

## Supporting Information

### A new type of surface-enhanced Raman scattering sensor for the enantioselective recognition of *D/L*-cysteine and *D/L*-asparagine based on helically arranged Ag NPs@homochiral MOF

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**Materials and General Procedures.** Cadmium nitrate tetrahydrate, l-leucine, d-leucine, d-asparagine, l-asparagine, l-cysteine, d-cysteine, l-alanine and d-alanine, sodium carbonate, silver nitrate, nitric acid, hydrobromic acid, potassium bromide, sodium borohydride and 4-pyridinecarboxaldehyde were obtained from Aladdin (Aladdin Chemistry Co. Ltd., Shanghai, China). Ultrapure water (18.2MU cm) was obtained from a Water Pro Water Purification System (Labconco Corporation, Kansas City, USA). Unless otherwise stated, all chemicals and reagents used were at least of analytical grade and as received without further purification.

**Apparatus.** The FT-IR (KBr pellet) spectrum was recorded (400-4000  $\text{cm}^{-1}$  region) on a Nicolet Magna 750 FT-IR spectrometer. Powder X-ray Diffraction (PXRD) patterns were measured at room temperature (298 K) on a Bruker SMART APEX CCD-based diffractometer (Cu  $K\alpha$  radiation,  $\lambda = 1.5418 \text{ \AA}$ ). The solid state CD spectra were recorded on a J-815 spectropolarimeter (Jasco, Japan). Transmission electron microscopy (TEM) was carried out on a JEM-100CX II electron microscope. The SEM images were recorded on a FEI QUANTA FEG250 scanning electron microscope at 15.0 kV. SERS spectra were measured using a LabRAM HR-800 (HORLBA JY, France).

**Synthesis of ligand [N-(4-Pyridylmethyl)-L-leucin·HNO<sub>3</sub>] (l-HNO<sub>3</sub>).** The ligand [N-(4-Pyridylmethyl)-L-leucin·HNO<sub>3</sub>] (l-HNO<sub>3</sub>) was synthesized according to the previously reported literature with minor modifications. Typically, a solution of 4-pyridinecarboxaldehyde (2.14 g, 20 mmol) in MeOH (10 mL) was added dropwise to a water solution (40 mL) of L-leucine (2.7 g, 20 mmol) and sodium carbonate (1.06 g, 10 mmol). The mixture was stirred at room temperature for 2 h, and then cooled in an ice bath. A solution of sodium borohydride (0.91 g, 24 mmol) in water (10 mL) was added. The mixture was stirred for 1 h and acidified to pH = 6 by adding nitric acid. The solution was stirred for another 2 h and then evaporated to dryness. The solid (residue) was extracted with MeOH (10 mL), and the extract was evaporated to get a white powder. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{O-H}}$ , 3419;  $\nu_{\text{C=O}}$ , 1568 (vas) and 1374 (vs).

**Synthesis of ligand [N-(4-Pyridylmethyl)-D-leucin·HNO<sub>3</sub>] (d-HNO<sub>3</sub>).** The synthesis of ligand [N-(4-Pyridylmethyl)-D-leucin·HNO<sub>3</sub>] (d-HNO<sub>3</sub>) was similar to that for [N-(4-Pyridylmethyl)-L-leucin·HNO<sub>3</sub>] except D-leucine was used instead of L-leucine.

**Synthesis of ligand [N-(4-Pyridylmethyl)-L-leucine·HBr] (l-HBr).** The synthesis of ligand [N-(4-Pyridylmethyl)-L-leucine·HBr] (l-HBr) was similar to that for [N-(4-Pyridylmethyl)-L-leucin·HNO<sub>3</sub>] except hydrobromic acid was used instead of nitric acid for acidification.

**Synthesis of ligand [N-(4-Pyridylmethyl)-D-leucine·HBr] (d-HBr).** The synthesis of ligand [N-(4-Pyridylmethyl)-D-leucine·HBr] (d-HBr) was similar to that for [N-(4-Pyridylmethyl)-D-leucin·HNO<sub>3</sub>] except hydrobromic acid was used instead of nitric acid for acidification.

**Synthesis of homochiral MOF-1 and MOF-2.** Homochiral porous MOF-1 was synthesized by mixing the ligand l-HNO<sub>3</sub> (0.023 g, 0.1 mmol), potassium bromide (1.48 mg, 0.0125 mmol) in 1 mL of water and cadmium nitrate tetrahydrate (0.03 g, 0.1 mmol) in 1 mL of ethanol at room temperature (25 °C). The mixture turned turbid immediately. After 5 min ultrasound-guided

treatment, nanometer sized colorless rod-shaped crystals were obtained. The synthesis of MOF-2 was similar to that for MOF-1, except  $\text{d-HNO}_3$  was used instead of  $\text{l-HNO}_3$ .

