Supporting Information

Triazole-Modified Calix[4]crown as a Novel Fluorescent On-Off Switchable Chemosensor

Kai-Chi Chang, In-Hao Su, Annamalai Senthilvelan and Wen-Sheng Chung*

Department of Applied Chemistry, National Chiao-TungUniversity, Hsinchu, 30050, Taiwan-ROC

Table of contents

S14. Changes in fluorescence emission spectra of **1** (10 μM) upon titration with $Cr(ClO_4)_3$ in MeCN/$CHCl_3$ (v/v = 1000:4) (Figure S15) & Job plot of a 1:1 complex of **1** and Cr^{3+}. (Figure S16)

S15. Changes in fluorescence emission spectra of **2** (10 μM) upon titration with $Cu(ClO_4)_2$ in MeCN. (Figure S17) & Job plot of a 1:1 complex of **2** and Cu^{2+}. (Figure S18)

S16. Changes in fluorescence emission spectra of **2** (10 μM) upon titration with $Hg(ClO_4)_2$ in MeCN. (Figure S19) & Job plot of a 1:1 complex of **2** and Hg^{2+}. (Figure S20)

S17. Changes in fluorescence emission spectra of **2** (10 μM) upon titration with $Cr(ClO_4)_3$ in MeCN. (Figure S21) & Job plot of a 1:1 complex of **2** and Cr^{3+}. (Figure S22)

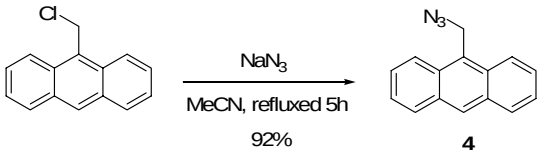
S18. Fluorescence emission changes of **1**•Hg^{2+}, **1**•Cu^{2+} and **1**•Cr^{3+} complexes in MeCN/$CHCl_3$ (v/v = 1000:4) upon addition of K^+ (Figure S23). & Fluorescence emission changes of **1**•Pb^{2+} complex in MeCN/$CHCl_3$ (v/v = 1000:4) upon addition of Ba^{2+} (Figure S24).

S19. Fluorescence emission changes of **1**•Pb^{2+} complex in MeCN/$CHCl_3$ (v/v = 1000:4) upon addition of Zn^{2+} (Figure S25). & Fluorescence emission changes for the **1** (10 μM) with 10 equiv of $Pb(ClO_4)_2$ in MeCN/$CHCl_3$ (v/v = 1000:4) upon addition of various amount of K^+ ion (Figure S26).

S20. Fluorescence emission changes for the **1** (10 μM) with 10 equiv of $K(ClO_4)$ in MeCN/$CHCl_3$ (v/v = 1000:4) upon addition of various amount of Pb^{2+} ion (Figure S27).

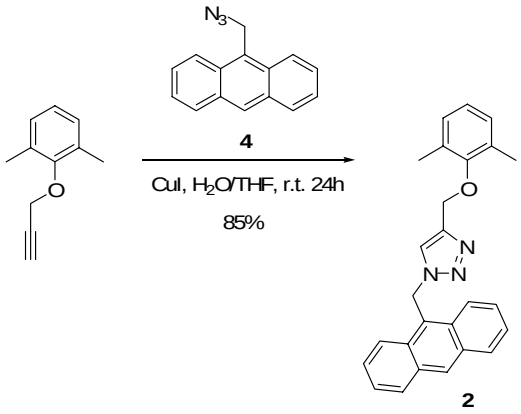
General Information. All melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on 300 MHz and 500 MHz instruments. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, bs = broad singlet, m = multiplet), coupling constant (Hz), integration, and interpretation. Mass spectra were obtained on a Micromass-Trio 2000 GCMS instrument. High resolution mass spectra were recorded on JMS-700 High performance mass spectrometer. Column chromatography was performed with SiO_2 (Merck Silica Gel 60 (230-400 mesh)). UV-vis spectra were recorded by using HP-8453 spectrophotometer with a diode array detector, and the resolution was set at 1 nm. Fluorescence spectra were recorded on an Aminco Bowman Series-2 Luminescence spectrophotometer.

Synthesis of 9-(azidomethyl)-anthracene 4:



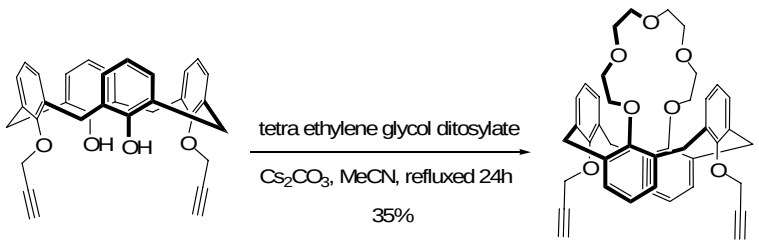
A mixture of 9-(chloromethyl)anthracene (1.00 g, 4.41 mmol) and sodium azide (0.43 g, 6.62 mmol) in 30 mL of MeCN was refluxed for 5 h. After completion of the reaction, the solvent was removed under reduced pressure and the resulting solid was recystallized from CH_2Cl_2/methanol mixture to give **4.** Yield= 0.95g, (92%)**;** yellow solid.; mp 80-82 ^{o}C; R_f = 0.7 (hexane/EtOAc = 3/1); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.52 (s, 1H), 8.30 (d, J = 8.8 Hz, 2H), 8.06 (d, J = 8.3 Hz, 2H), 7.70-7.43 (m, 4H), 5.35 (s, 2H)); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 131.3 (Cq), 130.6 (Cq), 129.2 (CH), 128.9 (CH), 126.8 (CH), 125.7 (CH), 125.1 (CH), 123.4 (CH), 46.2 (CH_2); FABMS m/z 233 (M^+, 46), 234 (M^+ + 1, 13), 204 (35), 191 (100); HR FABMS Calcd for $C_{15}H_{11}N_3$ 233.0953; Found 233.0947.

Synthesis of 4-((2,6-dimethylphenoxy)methyl)-1-[(anthracen-10-yl)methyl]-1*H*-1,2,3-triazole 2:



A heterogeneous mixture of 1,3-dimethyl-2-(prop-2-ynyloxy)benzene (0.35 g, 2.19 mmol), 9-(azidomethyl)anthracene (0.77 g, 3.29 mmol) and CuI (about 5 mg) in THF and water (v/v = 2:1, 30.0 mL) was stirred vigorously at room temperature for 24h. The mixture was extracted thrice with chloroform. The chloroform layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue obtained was purified over silica gel column eluting with hexane/ethyl acetate (v/v = 8/1) to give **2.** Yield= 0.73g (85%); light-yellow solid; mp 192-194 ^oC; R_f = 0.23 (hexane/EtOAc = 5/1); ^1H NMR ($CDCl_3$, 300 MHz) δ 8.60 (s, 1H), 8.33 (d, J = 8.5 Hz, 2H), 8.10 (d, J = 8.5 Hz, 2H), 7.68-7.45 (m, 4H), 7.15 (s, 1H), 6.93-6.75 (m, 3H), 6.57 (s, 2H), 4.80 (s, 2H), 2.10 (s, 6H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 155.1 (Cq), 131.4 (Cq), 130.9 (Cq), 130.8 (Cq), 129.9 (CH), 129.5 (CH), 128.7 (CH), 127.7 (CH), 125.4 (CH), 124.1 (CH), 123.6 (Cq), 123.0 (CH), 122.1 (CH), 65.4 (CH_2), 46.5 (CH_2), 16.2 (CH_3); EIMS m/z 393 (M^+, 4), 244 (19), 191 (35), 57 (100); HR EIMS Calcd for $C_{26}H_{23}N_3O$ 393.1841; Found 393.1828.

