

Supporting Information

Silver(I) ion detection in aqueous media based on “off-on” fluorescent probe

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1. Experimental

Apparatus and reagents

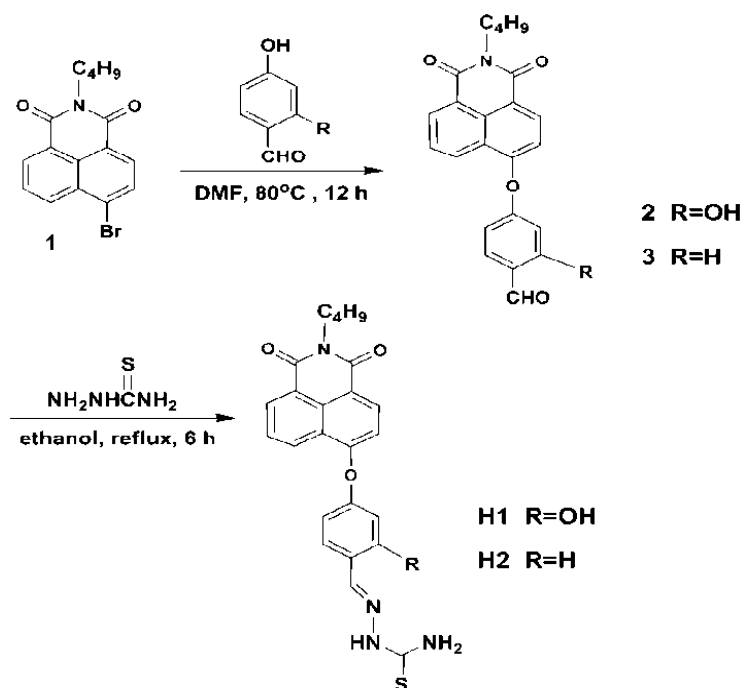
^1H NMR and ^{13}C NMR spectra were obtained on a Bruker WM-300 spectrometer, and chemical shifts were given in ppm from tetramethylsilane (TMS). Melting points were measured with a WRS-1B digital melting point apparatus (Shanghai, China). Electrospray ionization (ESI) spectroscopy was performed on a Thermo TSQ Quantum Mass Spectrometer. Fluorescence emission spectra were conducted on a HORIBA Fluoromax-4 spectrofluorometer. The pH measurements were carried out on a PHS-3C meter.

Doubly distilled water was used throughout the experiments. All the materials were used as received.

General procedure for spectroscopic measurements

A stock solution of **H1** (1.0 mM) was prepared in DMSO. To 5 mL glass tubes, 0.050 mL **H1** (1.0 mM) and a proper amount of Cu^{2+} stock solution (1.0 mM) were added subsequently and then diluted with ethanol/HEPES buffer (8:2, v/v, pH 6.5, 50 mM). The resulting solution was mixed thoroughly. For all measurements, excitation and emission slit widths were 7 nm and 3 nm, respectively, excitation wavelength was 370 nm.

Synthesis of compound 2, 3, H1, H2



Compound **2**

Under N₂ gas, compound **1** (300 mg, 0.90 mmol) and K₂CO₃ (500 mg, 3.62 mmol) were combined in DMF (10 mL) and stirred. 2, 4-dihydroxybenzaldehyde (130 mg, 0.9 mmol) in DMF (10 mL) was added dropwise. The reaction mixture was stirred at 80 °C for 12 h, filtered through Celite and the solvent was evaporated under reduced pressure, purification with silica gel column chromatography (CH₂Cl₂/petroleum ether=15:1, v/v) afforded as a yellow solid. Yields: 245 mg (70 %). ¹H NMR (δ: ppm, CDCl₃): 11.37 (s, 1H, CHO), 9.85 (s, 1H, OH), 8.65-8.67 (d, 1H, ArH), 8.56-8.57 (d, 1H, ArH), 8.44-8.46 (d, 1H, ArH), 7.76-7.79 (t, 1H, ArH), 7.59-7.61 (d, 1H, ArH), 7.26-7.27 (t, 1H, ArH), 6.73-6.76 (d, 1H, ArH), 6.61-6.62 (d, 1H, ArH), 4.18-4.21 (t, 2H, -NCH₂), 1.70-1.76 (m, 2H, CH₂), 1.42-1.49 (m, 2H, CH₂), 0.97-1.00 (t, 3H, CH₃). ¹³C NMR (δ: ppm, CDCl₃): 194.94 (CHO), 164.08, 163.48 (C=O), 156.48, 136.03, 132.55, 132.25, 132.05, 131.03, 129.81, 128.08, 127.19, 124.74, 123.03, 119.12, 117.62, 115.10, 110.73, 106.80, 40.30, 30.23, 20.39, 13.85. MS (ESI) m/z: 388.11 [M-H]⁻

