

Unlocking Enhanced Detection of Perfluoroalkanesulfonic Acids via Fluorinated Nonpolar 3D Covalent Organic Frameworks-Based Ambient Probe Nanoelectrospray Ionization Mass Spectrometry

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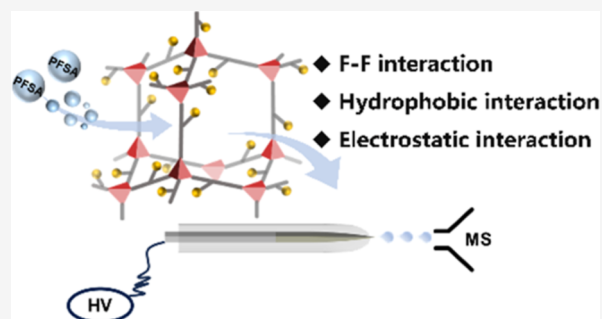


Article Recommendations



Supporting Information

ABSTRACT: The trace levels and severe matrix interferences greatly limited the determination of stable, persistent, and long-range-transported perfluoroalkanesulfonic acids (PFSAs) in complex environments. Here, we design and prepare the first fluorinated nonpolar 3D COF (TFPM-Pa- CF_3) as an adsorbent, consisting of tetrakis(4-formylphenyl)methane (TFPM) and 2,5-diaminobenzo-trifluoride (Pa- CF_3) for adsorption and extraction of PFSAs. The proposed TFPM-Pa- CF_3 demonstrates excellent adsorption capacity (509.1 mg g^{-1}) and rapid adsorption kinetics (5 min) for PFSAs attributed to the synergistic effects of F–F, hydrophobic, and electrostatic interactions. Furthermore, TFPM-Pa- CF_3 is grown in situ on a stainless needle and coupled with ambient probe nanoelectrospray ionization mass spectrometry (PESI-MS) to develop a rapid and direct determination method with a low limit of detection ($0.05\text{--}0.86 \text{ ng L}^{-1}$) and wide linear range ($1\text{--}10,000 \text{ ng L}^{-1}$) for trace perfluorooctanesulfonate and its alternatives in environmental soil, algae and water. This work unlocks the efficient determination or removal of PFSAs in a complex environment, facilitating the solution of critical environmental PFSAs problems.



INTRODUCTION

Extensive consumption in industry has led to the widespread distribution of perfluoroalkanesulfonic acids (PFSAs) in a diverse array of environmental matrices.^{1–3} The high dissociation energy of the C–F bond makes PFSAs extremely stable, persistent, and long-range-transported in the environment, increasing their bioaccumulation as well as potential ecological and health risks.^{4,5} Perfluorooctanesulfonate (PFOS) and its alternatives thereby have already been classified as a persistent organic pollutant under the Stockholm Convention and also subjected to strict regulations with a maximum concentration limit of 70 ng L^{-1} by the U.S. Environmental Protection Agency.^{6,7} Consequently, effective detection methods are urgently required to control the risks of PFSAs, which remains challenging due to the coexistence of complex environmental matrices and the presence of PFSAs at trace or ultratrace levels.

Solid adsorbents can serve the purpose of enriching target analytes and removing matrix interference, so adsorbents with excellent selectivity and kinetics are crucial for accurate detection of PFSAs.^{8–11} A range of adsorbents, such as activated carbon,^{12,13} anion exchange resins,¹⁴ and molecularly imprinted polymers,¹⁵ have been reported to effectively extract or remove PFSAs. However, these existing adsorbents suffer from uncontrollable and amorphous structures, leading to the limitation in selectivity and kinetics for PFSAs.¹⁶ Covalent

organic frameworks (COFs) are well-known for their highly designable ordered structure with tunable functionalities and good stability,^{17–20} thereby being regarded as a promising candidate adsorbent for PFSAs.

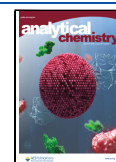
Currently, diverse two-dimensional (2D) COFs have achieved great analytical performance for PFSAs attributed to the well-organized ordered structure and introduced specific F–F interaction.^{21–24} However, the hierarchical stacking polar structures of 2D COFs with only one-dimensional pore channels are inadequate for the mass transfer and adsorption of PFSAs with long hydrophobic carbon chains, resulting in preventing promotion of the selectivity and kinetics of COFs for PFSAs.^{25–27} In contrast, 3D COFs possess a nonpolar pore environment, consisting of rich pore channels and large cage-like cavities.^{28–32} This property makes 3D COFs theoretically more favorable for the diffusion and mass transfer of hydrophobic PFSAs,^{33,34} but the practical potential of nonpolar 3D COFs as adsorbents for adsorption or extraction of PFSAs has not yet been explored.

