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A Lanthanide Complex-Based Molecularly Imprinted Luminescence Probe for Rapid and Selective Determination of λ-Cyhalothrin in Environment

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Abstract

The molecularly imprinted polymers cladding lanthanides complex were synthesized by precipitation polymerization. The luminescent molecularly imprinted polymers were characterized by scanning electron microscopy, Fourier transform infrared spectroscopy and thermogravimetric analysis. The optical properties of the imprinted polymers were determined by fluorescence spectroscopy. Due to the highly selective cavities of surface imprinted layer of the polymers, the imprinted polymers could be applied in rapid, selective and sensitive determination of the λ-cyhalothrin. Based on the quenching mechanism, a stage of quantitative determination λ-cyhalothrin was proposed by using luminescent molecularly imprinted polymers as fluoroprobe. Under the optimized experimental conditions, our fluoroprobe was used for the recognition of λ-cyhalothrin selectively and rapidly successfully. The fluorescent intensity of the fluoroprobe gave a linear response in the 10−100 μM concentration range with a correlation coefficient of 0.9963. At last, the luminescence probe was proven to be suitable for the determination of the λ-cyhalothrin residues in real environment examples.

Keywords: λ-cyhalothrin, Surface molecularly imprinted polymers, lanthanides, determination, Selective recognition.

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1. Introduction

Pyrethroids, as an important kind of synthetic pesticides, are widely used in the agricultural production[1, 2], because of its advantages of the efficient and broad-spectrum deinsectization. However, pyrethroids inflowed into farmland by drainage and atmospheric rainfall which poisoned aquatic animals, even causing serious damage to human health [3, 4]. The world health organization (WHO)'s standard requires that acceptable daily intake (ADI) of pyrethroids to be 0–0.03 milligrams per kilogram of body weight per day[5, 6]. Thus, a rapid, sensitive, and selective analytical technique for determination of the pesticide residues in environmental have been long-cherished for practical purposes.

Much attention has recently been focused on the use of molecularly imprinted polymers (MIPs) for determination of template molecules due to their special abilities to recognize a certain molecule[7]. Molecularly imprinted polymers possesses advantages over biological recognition elements including low cost, high mechanical stability, and reutilization[8], which have been extensively used to improve the separation efficiency for chemical analytes[9, 10]. Surface MIPs have enjoyed widespread attention because of complete removal of templates, accessibility to the target molecules, high adsorption capacity and ease of preparation[11, 12]. Surface MIPs has been widely applied for the pretreatment of examples, such as separation and enrichment[13-15]. However, pretreatment process was complicated and time-consuming. Moreover, pretreatment demanded a great deal of organic solvents, thus, causing more environmental problem. Therefore, the great priority has been given to the development of novel in situ molecular recognition techniques.

Luminescent analysis is appealing because of the characterization of high sensitivity, undamaged for the sample and low-cost instruments[16-18]. It can achieve an effective, simple and environmentally friendly in situ analysis for high-efficiency detection of pollution. Lanthanides fluorescent analysis have been reported widely because of their large Stokes shifts and narrow spectra[19, 23]. Lanthanides based on luminescence probes were promising candidates for in situ recognition. But, several deficiencies need to solve for lanthanides in detection of the pesticides. Firstly, although the lanthanides can be used as the probe to label the target molecules, fluorescence intensity would be interfered by substances with similar fluorescent characteristic. It meant that similar structure of pesticides cannot detected specifically in a complex system, in other words, the selectivity of the probe was poor. Secondly, the lanthanide probe was vulnerable to the environmental impact, such as pH and common existence ions. In order to solve these problems, surface imprinted luminescence probe was proposed based on surface molecularly imprinted polymers and fluorophore. It can specifically and fast recognize target analytes by accessible imprinted sites, quickly mass transfer in a low detection background[24]. Our previous efforts to detect pyrethroids based on molecular imprinting fluorescent particles were stabilized Pickering emulsion[25]. Although we were able to detect pyrethroids by the imprinting polymers, the synthesis of lanthanide based MIPs was complex. Further, we prepared core–shell structured

