Supplementary information for

Visual Detection of Cu(II) Ions Based on a Simple Pyrene Derivative Using Click Chemistry

Materials: All chemicals were obtained from Sigma-Aldrich, Alfa Aesar, Aladdin, and Beijing chem. Reagents Co. (Beijing, China) and used without further purification. 1-(4-azidobutyl)pyrene (PyN_3), and N,N,N-trimethylprop-2-yn-1-ammonium bromide (TAB) were synthesized and purified as follows.

Measurements: ^{1}H-NMR spectrum was recorded on a Bruker Avance 500MHz NMR Spectrometer. UV-vis spectra were recorded on a HITACHI U-3900 UV-VIS spectrophotometer. Fluorescence spectra were recorded on a Horiba Fluorolog-3 FL3-21 fluorescence spectrophotometer with excitation wavelength 342 nm. FT-IR spectra were obtained through Thermo Fisher iN10.

Sample preparation: For Cu^{2+} sensing, the stock solution of PyN_3 (10 mM) was prepared by dissolving in DMSO, Stock solutions of Cu^{2+}, TAB, SA and various other metal ions were prepared by dissolving them in water. The test solution was prepared by adding the requisite amounts of stock solutions together, then diluting with 10mM HEPES buffer (pH 7.4), the final solvent was HEPES-buffered (pH 7.4) water-DMSO (999.5:0.5, v/v). Upon addition of analyte, the solution was stirred for 15 mins at 25 ℃, then the fluorescence spectra were recorded, λ_{ex} = 342 nm, ex slit = 2 nm, em slit = 2 nm. The real sample preparation in tap water to evaluate the potential of this strategy for on-site sensing applications is the same to those conducted in buffer solution stated above.

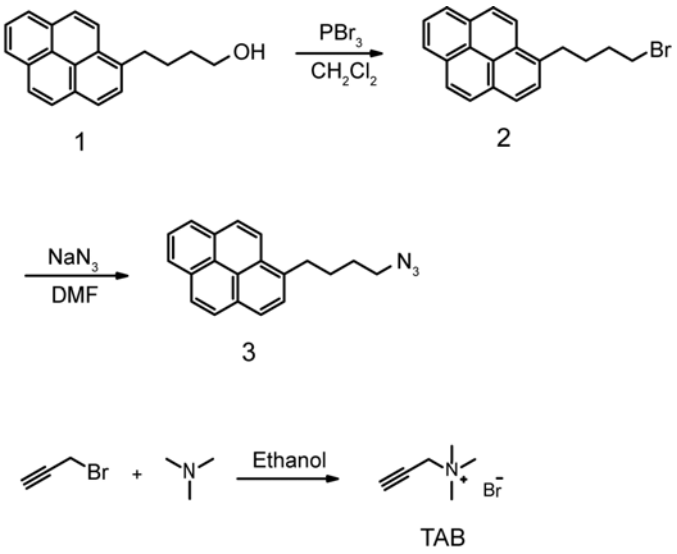

Figure S1. Synthesis route for PyN_3 (**3**) and TAB.

Synthesis of 1-(4-bromobutyl)pyrene (2). To a solution of 1-pyrenebutanol (0.5 g, 1.8 mmol) in anhydrous CH_2Cl_2 (30 mL) at 0℃, a solution of PBr_3 in CH_2Cl_2 (1.98 mmol, 20 mL) was added dropwise in 30 min. The reaction mixture was then stirred at room temperature for 2 h. After washing several times with water, the organic phase was dried and evaporated. The residue was purified by chromatography on silica gel eluted with ether/petroleum ether (5:95, v/v) to give the bromide derivative 2 (0.42 g, yield 67.5%). δ_H (500 MHz, $CDCl_3$) 8.17 (1H, d, J = 9.3), 8.13-8.08 (2H, m), 8.06-8.00 (2H, m), 7.98-7.94 (2H, m), 7.92 (1H, d, J = 7.6), 7.80-7.73 (1H, m), 4.08-3.99 (2H, m), 3.28 (2H, t, J = 7.5), 1.88 (2H, ddd, J = 10.9, 8.6, 4.8), 1.76 (2H, dt, J = 11.6, 6.1).

