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Supplementary Information

Preparation of a microporous organic polymer by thiol-yne addition reaction and formation of Au nanoparticles inside the polymer

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Materials

Tetrakis(4-iodophenyl)adamantane was prepared according to the reported procedure.[1] 1-Bromoadamantane, triethylamine, $AlCl_3$, trimethylsilylacetylene, $NaBH_4$, 4-nitrophenol, K_2CO_3, thiophenol, CuI, dichlorobis(triphenylphosphine)palladium(II), phenylacetylene and gold chloride hydrate ($HAuCl_4$) were purchased from Aldrich and used as received. 1,3,5-Benzenetrithiol and iodine were purchased from TCI and used as received. Other reagent-grade solvents were used as received. Azobisisobutyronitrile (AIBN) was recrystallized in methanol before use.

Characterization

^1H NMR measurement was carried out on a Bruker Avance-300 (300 MHz). ^{13}C Solid state NMR measurement was carried out on a Bruker 400 Solid/Micro-Imaging High Resolution NMR (100 MHz). N_2 uptake amounts were measured by using a Belsorp-Max (BEL Japan, Inc.) apparatus. FT-IR spectra were recorded on a PERKIN ELMER Spectrum GX I using KBr pellets. High resolution TEM image was obtained by using a JEM-2100F (JEOL). Field emission SEM image was obtained by using a JSM-6700F. Elemental analyses were performed by a Flash 1112 (Thermo Electron corporation). UV-Vis spectra were obtained by using a SCINCO S-3150 spectrometer. Wide-angle X-ray diffraction (WXRD) was recorded by a Bruker Xps GADDS (Cu Kα radiation, $\lambda = 1.54$ Å). Powder X-ray diffraction (PXRD) was recorded by a Bruker D5005. X-ray photoelectron spectroscopy (XPS) spectra were collected on a KRATOS AXIS-Hsi spectrometer equipped with a Mg K_α X-ray source. Mass spectra were obtained by a JEOL JMS-700 in the fast atom bombardment mode. Thermogravimetric analyses (TGA) were performed on a TA modulated TGA2050 with a heating rate of 10 °C/min under nitrogen.

Synthesis of tetrakis(4-ethynylphenyl)adamantane

This compound was prepared according to the reported procedure.[2] To a solution of tetrakis(4-iodophenyl)adamantane (1 g, 1.06 mmol) in toluene (80 mL) were added trimethylsilylacetylene (0.416 g, 4.24 mmol), TEA (30 mL), CuI (0.025 g, 0.13 mmol), and dichlorobis(triphenylphosphine)palladium (0.050 g, 0.07 mmol) at room temperature. The solution was refluxed for 10 h. After evaporation of the solvent, the product was dissolved in $CHCl_3$ (50 mL) and washed with water. The organic phase was dried by anhydrous magnesium sulfate. After filtration and evaporation, the product [tetrakis(4-trimethylsilylethynylphenyl)adamantine] was isolated by recrytallization from MeOH. Yield: 0.850 g, 97 %. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.44 (d, 8H, ArH), 7.38 (d, 8H, ArH), 2.05 (s, 12H, adamantine H), 0.27 (s, 36H, $SiCH_3$). Tetrakis(4-trimethylsilylethynylphenyl)adamantane (0.5 g, 0.932 mmol) was dissolved in THF/MeOH (100 mL, 1:1 v/v). After addition of K_2CO_3 (1.03 g, 7.45 mmol), the solution was stirred at room temperature for 10 h. After evaporation of the solvent, the product was dissolved in dichloromethane (50 mL) and washed with water. The organic phase was dried by anhydrous magnesium sulfate. After filtration and evaporation, the product was isolated by recrytallization from MeOH. Yield: 0.252 g, 77 %. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.49 (d, 8H, ArH), 7.42 (d, 8H, ArH), 3.05 (s, 4H, CH), 2.12 (s, 12H, adamantane H).

