

Conductive Organic Cages Enable Efficient Capture and Transistor Detection of ppq-Level Perfluorooctanoic Acid

Qiang YAN

yanq@fudan.edu.cn

Fudan University <https://orcid.org/0000-0001-5523-2659>

Chao-Wang Tang

Fudan University

Wen-Wen Wang

Fudan University

Jing-Yan Tang

Henan University of Science and Technology

Yixin Wang

Fudan University

Yang-Yang Wang

Fudan University

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Conductive Organic Cages Enable Efficient Capture and Transistor Detection of ppq-Level Perfluorooctanoic Acid

Chao-Wang Tang,¹ Wen-Wen Wang,¹ Jing-Yan Tang,² Yixin Wang,^{1,*} Yang-Yang Wang,¹ and Qiang Yan^{1,*}

¹State of Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, China. ²School of Chemistry & Chemical Engineering, Henan University of Science and Technology, Henan 471023, China

The emission of per- and polyfluoroalkyl substances (PFAS) resulted from surging industrialization poses environmental threat and health risk second to none. Strategies for efficient removal and ultrasensitive detection of PFAS from contaminated water is therefore sought after. Yet, achieving both missions simultaneously with a single material remains a great challenge. Here we report a conductive organic cage with tetrathiafulvalene facets (ReTTFcage) that can serve as high performance adsorbent to capture trace perfluorooctanoic acid (PFOA) and be made into a cage-based field-effect transistor (cageFET) for on-site, ppq-level PFOA sensing from water bodies. By designing the synergy of charge-transfer, hydrogen bonds and electrostatic interactions, this cage manifests high affinity to PFOA and thus break the trade-off between the maximum adsorption capacity (Q_m) and adsorption kinetics (k_{obs}), attaining PFOA uptake of 4210 mg g⁻¹ and an uptake rate up to 60500 g mg⁻¹ h⁻¹. It can also decontaminate PFOA in flowing water down to a picogram level (82 pg L⁻¹) that is otherwise unattained by other materials, far below the strictest international criteria (4 ng L⁻¹). Moreover, the electroactive TTF units endow the molecular cages with tunable conductivity upon hosting PFOA, allowing a transistor sensing with limit of detection (LoD) as low as 0.6 ppq (0.6 pg L⁻¹), on par with LC-MS gold standard but offering a miniature size (1 × 1 cm) and swift response (~30 s) absent in LC-MS technique. This study translates cage materials into a two-in-one platform for on-site remediation and synchronized assessment of environmental PFAS.

Main

Increasing industrialization aggravates the contamination of water resources by industrial persistent organic pollutants.¹ Per- and polyfluoroalkyl substances (PFAS), as a family of highly persistent compounds, pose serious environmental and health hazards due to their remarkable chemical inertness, bioaccumulation potency, and migration through water bodies.²⁻⁴ Among them, the crisis of perfluorooctanoic acid (PFOA) to human leads particular attention, since it has strong resistance to degrade (C-F bonds, 485 kJ mol⁻¹) and correlation to a range of pathological effects, including kidney damage, hepatotoxicity, immunotoxicity, and cancer induction.⁵⁻⁷ For this, the U.S. Environmental Protection Agency (USEPA) in 2024 has re-enacted an enforceable rule of 4 ng L⁻¹ for PFOA in drinking water.⁸ Unfortunately, PFOA levels in groundwaters and surface waters worldwide mostly exceed this threshold.⁹ These highlight the urgent need for methods and techniques that allow for efficient removal and ultrasensitive detection of PFOA from contaminated water, especially desiring one function-integrated material capable of simultaneously serving both missions.

In the respect of PFOA elimination, current industrial adsorbents often adopt the activated carbons^{10,11} and resins.¹² Despite low cost and easy to handle, they are limited by poor uptake capacity and reusability.¹⁰ To replace these industrial adsorbents, a variety of new PFOA-absorbing materials have been developed in recent years,^{13,14} such as porous organic polymers (POPs),¹⁵⁻¹⁷ metal-organic frameworks (MOFs),¹⁸⁻²⁶ covalent organic frameworks (COFs),²⁷⁻³² gels,^{33,34} nonporous adaptive crystals (NACs),^{35,36} and molecular cages,³⁷⁻⁴⁰ a few of which show ultrahigh uptake amount (~2000 mg g⁻¹),¹⁶ while others realize fast equilibrium uptake time (<1 min).³⁶ Nevertheless, a fundamental issue is the performance trade-off between the maximum adsorption capacity (Q_m) and adsorption kinetics (k_{obs}) existing in these materials, where the former is essential for ensuring the massive PFOA removal in still water, but the latter determines the capture efficiency of trace PFOA in fast-flowing water bodies.⁴¹ In addition, most innovative adsorbents are implicated in the installation of fluorinated groups to remove PFOA by exploiting F $\cdots$ F interactions, but this way is likely to cause unforeseen “fluorine forever” risks.⁴²

On the side of PFOA detection, liquid chromatography-mass spectrometer technology (LC-MS) is considered as the gold standard.^{43,44} It has a very low limit of detection (LoD~0.1 ppt) and good reproducibility, but this technique requires expensive and bulky instruments, well-trained personnel,

and tedious procedures that does not meet the needs of on-site monitoring in complex aquatic environment.⁴⁵ Recently, most efforts focused on optical sensing methods (e.g. fluorometric or colorimetric analysis) owing to their rapid response and reliability.^{46,47} Yet, their LoD lies in ppb level ($\mu\text{g L}^{-1}$), insufficient to match the practical PFOA detecting scenarios.

