**Direct Detection of Potential Pyrethroids in Yangtze River via an Imprinted Multilayer Phosphorescence Probe**

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A novel tailored multilayer probe for monitoring potential pyrethroids in the Yangtze River was proposed. The room-temperature phosphorescence method was applied to realize a detection strategy that is superior to the fluorescence method. Efficient Mn-doped ZnS quantum dots with uniform size of 4.6 nm were firstly coated with a mesoporous silica to obtain a suitable intermediate transition layer, then an imprinted layer containing bifenthrin specific recognition sites was anchored. Characterizations verified the multilayer structure convincingly and the detection process relied on the electron transfer-induced fluorescence quenching mechanism. Optional detection time and standard detection curve were obtained within a concentration range from 5.0 to 50 µmol L⁻¹. The stability was verified to be good after 12 replicates. Feasibility of the probe was proved by monitoring water samples from the Zhenjiang reach of the Yangtze River. The probe offers promise for direct bifenthrin detection in unknown environmental water with an accurate and stable phosphorescence analysis strategy.

**Keywords** Room temperature phosphorescence probes, molecular imprinting technique, semiconductor nanocrystals, bifenthrin detection, Yangtze River sample

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**Introduction**

Bifenthrin (BF) is an efficient pyrethroid insecticide used in agriculture, forestry and households.¹⁻³ It is expected to be applied even more widely in agriculture since the application of organophosphorus and organochlorine insecticides are under restriction.⁴⁻⁵ However, BF has nonnegligible toxicity, especially to aquatic organisms, even at a low dose.⁶⁻⁸ Monitoring trace BF residues in surface water is thus important.⁹ Traditional detection methods such as gas chromatography¹⁰ and high performance liquid chromatography¹¹,¹² are usually complex, expensive, time consuming and offer low selectivity. As a result, a simple, fast and efficient monitoring strategy for trace BF in human habitats is crucial.

As is well-known, the low-dimensional material, semiconductor nanocrystal (also known as quantum dots) exhibits exceptional optoelectronic performance due to the “quantum confinement effect”¹³. The material has a tunable emission profile, wide excitation spectrum, narrow spectral band and high emission quantum yield. Beyond that, the chemical tunable surface and size makes semiconductor nanocrystals a promising probe technique.¹³,¹⁴ Ríos et al.¹⁵ had recently reviewed the strategies for probes applying semiconductor nanocrystals. Among all the monitoring techniques, room temperature phosphorescence (RTP) provides a longer lifetime, more efficient selectivity, lower level of interference from autofluorescence and scattering light of matrices over fluorescence (FL).¹⁵,¹⁷ Table 1 below lists some of the recently reported representative articles aiming at the selective detection of insecticides using optical techniques.¹⁸⁻²⁹

As Table 1 implies, RTP receives much less attention than FL. The coexistence substances may be the main obstacle interfering with the detecting accuracy of RTP. As a resolution, researchers recently applied a tailored technique, named molecular imprinting technique (MIT), to the RTP detection process for insecticides.²⁸ MIT is widely applied in selective separation and for purifying species with similar structures and sizes. It will provide the RTP probes with tailored cavities for target molecules. Hence the combination of MIT and RTP probes should be promising.

Previously, our team had explored several types of fluorescent molecularly imprinted composite probes,¹⁸⁻²⁸,²⁹ but on RTP strategy is quite limited. One previous study³⁰ focused on surface molecular imprinted polymers based on atom transfer radical polymerization of an RTP probe used to detect bifenthrin from Taihu Lake samples. Results showed that the RTP probe was a promising detection and monitoring strategy for environmental water samples. So in this article, from the view of developing a more low-cost and time and reagent-saving method over previous strategies, a tailored multilayer RTP probe was synthesized based on semiconductor nanocrystals for the specific identification of BF from the Yangtze River. Multiple layers including a mesoporous silica colloid layer and an imprinted layer, were coated on the surface of nanocrystals respectively for BF templates recognition. The monitoring
**Reagents and chemicals**

Experimental were verified to be feasible for the monitoring of direct samples quencher. The sensitivity and stability of the synthesized probe quenching mechanism, and BF performed as an efficient principle relied on the electron transfer-induced fluorescence quenching mechanism, and BF performed as an efficient quencher. The sensitivity and stability of the synthesized probe were verified to be feasible for the monitoring of direct samples from the Yangtze River.