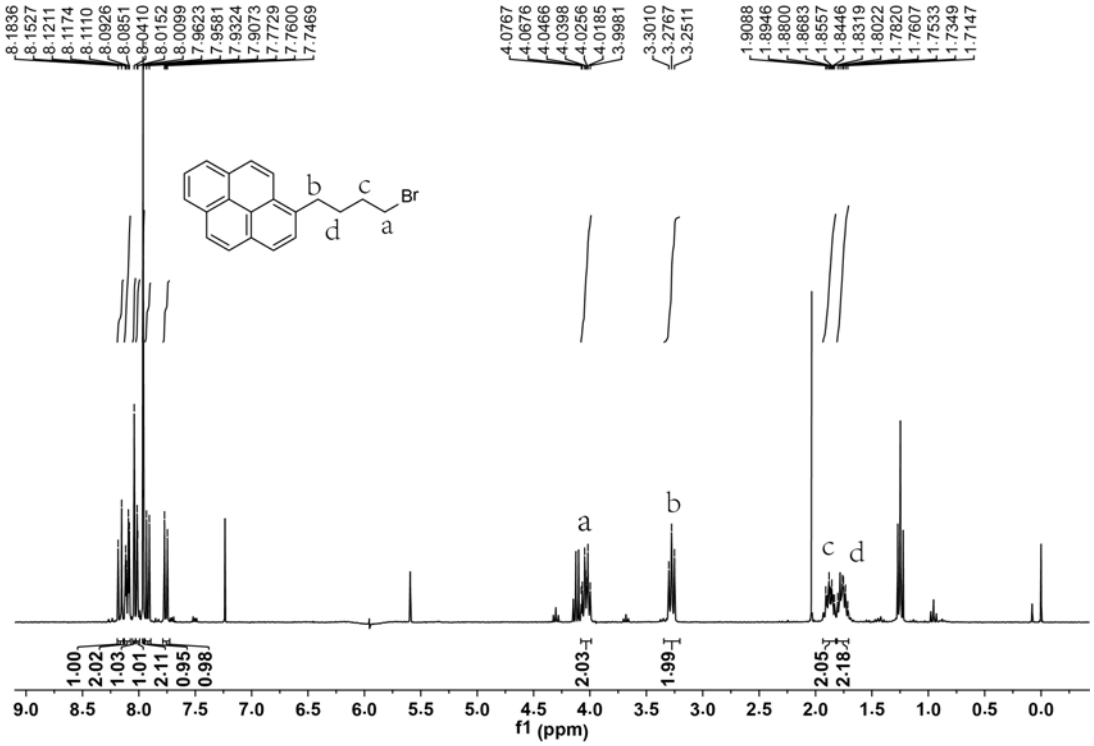

Figure S2. ^{1}H NMR spectrum of 1-(4-bromobutyl)pyrene (**2**) in $CDCl_3$.

Synthesis of 1-(4-azidobutyl)pyrene (3). 1-(4-bromobutyl)pyrene (200 mg, 0.67 mmol) were stirred with 52.2 mg sodium azide (0.81 mmol, 1.2 eq.) in 12 mL DMF for 24 h at 80 ℃. The reaction was quenched with 10 mL H_2O, subsequently extracted with DCM (15 mL×3). The organic layer was dried over $MgSO_4$, filtered, and evaporated. The crude product was isolated by column chromatography (silica gel, CH_2Cl_2/petroleum ether (1:1)) to give desired product (169 mg, 95%). δ_H (500 MHz, $CDCl_3$) 8.28 (1H, d, J = 9.2), 8.20 (2H, dd, J = 7.6, 3.7), 8.14 (2H, d, J = 8.5), 8.09-7.99 (3H, m), 7.89 (1H, d, J = 7.7), 3.39 (4H, dt, J = 13.8, 7.3), 2.02-1.94 (2H, m), 1.84-1.76 (2H, m). The results are in line with literature values.[19]

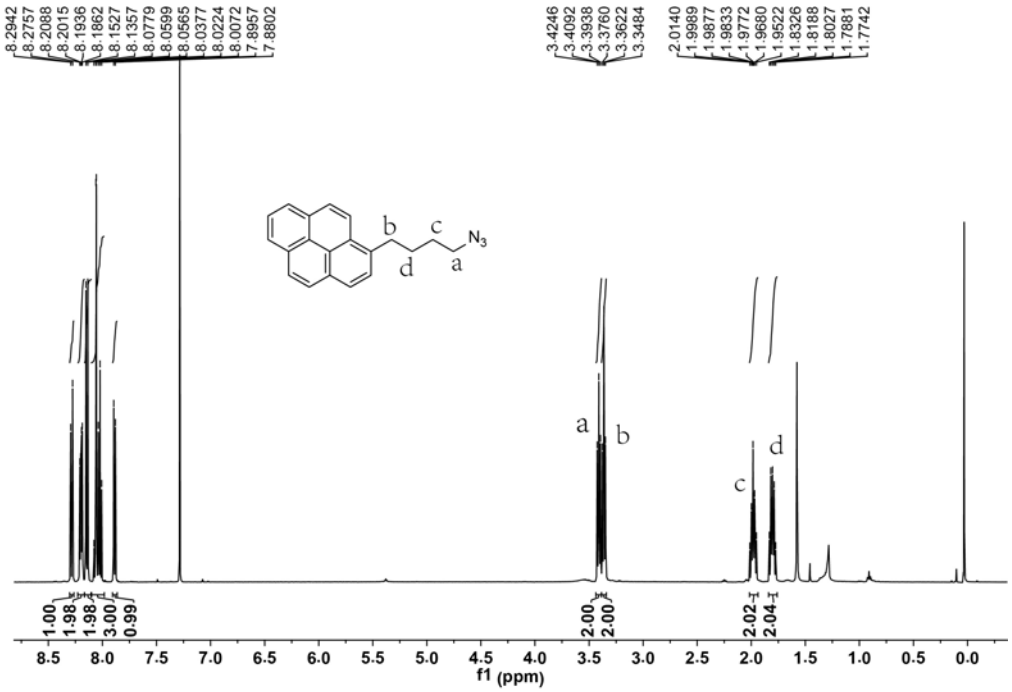

Figure S3. ^{1}H NMR spectrum of 1-(4-azidobutyl)pyrene (**3**) in $CDCl_3$.

