Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.

Supporting Information (SI)

Simple and Selective Method for Simultaneous Removal of Mercury(II) and Recovery of Silver(I) from Aqueous Media by Organic Ligand 4,4′-Azo-1,2,4-triazole

Panpan Peng[1], Chaofeng Zhao[1], Jie Ji[1], Weixing Chen[1], Ning Ding[1], Shenghua Li[1]*, and Siping Pang[1]*

[1]School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, PR China.

*Correspondence to: lishenghua@bit.edu.cn, pangsp@bit.edu.cn

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SI 1. Materials and chemicals

Synthesis of Atrz. The 4,4′-azo-1,2,4-triazole (Atrz) was prepared through 4-amino-1,2,4-triazole dehydrogenation of two molecules and formation of azo bonds. Typically, 2.5 g sodium dichloroisocyanurate and 3 mL acetic acid were added into 20 mL water, stirred until the solution was emulsion-like, then 1 g 4-amino-1,2,4-triazole was added for 4 h. The crude brown-yellow solids were filtered, washed with water, recrystallized in boiling water, and finally vacuum-dried, to get 0.60 g light yellow acicular crystal product with a yield of 58%.

Melting: mp 300 °C (dec.); IR (KBr, cm^{-1}): ν = 3167 (m), 3126 (m), 1498 (s), 1478 (s), 1390 (s), 1305 (s), 1200(s), 1060(s), 987 (s), 906 (s), 890 (s), 707 (s), 623 (s), 515 (s); ^1H NMR (400 MHz, D_2O, δ ppm): $\delta = 9.21$ (s, 4H); ^{13}C NMR (400 MH_Z, D_2O, δ ppm): $\delta = 138.84$ (s) ppm.

Preparation of Atrz aqueous solution. The solid sample of 0.164 g Atrz was dissolved in 50 mL distilled water to prepare 20 mmol/L aqueous solution. All Atrz solutions of different concentrations used in the experiment were diluted by the solution of this concentration.

Preparation of single metal ion aqueous solution. Thirteen kinds of metal nitrates in 0.202 g $Fe(NO_3)_3$ $9H_2O$, 0.146 g $Co(NO_3)_2$ $6H_2O$, 0.145 g $Ni(NO_3)_3$ $6H_2O$, 0.121 g $Cu(NO_3)_2$ $3H_2O$, 0.043 g $NaNO_3$, 0.126 g $Mn(NO_3)_2$ $4H_2O$, 0.131 g $Ba(NO_3)_2$, 0.149 g $Zn(NO_3)_2$ $6H_2O$, 0.08 g $AgNO_3$, 0.200 g $Cr(NO_3)_3$ $9H_2O$, 0.188 g $Al(NO_3)_3$ $9H_2O$, 0.167 g $Hg(NO_3)_2$ H_2O, and 0.166 g $Pb(NO_3)_2$ were dissolved in 50 mL distilled water to prepare 10 mmol/L single metal ionic solution. All metal ions solutions of different concentrations used in the experiment were diluted by the solution of this concentration.

SI 2. Adsorption experiment of metal ions by Atrz

Adsorption of single metal ions. Diluting all the above metal ion salts at 3 mL by 10 times, the metal ion solution with 1 mmol/L concentration can be successfully prepared. The initial concentration C_0 of metal ions in each solution was measured by ICP-AES. Then, 3 mL Atrz solution with a concentration of 20 mmol/L was added to each metal ion solution. Stay at room temperature for 4 h and then filter to obtain clarified filtrate. ICP-AES was used to test the final concentration C_f of metal ions in each solution. At last, the % removal efficiency and mass-weighted distribution coefficient K_d were calculated by formula.

Adsorption of mixed metal ions. Diluting all the above metal ion salts at 3 mL by 10 times, the metal ion solution with 1 mmol/L concentration can be successfully prepared. A 39 mL solution containing 13 mixed metal ions was obtained by mixing 3 mL of 1 mmol/L metal ion solution, and 30 mL of the mixed ions solution with about 0.77 mmol/L concentration was obtained from the 39 mL solution. The initial concentration C_0 of each metal ions was measured by ICP-AES. Then, 3 mL Atrz solution with a concentration of 20 mmol/L was added to mixed metal ion solution. Stay at room temperature for 4 h and then filter to obtain clarified filtrate. ICP-AES was used to test the final concentration $C_\mathbf{f}$ of each metal ions. At last, the % removal efficiency and mass-weighted distribution coefficient K_d were calculated by formula.