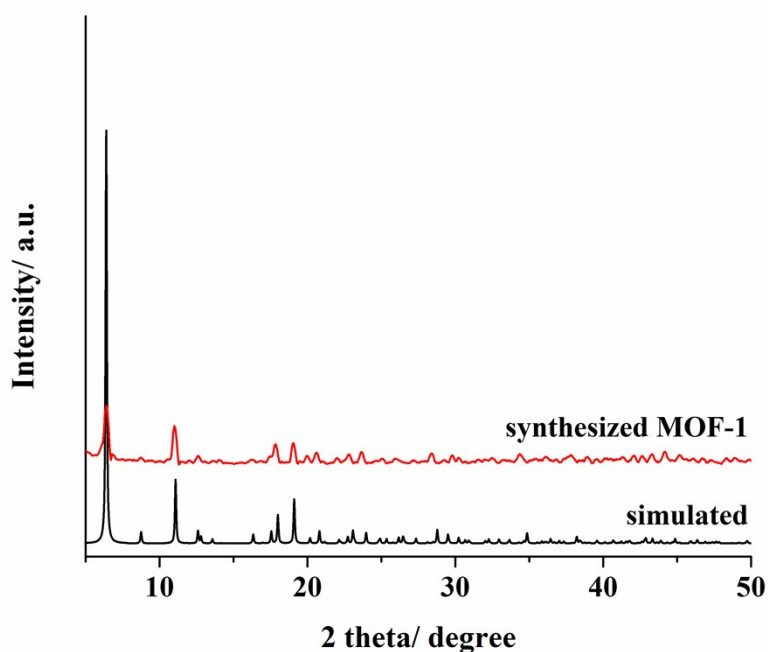
**Synthesis of *h*-Ag NPs@MOF-1 and *h*-Ag NPs@MOF-2.** MOF-1 were soaked in 0.3 mL of silver(I) nitrate (6.34 mg, 0.0625 mmol) for 12 h at 30 °C, removed from the solution, and rinsed with ethanol three times. The mixture of AgBr@MOF-1 was then exposed to an ultraviolet lamp (8 W) for 12 h at 25 °C. Final powder products with a brown color (denoted as *h*-Ag NPs@MOF-1), were isolated by centrifugation. The distance of the sample from the ultraviolet lamp was 10 cm and the mixture was stirred vigorously throughout the whole process. Ag NPs@MOF-2 was synthesized by using the same method as Ag NPs@MOF-1, except MOF-2 was used instead of MOF-1.

**Preparation of Ag NPs from *h*-Ag NPs@MOF-1**

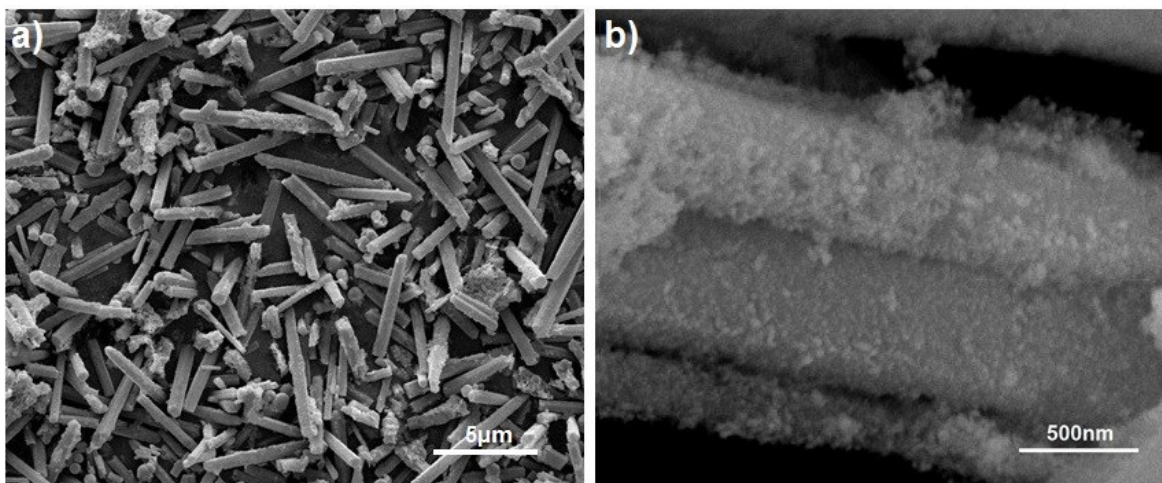
The Ag NPs@MOF-1 was firstly immersed in water, then a solution of sodium citrate (2%, 10 mL) as aggregation inhibitor was added simultaneously. After the ultrasound-guided treatment at room temperature for 30 min, the sample was centrifuged, washed with water and ethanol three times, respectively.

