

## Supporting information

### **Impact of the capping agent removal from Au NPs@MOF core-shell nanoparticles heterogeneous catalysts**

Shan Dai,<sup>a,c</sup> Kieu Phung Ngoc,<sup>a</sup> Laurence Grimaud,<sup>b</sup> Sanjun Zhang,<sup>c</sup> Antoine Tissot,<sup>a†</sup>  
Christian Serre<sup>a†</sup>

*a.* Institut des Matériaux Poreux de Paris, Ecole Normale Supérieure, ESPCI Paris, CNRS, PSL University, 75005 Paris, France.

*b.* Laboratoire de biomolécules (LBM), Département de chimie, Sorbonne Université, École Normale Supérieure, PSL University, Sorbonne Université, CNRS, 75005 Paris, France.

*c.* State Key Laboratory of Precision Spectroscopy, East China Normal University, No. 3663, North Zhongshan Road, Shanghai 200062, China.

## Experimental

Ambient Powder X-ray Diffraction (PXRD) data were recorded on a high-throughput Bruker D8 Advance diffractometer working on transmission mode and equipped with a focusing Göbel mirror producing CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) and a LynxEye detector. *In-situ* thermal PXRD data were collected using Malvern Panalytical Empyrean diffractometer (CuK $\alpha$  radiation,  $\lambda = 1.5418 \text{ \AA}$ ), equipped with GaliPIX<sup>3D</sup> detector and temperature-controlled HTK-1200N furnace. Nitrogen porosimetry data were collected on a Micromeritics Tristar/ Triflex instrument at 77 K (pre-activating samples at 150 °C under vacuum, 12 hours). Scanning Electron Microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX) results were recorded with FEI Magellan 400 scanning electron microscope. Infrared spectra were measured with a Nicolet iS5 FTIR ThermoFisher spectrometer. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance 300 spectrometer. ICP-MS was carried out with an Agilent 7850 elemental analyzer. For the ICP-MS tests, 2~3 mg of hybrid Au@MOF-808 composites were dissolved in 0.4 mL of aqua regia at 70 °C for 5 hours. The dilution method was based on the reported method while with small modification, where 0.18% w/v cysteine in 5% HCl aqueous solution was used to overcome the memory effect.<sup>1</sup>

## Chemicals

All chemicals were purchased from commercial suppliers and used as received without further purification. Trimesic acid, 98%, Alfa Aesar. ZrCl<sub>4</sub> anhydrous, 98%, Acros. Zirconyl chloride octahydrate, 98%, Acros. Isopropyl alcohol, 99+%, Sigma. Formic acid, 98%, Acros. Acetone, 99%, Acros. Methanol absolute,  $\geq 99\%$ , Acros. NaBH<sub>4</sub>,  $\geq 98\%$ , Aldrich. Polyvinylpyrrolidone, average mol. Wt. 10.000, Aldrich. HAuCl<sub>4</sub>·3H<sub>2</sub>O, 99.99%, Alfa Aesar. Distilled water, Millipore system.

## Synthesis of Au NPs:

The synthesis of Au NPs was performed following a previously published work.<sup>2</sup> An aqueous solution of HAuCl<sub>4</sub> (1 mM) was added to a solution of PVP (K-90) (277.9 mg) in 30 mL of H<sub>2</sub>O (MiliQ grade) so that the molar ratio of AuCl<sub>4</sub><sup>-</sup> and the monomeric unit of PVP was kept at 1:100. The mixture was kept stirring for 30 minutes at 0 °C, followed by the addition of an aqueous solution of NaBH<sub>4</sub> (100 mM, 2.5 mL). The resulted clear dark mixture was kept stirring at 0 °C for 15 minutes more before collecting the particles by centrifugation. The solid was then washed three times with an acetone/H<sub>2</sub>O (7:1) mixture. The final Au NPs were dried in air to remove completely acetone, dispersed in H<sub>2</sub>O (3.25 mL) and stored in the fridge for further use.