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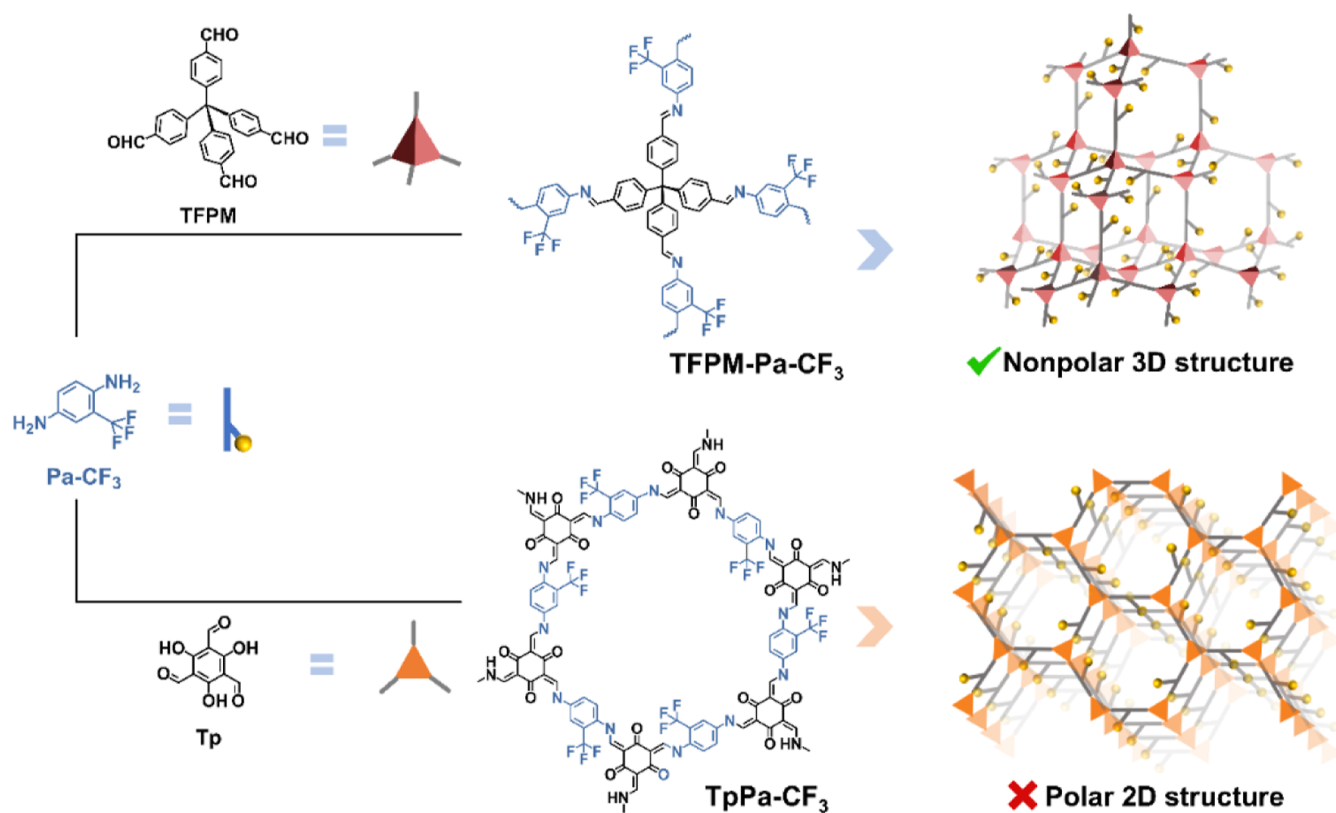


Figure 1. Schematic for the preparation of TFPM-Pa-CF₃.

Herein, we rationally designed the synthesis of the first fluorinated nonpolar 3D COF to serve as an adsorbent for the efficient adsorption of PFSA (Figure 1). The tetrahedral monomer of tetrakis(4-formylphenyl)methane (TFPM) lays the foundation for the formation of a nonpolar 3D structure, while the 2,5-diaminobenzo-trifluoride (Pa-CF₃) monomer can offer a specific F–F interaction. The properties of the as-prepared 3D COF (denoted as TFPM-Pa-CF₃) were in-depth characterized, and its adsorption efficiency for PFSA was further evaluated. Moreover, the 3D COF was further in situ grown on a stainless needle to apply in ambient probe nanoelectrospray ionization mass spectrometry (PESI-MS) for rapid and direct determination of trace PFOS and its alternatives in complex environmental samples including soil, algae and water. This work unlocks the efficient determination or removal of PFSA in complex environments, facilitating the solution of critical environmental PFSA problems.

MATERIALS AND METHODS

Materials and Chemicals. All chemicals are of analytical grade or higher purity and used without additional purification. TFPM was purchased from Yanshen Technology Co., Ltd. (Jilin, China). Acetonitrile (ACN), acetic acid (HAc), tetrahydrofuran (THF), hydrochloric acid, ammonium hydroxide, and sodium chloride were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Pa-CF₃, dopamine (DA), perfluorohexanesulfonate (PFHxS), perfluorobutanesulfonate (PFBS), PFOS, and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane-1-sulfonic acid (6:2 FTS) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Sodium *p*-perfluoroox nonenoxybenzenesulfonate (OBS) was bought from Macklin Biochemical Co., Ltd. (Shanghai, China). The internal standard compound (IS) of ¹³C₄-PFOS was obtained

from Wellington laboratories Inc. (Guelph (ON), Canada). Chromatography grade methanol was purchased from Fisher Chemical (Shanghai, China). Stainless needles (diameter ca. 0.25 mm, length 40 mm) were bought from Huaer Medical Instrument Co., Ltd. (Hebei, China).

Synthesis of TFPM-Pa-CF₃. Typically, TFPM (0.05 mmol, 21.6 mg) and Pa-CF₃ (0.1 mmol, 17.6 mg) were mixed in 1 mL of ACN, and then acetic acid (6.0 M, 0.1 mL) was added under sonication for 10 min. Afterward, the mixture was degassed by three cycles of freeze–pump–thaw and reacted at 90 °C for 3 days. The resulting yellow product was collected by centrifugation, sufficiently washed by THF, and then dried in a vacuum oven at 60 °C overnight to achieve TFPM-Pa-CF₃ (yield, 87.3%).