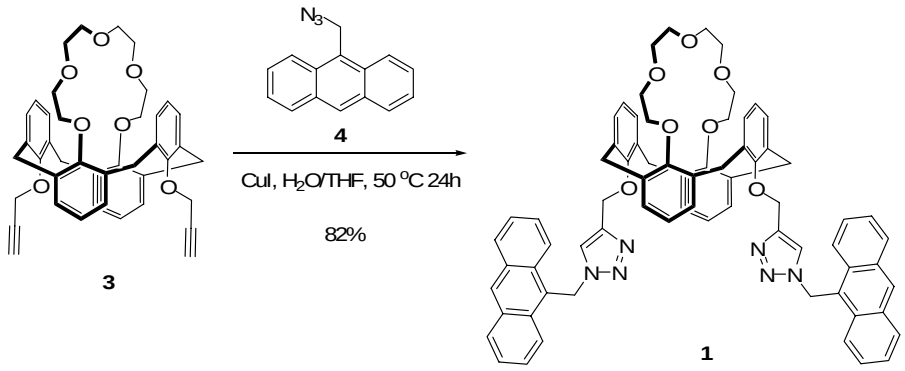
Synthesis of 25, 27-bis-(*O*-propargyloxy)calix[4]crown in the 1, 3-alternate conformation 3:



3

A mixture of 25, 27-dipropargyloxy-26, 28-dihydroxycalix[4]arene (0.50 g, 1.00 mmol), Cs_2CO_3 (1.63 g, 5.02 mmol) and tetra ethylene glycol ditosylate (0.80 g, 1.47 mmol) in 100 mL of MeCN was refluxed for 24 h. The solvent was removed under reduced pressure, to the resulting white solid 5% aqueous HCl (100 mL) and CH_2Cl_2 (50 mL) were added. The organic layer was separated, washed three times with water (50 mL), dried over $MgSO_4$ and concentrated to give white solid. It was purified by chromatography on silica gel column eluting with hexane/ethyl acetate (v/v = 1/1) gave **3.** Yield= 0.23g (35 %); white solid; mp 123-125 ^oC; R_f = 0.5 (hexane/EtOAc = 3/2); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.17-7.11 (m, 8H), 6.94-6.88 (m, 4H), 3.99 (d, *J* = 15.8 Hz, 4H), 3.82 (d, *J* = 15.8 Hz, 4H), 3.81 (d, *J* = 2.4 Hz, 4H), 3.57 (s, 8H), 3.38-3.36 (m, 4H), 3.28-3.26 (m, 4H), 2.32 (t, *J* = 2.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 156.0 (Cq), 155.4 (Cq), 134.9 (Cq), 134.3 (Cq), 130.1 (CH), 129.8 (CH), 123.2 (CH), 123.2 (CH), 80.6 (Cq), 74.3 (Cq), 72.3 (CH_2), 70.5 (CH_2), 70.1 (CH2), 69.1 (CH2), 58.1 (CH2), 38.1 (CH_2); FABMS m/z 659 (M^+ + 1, 5), 658 (M^+, 15), 619 (40), 144 (100); HR FABMS Calcd for $C_{42}H_{42}O_7$ 658.2931; Found 658.2938.

Synthesis of 25, 27-bis-[1-((anthracen-10-yl)methyl)]-1*H*-1,2,3-triazole calix[4]crown in the 1, 3-alternate conformation 1:



A mixture of **3** (0.20 g, 0.30mmol), 9-(azidomethyl)anthracene (0.28 g, 1.20 mmol) and CuI (about 5 mg) in THF and water (v/v = 2:1, 30.0 mL) was stirred vigorously at 50 ^{o}C for 24h. The mixture was extracted thrice with chloroform. The chloroform layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue obtained was purified over silica gel column eluting with hexane/ethyl acetate (v/v = 1/1) gave **1.** Yield= 0.28g (82%); light-yellow solid; mp 245-247 ^{o}C; R_f = 0.5 (MeOH/$CHCl_3$ = 1/3); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.53 (s, 2H), 8.29 (d, J = 8.6 Hz, 4H), 8.01 (d, J = 8.6 Hz, 4H), 7.69-7.58 (m, 4H), 7.52-7.47 (m, 4H), 6.71 (d, J = 7.4 Hz, 4H), 6.56 (t, J = 7.4 Hz, 2H), 6.42 (s, 4H), 6.40 (d, J = 7.8 Hz, 4H), 6.24 (s, 2H), 5.67 (t, J = 7.8 Hz, 2H), 4.25 (s, 4H), 3.50-3.38 (m, 8H), 3.40 (d, J = 15.6 Hz, 4H), 3.25 (d, J = 15.6 Hz, 4H), 3.18-3.09 (m, 4H), 3.07-3.02 (m, 4H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 155.3 (Cq), 155.1 (Cq), 144.1 (Cq), 134.5 (Cq), 133.6 (Cq), 131.3 (Cq), 130.7 (Cq), 129.7 (CH), 129.6 (CH), 129.4 (CH), 129.2 (CH), 127.4 (CH), 125.3 (CH), 123.9 (Cq), 123.1 (CH), 122.6 (CH), 122.5 (CH), 121.5 (CH), 71.9 (CH_2), 70.1 (CH_2), 70.1 (CH_2), 69.1 (CH_2), 63.3 (CH_2), 46.2 (CH_2), 37.4 (CH_2); FABMS m/z 1127 (M^+ + 2, 1), 647 (3); HR FABMS Calcd for $C_{72}H_{64}N_6O_7$ 1124.4836; Found 1124.4862.

Figure S1. ^{1}H NMR Spectrum of **4**.

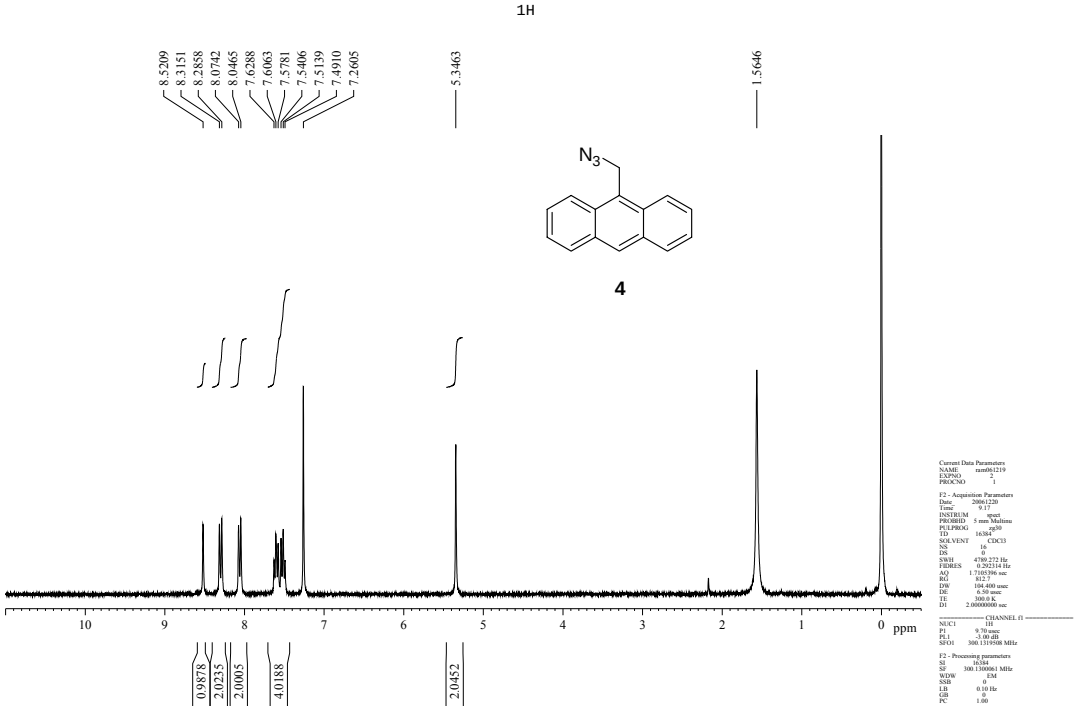


Figure S2. ^{13}C NMR Spectrum of **4**.