## Synthesis of Au NPs@MOF-808:

Zirconium oxoclusters ( $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{C}_2\text{H}_3\text{O}_2)_8\text{Cl}_4$ , 120 mg, 0,16 mmol) were stirred in  $\text{HCOOH}$  (600  $\mu\text{L}$ ) until well dissolved. Then, an aqueous solution of Au NPs capped with PVP (1 mL, 10 mM) was added to the solution. The mixture was kept stirring for around 15 minutes until observation of clear dark solution. Then, trimesic acid (20 mg, 0.095 mmol) was added and the resulted mixture was kept stirring overnight until the observation of cloudy purple solution. The solid was collected by centrifugation and washed three times with  $\text{H}_2\text{O}$ , three times with MeOH and three times with acetone. The purple solid (105 mg) was finally dried under vacuum.

### **Removal of PVP capping agent on Au NPs@MOF-808 particles:**

Several treatments were applied to the Au NPs@MOF-808 composites in order to remove the PVP capping the Au NPs. In each case, the resulting composite crystallinity was confirmed by PXRD and the compound was then used directly for other characterizations and for catalytic experiments.

#### **- thermal treatment:**

The well-washed dry composite was heated in the oven for 4 hours at 200 °C. A slight color change from dark purple to lighter purple was observed.

#### **- UV radiation treatment:**

The well-washed dry composite was positioned under an ultraviolet lamp (365 nm) in a chamber for 24 hours.

#### **- acidic solution treatment:**

The well-washed dry composite (17 mg) was dispersed in  $\text{H}_2\text{O}$  (2 mL) by sonification until the entire solid was well-dispersed in the solution. Different amounts of HCl were then added to the mixture to reach the 0.5M and 2M final concentrations and the solution was then kept stirring for 2 hours. The resulting solid was washed with acetone and dried under air.

#### **- $\text{NaBH}_4$ treatment:**

The well-washed dry composite (17 mg) was suspended in 2 mL acetone followed by the addition of a solution of  $\text{NaBH}_4$  (0.04 mg, 0.1 eq.) in acetone. The mixture was kept stirring at room temperature for 30 minutes. The final catalyst was collected by centrifugation, then washed with acetone three times and dried under air. This protocol was applied for the different treatments with  $\text{NaBH}_4$  using various amounts of  $\text{NaBH}_4$  as well as different reaction times.

#### **- $\text{NaBH}_4$ treatment in the co-solvent of DCM and EtOH:**

The catalyst (10.1 mg) was dispersed in a mixture of  $\text{NaBH}_4/\text{DCM}/\text{EtOH}$  (0.068 mg/ 527  $\mu\text{L}$ / 63.3  $\mu\text{L}$ ) and kept stirring for 30 minutes at room temperature. The final solid was collected by centrifugation, washed with DCM three times and acetone three times before drying under air.

### - double solvent treatment:

The well-washed dry composite (35 mg) was dispersed in a H<sub>2</sub>O (2 mL) in a round bottom flask, following by the addition of acetone (2 mL). The mixture was refluxed overnight. Final solid was collected by centrifugation and washed with a mixture of H<sub>2</sub>O/acetone (1:1), then three times with acetone followed by drying under air.