Preparation of microporous polymer by Thiol-Yne reaction

To a solution of tetrakis(4-ethynylphenyl)adamantane (0.126 g, 0.235 mmol) and 1,3,5-benzenetrithiol (0.109 g, 0.628 mmol) in DMF (80 mL) were added AIBN (0.154 g, 0.942 mmol) at room temperature. The solution was stirred at 130 ^{o}C for 24 h. The precipitated polymer was isolated by filtration and washed with THF, dichloromethane, MeOH, and water. The polymer was further purified by soxhlet-extraction with MeOH for 12 h and dried in vacuum. Yield: 0.165 g, 70.2 %. Anal. Calcd for $C_{58}H_{48}S_8$: C, 69.56; H, 4.83; S, 25.61. Found: C, 64.24; H, 4.27; S, 23.79.

Model reaction for Thiol-Yne reaction

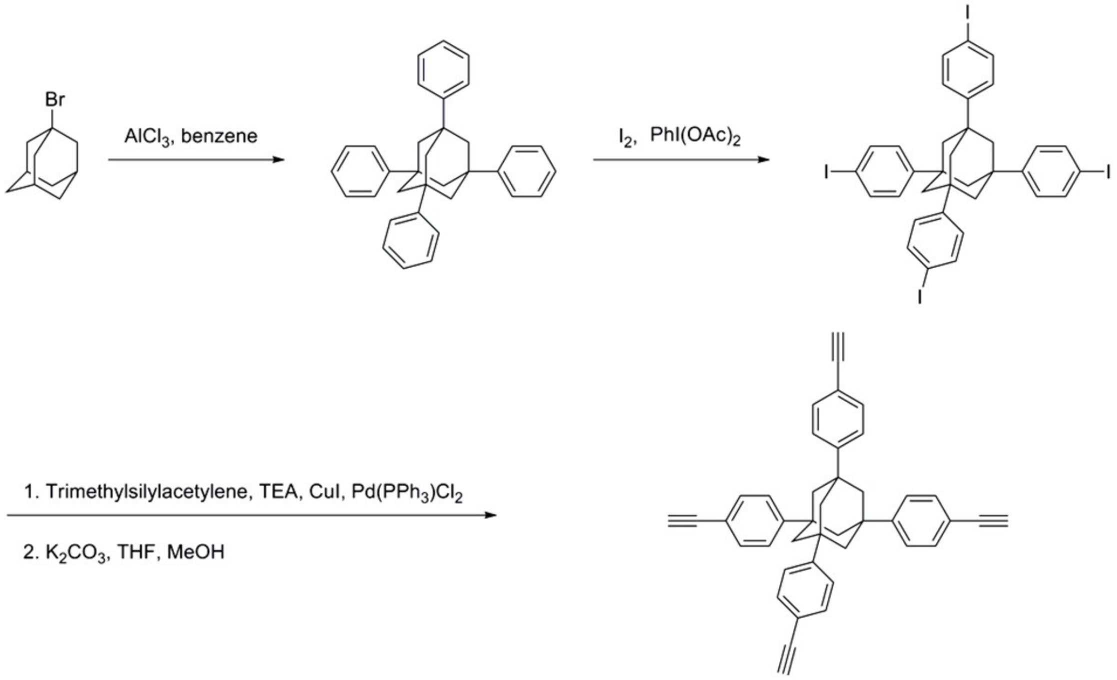
To a solution of phenylacetylene (0.1 g, 0.98 mmol) and thiophenol (0.216 g, 1.96 mmol) in DMSO-d_6 was added AIBN (0.016 g, 0.1 mmol). The solution was stirred at 100 ^{o}C.

