Electronic Supplementary Information

Hollow porous molecularly imprinted polymer nanosphere for fast and efficient recognition of bisphenol A

Xue-Bin Zhang, Jin Li, Bo You, Guo-Ping Yong, Hong-Wu Tong, Shao-Min Liu*

Department of chemistry, University of Science and Technology of China, Hefei, Anhui, 230026, China

E-mail: liusm@ustc.edu.cn

Fax: +86 551 3492065; Tel: +86 551 3492147

Experimental details

Materials

Bisphenol A (BPA, purity > 95%), phenol, o-phenylphenol (OPP, purity > 99%) and p-tert-butylphenol (PTBP, purity > 99%) were purchased from Aladdin reagent (Shanghai) Co., LTD. 4-Vinylpyridine (4-VP, Alfa Aesar, 96%) and ethylene glycol dimethacrylate (EGDMA, Alfa Aesar, 98%) were purified by distillation under vacuum. Azobisisobutyronitrile (AIBN, chemical grade) was purchased from Shanghai No.4 Reagent & H.V. Chemical Company (Shanghai, China), which was recrystallized with ethanol and then dried at room temperature in a vacuum condition prior to use. HPLC grade methanol was purchased from Tedia (Fairfield OH, USA). Cetyltrimethylammonium bromide (CTAB, 99.8 wt %), tetraethyl orthosilicate (TEOS), ammonium hydroxide (28 wt % NH_3 in water), HF solution (40%), toluene and ethanol were purchased from Shanghai Chemical Reagent Co., Ltd and were used as received without any further purification. Doubly distilled water was used in all experiments.

Synthesis

Preparation of MCM-48 spheres

In a typical synthesis, 2.6 g aliquot of *N*-hexadecyltrimethylammonium bromide was dissolved in 120 mL of doubly distilled water and 50 mL of ethanol, and 10 mL of aqueous ammonia (28 wt %) was added to the surfactant solution. The solution was stirred for 20 min at room temperature (450 r·min^{-1}), and 3 mL of TEOS was added at one time. After being stirred for 10 h,

the resulting solid was recovered by filtration, washed with distilled water and ethanol, and dried at 60 °C for 12 h. The template was removed by calcination at 823 K (2 ℃·min^{-1}) for 6 h.

Preparation of HPMIPs and HPNIPs

In a typical synthesis, 0.047 g of bisphenol A (BPA) and 0.074 g of 4-vinyl pyridine (4-VP) were resolved in 6 mL toluene at room temperature. 0.512 g of ethylene glycol dimethacrylate (EGDMA) and 60 mg azobisisobutyronitrile (AIBN) were added, the amount of imprint precursor mixture equaled to 0.6 times volume of MCM-48 (V=0.98 cm^3·g^{-1}), then purged with N_2, sealed up and stirred for 1 h at 40 °C. Next, 1 g MCM-48 spheres were added, ultrasound repeatedly, purged with N_2, sealed up and stirred for 6 h at 40 °C, heated up to 65 °C for 24 h and 80 °C for 6 h. Then washed with ethanol and immersed in ethanol solution of HF for 6 h to removal matrix MCM-48 and imprint molecule BPA, the resulting solid was recovered by filtration, washed with ethanol, and denoted as HPMIP-0.6. HPMIPs synthesized with imprint precursor equals to 0.8 and 1.0 times of pore volume of MCM-48 were denoted as HPMIP-0.8 and HPMIP-1.0, respectively. For comparison, the corresponding non-imprinted polymer (HPNIP) was also prepared in the same way in the absence of a template.

Characterization of the samples

The powder X-ray diffraction (PXRD) patterns of the samples were collected on a Philips X'Pert PRO SUPER diffractometer operating with nickel-filtered Cu-Kα radiation (λ = 1.540598 Å) at 40 kV and 200 mA. The diffractograms were recorded in the 2θ range of 0.8–10°. Nitrogen sorption isotherms were measured at 77 K with a Micromertics ASAP 3020 analyzer (Micromertics, USA), before measurements, the samples were degassed in a vacuum at 200 °C for at least 15 h. The Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) model were utilized to calculate the specific surface areas (BET), and pore size distributions, respectively. Fourier transform infrared (FT-IR) experiments were performed with EQUINOX55 (Bruker, Germany) using KBr pellets of the solid samples. The comparison of extract efficiency of

