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Molecularly imprinted photonic polymer based on β-cyclodextrin for amino acid sensing

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ABSTRACT

A novel molecularly imprinted photonic polymer (MIPP) using maleic anhydride modified β-cyclodextrin (β-CD) and acrylic acid as functional monomers has been presented for amino acid sensing. Reactive β-CD monomer carrying vinyl carboxylic acid functional groups was first synthesized. MIPP was fabricated by filling precursor solution into the interstitial spaces of polystyrene photonic crystal templates, followed by a thermal polymerization at 55 °C. Characterization showed that the MIPP possessed an opal photonic crystal structure. This β-CD-based MIPP could undergo a swelling change from 590 nm to 704 nm and still retain the molecular imprinting recognition ability during the sensing of L-phenylalanine (L-Phe). A function relationship was found between the diffraction wavelength shift and the logarithm of L-Phe concentration in the range of 10^{-8} M to 10^{-4} M at pH 6. A wavelength shift of 114 nm for L-Phe was observed within 30 s, whereas there were no obvious shifts for D-Phe, L-tyrosine and L-tryptophan, indicating that the β-CD-based MIPP had high specificity and rapid response to L-Phe. The developed MIPP sensor has been applied to detect L-Phe in compound amino acid injection sample.

1. Introduction

In recent years, much work has been focused upon developing molecularly imprinted photonic polymer (MIPP) as high effective sensor for environmental monitoring and chemical and biological detections. In many cases, design of MIPP was on the basis of combination of photonic crystal templating method and molecular imprinting technique [1–16]. In MIPP, photonic crystal template was used to create periodic structures for enduing photonic lattice properties to the MIPP. Meanwhile, molecular imprinting technique was used to synthesize molecular imprinted polymers with specific molecular recognition nanocavities. Stimuli-responsive hydrogels were commonly used as molecular imprinting functional monomers as well as high-sensitive transducers in MIPP. The sensing of MIPP was realized by the infiltrated hydrogels swelling and deswelling in response to environmental stimulus, which can give measurable signals upon binding guest molecules to detect and quantify the target analyte directly [17]. Previous research demonstrated that MIPP was an ideal sensing material due to its distinct advantages such as high selectivity, rapid response and signal self-reporting [1].

MIPP was introduced and then has been further developed by Li's group [2–6]. They reported a general protocol for the synthesis of MIPP films with inverse opal structure for specific recognition of L-dopa [2], protein [3], cholic acid [4], alkaloids [5] and atrazine [6]. Zhao et al. reported a new type of suspension array, which are molecularly imprinted polymer beads with photonic crystal structure, for the multiplex label-free detection of biomolecules [7]. Griffete et al. prepared a three-dimensional macroporous array for pH sensing [8] and made a development of MIPP by introduction of a planar defect in the sensor [9]. Recently, MIPP was reported for detection of trace cholesterol [10], organophosphorus [11], vanillin [12], 3-pyridinecarboxamide [13], chloramphenicol [14], and bisphenol A [15]. We have also demonstrated the application of MIPP for analysis tetracyclines in food [16].

Although all the above mentioned work demonstrated a very promising sensor platform of MIPP, the imprinting specific recognition of previous works was limited in aqueous media due to their common use of methacrylic acid and/or acrylic acid as the monomers. Hydrogen bonding interactions between template and acrylic acid functional monomers are easily destroyed in aqueous media because aqueous solvents can compete with the template [18,19]. Therefore, combining molecular imprinting with hydrogels photonic crystal is an emerging and promising technique that requires a systematic development. Attempts should be made to seek new functional monomers that can interact with templates in aqueous media to further exploit the potential of MIPP and make it applicable for more systems.

Due to some unique superior features compared to traditional functional monomers such as acrylic acid, β-cyclodextrins (β-CDs)

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have aroused extensive interest as attractive candidate monomers for molecular imprinting. β-CDs are a series of cyclic oligosaccharides with a hydrophilic exterior and a hydrophobic cavity capable of binding small hydrophobic structures, e.g., phenyl and indole ring systems [20]. Due to the rigidity and intrinsic chirality of hydrophobic cavity, β-CD unit can form complex with the target analyte through various kinds of intermolecular interactions such as Van der Waals force, hydrophobic, electrostatic, dipole–dipole, and hydrogen bond interaction during the imprinting process. Therefore, β-CDs are helpful to obtain high affinity binding sites [21,22] and separate chiral compounds [23] in aqueous solution.

Amino acids are important bioactive substances and widely used in the food, chemical and pharmaceutical industries. Artificial recognition systems for amino acids can be of great utility in modeling biological molecular recognition and also in the detection and separation of complex mixtures. Although molecularly imprinted polymers have been successfully applied for chiral separation of amino acids [24,25], the rational use of hydrophobic effect-based recognition is especially important for molecular imprinting aromatic amino acids. β-CDs have previously been shown to be capable of binding aromatic amino acids, and a variety of molecular imprinting receptors based on β-CDs, therefore, have been designed to recognize aromatic amino acids [21,26,27].

