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

Xuan Kuang, Sujuan Ye, Xiangyuan Li, Yu Ma*, Caiyun Zhang, and Bo Tang*

College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Functionalized Probes for Chemical Imaging in Universities of Shandong, Key Laboratory of Molecular and Nano Probes, Ministry of Education, Shandong Provincial Key Laboratory of Clean Production of Fine Chemicals, Shandong Normal University, Jinan 250014, P. R. China

Corresponding author e-mail: tangb@sdnu.edu.cn

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 were used at least of analytical grade and as received without further purification.

Apparatus. The FT-IR (KBr pellet) spectrum was recorded (400-4000 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 Kα radiation, λ = 1.5418 Å). 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 (HORIBA JY, France).

Synthesis of ligand [N-(4-Pyridylmethyl)-L-leucine-HNO₃] (l-HNO₃). The ligand [N-(4-Pyridylmethyl)-L-leucine-HNO₃] (l-HNO₃) 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, cm⁻¹): γ(O-H) 3197; γ(C=O) 1658 (vs) and 1374 (vs).

Synthesis of ligand [N-(4-Pyridylmethyl)-D-leucine-HNO₃] (d-HNO₃). The synthesis of ligand [N-(4-Pyridylmethyl)-D-leucine-HNO₃] (d-HNO₃) was similar to that for [N-(4-Pyridylmethyl)-L-leucine-HNO₃] 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-leucine-HNO₃] 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-leucine-HNO₃] 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-HNO₃ (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 d-HNO₃ was used instead of l-HNO₃.

**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 Ag(NO₃)₂.** Firstly, Ag(NO₃)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 μL of l-cysteine, d-cysteine, l-asparagine, d-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 μm, 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.