Compound **3**

Under N₂ gas, compound **1** (500 mg, 1.5 mmol) and K₂CO₃ (900 mg, 6.52 mmol) were combined in DMF (50 mL) and stirred. 4-hydroxy benzaldehyde (220 mg, 1.8 mmol) in DMF (10 mL) was added dropwise. The reaction mixture was stirred at 80 °C for 12 h. The mixture was cooled and poured into ice-water. The precipitate produced was filtered and further purified by recrystallization from ethanol. Yields: 448 mg (80 %). ¹H NMR (δ: ppm, CDCl₃): 10.03 (s, 1H, CHO), 8.67-8.69 (d, 1H, ArH), 8.53-8.57 (m, 2H, ArH), 8.00 (t, 1H, ArH), 7.98-7.99 (t, 1H, ArH), 7.78-7.81 (m, 1H, ArH), 7.29-7.30 (t, 1H, ArH), 7.28 (s, 1H, ArH), 7.14-7.16 (d, 1H, ArH), 4.18-4.22 (t, 2H, -NCH₂), 1.71-1.77 (m, 2H, CH₂), 1.43-1.51 (m, 2H, CH₂), 0.98-1.01 (t, 3H, CH₃). ¹³C NMR (δ: ppm, CDCl₃): 190.50 (CHO), 164.12, 163.52 (C=O), 160.89, 157.54, 133.12, 132.36, 132.23, 132.05, 129.80, 128.15, 127.05, 124.48, 122.96, 119.77, 118.47, 113.50, 40.27, 30.24, 20.39, 13.85. MS (ESI) m/z: 374.13 [M+H]⁺.

Compound **H1**

Under N₂ gas, compound **2** (582 mg, 1.5 mmol) and thiosemicarbazide (164 mg, 1.8 mmol) were combined in ethanol (50 mL). The reaction solution was refluxed for 6 h and stirred for another 1 h at room temperature to form a lot of white precipitate. The solid was filtrated,

washed with ethanol three times. Crude product was purified by recrystallization from ethanol to give **H1** (554 mg, 80 %). ^1H NMR (δ : ppm, DMSO- d_6): 11.41 (s, 1H, OH), 10.34 (s, 1H, NH), 8.58-8.60 (d, 1H, ArH), 8.52- 8.55 (d, 1H, ArH), 8.41-8.43 (d, 1H, ArH), 8.38 (s, 1H, N=CH), 8.11-8.12 (s, 2H, NH₂), 7.96 (s, 1H, ArH), 7.86-7.90 (t, 1H, ArH), 7.15-7.18 (d, 1H, ArH), 6.72-6.74 (d, 1H, ArH), 6.71 (s, 1H, ArH), 4.02-4.05 (t, 2H, CH₂), 1.59-1.64 (m, 2H, CH₂), 1.32-1.39 (m, 2H, CH₂), 0.92-0.95 (t, 3H, CH₃). ^{13}C NMR (δ : ppm, DMSO- d_6): 178.14 (C=S); 163.84, 163.20 (C=O); 158.51, 158.42, 157.51, 138.97, 133.03, 131.92, 129.39, 129.08, 128.57, 127.69, 123.93, 122.65, 118.44, 117.22, 112.88, 111.62, 107.62 (ArC); 56.49, 30.14, 20.27, 14.18. MS (ESI): 461.01 [M]⁻, 922.60 [2M]⁻

Compound **H2**

Under N₂ gas, compound **3** (560 mg, 1.5 mmol) and thiosemicarbazide (164 mg, 1.8 mmol) were combined in ethanol (50 mL). The reaction solution was refluxed for 6 h and formed a lot of white precipitate. The solid was filtrated, washed with hot ethanol three times to give **H1** (468 mg, 70 %). Mp: 240.9-241.4°C; ^1H NMR (δ : ppm, DMSO- d_6): 11.48 (s, 1H, NH), 8.65-8.67 (d, 1H, ArH), 8.57-8.59 (d, 1H, ArH), 8.43-8.45 (d, 1H, ArH), 8.20 (b, 1H, NH), 8.12 (s, 1H, HC=N), 8.05 (b, 1H, NH), 7.96-7.98 (d, 2H, ArH), 7.91-7.93 (t, 1H, ArH), 7.31-7.32 (d, 2H, ArH), 7.10-7.12 (d, 1H, ArH), 4.04-4.07 (t, 2H, CH₂), 1.59-1.65 (m, 2H, CH₂), 1.32-1.39 (m, 2H, CH₂), 0.92-0.94 (t, 3H, CH₃). ^{13}C NMR (δ : ppm, DMSO- d_6): 178.48 (C=S); 163.85, 163.20 (C=O); 158.83, 156.40, 141.63, 133.07, 131.99, 131.93, 129.99, 129.40, 128.58, 127.66, 123.86, 122.63, 120.98, 117.08, 112.35, 55.38, 30.14, 20.26, 14.18. MS (ESI): 445.20 [M-H]⁻, 890.95 [2M-H]⁻