Adsorption experiment of Atrz solution with different concentration. Single metal ion Ag^+ solutions with concentration of 1, 2, 5 and 10 mmol/L were prepared. And Pb^{2+}, Hg^{2+} solutions were prepared repeatedly. Then, 3 mL Atrz solution with a concentration of 20 mmol/L was added to each single metal ion solution. Other experimental procedures repeat the above operations.

Adsorption experiments of ATRZ and metal ions at different molar ratios. Ag^+ and Hg^{2+} single ion solution with concentration of 20 mmol/L and Atrz solution with concentration of 80 mmol/L were prepared. Two kinds of heavy metal ions 20 mL were mixed with 1, 1,5, 2, 2.5 mL Atrz solution, respectively. So, the molar ratios of Atrz to metal ions are 2:1, 3:1, 4:1 and 5:1, respectively. Other experimental procedures repeat the above operations.

SI 3. Removal of Hg^{2+} and Recovery of Ag^+.

Removal of Hg^{2+}. Atrz@Hg(II) (200 mg) dissolved in 10 mL DMSO was added into a 3 mL Na_2S (10 mmol/L) aqueous solution. The mixed solution was stirred for 10 min under room temperature, and then the resulting solution was filtered. The black insoluble precipitate is HgS. The concentration of Hg^{2+} in the transparent solution was detected by ICP-MS, and the final equilibrium concentration is 0.003 ppm.

Recovery of Ag^{+}. Atrz@A(I) (200 mg) dissolved in 5 mL $NH_3 \cdot H_2O$ (25%), then slowly add 1.5 mL (40%) acetaldehyde solution to the above solution, reaction under stationary condition for 2 h in 80 °C. Bright white Ag(0) began to precipitate at the bottom of glass vial within 15 min, and a total of nearly 5 mg Ag(0) was obtained until the end of the reaction. After filtering the resulting solution, the concentration of Ag^{2+} was 0.002 ppm in the transparent solution was detected by ICP-MS. The purity of Ag(0) detected by XPS was 93.25%.

SI 4. Instruments and characterizations

FT−IR spectra of the samples were recorded on a Nicolet-380 Fourier-transform infrared spectrometer using the KBr pellet method. Raman spectra were recorded on a microscopic confocal Raman spectrometer, using a 633 nm He-Ne laser. NMR spectroscopy was performed on a Bruker AVANCE III 600 instrument with Me4Si as an internal standard. Powder X-ray diffraction patterns were obtained at ambient (30 °C) temperature by a Bruker D2 with a Cu-Kα radiation (λ=1.5406 Å) at 30 kV and 10 mA. The samples were placed onto a circular sample holder and levelled with a glass slide. The sample was scanned within the scan range of 2θ from 5° to 90° continuous scan with a step size of 0.02° and a scan speed of 0.2 s per step. X-ray photoelectron spectroscopy (XPS) was performed on a Quantrea II energy spectrometer. SEM measurements were carried out using a Hitachi SU1510 microscope. EDS testing was carried out with a Natten Genensis Apollo X/XL X-ray energy spectrometer. The single crystal diffraction structure was determined by a Rigaku RAXIS IP diffractometer and SHELXTL crystallographic software package of molecular structure. The single crystals were mounted on a Rigaku RAXIS RAPID IP diffractometer equipped with a graphite-monochromatized MoKα radiation (λ= 0.71073 Å). Data were collected by the ω scan technique. The structure was solved by direct methods with SHELXS-97 and expanded by using the Fourier technique. The non-hydrogen atoms were refined anisotropically. The hydrogen atom was determined with theoretical calculations and refined with an isotropic vibration factor. The concentration of each metal ions in aqueous solution were analysed by using a PerkinElmer Optima 7300V ICP-OES with Syngistix for ICP, Version 2.0. software.