nanocomposite (YVO_4:Eu^{3+} @MIPs), but the fluorescence intensity of rare earth oxide is lower than rare earth complex. Meanwhile, the rare earth complex was strongly shifted long-lived emission may allow the development of simple instrumentation to carry out in situ analyses. As we know, there are few researches about the surface imprinted fluorescent probe in situ analyses for the determination of λ-cyhalothrin (LC)[26, 27]. In this paper, we make an attempt to use dysprosium(III) complex silicon as a fluorophore, coated MIPs to prepare a high sensitive and selective sensor for the detection of λ-cyhalothrin. Molecularly imprinted luminescence probe was first achieved in step with Dy complex doped into SiO_2. Because the surface of the Dy(III)@SiO_2 is rich in silanol hydroxyl, the surface imprinted polymerization was taken place by precipitation polymerization. Subsequently, templates (LC) were removed by solvent extraction. The characterization, evaluation of optical performance, effect of pH, selective and sensitive detection of pesticides were investigated. At last, the probe was investigated for selective and sensitive determination of λ-cyhalothrin from actual water samples.

2. Experimental

2.1 *Equipment*

Infrared spectra (4000−400 cm^{-1}) were collected on a Nicolet NEXUS-470 FT-IR apparatus (U.S.A.) using KBr disks. The morphology images were recorded by Scanning electron microscopy (SEM, JSM-7001-F). The thermogravimetric analysis (TGA) of samples was measured using a Diamond TG/DTA Instruments (STA 449C Jupiter, Netzsch, Germany) under a nitrogen atmosphere up to 1000 ˚C with a heating rate of 10.0 ˚C min^{-1}. Fluorescence spectra was taken on a QuantaMaster and TimeMaster spectro fluorometer (Photon Technology International, Inc.).

2.2 *Reagents and solutions*

λ-cyhalothrin (LC), β-cyfluthrin (CI), bifenthrin (BI) and fenvalerate (FE) were purchased from Yingtianyi standard sample company (Bei Jing, China), ammonia solution($NH_3 \cdot H_2O$; 25−28%), 1,3,5-Benzenetricarboxylic acid (BTC), HCl and acetonitrile were purchased from Sinopharm Chemical Reagent Co. Tetraethoxysilane (TEOS≥99.9%), methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), 2,2′-azobis(2-methylpropionitrile) (AIBN), Dy_2O_3, $C_{12}H_8N_2 \cdot H_2O$ (phen), Tetraethoxysilane (TEOS), Doubly distilled water was used for preparing all aqueous solutions and cleaning processes. The chemical structures of templates can be viewed in Fig. 1.

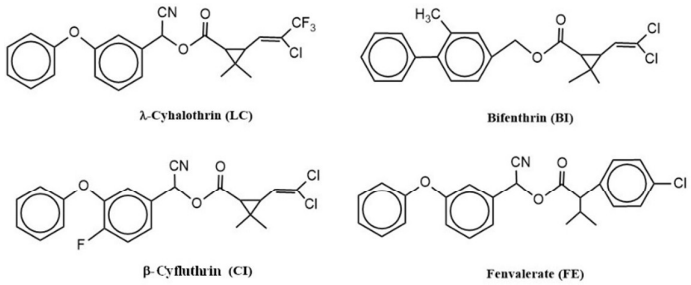


Fig. 1 Chemical structure of template and its structure analogous compounds

2.3 *Synthesis of Dy(III) complex*

1.0 g of Dy_2O_3 was added into a 100 mL flask, then slowly poured to a certain amount of dilute hydrochloric acid, magnetic stirring the mix to gradually dissolve Dy_2O_3. The residual HCl was removed by heating and evaporation to obtain a clear stock solution. Subsequently, evaporating the solution, until the solution appearing crystalline membrane. Then the flask was put in the oven at 120 °C, and the $DyCl_3$ was obtained over a night for the following use.