To the best of our knowledge, MIPP sensor based on β-CD is still lacking in the literatures. Our present work was intended to introducing β-CD as functional monomer into MIPP for chiral separation of aromatic amino acids. D-Phenylalanine (D-Phe) and L-phenylalanine (L-Phe) were chosen as template molecules since Phe was widely used in healthy, pharmaceutical and food products [28,29]. Maleic anhydride (MAH) modified β-CD carrying vinyl carboxylic acid groups was designed in order to obtain a reactive β-CD monomer which is water-soluble as well as can be copolymerized and cross-linked with acrylic acid component to form a hydrogel [30]. Precursor solution containing functional monomers, crosslinker (*N*,*N*′-methylene bisacrylamide), initiator (ammonium persulfate) was infiltrated into photonic crystal template which was self-assembled by monodisperse polystyrene colloids. After a thermal polymerization in an oven at 55 °C, the MIPP film with an opal structure was obtained. The sites which were complementary with the template were created when the imprinted molecules template was removed. Throughout a rigorous optimization of polymerization, pH, and response time, β-CD-based MIPP sensing for Phe with rapid, direct and sensitive detection has been achieved. The optical changes of diffraction wavelength resulted from the responding of the target molecules were detected directly by fiber optic spectrometer. The proposed MIPP has been applied to detect L-Phe in compound amino acid injection sample.

2. Experimental

2.1. Materials

D-Phenylalanine (D-Phe) was purchased from Aladdin Reagent (Shanghai, China), L-phenylalanine (L-Phe), L-tyrosine (L-Tyr), L-tryptophan (L-Trp), β-cyclodextrin (β-CD), maleic anhydride (MAH), ammonium persulfate (APS), acrylic acid (AA), *N*,*N*′-methylene bisacrylamide (BIS), dimethylformamide (DMF), $CHCl_3$, acetone, were analytical reagent grade and from local suppliers. Structures of β-CD, D-Phe, L-Phe, L-Tyr and L-Trp were shown in Fig. 1. β-CD was recrystallized two times from water prior to use. DMF was vacuum distilled before used. All other reagents were used without further purification. All containers and glass slides (50 × 20 mm) for photonic crystal growth were cleaned by rinsing with a H_2SO_4–H_2O_2 (7/3, v/v) mixture and deionized water.

Buffer solution was prepared by mixing 0.2 M disodium phosphate and 0.2 M sodium dihydrogen phosphate according to certain proportion, and its pH was adjusted by adding additional phosphoric acid or sodium hydroxide if necessary. Stock solutions of amino acids were prepared by dissolving them in pH 6 phosphate buffer solution.

2.2. Preparation of photonic crystal templates

The monodispersed polystyrene colloids were synthesized via emulsion polymerization in the same way as described in reference [31]. Then, templates of photonic crystal were prepared from the obtained monodispersed polystyrene colloids by using the vertical deposition method. Polystyrene colloids particles in aqueous media with a concentration of about 5% (v/v) were placed into treated containers. A treated glass slide was put into each container vertically for photonic crystal growth. Containers were laid in a 43 °C water bath until the solvent was evaporated completely, then templates of close-packed face-centered-cubic (fcc) photonic crystal were obtained.

2.3. Synthesis of maleic anhydride modified β-cyclodextrin (MAH-β-CD)

Modified β-CD carrying vinyl carboxylic acid groups was synthesized according to the reference [32]. Briefly, 5.68 g of β-CD (0.005 mol) was dissolved in 30 mL DMF, and 4.90 g of MAH (0.05 mol) was added afterwards. The mixture solution was heated at 80 °C for 10 h under the vigorously stirring. The mixture was allowed to cool to room temperature, and then, 30 mL of $CHCl_3$ was added. A white precipitate obtained was filtrated, and washed at least three times using large amount of acetone, finally, dried in a vacuum oven at room temperature for 1 day, and 80 °C for 3 days.

2.4. Fabrication of MIPP films

MAH-β-CD and AA were both chosen as functional monomers to prepare Phe-imprinted photonic polymer. In a typical experiment, MAH-β-CD (0.5 g) and AA (1.5 mL) were mixed with L-Phe (0.0165 g) in 3.5 mL deionized water for sufficient intermolecular interaction to form a stable complex. BIS (0.1 g) as cross-linker and APS (0.08 g) as initiator were added in this solution. Following a sufficient homogenization, the mixture of precursors was infiltrated into the above polystyrene photonic crystal template by capillary-attraction-induced method until the interstitial spaces among the close-packed spheres were filled with the solution. After polymerization in an oven at 55 °C for 4 h, the obtained MIPP was washed with 30 mL water and subsequently with methanol/acetic acid (9/1, v/v) to remove unreacted monomers and L-Phe. Herein, MIPPL and MIPPD were prepared using L-Phe and D-Phe respectively as the imprinted template. The corresponding non-molecularly imprinted photonic polymer (NIPP) was prepared in the same manner except for the absence of the imprinted templates.