Preparation of the TFPM-Pa-CF₃-Based Probe. A stainless needle (0.25 × 40 mm) was first soaked in aqua regia (depth of ~2 cm) for 10 min, then washed with ultrapure water, and dried in air. Subsequently, the etched needle was immersed in stirred dopamine solution (2 mg mL^{−1}, pH 8.5) at room temperature for 12 h, then rinsed with ultrapure water, and dried in an oven at 80 °C for 12 h to acquire a polydopamine (PDA)-modified needle. Finally, the dried PDA-modified needle was immersed in 1 mL of ethanol solution of Pa-CF₃ (0.1 mmol L^{−1}) at 90 °C for 4 h, further reacted with a mixture of TFPM (21.6 mg), Pa-CF₃ (17.6 mg), ACN (1 mL), and acetic acid (6 M, 0.1 mL) at 90 °C for 72 h, then washed with THF, and dried in a vacuum oven at 60 °C to obtain the TFPM-Pa-CF₃-based probe.

Adsorption Experiments. Typically, 1 mg of TFPM-Pa-CF₃ was mixed with 1 mL of PFSA solution with a certain concentration and pH under sonication. The mixture was then placed in a shaker at 200 rpm for a certain time and then filtered with a syringe filter (0.45 μm). The resulting filtrate

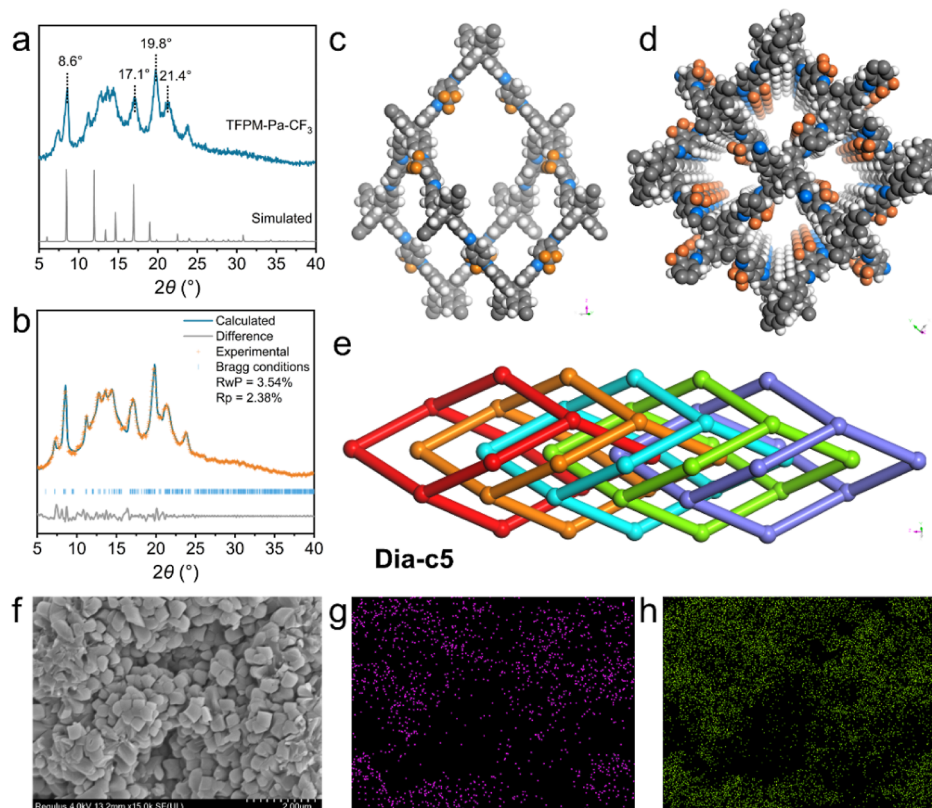


Figure 2. (a) Experimental and calculated PXRD patterns of TFPM-Pa-CF₃. (b) Refinement result for the simulated structure of TFPM-Pa-CF₃. (c) Structural representation of the crystal unit of TFPM-Pa-CF₃ (gray, C; white, H; blue, N; orange, F). (d) 3D porous framework in the space-filling model. (e) 5-fold interpenetrated dia net (dia-c5) of TFPM-Pa-CF₃. (f) Scanning electron microscopy (SEM) image of TFPM-Pa-CF₃. (g,h) EDS N and F mapping images of TFPM-Pa-CF₃.

was diluted with ultrapure water for determination of residual PFSA with a liquid chromatograph mass spectrometer (LC–MS). All adsorption experiments were repeated three times. The adsorptions under different conditions including pH (3–11), initial concentration of PFSA (1–200 mg L^{−1}), and adsorption time (1–30 min) were investigated in detail to evaluate the adsorption performance of TFPM-Pa-CF₃ for PFSA.

Preparation of Samples. Soil samples from Taihu Lake and Lihu Lake, as well as algae samples from Lihu Lake, were freeze-dried to remove moisture and then ground into powder. 0.5 g of the dried powder was weighed and mixed with 4 mL of methanol solution of ammonium hydroxide (0.1 mol L^{−1}). The mixture was sonicated for 30 min and centrifuged to collect the supernatant. After four repetitions of the above treatment, all the collected supernatant was dried by a nitrogen flow. The resulting residue was reconstituted in 10 mL of a mixture of ultrapure water (pH 5) and methanol (1/9, v/v) for further determination using TFPM-Pa-CF₃-based PESI-MS. The river water samples were directly analyzed with TFPM-Pa-CF₃-based PESI-MS after simple filtration by a 0.22 μm membrane.