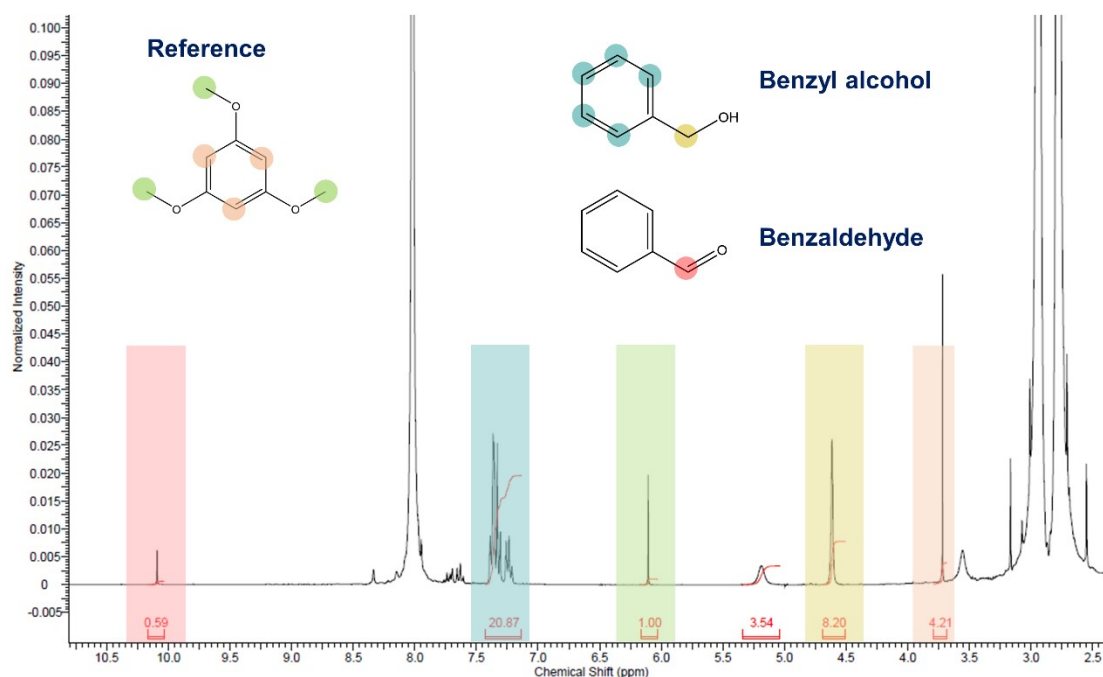
### Catalytic activity of the Au NPs@MOF-808 particles:

#### Catalytic experiments:

Benzyl alcohol (64.8 μL) was added to a well-dispersed solution of Au@MOF-808 (10 mg, corresponding to an Au:BA molar ratio of 1:100) in DMF (1.44 mL). The mixture was stirred at 100°C under air flow. The catalytic activity was evaluated after different reaction times in order to evaluate the reaction kinetics.

#### Quantitative method:

Quantitative-<sup>1</sup>H NMR experiment were performed in order to evaluate the catalyst activity in the presence of 1,3,5-trimethoxybenzene in a coaxial insert used a reference. The conversions were calculated according to the integrated area of each peak.



Representative <sup>1</sup>H NMR spectrum of the reaction mixture used to quantify the catalytic activity of the Au NPs@MOF-808 compound.

