Supporting Information

A Highly Sensitive, Selective, Colorimetric and Near-Infrared Fluorescent Turn-on Chemosensor for Cu^{2+} Based on BODIPY

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Experimental – General: 3,5-dichloro-8-(4-tolyl)BODIPY[1] and 1-ethynyl-4-(trimethylsilylethynyl)benzene[2] were synthesized according to literature procedures. Di(2-picolyl)amine, bis(triphenylphosphine)palladium(II) chloride [$Pd(PPh_3)_2Cl_2$], and tetrabutylammonium fluoride (1 mol/L solution in THF) were purchased from Aldrich and used without further purification. THF and toluene were distilled from sodium prior to use. The metal salts [AgOAc, $Ba(ClO_4)_2$, $Ca(ClO_4)_2$, $Cd(ClO_4)_2$, $Co(OAc)_2 \cdot 4H_2O$, $Cu(ClO_4)_2 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, $Hg(OAc)_2$, KOAc, $Mg(ClO_4)_2$ $NaOAc \cdot 3H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$, $Pb(OAc)_2 \cdot 3H_2O$ and $Zn(ClO_4)_2$] were purchased from Aldrich and used as such.

^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker Avance 300 operating at a frequency of 300 MHz for ^{1}H and 75 MHz for ^{13}C. UV–vis absorption spectra were recorded on a Perkin Elmer Lambda 40 UV–vis spectrophotometer. Melting points were taken on a Reichert Thermovar and are uncorrected. Corrected steady-state excitation and emission spectra were obtained using a SPEX Fluorolog. Mass spectra were recorded on a Hewlett-Packard 5989 A mass spectrometer (ESI mode). High-resolution mass data were obtained with a Kratos MS50TC instrument.

Determination of Quantum Yields: For the determination of the fluorescence quantum yields Φ_f of **1**, only dilute solutions with an absorbance below 0.1 at the excitation wavelength λ_{ex} were used. Relative quantum yields were obtained by comparing the areas under the corrected emission spectra of sample and fluorescence standard. Cresyl violet in methanol (λ_{ex} = 620 nm, Φ_f = 0.55) was used as fluorescence standard. In all cases, correction for the solvent refractive index was applied. All spectra were recorded at 20 °C using undegassed samples.

Determination of Ground-State Dissociation Constant K_d: The ground-state dissociation constant K_d of the complex between **1** and Cu^{2+} was determined in CH_3CN solution at 20 °C by *direct* fluorometric titration as a function of Cu^{2+} using the fluorescence emission spectra. Nonlinear fitting of eqn (1) to the steady-state fluorescence data F recorded as a function of $[Cu^{2+}]$ yields values of K_d, F_{min}, F_{max}, and n.

$$F = \frac{F_{\max}\left[\mathrm{Cu}^{2+}\right]^n + F_{\min}K_\mathrm{d}}{K_\mathrm{d} + \left[\mathrm{Cu}^{2+}\right]^n} \qquad (1)$$

In eqn (1), F stands for the fluorescence signal at $[Cu^{2+}]$, whereas F_{min} and F_{max} denote the fluorescence signals at minimal and maximal $[Cu^{2+}]$, respectively, and n is the number of Cu^{2+} ions bound per probe molecule (i.e., stoichiometry of binding).[3]

5-Chloro-4,4-difluoro-3-(4-(trimethylsilylethynyl)phenylethynyl)-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene 2: 130 mg (0.37 mmol) 3,5-dichloro-8-(4-tolyl) BODIPY and 80 mg (0.4 mmol) 1-ethynyl-4-(trimethylsilylethynyl)benzene were dissolved in 25 mL of THF and 100 µL of Et_3N under argon. To this solution 14 mg (0.02 mmol) $PdCl_2(PPh_3)_2$ and 4 mg (0.02 mmol) CuI were added. The reaction mixture was heated at 60 °C for 12 h. After evaporating the solvent, the crude product was extracted with CH_2Cl_2 (3 × 40 mL), dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. Purification was performed by chromatography on silica gel with petroleum ether/ethyl acetate (4:1, v/v) as eluent and afforded 59 mg purple solid **2** (31% yield). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.58 (2H, d, $J = 8.2$ Hz,), 7.46 (2H, d, $J = 8.2$ Hz), 7.39 (2H, d, $J = 8.2$ Hz), 7.30 (2H, d, $J = 8.2$ Hz), 6.87

(2H, dd, *J* = 3.7 Hz), 6.71 (1H, d, *J* = 4.6 Hz), 6.43 (1H, d, *J* = 3.7 Hz), 2.46 (3H, s, CH_3), 0.27 (9H, s, $Si(CH_3)_3$)). ^{13}C NMR (75 Mz, $CDCl_3$), δ (ppm): 144.9, 144.5, 143.6, 141.7, 141.5, 137.2, 135.9, 134.7, 133.8, 132.1, 131.7, 131.5, 130.7, 130.3, 129.6, 129.4, 124.3, 124.0, 122.1, 118.9, 104.7, 101.7, 97.4, 84.6, 21.5, 0.0005. ESI-MS: *m/z* 535.5 $[M+Na]^+$.

