Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Developed a Unimolecular Conjugated Polymeric Micelles for highly Selective Detection and Recovery of Gold from Electronic Wastes

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Content

1. *Reagents and Apparatus*

All reagents and solvents were commercially purchased. Thin-layer chromatography (TLC) was performed on efficient silica gel plates. 200-300 mesh chromatography silica gel was used for Chromatographic purification of chemical products. 1H NMR spectra were recorded in the particular solvent stated by using Bruker Avance III. Mass spectra were carried out by using Brucker Hct-High capacity ion trap mass spectrometer. Facility at Jilin University. The gel permeation chromatography (GPC) was analyzed on Waters 2690 high performance liquid chromatography with THF as eluent and polystyrene as standard. All fluorescence measurements were recorded on Hitachi Fluorescence Spectrophotometer F-2700. UV absorption spectrum measurements were recorded by using Shimadzu UV-3100 The ***fluorescence quantum yields*** were performed by using Edinburgh Instrument FLS920. All pH measurements were carried out on Sartorious PB-10.

The metal chloride salts were dissolved in distilled water for obtaining the stock solutions of metal ions: Co^{2+}, Ag^{+}. Cr^{3+}, Cd^{2+}, Pb^{2+}, Fe^{2+}, Ba^{2+}, Mn^{2+}, Ni^{2+}, Mo^{+6}, Ca^{2+}, Mg^{2+}, Al^{3+}, Cu^{2+} and Zn^{2+} (1 mM). Other concentrations of metal ions can be obtained by gradual dilution. Probe was dissolved in PBS buffer (0.05 M, pH=7.2) to get a 0.5 mM stock solution.

The testing system for the effect of Au(III) on absorption and emission spectroscopic properties towards PPE-OB-PEG was set: 30 μL of probe stock solution, 30 μL metal ions stock solution, and then added 2940 μL PBS buffer (0.05 M, pH 7.2) finally get a 3000 μL solution system. For all measurements, the excitation wavelength was set at 370 nm; The excitation slit widths was set at 10 nm and the emission slit widths was set at 5 nm; the photomultiplier voltage was set at 400 V. After incubating with various analytes for 2 min, the emission spectrum was measured and scanned from 390 nm to 650 nm at 1200 nm/min by fluorescence spectrophotometer.

2. *Extraction Procedures*

Preparation of electronic waste samples

The collected electronic waste was crushed, weighing 5 g of powder and dissolved in 20 mL of aqua regia. After the powder is completely dissolved, the solvent evaporates, and the residual solid is dissolved in HCl (0.01M, 20 mL). The solution is filtered and clarified, and the solution is fixed to 50mL. The sample of electronic waste is obtained.

The extractions of Au from single-Au solution of water into chloroform using PPE-OB-PEG.

The extraction was carried out, Au(III) solution (5 mL, 0.50 mM) containing PPE-OB-PEG (2.00 mM, repeat unit) was contacted with chloroform (4 mL) at room temperature for 30 min with magnetic stirring. The contents of Au(III) extracted into the organic phase were determined using ICP-OES by dissolving with HCl (0.01M, 50 mL) after drying the solvent.

The extractions of Au from electronic waste samples into chloroform using PPE-OB-PEG.

The extractions were carried out, 5 mL of electronic waste streams containing PPE-OB-PEG (2.00 mM, repeat unit) was contacted with chloroform (4 mL) at room temperature for 30 min with magnetic stirring. The contents of Au(III) extracted into the organic phase were determined using ICP-OES by dissolving with HCl (0.01M, 50 mL) after drying the solvent.

3. Synthesis of compounds

Synthesis of 1,4- di (ethyl 4-oxybutyrate) benzene (M_1)

The potassium hydroxide powder (2.24 g, 40 mmol) was dispersed in 20 mL DMSO and agitated violently. After rapid addition of hydroquinone (0.88 g, 8 mmol) in argon atmosphere, ethyl 4-bromobutyrate (4.60 mL, 32 mmol) was injected slowly into the mixture. After stirring for 48 h, the reaction mixture was extracted with dichloromethane, then washed with saturated salt water. The crude product was purified by column chromatography (Ethyl acetate / petroleum ether, V/V=1:5) after vacuum distillation to remove the solvent, the white powder $\mathbf{M_1}$ was obtained. Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.83 (s, 4H, Ar H), 4.22 – 4.09 (m, 4H, CH_2), 3.97 (t, *J* = 6.1 Hz, 4H, CH_2), 2.52 (t, *J* = 7.3 Hz, 4H, CH_2), 2.14 – 2.04 (m, 4H, CH_2), 1.28 (t, *J* = 7.1 Hz, 6H, CH_3). MS (ESI) *m/z*: [M + Na]: 362.3.

Synthesis of 1,4-di (ethyl 4-oxybutyrate)-2,5-diiodobenzene (M_2)

KI (0.31 g,1.44 mmol) and I_2(0.80 g,3.15 mmol) was dissolved in a mixture of 12 mL ethanol, 0.2 mL sulfuric acid and 0.6 mL water. The reaction mixture was stirred for 24 hours at 60°C after adding the compound $\mathbf{M_1}$(0.98 g,2.9 mmol), the reaction was monitored by TLC (Ethyl acetate / petroleum ether, V/V=1:5). Finally, the crude product was added to 500 mL of ice water, then vacuum was pumped and washed with a large amount of cooled ethanol. The final product was collected as white powder. Yield: 80%.^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.18 (s, 1H, Ar H), 4.16 (q, J = 7.1 Hz, 2H, CH_2), 4.00 (t, J = 6.0 Hz, 2H, CH_2), 3.80 – 3.62 (m, 1H , CH_2), 2.59 (t, J = 7.3 Hz, 2H, CH_2), 2.17 – 2.04 (m, 2H, CH_2), 2.19 – 2.02 (m, 2H, CH_2), 1.36 – 1.14 (m, 4H, CH_3). MS (ESI) *m/z*: [M + Na] $^+$: 613.0.