10% HF water solution and 10% HF ethanol solution for BPA in the as-made samples was performed on high-performance liquid chromatography-diode array detection (HPLC-DAD) (weigh accurately 10 mg of the HPMIPs etching with 10% HF water solution and etching with 10% HF ethanol solution into two 25 mL conical flasks, then 10 ml methanol were added, respectively. The systems were shaked for 12 h at 40 °C, filtration using a 0.22 μm Millex-GVMilli pore filter, and the filtrate was analyzed by HPLC-DAD with methanol as mobile phase, flow rate 0.8 $mL \cdot min^{-1}$, detector wavelength was 228 nm). Scanning electron microscopy (SEM) measurements were taken on a Sirion 200 microscope (FEI, USA) operated at 5 KV. Transmission electron microscopy (TEM) measurements were taken on a JEOL 2010 microscope (JEOL, Japan) operated at 200 KV. Thermogravimetric analysis of the samples were monitored using SDT Q600 thermal analyzer (TA, USA) from room temperature to 600 °C under air with a heating rate of 10 $°C \cdot min^{-1}$.

Equilibrium template binding experiments with the HPMIPs and HPNIPs

Equilibrium template binding experiments were investigated using high-performance liquid chromatography. 10 mg of the samples were first suspended in 10 mL of toluene solution with various concentrations of BPA. After incubation at room temperature for 2 h, filtration using a 0.22 μm Millex-GVMilli pore filter, and the filtrate was analyzed by HPLC-DAD (Agilent 1100) with methanol as mobile phase, flow rate 0.8 $mL \cdot min^{-1}$, detector wavelength was 228 nm. The binding amount of BPA was determined by measuring the difference between the total BPA amount and the residual amount in solution. All the above binding analyses were performed in duplicate and the mean values. Meanwhile, the binding kinetics of HPMIPs for BPA was tested by monitoring the temporal evolution of BPA concentration in the solutions.

Competitive binding experiments

The binding selectivity of the HPMIP-0.6 was evaluated by measuring their competitive binding capacities towards BPA and its structurally related compounds (4,4-Dihydroxybiphenyl (BIP), phenol, o-phenylphenol (OPP) and p-tert-butylphenol (PTBP)) with the same concentration. 10 mg of HPMIP-0.6 were incubated with 10 mL of a mixed solution of BPA, BIP, phenol, OPP and PTBP in toluene at 25 °C for 2 h and the amounts of BPA, BIP, phenol, OPP and PTBP bound to the HMMIP-0.6 were quantified by HPLC-DAD. The

wavelength used for the determination of the mixed solution of BPA, BIP, phenol, OPP and PTBP was 276 nm. Methanol and water with volume ratio equals to 7:3 were used as the mobile phase at a flow rate of 1 mL·min^{-1}. All the above binding analyses were performed in duplicate and the mean values.

The relative selectivity coefficient (k') were calculated according to the following equation:

$$K_d = \frac{C_i - C_f}{C_f} \times \frac{V}{W} \quad (1)$$

$$k = \frac{K_{dBPA}}{K_{danalogue}} \quad (2)$$

$$k' = \frac{K_{imprinted}}{K_{nonimprinted}} \quad (3)$$

Where distribution coefficient (K_d) stood for the character of a substance adsorbed by a sorbent, selectivity coefficient of the sorbent (k) represented the otherness of two analogues adsorbed by the same sorbent, while relative selectivity coefficient (k') suggested the otherness of two different sorbents. C_i and C_f represent the initial and final concentrations (μmol L^{-1}), V (L) and W (g) are volume of solution and mass of sorbent.