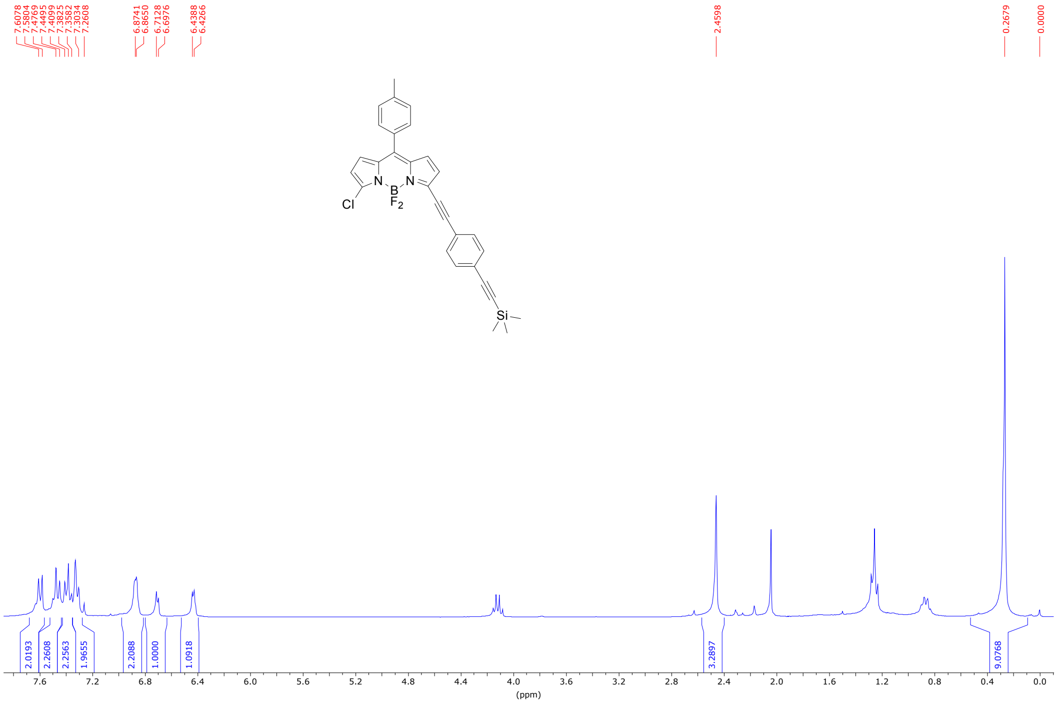
5-Chloro-4,4-difluoro-3-(4-(ethynyl)phenylethynyl)-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene 3: A solution of **2** (82 mg, 0.16 mmol) in 30 mL of THF was stirred at –78 °C under argon while 160 μL of tetrabutylammonium fluoride (1.0 M in THF) was added. Then the solution was stirred at this temperature for 15 min. After evaporating the solvent, the residue was poured into 50 mL of water and extracted with CH_2Cl_2 (3×40 mL), dried by $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel, eluting with a mixture of petroleum ether and ethyl acetate (4:1, v/v) to give purple solid **3** (43 mg, 61% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.62 (2H, d, *J* = 8.2 Hz), 7.49 (2H, d, *J* = 8.2 Hz), 7.42 (2H, d, *J* = 8.2 Hz), 7.32 (2H, d, *J* = 8.2 Hz), 6.88 (2H, dd, *J* = 4.6 Hz), 6.72 (1H, d, *J* = 4.6 Hz), 6.44 (1H, d, *J* = 4.6 Hz), 3.22 (1H, s, ≡CH), 2.47 (3H, s, CH_3). ^{13}C NMR (75 Mz, $CDCl_3$), δ (ppm): 145.0, 143.6, 141.4, 137.0, 135.8, 134.7, 132.1, 131.5, 130.6, 130.3, 129.3, 123.8, 123.2, 122.5, 118.9, 101.3, 84.5, 83.3, 79.7, 21.5. ESI–MS: *m/z* 904.6 $[2M+Na]^+$.