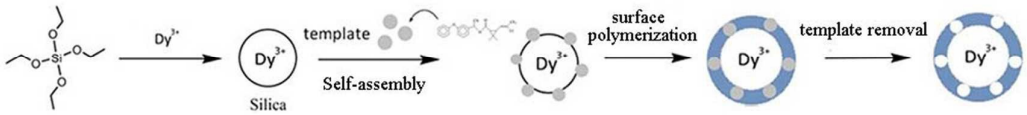
The Dy(III) complex was synthesized according to the conventional route as follows:[28] Briefly, $DyCl_3$ (0.5 mmol) and phen (0.75 mmol) were dissolved in ethyl alcohol (100 mL) under stirring at 80 °C. Then $NH_3 \cdot H_2O$ was added to adjust the pH to 6.0. Afterward, BTC (0.5 mmol) dissolved in ethyl alcohol (5 mL) was added dropwise. After complete addition, adjust the pH to 6.0 again. The solution was stirred for 4.0 h to ensure complete precipitation. The precipitate was filtered out and washed repeatedly with ethanol and water, and was dried overnight in vacuum at 60 °C. The result product was noted as Dy(III) complex.

2.4 *Synthesis Dy(III) complex modified with silica*

Dy(III) complex modified with silica were prepared as followed. Briefly, Dy(III) complex (20 mg) was first dissolved in 5 mL of acetone. The above solution and 1 mL of tetraethyl orthosilicate were codissolved in 25 mL of ethanol to form solution A. And the solution B was consisted of 14 mL of ethanol, 5.0 mL of distilled water and 1 mL of ammonia. Solution A was poured into solution B quickly under vigorous stirring. The solution became turbid after stirring for 2 h due to the formation of silica spheres. After the reaction, the mixture was centrifuged at 3700 rpm for 5 min, and the suspension was removed. The residuals were washed thoroughly with ethanol and distilled water until the pH of the suspension was equal to 7. The obtained product was Dy(III) complex doped SiO_2 and recorded as Dy(III)@SiO_2.

2.5 *Preparation of molecularly imprinted polymers (MIPs)*

0.1 g of Dy(III)@SiO_2 was dispersed in 30 mL of ethanol in a 100 mL round-bottomed flask, then 0.1 mmol of LC, 1.5 mL of EGDMA and 0.4 mmol of MAA were added into the system, ultrasonic degassing for 5 min. Then the flask was put in the chader for self-assembly 3 h under N_2 protection at 30 °C, then the temperature rose to 60 °C and 30 mg of AIBN was added to trigger the reaction. After 12 h, system became turbid, and the mixture was centrifuged at 3000 rpm, and the supernatant was removed. Solid particles were washed with ethanol and water three times. Then solid polymers were eluted with methanol/acetonitrile (v/v, 20:1) to removal of the templates (LC) by Soxhlet extraction until the LC would not be detected in the eluent by ultraviolet and visible spectrophotometer, and was dried in a vacuum chamber. Non-imprinted nanoparticles (NIPs) as a control to evaluate the molecular recognition properties of imprinted materials were synthesized same as MIPs without addition of LC. MIPs and NIPs were dispersed in 50% (v/v) ethanol-water for follow-up of fluorescence detection. Synthesis routes of MIPs were shown in Scheme.



Scheme. Schematic representation of Dy(III)@SiO_2@MIPs

3. Results and discussion

3.1 *Characterization of MIPs and NIPs*

Morphology of MIPs and NIPs was observed by SEM. SEM images of Dy(III) complex, Dy(III)@SiO_2, MIPs, and NIPs are shown in Fig. 2. It could be obviously observed that the Dy(III) complex is doped into SiO_2 successfully in Fig. 2B. Fig. 2C and 2D represent the surface morphology of MIPs and NIPs. Both of them are polyporous compare with Dy(III)@SiO_2 in Fig. 2B. It shows clearly that MIPs was synthesized on the surface of the Dy(III)@SiO_2. It indicates that fluorescent probe MIPs are successfully synthesized.

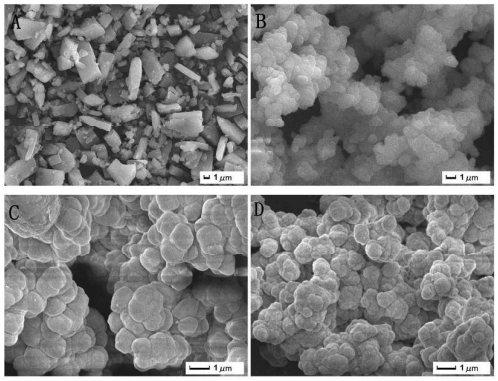


Fig. 2 SEM images Dy(III) complex (A), Dy(III)@SiO_2(B), MIPs(C) and NIPs(D)