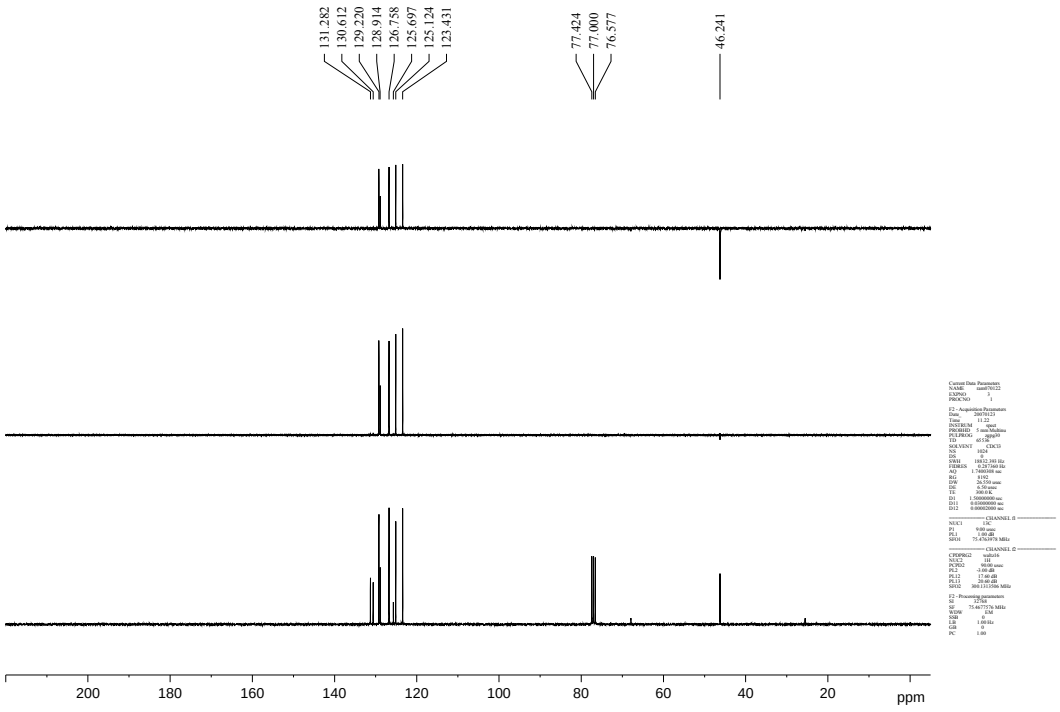


Figure S3. ^{1}H NMR Spectrum of **2**.

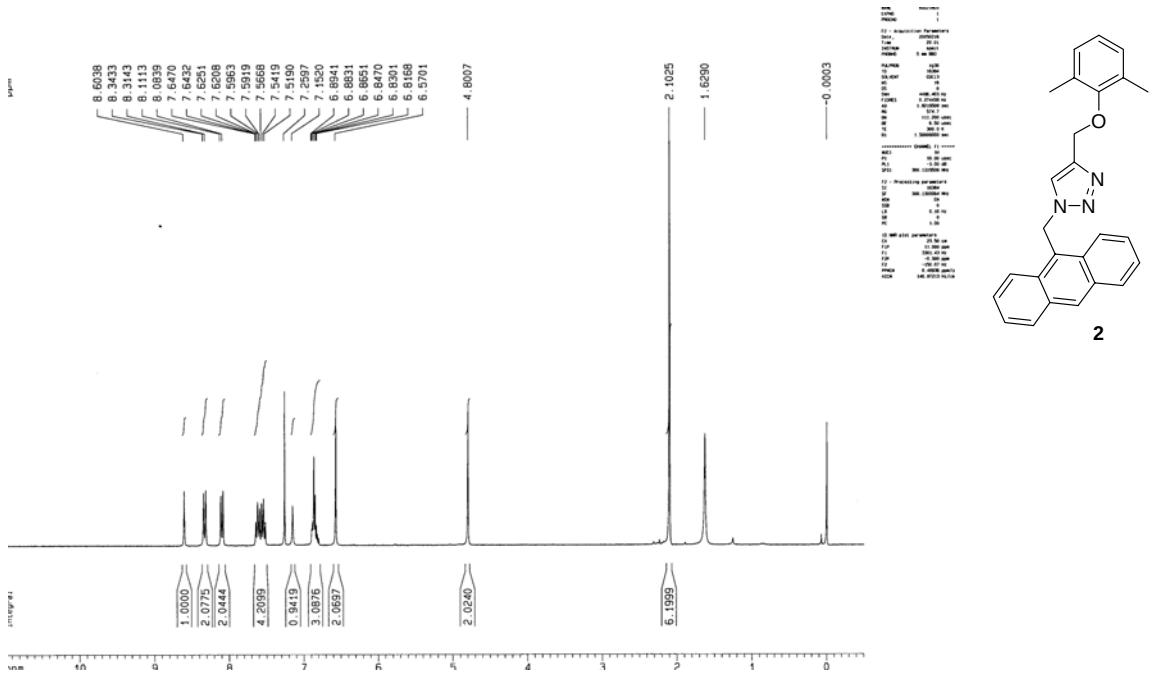


Figure S4. ^{1}H NMR Spectrum of **2**.

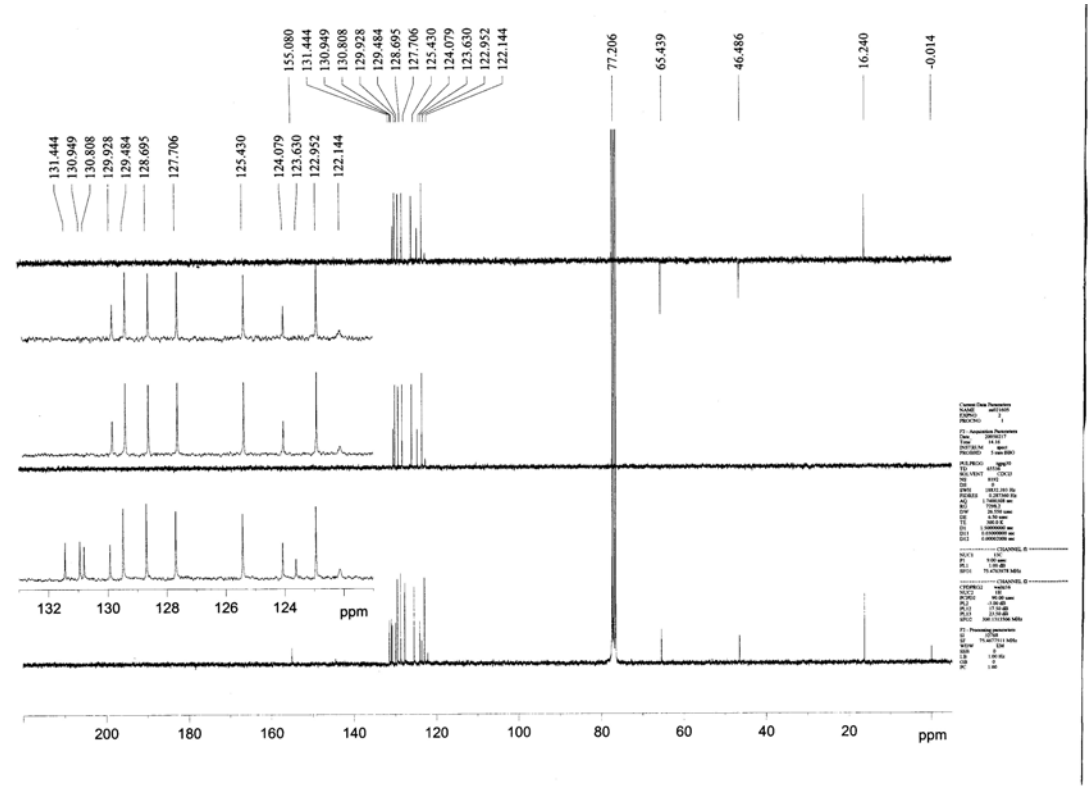


Figure S5. ^{1}H NMR Spectrum of **3**.