Synthesis of poly (2,5-bis (ethyl oxbutyrate)-1,4-phenylethynylene-alt-1,4-phenyleneethynylene) (PPE-OBE)

A mixture of 1,4-diethynylbenzene (201.60 mg, 1.60 mmol), $Pd(PPh_3)_4$ (23.04 mg, 0.02 mmol), CuI (3.82 mg, 0.02 mmol) and compound $\mathbf{M_2}$ (973.5 mg, 1.65 mmol) was poured into a 100mL flask. Then a mixture of 36 mL chloroform and 6 mL triethylamine was added into the flask, after stirring at 50°C for 24 h under nitrogen protection, the mixture was cooled to room temperature. The coarse product was slowly added into 200mL of ether, and the pure product was collected by centrifugation, then dried and collected in a vacuum dryer, and the golden powder PPE-OBE was observed. Yield: 76% ^{1}H NMR (400MHz, $CDCl_3$, δ): 7.53 (s, 4H, *J* = 4.5 Hz, H_g), 7.03 (s, 2H, H_a), 4.24-4.04 (m, 8H, H_b, H_e), 2.63 (d, *J* = 7.6 Hz, 4H, H_d), 2.18 (d, *J* = 6.2 Hz, 4H, H_c), 1.26 (t, *J* = 6.7 Hz, 6H, H_f)

Synthesis of poly (2,5-bis (Polyethylene glycol oxybutyrate)-1,4 phenylethynylene-alt-1,4-phenyleneethynylene) (PPE-OB-PEG)

A mixture of M-PEG (10.00 g, 5mmol), K_2CO_3(0.028 g, 0.2mmol) and PPE-OBE (0.477g, 1mmol, repeat unit) was dissolved into 50mL DMSO and Stirred for 6 h at 70 °C under decompression. The coarse product was poured into ether and stirred for

1h at room temperature. The yellow powder PPE-OB-PEG was observed. Yield: 80%. GPC measurement indicated that the weight-average molecular weight was 21170 with a polydispersity of 1.27. ^{1}H NMR (400MHz, $CDCl_3$, δ): 7.53 (4 H, d, *J* = 9.7), 7.02 (2 H, s), 4.39 – 3.95 (4 H, m), 3.66 (357 H, s), 3.40 (6 H, s), 2.09 (8 H, d, *J* = 6.2)