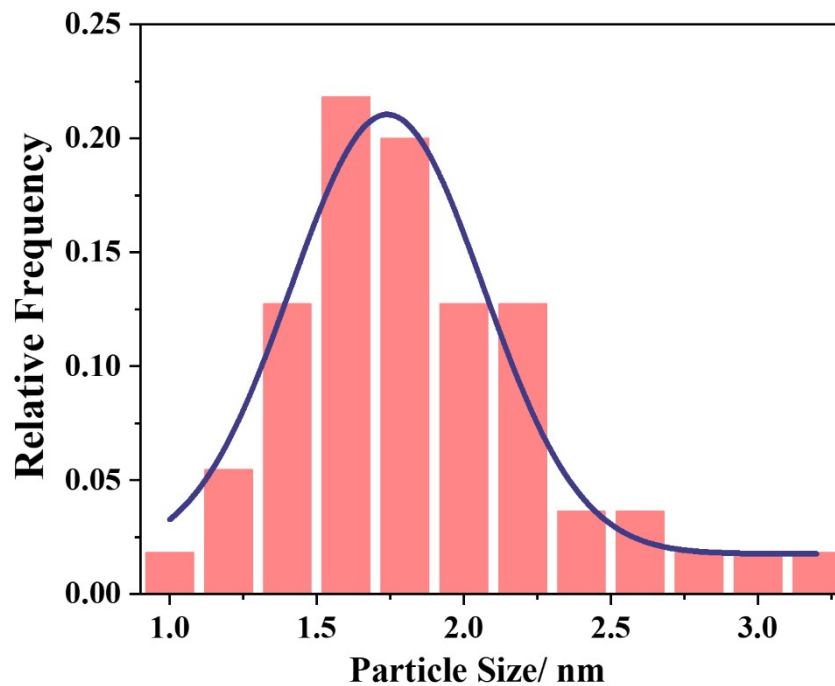


Figure S1. Particle size distribution histogram corresponding to the Au NPs in original solution.

Table S1. EDX and ICP-MS characterizations of Au NPs@MOF-808 following different treatments.

	Au/ Zr (atom%) (EDX)	Au/ Zr (atom%) (ICP- MS)
As-synthesized Au NPs@MOF-808	3.5%	4.0%
20 times water washing	3.3%	3.8%
2M HCl, double solvent	3.2%	3.8%

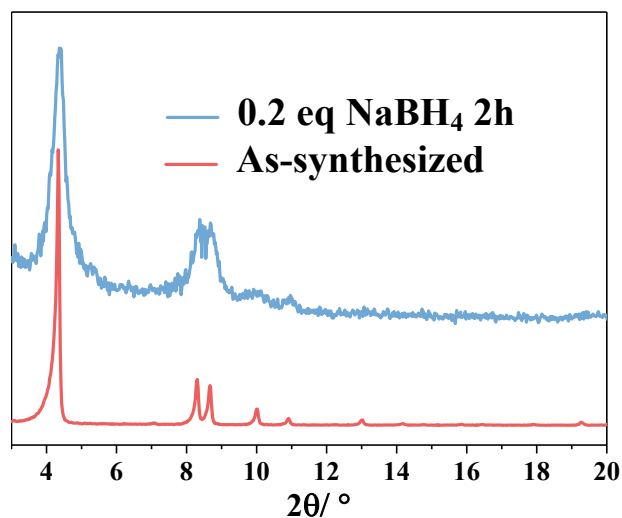


Figure S2. PXRD patterns of the as-synthesized Au NPs@MOF-808 and the one after treatment with 0.2 eq NaBH<sub>4</sub> for 2h.

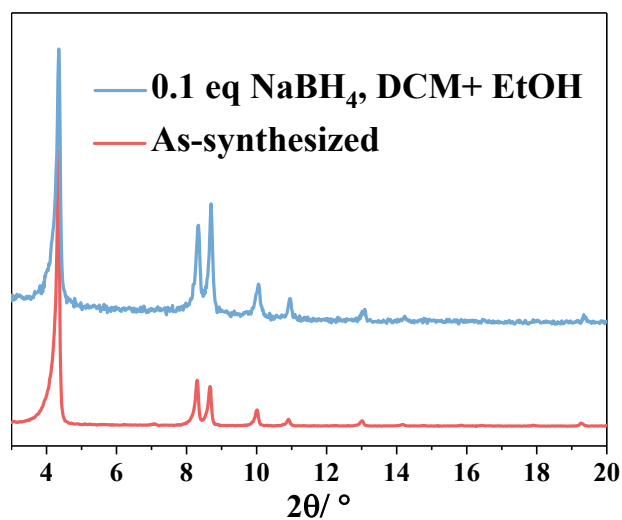


Figure S3. PXRD patterns of the as-synthesized Au NPs@MOF-808 and the one after treatment with 0.1 eq NaBH<sub>4</sub> in the mixture of DCM and EtOH as solvent.

