene

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Table of Contents

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1. General Information for Synthesis, Characterization and Spectroscopy Measurements

All solvents for reactions and column chromatography were used directly as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 MHz and 100 MHz instruments. Chemical shifts were expressed in parts per million (δ: ppm) TMS (δ = 0 ppm) as an internal standard. Coupling constants (*J* values) were given in hertz (Hz). HRMS analysis was performed using a MALDI-TOF or ESI mass spectrometer.

Commercial CHCl$_3$ was first washed with deionized water three times and then dried over anhydrous Na$_2$SO$_4$. Fresh CHCl$_3$ was distilled from P$_2$O$_5$ before spectroscopic measurements. CH$_3$CN for spectroscopy measurement was distilled. UV-vis spectra and the fluorescent emission spectra were recorded on an Olis DSM 172 spectrophotometer. 10 mm × 10 mm cuvettes were used. Usually, data were collected at 1 nm intervals. The slitwidth was fixed at 2.5 mm and the integration time was set as 0.1 s. High resolution mass spectra (HRMS) analysis was performed with a Waters Xevo G2-S Q-TOF mass spectrometer.

The chemicals were used directly as purchased from Energy Chemical Reagents, Aladdin Reagents, J&K Chemical Reagents.

2. Synthetic Details and Characterization Data for New Compounds
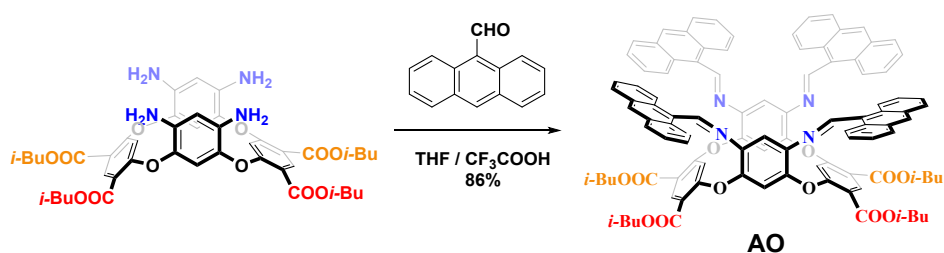
Tetraaminooxacalix[4]arene (0.33 g, 0.4 mmol, 1 equivalent) and 9-anthracaldehyde (0.34 g, 1.6 mmol, 4 equivalents) were dissolved in 20 mL anhydrous THF. Then catalytic amount of CF$_3$COOH was added to the reaction mixture. The reaction mixture was heated to reflux for 3 hours. After evaporation of solvent under reduced pressure, the residue was purified *via* column chromatography (silica gel, CH$_2$Cl$_2$: EtOAc = 30:1 as eluent). The product (0.54 g, 86%) was a yellow solid.

m. p.: 283–284 °C.

^{1}H NMR (400 MHz, CDCl$_3$ (passing through a K$_2$CO$_3$ column before use), TMS, 298 K, ppm): δ 9.42 (s, 4H, Ar-*H*-anthracene), 8.96 (s, 2H, Ar-*H*), 8.25 (d, *J* = 8.3 Hz, 8H, Ar-*H*-anthracene), 7.85 (s, 4H, N=C*H*), 7.45-7.37 (m, 8H, Ar-*H*-anthracene), 7.27 (s, 2H, Ar-*H*), 7.16 (s, 2H, Ar-*H*), 7.00-6.85 (m, 16H, Ar-*H*-anthracene), 6.25 (s, 2H, Ar-*H*), 4.13 (d, *J* = 6.4 Hz, 8H, COOC*H*$_2$), 2.10-1.90 (m, 4H, C*H*), 0.97-0.92 (m, 24H, C*H*$_3$).

^{13}C NMR (75 MHz, CDCl$_3$ (passing through a K$_2$CO$_3$ column before use), TMS, 298 K, ppm): δ 164.5, 163.6, 163.3, 146.9, 143.5, 138.1, 131.4, 130.13, 130.06, 128.5, 126.8, 124.6, 123.9, 123.5, 119.2, 113.2, 112.7, 101.7, 71.3, 27.9, 19.2.

