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Research Paper

Irreversible fluorine covalent organic framework based probe nanoelectrospray ionization mass spectrometry for direct and rapid determination of perfluoroalkyl carboxylic acids

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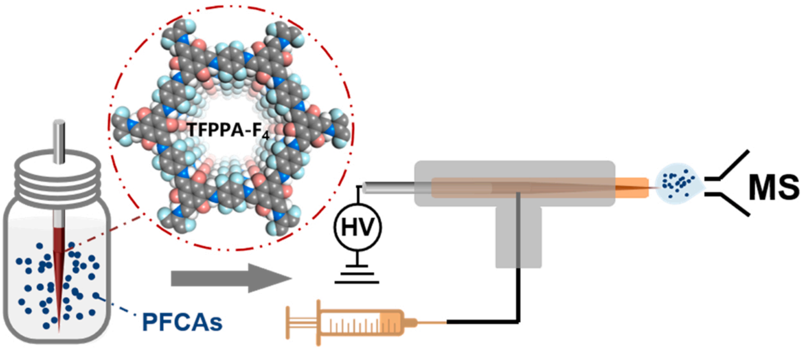
HIGHLIGHTS

- Irreversible fluorine COF (FCOF) bonded probe was fabricated via in-situ growth.
- Chemical bonding of irreversible FCOF improved the stability of probe.
- FCOF based PESI-MS was developed for perfluoroalkylcarboxylic acids.
- Mechanism involves hydrophobic, hydrogen bonding and F−F interactions.

GRAPHICAL ABSTRACT



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ABSTRACT

Probe nanoelectrospray ionization mass spectrometry (PESI-MS) is practically desirable for rapid and ultra-sensitive analysis of trace contaminants in environment, but limited with the stable and selective probe coating. Herein, we show the design and preparation of irreversible fluorine-based covalent organic framework (TFPPA-F_4) covalently bonded probe to couple with ESI-MS (TFPPA-F_4-PESI-MS) for direct and rapid determination of perfluoroalkyl carboxylic acids (PFCAs) in environmental water. Chemical bonding coating of irreversible crystalline TFPPA-F_4 not only improved stability of the probe, but also offered accessible multiple interactions including hydrophobic, hydrogen bonding and F-F interactions to promote the kinetics and selectivity for PFCAs. The proposed TFPPA-F_4-PESI-MS realized rapid determination of PFCAs (about 4 min) with low limits of detection of 0.06–0.88 ng L^{-1} and wide linear range of 1–5000 ng L^{-1} (R^2 of 0.9982–0.9998). Recoveries for the spiked lake and pond water were 85.9–111.1 %. TFPPA-F_4 based probe can maintain the extraction performance after 100 times of extraction. This work shows the great potential of the irreversible covalent organic framework based PESI-MS in rapid and ultra-sensitive determination of contaminants in environmental samples.

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1. Introduction

Protection of water resource is attracting worldwide attention in coming century due to the irreplaceability of water resource [22,36]. As new emerging contaminant, perfluoroalkyl carboxylic acids (PFCAs), typically represented with perfluorooctanoic acid (PFOA), widely exist in environmental water owing to their extensive application in various industries including aerospace, textile, packaging, automobile, and decoration [28,37]. The abundant C-F bonds with high bond energy make PFCAs extremely stable and difficult to degrade in the environment, resulting in the high bioaccumulation and potential risk for organisms [1,24,5]. Many national regulatory agencies start to monitor PFCAs levels in water (Committee POPRC, 2011; Committee JISC, 2022). A rapid and ultra-sensitive analytical method for PFCAs in environmental water remains indispensable and significant for investigation of the environmental exposure level and toxicological effect of PFCAs.

Trace level and serious interference of complex matrix from real samples make extraction necessary for determination of PFCAs with the primarily performed liquid chromatography-mass spectrometry (LC-MS) [8,30]. However, time-consuming and tedious processes of extraction and separation limit rapid determination of PFCAs with LC-MS [15,16,38]. Probe nanoelectrospray ionization mass spectrometry (PESI-MS) opens up a new stage for the determination of PFCAs [35,3,7]. Different from traditional LC-MS isolated with extraction, PESI-MS can utilize charged solvent to achieve on-line elution of enriched target from the coating of probe to produce spray ions of target for direct MS analysis [23,4,2], offering the opportunity for rapid and ultra-sensitive determination of PFCAs. However, the coatings of commercial probes including polydimethylsiloxane, divinyl-benzene and poly(acrylate) are not particularly selective for the enrichment of PFCAs [34]. Novel efficient coatings of probe for PFCAs are still extremely urgent.

