



Contents lists available at ScienceDirect

Analytica Chimica Acta

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# Rapid, low temperature synthesis of molecularly imprinted covalent organic frameworks for the highly selective extraction of cyano pyrethroids from plant samples

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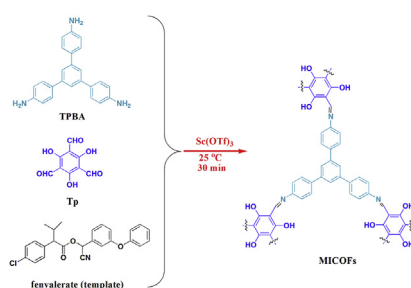
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## HIGHLIGHTS

- New molecularly imprinted covalent organic frameworks (MICOFs) are synthesized.
- The prepared MICOFs exhibit specific recognition toward cyano pyrethroids.
- The advantages are confirmed by the quantitative analysis of cyano pyrethroids in different plant samples.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 1 August 2017

Received in revised form

12 December 2017

Accepted 12 December 2017

Available online xxx

### Keywords:

Molecularly imprinted covalent organic frameworks

Pyrethroids

Solid phase extraction

High-performance liquid chromatography

Complex matrices

## ABSTRACT

New imine-linked molecularly imprinted covalent organic frameworks (MICOFs) were successfully prepared, using fenvalerate as the dummy template. Schiff base reaction between 1,3,5-tris(4-aminophenyl)benzene and 1,3,5-triformylphloroglucinol was rapidly achieved at room temperature, using  $\text{Sc}(\text{OTf})_3$  as the catalyst. The surface groups and morphologies of MICOFs were assessed by Fourier transform infrared spectroscopy, Brunauer-Emmett-Teller surface area analysis, and scanning electron microscopy. The MICOFs exhibited high selectivity toward four structurally similar cyano pyrethroids, including fenvalerate, flucythrinate,  $\beta$ -cyfluthrin and  $\lambda$ -cyhalothrin. A method based on solid phase extraction using MICOFs coupled to high performance liquid chromatography was established for the determination of cyano pyrethroids in plant samples. Linearity in the range  $0.1\text{--}200\text{ ng g}^{-1}$ , with correlation coefficients of  $0.9981\text{--}0.9993$ , was obtained for the four cyano pyrethroids. Detection limits and quantification limits were in the range  $0.011\text{--}0.018\text{ ng g}^{-1}$  and  $0.036\text{--}0.060\text{ ng g}^{-1}$ , respectively. Recoveries at three spiked levels ranged from 94.3% to 102.7%. The developed method is thus a promising technique for the selective extraction of cyano pyrethroids from complex matrices.

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## 1. Introduction

Covalent organic frameworks (COFs) represent a class of porous materials with inherent porosity and structural periodicity [1]. Because of their low density, high thermal stability and high surface

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area, COFs show considerable promise in the field of analytical chemistry, especially for sample preparation, sensing and chromatographic analysis [2–11]. Generally, COFs are prepared by Schiff base reactions (amine-aldehyde condensations) [12], self-condensation of aromatic diols and polycondensation with boronic acid [13] or dimerization of nitroso compounds [14]. Among these methods, the formation of Schiff bases (imines) is the only covalent chemistry suitable for constructing  $\pi$ -conjugated COFs [15]. Imine-linked COFs are traditionally synthesized under similar conditions, using  $\text{CF}_3\text{CO}_2\text{H}$  or  $\text{CH}_3\text{CO}_2\text{H}$  to catalyze imine formation and exchange [16,17]. These conditions, however, require long reaction times (>72 h) and the tedious procedures required create hurdles to the exploration of potential applications of imine-linked COFs. Their lack of specific molecular recognition ability also means that previously reported imine-linked COFs have poor efficiency for the purification and extraction of target compounds in complex matrices. The development of facile protocols for the synthesis of imine-linked COFs with specific molecular recognition ability thus represents a formidable scientific challenge.

Molecularly imprinted polymers (MIPs) have received much attention as artificial recognition materials because of their excellent recognition properties, easy preparation, low cost, and high chemical and mechanical stability [18–21]. MIPs have been prepared by free-radical polymerization [22–25], sol-gel processes [26–29] and click reactions [30], which are all carried out in the presence of the template. Removal of the template reveals specific binding sites, which can specifically rebind the target compound or other compounds with a similar structure [31]. Yan et al. have described the synthesis of hydrophilic molecularly imprinted polyphenol-formaldehyde-melamine resin, using a process that was quite different from the general methods used for the polymerization reaction [32,33]. Nevertheless, all of these methods are time-consuming (>24 h) and too cumbersome for routine application. A rapid synthesis of MIPs is thus urgently needed.