HRMS (ESI$^+$) calcd. for [C$_{104}$H$_{84}$N$_4$O$_{12}$ + H]$^+$ 1581.6159, found: 1581.6210.
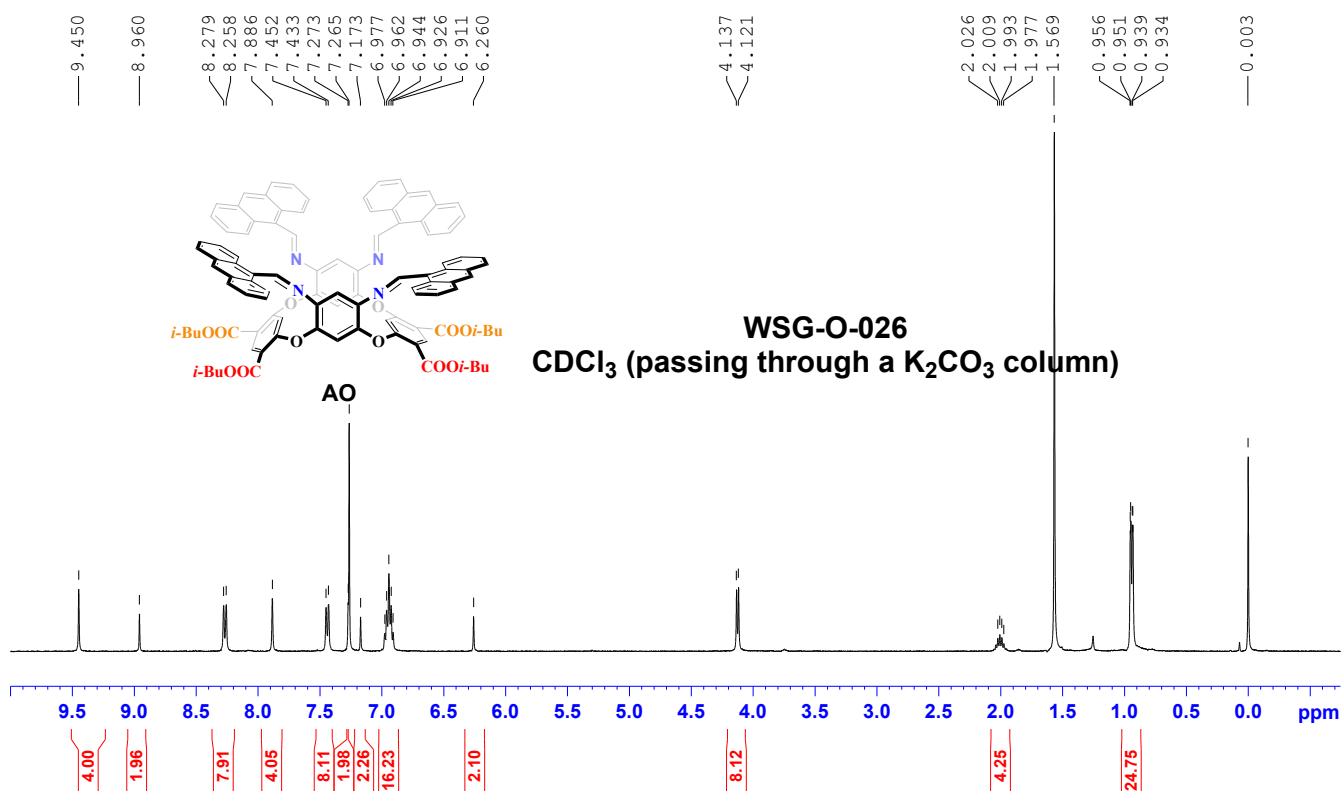
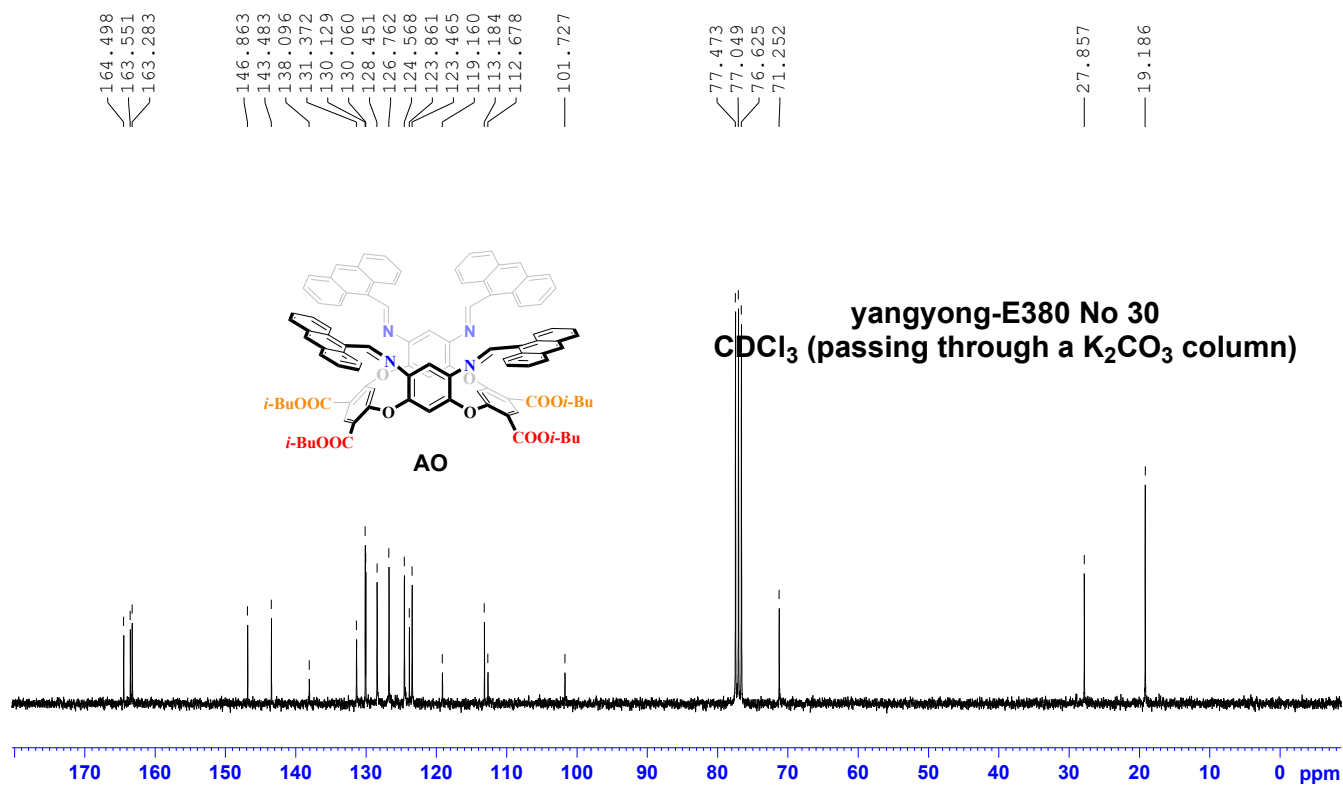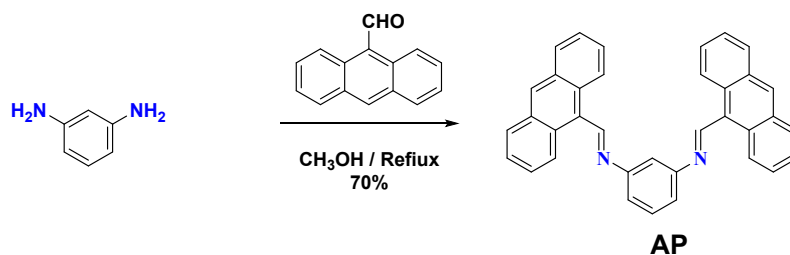Figure S1. ^{1}H NMR spectrum of compound **AO**, CDCl$_3$, 298 K, 400 MHz.