**Experimental**

**Reagents and chemicals**

All chemicals were of analytical grade. ZnSO$_4$·7H$_2$O, MnCl$_2$·4H$_2$O, Na$_2$S·9H$_2$O, 3-mercaptopropyltrimethoxysilane (MPTS), cetyltrimethylammonium bromide (CTAB), sodium hydroxide (NaOH), tetraethoxysilane (TEOS) and ethanol were all purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). The pyrethroid pesticides, BF, fenvalerate, cypermethrin and cyhalothrin were obtained from Yingtianyi Standard Sample Co. (Beijing, China) and the corresponding structures are displayed in Supporting Information (Fig. S1). Double distilled water was applied throughout the experimental procedure.

**Apparatus**

Infrared spectra (4000 – 400 cm$^{-1}$) in KBr were recorded using Nicolet NEXUS-470 FTIR apparatus (USA). The X-ray diffraction (XRD) spectra were collected on an XRD-6100Lab X-ray diffractometer (Shimadzu, Japan) with Cu $K\alpha$ radiation over the 2$\theta$ range of 10 – 80$^\circ$. The morphology and structure of prepared samples were observed by transmission electron microscope (TEM, JEOL, JEM-2100), and the phosphorescence measurements were performed on a Cary Eclipse spectrofluorometer (Varian, USA) equipped with a plotter unit and a quartz cell (1.0 x 1.0 cm).

**Preparation of silica layer coated nanocrystal**

Mn-doped ZnS nanocrystals coated with mesoporous silica were synthesized by a previously published method. First, 12.5 mmol of ZnSO$_4$·7H$_2$O, 1.0 mmol of MnCl$_2$·4H$_2$O and 40 mL of double distilled water were added to a three-necked flask by magnetic stirring under the protection of nitrogen gas for 10 min. Then, 10 mL of watery solution containing 12.5 mmol of Na$_2$S·9H$_2$O was added dropwise under magnetic constant-speed agitation for half an hour. Next, 10 mL of alcoholic solution containing 0.625 mmol MPTS was added in the same manner and the mixture solution was agitated magnetically for 20 h. The whole synthesis process was conducted at room temperature. The preparative polymers were centrifuged repeatedly, then washed with double distilled water and absolute ethanol three times, then dried in vacuum.

**Synthesis of the tailored layer on silica coated nanocrystal**

The imprinted polymer layer was anchored on the synthesized silica coated nanocrystals via one-step with the Stöber method. CTAB, NaOH, TEOS and BF$^-$ were applied as surfactant, catalyst, cross-linker and template molecule, respectively. First, 30 mg synthesized silica coated nanocrystals was dispersed into 60 mL double distilled water in a flask and then ultrasonicated for 10 min, followed by adding 0.8 mL CTAB (0.2 M), 0.1 mL NaOH (0.2 M) and 10 mg BF (template). After stirring for 30 min at room temperature, 0.2 mL of alcoholic solution containing 0.1 mL TEOS was added. The mixture solution was stirred at 35°C for 24 h. The preparative polymers were centrifuged repeatedly, then washed with double distilled water and absolute ethanol three times. The removal of the BF template was conducted with 100 mL of acetic acid/methanol (10:90 v/v) by Soxhlet extractor. This process continued until the BF template did not exist in the eluent. After that the material was dried under vacuum for 12 h at 40°C. The non-imprinted polymers were also prepared with the same method without the addition of BF.

**RTP measurement procedure**

RTP measurements were conducted in the same conditions under the phosphorescence mode by spectrophotometer. The photomultiplier tube voltage was set at 700 V, with the slit widths of the excitation and emission of 10 nm. The excitation wavelength was set at 320 nm with a recording emission range of 500 – 700 nm. Synthesized materials were dissolved in double distilled water to get a fresh-made stock solution (24 mg L$^{-1}$). BF stock solution (1 mol L$^{-1}$, in double distilled water) was stocked at 4.0°C. A suitable quantity of synthesized materials was added to a 10-mL colorimetric tube, respectively, and the corresponding structures were displayed in Supporting Information (Fig. S1). Double distilled water was applied throughout the experimental procedure.