4. *Characterization of PPE-OB-PEG*

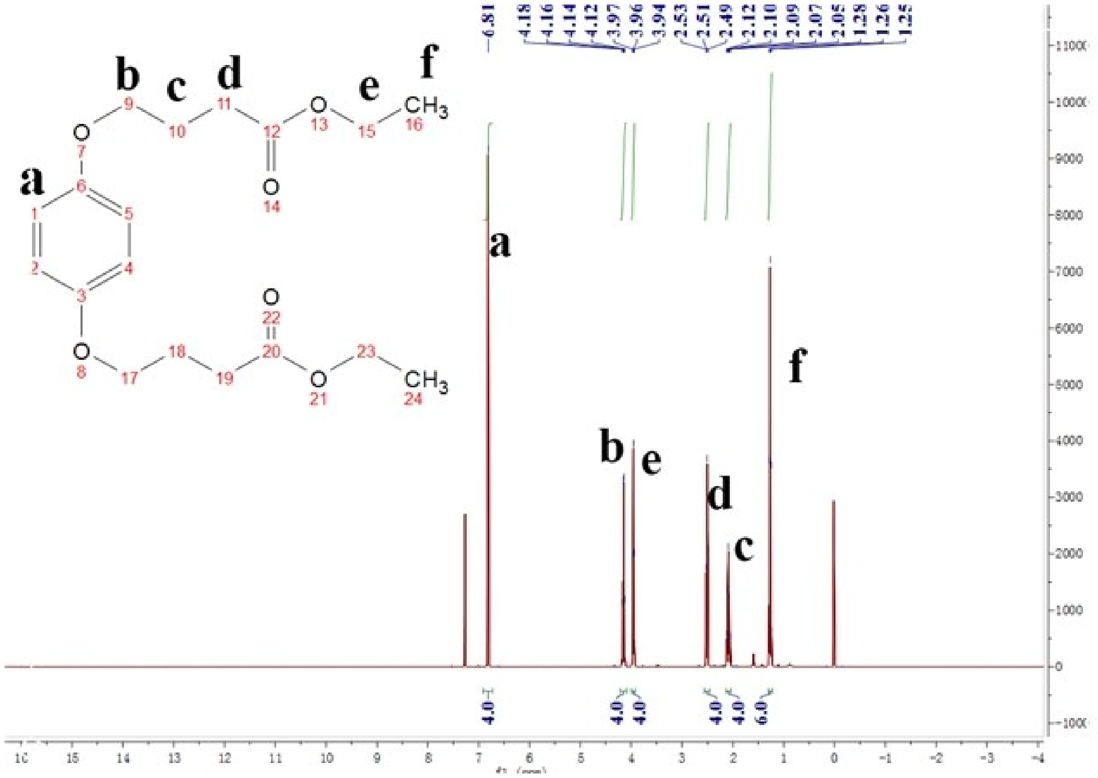

Fig.S1 ^{1}HNMR data for compound M_1 in $CDCl_3$

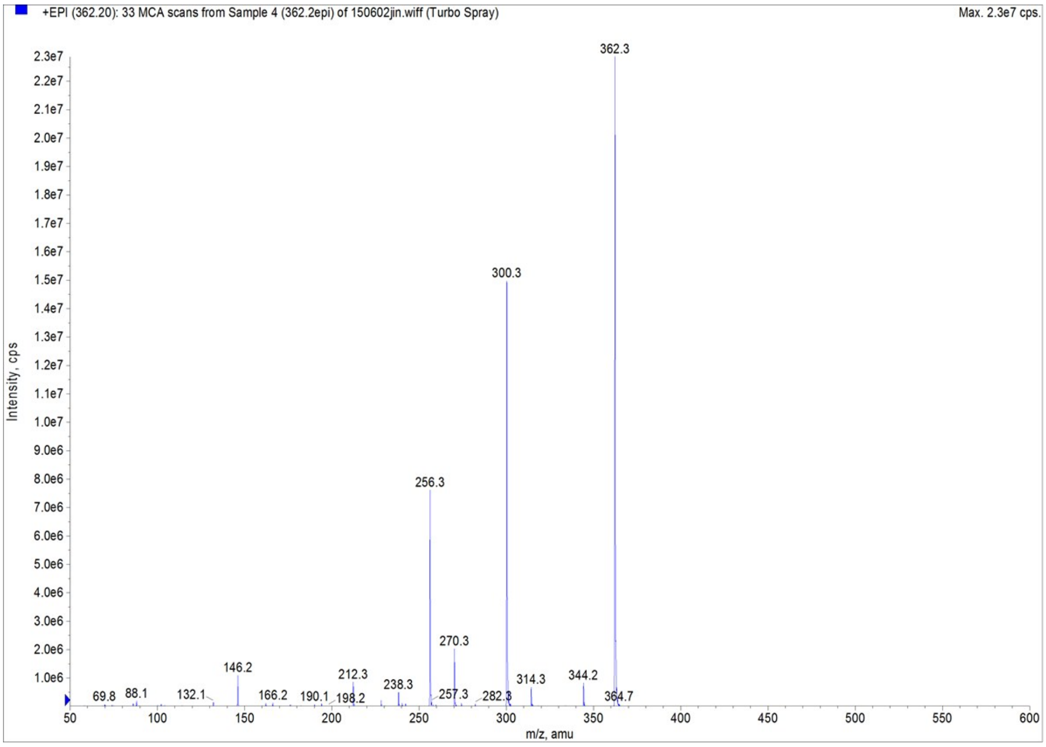

Fig.S2 ESI-MS of Compound M_1 in ethanol

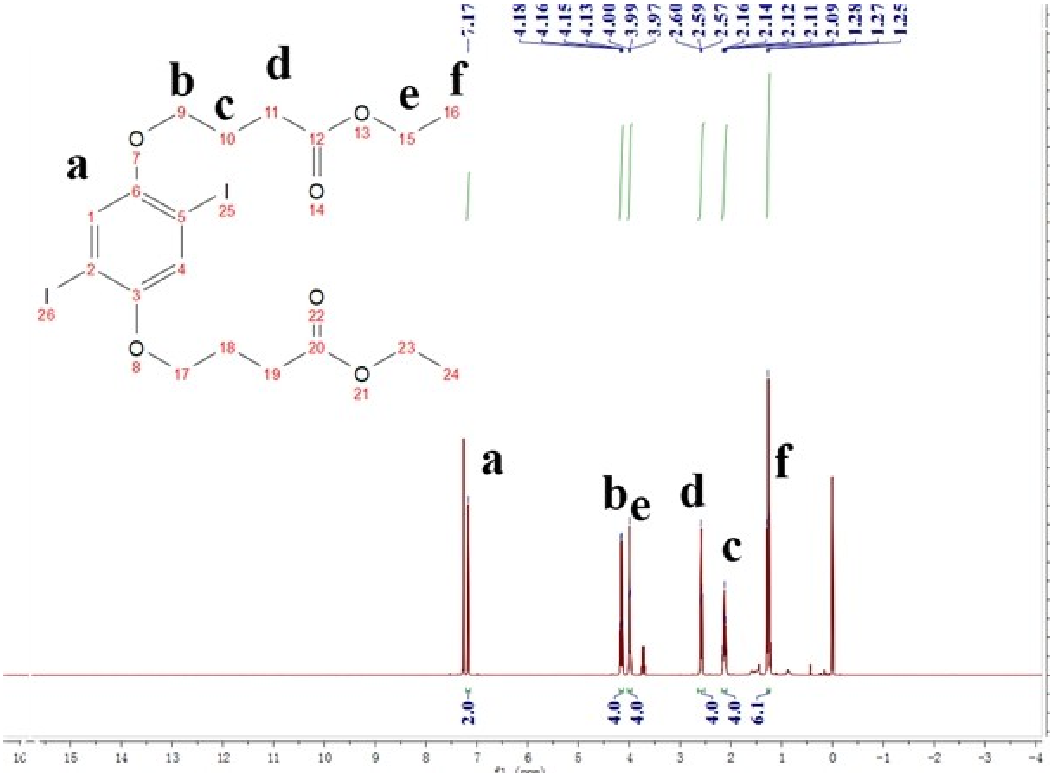

Fig.S3 ^{1}HNMR data for compound M_2 in $CDCl_3$

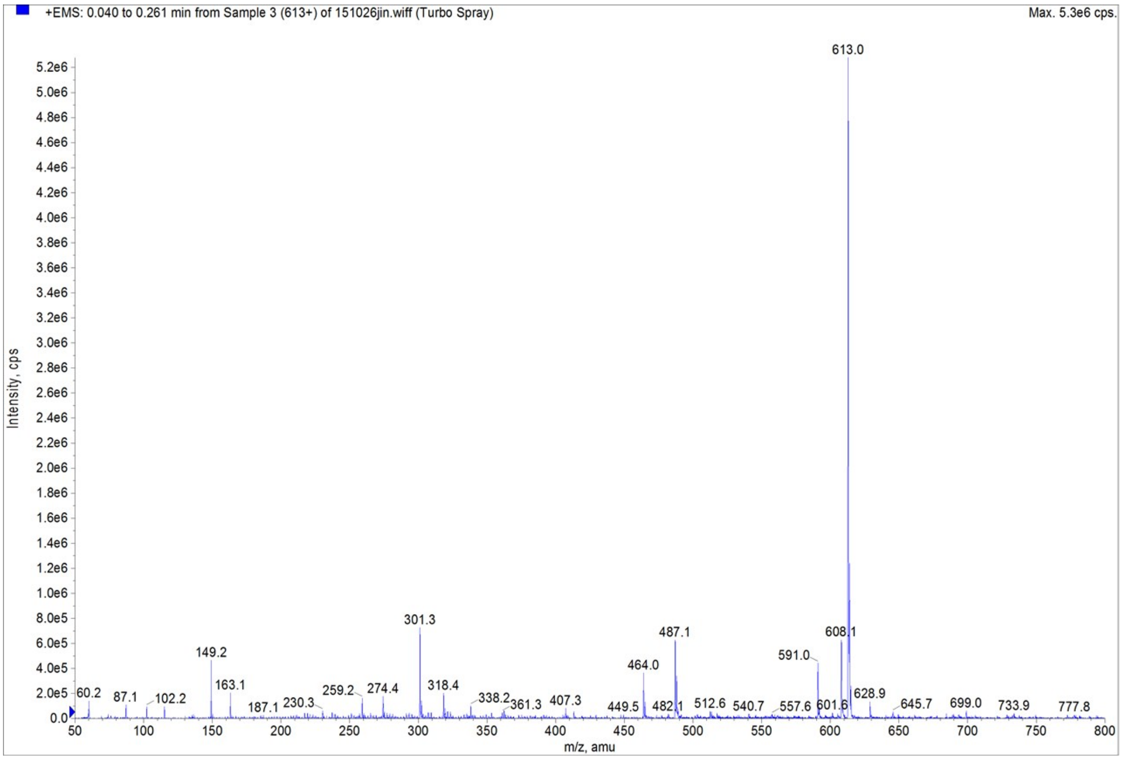

Fig.S4 ESI-MS of Compound M_2 in ethanol

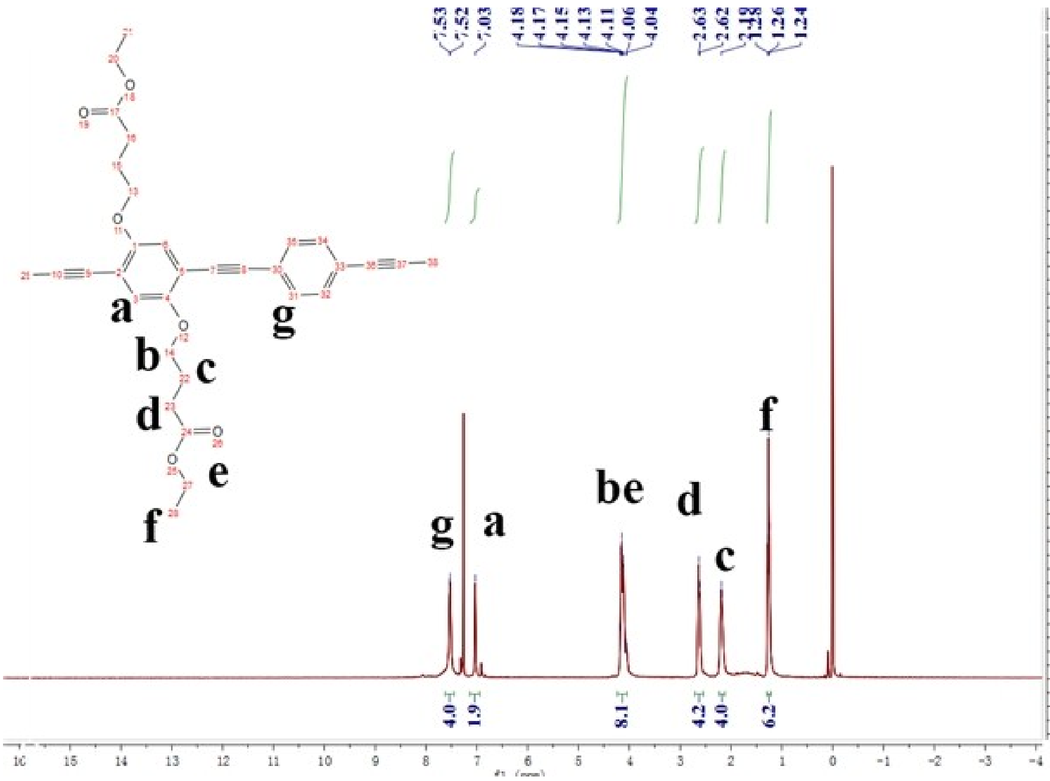