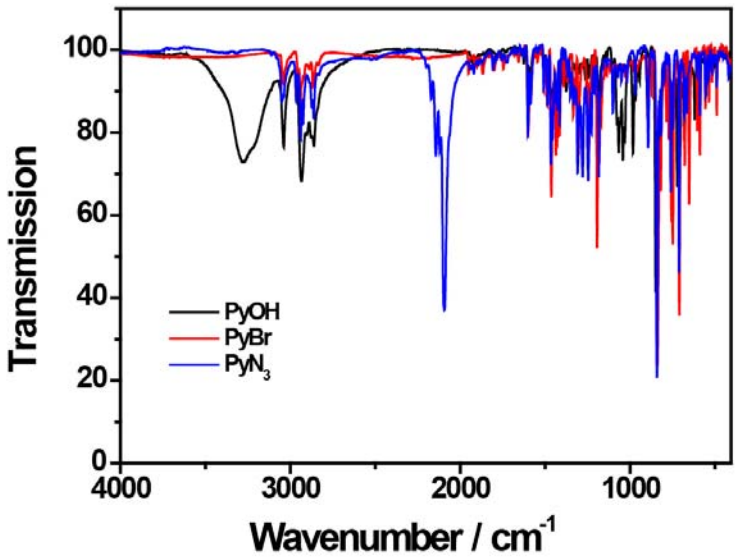

Figure S4. FT-IR spectra of 1-(4-azidobutyl)pyrene (blue), 1-(4-bromobutyl)pyrene (red), and the raw material1-pyrenebutanol (black). The typical stretching vibration peak of hydroxyl group at 3272 cm^{-1} of 1-pyrenebutanol (black) disappeared after bromination by PBr_3. 1-(4-azidobutyl)pyrene (blue) was obtained by azidation from 1-(4-bromobutyl)pyrene (red), which was confirmed by the sharp peak at 2092 cm^{-1} of the azide group.

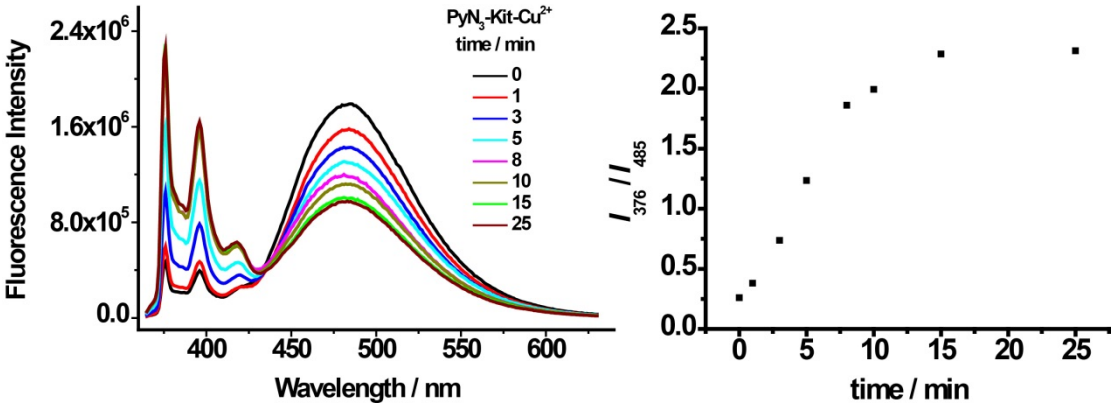

Figure S5. Fluorescence emission spectra of 5 μM PyN_3-kit-Cu^{2+} with increasing reaction time in HEPES buffer (10 mM, pH 7.4, containing 0.05% (v/v) DMSO). [Cu^{2+}] = 5 μM.