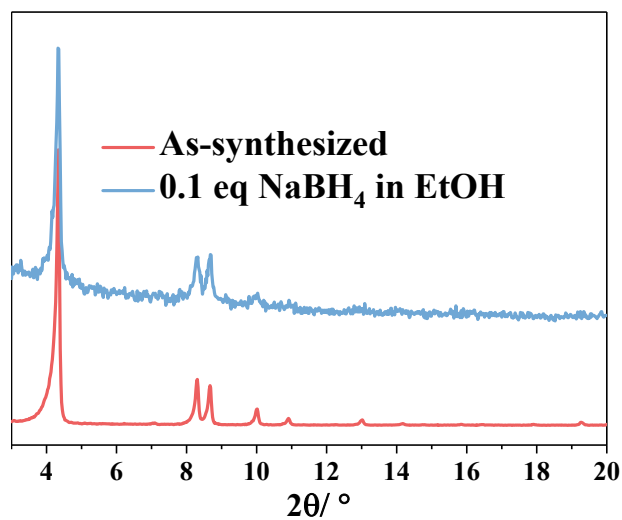


Figure S4. PXRD patterns of the as-synthesized Au NPs@MOF-808 and the one after treatment with 0.1 eq  $\text{NaBH}_4$  in EtOH.

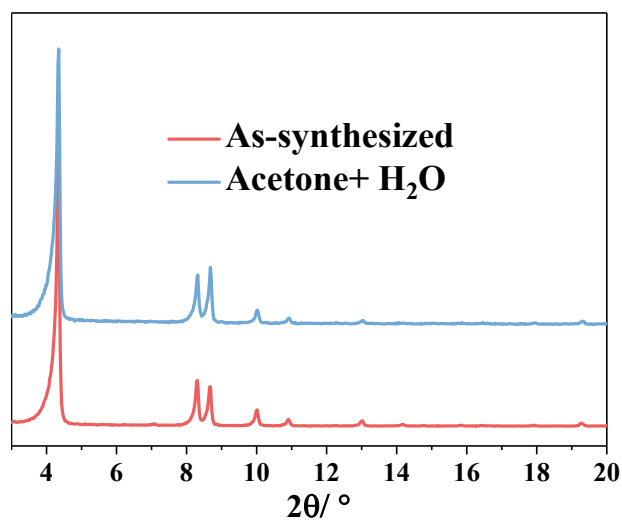


Figure S5. PXRD patterns of the as-synthesized Au NPs@MOF-808 and the one after treatment in a mixture of solvents (acetone+  $\text{H}_2\text{O}$ ).