Fig.S5 ^{1}HNMR data for PPE-OBE in $CDCl_3$

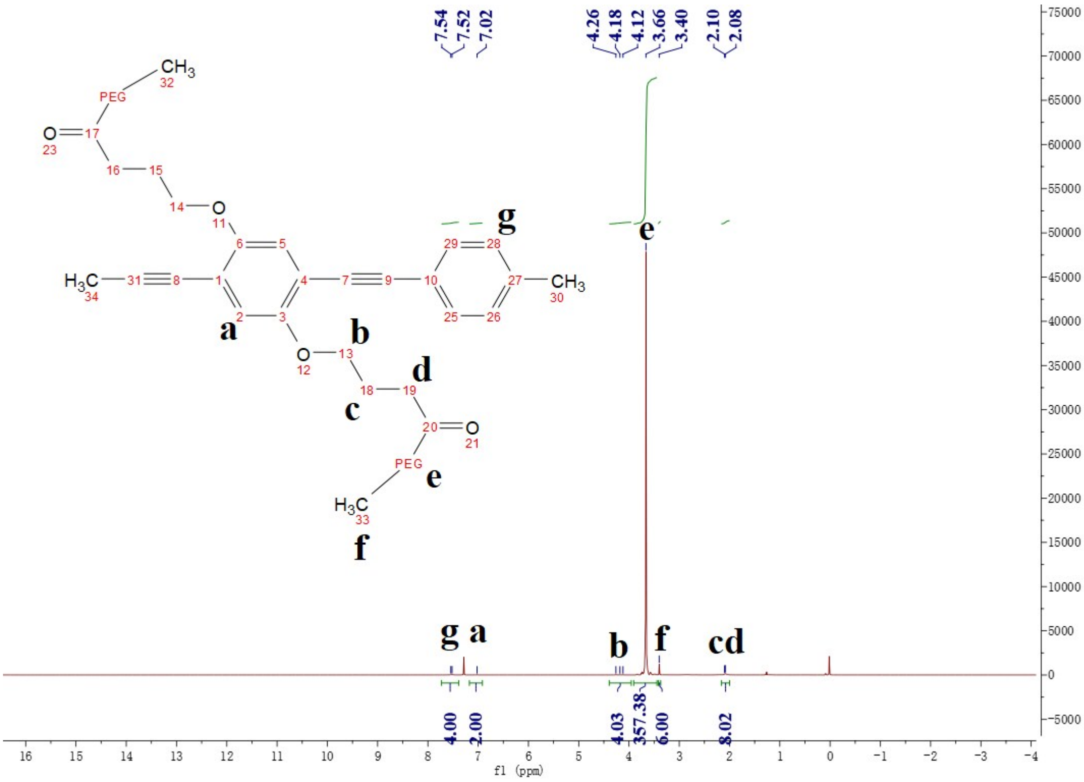

Fig.S6 ^{1}HNMR data for PPE-OB-PEG in $CDCl_3$

5. Supplementary Figures and Table

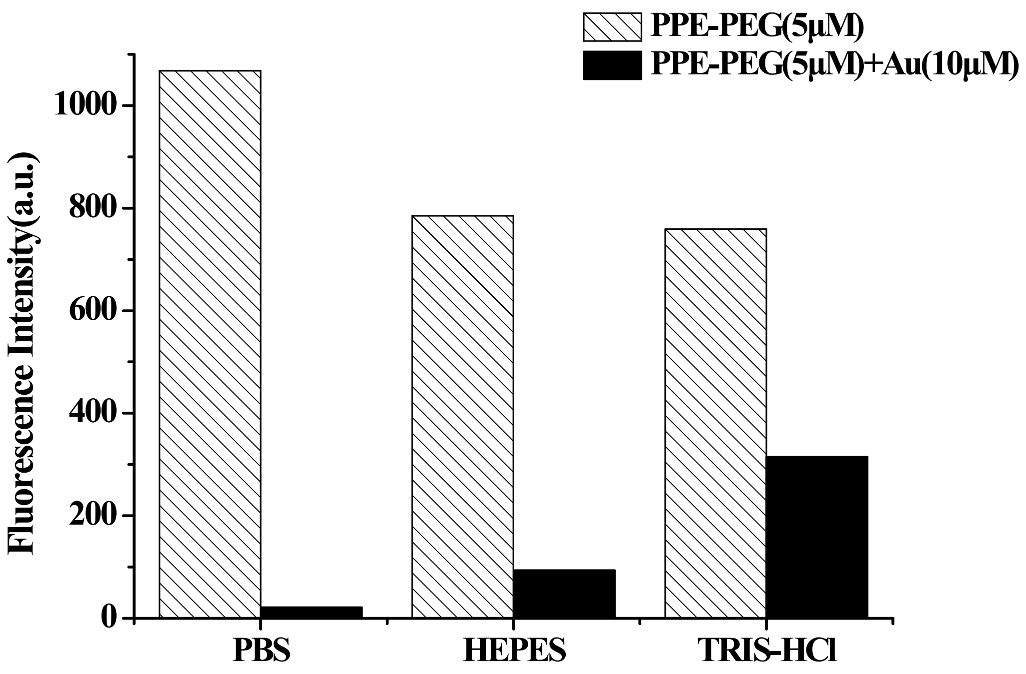

Fig.S7 The effect of different Buffers to the fluorescence intensity of PPE-OB-PEG (5 μM) in presence of Au(III) (10 μM) and in absence of Au(III)

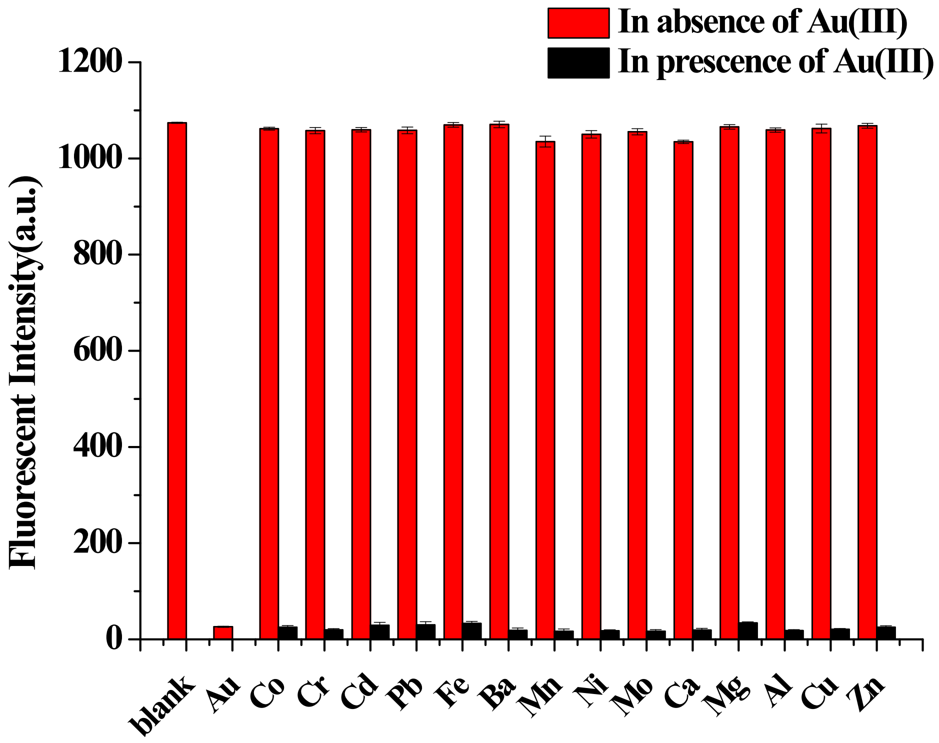