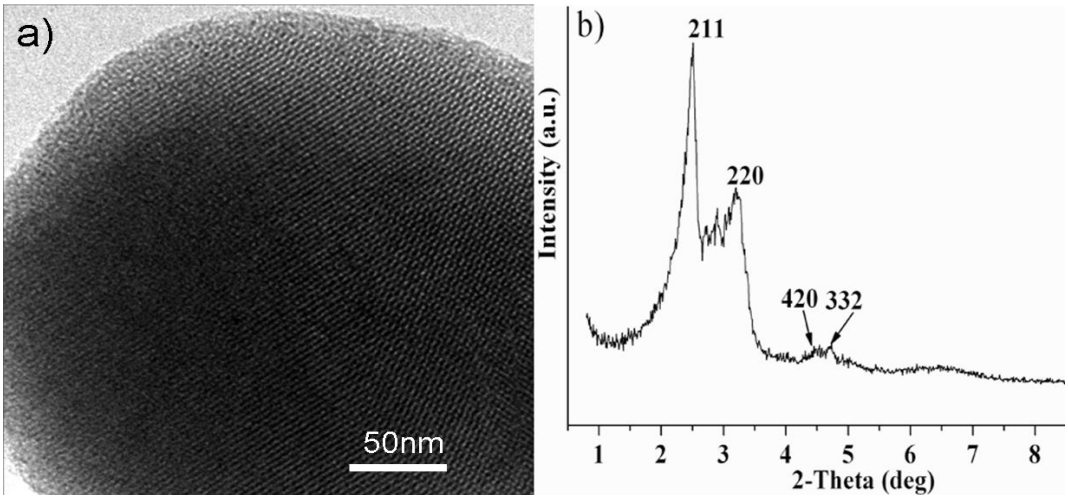

Fig. S1 HRTEM and XRD patterns of mesoporous MCM-48 sphere.

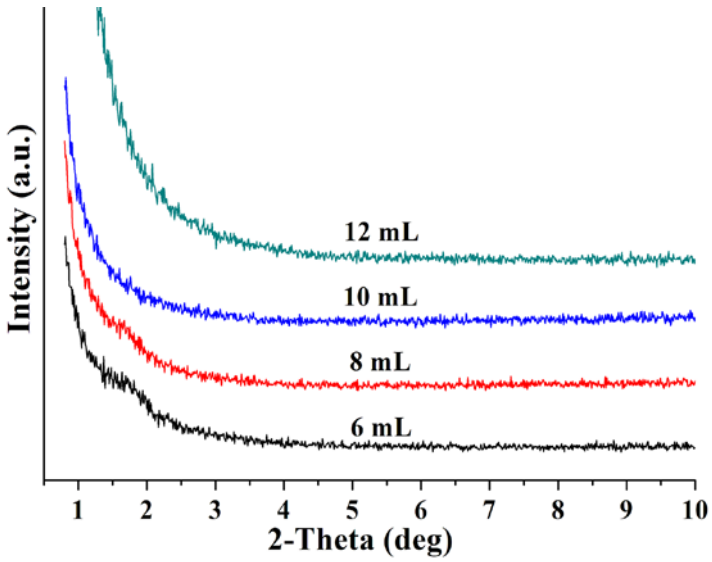

Fig. S2 Small angle XRD patterns of HPMIPs prepared with different solvent volume.

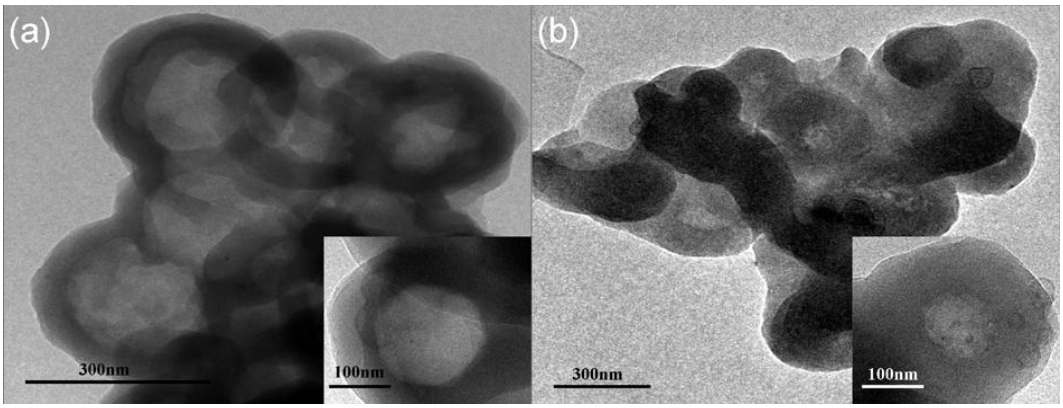

Fig. S3 TEM images of the synthesis HPMIPs with imprint precursor equals to 0.8 (a), and 1.0 (b) times of pore volume of MCM-48.