Subsequently, the optical properties of Dy(III) complex, Dy(III)@SiO_2, MIPs and NIPs were also investigated in 50% (v/v) ethanol-water. In Fig. 3, the free Dy(III) complex fluorescence in ethanol shows the characteristic sharp emission at 574 nm due to the $4F_{9/2}$-$6H_{13/2}$ transitions from the Dy(III)[29]. The emission intensity of MIPs is slightly higher than NIPs, it might because template molecules (LC) was added during the synthesis of the MIPs which impact the properties of the probe by surface modification [30]. By the same reason, the baseline of the NIPs is different with the MIPs.

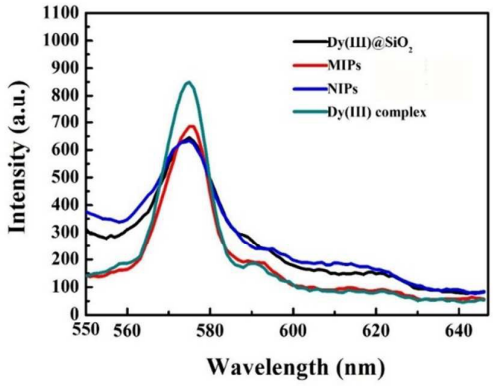


Fig. 3 Emission spectra of the free Dy(III) complex, Dy(III)@SiO_2, Dy(III)@SiO_2@MIPs and Dy(III)@SiO_2@NIPs. The concentrations of them remain to be 1 g/L in solution for all samples (λ_{ex}=265 nm)

The FT-IR spectra of free Dy(III) complex, Dy(III)@SiO_2, MIPs and NIPs also confirmed the surface covalent modifications. In Fig. 4, the absorption peaks at 1098 cm^{-1} and 3438 cm^{-1} could attribute to Si-O-Si asymmetric stretching vibration and Si-OH stretching vibration respectively. In addition, the characteristic peaks of Dy(III) complex disappear, they both suggest that the complex is enshrouded by SiO_2 successfully. The FT-IR spectra of MIPs and NIPs possessed the same absorption bands around 1731, 1259, and 1161 cm^{-1}, which are assigned to C=O stretching vibration of carboxyl (MAA), C–O asymmetric and symmetric stretching vibration of ester (EGDMA), respectively [31]. Meanwhile, the absorption band at 3446 cm^{-1} of the MIPs and NIPs could attribute to the stretching vibration of O–H bonds from MAA molecules. All the results confirm that the cross-linking reaction was successfully initiated by AIBN.

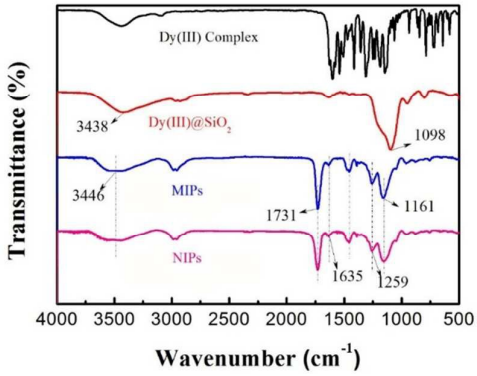


Fig. 4 FT-IR spectra of Dy(III) complex, Dy(III)@SiO_2, MIPs and NIPs

3.2 *Effect of pH*

The pH effect in a range between 1.0 and 12.0 was studied for MIPs (squares) and NIPs (circles) in Fig. 5. Because the fluorescence probe was doped into SiO_2 and MIPs, the fluorescence intensity of MIPs at the range of 5.0 to 12.0 was considerably stable, which greatly advanced the application of the fluorescence probe. As the pH reduces from 4.0 to 1.0, the fluorescence intensity decreases quickly, which probably because the coordination compound of Dy(III) decomposed in strong acidic system and weakened the energy transfer. Similar phenomena is occurred in NIPs as well. Comparing with the NIPs, the pH of 7.0 is selected for the further experiments.