Procedure of TFPM-Pa-CF₃-Based PESI-MS. The TFPM-Pa-CF₃ probe was inserted into the prepared samples or standard solutions for 2 min at 800 rpm, then rinsed with ultrapure water for 10 s, and moved on a homemade PESI-MS system with a moving platform and digital microscope to control and monitor the position of the probe as described in our previous work.³⁵ After application with a voltage of −3.2 kV, the PFSA-adsorbed TFPM-Pa-CF₃ probe acted as an ESI emitter. Then methanol (20 μL min^{−1}) was delivered to elute

the adsorbed PFSA and directly produce the charged spray of PFSA into the MS for analysis. Finally, the TFPM-Pa-CF₃ probe was rinsed with methanol and water for recycle, respectively.

RESULTS AND DISCUSSION

Preparation and Characterization of TFPM-Pa-CF₃. Fluorinated nonpolar structures can render specific F–F and hydrophobic interactions for selective adsorption of PFSA with a fluorinated carbon chain. Thus, the tetrahedral TFPM and linear Pa-CF₃ were applied to fabricate a new fluorinated nonpolar 3D COF TFPM-Pa-CF₃. The successful formation of a crystalline structure was achieved via the optimization of condensation conditions including solvent, temperature, time, and concentration of catalyst (Figures S1–S4). The as-prepared TFPM-Pa-CF₃ gave some major powder X-ray diffraction (PXRD) characteristic peaks at 8.6°, 17.1°, 19.8°, and 21.4°, which matched well with the simulated PXRD with a dia-c5 structure (Figure 2a). Further refinement with experimental PXRD data indicates that the specific simulated unit parameters were adopted with space group *P1* with *a* = 20.5830 Å, *b* = 20.5830 Å, *c* = 12.2852 Å, and $\alpha = \beta = \gamma = 90^\circ$ (Figure 2b–e and Table S1). No significant change in the PXRD pattern after treatment with different solvents proved the high chemical stability of TFPM-Pa-CF₃ (Figure S5).

The significant characteristic peak of the imine (1625 cm^{−1}) in the Fourier transform infrared (FTIR) spectra of TFPM-Pa-CF₃ confirms the successful polymerization of monomers through the Schiff-base reaction. Additionally, the intense stretching FTIR peak at 1139 cm^{−1}, assigned to C–F, indicates