SI 5. Experimental data and spectrum

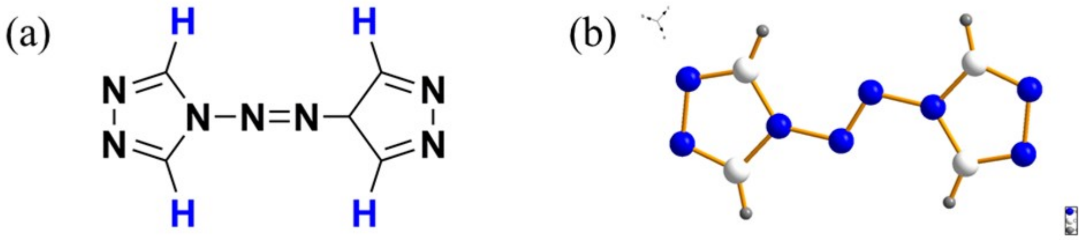

Figure S1. (a) Chemical formula and (b) single crystal X-ray diffraction structure of the organic ligand Atrz.

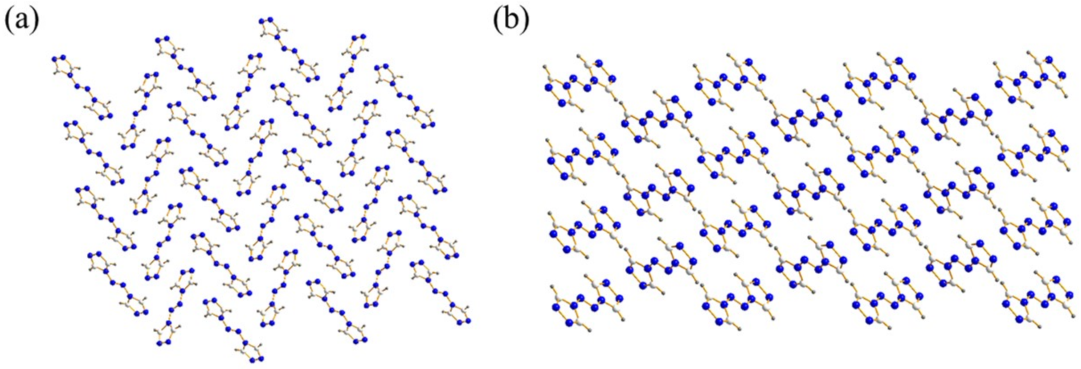

Figure S2. Extended packing of the organic ligand Atrz: (a) view of *a*-axis and (b) side view of *a*-axis.

Table S1. Crystallographic data and structure refinement parameters of the Atrz

Cocrystal	Atrz
Formula	$C_4H_4N_8$
T / K	296(2)
Mr	164.15
Crystal system	Monoclinic

Space group, Z	P-21/n, 2
a / Å	5.021(2)
b / Å	6.475(3)
c / Å	10.281(4)
α / °	90
β / °	91.453(5)
γ / °	90
V / Å^3	334.2(2)
μ(Mo-Kα) / mm^{-1}	0.123
D_{calc} /g·cm^{-3}	1.631
F(000)	168
2θ max / °	55.002
Reflections Collected	1974
Independent reflections	769
R_{int}	0.0242
Data/restraints/parameters	769/0/55
Goodness-of-fit on F^2	1.047
R_1, wR_2 [$I > 2\sigma(I)$]	0.0532, 0.1347
R_1, wR_2 (all data)	0.0556, 0.1422

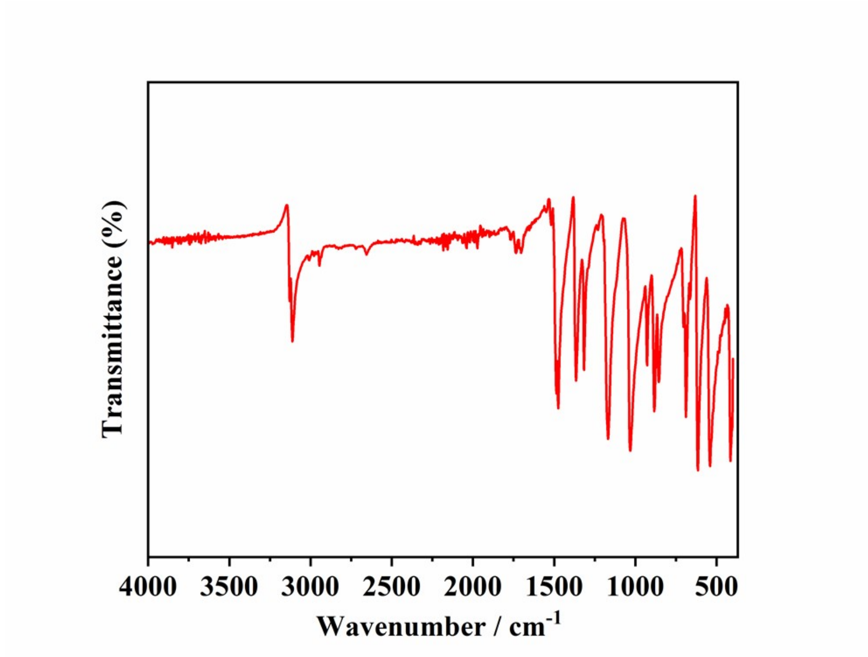

Figure S3. The FT-IR spectra of organic ligand Atrz.