2. NMR and MS spectra of compound 2, 3, H1 and H2

Fig. S1

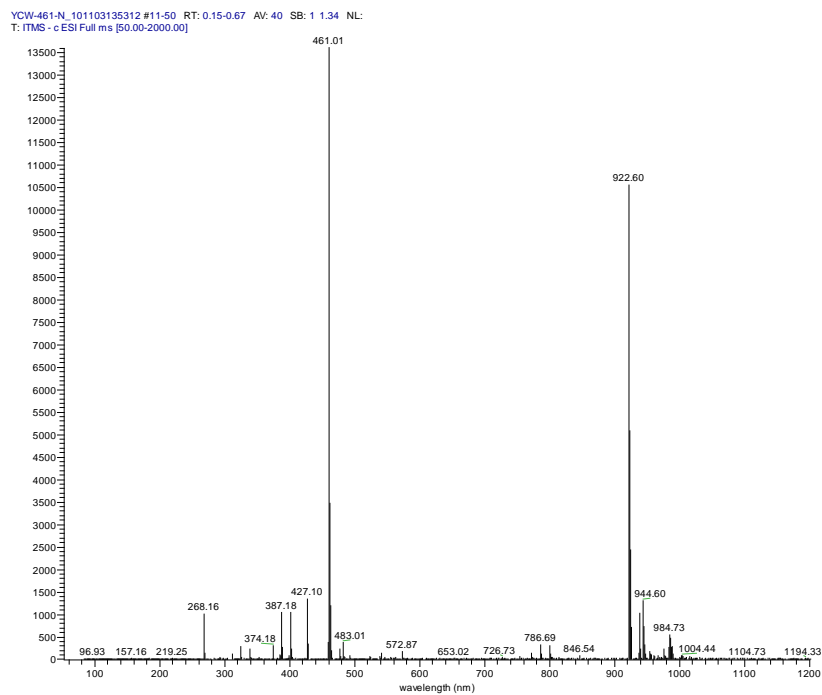


Fig. S2

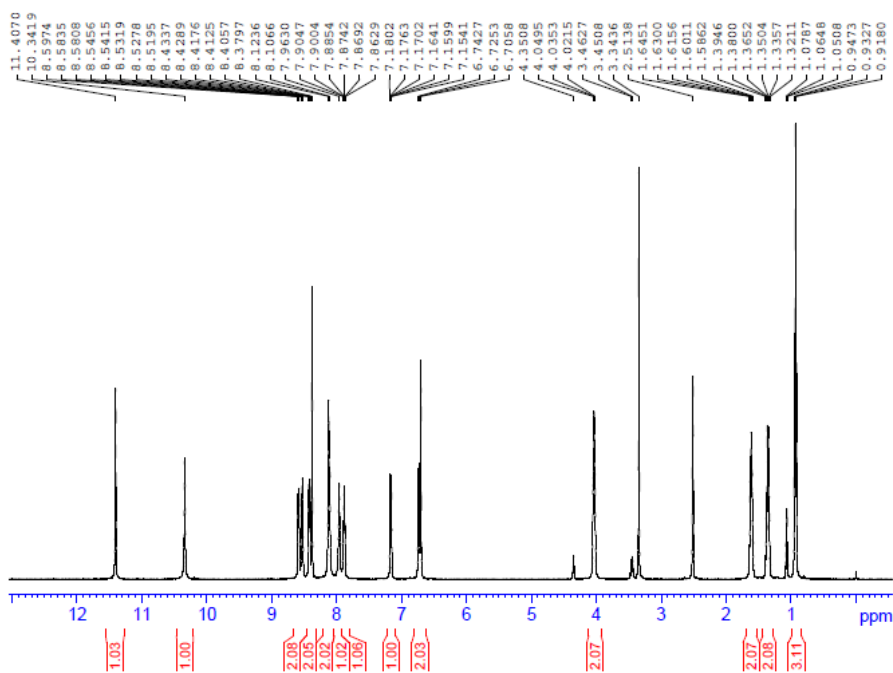


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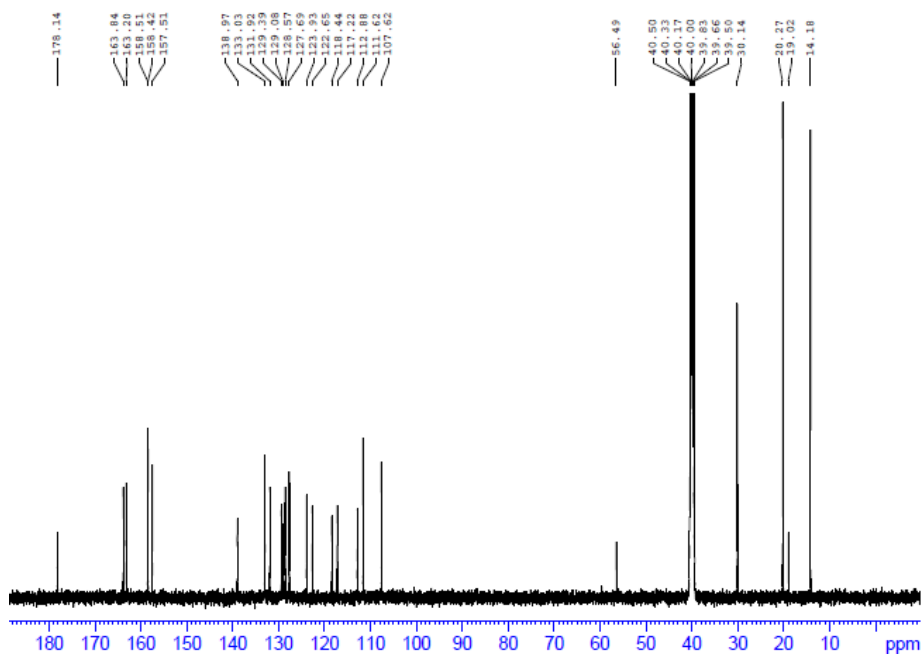