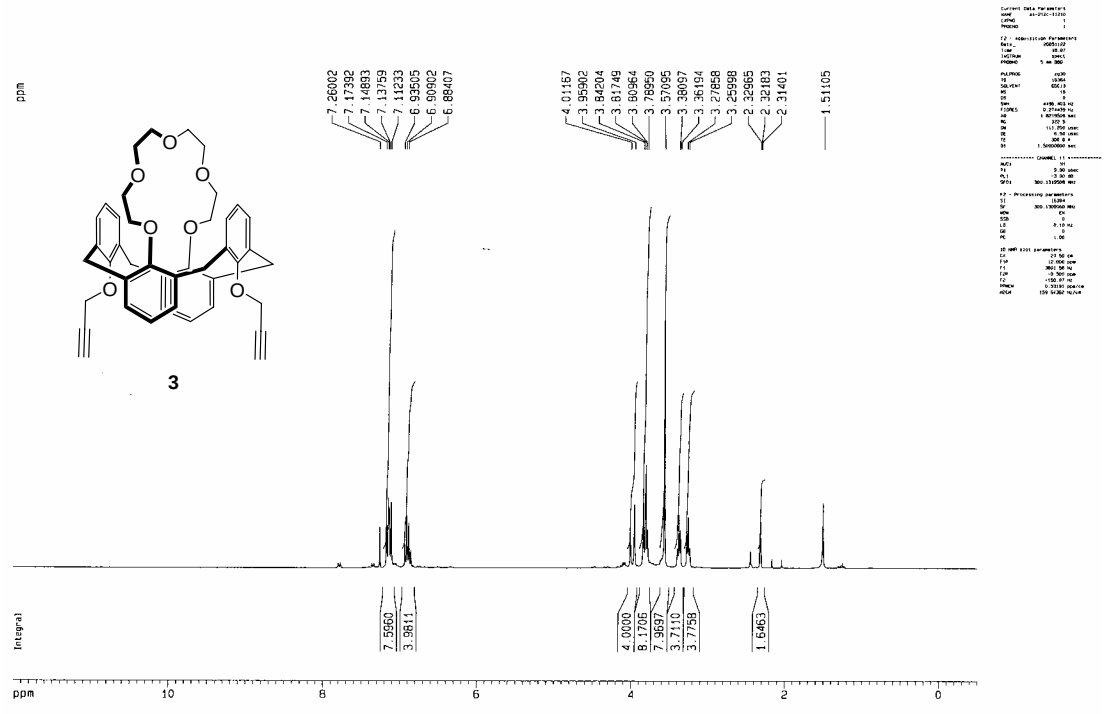


Figure S6. ^{13}C NMR Spectrum of **3**.

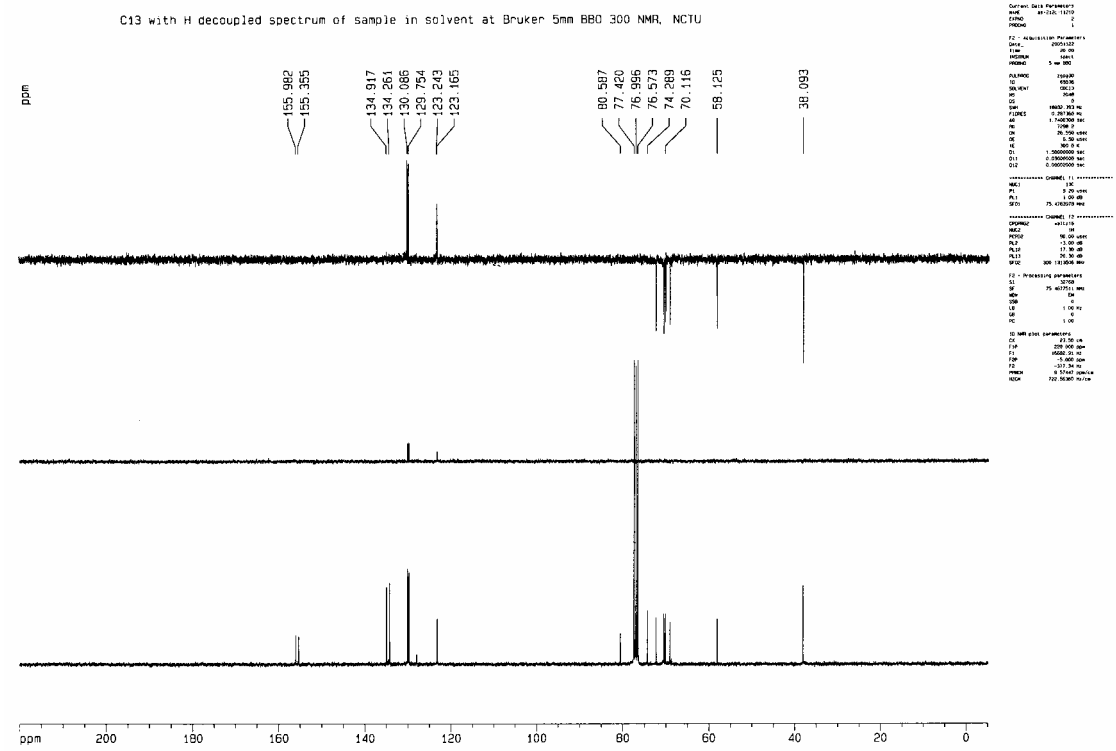


Figure S7. ^{1}H NMR Spectrum of **1**.