**Results and Discussion**

**Table 1 Related articles aiming at the selective detection of insecticides**

| Insecticide type      | Sensing technique | Semiconductor nanocrystals | Detection limit or sensitive range |
|-----------------------|-------------------|-----------------------------|-----------------------------------|
| Pentachlorophenol$^{28}$ | RTP-MIT           | MPTS/Mn:ZnS/MIP             | 86 nM                             |
| Organophosphorus pesticide$^{27}$ | RTP            | Mn:ZnS                      | –0.1 pM                           |
| 2,4,5-Trichlorophenol$^{26}$ | RTP-MIT         | Mn-doped ZnS                | 5.0 – 50 μM                       |
| Cyhalothrin$^{25}$    | FL-MIT            | SiO$_2$@KH570               | 0 – 2.5 nM                        |
| α-Cyhalothrin$^{19,20,24,29}$ | FL-MIT         | SiO$_2$-MPS@FMI              | 0.0037 nM                         |
| Bifenthrin$^{25}$     | FL-MIT            | SiO$_2$@FITC-APTS           | 9.17 nM                           |
| Fenvalerate$^{27}$    | FL-MIT            | OVDAC/CdTe/PAM              | 0.1 – 16 μM                       |
| Pyrethroids$^{30}$    | FL-MIT            | Dy$^{3+}$@SiO$_2$/PMMA       | 10 – 100 μM                       |
| Cyhalothrin$^{25}$    |                  | OVDAC/CdTe/PS               | 0.08 μM                           |
| Alkyd fluorescein@MIP |                  | SiO$_2$/ZnO/PAM             | 0.13 μM                           |

The morphology and structure of prepared samples were observed by transmission electron microscope (TEM, JEOL, JEM-2100), and the phosphorescence measurements were performed on a Cary Eclipse spectrofluorometer (Varian, USA) equipped with a plotter unit and a quartz cell (1.0 x 1.0 cm).

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**Results and Discussion**

**Structure illustration and detection principle**

Scheme 1 illustrates the synthesis process and the designed multilayer structure of this tailored multilayer RTP probe. The silica layer (Scheme 1B) located on the surface of the Mn:ZnS nanocrystal (Scheme 1A) was proved an ideal choice because of its inertia and optical transparence. This thin silica layer would not only protect the semiconductor nanocrystals from interference from the external environment, but also acted as a supporting material for the following molecular imprinting...
process. The mesoporous structural silica shell encloses the phosphorescence of the nanocrystal to facilitate the mass transfer between binding sites and template molecules on the imprinted layer (Scheme 1C). Removal of the template molecule (Scheme 1D) would realize the specific recognition sites being rebound with BF molecules selectively and repeatedly. The detection principle was illustrated from the rebinding process of BF (Schemes 1D to 1C). The existence of BF in samples could be monitored by phosphorescence quenching when the imprinted cavity rebound with BF.

Characterizations

As shown in Fig. 1, the morphological and structural characterizations of the tailored multilayer RTP probe and its precursor materials were observed by TEM. Mn:ZnS nanocrystals (Fig. 1(a)) had a uniform size of 4.6 nm, and the silica coating layer (Fig. 1(b)) on the nanocrystal was obvious since the tiny dots became connected by a thin continuous layer. As for the final tailored multilayer RTP probe (Fig. 1(c)), its dimension was greater than that of the precursors (Figs. 1(a) and 1(b)). This implies the nanocrystals incorporated by multiple layers, the mesoporous silica layer and the tailored imprinted layer, were synthesized successfully.

The XRD spectra of the tailored multilayer RTP probe and its precursor materials were evaluated on an X-ray diffractometer. As shown in Supporting Information (Fig. S2), both patterns showed a crystal structure with peaks indexed as (1 1 1), (2 2 0), (3 1 1) lattice planes. The peak (1 1 1), referring to the ZnS diffraction peak, of the silica coated nanocrystal (curve 1) was stronger than that of imprinted multilayer RTP probe (curve 2). The probable reason may lie in the more amorphous silica materials emerged in the tailored multilayer RTP probe than that of its precursor monolayer material. The result was in good accordance with our previous research.26

Infrared spectra of the tailored multilayer RTP probe and its precursor materials are shown in Supporting Information (Fig. S3). In curve 1, the observed bands of silica coated nanocrystal at round 3391, 1635 and 1113 cm⁻¹ displayed -OH and Si-O absorption vibrations. For BF imprinted and non-imprinted multilayer RTP probes (curves 2 and 3), the strong band at round 1115 cm⁻¹ indicated the peaks of Si-O-Si asymmetric stretching. Other observed peaks of 770 and 675 cm⁻¹ also indicated its characteristic vibrations. The consequences further explained that the synthesized tailored multilayer RTP probe from sol-gel polymerization of CTAB and TEOS were faultlessly covered on the support materials.