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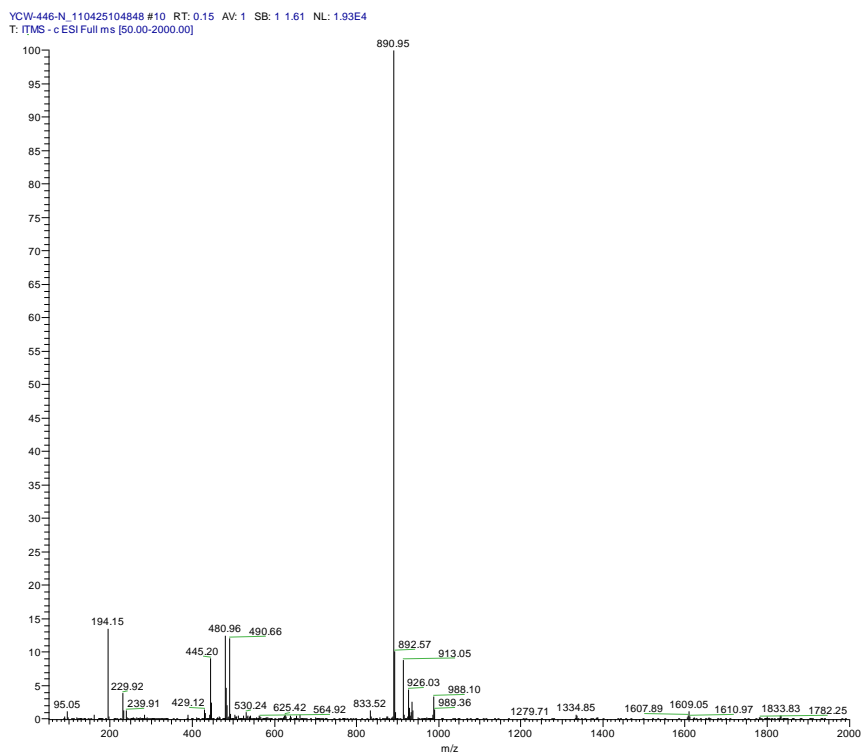


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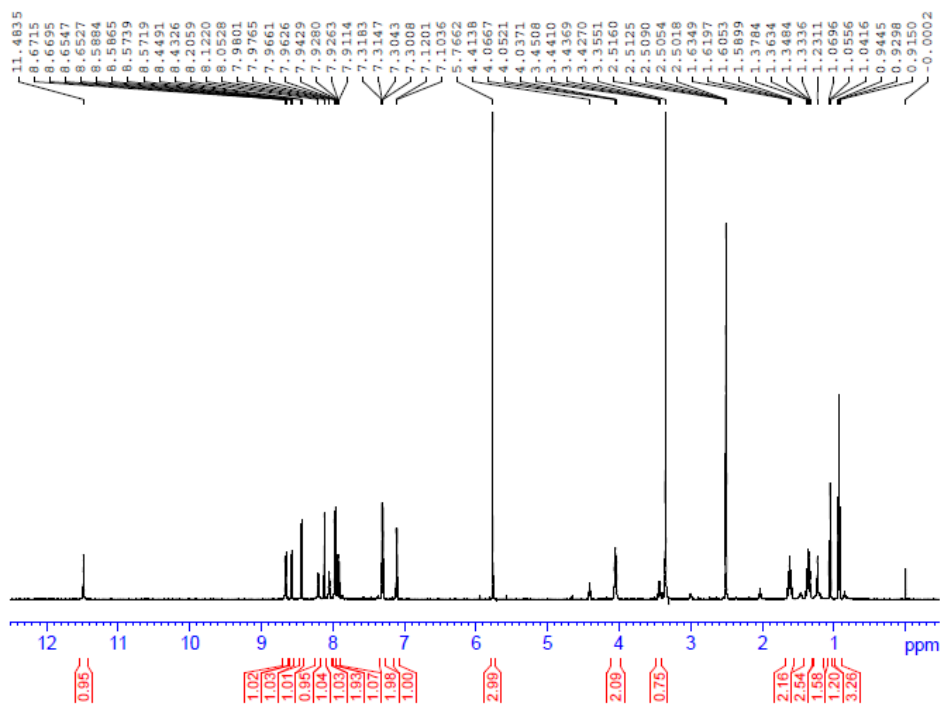