Crystalline porous materials of covalent organic frameworks (COFs), linked with organic monomers by covalent bonds, have already shown up-and-coming talents as adsorbents for sample pretreatment [9,21,26,27,6]. High stability, ordered porosity, designable structure and tunable functionality allow COFs to rapidly and selectively interact with analytes. Thus, development of COFs based PESI-MS is promising in rapid and ultra-sensitive analysis of complex samples, but still in preliminary stage [10,11,13]. The majority of reported COFs in PESI-MS are reversible, and the COFs are physically adhered on the probe, which greatly compromises the stability and durability of the COFs based probe.

Herein, we intentionally designed to prepare irreversible COF covalently bonded probe to couple with ESI-MS for direct and rapid determination of PFCAs in environmental water. An irreversible crystalline fluorine-based COF (TFPPA-F_4) condensed with 1,3,5-triformylphloroglucinol (TFP) and 2,3,5,6-tetrafluoro-1,4-phenylenediamine (PA-F_4) was selected and covalently in-situ grown on stainless steel probe (SS). The highly ordered structure of TFPPA-F_4 with rich F-F, H-bonding and hydrophobic interactions would render the TFPPA-F_4 bonded probe superior sensitivity and rapid kinetics for PFCAs, allowing TFPPA-F_4-PESI-MS for rapid and ultra-sensitive determination of PFCAs in real environmental water. This work not only expands the talent of irreversible COFs in PESI-MS, but also reveals the great potential of COFs based PESI-MS in rapid and ultra-sensitive determination of contaminants in environmental samples.

2. Materials and methods

2.1. Materials and chemicals

All chemicals and reagents are commercially available and used without further purification. TFP was obtained from Yanshen Technology Co., Ltd. (Jilin, China). PA-F_4 was bought from Tokoy Chemical Industry Co., Ltd. (Shanghai, China). 1,4-Dioxane, mesitylene, acetic acid (HAc), tetrahydrofuran (THF), (3-aminopropyl)triethoxysilane (APTES), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA) and perfluoroundecanoic acid (PFUnDA) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Perfluoro-n-(1,2,3,4-$^{13}C_4$) octanoic acid ($^{13}C_4$-PFOA) as the internal standard compound (IS) was obtained from Wellington laboratories Inc. (Guelph (ON), Canada). HPLC grade methanol (MeOH) was gotten from Fisher Chemical (Shanghai, China). Ultrapure water was purchased from Wahaha Foods Co., Ltd. (Shanghai, China). SS (diameter ca. 0.25 mm, length 40 mm) was purchased from Huaer Medical Instrument Co., Ltd (Hebei, China). Fused silica capillary (o.d. 0.53 mm) was purchased from Yongnian Optic Fiber Plant (Hebei, China). Environmental water samples were collected locally and directly used as matrix samples without any pretreatment.

2.2. Instrumentation

Powder X-ray diffraction (PXRD) patterns were recorded on a D2 PHASER X-ray diffractometer (Bruker, German) using Cu Kα radiation ($\lambda = 1.5418$ Å) with a scanning speed of 8° min^{-1} and a step size of 0.05° in 2θ. Scanning electron microscopy (SEM) images were recorded on an S-3500 N (Hitachi, Japan) scanning electron microscope. Fourier transform infrared (FTIR) spectra were measured on a Nicolet IR IS10 spectrometer (Nicolet, USA). X-ray photoelectron spectroscopy (XPS) exeriments were performed on Axis supra (Kratos, UK). N_2 adsorption experiments were performed on Autosorb-iQ (Quantachrome, USA) using N_2 adsorption at 77 K. Mass spectra were obtained on QTRAP 4500 mass spectrometer (AB SCIEX, USA) equipped with a Nanospray II Source (P/N #1004600, AB SCIEX) and analyst software (AB SCIEX, USA) to control equipment and acquire data.