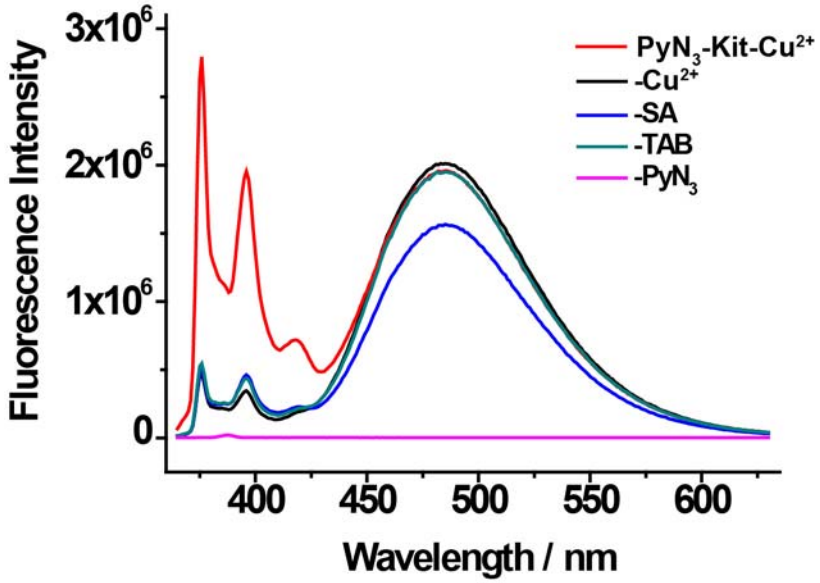

Figure S6. The emission spectra of PyN_3-kit-Cu^{2+} lack of Cu^{2+}, SA, TAB, PyN_3 respectively in HEPES buffer (10 mM, pH 7.4, containing 0.05% (v/v) DMSO). [PyN_3] = 5 μM, [SA] = 100 μM, [TAB] = 100 μM, [Cu^{2+}] = 5 μM.

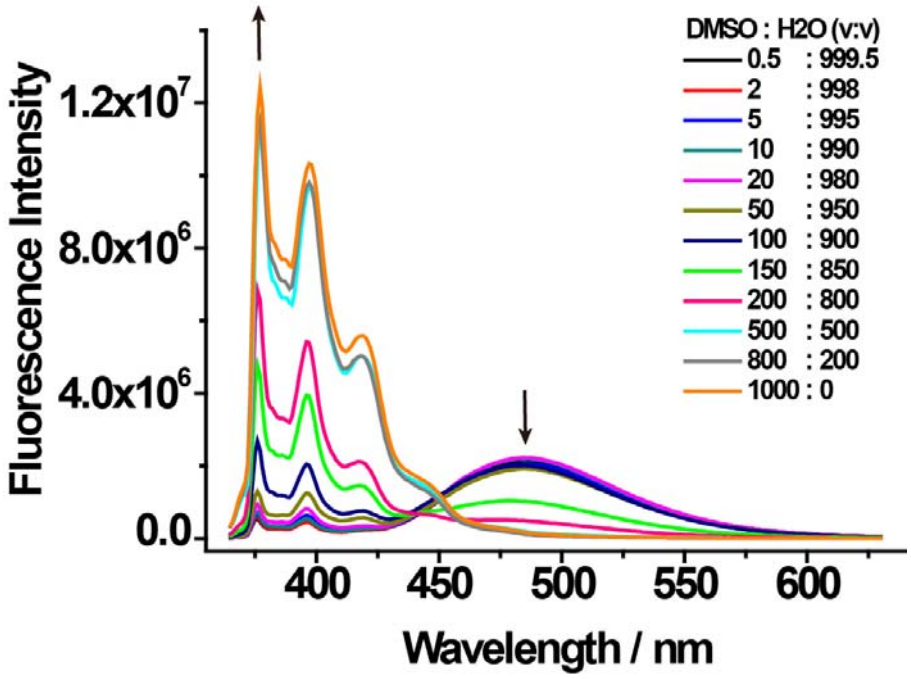

Figure S7. Fluorescence response of PyN_3 (5 μM) in HEPES buffer (10 mM, pH 7.4) when increasing the ratio of DMSO from 0.05% to 100% (v/v).

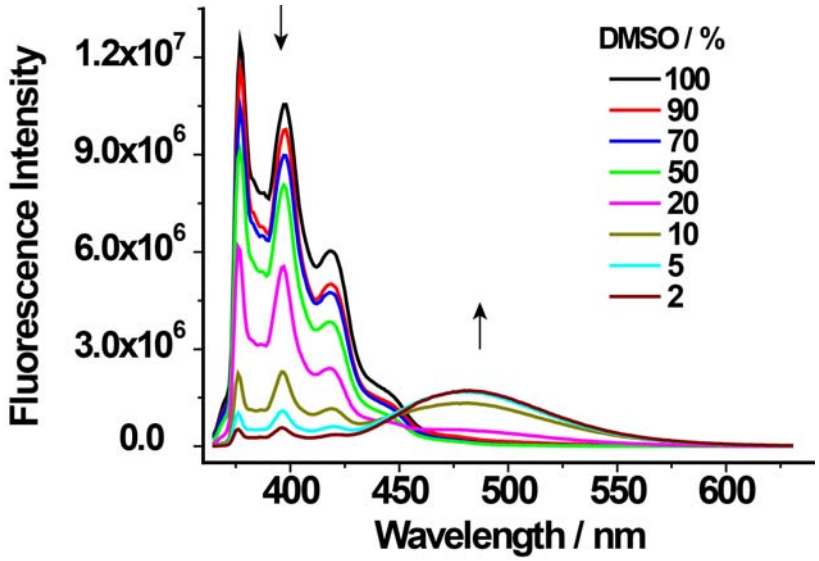

Figure S8. Fluorescence responses of PyN_3 (5 μM) in DMSO with the increasing ratio of water from 0% to 98% (v/v).