To solve the above unmet issues in PFOA removal and detection at one time, here we report a conductive organic cage composed of electroactive tetrathiafulvalene units and reduced imine linkers (ReTTFcage) that manifests two-in-one function. Selecting TTF-decorated cages as primary materials to capture and sense PFOA has triple advantages. First, porous organic cages (POCs) feature more favorable guest recognition and solution processability as compared to MOFs and COFs because of their discrete structure, persistent shape, and intrinsic cavity.⁴⁸⁻⁵⁰ Second, TTF units and amine groups on the cage are respectively expected as electron and hydrogen donors, which could bind electron-deficient fluorocarbon chain and carboxyl end in PFOA via charge-transfer, hydrogen bonds and electrostatic interactions, thus enhancing uptake selectivity and efficacy of PFOA.⁵¹ Third, the electroactive TTF groups could impart increased conductivity to the molecular cage upon binding guests. This electrical modulation permits it to potentially serve as a miniature cage-based field-effect transistor device (cageFET) for probing PFOA. With the design idea in mind, ReTTFcage can not only capture PFOA in still water, breaking the dilemmatic concession on the maximum adsorption capacity ($Q_m = 4210 \text{ mg g}^{-1}$) and fast adsorption rate ($k_{\text{obs}} = 60500 \text{ g mg}^{-1} \text{ h}^{-1}$), far higher than that of activated carbons and other state-of-the-art materials, but also attain a picogram-level PFOA decontamination in flowing water for the first time (1000 ng L^{-1} to 82 pg L^{-1}), below one-fiftieth of USEPA's threshold. More critically, we discover that ReTTFcage can be fabricated into a category of FET sensor that enables PFOA detection in ultrasensitive, real-time, and portable manners (Figure 1a). Its LoD is as low as 0.6 pg L^{-1} , which far exceeds the spectroscopic methods by 10^6 and better than LC-MS technique by 10^2 , while featuring fast response time ($\sim 30 \text{ s}$) and chip-scale footprint ($1 \times 1 \text{ cm}$). This conductive organic cage could play as an integrated platform for achieving the two missions on adsorbing and detecting PFOA, and help to take a step of performance limits forward an unreported parts-per-quadrillion level (ppq, $10^{-15} \text{ g/g} = 1 \text{ pg L}^{-1}$).