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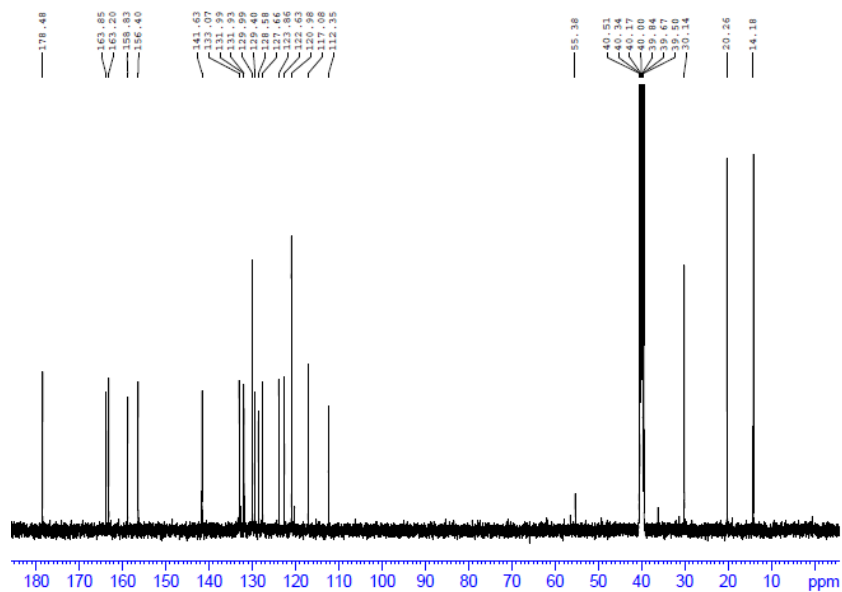


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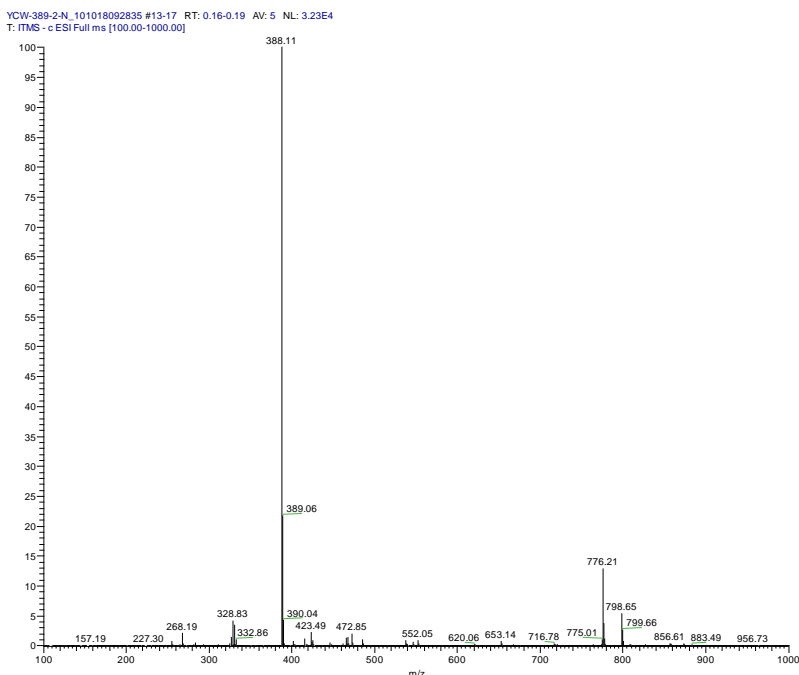


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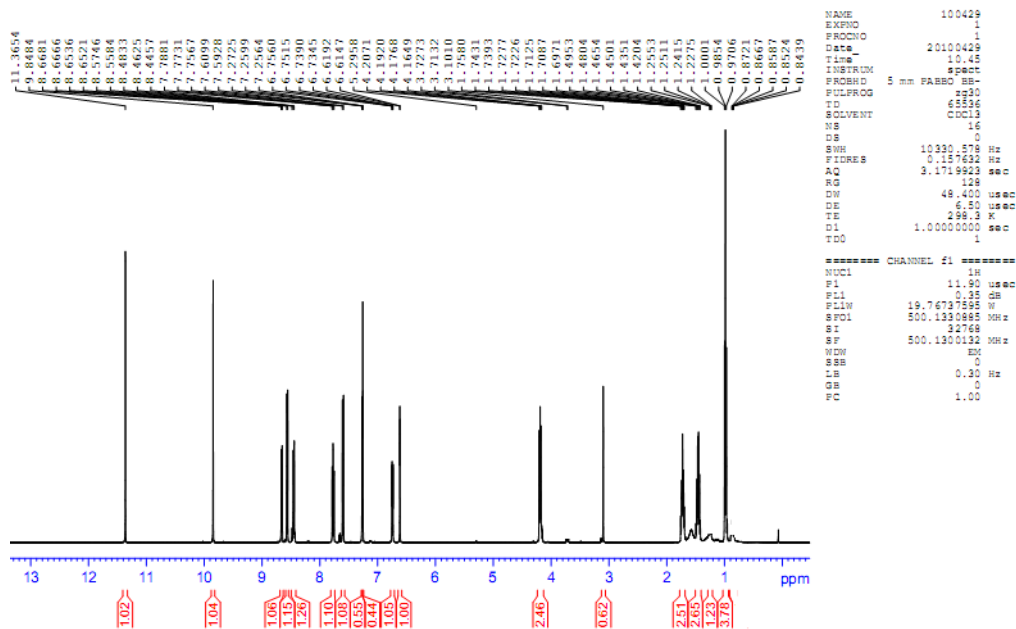