5-*N*-(2-picolyl)amine-4,4-difluoro-3-(4-(ethynyl)phenylethynyl)-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene 1: To a solution of **3** (110 mg, 0.25 mmol) in 20 mL of acetonitrile di(2-picolyl)amine (80 mg, 0.4 mmol) was added. The reaction mixture was stirred at room temperature for 12 h under argon. After evaporating the solvent, 30 mL of water was added and the organic layer was extracted with CH_2Cl_2 (3×40 mL), dried by $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel, eluting with a mixture of CH_2Cl_2 and ethyl acetate (1:1, v/v) to give purple solid **1** (122 mg, 81% yield). M.p. 191 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.56 (2H, d, *J* = 3.7 Hz), 7.67 (2H, t, *J* = 7.8 Hz), 7.36 (6H, d), 7.34 (2H, d), 7.20 (4H, d), 6.84 (1H, d, *J* = 4.6 Hz), 6.59 (1H, d, *J* = 3.6 Hz), 6.35 (1H, d, *J* = 3.6 Hz), 6.30 (1H, d, *J* = 4.6 Hz), 5.29 (4H, s, $N(CH_2)_2$), 3.16 (1H, s, ≡CH), 2.42 (3H, s, CH_3). ^{13}C NMR (75 Mz, $CDCl_3$), *δ* (ppm): 164.2, 156.3, 149.5, 139.2, 137.0, 136.4, 135.5, 133.8, 131.9, 131.3, 130.4, 128.9, 125.2, 124.3, 122.6, 121.9, 121.3, 120.4, 119.3, 115.4, 94.9, 86.1, 83.6, 78.7, 58.0, 21.4. ESI–MS: *m/z* 626.6 $[M+Na]^+$. HRMS: calcd. for $C_{38}H_{28}BF_2N_5$ 603.24058, found 603.2447.

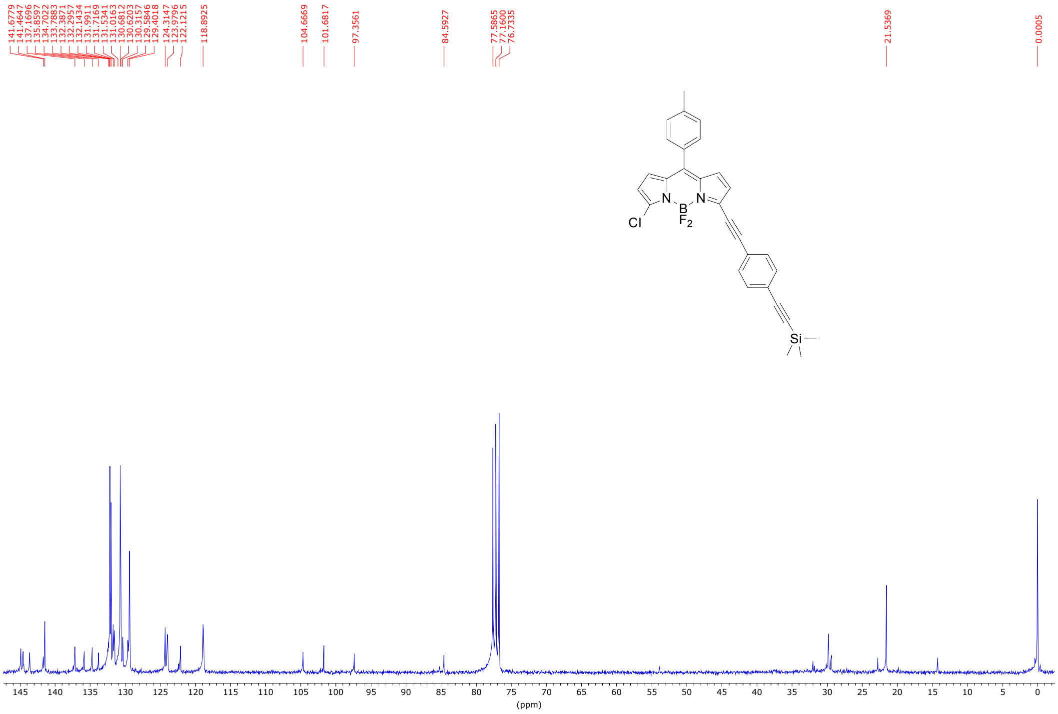
References:

1. T. Rohand, M. Baruah, W.W. Qin, N. Boens and W.Dehaen, *Chem. Commun*. 2006, 266.
2. Y. Shirai, Y. M. Zhao, L. Cheng and J. M. Tour, *Org. Lett.* 2004, **6**, 2129.
3. E. Cielen, A. Tahri, A. Ver Heyen, G. J. Hoornaert, F. C. De Schryver, N. Boens, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1573.