2.5. Characterization

Surface morphologies of the used photonic crystal templates and the imprinted films were observed by a field-emission scanning electron microscope (Nova NanoSEM 430, FEI) operating at 25 kV. Infrared spectroscopy measurements were performed on Fourier transform infrared spectrophotometer (Perkin-Elmer 1600, FT-IR) using KBr pellet techniques.

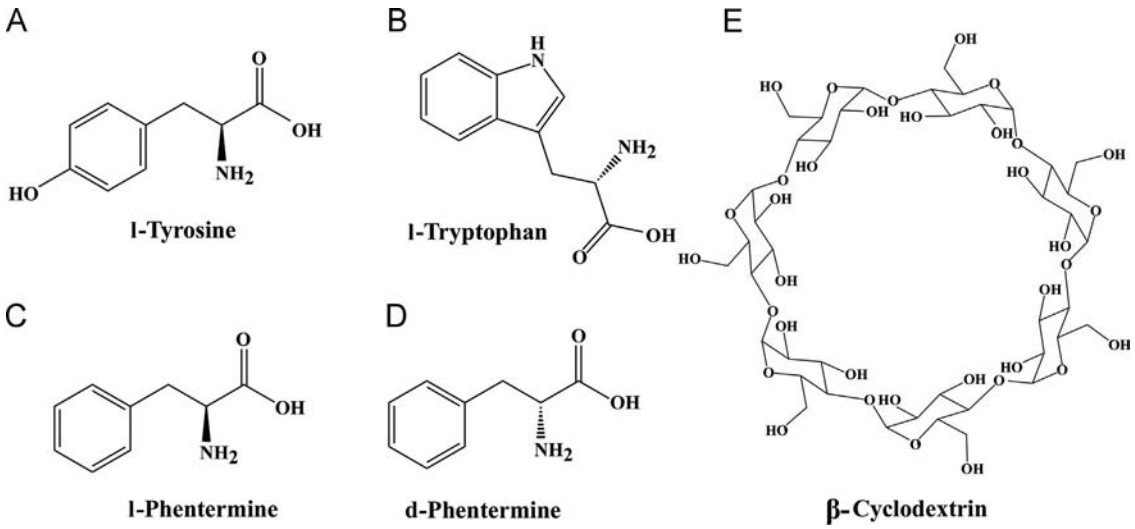

Fig. 1. Molecular structures of (A) L-Tyr, (B) L-Trp, (C) L-Phe, (D) D-Phe and (E) β-CD.

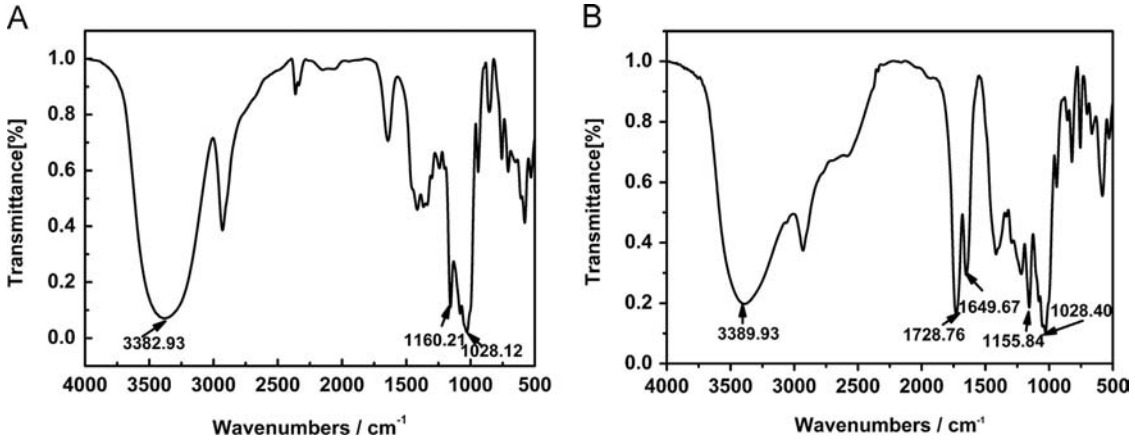

Fig. 2. FT-IR spectrums of (A) unmodified β-CD and (B) MAH-β-CD.

2.6. Determination of MIPP to recognition

Diffraction wavelengths of MIPP film to Phe were measured in buffer solutions of various chemicals by using a 380–1050 nm fiber optic spectrometer (JKHQ-D1, Tianjin, China) at the vertical direction. The fiber optic spectrometer is convenient to fix a same measurement location on the film by focusing the incident light on one dot; and always maximum diffraction wavelength was observed in our experiments. The recognition was performed in a range of concentration of the solution in the optimal pH condition. For a series of concentrations, the detection followed the sequence from low to high concentrations to eliminate interference.