2.3. Preparation of irreversible TFPPA-F_4 boned probe

SS was dipped into aqua regia (depth ca. 1.5 cm) for 1 min, then washed with ultrapure water continuously until pH reached 7.0, and finally dried at room temperature. The dried etched SS was immersed into a mixture of APTES/MeOH/H_2O (v/v/v, 4/5/1) solution for 4 h and dried in a vacuum oven at 120 °C for 1 h to obtain the amino-functionalized SS (NH_2-SS). The NH_2-SS was immersed in the mixture of TFP (31.5 mg), PA-F_4 (40.5 mg), 6 M HAc (0.1 mL), 1,4-dioxane (0.5 mL), and mesitylene (0.5 mL) with ultrasonic process for 10 min, degassed with freeze-pump-thaw cycles, reacted at 100 °C for 3 days, washed with THF and finally dried in a vacuum oven for 2 h to obtained TFPPA-F_4 bonded SS (TFPPA-F_4-SS).

2.4. Procedure of TFPPA-F_4-PESI-MS

All the samples were extracted with TFPPA-F_4-SS. Typically, the TFPPA-F_4-SS was first cleaned with MeOH and ultrapure water, immersed into 1 mL of IS ($^{13}C_4$-PFOA) mixed samples with vigorous stirring at room temperature for 2 min, then washed with ultrapure water for 10 s, and finally moved to a home-made probe holder (Fig. S1). The home-made probe holder with a three-dimensional moving platform and hand-held digital microscope can finely control and monitor the position of the TFPPA-F_4-SS (Fig. 1a). The distance between tip of TFPPA-F_4-SS and MS inlet was controlled as ca. 5 mm. The prepared TFPPA-F_4-SS also served as ESI emitter. A negative voltage of 3.2 kV, supplied by the MS-integrated high-voltage source, was applied to the end of COF-probe (Fig. 1b). An MS-integrated syringe pump was used to offer solvent as eluent. The eluent of MeOH at a flow rate of 20 μL min^{-1} was pumped to elute the TFPPA-F_4 coating on the probe. The produced charged spray of eluate was directly introduced into MS for data acquisition and analysis. The TFPPA-F_4-SS could be recycled by vigorous stirring with MeOH and water.

3. Results and discussion

3.1. *Preparation and characterization of irreversible TFPPA-F_4 boned probe*

Hydrophobic, hydrogen bonding, and F-F interaction are well-known for promoting the selectivity of adsorbent for PFCAs [13,14,19]. Ordered crystalline structure of adsorbents can facilitate mass transfer of analytes to achieve rapid adsorption [18,29]. Accordingly, irreversible crystalline COF TFPPA-F_4 with rich hydrophobic aromatic rings, H-bond acceptors (C=O), H-bond donors (N-H) and F groups was selected as the coating to promote the selectivity and kinetics of probe to PFCAs. The TFPPA-F_4 covalently bonded probe was synthesized via in-situ growth approach as shown in Fig. 2. The etched SS was first reacted with APTES to prepare NH_2-SS. Then, TFP and PA-F_4 were further introduced to react with NH_2-SS via the Schiff-base reaction to obtained TFPPA-F_4-SS.

Formation of TFPPA-F_4 and its bonded SS was first confirmed with PXRD. The prepared TFPPA-F_4 and TFPPA-F_4 scraped from TFPPA-F_4-SS gave an evident peak at 4.7° in PXRD pattern, which was in good consistent with the simulated PXRD pattern of TFPPA-F_4. The simulation and refinement gave the specific cell parameters of space group P6/m, $a = b = 21.8234$ Å, $c = 3.5031$ Å, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ for TFPPA-F_4 (Fig. 3a-c and Table S1). Irreversible COFs are famous for their superior stability [12,25,32,33]. The irreversible keto-enamine COFs can keep the crystallinity even in extreme acid/base condition [17]. Hydrolytic stability of TFPPA-F_4 was examined with the PXRD. No obvious change of the PXRD patterns for TFPPA-F_4 after immersing in different solvents demonstrated the high chemical stability of TFPPA-F_4 coating in 1 M NaOH/HCl, water and MeOH (Fig. 3d). In contrast, the reported reversible COF-F-1 for the PFCAs was totally hydrolyzed in 1 M HCl and lost the crystallinity in 1 M NaOH, MeOH and H_2O, indicating the practical potential of irreversible COFs in complex matrix (Fig. S2).