Fig. S9

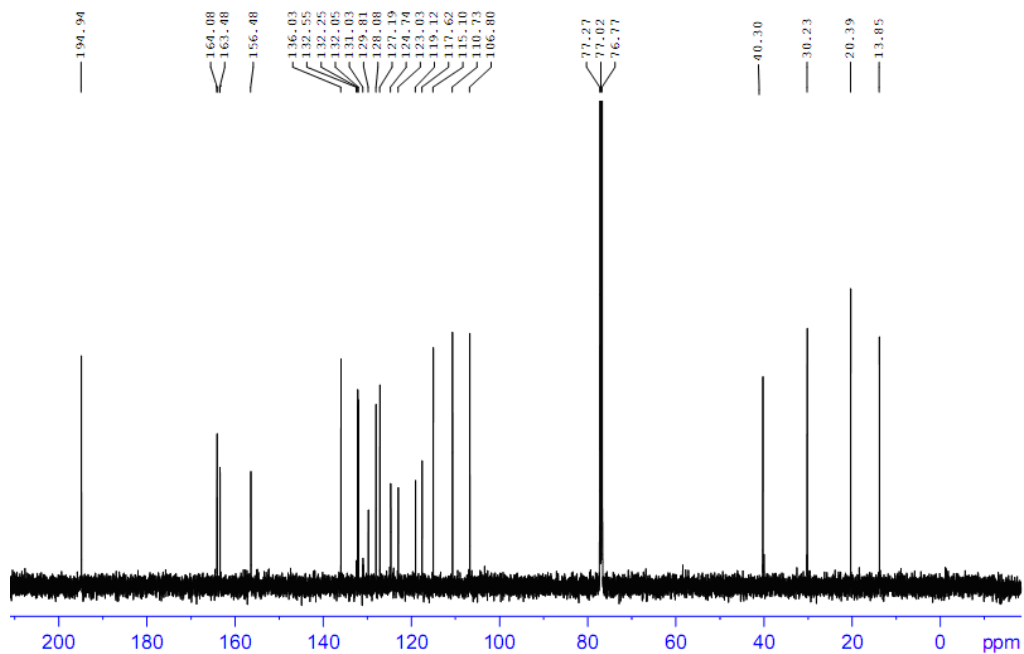


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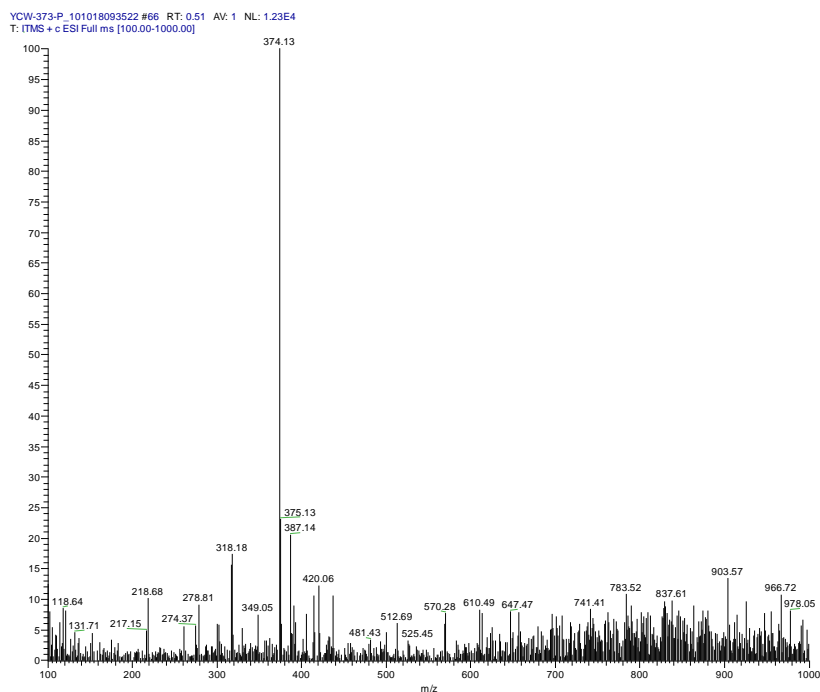