Fig.S8 Column diagram of metal ion selectivity of PPE-OB-PEG [PPE-OB-PEG 5 μM, Au(III) 10 μM and 10 μM for all remaining metal ions; Red bar: fluorescent emission intensity of PPE-OB-PEG with different metal ions; Black bar: different metal ions in the presence of Au(III)];

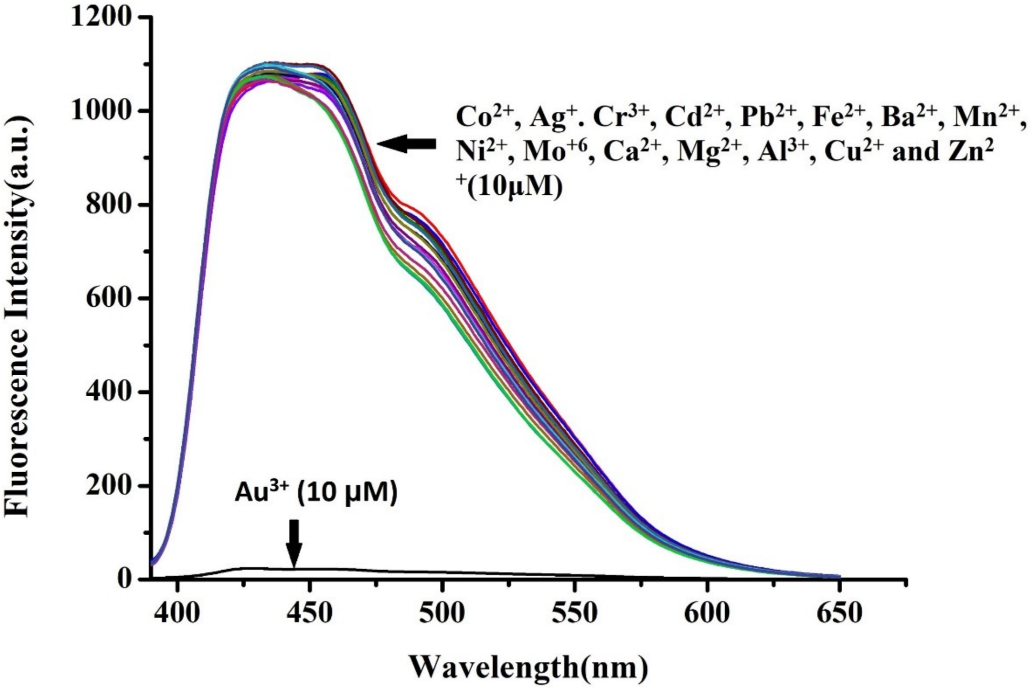

Fig.S9 Fluorescence spectra of PPE-OB-PEG (5 µM) towards various metal ions (10 µM) in PBS buffer (0.05 M, pH=7.2) at room temperature for 2 min.NO_3^-