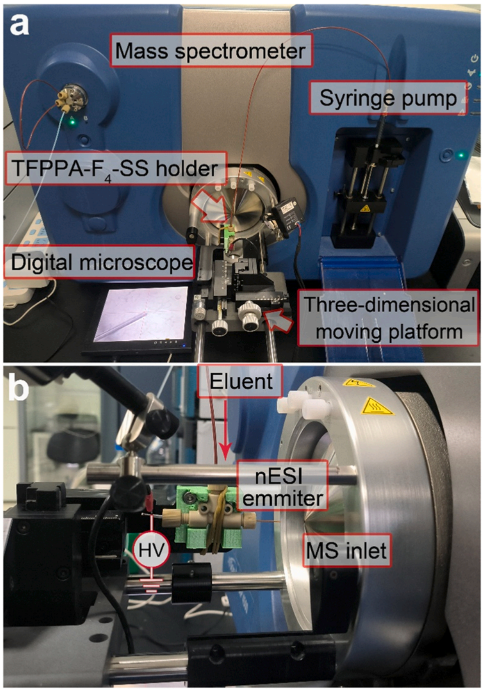

Fig. 1. (a) Photograph of TFPPA-F_4-PESI-MS system with home-made probe holder, three-dimensional fine moving platform, hand-held digital microscope, syringe pump, and mass spectrometer. (b) Detailed fittings including the home-made probe holder, TFPPA-F_4-SS served as nanoelectrospray ionization (nESI) emitter, MS-integrated high-voltage source and inlet of MS.

Change and formation of chemical bonds were verified with FTIR. The FTIR spectra of TFPPA-F_4 appeared a new shoulder peak at 1662 cm^{-1} (assigned to the stretching band of C=O), which overlapped with the strong band of C=C (1593 cm^{-1}), indicating formation of irreversible keto structure. Intense stretching peak at 1010 cm^{-1} revealed abundant C-F in the prepared TFPPA-F_4 (Fig. 3e). Evident peak of F 1s in wide XPS scanning spectra also conveyed the existence of rich F in the TFPPA-F_4 (Fig. 3f).

Optical photograph of TFPPA-F_4-SS showed evident orange red TFPPA-F_4 coating (about 1.5 cm) on the end of SS (Fig. 4a). SEM image revealed the sphere-like morphology of TFPPA-F_4 (Fig. 4b). Compared to NH_2-SS, TFPPA-F_4-SS offered larger density of TFPPA-F_4 particles on surface of SS (Fig. 4c and d), further confirming successful bonding of TFPPA-F_4 with SS. SEM image of cross-section for TFPPA-F_4-SS reveals about 25 μm thickness of TFPPA-F_4 (Fig. 4e).

N_2 adsorption experiment characterized the pore properties of the prepared irreversible TFPPA-F_4 with the BET surface area of 233 $m^2\ g^{-1}$ and narrow pore size distribution of 1.0–3.0 nm (Fig. S3 and S4). The main pores were distributed at ~1.79 nm. The large surface area and suitable pore size of TFPPA-F_4 with high chemical stability as well as rich aromatic ring, C=O, N-H and F groups make selective extraction of PFCAs with TFPPA-F_4 reasonable, inspiring us to explore the potential of TFPPA-F_4 based PESI-MS for the analysis of PFCAs.

3.2. *Development of TFPPA-F_4-PESI-MS*

TFPPA-F_4-SS was immersed into 1 mL of samples containing six PFCAs of PFHxA, PFHpA, PFOA, PFNA, PFDA, and PFUnDA. The PFCAs extracted TFPPA-F_4-SS (TFPPA-F_4-SS-PFCAs) was washed with water, then equipped on a home-made probe holder and linked with MS (Fig. 1 and S1). Eluent of MeOH was set at a flow rate of 20 μL min^{-1} under a negative voltage of 3.2 kV to elute the extracted PFCAs to produce charged spray of PFCAs for direct MS analysis. In order to investigate extraction time, signal intensities of PFCAs ($I_{analyte}$) was monitored at different time. It was found that the $I_{analyte}$ remained no evident change after 2 min (Fig. S5). Thus, the extraction time was considered to be 2 min. Elution profile showed complete elution of PFCAs from TFPPA-F_4 based probe in 1.5 min (Fig. 5a).