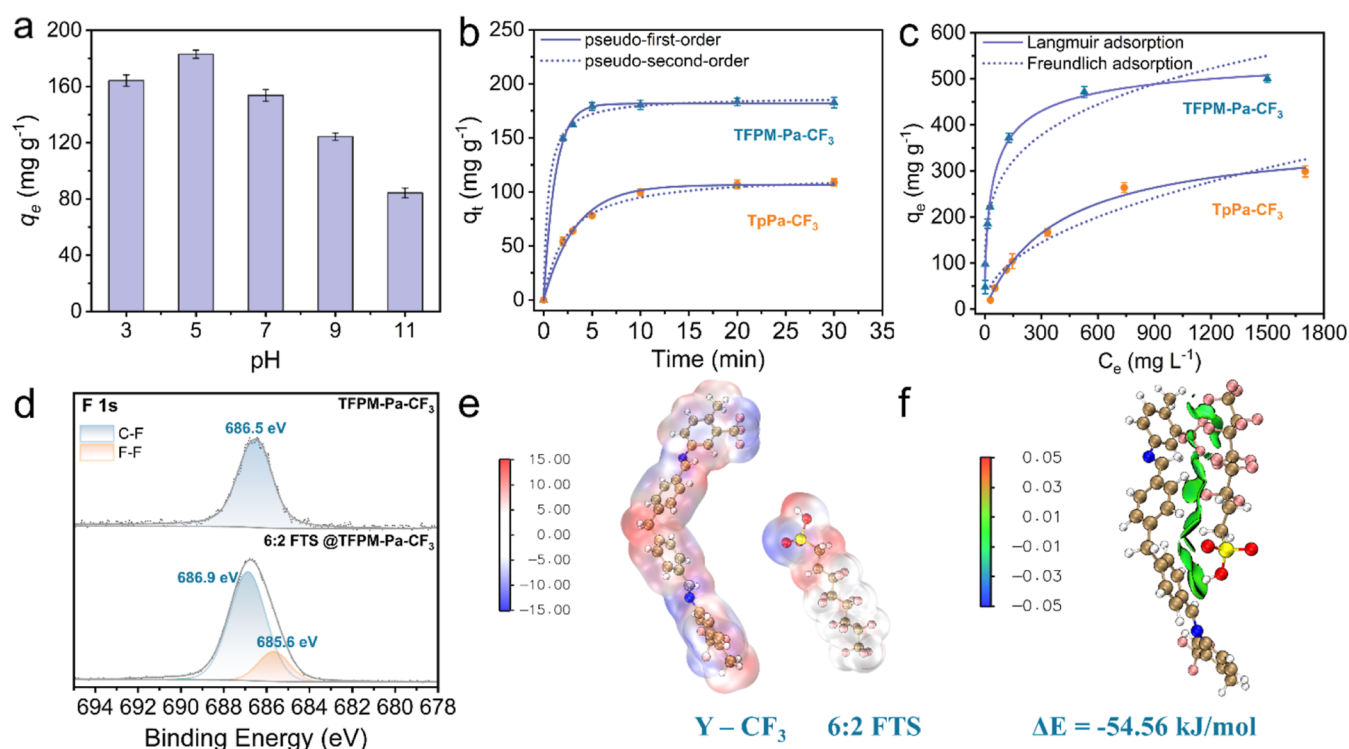


Figure 3. (a) Optimization of pH on the adsorption of 6:2 FTS on TFPM-Pa-CF₃. (b) Adsorption kinetics of 6:2 FTS on TFPM-Pa-CF₃ and TpPa-CF₃. (c) Adsorption isotherm of 6:2 FTS on TFPM-Pa-CF₃ and TpPa-CF₃. (d) F 1s XPS spectra of TFPM-Pa-CF₃ before and after adsorption of 6:2 FTS on TFPM-Pa-CF₃. (e) Corresponding electrostatic potential (ESP) distribution of Y-CF₃ and 6:2 FTS. (f) Molecular interactions and binding energy between 6:2 FTS and Y-CF₃ in their optimal configuration.

the presence of abundant fluorine groups in the prepared TFPM-Pa-CF₃ (Figure S6), which was further confirmed by the distinct peak of F 1s in the X-ray photoelectron spectroscopy (XPS) spectra of TFPM-Pa-CF₃ (Figure S7) and the uniform distribution F in energy-dispersive X-ray spectroscopy (EDS) elemental mapping images (Figure 2g,h).

Numerous nanosized cubic particles aggregated morphology of TFPM-Pa-CF₃ was observed using SEM (Figure 2f). The water contact angle (WCA) of TFPM-Pa-CF₃ was $83.6 \pm 3.4^\circ$, validating its nonpolar structure (Figure S8a). N₂ adsorption-desorption experiment revealed that the Brunauer-Emmett-Teller (BET) surface areas, main pore size distribution, and pore volume of TFPM-Pa-CF₃ were $491 \text{ m}^2 \text{ g}^{-1}$, 1.93 nm , and $0.347 \text{ cm}^3 \text{ g}^{-1}$, respectively (Figures S9 and S10). All of these characterizations demonstrate the stable fluorinated hydrophobic crystalline porous structure of prepared TFPM-Pa-CF₃, which would facilitate the subsequent selective adsorption of PFSA s from complex matrices.

Adsorption Performance. 6:2 FTS, as an alternative to PFOS, is receiving increasing attention and was therefore selected as a model target to evaluate the adsorption performance of TFPM-Pa-CF₃ for PFSA s. The best adsorption of PFSA s was achieved at pH 5 (Figure 3a). Adsorption equilibrium of 6:2 FTS on TFPM-Pa-CF₃ was reached in 5 min. The adsorption kinetics adopted with the pseudosecondary model rather than the pseudoprimary model according to the correlation coefficient (Figure 3b and Table S2). The rapid kinetics of TFPM-Pa-CF₃ for PFSA s contrast sharply with the long adsorption time of other adsorbent materials, often measured in hours (Table S4). The adsorption isotherms can be described better by the Langmuir isothermal model than the Freundlich model, indicating that 6:2 FTS is uniformly

adsorbed on the surface of TFPM-Pa-CF₃ in a monolayer. Moreover, TFPM-Pa-CF₃ gave a maximum adsorption capacity of 509.1 mg g^{-1} for 6:2 FTS (Figure 3c and Table S3), which ranks among the top reported PFSA s adsorbents (Table S4). Even in the presence of several antibiotics (SDM, OFLX, and BPA) and a cationic surfactant (CTAB), TFPM-Pa-CF₃ still demonstrated a high adsorption capacity for 6:2 FTS, while showing lower adsorption capacities for these interferents, highlighting the selectivity of TFPM-Pa-CF₃ for PFSA s (Figure S11).

Mechanism. The F 1s XPS spectra of TFPM-Pa-CF₃ gave a single C-F peak at 686.5 eV. After adsorption of 6:2 FTS, the C-F peak shifted to 686.9 eV and a new peak appeared at 685.6 eV, assigned to F...F (Figure 3d).³⁶ In addition, the potential of TFPM-Pa-CF₃ was significantly positive at pH < 6 (Figure S12), while PFSA s are always in the negatively charged form, due to the pK_a of PFSA s of 0.47–3.57 at the same conditions. Accordingly, electrostatic interactions are involved in the adsorption. In contrast, a fluorinated 2D COF (denoted as TpPa-CF₃) was prepared via replacing the tetrahedral monomer TFPM with Tp to react with Pa-CF₃ and also characterized (Figures 1 and S13). The small WCA ($27.8 \pm 5.8^\circ$) indicates polar TpPa-CF₃ (Figure S8b). The inferior adsorption capacity and equilibrium time of TpPa-CF₃ for 6:2 FTS at the optimal pH reveal more accessibility of the hydrophobic 3D structure for PFSA s under the hydrophobic interaction (Figures 3b,c and S14).

