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

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A hydrophilic molecularly imprinted polymer (H-MIP) for selective recognition of polycyclic aromatic hydrocarbons in an aqueous medium has been developed in which a hydrophilic functional co-monomer is used to improve the surface hydrophilicity. By using phenanthrene as a model, the proposed H-MIP exhibits remarkably improved selectivity in aqueous solution.

Polycyclic aromatic hydrocarbons (PAHs), a group of highly lipophilic organic compounds, have received considerable attention in recent years owing to their carcinogenicity and ubiquitousness in the environment.1 In view of their environmental importance, many analytical methods have been developed to measure PAHs, such as gas chromatography-mass spectrometry (GC-MS),² high-performance liquid chromatography (HPLC)³ and room temperature phosphorescence (RTP).⁴ Since PAHs are usually found at trace levels in environmental samples, separation and preconcentration steps are always required prior to measurements. Solid-phase extraction (SPE) has shown to be a promising technique for PAHs enrichment because of its lower consumption of organic solvents, shorter extraction time and easier automation compared to liquidliquid extraction. Many materials including polymer sorbents,⁵ graphite fibers6 and silica particles7 have been used as SPE sorbents. However, it should be noted that the SPE approaches based on these materials show rather poor selectivities because the enrichment is governed mainly by the polarities of PAHs, rather than specific molecular recognition.

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Molecularly imprinted polymers (MIPs) have gained wide acceptance as new molecular recognition materials for use in SPE since they have high affinities and excellent selectivities similar to those of antibodies, and are chemically stable and easy to produce.⁸ In recent years, MIPs with excellent recognition abilities have been developed for preconcentration and determination of PAHs such as pyrene, chrysene and benzo[*a*]pyrene in environmental samples.⁹ However, most of the MIPs developed for PAHs are compatible with organic solvents, and fail to show specific template bindings in aqueous solutions since the strong non-specific adsorption of PAHs to the hydrophobic surface of MIPs usually occurs in aqueous media. This significantly limits their practical application in such areas as molecularly imprinted sorbent assays.

Herein, we report the efficient synthesis of the hydrophilic MIP (H-MIP) for PAHs. Hydrophilic co-monomer glycidylmethacrylate (GMA) is introduced to improve the water dispersion stability and the surface hydrophilicity of MIPs. Phenanthrene (PHE) has been chosen as a model of PAHs because it is one of the most abundant PAHs in aquatic environment. 4-Vinylpyridine (4-VP) was used as functional monomer, and the effect of the mole ratio of co-monomer/functional monomer is shown in Fig. S-1 (see the ESI†). It will be shown that the proposed approach can offer remarkably improved selectivity for the PHE MIP in aqueous solution. To our knowledge, this paper reports for the first time the synthesis of H-MIP that can be used directly in aqueous samples for the specific recognition of PAH molecules.

The obtained H-MIP was characterized by scanning electron microscope (SEM). Fig. 1a shows the SEM images of the conventional MIP and H-MIP, respectively. Interestingly, significant differences in morphology and particle shape were observed. The structure of the conventional MIP consists of interconnected nodules with sizes of approximately 20–50 nm, while the H-MIP particles exhibit a flaky appearance. This is due to the incorporation of the GMA co-monomer on the MIP surface. In order to confirm the grafting of the hydrophilic functional groups, the infrared spectra of the conventional MIP

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Fig. 1 (a) SEM images of the conventional MIP and H-MIP particles. (b) Infrared spectra of the conventional MIP and H-MIP. (c) Photographs showing the dispersions of the conventional MIP and H-MIP particles in pure water (10 mg mL⁻¹) at ambient temperature after settling down for 6 h.

and H-MIP were compared. As shown in Fig. 1b, the H-MIP displays the characteristic peaks of the hydroxyl groups of C-OH at the range of 1090–1110 cm⁻¹ compared with the infrared data of the conventional MIP, indicating that hydrophilic –OH groups have been introduced into the H-MIP. It has been well established that the water dispersion stability of the polymer particles can be efficiently improved by the introduction of hydrophilic groups. Therefore, it is anticipated that the particles grafted with hydrophilic groups should show enhanced dispersion stability in water. As expected, the H-MIP particles were stable and well-dispersed in water. In contrast, the conventional MIP particles aggregate into clusters floating on water, which is probably due to the high hydrophobicity of the conventional MIP (Fig. 1c).

To evaluate the selective recognition and special binding properties of the proposed H-MIP, the PHE recognition abilities of the conventional MIP with high hydrophobicity, GMA inserted MIP (G-MIP), H-MIP, and hydrophilic nonimprinted polymer (H-NIP) were investigated by the classical steady-state binding method in aqueous solutions. As shown in Fig. 2a, all of the imprinted polymers (the conventional MIP, G-MIP and H-



Fig. 2 (a) Equilibrium binding isotherms for the uptake of phenanthrene by the conventional MIP, G-MIP, H-MIP and H-NIP. Error bars represent one standard deviation for three measurements. (b) Profiles of a water drop on the films of the conventional MIP ($\theta = 103^{\circ}$), G-MIP ($\theta = 25^{\circ}$), H-MIP ($\theta = 32^{\circ}$) and H-NIP ($\theta = 30^{\circ}$) particles.