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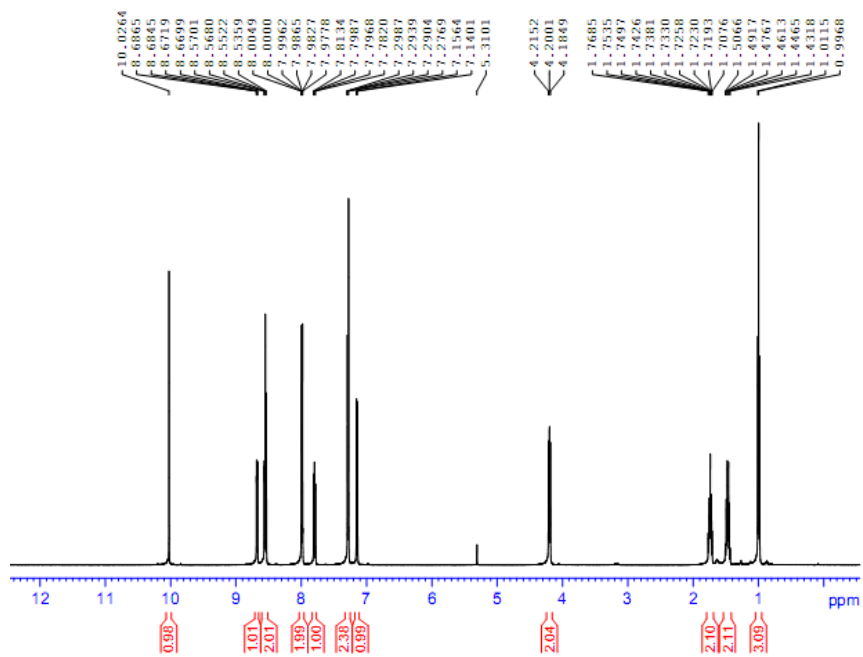
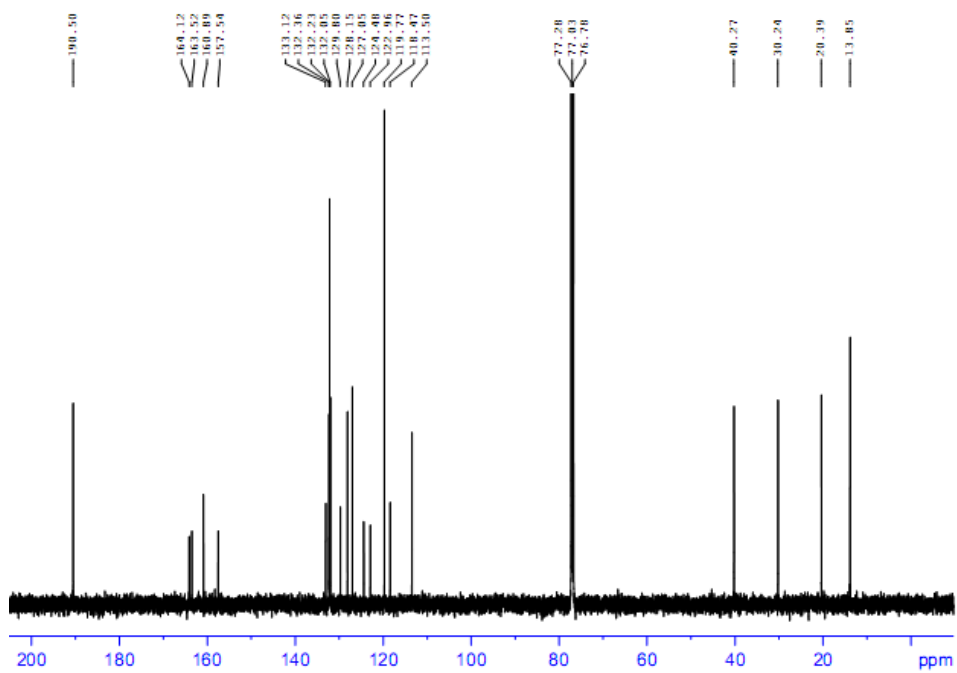