**Preparation of Ag NPs substrate from  $\text{Ag}(\text{NO}_3)_2$ .** Firstly,  $\text{Ag}(\text{NO}_3)_2$  (18 mg) was added to 100 mL boiling water solution. Then a solution of sodium citrate (1%, 2 mL) as reductant was added. The mixture was kept on boiling for 1 h. Subsequently, a layer of Ag nanocolloids was assembled via electrostatic interaction on glass slides that being hydroxylated.

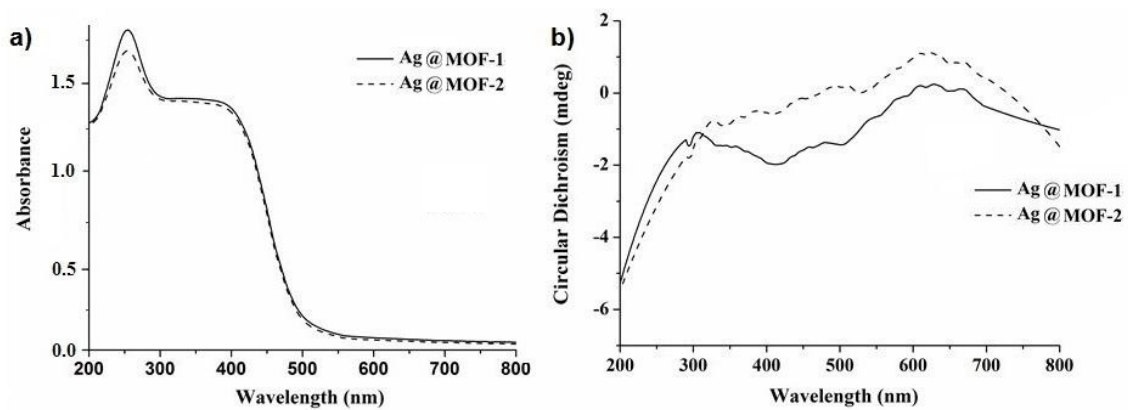
**SERS measurements.** 100  $\mu\text{L}$  of l-cysteine, d-cysteine, d-asparagine, l-asparagine, l-alanine, d-alanine, l-leucine or d-leucine (10 mmol/L) aqueous solution was mixed with 12 mg of *h*-Ag NPs@MOF-1, respectively. After being dried, the samples were scanned using a Horiba LabRAM HR-800 Raman spectrophotometer equipped with a 633 nm Ar ion laser. The laser power was 5 mW, the spot size was 3.2  $\mu\text{m}$ , and the collection time was 10 s.



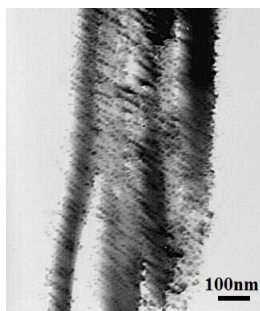
**Figure S1.** PXRD patterns of simulated Zn-MOF and synthesized MOF-1.



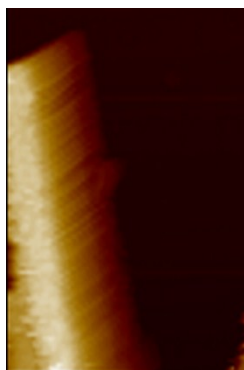
**Figure S2.** SEM images of (a) MOF-1 templates and (b) Ag NPs@MOF-1.