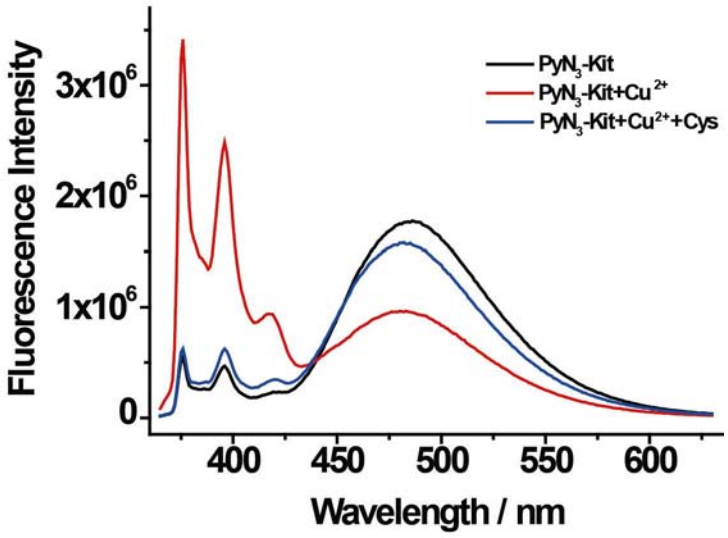

Figure S9. The emission spectra of PyN_3-kit, PyN_3-Kit-Cu^{2+}, PyN_3-kit-Cu^{2+}-Cys in HEPES buffer (10 mM, pH 7.4, containing 0.05% (v/v) DMSO). [PyN_3] = 5 μM, [Cu^{2+}] = 5 μM, [Cys] = 100 μM.

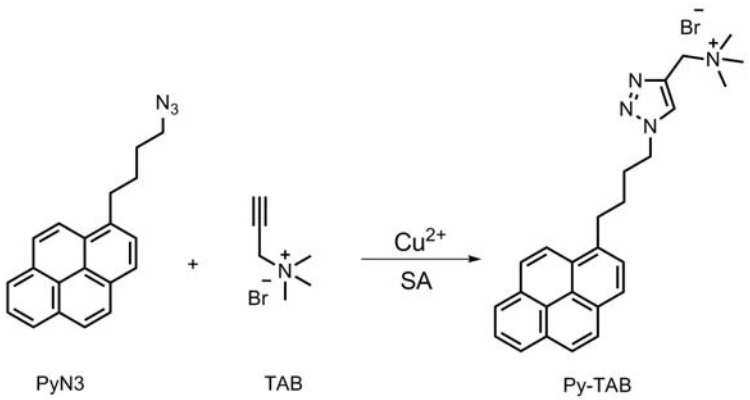

Figure S10. Synthesis of Py-TAB.

Synthesis of Py-TAB. 1-(4-azidobutyl)pyrene (35.4 mg, 0.12 mmol) in 10 mL DMSO was mixed with TAB (19.58 mg, 0.11 mmol) and sodium ascorbate (0.216 g, 0.13 mmol) in 5 mL water, and then copper sulfate pentahydrate (27.6 mg, 0.11 mmol) was added to the solution. The mixture was stirred overnight at room temperature. The product was filtered with 0.22 μm membrane and then extracted with ethyl ether. The aqueous phase was concentrated under reduced pressure and purified with HPLC (shim-pack PRC-ODS on SHIMADZU LC-6AD, acetonitrile/H_2O gradient elution, flow rate 2 mL/min) to give the desired product (22.73 mg, yield 40%). ^{1}H NMR (500 MHz, D_2O) δ 7.52 (1H, s), 7.21 (1H, s), 6.94 (7H, m), 6.56 (1H, s), 4.15 (2H, m), 3.32 (2H, s), 2.80 (9H, s), 1.93 (2H, s), 0.85 (2H, s), 0.51 (2H, s). ^{13}C NMR (125 MHz, D_2O) δ 135.52, 134.64, 130.52, 130.10, 128.75, 127.60, 126.88, 126.42, 126.03, 125.21, 124.17, 123.91, 122.67, 72.61, 59.36, 52.44, 31.21, 28.61, 27.05. HRMS (ESI), calcd $[M\text{-}Br]^+$ for $C_{26}H_{29}N_4$: 397.2387; found: 397.2381.