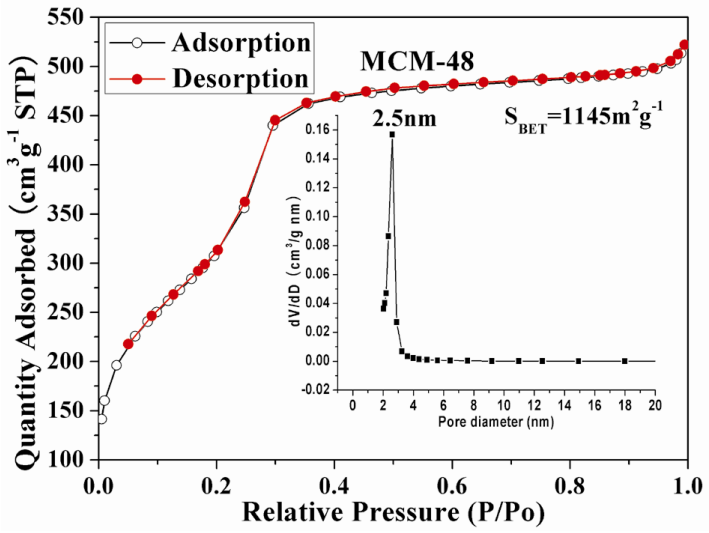

Fig. S4 N_2 sorption isotherms and pore size distribution curves of MCM-48.

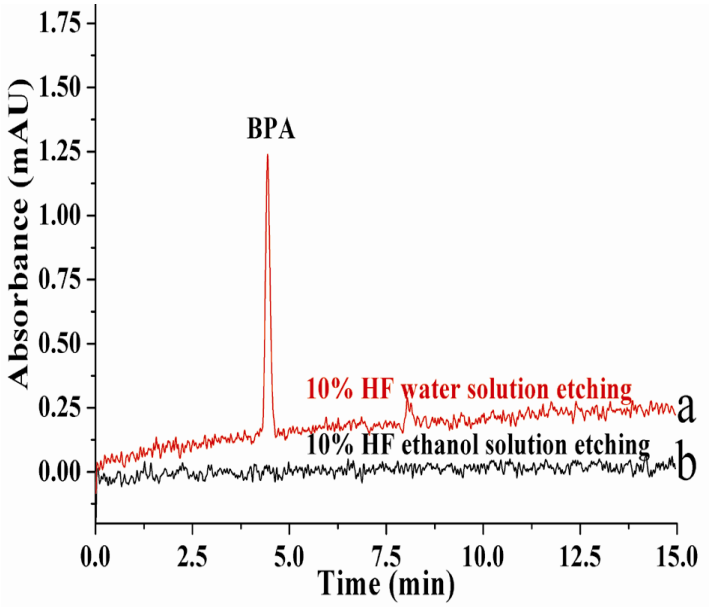

Fig. S5 The effect of etching solvent. (a) HPMIP etching with water solution of HF, (b) HPMIP etching with ethanol solution of HF, and then 10 ml methanol were added, respectively. The systems were shaking for 12 h at 40 °C, filtration using a 0.22 μm Millex-GVMilli pore filter, and the filtrate was analyzed by HPLC-DAD)

Seen from Fig. S5, if water solution of HF was used as etching solvent the imprint molecular can not be completely removed, while ethanol solution of HF could completely remove the imprint molecular.

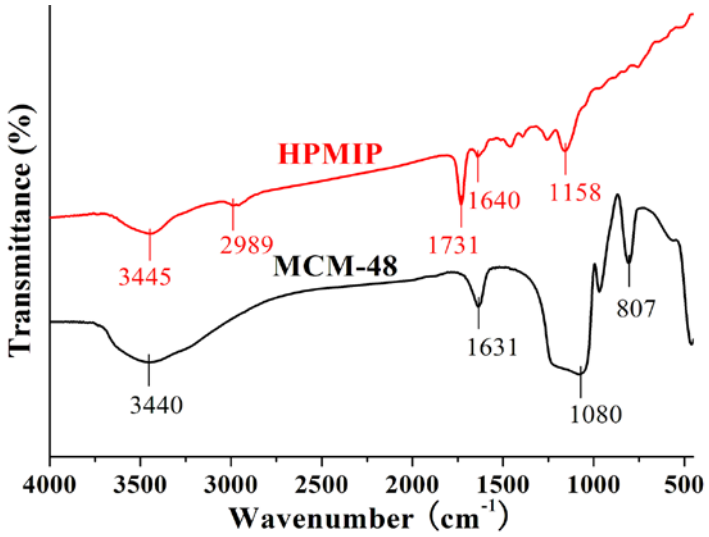

Fig. S6 FT-IR spectra of MCM-48, and HPMIP etching with 10% HF ethanol solution.