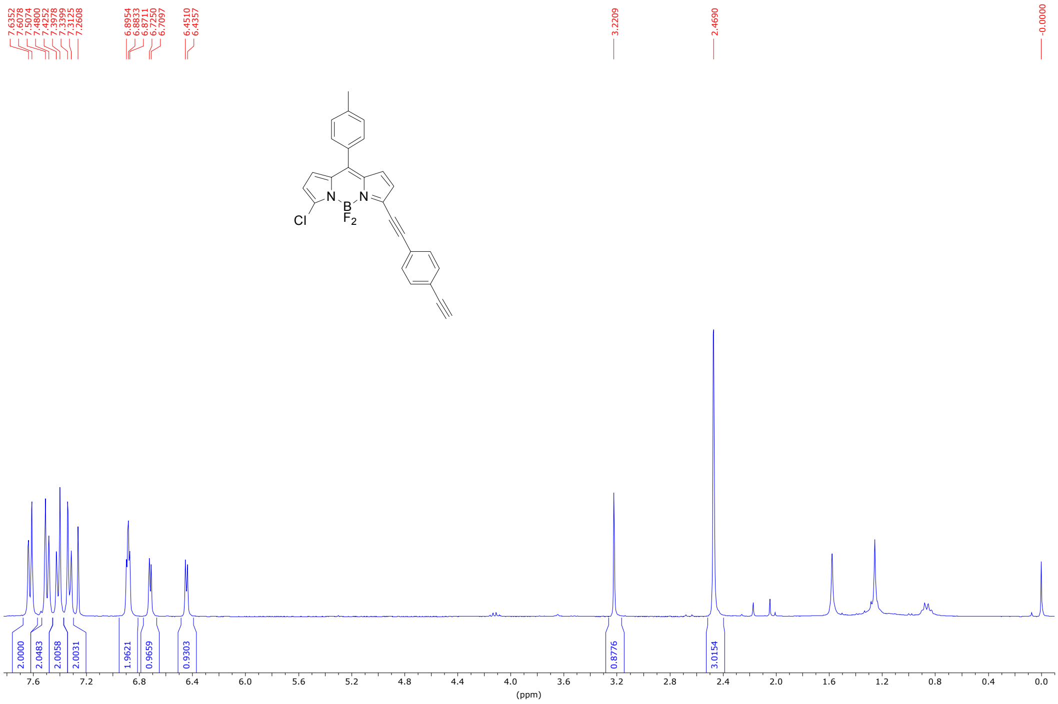
^{1}H NMR spectra of **2**.



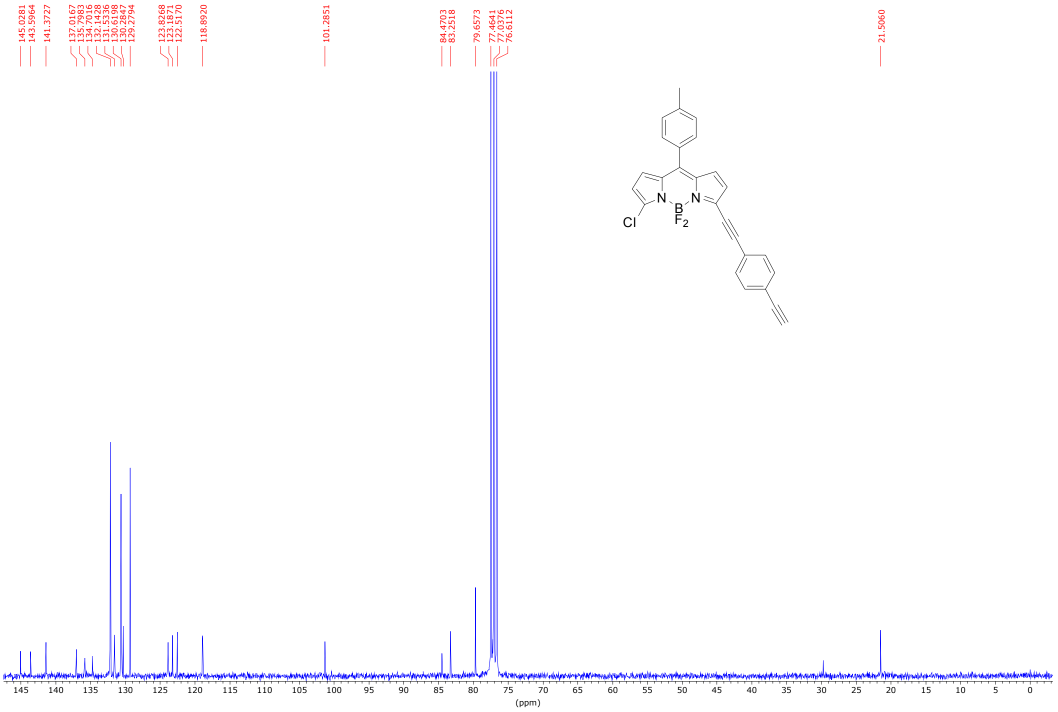
^{13}C NMR spectra of **2**.