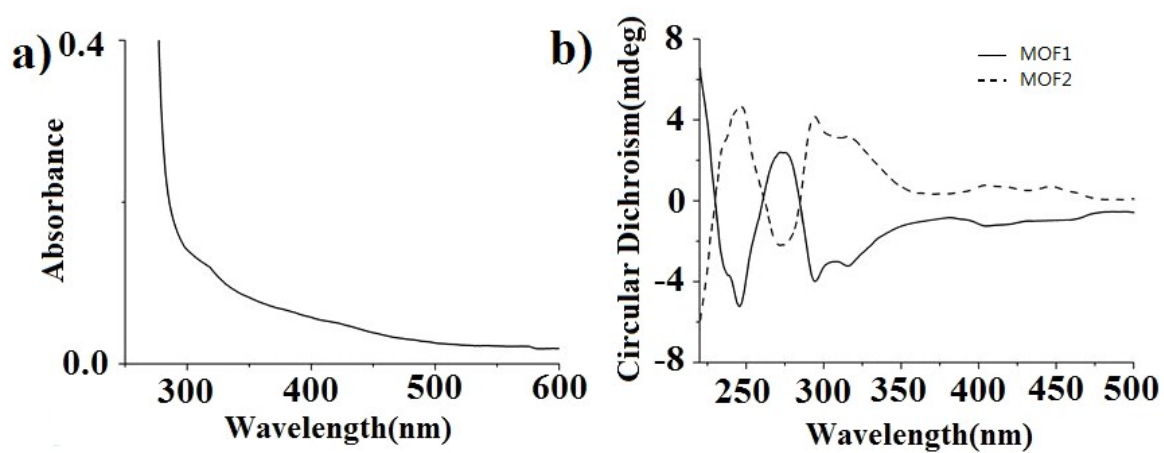
**Figure S3.** (a) UV-vis absorption spectra and (b) CD spectra of enantiomeric Ag NPs@MOF-1 and Ag NPs@MOF-2.



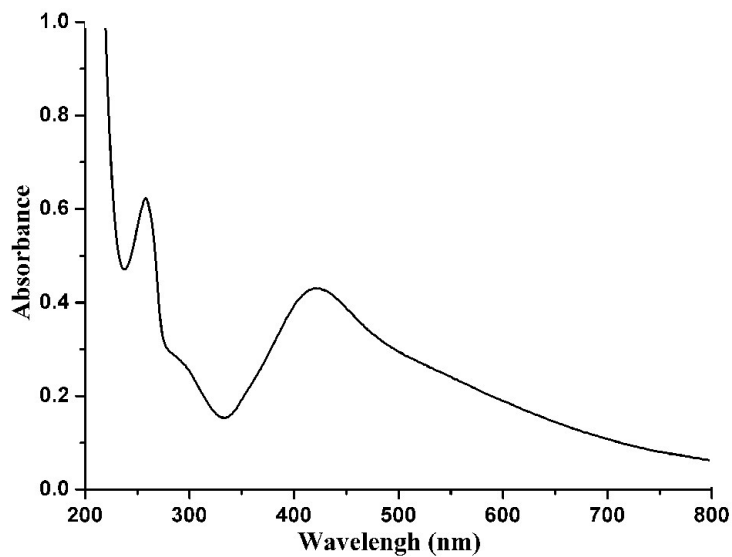
**Figure S4.** TEM image of *h*-Ag NPs@MOF-1