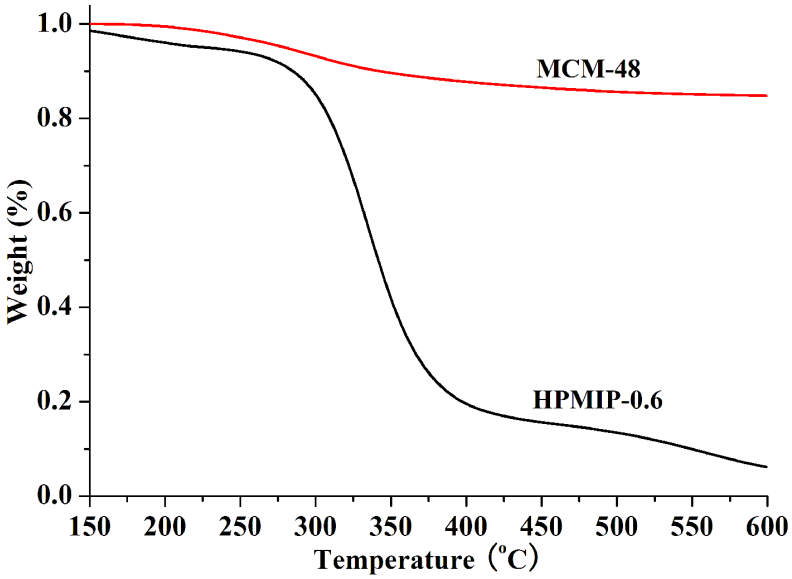

Fig. S7 Thermogravimetric (TG) curve of MCM-48 and HPMIP-0.6 recorded in air.

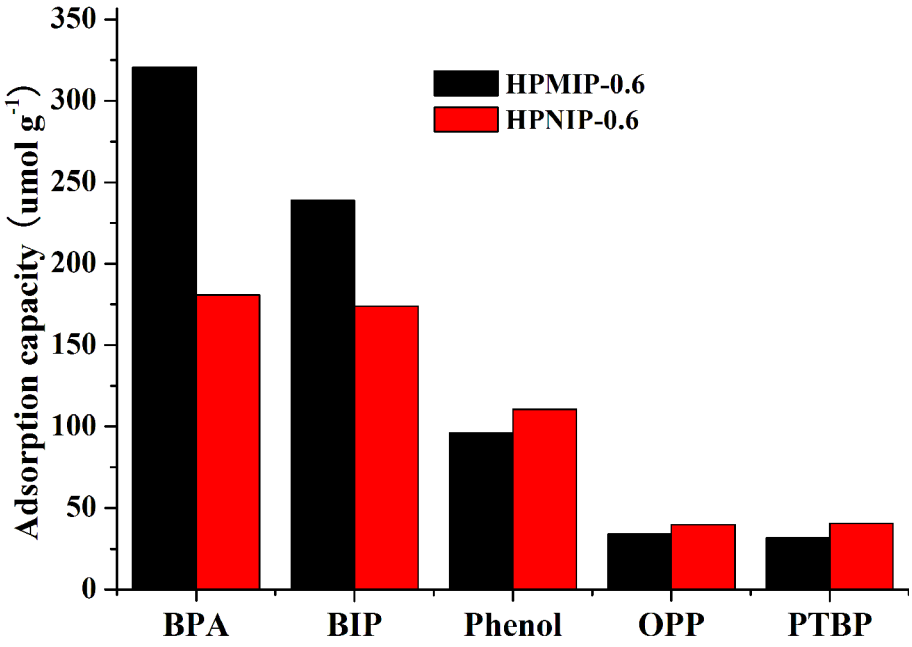

Fig. S8 Binding selectivity of HPMIP-0.6 and HPNIP-0.6 for BPA in mixture solution of 4,4-Dihydroxybiphenyl (BIP), phenol, o-phenylphenol (OPP), p-tert-butylphenol (PTBP) and bisphenol A (BPA).