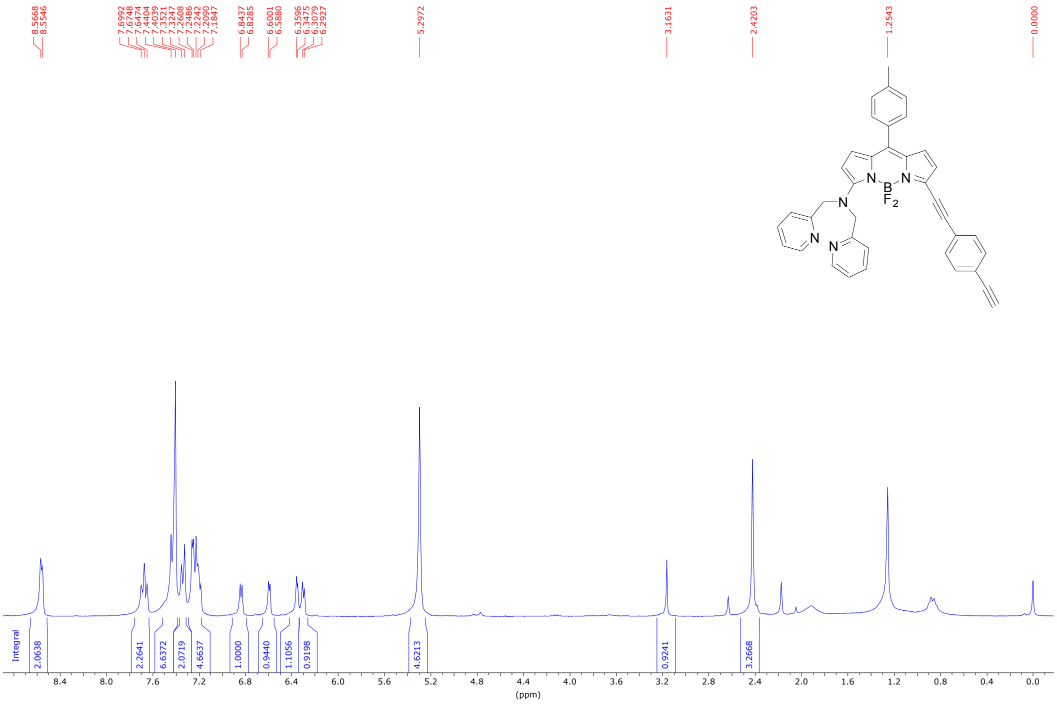
^{1}H NMR spectra of **3**.



^{13}C NMR spectra of **3**.



^{1}H NMR spectra of **1**.



^{13}C NMR spectra of **1**.