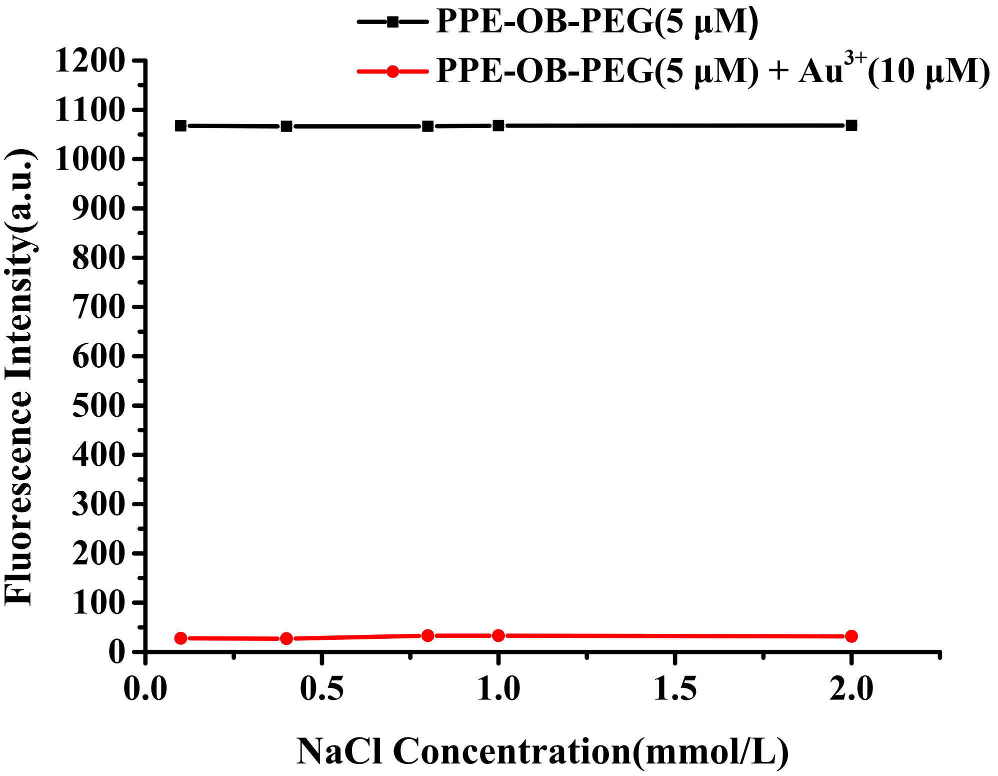

Fig.S10 The effect of the concentration of NaCl to the fluorescence intensity of PPE-OB-PEG (5 μM) in presence of Au(III) (10 μM) and in absence of Au(III)

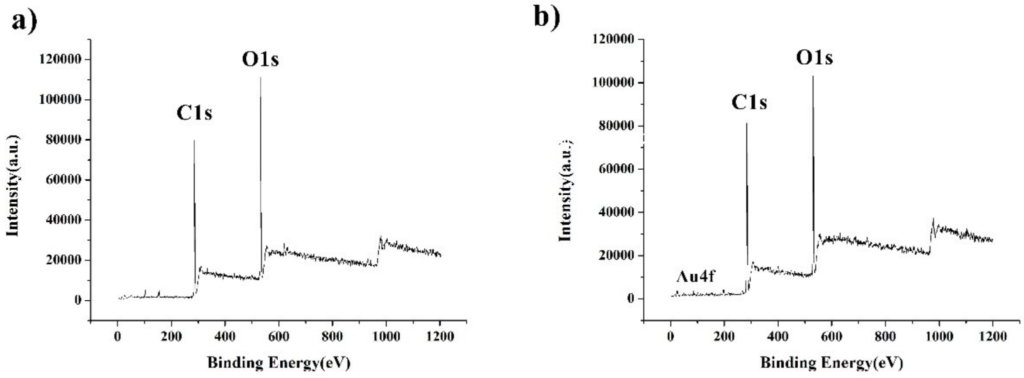

Fig.S11 XPS spectra of (a) free PPE-OB-PEG and (b) PPE-OB-PEG with Au(III)