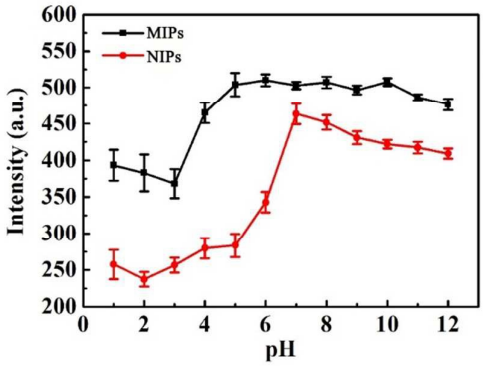


Fig. 5 Effect of pH on luminescence of the MIPs and NIPs (Experiment condition: MIPs 1.0 g·L^{-1}, LC 50 μM, Error bars represent the standard derivation)

3.3 *Determination time*

To confirm the optimal detection time, a certain amount of LC (50 μM) was added into MIPs solution. The fluorescence intensities were recorded at different interval time. The experiments were done three times and the average values are given in Fig. 6. Form the figure, the fluorescence intensity decreases quickly at the initial beginning, when time up to 7 min, the fluorescence intensity don't change. As a result, we choose 7 min for the optimal detection time.

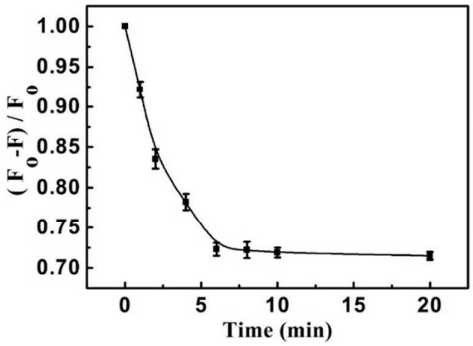


Fig. 6 Effect of time on fluorescent intensity (Experiment condition MIPs: 1.0 g·L^{-1}, LC 50 μM, λ_{ex}=265 nm, Error bars represent the standard derivation)

3.4 *Determination of Pyrethroids*

Under the optimal condition, the MIPs fluorescent probe was used for determination of LC in the samples. The results show the fluorescent intensity of MIPs decrease sensitively in the presence of LC in 50% (v/v) ethanol-water solution (Fig. 7). The possible mechanism is that LC could be selectively bonded by the specific recognition cavities of imprinted layer and quench the fluorophore. While the other pyrethroids cannot be adsorbed by the specific imprinted sites. The Dy complex is protected by the imprinted layer so that the fluorescence intensity will not make a significant change in a wide linear range. The relationship between the fluorescent intensity and the concentration of LC can be described by Stern−Volmer quenching the equation 1: [32, 33]

$$F_0/F = 1 + K_{sv} \cdot [c] \quad (1)$$

Where F and F_0 are the fluorescence intensities of the probe at a given related concentration of LC and LC free solution, respectively. K_{sv} is the Stern−Volmer quenching constant, and [c] stand for the concentration of LC.

The dependence of F_0/F as a function of [c] was shown in Fig. 7a and 7b. Based on the results, the linear dependence of the MIPs is F_0/F =-0.0047+4.41×10^{-3}c at the range from 10–100 μM (4.498–44.98 mg/L) with a correlation coefficient of 0.9963. The limit of detection is 1.6 μM (0.7197 mg/L) at S/N=3. Similarly, the linear dependence of the NIPs is F_0/F =-0.0137+3.85×10^{-3}c with the concentration range from 10 to 100 μM, the correlation coefficient is 0.9939. There are three conditions of fluorescence quenching mechanisms: static quenching, dynamic quenching, and a combination of the both of two. But for a single dynamic or static quenching, the change in the intensity of fluorescence (F_0/F) has a linear relationship with the quencher concentration (c), while the Stern–Volmer curve is non-linear when the quenching process is a combination of the static quenching and dynamic quenching. Moreover, for dynamic quenching, the maximum quenching constant of particles is usually less than 1×10^{-4} L·mol^{-1}. So if the quenching constant is more than 1×10^{-4} L mol^{-1}, the quenching mechanism is static[34]. In our experiments, the curve is linear (Fig. 7), and the quenching constants (4.41×10^{-3} L μmol^{-1}) are larger than 1×10^{-4} L·mol^{-1}. Hence, the mechanism of fluorescence quenching is reckoned to be static quenching. The K_{sv} value of the MIPs (4.41×10^{-3} L μmol^{-1}) is larger than that of NIPs (3.85×10^{-3} L μmol^{-1}), it is an important data to evaluate the sensitivity of the materials we obtain. From the above results, the MIPs get a better sensitivity than that of NIPs. Therefore, our analytical method is suitable for the on-site rapidly determination analysis.