The dependence of the recognition of MIPP film to L-Phe on the pH value was investigated as follows: the MIPP film was soaked in 10 mL buffer solution from pH 2 to 9 containing 10^{-5} M L-Phe at room temperature for 2 min, following a diffraction wavelength was recorded. After one detecting, the film was soaked again in methanol/acetic acid (9:1, v/v) for 10 min and then rinsed thoroughly with deionized water to recover the original state for the next detection. As a control, the blank experiment was performed in pure buffer solution without L-Phe.

For observing the responding time of the MIPP to the templates, the MIPP film was soaked in 10 mL 10^{-5} M l-Phe solution at optimum pH value at room temperature and diffraction spectra were measured as frequently as possible.

3. Results and discussion

3.1. FT-IR analysis of MAH-β-CD

In order to obtain a β-CD based reactive monomer which can be copolymerized and cross-linked with AA to form a hydrogel, a modified β-CD carrying five vinyl carboxylic acid groups was synthesized. According to reference [32], the synthesized β-CD tethered five vinyl groups on the smaller rim of β-CD (primary OH side). The structures of unmodified β-CD and the synthesized product were characterized by FT-IR. In Fig. 2A, a strong and wide band at 3382 cm^{-1} was the absorption from hydroxyl; meanwhile, evident C–O stretching vibration at 1028 cm^{-1} demonstrated the attachment of hydroxyl groups to β-CD ring. Compared to Fig. 2A, FT-IR spectrum in Fig. 2B showed a strong C=O stretching vibration at the 1728 cm^{-1} and C=C stretching vibration at 1649 cm^{-1}, which meant modified β-CD carrying vinyl carboxylic acid groups was successfully synthesized. In previous studies, it was found that when β-CD linked onto polymer backbone by a covalent bond, its inclusion ability was comparable to that of β-CD monomer [33].

3.2. Fabrication of Phe imprinted photonic polymer

To obtain highly specific imprinted photonic polymers, the formation of stable complexes between the template and their

functional monomers in the reaction mixture is crucial and should be preserved in the resulting polymers. Different ratios of monomers, cross-linker, and imprinted template molecule have a considerable influence on the sensing properties of the imprinted photonic materials [16]. In our experiments, the ratio of template, functional monomers, crosslinker and initiator was optimized.

Fig. 3 is an overall protocol for the fabrication, characterization and recognition process of MIPP. The steps for the construction of Phe imprinted photonic polymer including the preparation of the polystyrene photonic crystal template by using the vertical deposition method (Fig. 3A), the infiltration of liquid precursors and the complex of Phe with monomer into the voids of the photonic crystal template by using a capillary-attraction-induced method (Fig. 3B), polymerization of the complex of the template and functional monomers, and the removal of the imprinted Phe template (Fig. 3C). It is noteworthy that our procedure was somewhat different from the reported works [2–6]. First, polymethyl methacrylate (PMMA) substrates were not used. Second, the infiltration procedure was not fulfilled by dipping the photonic crystal template into the precursor solution. While infiltrating of liquid precursors, glass slide partly covered with the opal photonic crystal template was tilted by about 15° against the horizontal. The precursor was dropped directly onto the glass slide next to the up edge of the opal template and then infiltrated into the template slowly and filled the interstitial space by the capillary force and gravity.

Fig. 4A showed the SEM image of photonic crystal template formed with polystyrene spheres of diameter 200 nm, which had a highly ordered 3D structure. Fig. 4B showed the SEM top view photo of the obtained MIPP film. It can be seen that the MIPP film was faithfully duplicated the 3D highly ordered opal structure similar to the photonic crystal template. The thickness of our MIPP film was about 100 μm, and it was very easy to separate the polymerized MIPP film from glass slide by immersing in deionized water before the removal of the imprinted template. The effect of the thickness on the sensing properties of the MIPP film was controlled by using the same film throughout the experiments. Our MIPP film was robust enough to go through several hundred even as many as one thousand tests, as long as the film was not destroyed by external force and extreme condition such as ultra-strong acid or basic.

3.3. The response speed of MIPP film to template

The interval time required for the volume of a hydrogel to change is governed by the collective diffusion of the polymer network forming the MIPP film. Although it is commonly considered that bulk hydrogel polymer exhibits poor analyte accessibility and slow mass transport, it was found that the MIPP film in our experiments exhibited extremely rapid response to analytes within 30 s. Probably, affinitive binding sites formed on the surface of highly-ordered photonic crystal film promote the diffusion of analytes from the solution to the film, or the rapid response resulted from the suitable hydrophobic matching between of β-CD cavities and phenyl moiety of the template molecule.