Figure S2. ^{13}C NMR spectrum of compound **AO**, CDCl$_3$, 298 K, 75 MHz.

A mixture of 1, 3-phenylenediamine (0.05 g, 0.5 mmol) and 9-anthraldehyde (0.21 g, 1.0 mmol) in 40 mL anhydrous CH_3OH was heated to reflux for 15 min. The hot solution was filtered. The filtrate was left to cool down to 5 °C. Upon standing for 15 hours, the precipitated yellow solid (0.17 g, 70%) was collected by filtration and washed with CH_3OH.

m. p.: 207–208 °C.

^{1}H NMR (400 MHz, CDCl_3, TMS, 298 K, ppm): δ 9.83 (s, 2H, Ar-*H*-anthracene), 8.83 (d, *J* = 8.7 Hz, 4H, Ar-*H*-anthracene), 8.60 (s, 2H, C*H*=N), 8.08 (d, *J* = 8.2 Hz, 4H, Ar-*H*-anthracene), 7.65-7.50 (m, 10H, Ar-*H*-anthracene and Ar-*H*), 7.41 (dd, *J* = 7.8 Hz, *J* = 2.0 Hz, 2H, Ar-*H*).

^{13}C NMR (100 MHz, CDCl_3, TMS, 298 K, ppm): δ 160.4, 153.8, 131.4, 131.0, 130.8, 130.2, 129.1, 127.4, 127.1, 125.5, 124.8, 119.0, 113.6.
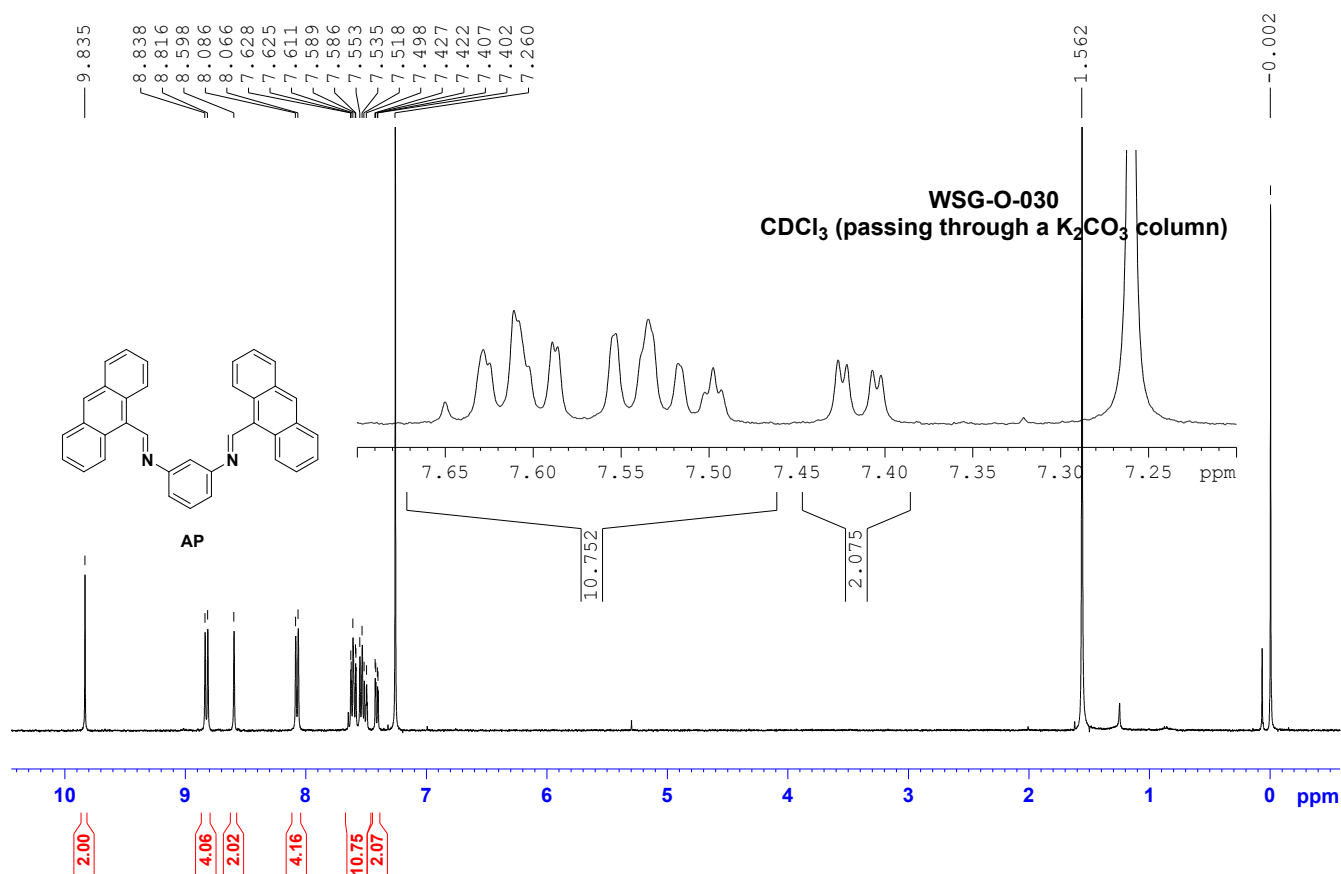

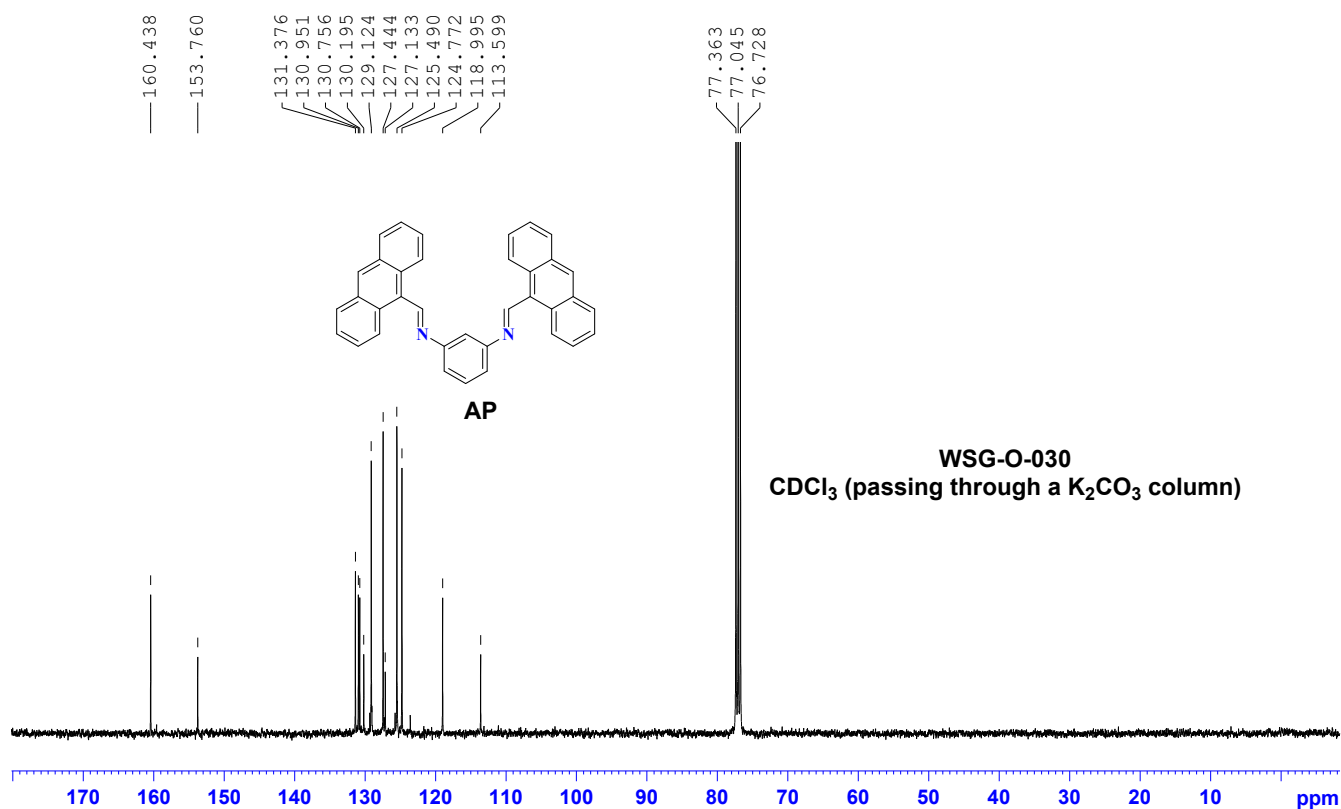Figure S3. ^{1}H NMR spectrum of compound **AP**, CDCl_3, 298 K, 400 MHz.