Fig. S12



3. Supplementary spectral data

Fig. S13

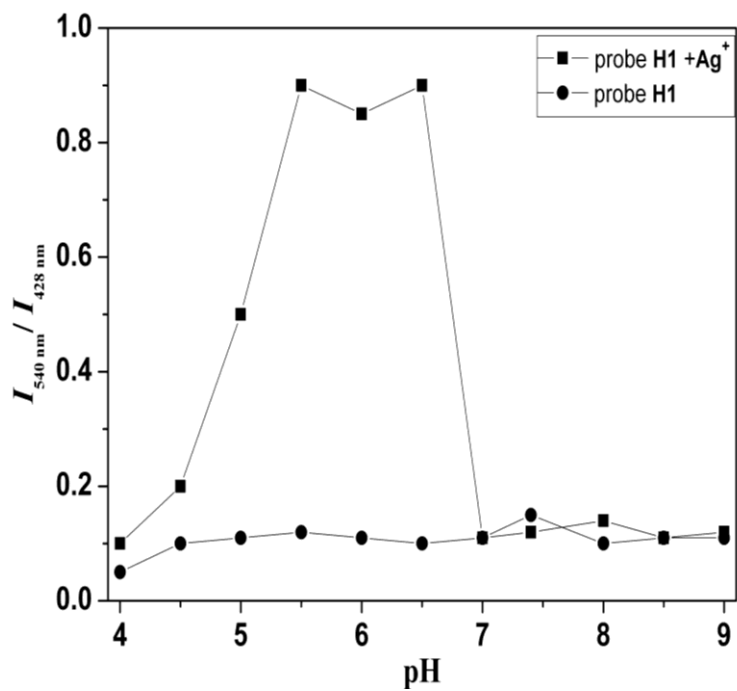


Fig. S14

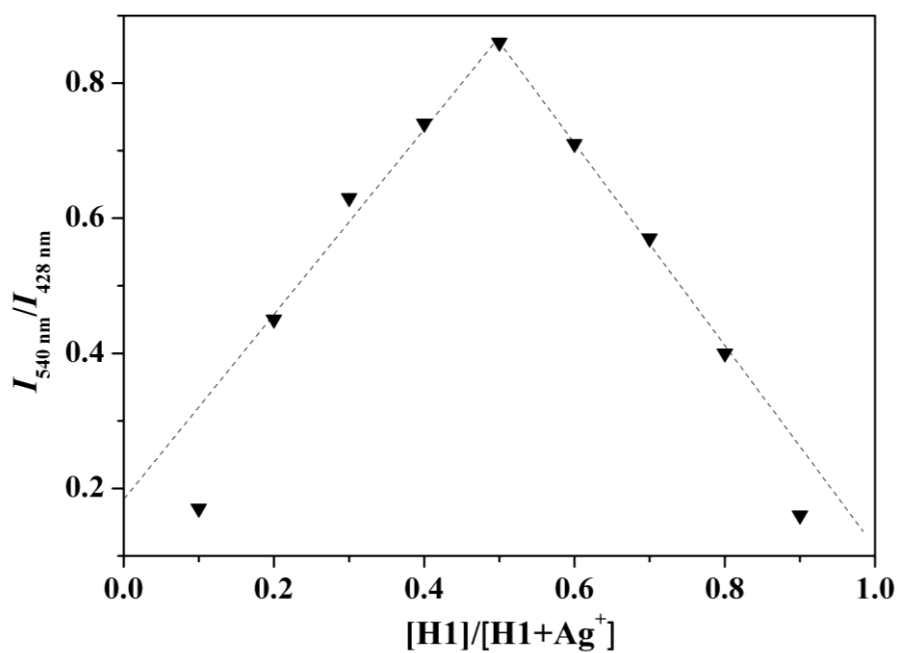


Fig. S15

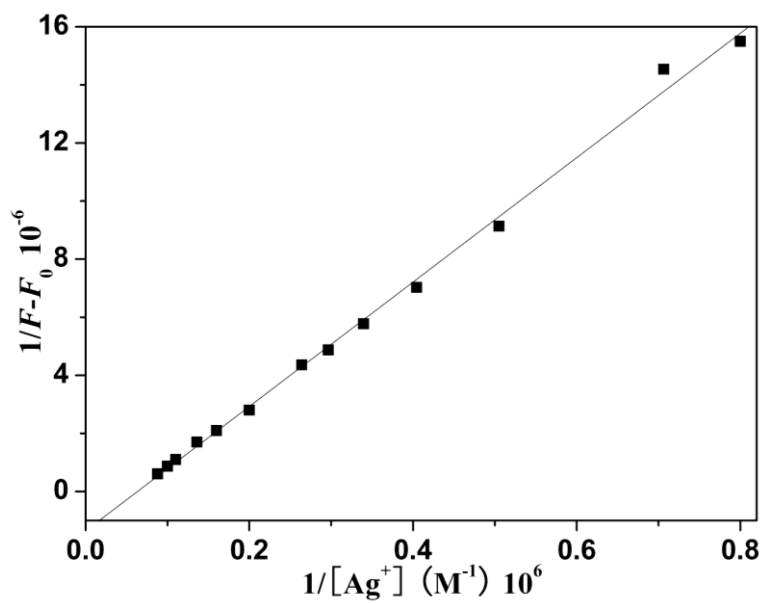


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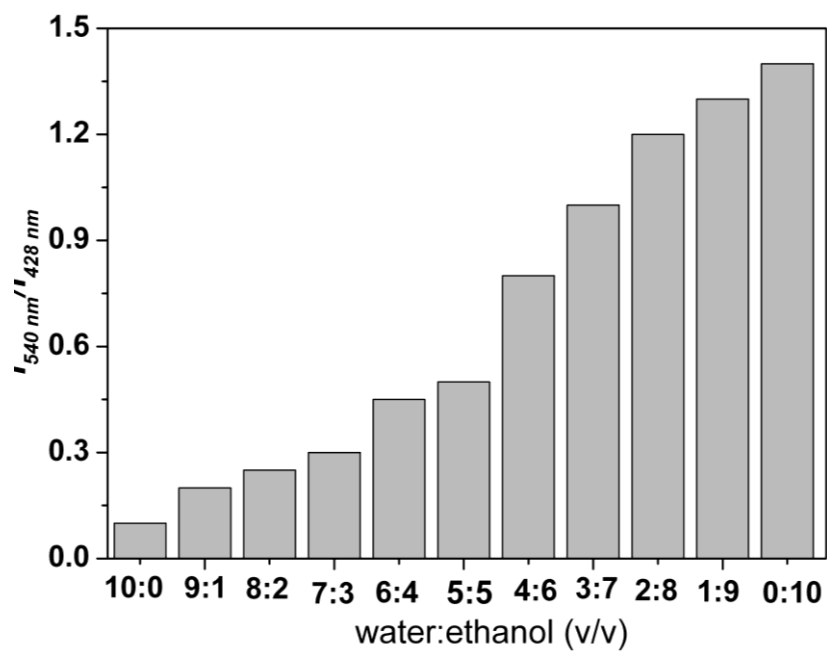


Table 1

Real sample	Ag ⁺ (10 ⁻⁶ M)	Sum results (n=3)	Recovery (%)
	Added		
Tap water	0.9	0.81	90
	3.0	3.6	120
	5.0	4.8	96