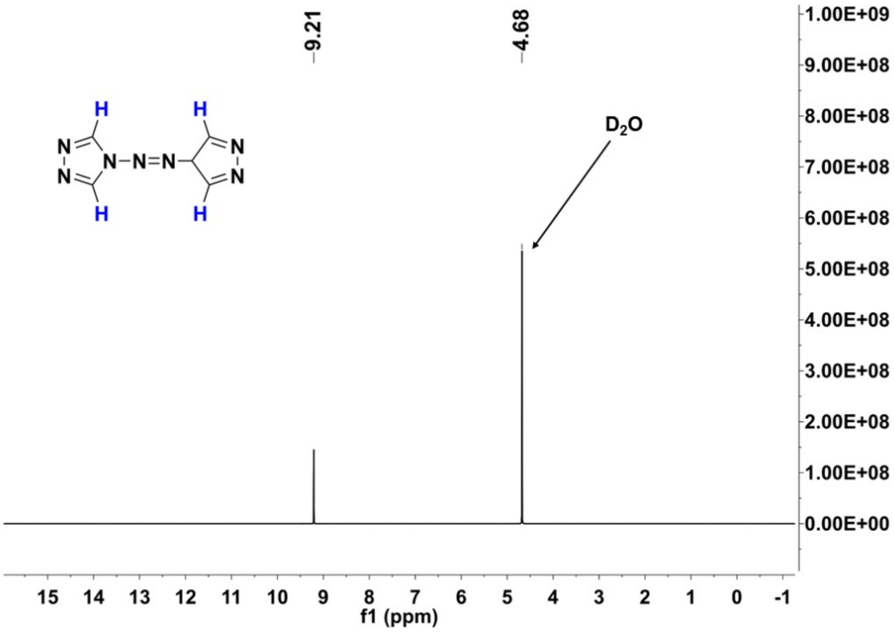

Figure S4. The ^{1}HNMR spectra of organic ligand Atrz.

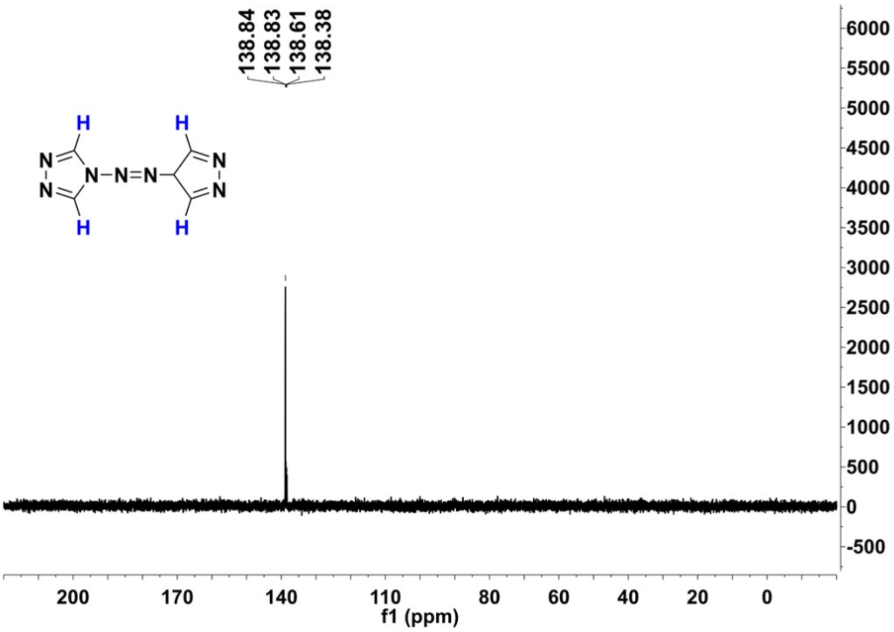

Figure S5. The ^{13}CNMR spectra of organic ligand Atrz.