A typical fragment of TFPM-Pa-CF₃, named Y-CF₃, was adopted as the theoretical model for discrete Fourier transform (DFT) calculations. The calculated ESP maps showed a strongly electronegative sulfonic acid group of 6:2 FTS and relatively concentrated positive benzene ring of TFPM-Pa-CF₃

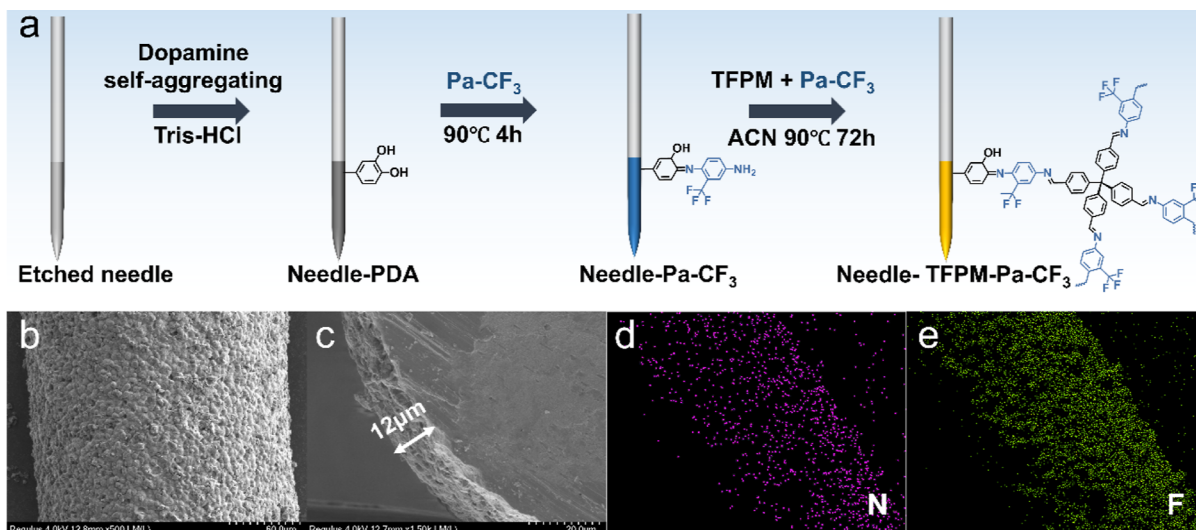


Figure 4. (a) Scheme for preparation of the TFPM-Pa-CF₃ probe via in situ growth. (b) SEM images of the TFPM-Pa-CF₃ probe. (c) SEM images of cross-section for the TFPM-Pa-CF₃ probe. (d,e) EDS N and F mapping images of the TFPM-Pa-CF₃ probe.

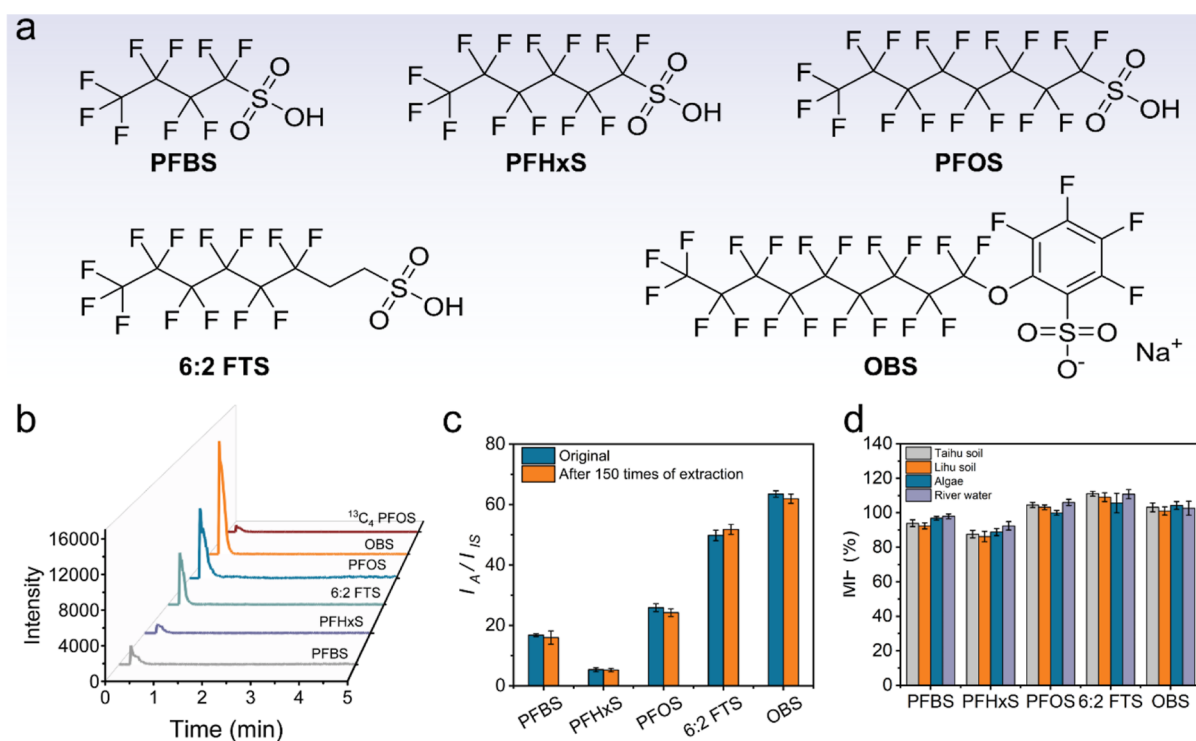


Figure 5. (a) Structures of PFSA, (b) elution profile for PFSA, (c) extraction performance of the TFPM-Pa-CF₃ probe after 150 cycles, and (d) matrix factor (MF) of real samples on the extraction of PFSA.