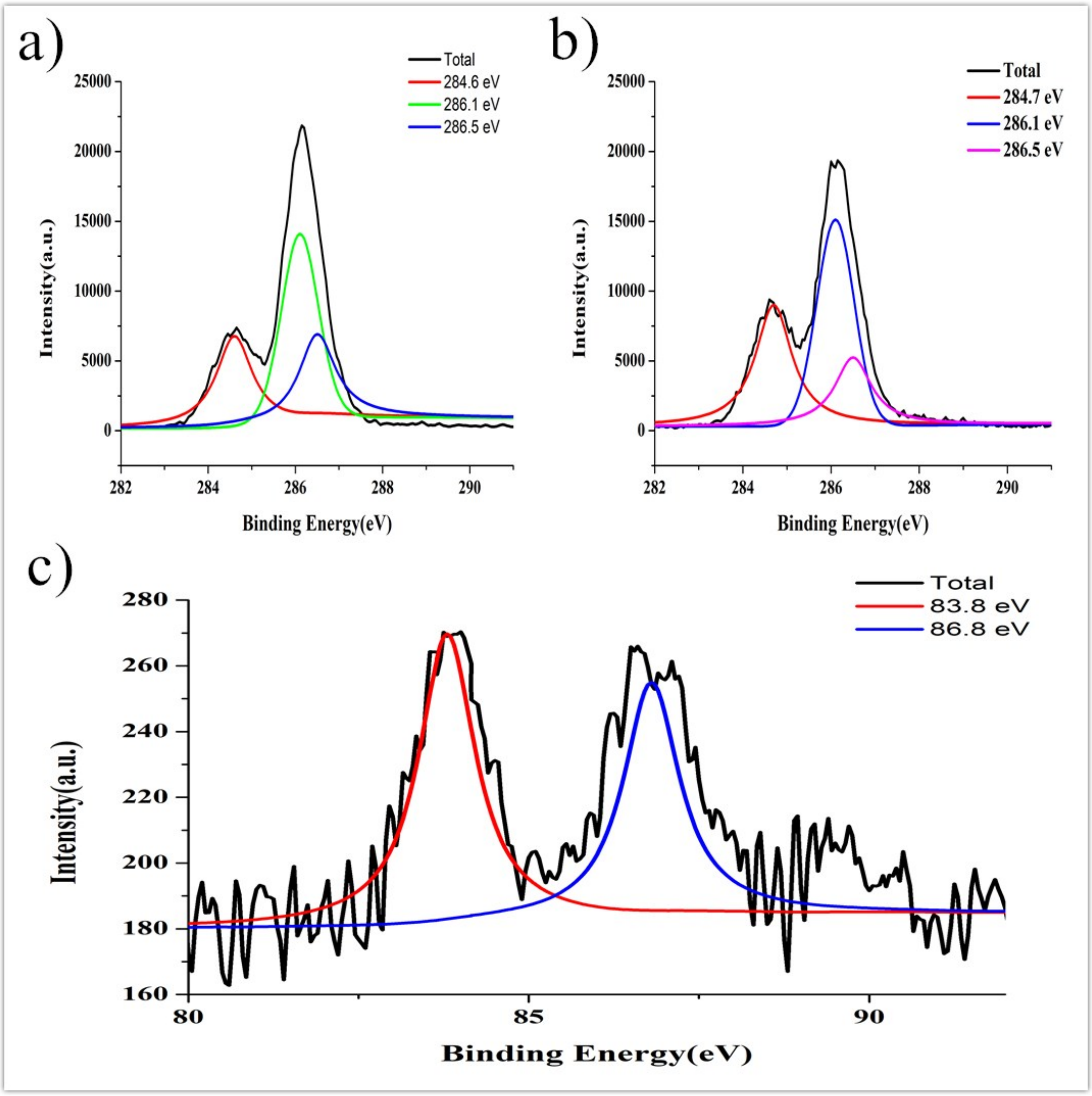

Fig.S12 High-resolution C1s XPS spectra of (a) free PPE-OB-PEG, (b) complexes of PPE-OB-PEG with Au(III) and (c) high-resolution Au4fs XPS spectra of complexes of PPE-OB-PEG with Au(III).

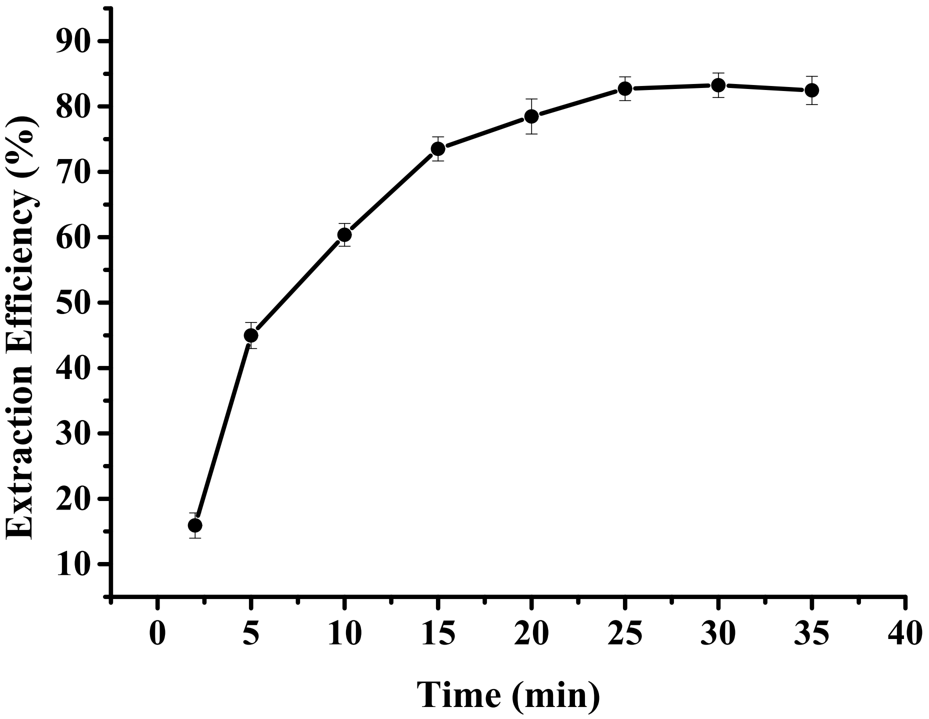

Fig.S13 Effect of extraction equilibrium time on Au (III) (0.5 mM) extraction efficiency (E %)