Preparation of the Au NPs loaded microporous polymer

The microporous polymer (30 mg) was dispersed in ethanol (5 mL). A $HAuCl_4$ aqueous solution (1 mL, 8 mg mL^{-1}) was added into the dispersion. A $NaBH_4$ aqueous solution (1 mL, 25 mM) was slowly added to the dispersion with stirring. The color of the mixture changed from yellow to dark brown. After 1 h, the microporous polymer was filtered and washed with water and ethanol. The Au NPs loaded microporous polymer was dried in vacuum. The concentrations of Au, S and C measured by XPS were 11.49, 14.3 and 74.21 wt%, respectively.

Catalytic activity study

An ethanol solution of 4-nitrophenol (5 mL, 0.05 mM) was added to an aqueous $NaBH_4$ solution (1 mL, 0.1 mM). Then, the Au NPs loaded microporous polymer (10 mg) was added to the solution with gentle stirring. The UV-Vis absorption spectra were recorded at regular intervals to monitor the catalytic reduction of 4-nitrophenol.



Scheme S1 Synthesis of tetrakis(4-ethynylphenyl)adamantane.

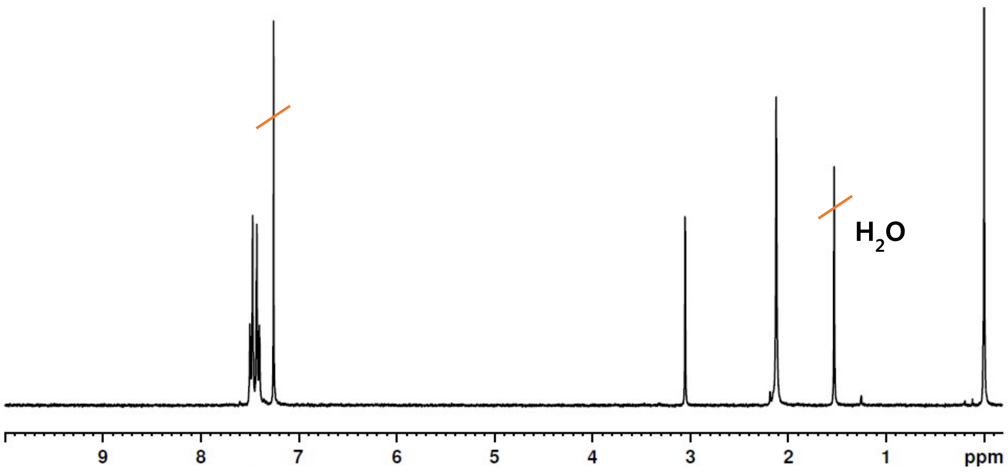


Fig. S1 ^{1}H NMR spectrum of tetrakis(4-ethynylphenyl)adamantane.

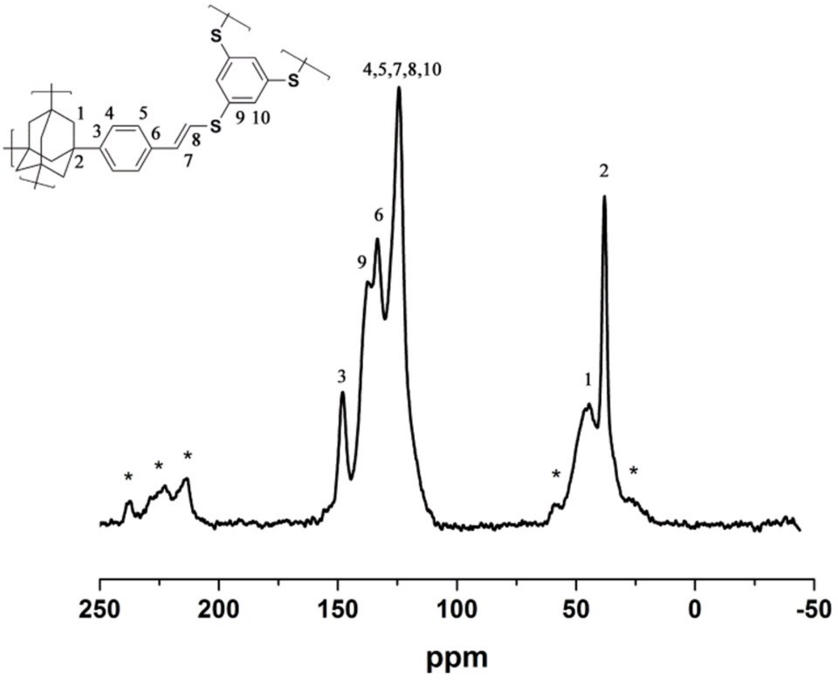


Fig. S2 ^{13}C solid state NMR spectrum of the microporous polymer.