Twenty precursor ion/product ion pairs of the six PFCAs and $^{13}C_4$-PFOA (IS) were monitored in MRM model to qualitatively and quantitatively analyze PFCAs under the optimal conditions in Table S2, Fig. 5 and Fig. S6. Quantitative performance of the established TFPPA-F_4-PESI-MS method was assessed via analyzing pure water samples spiked with 0.5 – 5000 ng L^{-1} of PFCAs and 100 ng L^{-1} of $^{13}C_4$-PFOA as IS. Ratio of signal intensities for PFCAs and IS ($I_{analyte}/I_{IS}$) was used for construction of calibration curve and quantitative calculation. The $I_{analyte}/I_{IS}$ linearly increased with the concentration of PFCAs from 5 to 5000 ng L^{-1} except of PFNA and PFDA (1–5000 ng L^{-1}) with determination coefficients (R^2) of 0.9982–0.9998 (Table 1 and Fig. S7). Limits of detection (LODs, S/N = 3) and quantification (LOQs, S/N = 10) of TFPPA-F_4-PESI-MS for the PFCAs were 0.06–0.88 and 0.20–2.92 ng L^{-1}, respectively (Table 1).

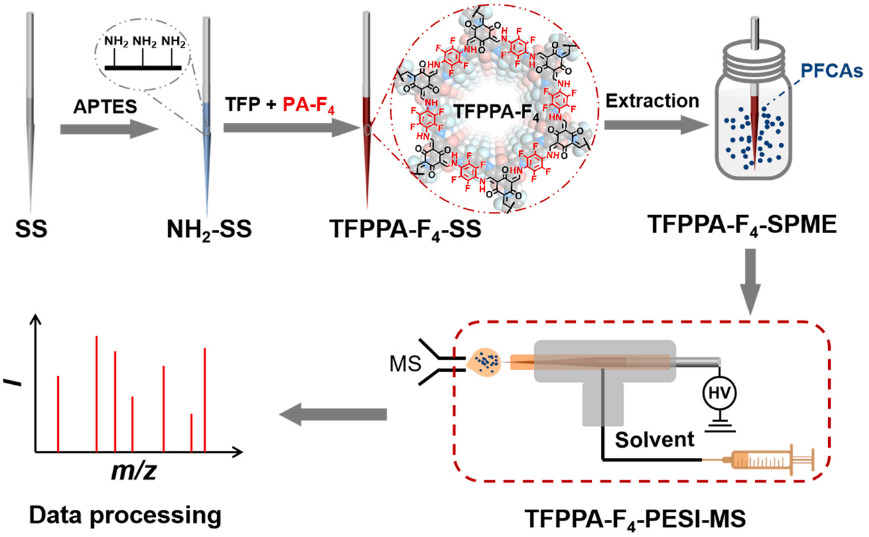

Fig. 2. Schematic illustration of the preparation of TFPPA-F_4-SS for PESI-MS analysis of PFCAs.