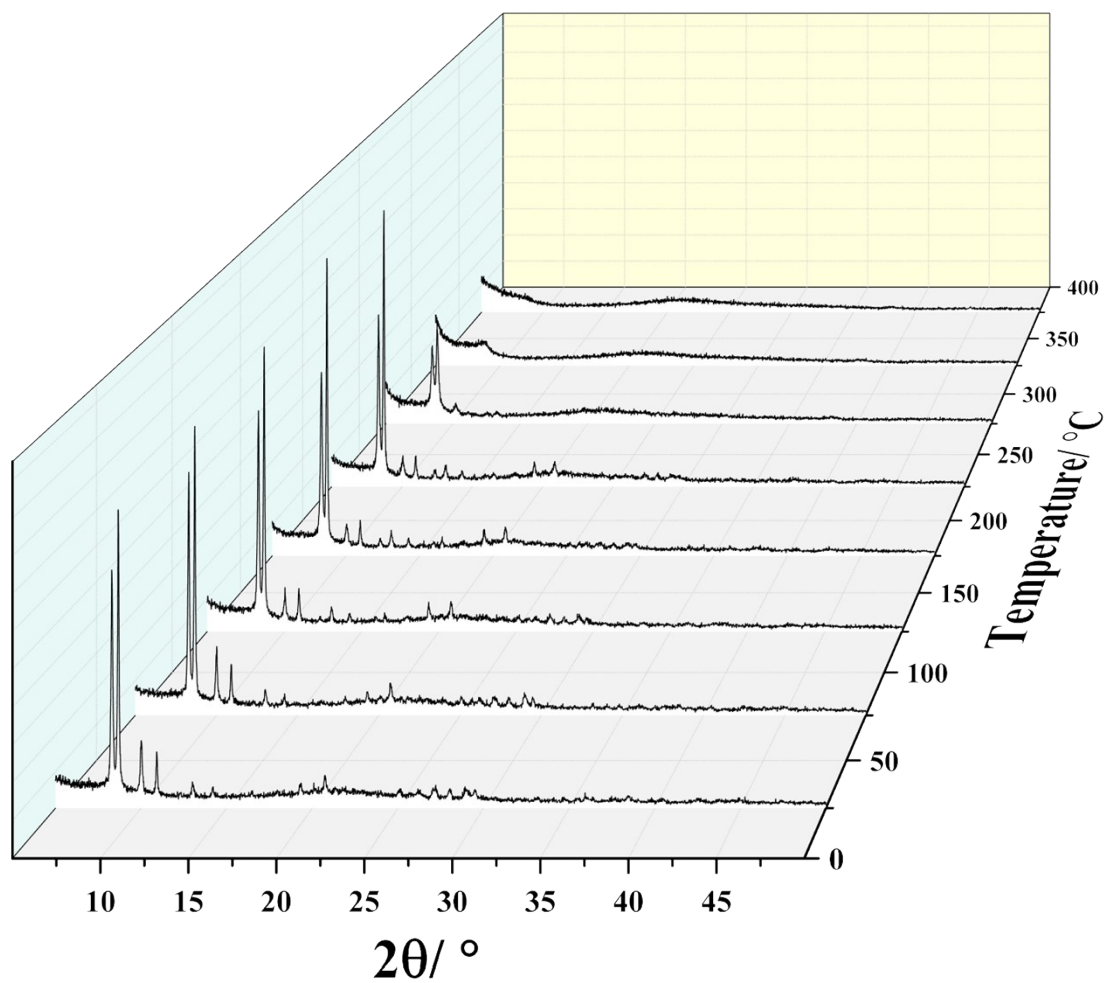


Figure S6. In-situ temperature-dependent PXRD of Au NPs@MOF-808 (heating rate 10  $^\circ\text{C}/\text{min}$ ).

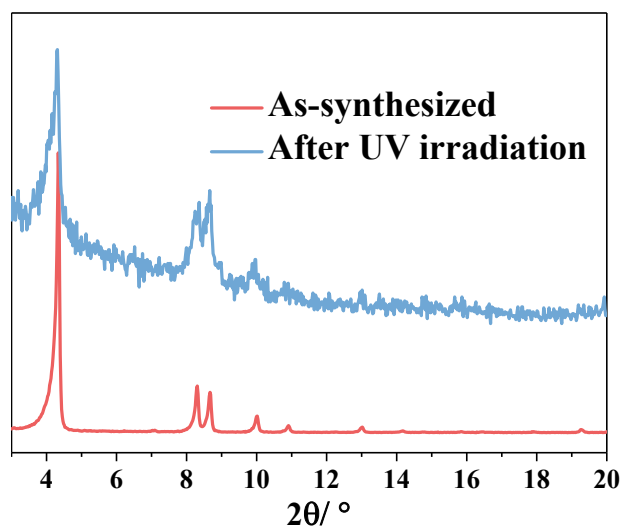


Figure S7. PXRD patterns of the as-synthesized Au NPs@MOF-808 and the one after treatment with 365 nm UV irradiation.