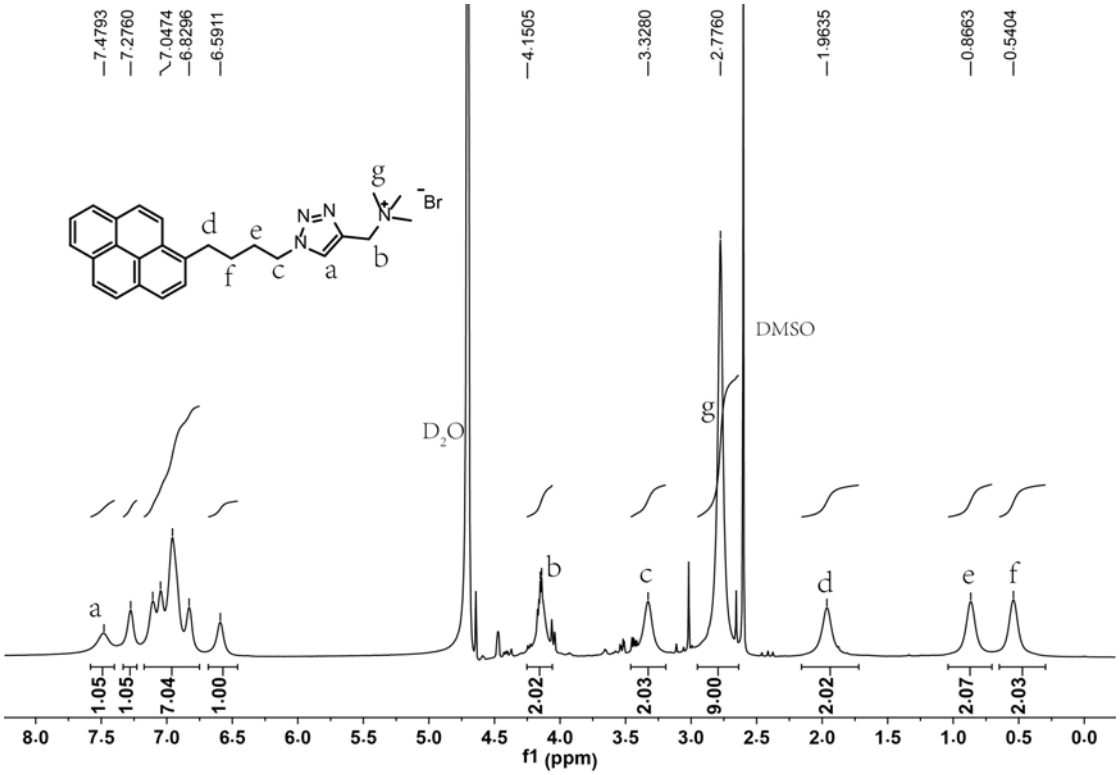

Figure S11.[1]H NMR spectrum of Py-TAB.

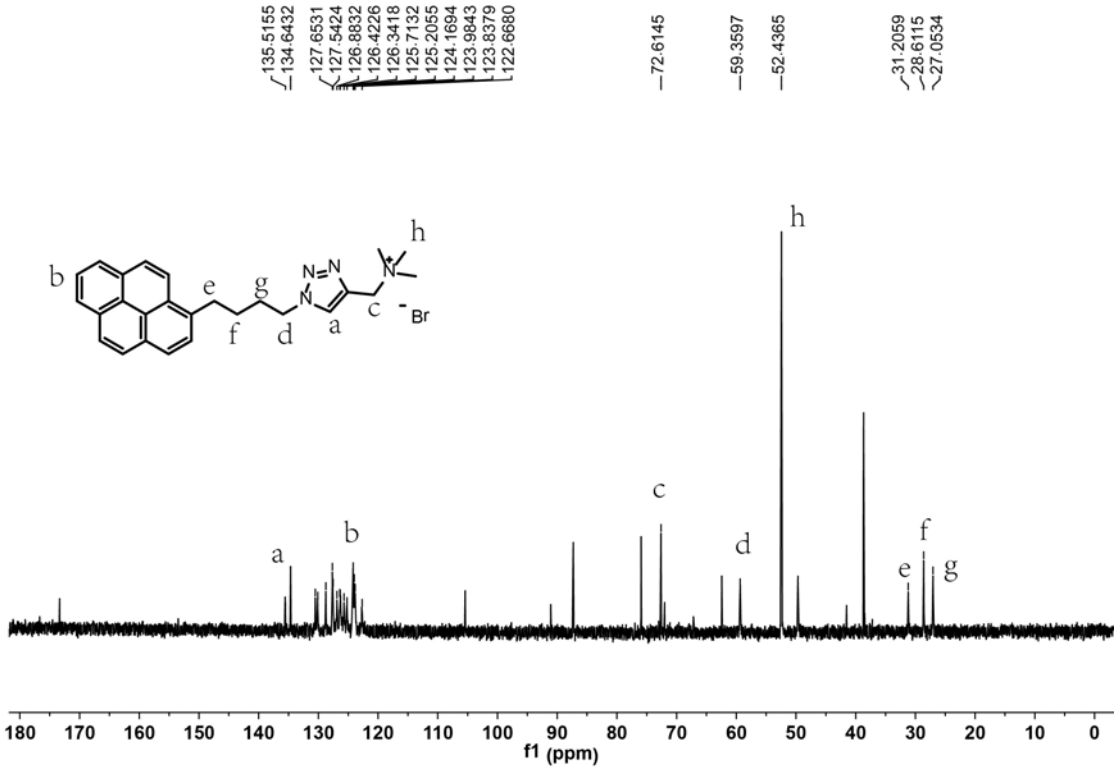

Figure S12.[13]C NMR spectrum of Py-TAB.