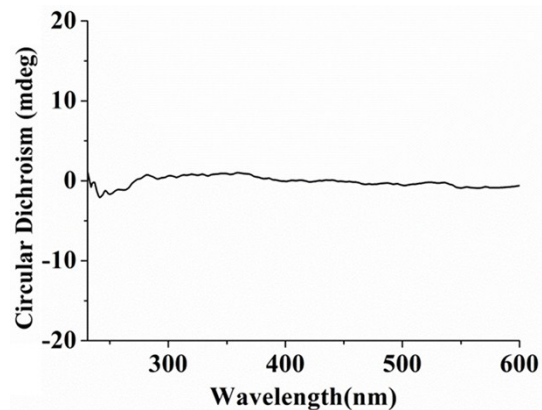


**Figure S5.** AFM image of *h*-Ag NPs@MOF-1

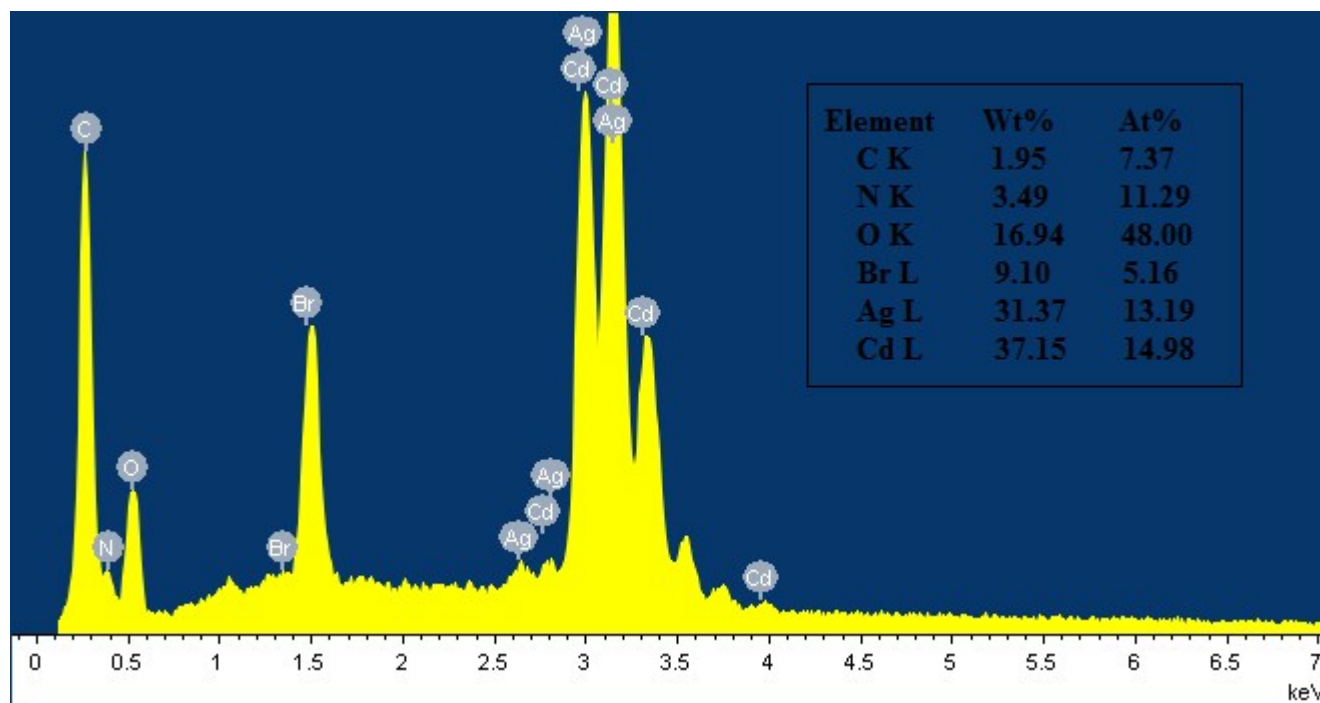


**Figure S6** (a) UV-vis absorption spectrum of MOF-1. (b) CD spectra of enantiomeric MOF-1 and MOF-2.

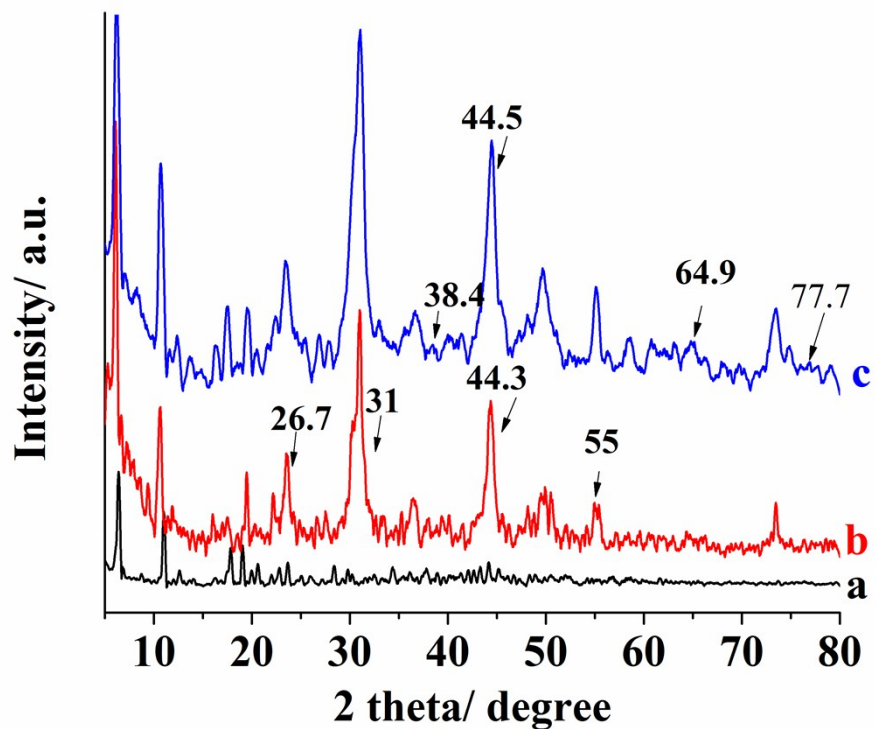




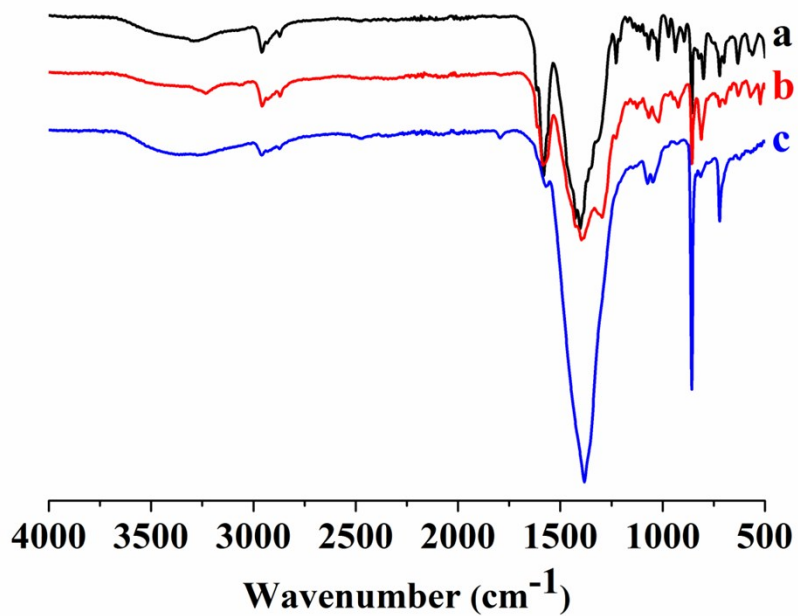
**Figure S7** UV-vis absorption spectrum of Ag NPs synthesized from *h*-Ag