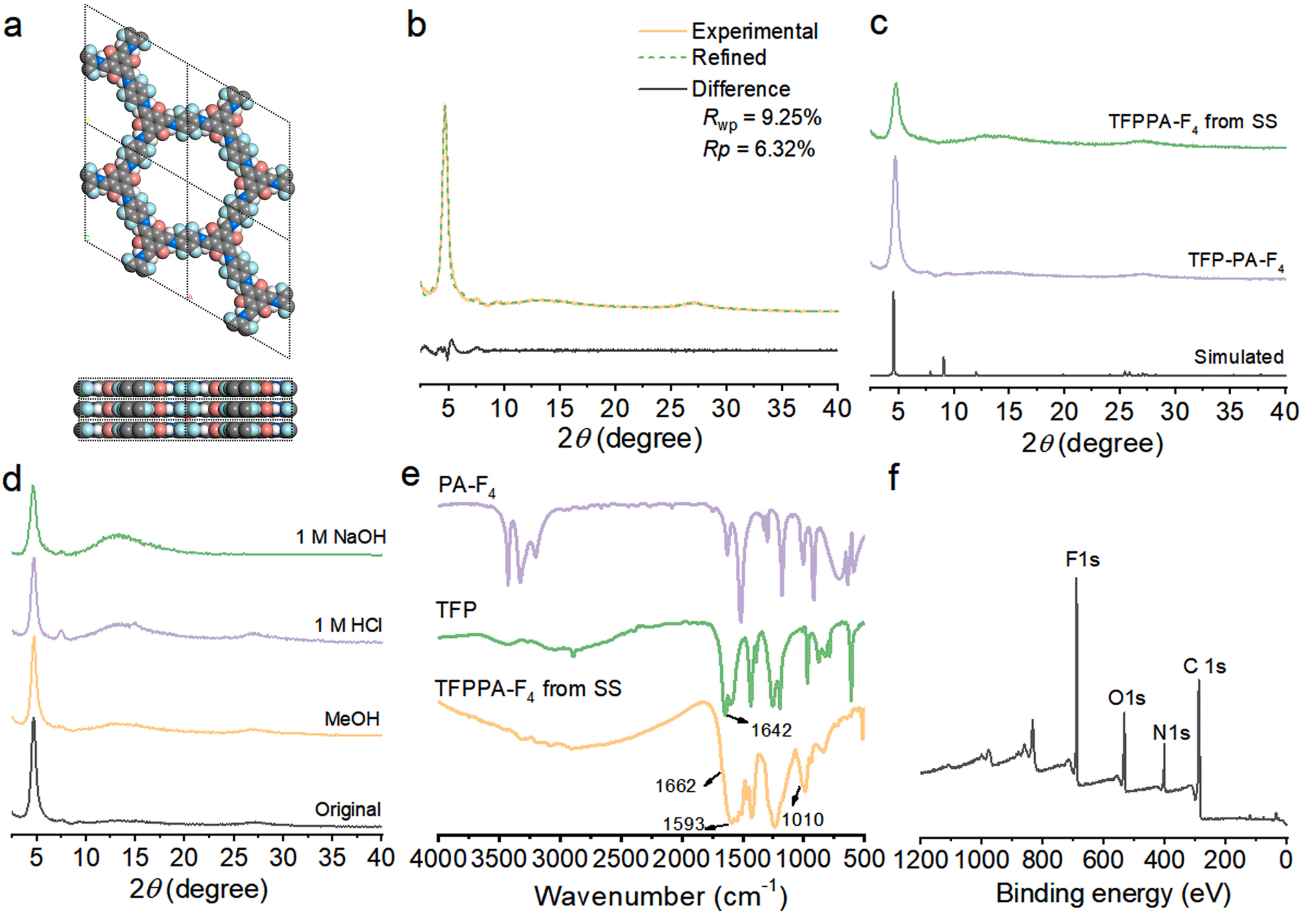

Fig. 3. (a) Unit cell of TFPPA-F_4. (b) Pawley refinement of TFPPA-F_4. (c) Experimental and simulated PXRD patterns of TFPPA-F_4. (d) PXRD patterns of TFPPA-F_4 treated with different solvents. (e) FTIR spectra of TFP, PA-F_4 and TFPPA-F_4. (f) Wide XPS scanning spectra of TFPPA-F_4.

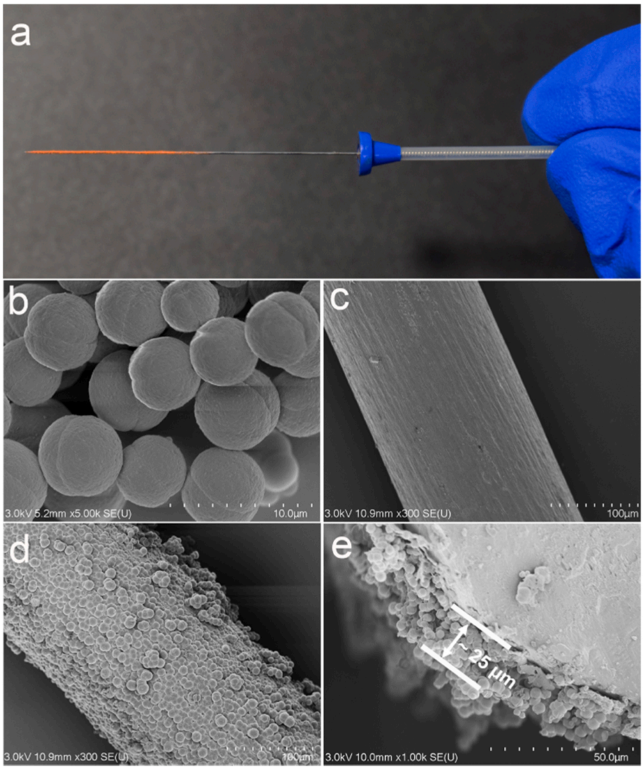

Fig. 4. (a) Optical photograph of TFPPA-F_4-SS. SEM images of (b) TFPPA-F_4, (c) etched SS, (d) TFPPA-F_4-SS and (e) cross-section for the TFPPA-F_4-SS.