Table S2. Adsorption Results of Atrz toward Individual Thirteen Ions at Different Molar Ratios

Single metal ions	**Molar ratios**	**C_0 (ppm)**	**C_f — 4 h (ppm)**	**removal (%)**
Hg^{2+}	2 : 1	401.68	182.5	54.56
	3 : 1	401.68	130.7	67.46
	4 : 1	401.68	141.5	64.77
	5 : 1	401.68	149.7	62.73
Ag^{+}	2 : 1	414.5	217.5	47.53
	3 : 1	414.5	190.9	53.94
	4 : 1	414.5	185.6	55.22
	5 : 1	414.5	189.2	54.35

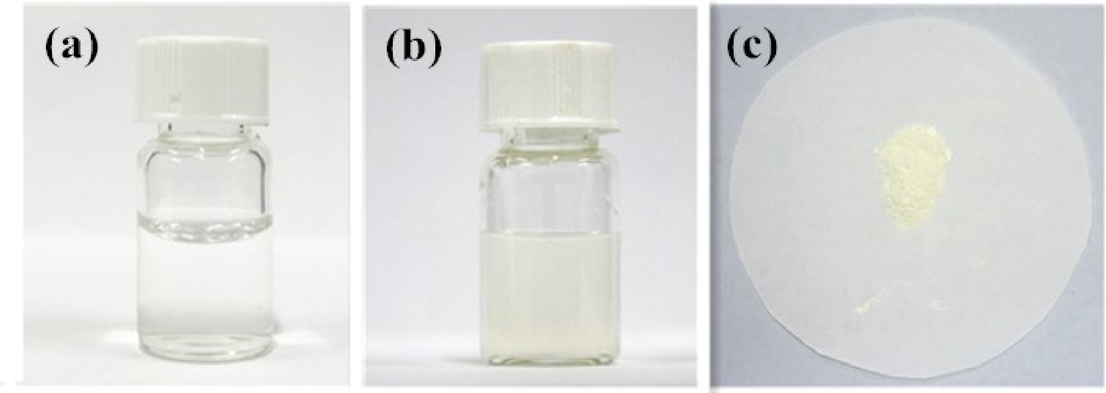

Figure S6. (a) Ag^{+} or Hg^{2+} single metal ion solution before ATRZ adsorption. (b) Adsorption of Ag^{+} or Hg^{2+} resulted in white coprecipitation, and (c) Precipitated solid sample after drying.

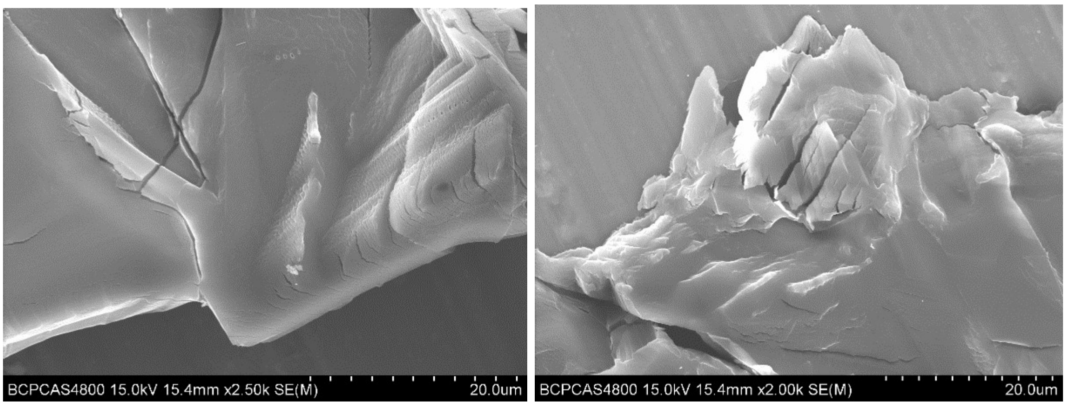

Figure S7. SEM images of the Atrz solid samples with magnification of (left) ×2.5 k and (right) ×2.0 k showing typical square block structure.