NPs@MOF-1 (up); CD spectra of Ag NPs synthesized from *h*-Ag NPs@MOF-1 (below)



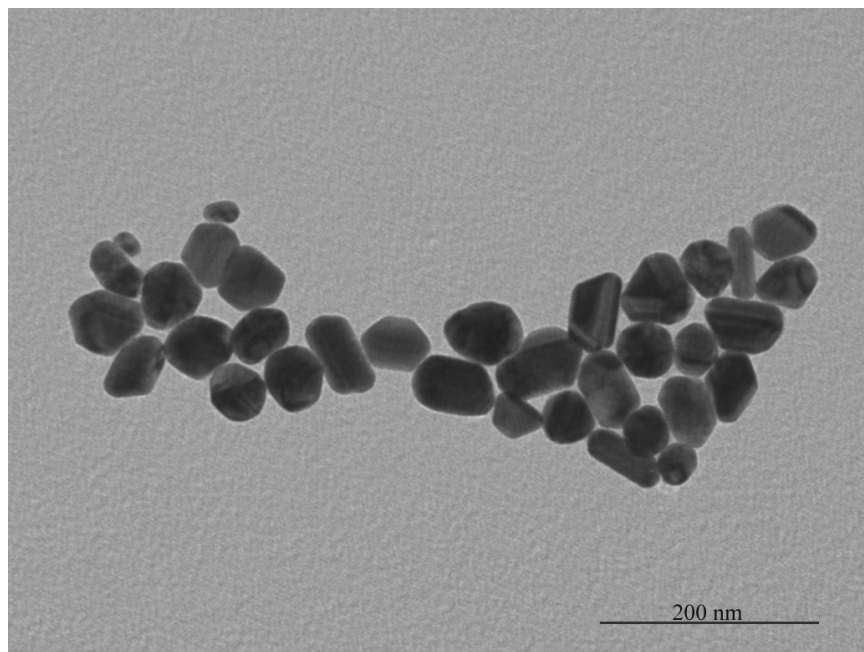
**Figure S8.** EDX spectrum of *h*-Ag NPs@MOF-1.



**Figure S9.** XRD pattern of (a) MOF-1 template, (b) AgBr@MOF-1 and (c) *h*-Ag NPs@MOF-1.



**Figure S10.** FTIR spectra of (a) MOF-1, (b) AgBr@MOF-1 and (c) *h*-Ag NPs@MOF-1.



**Figure S11.** TEM image of achiral Ag NPs.