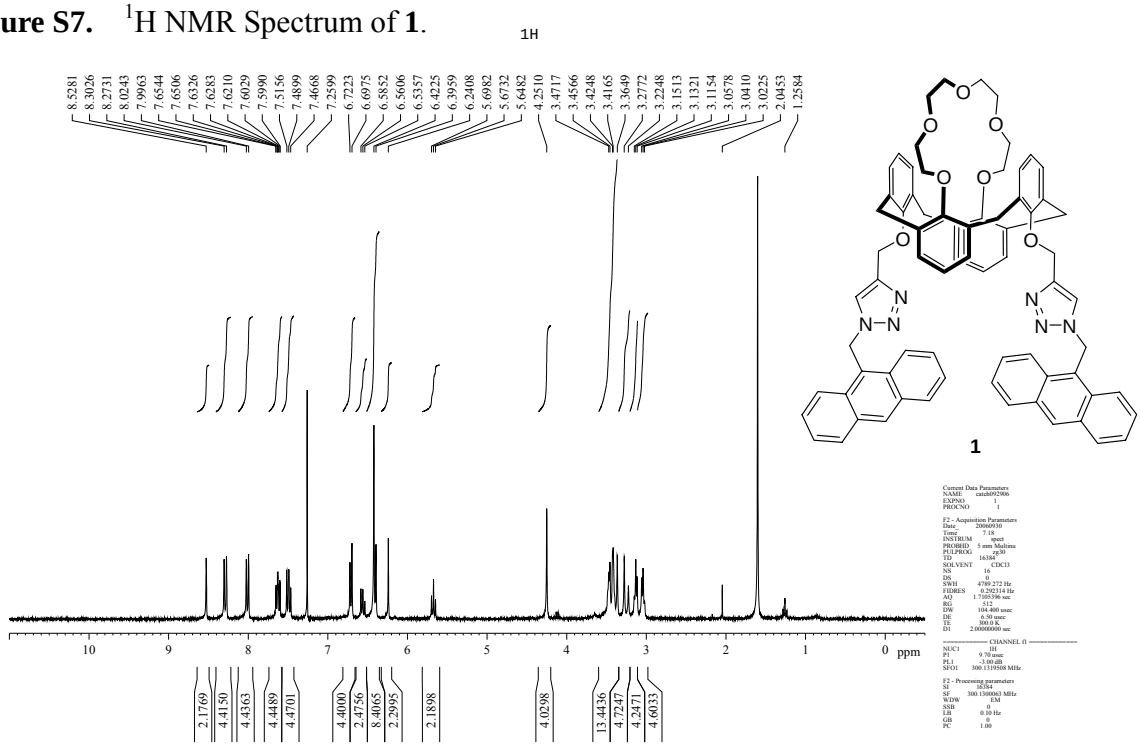


Figure S8. ^{13}C NMR Spectrum of **1**.

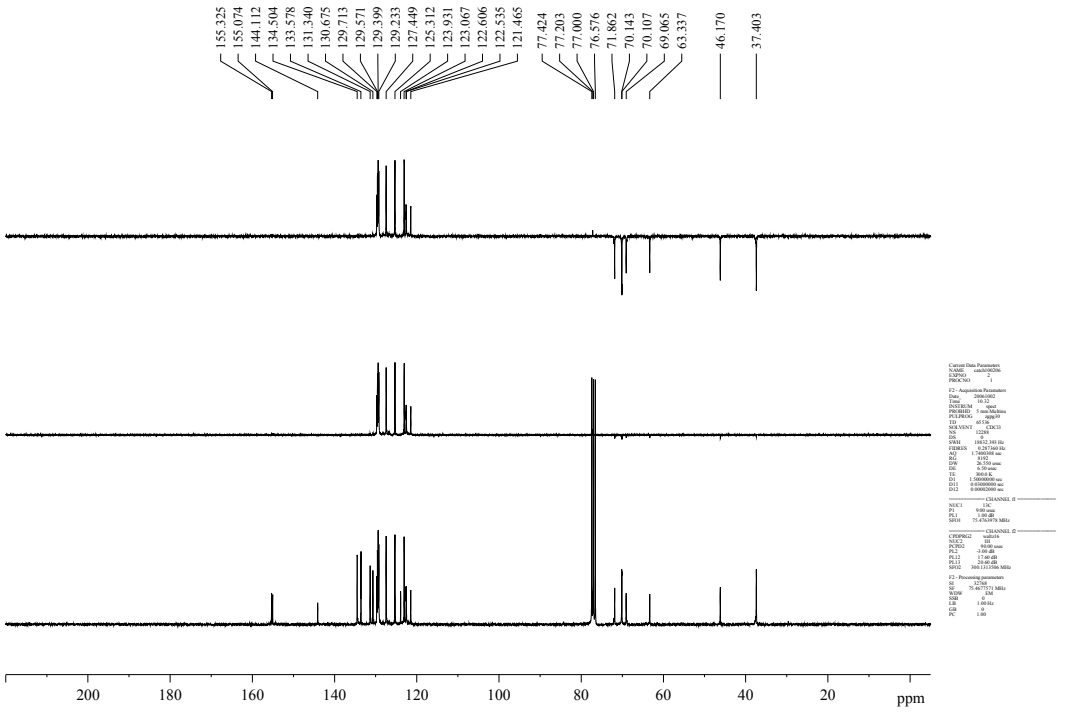


Figure S9. Fluorescence emission spectra of **1** (solid line) and **2** (dash line) (10 μM) in MeCN/$CHCl_3$ (v/v = 1000:4).

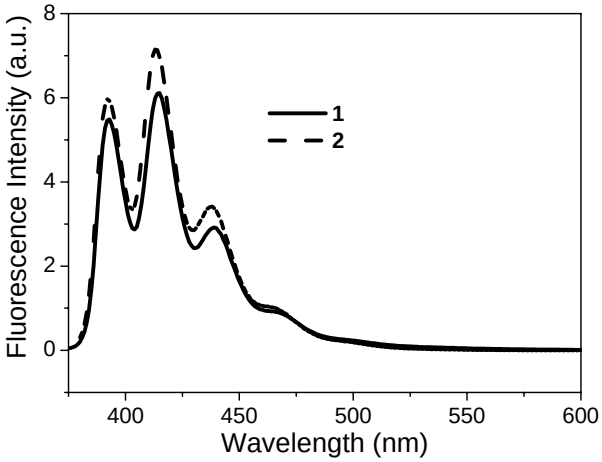


Figure S10. ^{1}H NMR spectra of **2** (2.5 mM) in $CDCl_3/CD_3CN$ (3:1) solution in the presence of various metal perchlorates (1.0 equiv): (a) **2**, (b) **2** + Hg^{2+}, (c) **2** + Cr^{3+}, (d) **2** + Cu^{2+}, where * denotes NMR solvent peaks.

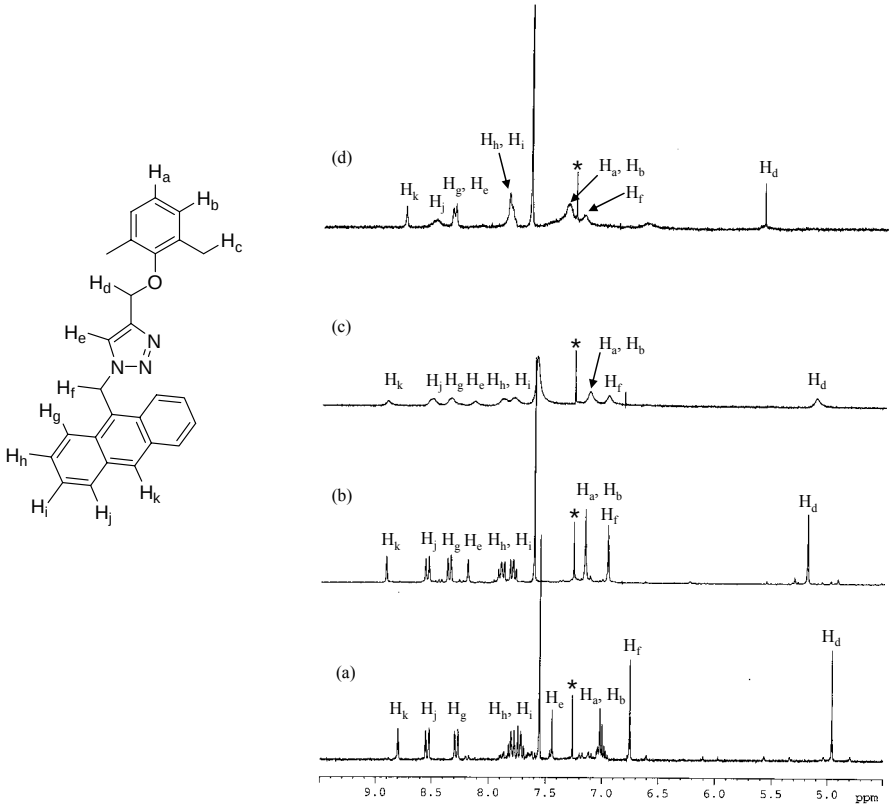


Figure S11. Changes in fluorescence emission spectra of **1** (10 μM) upon titration with $Cu(ClO_4)_2$ in $MeCN/CHCl_3$ (v/v = 1000:4). (The excitation wavelength was 367 nm.)

