

Supporting Information

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Hydrophilic molecularly imprinted polymers for selective recognition of polycyclic aromatic hydrocarbons in aqueous media

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1 **1. Reagents**

2 Naphthalene (NAP), acenaphthylene (ANY), acenaphthene (ACE), phenanthrene (PHE),
3 fluoranthene (FLT), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene
4 (BbK), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IPY),
5 dibenzo[a,h]anthracene (DBA), benzo[ghi]perylene (BPE), 4-vinylpyridine (4-VP), divinyl benzene
6 (DVB) (technical grade, 80%; treated successively with 1 M sodium hydroxide and washed with
7 ultrapure water), and glycidyl methacrylate (GMA) were purchased from Sigma-Aldrich. Cyclohexane,
8 2,2'-Azobis-isobutyronitrile (AIBN), dichloromethane (DCM), ethyl acetate, ethanol, sodium hydroxide,
9 sodium chloride, perchlorate, and acetone were obtained from Sinopharm Chemical Reagent Co., Ltd
10 (China). Methanol (MeOH) and acetonitrile (ACN) used for HPLC were obtained from Shanghai
11 ANPEL Scientific Instrument Co., Ltd. (Shanghai, China).

12 All other reagents were of analytical grade and used without any further purification. Freshly
13 deionized water (18.2 M Ω cm specific resistance) obtained by a Pall Cascada laboratory water system
14 was utilized for preparing aqueous solutions. The stock solutions of PHEs were prepared in ACN and
15 then diluted to appropriate concentrations of working solutions with deionized water.

16 **2. Synthesis of H-MIP**

17 The hydrophilic MIP (H-MIP) for PHE was synthesized according to the previously reported
18 method with some modifications.¹ Briefly, the template PHE (1 mmol), 4-VP (5 mmol), GMA (20
19 mmol), DVB (20 mmol) and AIBN (0.5 mmol) were dissolved in dichloromethane (30 mL). Then the
20 solution was purged with a stream of nitrogen gas for 10 min. Polymerization was done overnight at 70
21 °C in an oil bath. After polymerization, the obtained soft bulk polymer particles were ground manually
22 with a mortar and pestle. Removal of the template and unreacted monomers was done by Soxhlet
23 extraction with dichloromethane for 12 h. The resultant particles were oxidized by perchloric acid
24 (10%, v/v) for 24 h to make the epoxide ring of GMA opening and then washed with ethanol, and dried
25 overnight. In epoxide ring-opening reaction, H₂O was chosen as the nucleophile. It has been well
26 established that the rate of such reaction can be efficiently enhanced by the acids.² However, it should
27 be noted that chloride and nitrate which are strong nucleophiles can be added to the epoxide since
28 epoxide ring opening is a nucleophilic addition reaction. Perchlorate which is a very weak nucleophile
29 will not interfere with the above mentioned reaction. In addition, it has been proven that the presence of
30 a strong acid has no effect on the shape of a dense polymeric network.³ Thus, perchloric acid, rather

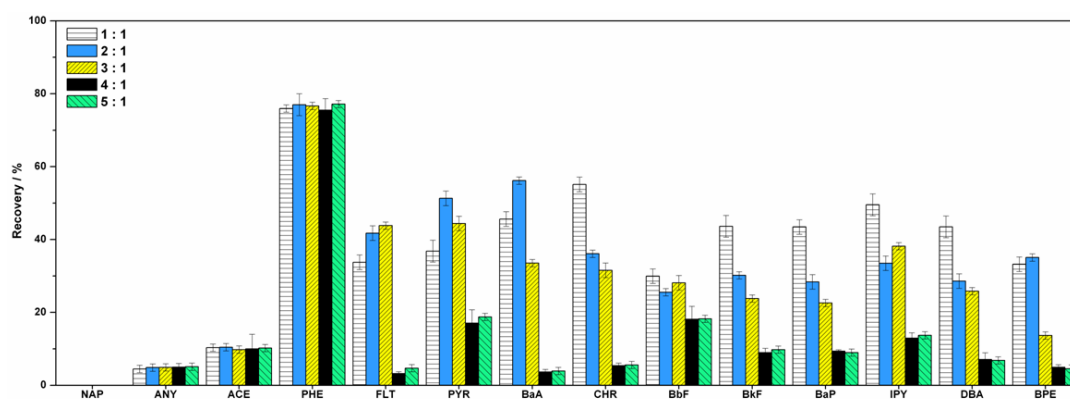
1 than HCl and HNO₃, was chosen as the agent for epoxide ring opening of GMA.