3.4. Effect of pH on responsiveness

To research the effect of pH on response ability, we soaked MIPP film in 10^{-5} M L-Phe buffer solution varying from pH 2 to

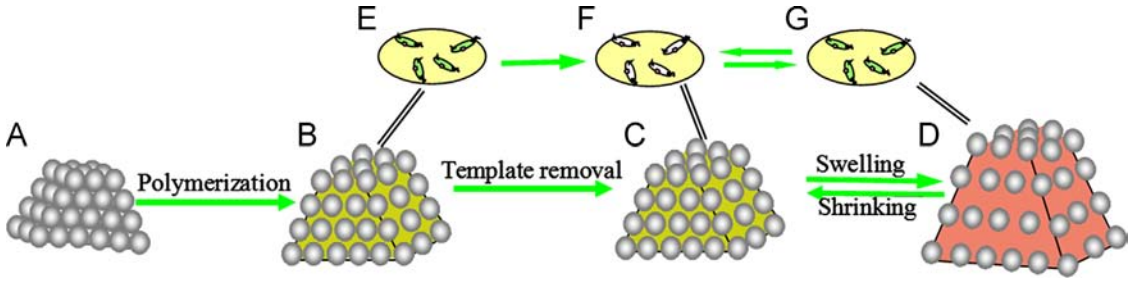

Fig. 3. Overall protocol for the fabrication, characterization and recognition process of MIPP. (A) polystyrene colloids self-assembled into photonic crystals; (B) polymerization of Phe imprinted photonic polymer; (C) MIPP film after the removal of Phe imprinted molecule template; (D) recognition of MIPP to the template molecules in solution; (E) complex of the monomer and imprinted template molecule; (F) imprinted cavities with complementary shape and binding sites to the template molecule; (G) imprinted molecules within the polymer networks.

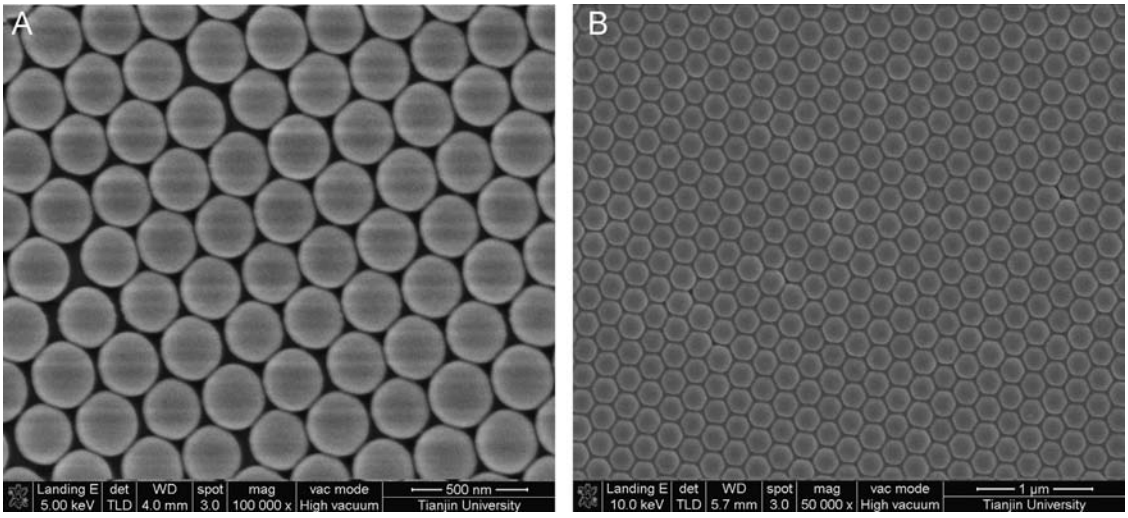

Fig. 4. Typical SEM images of (A) the used polystyrene colloidal crystal template and (B) the obtained MIPP film.

pH 9. Fig. 5 exhibited the dependence of diffraction wavelength shift with pH, in which $\Delta\lambda$ was the diffraction wavelength shift when MIPP film soaked in L-Phe solutions compared to it in pure buffer at the same pH without L-Phe. As the pH increasing from pH 2 to pH 6, the diffraction wavelength shift of MIPP increased, and then decreased when pH changed from pH 6 to pH 9. The maximum diffraction shift responding to L-Phe was up to 56 nm at pH 6. Since the isoelectric point of L-Phe is 5.48, more than 99% of the carboxyl and amino groups of L-Phe remain were as COO^- and NH_3^+ at pH 6 according to the Henderson–Hasselbach equation [34]. Under this condition, it was deduced that nonpolar L-Phe could be easily capped by the hydrophobic cavity of β-CD and the high binding affinities were resulted from the ionic bonding between the L-Phe template molecules and functional monomers.

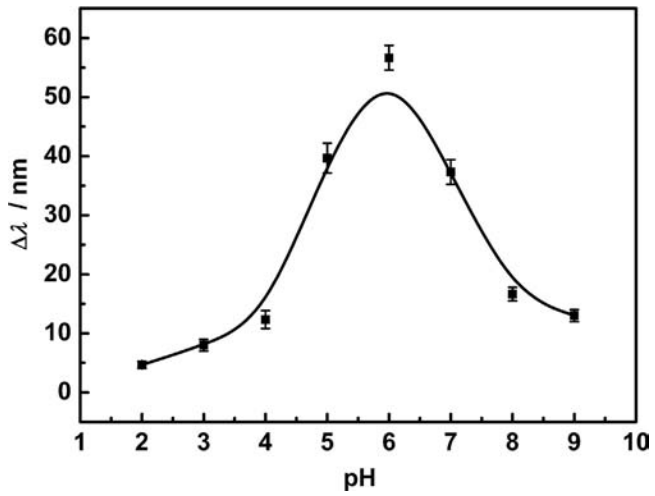

Fig. 5. Effect of pH on response properties of MIPP to L-Phe. $\Delta\lambda$ is the diffraction wavelength difference between 10^{-5} M L-Phe solution and pure buffer.