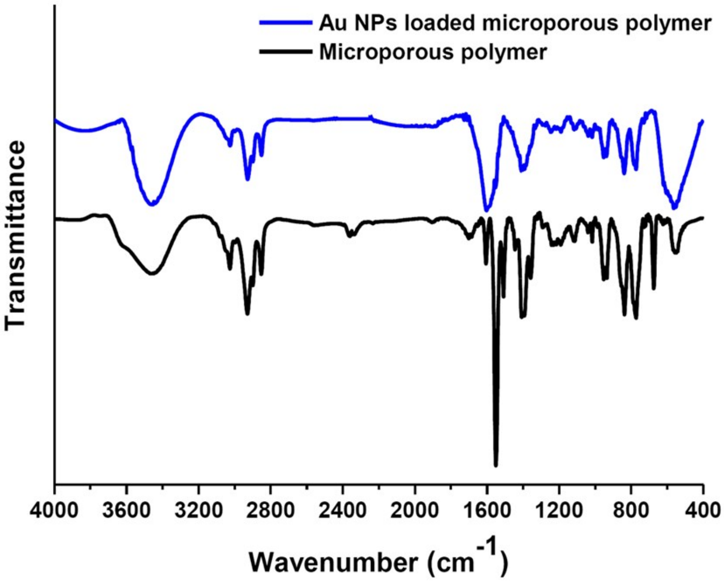
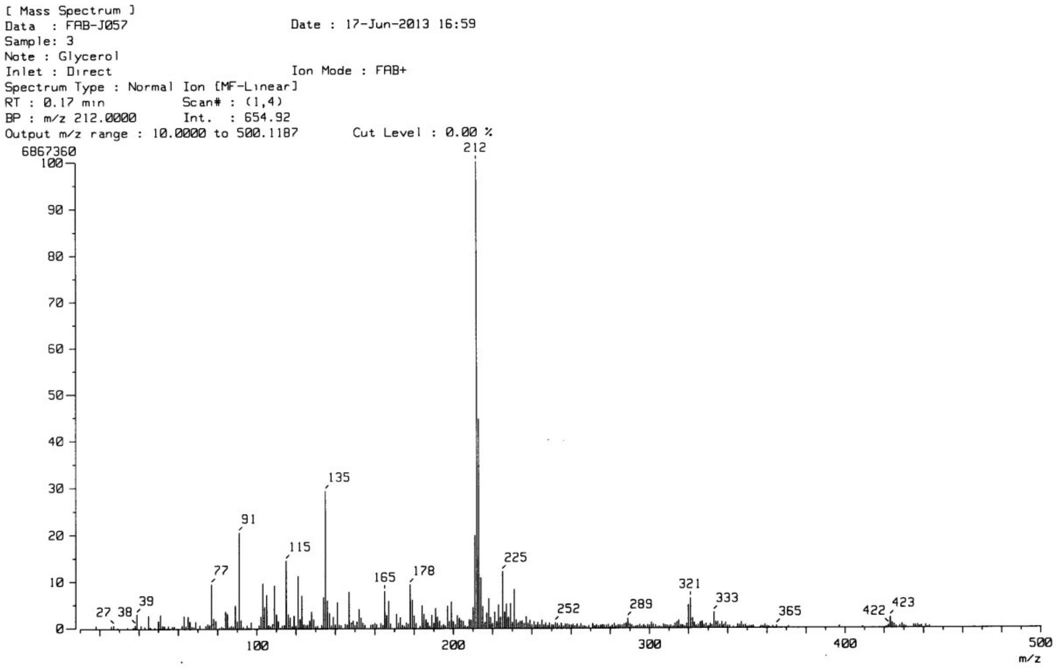


Fig. S3 FT-IR spectra of the microporous polymer and the Au NPs loaded microporous polymer.