2 The hydrophilic non-imprinted polymer (H-NIP) was synthesized by the similar procedure in the
3 absence of template molecules. GMA inserted MIP (G-MIP) was prepared under identical conditions
4 except for omission of the procedure for epoxide ring opening. The conventional hydrophobic MIP was
5 synthesized by the bulk polymerization method as described elsewhere.⁴

6 **3. Effect of the mole ratio of co-monomer/functional monomer**

7 To choose a suitable mole ratio of co-monomer/functional monomer for the polymerization
8 process, the effect of the mole ratio was investigated in the range of 1 to 5. The results are shown in Fig.
9 S-1. As can be seen, the variation of the ratio exhibits a significant difference in the selectivity of the
10 resultant H-MIP, and the mole ratio of 4 gives the highest selectivity in terms of the high ratios of the
11 binding capacity of the template PHE to those of other 13 PAHs. In addition, further increase in the
12 ratio would not significantly improve the selectivity. Thus, the mole ratio of 4 was employed for
13 subsequent experiments.

14



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16 Fig. S-1. Effect of the mole ratio of co-monomer/functional monomer on the recoveries of 14 PAHs.

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18 **4. Details for the analytical methods**

19 **4.1. Saturation binding curves**

20 Saturation binding curves were obtained by incubating the conventional MIP, G-MIP, H-MIP and
21 H-NIP with 1 μ M–7 μ M PHE following the steps as described elsewhere.⁵ The amounts of PHE in the
22 supernatants were determined by HPLC (Waters e2695-2998, US).

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1 4.2. *Competitive binding assays*

2 The competitive binding assays were carried out by incubating 50 mg of the conventional MIP, G-
3 MIP, H-MIP, H-NIP and Supelco-MIP (Sigma-Aldrich, US) in 2 mL of the H₂O/methanol solution (2:1,
4 v/v) containing 14 PAHs at the same concentration (1 μM) in a 5 mL polypropylene microcentrifuge
5 tube, respectively. Then the tube was shaken under agitation for 24 h. The polymer was removed by
6 centrifugation at 9,000 rpm for 6 min and the supernatant was collected. The amounts of free PAHs
7 were calculated by subtracting the final concentrations from the initial concentrations of PAHs in
8 solution. The recovery was calculated by subtracting the amount of unbound one from the initial
9 amount added to the mixture and then dividing by the initial amount:

$$10 \quad \%R = \frac{C_{\text{initial amount}} - C_{\text{free amount}}}{C_{\text{initial amount}}}$$

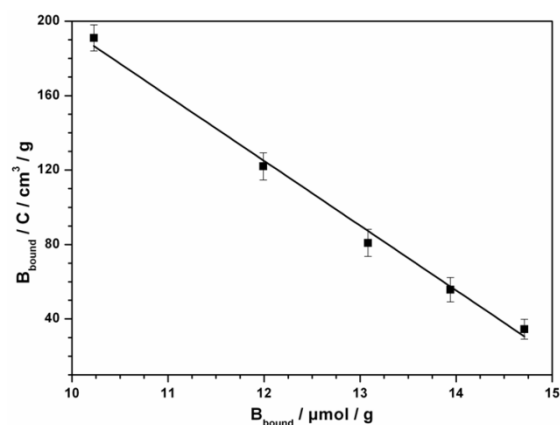
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12 5. *Scatchard analysis* ⁶

13 The Scatchard equation was employed to evaluate the relation between the concentration and
14 binding ability, and the equation is expressed as:

$$15 \quad \frac{Q}{C} = -\frac{1}{K_D}Q + \frac{Q_{\text{max}}}{K_D}$$

16 where Q stands for the binding capacity (μmol g⁻¹) of PHE on H-MIP, K_D represents the equilibrium
17 dissociation constant (μmol L⁻¹), Q_{max} (μmol g⁻¹) is the theoretical maximum adsorption amount of
18 template molecules on the H-MIP, and C (mol L⁻¹) is the equilibrium concentration of PHE in the
19 solution. In the case of one ligand and one type of binding site, a straight line would be generated with
20 a fixed slope rather than a curved one according to the Scatchard equation. Therefore, the values of
21 Q_{max} and K_D should be considered as good indicators for the evaluation of the binding ability of the H-
22 MIP. The application of the Scatchard equation to the calculations of the values for the binding
23 isotherms renders the plot and the corresponding values for the apparent Q_{max} and K_D (Q_{max} = 15.6
24 μmol/g, K_D = 28.7μM). The H-MIP curve shows a linear slope, indicative of one type of binding site
25 possessing high affinity (Fig. S-2).
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Fig. S-2. Scatchard plot of the H-MIP isotherm.

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