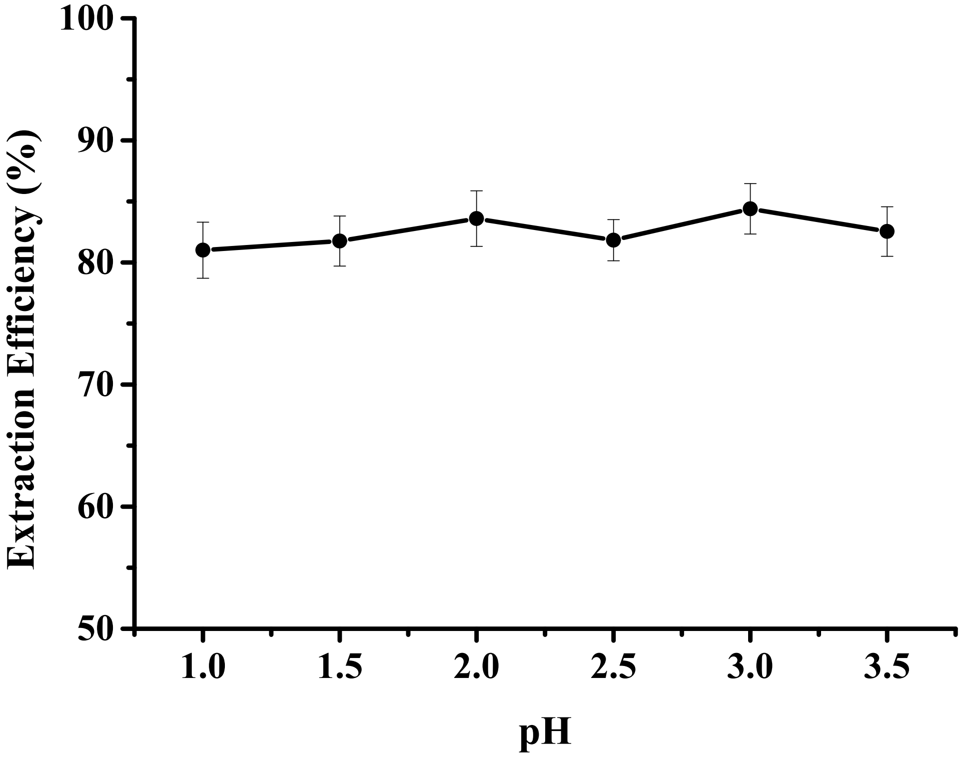

Fig.S14 effect of pH on Au (III) (0.5 mM) extraction efficiency (E%)

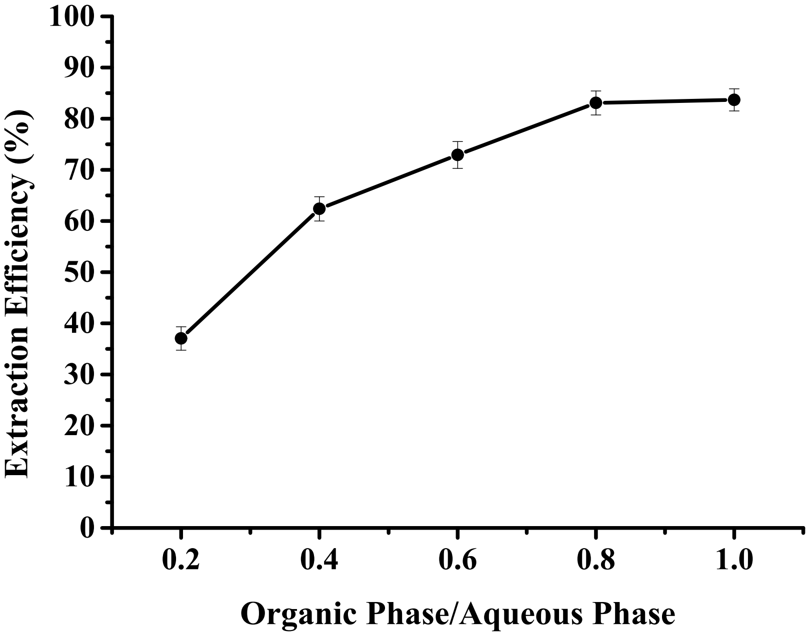

Fig.S15 effect of phase ratio on Au (III) (0.5 mM) extraction efficiency (E%)

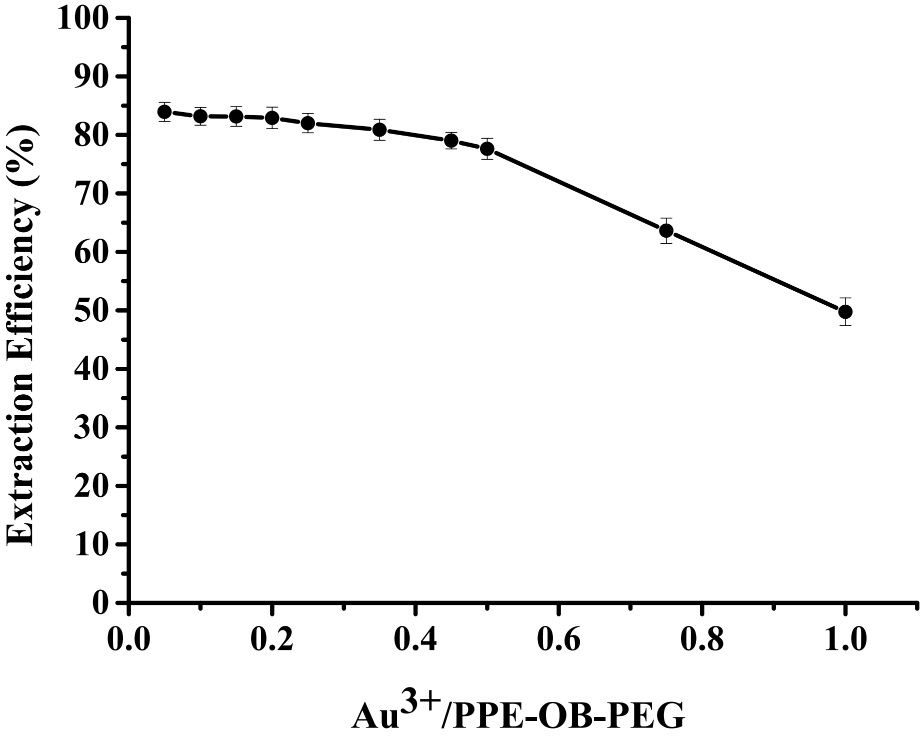

Fig.S16 effect of Au(III) content on Au (III) extraction efficiency (E%)

Table S1 Comparison of fluorescent methods for the detection of Au(III).

Fluorescent Probe	linearity range/μM	LOD/nM	Slovent	Ref.
diketopyrrolopyrrole	0.00-25.00	18.00	water/DMF	1
Fluorescein	0.07-60.00	70.00	water	2
BODIPY/pyridine	0.05-1.00	63.00	water/EtOH	3
SiNPs	0.50-100.00	23.00	water/EtOH	4
Cu_2S QDs	1.62-60.80	162.00	water	5
PPE-OB-PEG	0.004-1.50	1.32	water	This work

6. Detection of Au^{3+} with PPE-OB-PEG in electronic waste stream samples

Table. S2 Determination of Au(III) in electronic waste streams (n = 5)

Sample	ICP-AES (μM)	Found(μM)	Error/%
Electronic waste (1)	0.851	0.811	4.7
Electronic waste (2)	0.826	0.782	5.3
Electronic waste (3)	0.992	0.940	5.2
Electronic waste (4)	1.028	0.964	6.2

Table. S3 Comparison of this method and ICP-AES for detecting Au(III) in electronic waste stream

Sample	Number of tests	Average result(μM)	S	$t_{0.05,6}$	t
ICP-AES	3	0.992	0.044	1.94	
This method	5	0.940	0.042		1.65

Reference

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