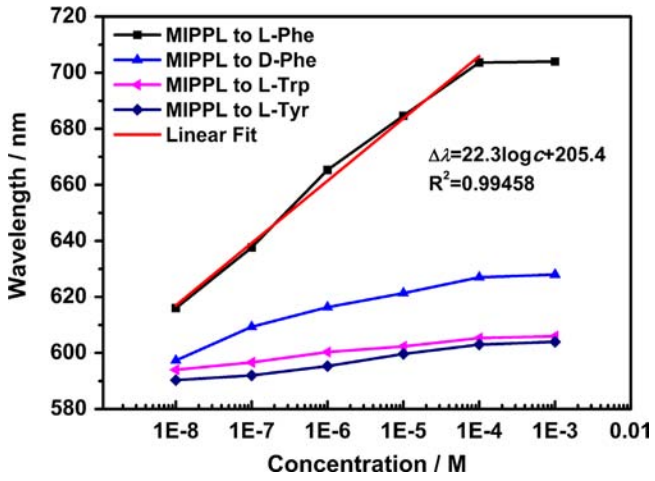

Fig. 6. Responses comparison of MIPPL to L-Phe, D-Phe, L-Tyr, and L-Trp. Superimposed line is the fitting functional relationship between the diffraction wavelength shift $\Delta\lambda$ and the concentration of L-Phe in the range of 10^{-8} M to 10^{-4} M.

3.5. Selectivity

The molecular selectivity and sensing specificity of the MIPP were investigated by using L-Phe as the template molecule, as well as D-Phe, L-Tyr and L-Trp as the control compounds. As can be seen from Fig. 6, MIPPL exhibited only a slight shift in the diffraction wavelength in the buffer solution of L-Tyr or L-Trp, compared to the distinct shift to L-Phe. Since the chemical structures of these two substrates are different from the template in terms of size and shape, thus, only target molecules can occupy the imprinted nanocavities within the MIPP network and cause a volume change in the MIPP film, thereby inducing a red-shift in the diffraction wavelength.

The cavities of CDs have been found to be very suitable for chiral selective analysis of chiral compounds, with the possibility of double selectivity: internal selectivity (i.e., inclusion type, dependent on the size of the cavity and the guest molecule) and external selectivity (dependent on the functional groups) [23]. Herein, we used modified β-CD as a functional monomer to fabricate MIPP films to detect L-Phe or D-Phe in pH 6 buffer solutions with varying concentrations. When immersing MIPPL film into L-Phe solution, a red shift of the diffraction wavelengths was observed. Moreover, it was found that the extent of the red shift was dependent on the concentration of L-Phe in the buffer solution. As shown in Fig. 7A, with the increase of concentration of L-Phe, the diffraction wavelength of MIPPL red-shifted gradually and a maximum red-shift was up to 114 nm until the L-Phe concentration was higher than 10^{-4} M. However, when the film exposed to D-Phe buffer solution of various concentrations, there was no distinct shift observed (Fig. 7B). The similar experiments were conducted by detecting the shifts of diffraction wavelength of MIPPD film to buffer solutions with D-Phe and L-Phe. The dependence of the diffraction wavelength of MIPPD in response to D-Phe and L-Phe was shown in Fig. 8. As it can be seen,

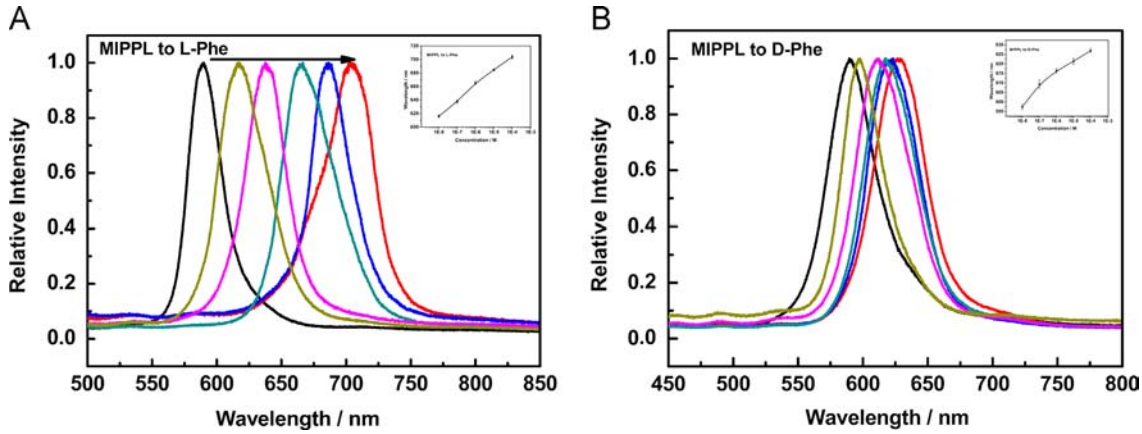

Fig. 7. Dependence of the diffraction wavelength of MIPPL in response to (A) L-Phe and (B) D-Phe in the range of 10^{-8} M to 10^{-4} M. Inset is the corresponding linear plot.