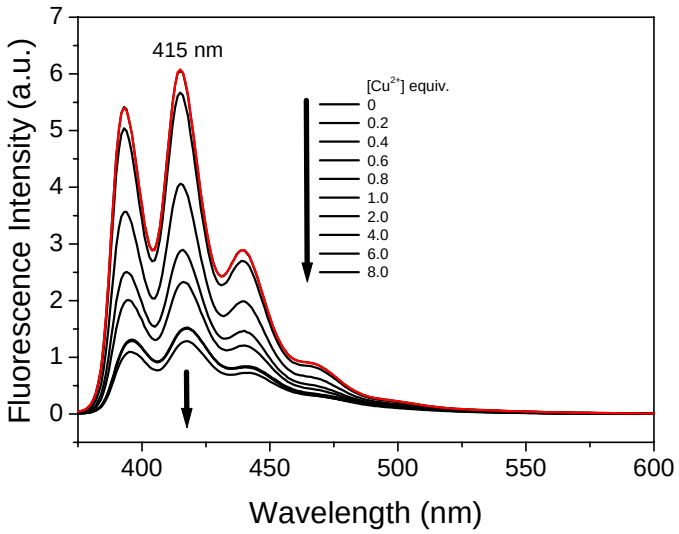


Figure S12. Job plot of a 1:1 complex of **1** and Cu^{2+}, where the difference in fluorescence intensity at 415 nm was plotted against the mole fraction of **1** at an invariant total concentration of 10 μM in $MeCN/CHCl_3$ (v/v = 1000:4).

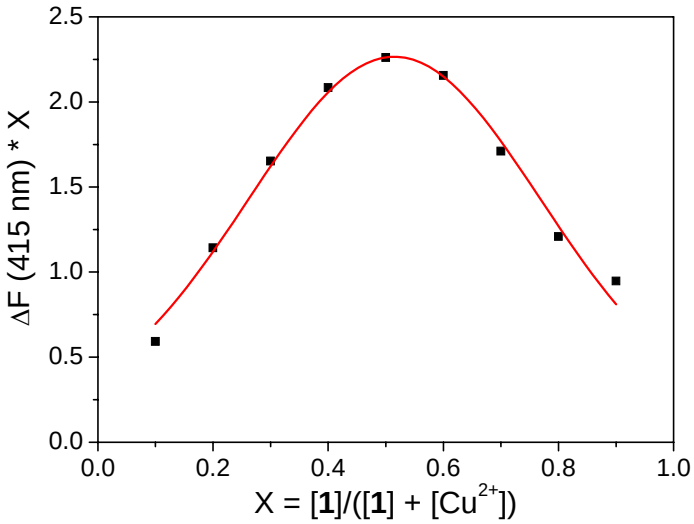


Figure S13. Changes in fluorescence emission spectra of **1** (10 μM) upon titration with $Hg(ClO_4)_2$ in MeCN/$CHCl_3$ (v/v = 1000:4). (The excitation wavelength was 367 nm.)

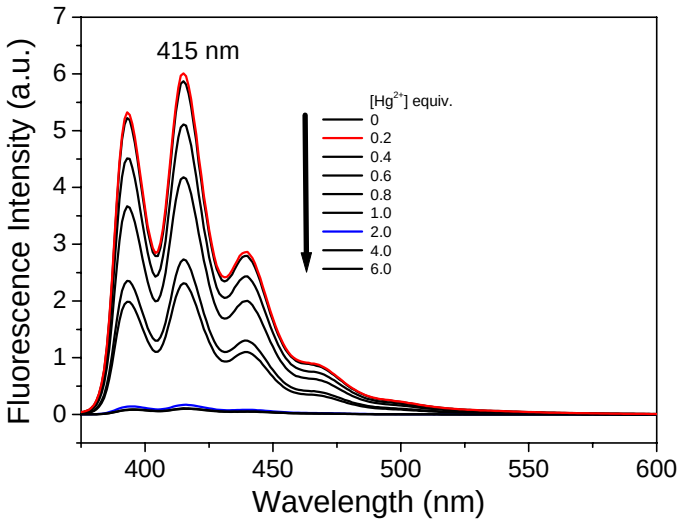


Figure S14. Job plot of a 1:1 complex of **1** and Hg^{2+}, where the difference in fluorescence intensity at 415 nm was plotted against the mole fraction of **1** at an invariant total concentration of 10 μM in MeCN/$CHCl_3$ (v/v = 1000:4).

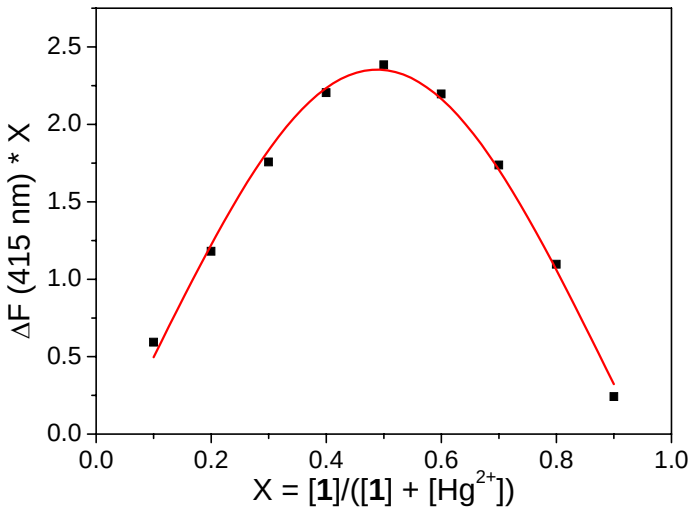


Figure S15. Changes in fluorescence emission spectra of **1** (10 μM) upon titration with $Cr(ClO_4)_3$ in $MeCN/CHCl_3$ (v/v = 1000:4). (The excitation wavelength was 367 nm.)

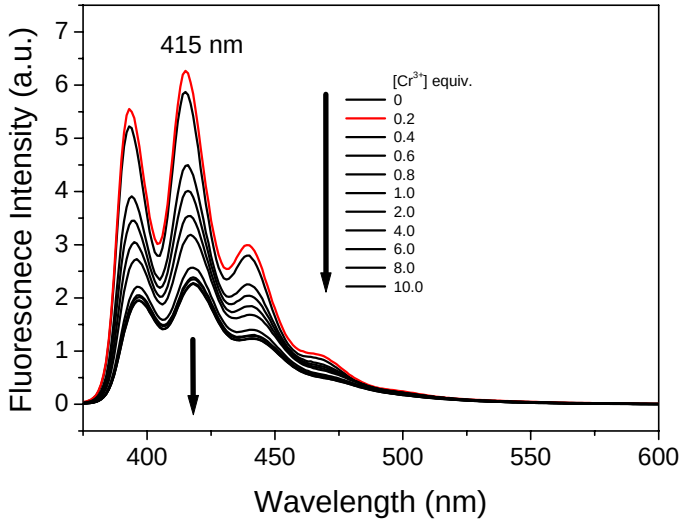


Figure S16. Job plot of a 1:1 complex of **1** and Cr^{3+}, where the difference in fluorescence intensity at 415 nm was plotted against the mole fraction of **1** at an invariant total concentration of 10 μM in $MeCN/CHCl_3$ (v/v = 1000:4).