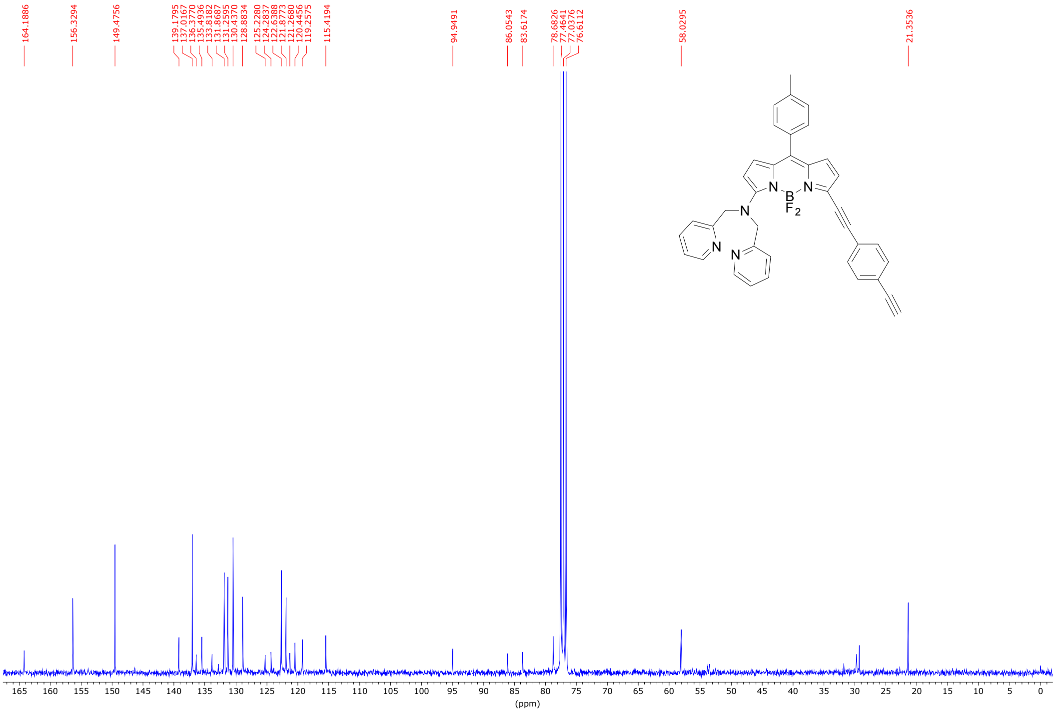


Figure S1. UV–vis absorption spectra of **1** in CH_3CN upon addition of various metal ions. The concentration of **1** was 2 μM and that of the selected metal ion was 100μM.

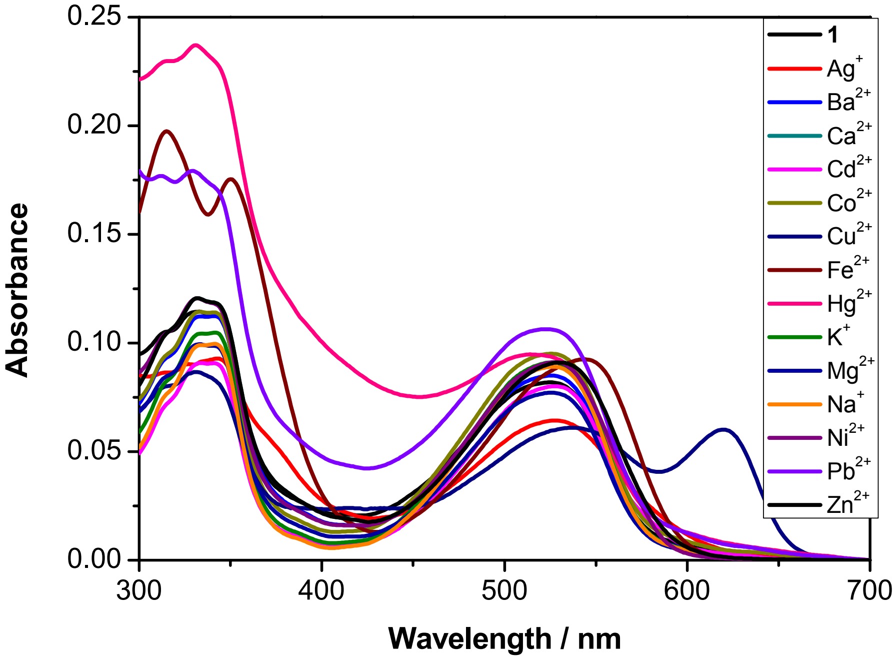


Figure S2. Photographs of solutions of **1** in CH_3CN upon addition of various metal ions. The concentration of **1** was 2 μM and that of the selected metal ion was 100 μM. Upper row: optical. Middle row: fluorescence observed upon excitation with 632-635 nm light from a laser pointer. The red speckles are reflections of the excitation laser light. Lower row: fluorescence observed upon excitation at 360 nm.