(Figure 3e). The obtained optimal configuration of Y-CF₃ and 6:2 FTS exhibited that the sulfonic acid group of 6:2 FTS trended to attach with the benzene ring of the absorbent, while the long C-F chains of 6:2 FTS affiliated with the -CF₃ group, indicating the existence of electrostatic and F-F interactions (Figure 3f). The calculated adsorption energy of 6:2 FTS on Y-CF₃ is -54.56 kJ/mol, confirming the strong and stable adsorption affinity of the fluorinated 3D COF for 6:2 FTS.

Preparation and Characterization of the TFPM-Pa-CF₃-Based Probe. The excellent selective adsorption of TFPM-Pa-CF₃ for PFSA incents us to explore the practical application potential of TFPM-Pa-CF₃. So, TFPM-Pa-CF₃ was

further anchored on a stainless needle via an in situ growth method to couple with PESI-MS for determination of trace PFSA in complex samples (Figure S15). The PDA layer was first grown on the surface of an etched needle to introduce quinone groups. Then the Pa-CF₃ monomer was subsequently grafted onto the needle by nucleophilic substitution of amino and quinone. Finally, the Pa-CF₃-grafted stainless needle was inserted into the mixture of TFPM and Pa-CF₃ for in situ preparation of the as-designed TFPM-Pa-CF₃-based probe (Figure 4a).

The PXRD pattern of powder scraped from the probe was in close agreement with that of the prepared TFPM-Pa-CF₃, verifying successful growth of TFPM-Pa-CF₃ (Figure S16).

Optical photographs showed that the color of the needle surface changed from gray to yellow after growth of the prepared COF (Figure S17), while SEM images directly exhibited dense spherical TFPM-Pa-CF₃ coating (thickness: ~12 μm) on the surface of the needle (Figures 4b,c and S18). The even distribution of N and F elements, as shown by EDS mapping images, validated the successful bonding of TFPM-Pa-CF₃ on the probe (Figure 4d,e).

Development of TFPM-Pa-CF₃-Based PESI-MS. The prepared TFPM-Pa-CF₃-based probe was designed to couple with PESI-MS for determination of five PFASs, including PFBS, PFHxS, PFOS, 6:2 FTS, and OBS (Figure 5a). After optimization of MS condition, 13 ion pairs of the five PFASs and ¹³C₄-PFOS (serving as IS) were monitored in the MRM model for qualitative and quantitative analysis (Table S5). Extraction conditions were optimized based on the ratio of quantitative ions intensity for PFASs and IS (I_A/I_{IS}). The I_A/I_{IS} rose with increase of stirring rates from 200 to 800 rpm (Figure S19), owing to the fact that appropriate stirring facilitated dispersion of the analytes on the probe. Further increase of stirring rates would decrease the I_A/I_{IS} , resulting from formation of vortices induced by too rapid stirring. The I_A/I_{IS} showed no significant change after 2 min (Figure S20), indicating the complete extraction. High extraction efficiency was also obtained at pH 5 (Figure S21), resulting from the electrostatic interactions, which was proved in the adsorption section. Compared with acetonitrile, ethanol, and isopropanol, methanol gave the highest I_A/I_{IS} and thereby was chosen as the eluent (Figure S22). Similarly, the eluent flow rate and spray voltage were set as 20 μL min⁻¹ and -3.2 kV according to the indicator of I_A/I_{IS} , respectively (Figures S23 and S24). No obvious ions could be detected in 1 min, demonstrating the complete elution (Figure 5b).

The figure of merit for the established TFPM-Pa-CF₃-PESI-MS was evaluated by analyzing pure water samples spiked with 1–10,000 ng L⁻¹ PFASs and 100 ng L⁻¹ ¹³C₄-PFOS. The I_A/I_{IS} linearized with the concentration of the five analyzed PFASs in a wide range of 1–10,000 ng L⁻¹ (R^2 : 0.9955–0.9996) (Figure S25). The limit of detection (LOD) ($S/N = 3$) and limit of quantification (LOQ) ($S/N = 10$) of the developed method for PFASs were 0.05–0.86 ng L⁻¹ and 0.18–2.88 ng L⁻¹, respectively. The analytical processes, including extraction and MS detection, took about 3 min owing to the rapid mass transfer of the crystalline COF and HPLC-free analysis. The TFPM-Pa-CF₃ probe demonstrated superior extraction efficiency for PFASs compared to bare and PDA-coated probes, confirming its dominance in extraction (Figure S26). These merits make the developed TFPM-Pa-CF₃-PESI-MS competitive in the determination of PFASs in complicated samples compared with many reported methods (Table S6).

Relative standard deviation of I_A/I_{IS} for PFASs with the same TFPM-Pa-CF₃ probe was 2.5%–7.5%, while that with three different probes was 3.6%–13.7%, indicating the capable repeatability and reproducibility of the developed methods (Table S7). PXRD and FTIR patterns of TFPM-Pa-CF₃ after extraction did not significantly change compared to the original pattern (Figure S27). No significant decrease of I_A/I_{IS} after 150 extraction cycles further demonstrates the high stability of the TFPM-Pa-CF₃ coating and great reusability of the developed TFPM-Pa-CF₃-based PESI-MS (Figure 5c).