all the results suggested that β-CD-based MIPP films had the ability to distinguish chiral molecules.

3.6. Sensitivity

Relationship between the diffraction wavelength of MIPP and the concentration of template was investigated experimentally. Fig. 6 indicated the results of the diffraction wavelength shift of MIPPL to L-Phe. As it can be seen, the diffraction wavelength shifted regularly to the longer wavelength region with the increasing concentrations. Superimposed line in Fig. 6 was the fitting functional relationship between the diffraction wavelength shift $\Delta\lambda$ and the concentration of L-Phe in the range of 10^{-8} M to 10^{-4} M. A function relationship was found between the diffraction wavelength shift $\Delta\lambda$ and the logarithm of L-Phe concentration in the range from 10^{-8} M to 10^{-4} M, and a function equation $\Delta\lambda = 22.3\log c + 205.4$ with R^2 of 0.99458 was obtained. A maximum wavelength shift from 590 to 704 nm for L-Phe was observed when the L-Phe concentration was up to 10^{-4} M. When the L-Phe concentration was as low as 10^{-8} M, an obvious red-shift as much as 26 nm still could be lead. The proposed MIPP should be able to resolve and sense a minimum L-Phe concentration of 6.3×10^{-10} M since the distinguishable diffraction wavelength of the fiber optic spectrometer is 0.23 nm.

It was also indicated that a superior sensitivity was endowed to MIPP because of introduction of β-CDs. In reference [29], a molecular imprinting-chemiluminescence sensor for the determination of L-Phe using molecularly imprinted polymer (MIP) as recognition element was reported. The Phe-MIP was synthesized using acrylamide (AM) as functional monomer and ethylene glycol dimethacrylate (EGDMA) as cross-linker, which responded linearly to the concentration of Phe in the range 1.3×10^{-6} to 5.44×10^{-4} M with a detection limit of 6.23×10^{-7} M. Our previous investigation [35] demonstrated that another MIPP using acrylamide in combination with methacrylic acid as functional monomers but in absence of β-CD showed linear response to L-pyroglutamic acid in the range of 1.0×10^{-5} to 5.0×10^{-4} M. As can be seen from the comparison, the present MIPP film was much more sensitive to amino acid and showed response to amino acid in a wider concentration range.

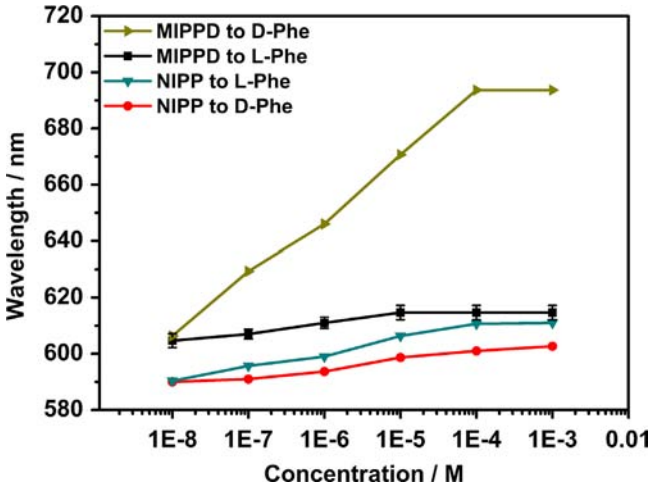

Fig. 8. Dependence of the diffraction wavelength of MIPPD in response to D-Phe and L-Phe, and NIPP in response to L-Phe and D-Phe in the range of 10^{-8} M to 10^{-4} M.

3.7. Recoverability

The recognition of the MIPP sensor to the template molecules is a reversible process as reported in previous works [2–16]. Since the MIPP film usually is required to be soaked in the solution and followed by washing with deionized water in every test, the recoverability of the sensor is very important for reproducibility. The MIPPL was soaked in 10 mL solution containing 10^{-5} M l-Phe at pH 6 for 2 min, and the diffraction wavelength was measured. Then, the MIPP was washed with methanol/acetic acid (9:1, v/v) for 10 min and then rinsed thoroughly with deionized water to recover to the blank state. The experiments indicated that the sensor had good recoverability without degradation of the response time or significant change in diffraction wavelength. A single MIPP film was used throughout a sequent investigation in our work.