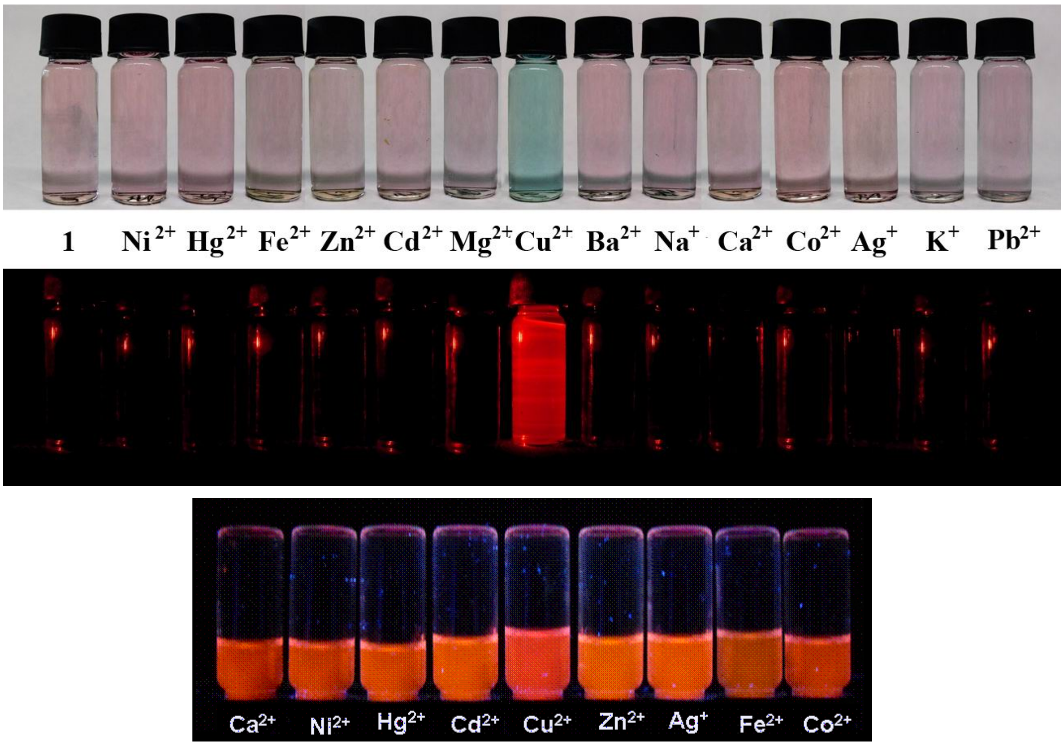


Figure S3. Fluorescence emission spectra of **1** (2 μM) in CH_3CN upon addition of various metal ions (100 μM) (λ_{ex} = 520 nm).

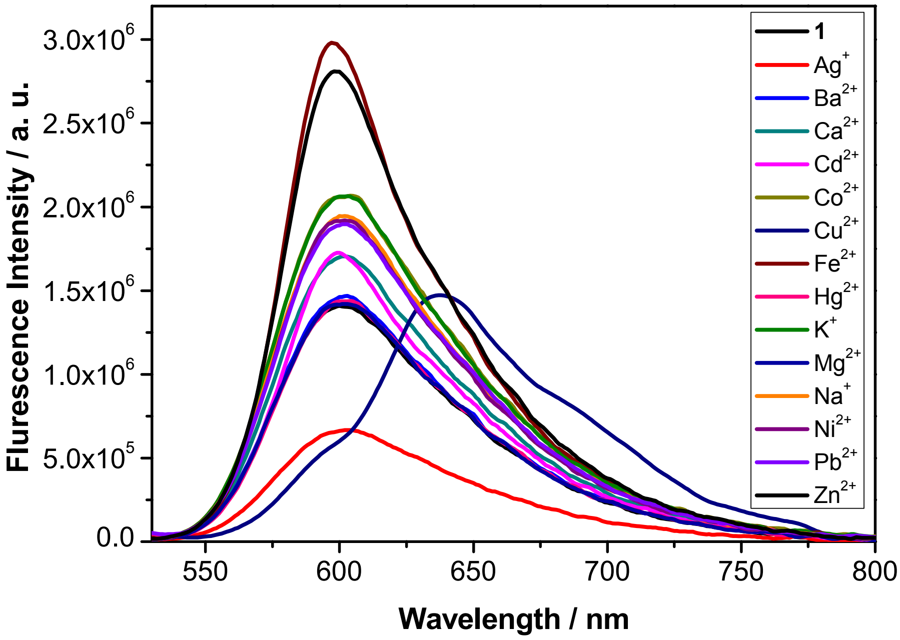


Figure S4. Fluorescence emission intensity of **1** (2 μM) in CH_3CN monitored at 650 nm as a function of Cu^{2+} concentration (λ_{ex} = 620 nm). The red line represents the best fit to the data (filled squares) according to eqn (1).

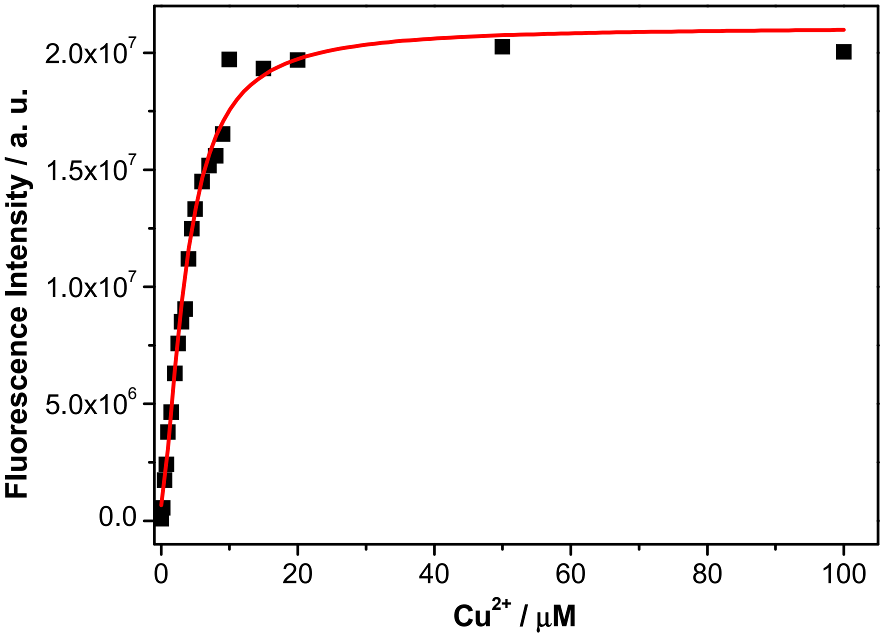


Figure S5. ESI ms spectra of **1** and **1**–Cu^{2+}.