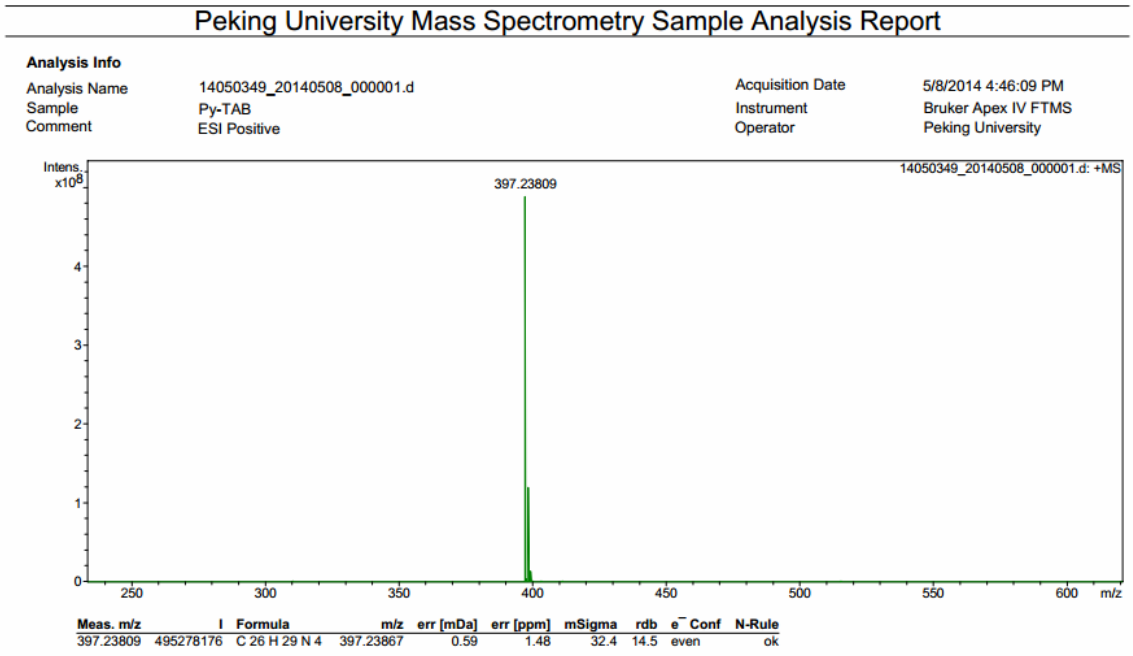

Figure S13. High resolution mass spectroscopy of Py-TAB.

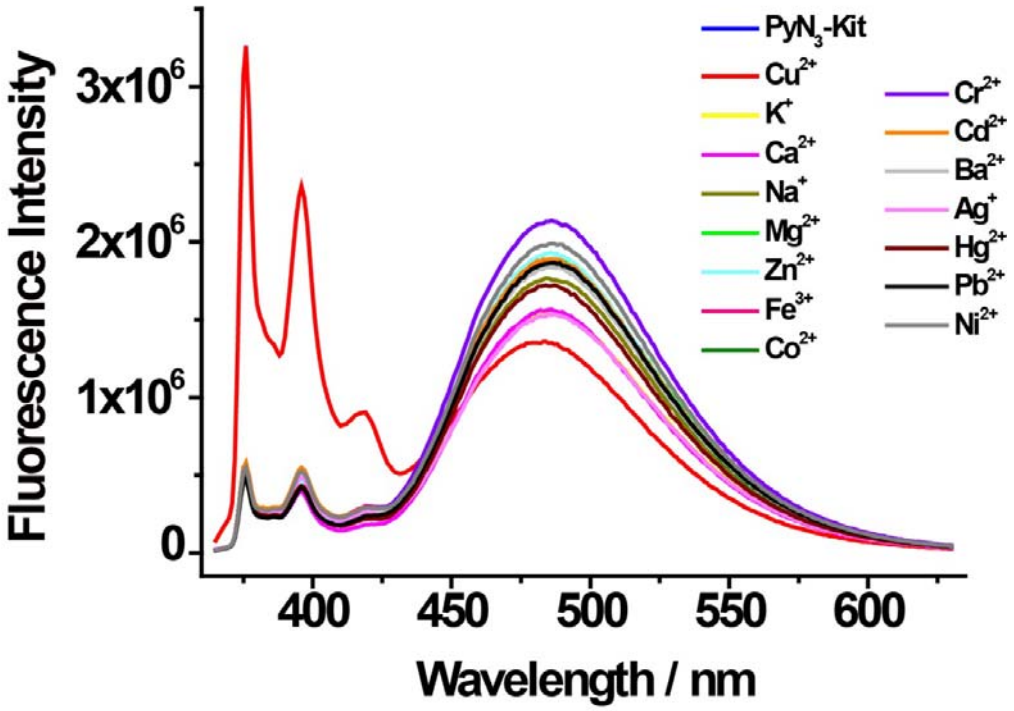

Figure S14. Fluorescent spectra of PyN_3-kit in the presence of Cu^{2+} and other metal ions in HEPES buffer (10 mM, pH 7.4, containing 0.05% (v/v) DMSO).