Figure S4. ^{13}C NMR spectrum of compound **AP**, CDCl$_3$, 298 K, 100 MHz.

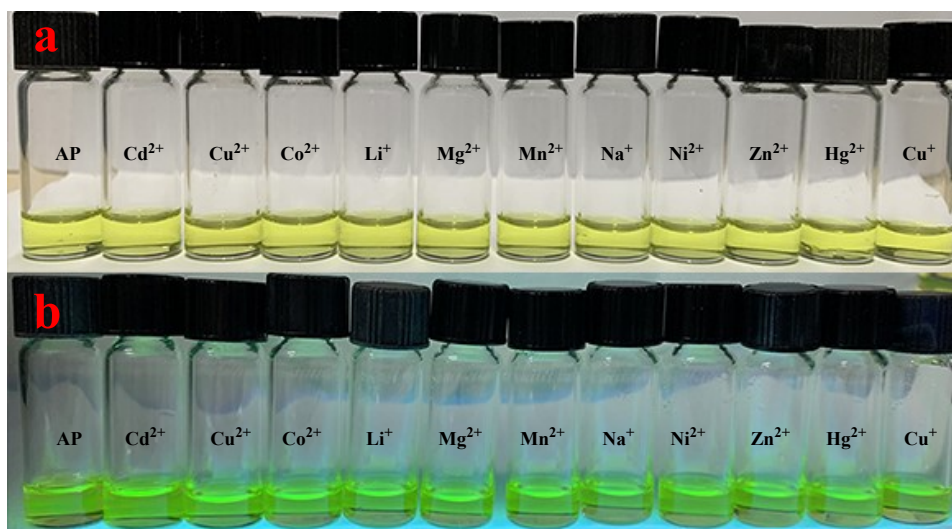## 3. Control Experiments with **AP**

Figure S5. Photographs of **AP** (2×10^{-5} M) upon addition of 2.5 equivalents of various metal ions in CH$_3$CN-CHCl$_3$ solution (1:1, v/v), (a) under natural light, and (b) under UV lamp $\lambda = 365$ nm.
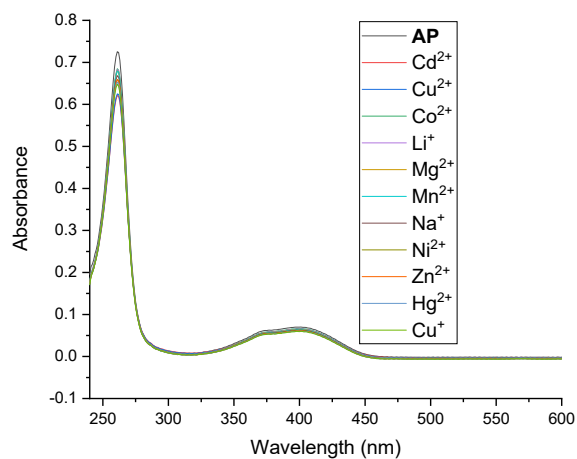
Figure S6. UV-vis absorption spectra of **AP** (2×10^{-5} M) in the absence and presence of Cd^{2+}, Cu^{2+}, Co^{2+}, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Zn^{2+}, Hg^{2+}, Cu^+ (each 2.5 equivalents) in $CH_3CN-CHCl_3$ solution (1:1, v/v).
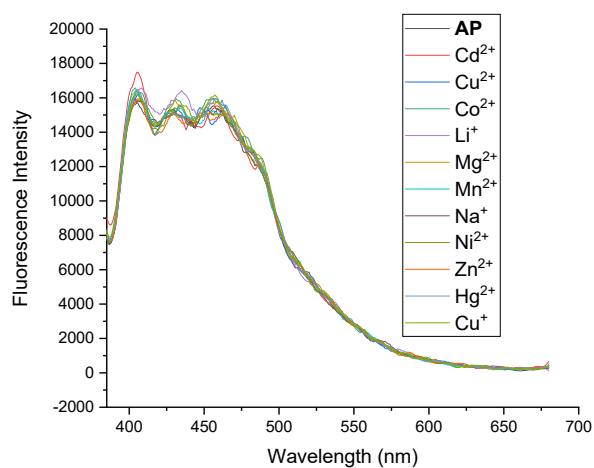
Figure S7. FL emission spectra for AP (2×10^{-5} M) in the absence and presence of Cd^{2+}, Cu^{2+}, Co^{2+}, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Zn^{2+}, Hg^{2+}, Cu^+ (each 2.5 equivalents) in $CH_3CN-CHCl_3$ solution (1:1, v/v), λ_{ex} = 365 nm.
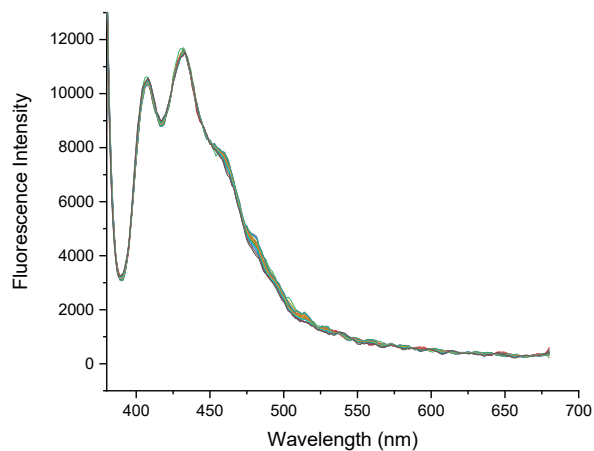
4. Determination of the Limit of Detection