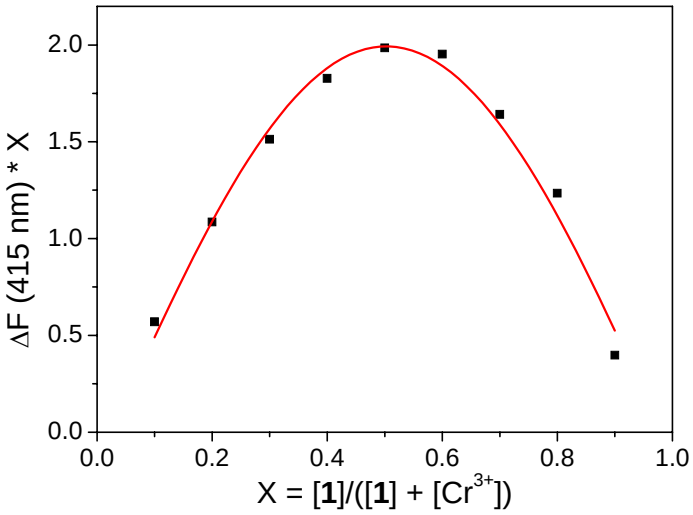


Figure S17. Changes in fluorescence emission spectra of **2** (10 μM) upon titration with $Cu(ClO_4)_2$ in $MeCN/CHCl_3$ (v/v = 1000:4). (The excitation wavelength was 350 nm.)

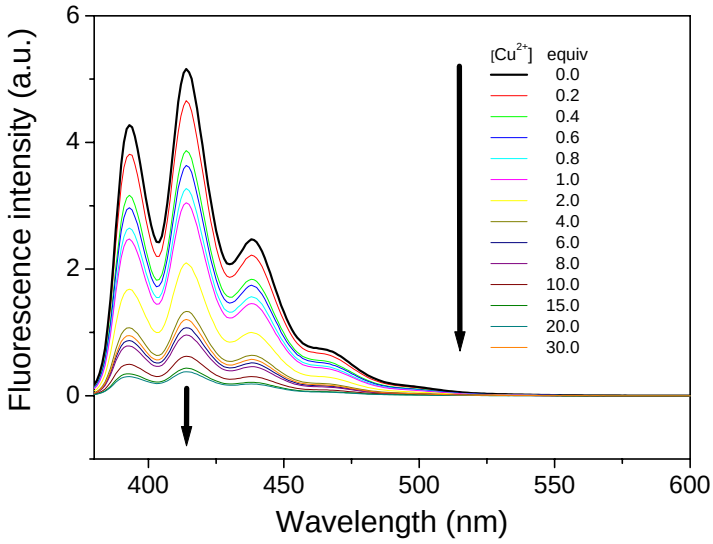


Figure S18. Job plot of a 1:1 complex of **2** and Cu^{2+}, where the difference in fluorescence intensity at 414 nm was plotted against the mole fraction of **2** at an invariant total concentration of 10 μM in $MeCN/CHCl_3$ (v/v = 1000:4).

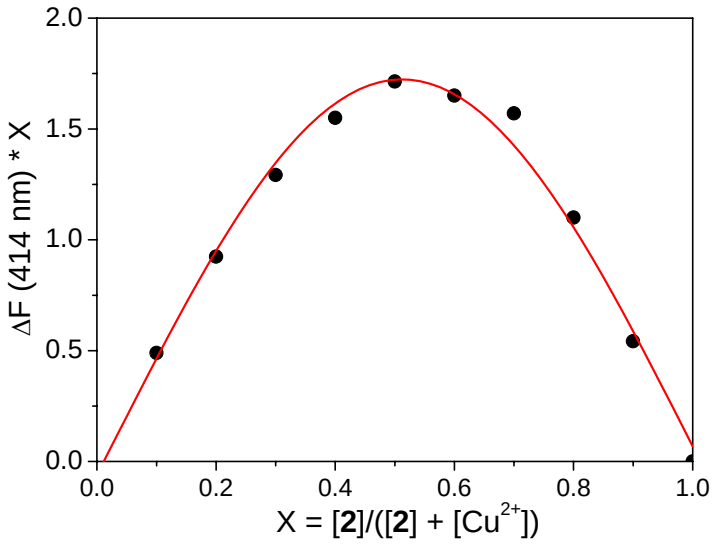


Figure S19. Changes in fluorescence emission spectra of **2** (10 μM) upon titration with $Hg(ClO_4)_2$ in MeCN/$CHCl_3$ (v/v = 1000:4). (The excitation wavelength was 350 nm.)

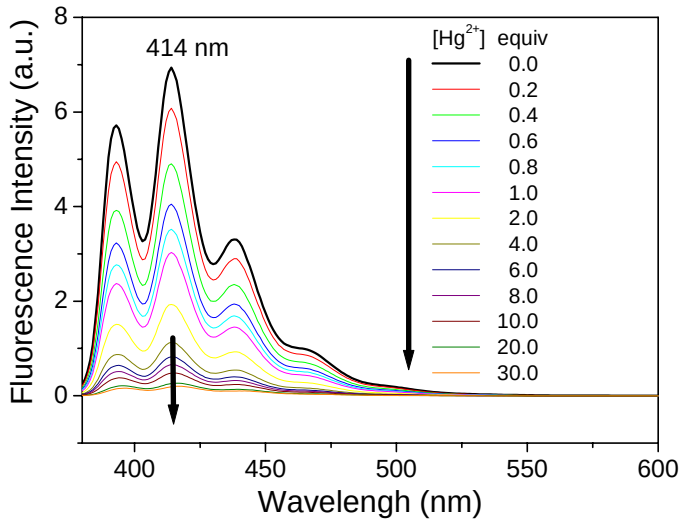


Figure S20. Job plot of a 1:1 complex of **2** and Hg^{2+}, where the difference in fluorescence intensity at 414 nm was plotted against the mole fraction of **2** at an invariant total concentration of 10 μM in MeCN/$CHCl_3$ (v/v = 1000:4).

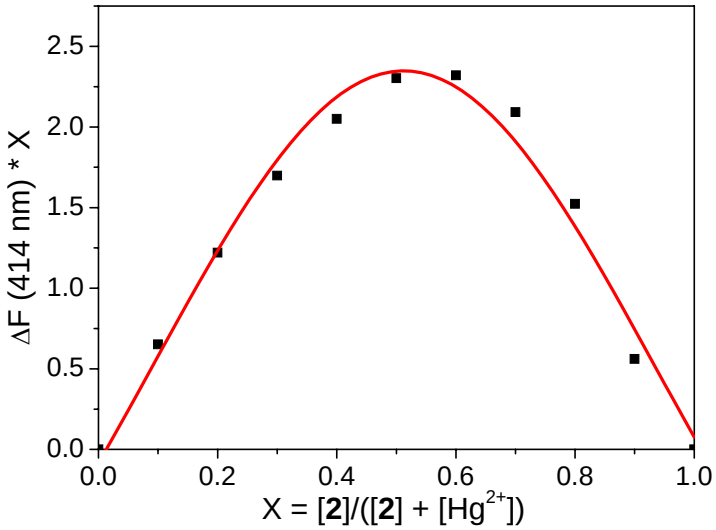


Figure S21. Changes in fluorescence emission spectra of **2** (10 μM) upon titration with $Cr(ClO_4)_3$ in $MeCN/CHCl_3$ (v/v = 1000:4). (The excitation wavelength was 350 nm.)

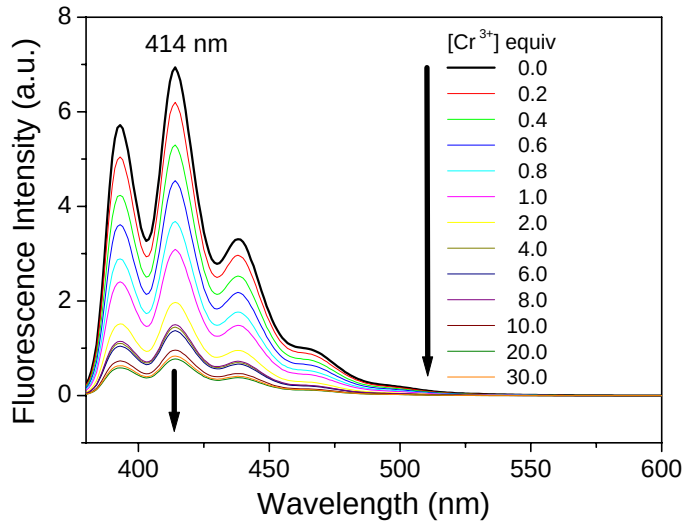


Figure S22. Job plot of a 1:1 complex of **2** and Cr^{3+}, where the difference in fluorescence intensity at 414 nm was plotted against the mole fraction of **2** at an invariant total concentration of 10 μM in $MeCN/CHCl_3$ (v/v = 1000:4).