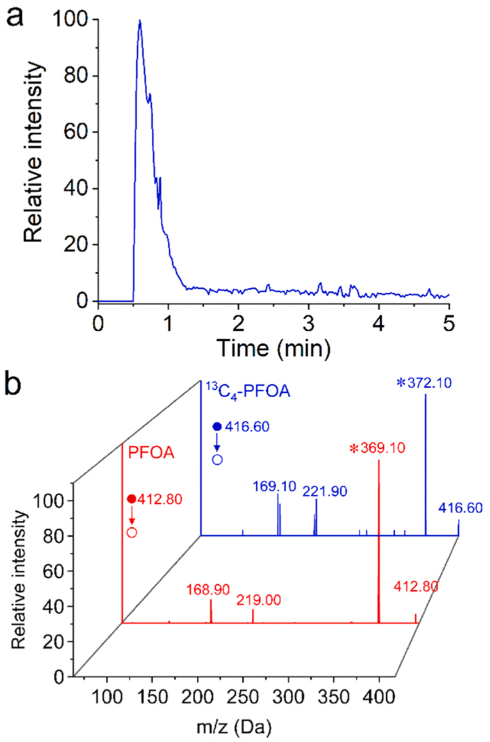

Fig. 5. (a) Elution profile for PFCAs (5 μg L^{-1}). (b) MS/MS spectra of PFOA and $^{13}C_4$-PFOA (The ions labeled with star were selected for quantitation).

Moreover, the developed TFPPA-F_4-PESI-MS not only did not require separation process of LC, but also facilitated extraction speed for PFCAs because of ordered crystalline structure of TFPPA-F_4, resulting in shorter analysis time of PFCAs (about 4 min) in contrast to traditional LC-MS. Compared with many other reported analytical methods for PFCAs, our proposed TFPPA-F_4-PESI-MS was quite competitive in sample throughput and sensitivity (Table S3).

Maximum molecular sizes of PFHxA-PFUnDA were calculated to be smaller than 14.9 Å (Fig. S8), which was covered by the pore size of TFPPA-F_4, favoring size exclusion effect and pore selection. XPS characterization was further applied to investigate the effect of TFPPA-F_4 on the extraction of PFCAs. The results showed O 1s, N 1s and F 1s spectra of TFPPA-F_4 changed after adsorption of PFCAs. XPS peaks of TFPPA-F_4 for N 1s at 404.20 eV, O 1s at 532.83 eV and F 1s at 691.32 eV likely resulted from the intramolecular hydrogen bonding. After the adsorption of PFCAs, binding energies of the aforementioned N 1s, O 1s and F 1s shifted to 403.53, 533.04 and 690.46 eV, respectively (Fig. S9). These changes indicate the formation of hydrogen bonding and F-F interaction of TFPPA-F_4 and PFCAs [20,31].

Repeatability and reproducibility are crucial for probe. Relative standard deviations (RSDs) of $I_{\text{analyte}}/I_{\text{IS}}$ for 12 replicate extractions of PFCAs with TFPPA-F_4-SS were 1.87–4.6 %. The RSDs of $I_{\text{analyte}}/I_{\text{IS}}$ for PFCAs with three different TFPPA-F_4-SS were 6.7–12.5 % (Table 1). The $I_{\text{analyte}}/I_{\text{IS}}$ of 100 ng L^{-1} PFCAs gave no significant change after 100 extraction cycles, indicating long-lasting reusability of the prepared TFPPA-F_4 bonded probe (Fig. S10). The stability of TFPPA-F_4 coating was also verified by PXRD and FTIR. Compared with original TFPPA-F_4 coating, the TFPPA-F_4 coating after extraction gave no obvious change in FTIR spectra and PXRD patterns (Fig. S11 and S12), indicating good retention and no hydrolysis of the crystalline structure of TFPPA-F_4 coating after extraction, which was attribute to the irreversibility of TFPPA-F_4 as well as the chemical bonding of TFPPA-F_4 and SS.