Figure S8. Twenty scans of fluorescence emission spectra of **AO** (2×10^{-5} M) in CH$_3$CN−CHCl$_3$ solution (1:1, v/v) , λ_{ex} = 365 nm. The standard deviation of the FL intnesity data at λ = 490 nm was 112.9. The limit of detection (LOD) was calculated based on the following equation.

$$\text{Limit of Detection (LOD)} = \frac{3\sigma}{K} = 3 \times \frac{112.9}{2.5 \times 10^9 \text{ M}^{-1}} = 1.4 \times 10^{-7} \text{ M} \qquad \text{(Eq. S1)}$$

σ: the standard deviation for FL intensity of AO solution at λ = 490 nm

K: the slope of the plot of changes in FL intensity at λ = 490 nm vs [Cu^{2+}]

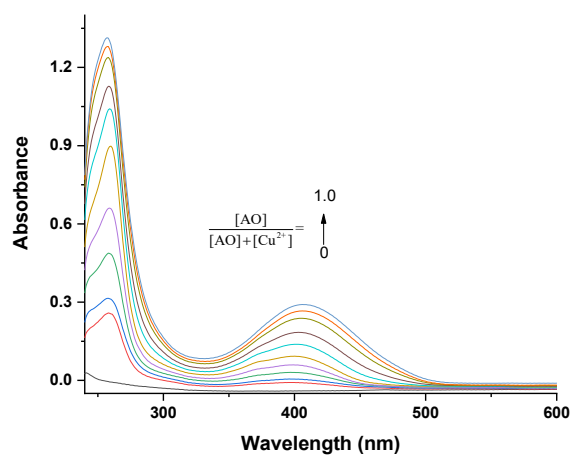# 5. Job Plots for Complex AO-Cu^{2+} using UV-vis and FL Measurements

Figure S9. UV-vis spectra of mixtures of **AO** and Cu^{2+} with different ratios in CH$_3$CN−CHCl$_3$ solution (1:1, v/v). The total concentration was fixed at 2×10^{-5} M.
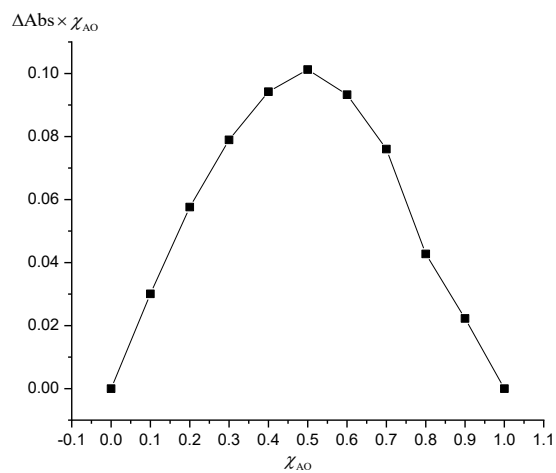