Herein, we address both the growing need for MIPs and the scientific challenge of COFs and present an efficient and general synthetic strategy for the preparation of the first imine-linked molecularly imprinted covalent organic frameworks (MICOFs). In the presence of fenvalerate (the template), reaction between 1,3,5-tris(4-aminophenyl)benzene (TAPB) and 1,3,5-triformylphloroglucinol (Tp) to form the Schiff base occurred rapidly at room temperature in the presence of  $\text{Sc}(\text{OTf})_3$ . The prepared imine-linked MICOFs were used to selectively adsorb cyano pyrethroids from plant samples, including vegetables, fruits and traditional Chinese medicines (TCMs). Cyano pyrethroids are an important class of insecticides that are widely used in agriculture but residues of these pesticides are potentially harmful to human health. It is essential, therefore, to develop a sensitive and selective detection method for cyano pyrethroids. Although some scientists have prepared COFs [11] and MIPs [34] for the detection of pyrethroids, to the best of our knowledge, the development of MICOFs has not been reported.

## 2. Materials and methods

### 2.1. Chemicals

Fenvalerate, flucythrinate,  $\beta$ -cyfluthrin,  $\lambda$ -cyhalothrin, empen-thrin and tetramethrin, for use as standards, were obtained from Aladdin Reagents (Shanghai, China). The structures are shown in Fig. 1. TAPB, Tp,  $\text{Sc}(\text{OTf})_3$ , 4-methylbenzenesulfonic acid (TsOH) and  $\text{CF}_3\text{CO}_2\text{H}$  were purchased from Tokyo Kasai Co. (TCI). HPLC-grade methanol and acetonitrile were purchased from Macron Fine Chemicals (USA). Other reagents were analytical grade and were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai,

China). Working solutions of the standards were prepared by dissolving the analytes in *n*-hexane. The solutions were stored at 4 °C before use.

### 2.2. Instruments

Scanning electron microscope (SEM) images were recorded using a SWPRATM55 microscope (Carl Zeiss AG, Aalen, Germany). Fourier-transform infrared (FT-IR) spectra were recorded using a Nicolet 710 FT-IR spectrometer. Nitrogen adsorption-desorption isotherms were recorded using an ASAP 2020 surface area measurement system (Micromeritics Instrument Corp., Norcross, GA, USA). The polymers were degassed for 12 h at 110 °C before recording the sorption measurements. Total pore volume and surface area were calculated using the Brunauer-Emmett-Teller (BET) method. The pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) model.

HPLC analyses were carried out using an Agilent 1120 LC system (Agilent Technologies, Inc., Palo Alto, CA, USA), equipped with an ZORBAX ODS column (5  $\mu\text{m}$ , 4.6  $\times$  250 mm, Agilent Technologies, Inc.) and a diode-array detector. The mobile phase was composed of water (A) and acetonitrile (B), with a flow rate of 1.0 mL min<sup>-1</sup> at 25 °C. The gradient elution program was: 0–5 min, 80.0% B; 5–7 min, 80.0–66.0% B; 7–20 min, 66.0% B; 20–25 min, 66.0–80.0% B. The detection wavelength was 230 nm and the injection volume was 20.0  $\mu\text{L}$ .

### 2.3. Synthesis of MICOFs

Fourteen MICOFs were prepared using different reaction conditions as previously described, with some modifications [17]. The synthesis of MICOF 7 serves as an example (Table 1). A 10-mL round-bottomed flask was charged with TPBA (0.15 g, 0.4 mmol), Tp (0.09 g, 0.4 mmol) and fenvalerate (0.04 g, 0.1 mmol). Mesitylene (2 mL) was added and the resulting suspension was sonicated at 25 °C until the monomers were fully dissolved. After standing for 30 min,  $\text{Sc}(\text{OTf})_3$  (4 mg, 0.008 mmol) was added and the resulting suspension was sonicated briefly. The flask was closed with a plastic cap and allowed to stand for 30 min. The reaction mixture was transferred to a container and while precipitates were activated by Soxhlet extraction using MeOH/ $\text{CH}_3\text{COOH}$  (9:1, v/v) for 12 h to removing fenvalerate. After washing with MeOH until neutral, the particles were dried under vacuum for 12 h at 60 °C to provide MICOF 7 (0.21 g, 95%). Before used, the polymers were sieved through a 35–45  $\mu\text{m}$  sieve.

The corresponding non-imprinted covalent organic frameworks (NICOFs) were synthesized in the same manner, except that no fenvalerate was added.

### 2.4. Binding experiments

**Isothermal adsorption:** Fenvalerate working solutions (0.01–1.0 mmol L<sup>-1</sup>) were prepared in *n*-hexane. Aliquots (5 mL) of each solution was mixed with MICOFs (20 mg) in separate 10.0-mL flasks. The flasks were then shaken at 25 °C for 4 h. After binding, the mixtures were filtered through 0.45  $\mu\text{m}$  membranes. The free concentration of fenvalerate in each supernatant solution was measured by HPLC. The quantity ( $Q_e$ , mmol g<sup>-1</sup>) of fenvalerate bound to MICOFs and NICOFs was calculated using the following equation [31]:

$$Q_e = (C_i - C_e) v/m$$

where  $m$  (mg) is the mass of sorbents and  $v$  (mL) is the volume of the sample.  $C_i$  (mmol L<sup>-1</sup>) and  $C_e$  (mmol L<sup>-1</sup>) are the initial

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