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[ Mass Spectrum ]
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Sample: 3
Note : Glycerol
Inlet : Direct                       Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.17 min          Scan# : (1,4)
BP : m/z 212.0000      Int.   : 654.92
Output m/z range : 10.0000 to 500.1187       Cut Level : 0.00 %
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Fig. S4 Mass spectrum of the reaction mixture of thiophenol and phenylacetylene isolated after stirring at 100 °C for 3 h in DMSO-d_6

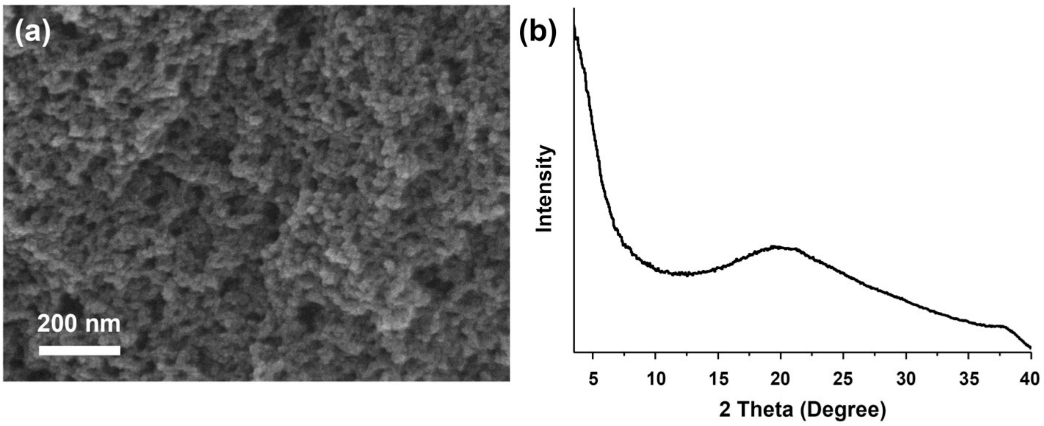

Fig. S5 (a) SEM image and (b) WXRD pattern of the microporous polymer.