Figure S10. Job plot for the complex between **AO** and Cu^{2+} in CH$_3$CN−CHCl$_3$ solution (1:1, v/v), using UV-vis absorption values at $\lambda =$ 408 nm, showing a 1:1 stoichiometry.
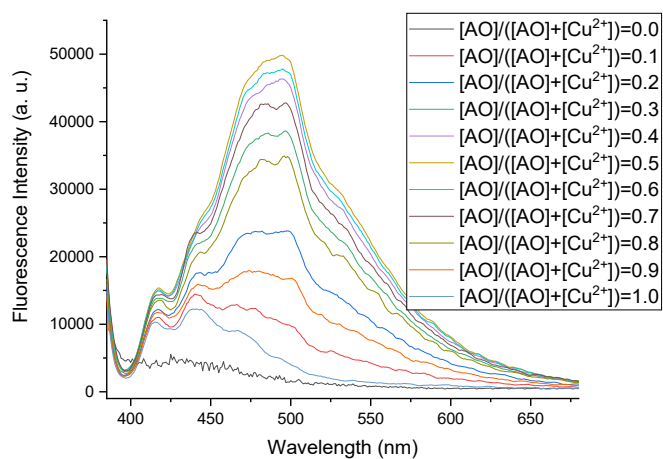
Figure S11. Fluorescence spectrum of mixtures of **AO** and Cu^{2+} with different ratios in $CH_3CN-CHCl_3$ solution (1:1, v/v). The total concentration was fixed at 2×10^{-5} M, $\lambda_{ex} = 365$ nm.
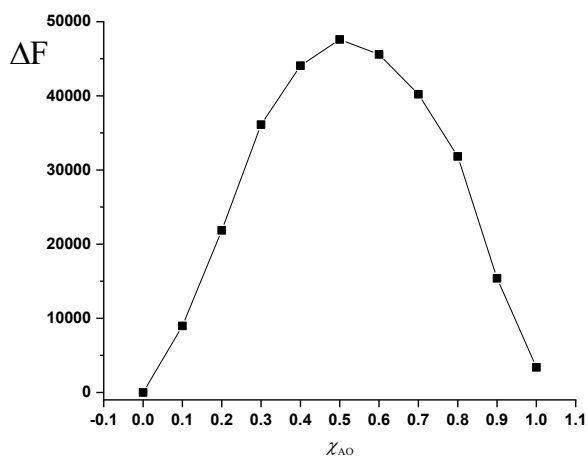

Figure S12. Job plot for the complex between **AO** and Cu^{2+} in $CH_3CN-CHCl_3$ solution (1:1, v/v), using fluorescence intensity values at $\lambda = 490$ nm, showing a 1:1 stoichiometry.

6. The Nonlinear Fitting Equation for the 1:1 Binding Mode Using FL Titration Data

The nonlinear fitting equation for determination of association constant (K_a) of **AO**-Cu^{2+} complex was based on the following 1:1 bind mode. The FL intensities at $\lambda = 490$ nm was used for fitting. [S1]
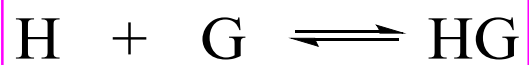
$$H \; + \; G \; \rightleftharpoons \; HG$$

$$K_a = \frac{[HG]}{[H][G]}$$

$$[H] = [H]_0 - [HG]$$

$$[G] = [G]_0 - [HG]$$

$$[HG] = \frac{[G]_0 + [H]_0 + \dfrac{1}{K_a} - \sqrt{([G]_0 + [H]_0 + \dfrac{1}{K_a})^2 - 4[G]_0[H]_0}}{2}$$

$$F = k_H[H] + k_{HG}[HG]$$
$$= k_H([H]_0 - [HG]) + k_{HG}[HG]$$
$$= k_H[H]_0 + (k_{HG} - k_H)[HG] \qquad F_0 = k_H[H]_0$$

$$F - F_0 = (k_{HG} - k_H)[HG]$$

$$\Delta F = F - F_0 \qquad C = k_{HG} - k_H$$

$$\Delta F = C \frac{[G]_0 + [H]_0 + \dfrac{1}{K_a} - \sqrt{([G]_0 + [H]_0 + \dfrac{1}{K_a})^2 - 4[G]_0[H]_0}}{2}$$