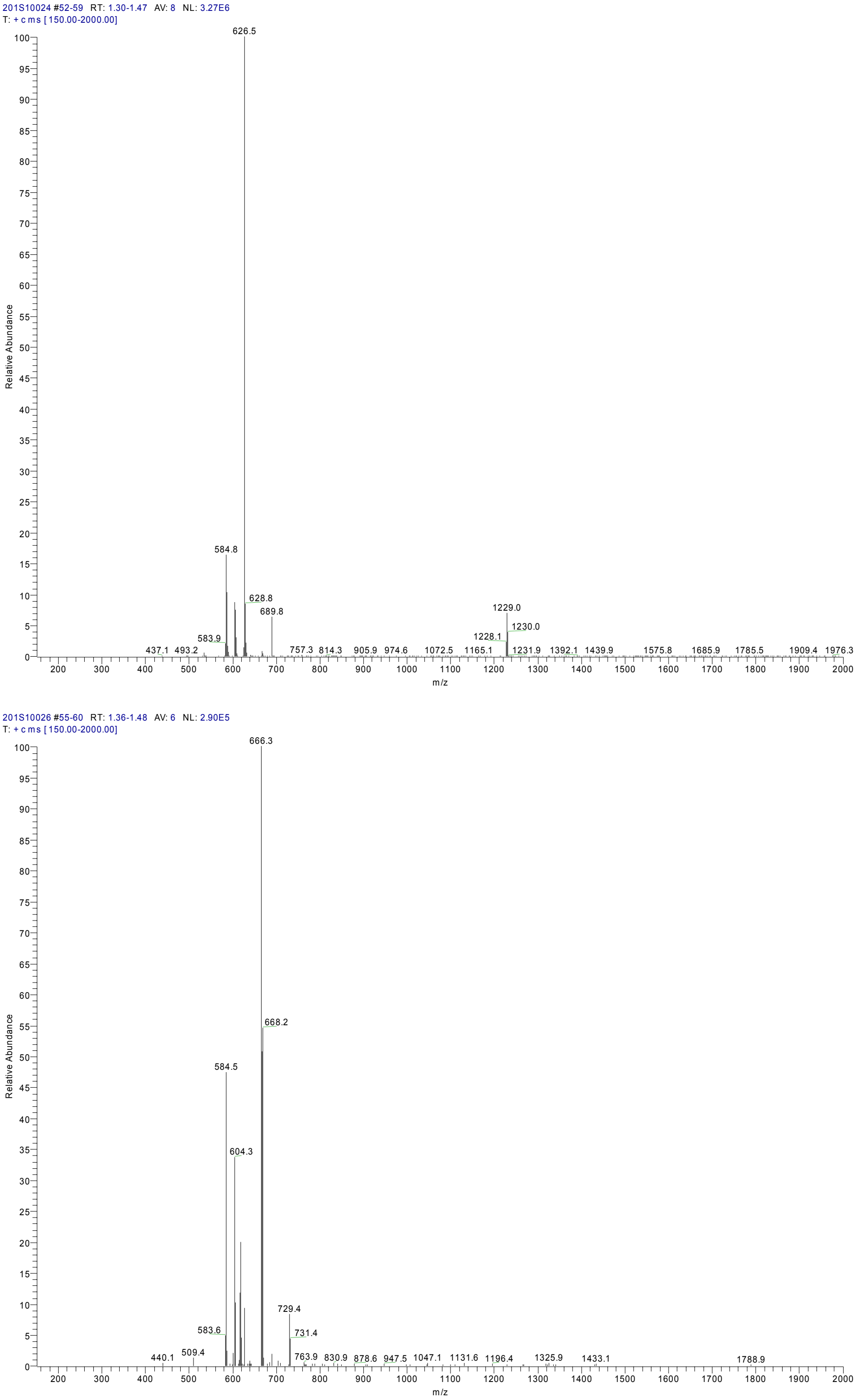


Figure S6. Fluorescence emission spectra of **1** (2 μM) in CH_3CN in the presence of Ag^+ (50 μM) upon addition of different concentrations of Cu^{2+} (see insert) (λ_{ex} = 620 nm).