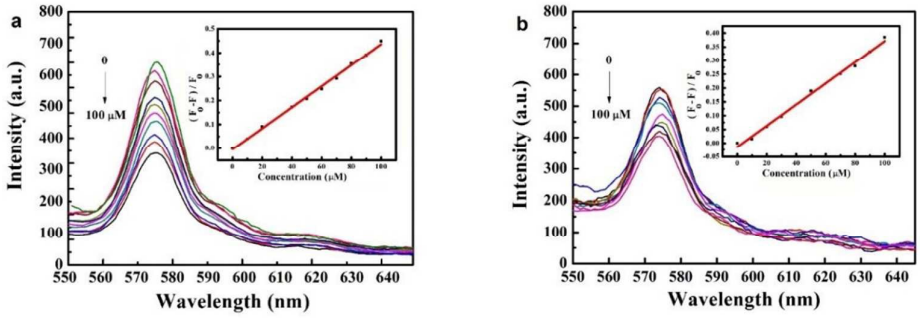


Fig. 7 Fluorescence spectra of the MIPs (a) and NIPs (b) with the increasing concentrations of LC. Inset: description of the data showing a linear fit throughout the LC concentration range with a correlation coefficient R^2= 0.9963 for MIPs and R^2= 0.9939 for NIPs (Experiment condition: MIPs and NIPs: 1.0 g·L^{-1}, λ_{ex}=265 nm)

3.5 *Selectivity Determination*

Selectivity is a significant property to evaluate the probe performance. So the selectivity test of sensor allowed various pesticides was examined. The initial concentration of each pyrethroids was 50 μM in 50% (v/v) ethanol-water solution. The experiments were done three times and the results of selectivity determination were exhibited in Fig. 8. As is evident from Fig. 8, the

emission intensity of the fluoroprobes decreases with the amount of the pesticide. This is probably because lots of cavities exist in the surface of MIPs due to the imprinting process, and when templates are adsorbed into cavities and quenching the probe. The quenching amount $[(F_0-F)/F_0]$ of MIPs for the four compounds followed the order LC > CI > FE > BI. The quenching amounts of MIPs are 0.2801, 0.1715, 0.1298 and 0.1325 for LC, CI, BI and FE by calculation, respectively. In contrast, because of no presence of templates, the surface polymeric layer for the NIPs had no cavities. So, just a trivial molecule adsorbed on the non-imprinting layer, leading a weaker fluorescence quenching[35]. The quenching amount $[(F_0-F)/F_0]$ of NIPs for the four compounds are 0.2169, 0.2465, 0.2334 and 0.2375. The results suggest that MIPs are more specific to LC and nonspecific to other pesticides. Due to the structures and functional groups of the template, different binding forces form between LC and MAA, resulting in a distinct recognition effect. Moreover, CI has almost the same structure as LC except for the different position of the substituted chlorine and fluorine functional groups, but the removal rate of MIPs for CI is still lower than that for LC, suggesting that the memory of specific functional groups also played an important role in the formation of tailored stereo binding sites [36]. To further investigate the competitive quench amount of LC, CI and BI, two competitive pesticides were added into LC solution in turn to form mixture solutions, and the concentrations of both LC and the competitive pesticides were 50 μM. There is no obvious effect on florescence intensity of MIPs by the two competitive pesticides, and the interference of CI and BI are too weak to be ignored in Fig. 9. But for NIPs, shown in the inset of Fig. 9, it is necessary to consider the significant influence by the two competitive pesticides.