$[H]_0$: the initial concentration of Host

$[H]$: the concentration of free Host

$[G]_0$: the initial concentration of Guest

$[G]$: the concentration of free Guest

$[HG]$: the concentration of Host-Guest complex

K_a: association constant

k_H: coefficient

k_{HG}: coefficient

F_0: the initial FL intensity of Host

F : FL intensity for each titration

ΔF: changes of the FL intensity

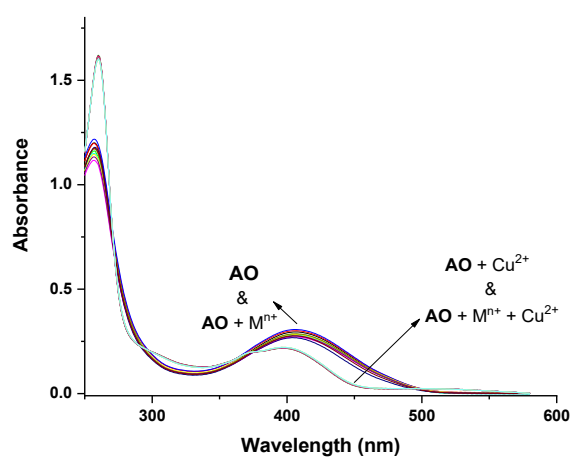C : constant

7. Interference Studies

Figure S13. UV–vis spectra of **AO** (2×10^{-5} M) with various metal ions M^{n+}: Cd^{2+}, Co^{2+}, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Zn^{2+}, Hg^{2+}, Cu^+ (25 equivalents) in the absence and presence of Cu^{2+} (2.5 equivalents) in $CH_3CN-CHCl_3$ solution (1:1, v/v).
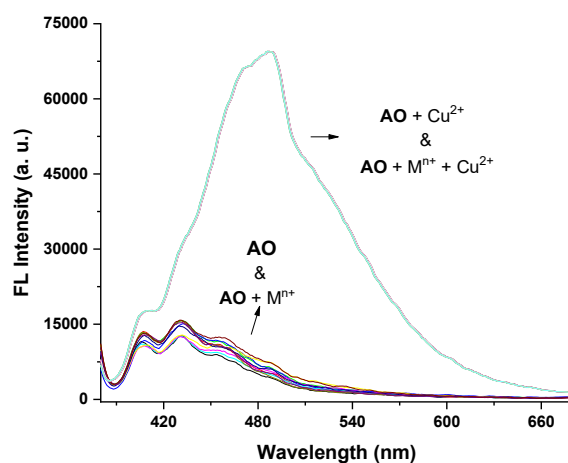
Figure S14. FL emission spectra of **AO** (2×10^{-5} M) with various metal ions M^{n+}: Cd^{2+}, Co^{2+}, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Zn^{2+}, Hg^{2+}, Cu^+ (25 equivalents) in the absence and presence of Cu^{2+} (2.5 equivalents) in $CH_3CN-CHCl_3$ solution (1:1, v/v), $\lambda_{ex} = 365$ nm.

8. Protocol to analyze Cu^{2+} in aqueous samples

Bulk solution of the sensor **AO** (1×10^{-3} M) was prepared by dissolving **AO** (4.7 mg, 3.0 μmol) in 3 mL CH_3CN-$CHCl_3$ solution (1:1, v/v). Bulk solution of $Cu(ClO_4)_2$ (1×10^{-3} M) was obtained by dissolving solid (1.1 mg, 3.0 μmol) in 3 mL water. In the following six parallel experiments, 60 μL of **AO** solution and different volume (3 μL, 9 μL, 21 μL, 36 μL, 45 μL, 60 μL) of the above $Cu(ClO_4)_2$ solution were mixed in 3 mL CH_3CN-$CHCl_3$ solution (1:1, v/v) and 3 mL water. Then the solutions were heated to reflux in sealed tubes for 24 h. Solvent was removed in vacuo and the solids were dried at 100 °C for 24 hours to remove all solvent. Each sample was prepared by dissolving the above dried solid in 3 mL CH_3CN-$CHCl_3$ solution (1:1, v/v) and the fluorescence spectra were recorded (see below).
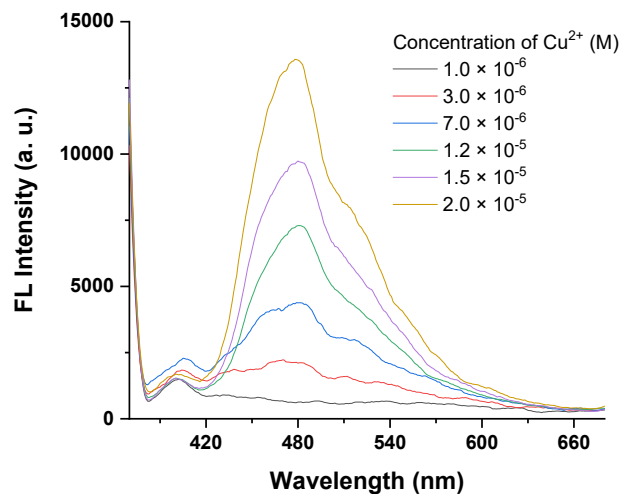

Figure S15. Fluorescence spectra of sensor **AO** (2×10^{-5} M) and with varied concentration of Cu^{2+} from aqueous sample mixed in CH_3CN-$CHCl_3$ solution (1:1, v/v) , $\lambda_{ex} = 365$ nm.

$$F = K[Cu^{2+}] + C$$
$$K = 575 \text{ M}^{-1}$$
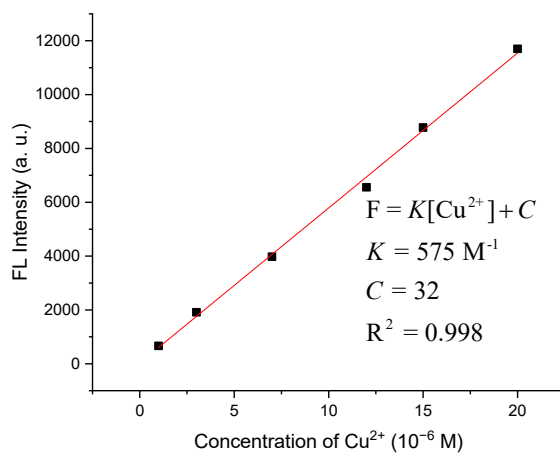$$C = 32$$
$$R^2 = 0.998$$

Figure S16. Linear fitting result of the fluorescence intensity data at $\lambda = 490$ nm *vs* concentration of Cu^{2+}, demonstrating a linear response.

9. Reference

S1 P. Thordarson, Determining association constants from titration experiments in supramolecular chemistry, *Chem. Soc. Rev.*, 2011, **40**, 1305-1323.