3.3. TFPPA-F_4-PESI-MS for real samples

Practicability of the developed TFPPA-F_4-PESI-MS method was verified by analyzing environmental water samples. Matrix factor (MF) of three environmental water samples was 85.7–114.7 % (Fig. S13), indicating that the standard calibration curves obtained with pure water are available for quantitative calculation of real samples. PFCAs were found in all the three samples. In lake water I, PFHxA, PFHpA, PFOA, PFNA and PFDA were found to be 9.4 ± 1.2, 19.0 ± 0.2, 4.5 ± 0.2, 18.2 ± 0.2, and 10.9 ± 0.2 ng L^{-1}, respectively. In lake water II, PFOA, PFNA and PFDA were detected to be 3.4 ± 0.2, 8.3 ± 0.4, and 2.4 ± 0.2 ng L^{-1}, respectively. In pond water, PFHxA, PFHpA, PFOA, PFNA and PFDA was found to be 20.3 ± 1.6, 27.1 ± 1.0, 4.9 ± 0.6, 8.5 ± 0.7, and 3.5 ± 0.5 ng L^{-1}, respectively (Table S4). Recoveries of spiked 100 ng L^{-1} of PFCAs in the three water samples were 82.9–111.1 % (Table S4), indicating good accuracy of the TFPPA-F_4-PESI-MS for direct determination of trace level PFCAs in real samples.

4. Conclusions

In summary, an irreversible fluorine-based COF TFPPA-F_4 bonded probe coupled with ESI-MS was firstly designed for determination of PFCAs. The rich hydrophobic aromatic rings, H-bond acceptors/donors and F groups of TFPPA-F_4 provided the conjunction of hydrophobic, hydrogen bonding, and F-F interactions to promote the selectivity of TFPPA-F_4 for PFCAs. The irreversible TFPPA-F_4 with ordered structure and great stability further served as probe coating via chemical bonding method to render the TFPPA-F_4 based probe of PFCAs with fast kinetics

Table 1
Validation of TFPPA-F_4-PESI-MS for PFCAs.

Analyte	Linear range (ng L^{-1})	Regression equation	R^2	LOD (ng L^{-1})	LOQ (ng L^{-1})	Repeatability (RSD, %)[a]	
						One probe (n = 6)	Probe-to-probe (n = 3)
PFHxA	5–5000	Y = 0.0038X + 0.0716	0.9984	0.88	2.92	4.6	6.7
PFHpA	5–5000	Y = 0.0161X + 0.2132	0.9998	0.78	2.60	2.1	7.5
PFOA	5–5000	Y = 0.0619X + 0.5404	0.9996	0.26	0.87	2.2	10.9
PFNA	1–5000	Y = 0.0260X + 0.2428	0.9982	0.41	1.35	1.9	8.6
PFDA	1–5000	Y = 0.0728X + 0.7818	0.9996	0.30	0.99	4.1	6.8
PFUnDA	5–5000	Y = 0.2310X + 22.517	0.9991	0.06	0.20	2.5	12.5

[a] 100 ng L^{-1} of PFCAs.

and high selectivity. Coupled with ESI-MS, the proposed TFPPA-F_4-PESI-MS achieved rapid and ultra-sensitive analysis of trace PFCAs in environmental samples. Moreover, the chemical bonding coating improved the stability of the COF based probe. This work not only offers an efficient analytical method for trace PFCAs, but also reveals the great potential of irreversible COFs-PESI-MS technology in rapid and accurate determination of pollutants in environmental samples.

Environmental Implication

As new emerging contaminant, perfluoroalkyl carboxylic acids (PFCAs) widely exist in environmental water. Compared with the traditional LC-MS, probe nanoelectrospray ionization mass spectrometry (PESI-MS) opens up a new stage for rapid and sensitive determination of PFCAs owing to the high selectivity and no LC separation, but is limited by the efficient coating of probe. Here, an irreversible fluorine-based covalent organic framework (TFPPA-F_4) covalently bonded probe coupled with ESI-MS (TFPPA-F_4-PESI-MS) was designed and prepared for direct and rapid determination of PFCAs in environmental water.

CRediT authorship contribution statement

Xu-Qin Ran: Conceptualization, Investigation, Methodology, Data curation, Writing – original draft. **Shu-Ting Xu:** Methodology, Resources. **Hai-Long Qian**: Conceptualization, Methodology, Writing – review & editing, Supervision, Funding acquisition. **Xiu-Ping Yan:** Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2023.131584.

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