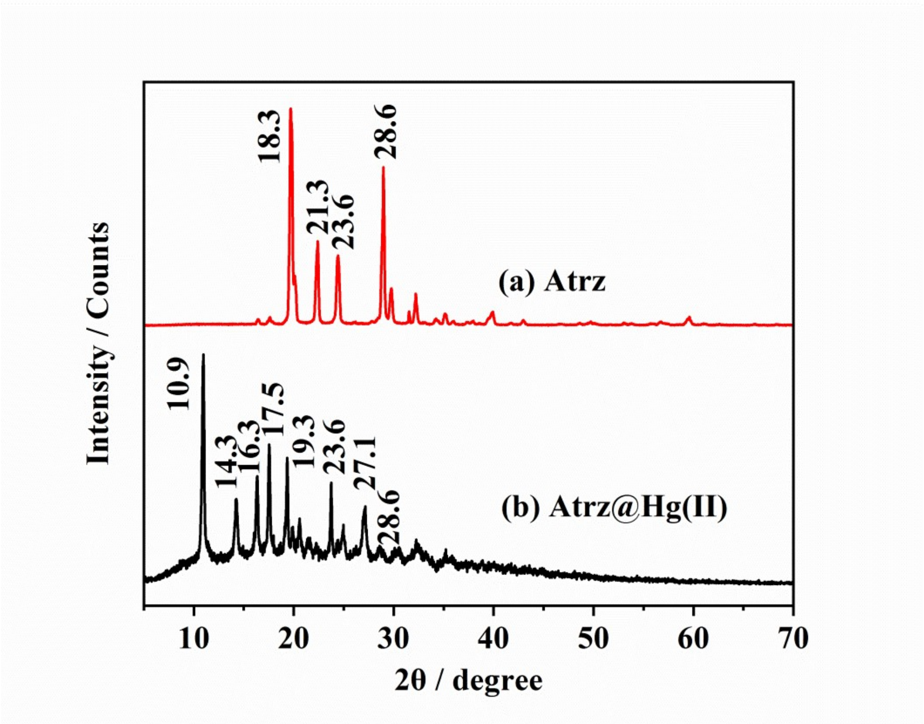

Figure S8. XRD patterns of (a) Atrz and (b) Atrz@Hg(II).

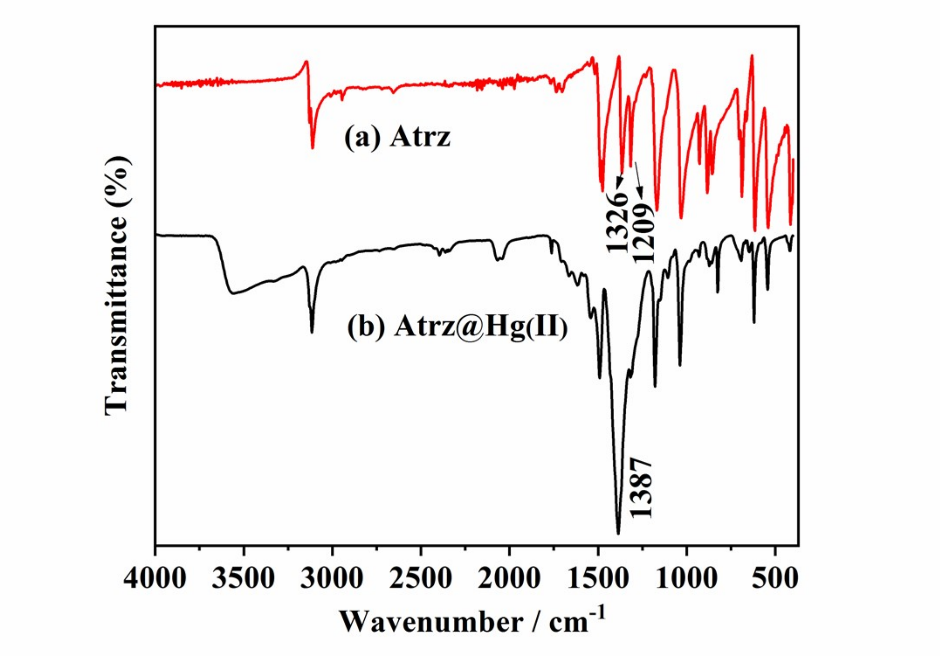

Figure S9. FT-IR spectra of (a) Atrz and (b) Atrz@Hg(II).