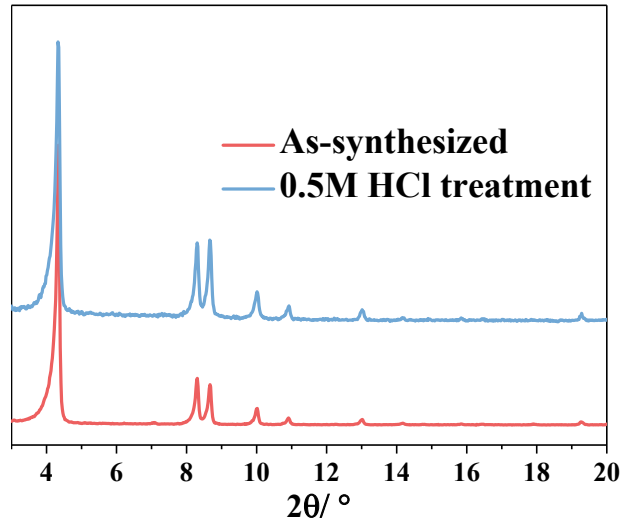


Figure S8. PXRD patterns of the as-synthesized Au NPs@MOF-808 and the one after 0.5M HCl treatment.

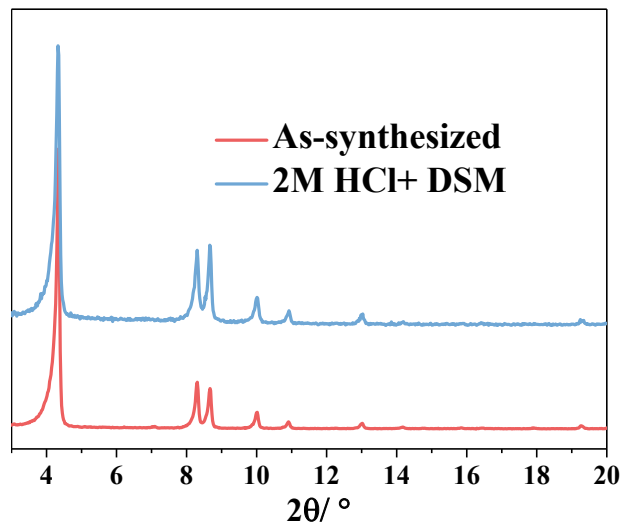


Figure S9. PXRD patterns of the as-synthesized Au NPs@MOF-808 and the one after treatment with 2M HCl in the Acetone and H<sub>2</sub>O (1:1) solvent mixture.

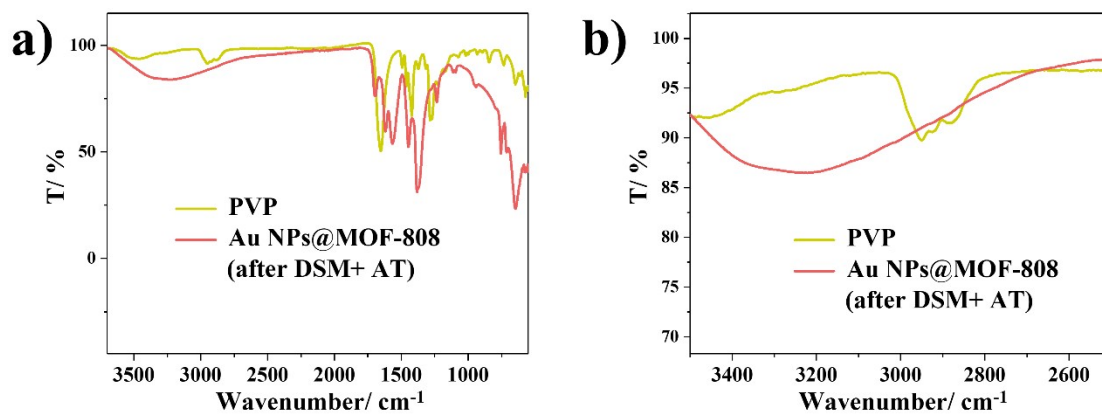


Figure S10. a) FT-IR spectra of PVP, and Au NPs@MOF-808 (after acid treatment in double solvent), b) zoom in figure of a).

1. Y. Li, C. Chen, B. Li, J. Sun, J. Wang, Y. Gao, Y. Zhao and Z. Chai, *J. Anal. At. Spectrom.*, 2006, **21**, 94-96.
2. H. Tsunoyama, H. Sakurai, N. Ichikuni, Y. Negishi and T. Tsukuda, *Langmuir*, 2004, **20**, 11293-11296.