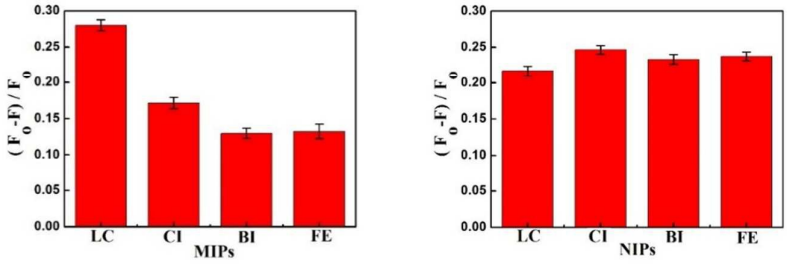


Fig. 8 The selectivity of MIPs and NIPs by different kinds of 50 μM pyrethroids (LC; CI; BI; FE) and Error bars represent the standard derivation

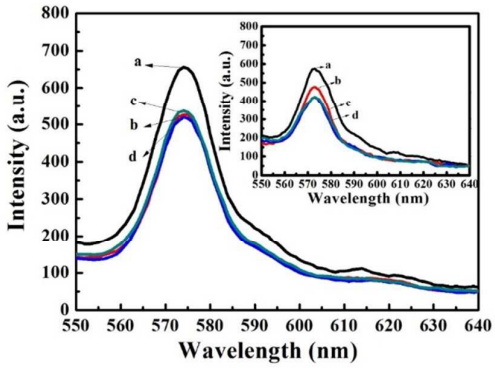


Fig. 9 Test for the interference of different pyrethroids on the fluorescence response toward LC of MIPs. (a) MIPs, (b) MIPs + LC, (c) MIPs + LC + CI, (d) MIPs + LC + BI, Inset: the interference for NIPs. (a) NIPs, (b) NIPs + LC, (c) NIPs +LC + CI, (d) NIPs + LC + BI (50 μM of LC and competitive pyrethroids)

The investigation of the interfering effects of sample matrix components on the properties of the surface MIPs-based fluorescent probe were carried out. Several possible components in the environmental condition, such as K^+, Na^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, CO_3^{2-}, SO_4^{2-} and NO_3^- were added into the incubation solution containing 50 μM LC, respectively. As are shown in Table 1, the interfering ions doesn't affect the change of fluorescent intensity to target LC alone obviously. Cu^{2+} is a kind of strong quencher for lanthanide complex. However, the effect of Cu^{2+} for our probe is significantly decrease due to imprinted layer. Therefore, MIPs could be applied for the rapid and selective analysis for LC in the complex environmental system. It is rational that the high specificity of the sensor might be contributed to the memory of specific imprinted binding cavities in MIPs.

Table 1. Test for the Interference of different substances on the change of fluorescence

Coexisting substance	Coexisting concentration (μM)	Change of fluorescence intensity (%)
K^+	50.0	0.43
Na^+	50.0	0.63
Ca^{2+}	20.0	1.97
Mg^{2+}	20.0	2.16
Cu^{2+}	20.0	7.82
CO_3^{2-}	10.0	1.20
SO_4^{2-}	20.0	0.54
NO_3^-	20.0	0.71

3.6 *Application to environmental sample analysis*

The analytical method was applied in the actual water samples. The water samples were taken from a local river. The samples were stored in precleaned glass bottles and calibrate pH=7.0. As no λ-cyhalothrin in the river samples were detected by the proposed method, a recovery study

was carried out on the samples spiked with 10−100 μM LC to evaluate the developed method. A certain amount of LC was first dissolve in methanol and then diluted with river sample (methanol: river sample=1:10) to prepare solutions with the concentration of 10−100 μM. The as-prepared samples were measured by using the fluorescence spectra and ultraviolet spectra as a secondary method. The results are listed in Table 2. Compared with the UV method, the results are more accurate and sensitivity. The results reveal that a good accordance between both analytical methods. It can find that our method is suitable to detect LC at the low concentration. It is sufficiently to obtain a quantitative recovery (99.42−106.6%) of spiked LC to use a simple aqueous standard solution for the accurate quantification of LC, thereby the MIPs can be regarded as an optional probe for determination of LC.