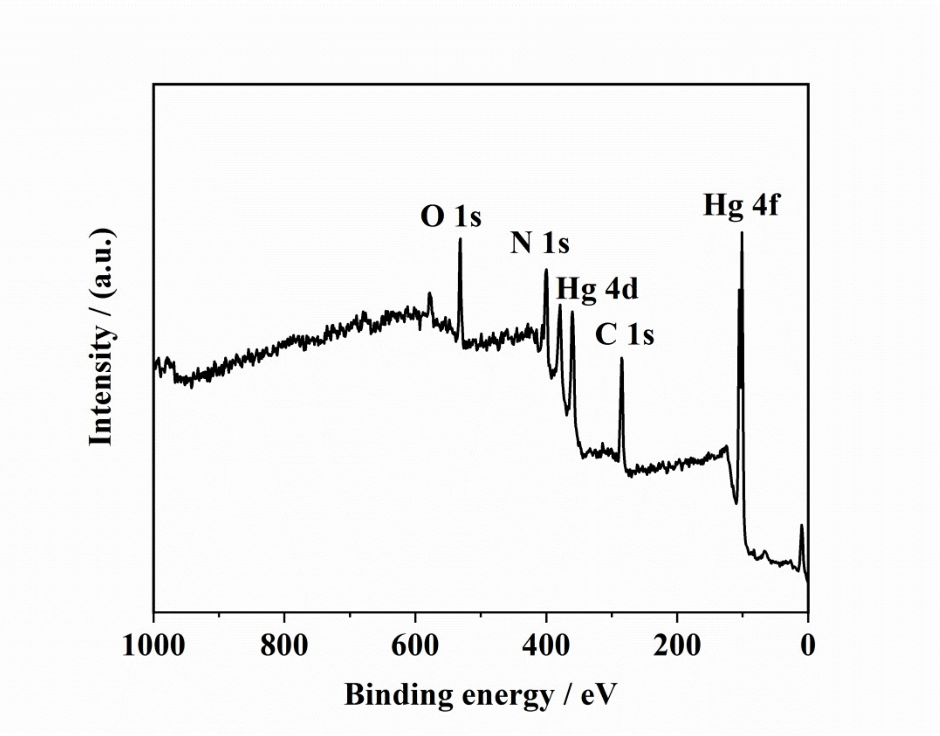

Figure S10. XPS full-spectra of the Atrz@Hg(II).

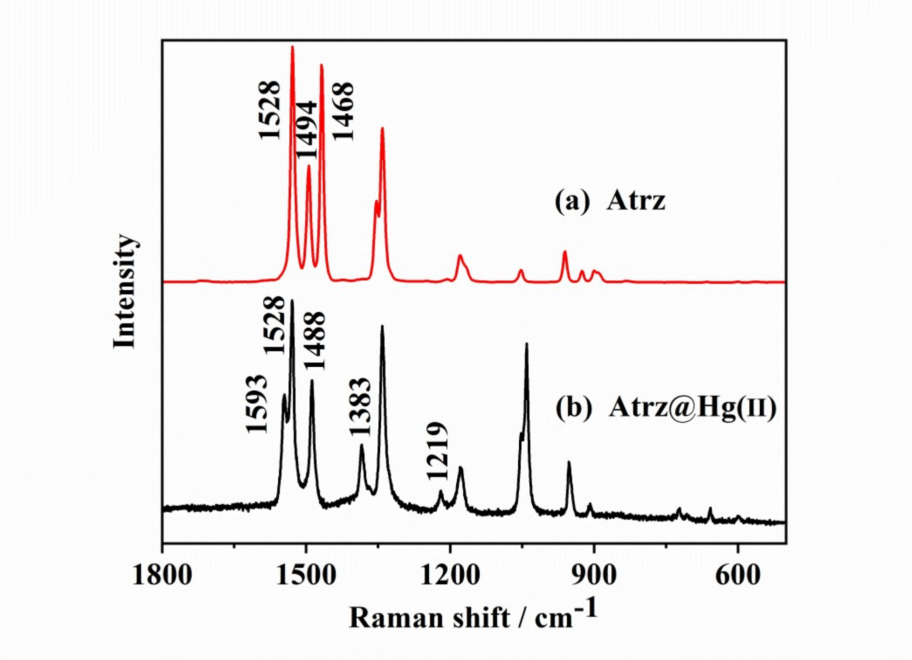

Figure S11. Raman data of (a) Atrz and (b) Atrz@Hg(II).