3.8. Sensing mechanism

In theory, to gain insight into the adsorption mechanism of MIPP, the adsorption data or isotherm models should be analyzed. In our experiments, we have tried to perform an adsorption analysis of MIPP film. But unfortunately, we could not obtain satisfactory and useful adsorption analysis because the free Phe concentration in the supernatant after adsorption was too low to be accurately analyzed by UV–vis spectroscopy.

To further elucidate the high binding affinity of MIPP attributing to the imprinting effect, the optical response of NIPP was investigated in various concentrations of Phe as control experiments. As it can be seen in Fig. 8, there was almost no obvious diffraction wavelength shift when NIPP film exposed to L-Phe and D-Phe. The shift of NIPP film in response to L-Phe was larger than to D-Phe, which may arise from the inherent chiral selectivity of the β-CD monomers to molecule in L form. All the results indicated that the microenvironments created by molecular imprinting are responsible for the observed responses of MIPP to templates.

Usually, hydrogen bonding is the most commonly exploited interaction for the non-covalent molecular imprinting. However, it is easily destroyed in aqueous media because aqueous solvents can compete with the template for the functional monomers. In this case, MAH modified β-CD as well as AA were chosen as functional monomers to interact with Phe, the hydrophobic cavities of modified β-CD can bind the template phenyl moiety through hydrophobic interaction [21,27,36,37] and carboxyl of MAH-β-CD can interact with the amine and carboxyl through ion pairing and

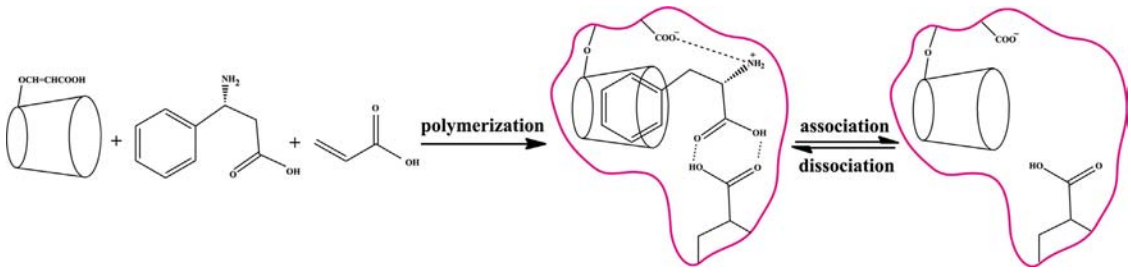

Fig. 9. The schematic illustration for establishment imprinting process between functional monomers and Phe template molecule.

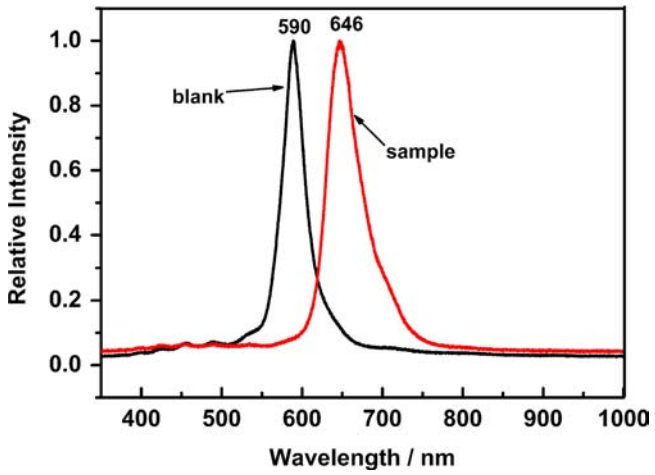

Fig. 10. Diffraction wavelength comparison between MIPPL in the blank buffer solution and compound amino acid injection sample.

hydrogen bonding. Moreover, AA may also form hydrogen bonding and electrostatic interactions [38]. The possible establishment and interruption process between the two functional monomers and template was shown schematically in Fig. 9, in which multiple binding sites are expected to occur among MAH-β-CD, AA and Phe.

3.9. Application

Compound amino acid injection (15-HBC, Tianan Pharmaceuticals Company, Tianjin) with the L-Phe certified value of 2×10^{-3} M was purchased from local drugstore and then diluted to the concentration of 10^{-5} M by pH 6 buffer solution for analysis. The optical response when soaking MIPPL film into the prepared sample solution was shown in Fig. 10. A significant diffraction wavelength red-shift up to 56 nm was observed, which indicated the sensitive response of MIPPL to the L-Phe in compound amino acid injection. L-Phe was detected in the sample and the obtained concentration agreed with the certified value. The recoveries of L-Phe in the diluted samples ranged from 95 to 109%. The precision (RSD) of the diffraction wavelength shift for seven successive tests of a sample were 3%.

4. Conclusions

In this work, we have utilized MAH modified β-CD as a novel functional monomer in MIPP for Phe sensing in aqueous solution. We believe it is of great significance of our attempts to further exploit the potential of MIPP sensing methodology and it will open new opportunities for sensitive detection of biomolecules.

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