MIP) exhibit much higher capacities than the control polymer (H-NIP) for PHE. These results indicate that the functionalities of the PHE molecules are responsible for the imprinting effect of MIP. However, it should be noted that the binding capacities of the conventional MIP and G-MIP are higher than that of H-MIP. This observation might be attributed to the fact that the conventional MIP is more hydrophobic than the H-MIP, which can be confirmed by the reduced water contact angle of the H-MIP (Fig. 2b). In this case, more templates can be adsorbed onto the hydrophobic polymer surface through the non-specific hydrophobic interactions. The G-MIP can bind more of the template molecules than the H-MIP owing to the additional charge-transfer complexing interactions between the epoxide group of GMA and PHE although their static water contact angles are rather close (Fig. 2b). In addition, the Scatchard analysis was employed to evaluate the relation between the concentration and binding ability of H-MIP (see Fig. S-2 in the ESI[†]). As illustrated, the Scatchard plot of the H-MIP isotherm shows a linear slope, indicative of one type of binding site possessing high affinity. A K_D value (K_D represents the equilibrium dissociation constant) of 28.7 μ mol L⁻¹ was obtained.

The binding selectivity of the H-MIP in aqueous solution was evaluated by measuring the competitive binding capacities towards PHE and other 13 PAHs (see the ESI[†] for details). As a comparison, the conventional MIP, G-MIP, H-NIP and commercially available Supelco-MIP were chosen as reference polymers. Fig. 3 shows the results of competitive bindings of PHE and 13 PAHs competitors on these five polymers. Surprisingly, the specific template binding abilities (i.e., the binding differences between the template and other PAHs) of the conventional MIP and Supelco-MIP almost completely disappear in aqueous media although these polymers exhibit rather high binding capacities towards the 11 PAHs such as PHE, PYR, FLT, BkF and BbF. In sharp contrast, the H-MIP shows unique specific template bindings and high selectivity for PHE, which is probably attributed to its largely improved surface hydrophilicity. Note that, with hydrophilic modification, the non-specific adsorption is reduced owing to the decrease of the hydrophobicity of the MIP. In this case, the specific molecule recognition



Fig. 3 Competitive bindings assays of the Supelco-MIP, conventional MIP, G-MIP, H-MIP and H-NIP particles in 14 PAHs, including naphthalene (NAP), acenaphthylene (ANY), acenaphthene (ACE), phenanthrene (PHE), fluoranthene (FLT), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IPY), dibenzo[a,h]anthracene (DBA), benzo[ghi]perylene (BPE), mixed aqueous solutions. Error bars represent one standard deviation for three measurements. The concentrations of PHE and other 13 PAHs are 1 μ M.

interactions dominate the binding selectivity of the MIP. These results clearly confirm the excellent specific molecularrecognition ability of the H-MIP in the aqueous solution. Compared with the H-MIP and other reference polymers, the H-NIP exhibits the lowest binding capacity towards the template PHE. Above all, no specific template binding ability towards the 14 PAHs can be observed for the H-NIP, which further confirms the imprinting effect of the H-MIP. In addition, it should be noted that the hydrophilic G-MIP also exhibits no specific binding ability. Thus, it can be demonstrated that hydrophilic -OH groups of the H-MIP can not only improve the surface hydrophilicity but also act as a protective layer to prevent the non-specific adsorption of the hydrophobic interferents on the polymer surface.

Conclusions

A few approaches for synthesis of hydrophilic MIPs have been reported. Direct modifications based on the additions of hydrophilic monomers,10 co-monomers8d and crosslinkers11 in the molecular imprinting polymerization systems have been described for water-compatible MIPs. However, these approaches suffer from problems of the formation of unexpected hydrogen bonds between functional monomers and hydrophilic co-monomers or crosslinkers. A general and successful approach for synthesis of hydrophilic MIPs has been developed based on reversible addition-fragmentation chaintransfer precipitation polymerization mediated by hydrophilic macromolecular chain-transfer agents.8b Despite its excellent performance, the proposed approach referred to complicated synthesis processes. In this work, we report a simple approach for efficient synthesis of hydrophilic MIP with excellent specific recognition ability in aqueous media for PAHs. The water dispersion stability and surface hydrophilicity of the conventional PHE MIP have been significantly improved by the introduction of the hydrophilic functional co-monomer GMA. Although the proposed H-MIP exhibits a slightly lower binding capacity for PHE than the conventional MIP and G-MIP, it shows specific template binding ability and high template selectivity in aqueous solution. It is expected that such polymer

can be used as SPE sorbent for the efficient enrichment of PHE in real aqueous samples such as environmental waters and biological fluids. Since many hydrophilic co-monomers and MIPs have been extensively exploited in analytical chemistry, it is very promising to develop hydrophilic imprinted polymers for selective recognition of other organic species in aqueous media.

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