Effect of pH

The three dimensional structure and the RTP intensity of the synthesized material would be greatly influenced by pH value, according to previous studies.24,27 As is well understood, pH value affects the stability of the RTP probe. When pH value is below 4.0, the Mn:ZnS nanocrystal decomposition will be observed from the fact of obvious smelly H2S gas. As a result, we tested the RTP intensity variation along with the increasing of pH value from 4.0 to 11.0. In Supporting Information (Fig. S4), the RTP intensity reached the maximum value at pH 7.5 for both BF imprinted and non-imprinted multilayer RTP probes (curves 1 and 2). When the pH value was above 10, the RTP intensity decreased because of the ionization of the silica layer under high concentration of OH⁻, together with the destruction of the recognition sites on the surface layer. This phenomenon exactly proved the protection performance of the silica layer for Mn:ZnS nanocrystals; protection from interference from the external environment and support for the molecular imprinted layer. From Supporting Information (Fig. S4), it can be seen that the intensities of both BF imprinted and non-imprinted multilayer RTP probes remained constant in the pH range

![Scheme 1](image)

Scheme 1  Schematic illustration of the synthesis process of the tailored multilayer RTP probe and its detection principle for BF.

![Fig. 1](image)

Fig. 1  TEM images of Mn:ZnS nanocrystals (a); silica coated nanocrystals (b); tailored multilayer RTP probe (c).
between 6.0 and 8.0. So 7.5 was selected as the most suitable pH value for optional detection throughout the experimental procedure.

Detection time and stability

It is necessary and practical to determine an optional detection time. The long-lived RTP offers a sufficient delay time so that background fluorescence emission interference and scattering light encountered from the environment could be avoided as a result. As shown in Fig. 2, the series data were tested at different time intervals. The results show clearly that the RTP intensity decreased sharply in the first 3 min, and the tendency reached a relatively steady state from 5 to 35 min. For time-saving considerations for a fast analysis strategy, 20 min was selected as the optional detection time throughout the experimental procedures.

In Fig. 3, the stability of the probe is shown clearly. The RTP intensity for both BF imprinted and non-imprinted multilayer RTP probes were repeatedly tested in watery solution (pH 7.0) at room temperature. As displayed in Fig. 3, the phosphorescent intensity of both BF imprinted and non-imprinted probes were stable after 12 measurements in 35 min. The trend of the data showed that the probes were stable with the presence of the mesoporous intermediate transition silica layer, as explained above.

Effect of BF concentration and the quenching mechanism

As designed originally, the detection sensitivity and selectivity of the imprinted probe should be superior to the non-imprinted probe because of the improved recognition cavities on the imprinted surface layer. As displayed in Fig. 4, the intensities of both BF imprinted and non-imprinted probes were tested under diverse BF concentrations. Under the optimized conditions, the fluorescence intensity ($I/I_0$) showed a linear relationship with the quenching reagent concentration for both the imprinted and non-imprinted probes (figures embedded in Fig. 4). But the imprinted probe showed a much more sensitive and drastic decrease in phosphorescence intensity. These results proved that this imprinting strategy was more effective and suitable for the determination of BF.

In order to investigate the quenching mechanism of this tailored multilayer RTP probe with BF, the Stern-Volmer equation (Eq. (1)) was applied, which is shown as follows:

$$I/I_0 = 1 + K_{sv}C_{BF}$$  

(1)
The quenching efficiency of four similar pyrethroids by BF imprinted (red column) and non-imprinted (black column) multilayer RTP probes (both 18 mg L\(^{-1}\)).

Where, \(I_0\) and \(I\) are the RTP intensity of the probes with the absence and presence of the quencher BF, respectively. \(K_{sv}\) is the Stern-Volmer quenching constant in units of L mol\(^{-1}\), and \(C_{BF}\) is the concentration of quencher BF.

Static quenching, dynamic quenching and a combination of both are the three basic fluorescence-quenching mechanisms. For a static or dynamic quenching mechanism, the relationship between \(I/I_0\) and \(C_{BF}\) is usually linear; while for a combination of the two, the Stern-Volmer curve is usually nonlinear with an upward movement. And the value of the quenching constant \(K_{sv}\) is often the discriminating criterion that distinguishes a static or dynamic mechanism. If the value of \(K_{sv}\) is more than 100 L mol\(^{-1}\), the mechanism will be defined as a static process; while for biomolecules, the quenching constant is usually considered to be less than 100 L mol\(^{-1}\).