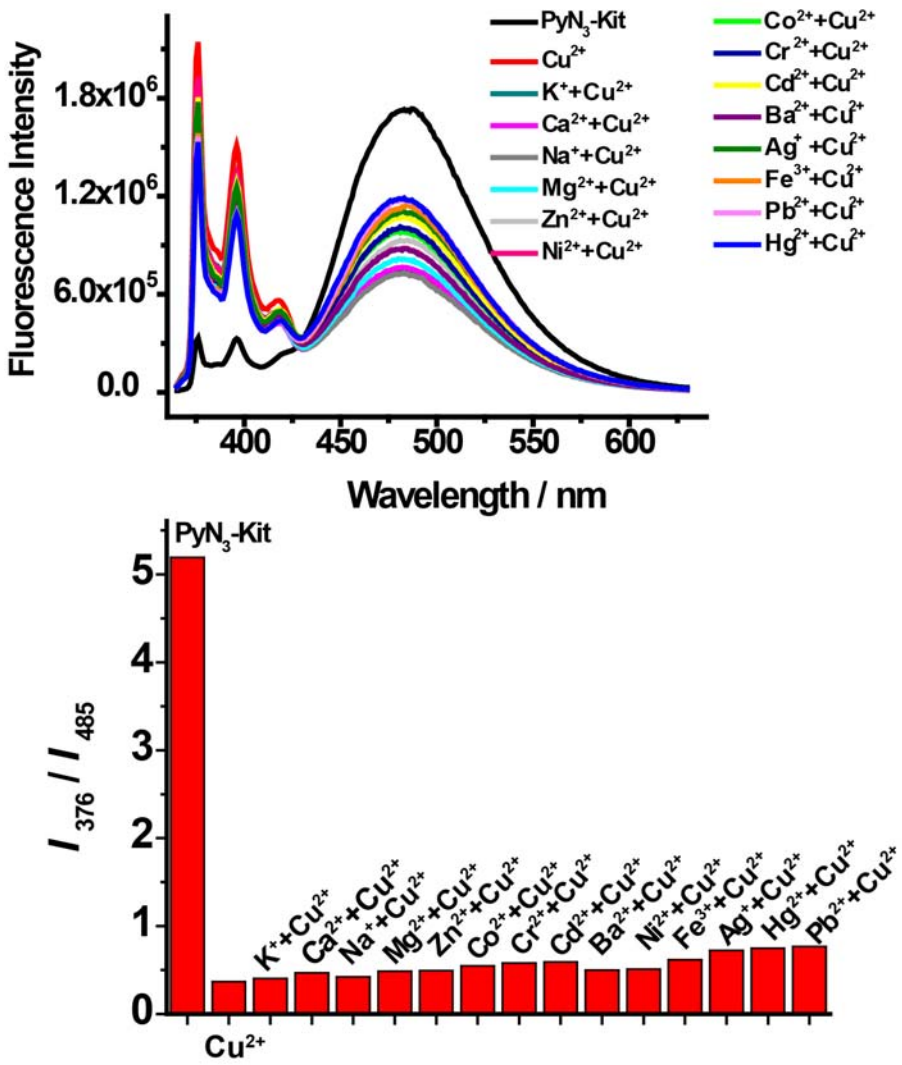

Figure S15. The specificity experiment of Cu^{2+} mixed with each metal ions in HEPES buffer (10 mM, pH 7.4, containing 0.05% (v/v) DMSO). Control: PyN_3-kit-Cu^{2+}, other metal ions: PyN_3-kit-Cu^{2+}+M. [PyN_3-kit] = 5 μM; [Cu^{2+}] = 5 μM; [other ions] = 5 μM.

Table S1. Comparison of advantages and disadvantages of this work and other reported methods (PL: photoluminescence)

	Detection limit	Response time	Advantage	Disadvantage
This work (click chemistry)	50 nM (PL) 5 μM (naked eye)	15 min	visual and fast detection, simple synthesis, high selectivity	visual detection with uv excitation
Other click chemistry	20 μM (naked eye)[20]	over night	visual detection, high selectivity	high detection limit, long response time, complicated probe preparation and modification
	0.8 μM (PL) 3 μM (naked eye)[12a]	15 min	visual and fast detection, simple synthesis, high selectivity	pre-treatment for real samples
	80 nM (PL)[21]	15 min	fast detection, simple synthesis	nonratiometric fluorescent probe, nonvisual detection
	65 nM (PL)[13]	90 min	excellent selectivity, Low detection limit	DNA modification needed, tedious detection steps
Pyrene based	40 nM (PL)[12c]	5 min	fast response, low detection	probe unstable and pH dependent
Tetraphenylethylene (TPE) Schiff base macrocycle	5 nM (PL) 10 μM (naked eye)[22]	8 h	high selectivity and sensitivity	complicated synthesis and long time of detection steps
Luminescent lanthanide chelates	1 μM (PL)[23]	1 h		complicated synthesis
QDs	10 nM (PL)[24]	2 h	excellent detection limit, detection of Cu^{2+} in live cells	complicated modification, tedious and long time of detection steps
	3 nM (PL)[10a]	20 min	high selectivity and sensitivity	pH dependent, system instability
ICP-MS	1 ng/g[8b]		simultaneous multiple element measurement, wide linear dynamic range	instruments, sample pretreatment
Electrochemical	0.48 nM[9]	30min	good stability, selectivity and reproducibility	electrode preparation

References

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