Real Samples Analysis. The developed TFPM-Pa-CF₃-based PESI-MS method was further applied to detect trace PFASs in soil, algae, and water. The MF for the three real

samples was 86.2%–111.1% (Figure 5d), indicating the excellent interference removal ability of TFPM-Pa-CF₃. All three environmental samples found the existence of PFASs (Table 1). PFBS, PFHxS, PFOS, and 6:2 FTS in the soil of

Table 1. Analytical Results for the Determination of PFASs in Real Samples ($n = 3$)

analyte	sample	spiked PFASs (ng L ⁻¹)	determined PFASs (ng L ⁻¹ , mean ± s)	recovery (%) (mean ± s)
PFBS	Taihu soil	0	24.8 ± 4.8	
		100	132.9 ± 3.6	108.0 ± 3.5
		0	ND ^a	
	Lihu soil	100	107.3 ± 3.4	107.3 ± 1.1
		0	ND ^a	
	algae	100	108.1 ± 2.4	108.1 ± 2.4
		0	20.6 ± 4.3	
		100	115.3 ± 2.3	94.7 ± 2.5
	Lihu water	0	20.5 ± 3.2	
		100	124.0 ± 4.9	103.4 ± 5.0
PFHxS	Taihu soil	0	9.0 ± 2.4	
		100	106.3 ± 2.8	97.3 ± 2.8
		0	18.7 ± 3.7	
	Lihu soil	100	117.7 ± 3.3	99.0 ± 3.3
		0	ND ^a	
	algae	100	103.6 ± 3.3	103.6 ± 3.3
		0	7.2 ± 2.1	
		100	99.3 ± 1.3	92.1 ± 1.3
	Lihu water	0	5.5 ± 1.1	
		100	104.4 ± 2.4	98.9 ± 2.3
PFOS	Taihu soil	0	3.2 ± 1.1	
		100	98.5 ± 4.8	95.3 ± 4.8
		0	16.2 ± 3.0	
	Lihu soil	100	116.2 ± 5.3	100.0 ± 2.4
		0	12.3 ± 5.7	
	algae	100	113.5 ± 5.6	101.2 ± 2.0
		0	3.9 ± 2.1	
		100	97.4 ± 2.1	93.5 ± 2.1
	Lihu water	0	102.2 ± 2.0	102.2 ± 2.0
		0	15.7 ± 2.4	
6:2 FTS	Taihu soil	100	122.7 ± 4.0	107.0 ± 4.9
		0	ND ^a	
		100	100.9 ± 1.3	100.9 ± 1.3
	Lihu soil	0	ND ^a	
		100	103.0 ± 3.6	103.0 ± 3.6
	algae	0	4.2 ± 1.7	
		100	106.9 ± 2.9	102.7 ± 3.6
		0	4.6 ± 2.4	
	Lihu water	0	102.7 ± 4.2	98.1 ± 5.9
		100		

^aND = not detected.

Taihu Lake were found to be 24.8 ± 4.8 , 20.5 ± 3.2 , 7.2 ± 2.1 , and 12.3 ± 5.7 ng L⁻¹, respectively. PFHxS, PFOS, and 6:2 FTS in the Lihu Lake soil were detected to be 9.0 ± 2.4 , 5.5 ± 1.1 , and 3.9 ± 2.1 ng L⁻¹, respectively. PFHxS, PFOS, and OBS in the algae were found to be 18.7 ± 3.7 , 3.2 ± 1.1 , and 4.2 ± 1.7 ng L⁻¹, respectively. PFBS, PFOS, 6:2 FTS, and OBS in the river water were found to be 20.6 ± 4.3 , 16.2 ± 3.0 , 15.7 ± 2.4 , and 4.6 ± 2.4 ng L⁻¹, respectively. All three environmental samples were further spiked with PFSA (100 ng L⁻¹). The recoveries of these spiked samples ranged from 92.1% to 108%, confirming the excellent accuracy of the developed method.

CONCLUSIONS

In summary, we first explored the capability of 3D COFs for adsorption of PFSA. For this purpose, a new 3D COF TFPM-Pa-CF₃ with rich fluorine groups and a nonpolar structure was designed as an adsorbent, and it achieved rapid adsorption kinetics and excellent adsorption capacity for PFSA. Furthermore, TFPM-Pa-CF₃-based PESI-MS was developed, showing a lower detection limit and wider linear range for determination of five PFSA than many reported methods as well. This work provides robust support for the excellent practical adsorption and extraction of PFSA in complex environments.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.analchem.5c00330>.

Additional instrumentation and methods, including DFT calculations, calibration curves, LODs and LOQs, MF, and additional figures and tables including PXRD patterns, FTIR spectra, wide XPS spectra, WCA, N₂ adsorption–desorption isotherms, pore size distribution, adsorption capacity and effects of pH on the zeta potential of TFPM-Pa-CF₃, effect of pH on the adsorption of 6:2 FTS on TpPa-CF₃, effects of stirring rate, extraction time, pH, eluent, voltage, and flow rate on the I_A/I_S of PFSA, optical pictures, SEM images, extraction performance of the needles for PFSA, fractional main atomic coordinates, kinetic and adsorption parameters, comparison of reported adsorbents for adsorption of PFSA and of the reported method for the detection of PFSA, multireaction monitoring conditions for qualitative and quantitative analysis of PFSA with PESI-MS, and validation of the TFPM-Pa-CF₃-based PESI-MS method (PDF)

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Notes

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