The equation is applied to determine the value of \(K_{sv}\) for each system quantitatively. The ratio of \(K_{sv}\) by BF imprinted and non-imprinted probe was defined as the imprinting factor (IF) to evaluate the selectivity of the probes. By calculation, \(K_{sv}\) of the non-imprinted probe was 2574 L mol\(^{-1}\), and the linearity of the standardization curve was also recorded from 5.0 to 50 \(\mu\)mol L\(^{-1}\) BF with a correlation coefficient of 0.9928. While the \(K_{sv}\) of the imprinted probe was calculated as 3147 L mol\(^{-1}\) and the linearity of the standardization curve was recorded with a correlation coefficient of 0.9916 ranging from 5.0 to 50 \(\mu\)mol L\(^{-1}\) BF. The values of \(K_{sv}\) proved that the imprinted RTP probe had better selectivity for BF and a static quenching mechanism as well.

Specific recognition of BF

Several similar structural pyrethroids, namely, bifenthrin, cyhalothrin, cypermethrin and fenvalerate, were examined to evaluate the selectivity of the synthesized probes with the original concentration of 18 mg L\(^{-1}\) each pyrethroid in a mixed solution. In Fig. 5, the RTP response of the probe for each pyrethroid was displayed. The quenching efficiency (\(I/I_0\) – 1) order for the four pyrethroids was: bifenthrin > cyhalothrin > cypermethrin > fenvalerate. The ratios between the quenching efficiencies of imprinted and non-imprinted probes were 0.125, 0.055, 0.076, and 0.027 for bifenthrin, cyhalothrin, cypermethrin and fenvalerate, respectively. The results thus indicate, the imprinted probe had a more sensitive selectivity toward the target BF.

Table 2 Recovery of potential BF in water samples from Zhenjiang reach of Yangtze River

| Concentration taken/\(\mu\)M | Detected/\(\mu\)M | Recovery, \% | RSD, \% |
|-----------------------------|-----------------|-------------|---------|
| 1                           | 5.0             | 5.39        | 107.8   | 3.2     |
| 2                           | 10.0            | 10.62       | 106.2   | 2.7     |
| 3                           | 15.0            | 15.18       | 101.2   | 1.6     |
| 4                           | 20.0            | 20.70       | 103.5   | 2.2     |

Application to Yangtze River sample analysis

Water samples, collected from the Zhenjiang reach of the Yangtze River, were tested to determine the feasibility of the synthesized probe. The samples were filtered through 0.45 \(\mu\)m Supor filters and stored in neat beakers. BF in amounts of 5.0 – 20 \(\mu\)mol L\(^{-1}\) was spiked into the samples since there were no pyrethroids being detected in the river samples by previous methods. The standard curve in Fig. 4(a) was applied to deduce the BF level in the samples. The analytical results are shown in Table 2. The RTP recovery varied from 101.2 to 107.8\% with the highest RSD value of 3.2\%. These results verified the synthesized tailored multilayer RTP probe was able to detect the BF concentration in direct unknown environmental water sample analysis with relatively high accuracy.

Conclusions

In summary, we integrated MIT and semiconductor nanocrystals to fabricate a novel tailored multilayer fluorescent probe for the monitoring of target BF, based on the mechanism of electron transfer-induced phosphorescence quenching. The synthesized RTP probe had a thin silica intermediate transition layer between the nanocrystal and the outer imprinted layer, which provided mesoporous channels to lower transfer resistance between the nanocrystals and the imprinted quencher BF. High selectivity for the target BF was realized and was attributed to the tailored design and stable structure. Under optional measurement conditions, this RTP responded effectively and sensitively to bifenthrin in direct environmental water samples. Above all, we feel more attention should be given to MIT research to motivate the development of new strategies for RTP detection techniques.

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Supporting Information

The chemical structures of the target detection template and its analogous compounds (Fig. S1), XRD spectra of silica coated nanocrystals and imprinted multilayer RTP probe (Fig. S2), infrared spectra of silica coated nanocrystals, BF imprinted multilayer RTP probe and non-imprinted multilayer RTP probe (Fig. S3), and the effect of \(pH\) value on RTP intensity of BF imprinted and non-imprinted multilayer RTP probes (Fig. S4).
This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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