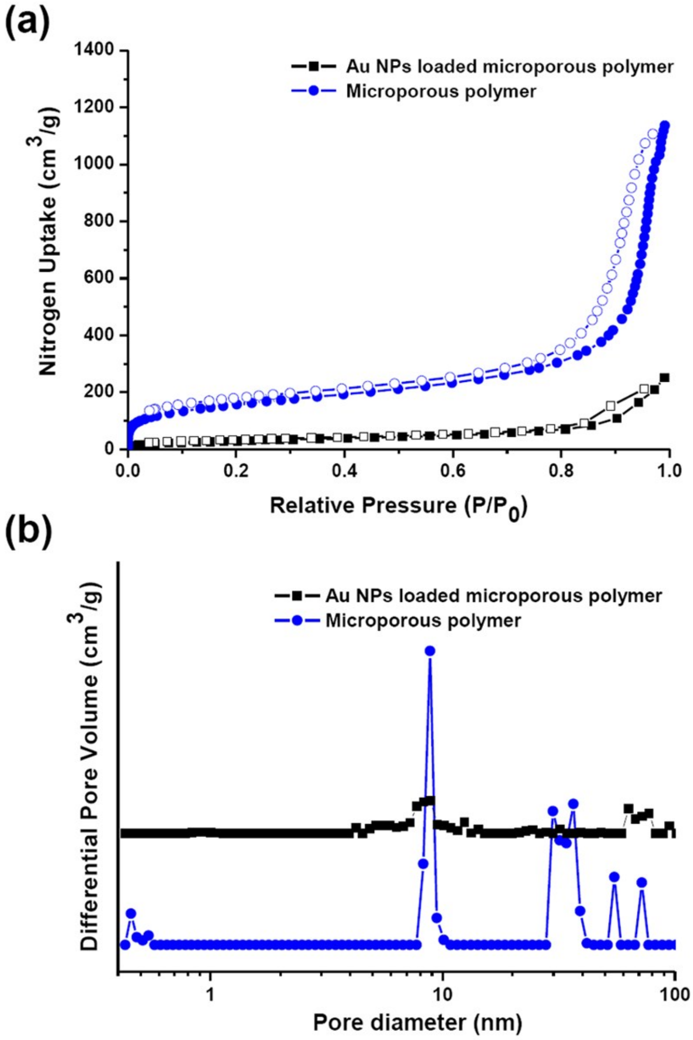

Fig. S6 (a) Nitrogen adsorption-desorption isotherms at 77 K and (b) NLDFT pore size distributions of the Au NPs loaded microporous polymer and the microporous polymer.

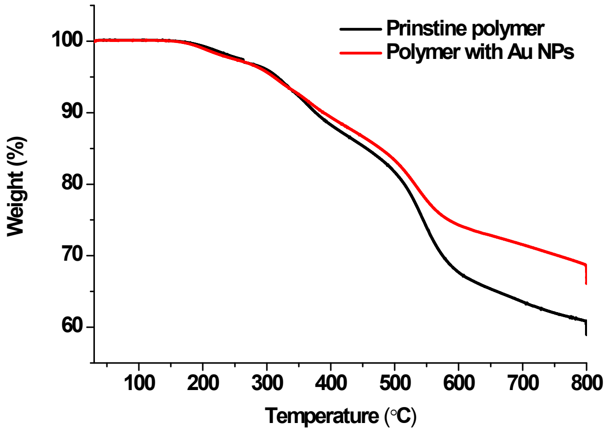

Fig. S7 TGA thermograms of microporous polymer before (black line) and after functionalization with Au NPs (red line).

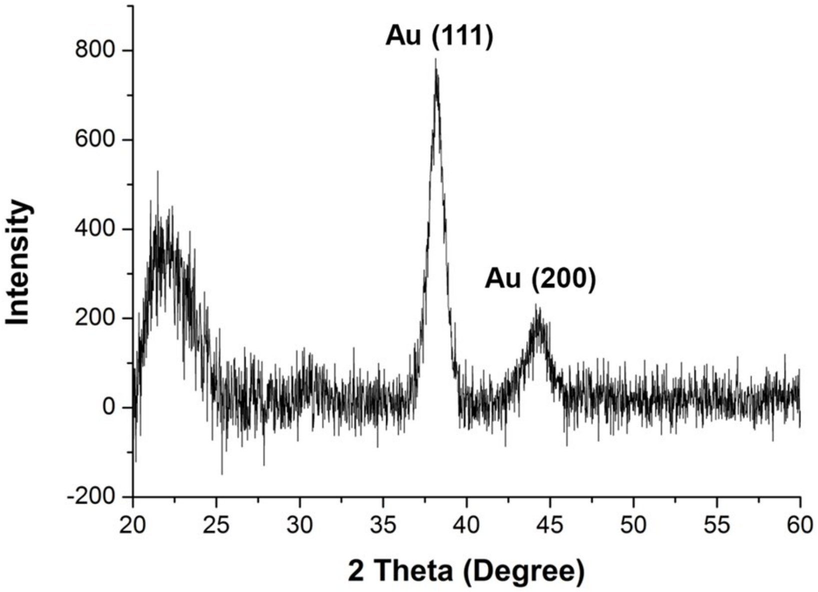

Fig. S8 Powder XRD pattern of the Au NPs loaded microporous polymer.