Table 2. Recovery study of LC in water samples with LC at different concentration

	Concentration taken (μmol/L)	Detected (μmol/L)		Recovery (%)	
		Fluorometry	UV	Fluorometry	UV
LC	10.0	10.12	9.75	101.2	97.5
LC	20.0	21.32	21.68	106.6	108.4
LC	40.0	41.61	46.95	104.0	117.4
LC	60.0	60.85	63.57	101.4	106.0
LC	80.0	79.54	81.31	99.42	101.6
LC	100.0	100.6	104.2	100.6	104.2

In addition, concerning the LC behavior in environment, LC is easily moved into soil. So the method application for soil samples was also performed. The soil samples were taken from a local farmland. We used 500 mL of ethanol immerse 500 g of soil for 24 h. This process was repeated in triplicate. The samples were filtered through 0.45 μm Supor filters and stored in precleaned glass bottles and calibrated pH=7.0. No λ-cyhalothrin in the soil samples were detected by the proposed method neither, and a recovery study was also carried out on the samples spiked with 10−100 μM LC to evaluate the developed method. A certain amount of LC (10-50 μmol) was first mixed with 500 g of soil. Then 500 mL of ethanol immersed the mixed soil. The ethanol solutions were filtered through 0.45 μm Supor filters and calibrated pH=7.0. The samples were measured by using the fluorescence spectra and ultraviolet spectra. The results are listed in Table 3. The quantitative recovery of LC is from 102.7 % to 107.9 % for the accurate quantification of LC. It proves that our MIPs can be applied for the rapid and selective determination of LC in environment samples.

Table 3. Recovery study of LC in soil samples with LC at different amounts

	Spiked amount (μmol)	Detected (μmol)		Recovery (%)	
		Fluorometry	UV	Fluorometry	UV
LC	10.0	10.79	11.72	107.9	117.2

LC	25.0	20.58	21.69	102.9	108.5
LC	50.0	51.37	53.94	102.7	107.9

4. Conclusion

The Dy(III) complex based on molecularly imprinted polymers were prepared by precipitation polymerization. The luminescent molecularly imprinted polymers were attempted to be applied as a luminescent probe which has an excellent sensitivity for optical recognition of λ-cyhalothrin, due to its properties of tolerance to environmental pH and interfering ions. It improves a potential application of molecularly imprinted polymers. A novel method of rapid and low cost determination of the pyrethroid in the environment is established. Compare to the higher sensitivity but the higher cost analysis chromatography to detect pesticide residues, our method based on our fluorescence probe for the detection of λ-cyhalothrin shows a simple, certain sensitivity and rapid detection of λ-cyhalothrin residues. Because of imprinting layer, the probe is under a wide linear range. In addition, our fluoroprobe with potential application in the recognition and sensitive sensing of analytes is applied in actual environmental sample test.

Acknowledgements This work was financially supported by the National Natural Science Foundation of China (No. 21107037, No. 21176107).

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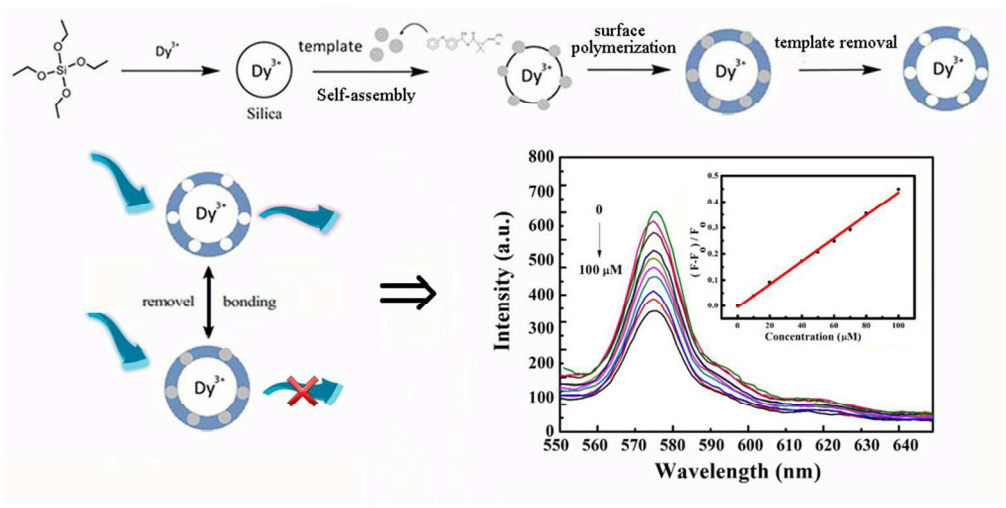

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