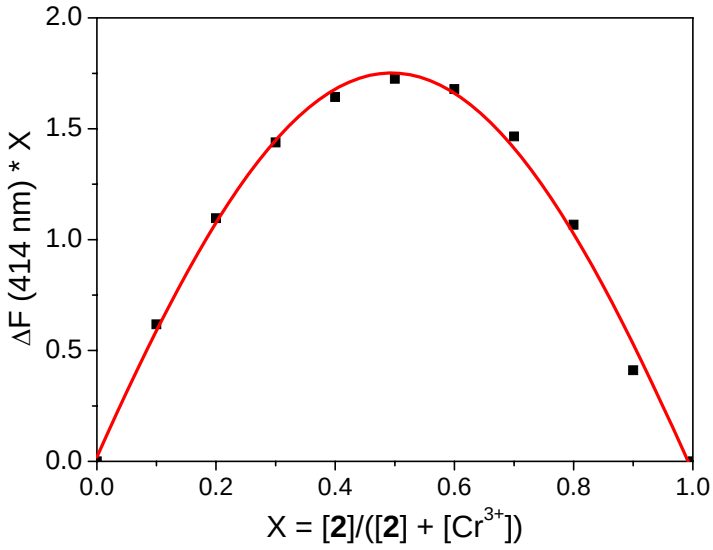


Figure S23. Fluorescence emission changes of **1**•Hg^{2+}, **1**•Cu^{2+} and **1**•Cr^{3+} complexes in $MeCN/CHCl_3$ (v/v = 1000:4) upon addition of K^+. (The excitation wavelength was 367 nm.)

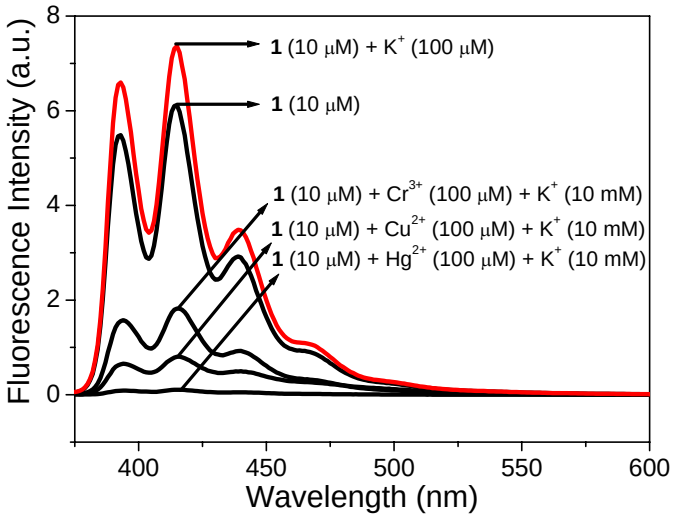


Figure S24 Fluorescence emission changes of **1**•Pb^{2+} complex in $MeCN/CHCl_3$ (v/v = 1000:4) upon addition of Ba^{2+}. (The excitation wavelength was 367 nm.)

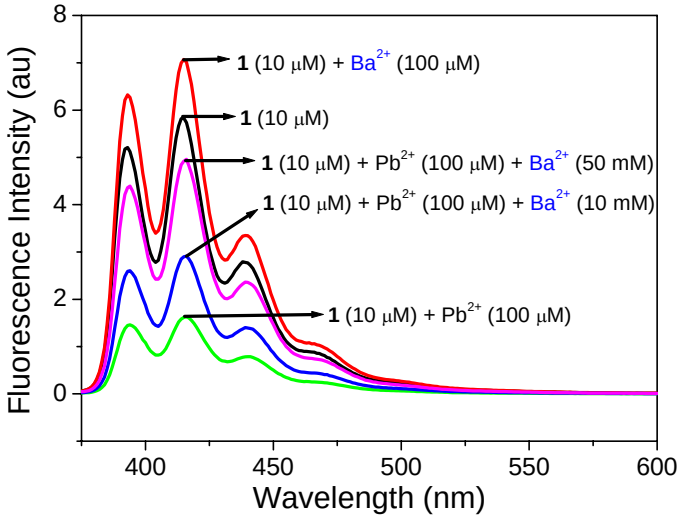


Figure S25 Fluorescence emission changes of **1**•Pb^{2+} complex in MeCN/$CHCl_3$ (v/v = 1000:4) upon addition of Zn^{2+}. (The excitation wavelength was 367 nm.)

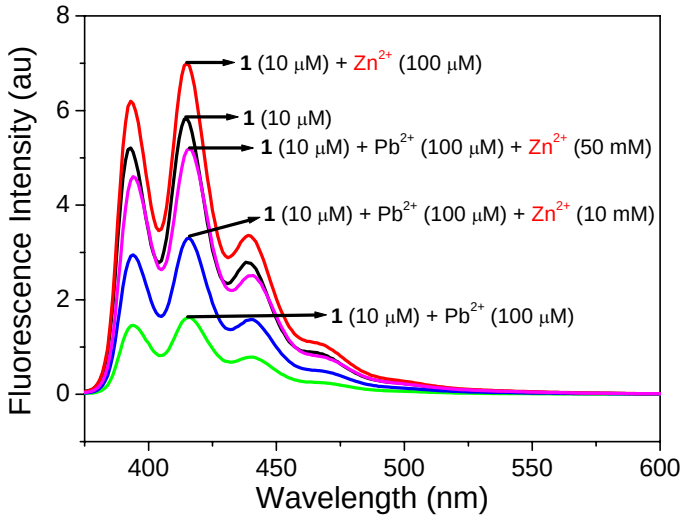


Figure S26 Fluorescence emission changes for the **1** (10 μM) with 10 equiv of $Pb(ClO_4)_2$ in MeCN/$CHCl_3$ (v/v = 1000:4) upon addition of various amount of K^+ ion ($\lambda_{excitation}$ = 367 nm).

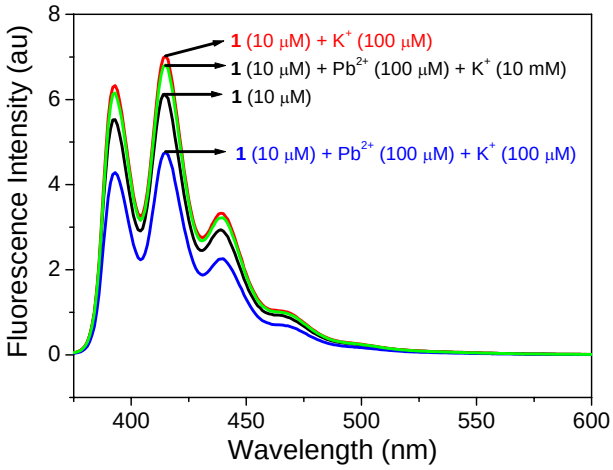


Figure S27 Fluorescence emission changes for the **1** (10 μM) with 10 equiv of $K(ClO_4)$ in $MeCN/CHCl_3$ (v/v = 1000:4) upon addition of various amount of Pb^{2+} ion ($\lambda_{excitation}$ = 367 nm).