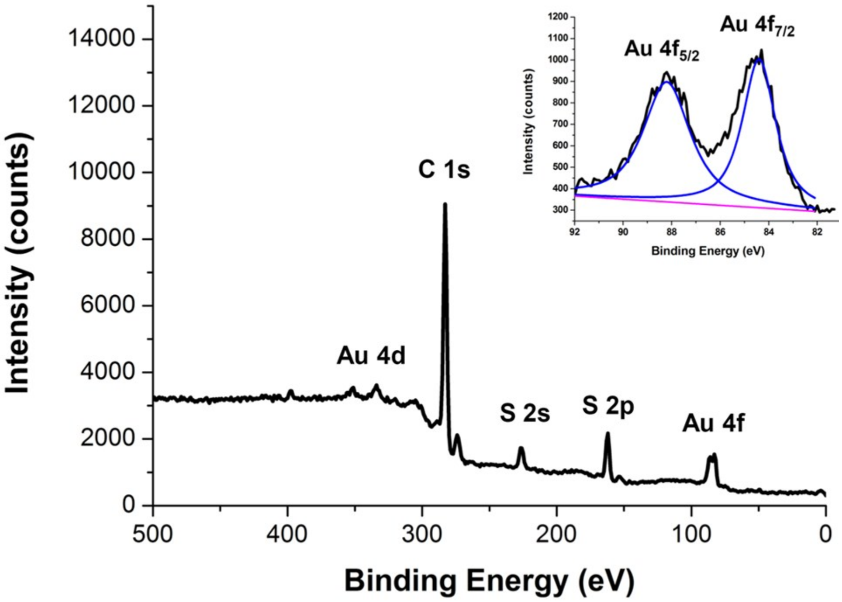

Fig. S9 XPS spectrum of the Au NPs loaded microporous polymer. High-resolution XPS spectrum is shown in inset.

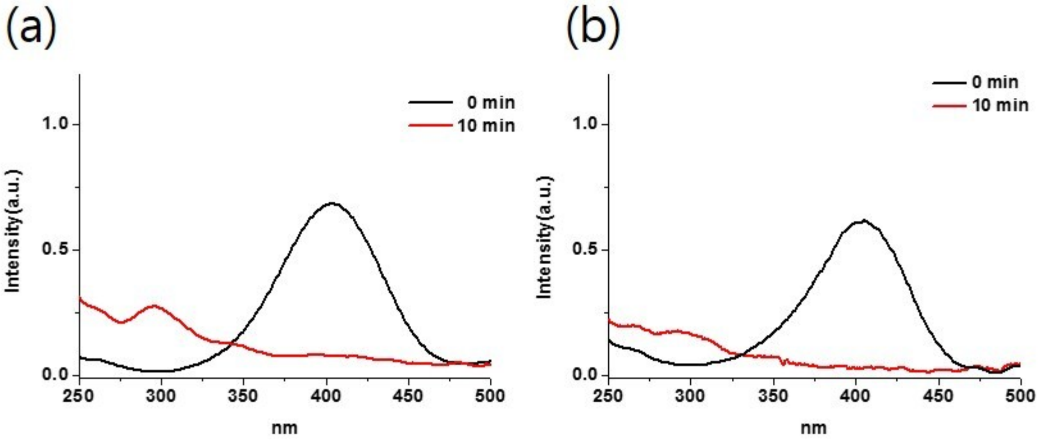

Fig. S10 UV-Vis spectra of (a) the 1st and (b) 5th cycle of the catalytic reduction of 4-nitrophenol with the Au NPs loaded microporous polymer.

References

1. H. Lim and J. Y. Chang, *Macromolecules*, 2010, **43**, 6943.
2. W. Lu, D. Yuan, D. Zhao, C. I. Schilling, O. Plietzsch, T. Muller, S. Bräse, J. Guenther, J. Blümel, R. Krishna, Z. Li and H.-C. Zhou, *Chem. Mater.,* 2010, **22**, 5964.