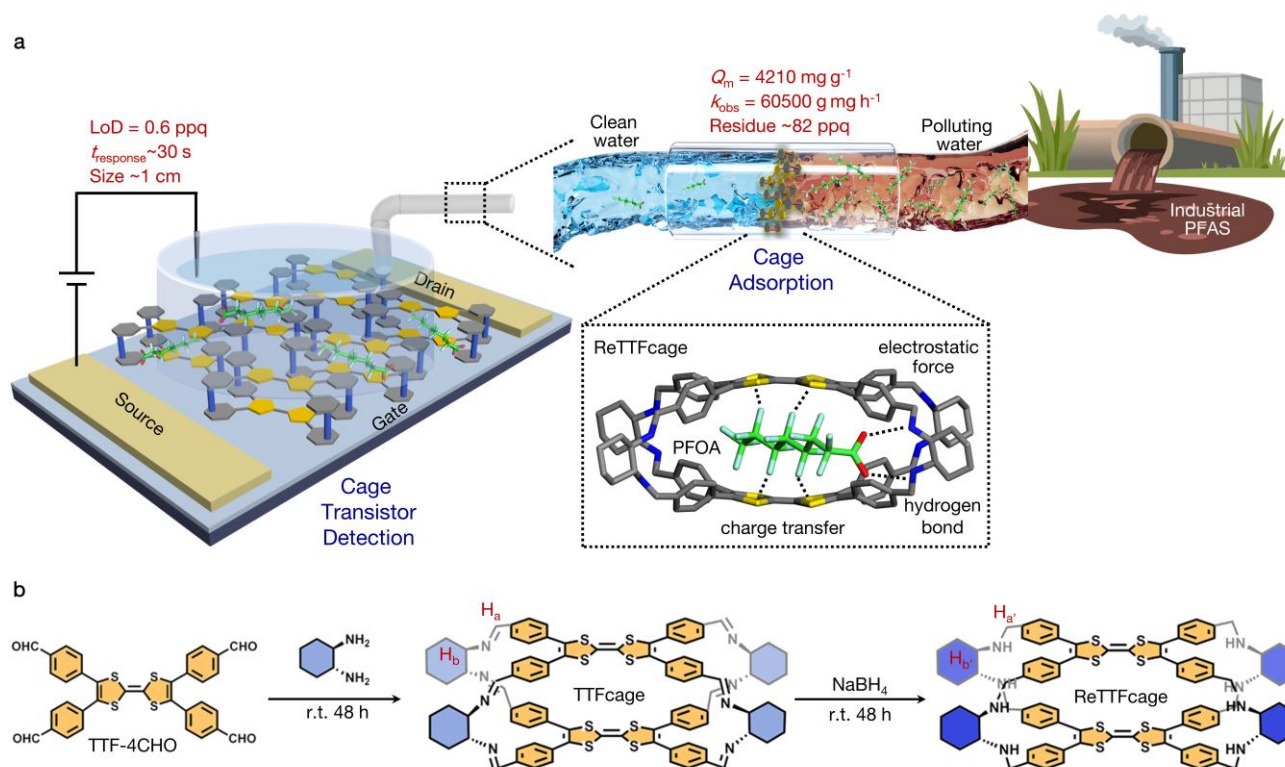


Figure 1. (a) Schematic illustration of function-integrated conductive organic cage (ReTTFcage) platform as an efficient adsorbent for PFOA uptake and as a cage-based field-effect transistor (cageFET) for PFOA detection. (b) Synthesis of TTF-functionalized molecular cages (ReTTFcage).

Results and Discussions

Design and synthesis of ReTTFcage. The ReTTFcage was synthesized through a one-step [2+4] imine condensation between para-formyl tetrathiafulvalene (TTF-4CHO) and cyclohexane-1,2-diamine to obtain TTFcage,⁵² followed by an imine-selective reduction using sodium borohydride (NaBH_4) to give the target cage. The synthetic route was depicted in Figure 1b and their cage-like structures were identified by ^1H , ^{13}C NMR and high-resolution electro-spray ionization mass spectrometry (HR-ESI-MS, Scheme S1 and Figure S1-S9 in Supporting Information). Single-crystal X-ray diffraction (SCXRD) analysis revealed that TTFcage precursor has a near cuboid shape, where the two TTF units adopt a face-to-face stacking fashion with a spacing of 8.1 Å, while the four imine edges arrange perpendicularly to the bottom panels with a rectangular size of 23.7×13.8 Å (Figure 2a and Table S1). TTFcage crystallizes in a monoclinic $P2_1$ space group, in which two neighboring cages are packed on each other via π - π interactions between the slipped TTF panels (3.4 Å) to form a 1D

columnar architecture along the x-axis (Figure 2b), while weak CH $\cdots$ S interactions (2.9 Å) facilitate the internal assembly in other directions (Figure S10). The channels formed between the cages offer possibility on binding of PFOA outside the cage.

After reduction by NaBH₄, the geometry of resulting ReTTFcage produces a certain change. The cavity height gives a slight decrease from 8.1 Å to 7.3 Å owing to the transition of connecting arms from rigid C=N bond to flexible C-N one, whereas the distance between the two adjacent arms increases a bit from 13.8 Å to 14.1 Å because of the electrostatic repulsion of the lone pairs in -NH- groups (Figure 2d). Compared to TTFcage, SCXRD indicated that ReTTFcage belongs to a tetragonal crystal system, with a higher symmetry of *I*4₁/a space group (Table S2). In a unit cell, the central cage adopts a near vertical conformation and is bound to other four ones in the plane via multiple CH $\cdots$ S interactions (2.9 Å, 3.2 Å and 3.4 Å), rather than the π -stacking (Figure 2e and Figure S11). Inside the cage, it is stabilized by polar- π interactions with hexafluorobenzene (HFB).⁵³ Although the internal cavity of individual cage has a small reduction (~9%), the exterior space and the affinity between the cages are improved. These features allow ReTTFcage not only to recognize guests via its intrinsic cavity but also to utilize the internal voids for nonporous adaptive adsorption, thus increasing the overall binding amount. In addition, powder X-ray diffraction (PXRD) analysis was conducted on the synthesized and recrystallized TTFcage and ReTTFcage. The results showed sharp diffraction peaks, which were highly consistent with the simulated spectra (Figure S12), proving that the cage-like frameworks have high crystallinity and structural order, ensuring their reliable adsorption capacity. The BET experiment of N₂ adsorption supported this point. The surface area of ReTTFcage was determined to be 245 m² g⁻¹ with a micropore of 1.5 nm (Figure S13). This value is smaller than that of conventional porous frameworks (>500 m² g⁻¹),¹⁵⁻³² but much larger than those reported NACs (<20 m² g⁻¹),^{35,36} which implies that ReTTFcage adopts a mixed-type adsorption to capture PFOA.

Other characterizations further confirmed the structural change from TTFcage to ReTTFcage. ESI-MS showed that before and after reduction the molecular ion peaks of the cage differed exactly by 16 ($\Delta m/z$ = 1569.5125 - 1553.4364), corresponding to the mass increase due to the hydrogenation of eight imine linkers (Figure 2c,f). The isotope series of 1⁺ and 2⁺ species were also probed, consistent well with the theoretical predications (bottom in Figure 2c,f and Figure S6,S9). ¹H NMR spectral analysis offered deep insight on this cage structural conversion. The doublet peak of CH=N proton (Ha, 7.71 and 7.61

ppm) totally vanished, instead, new peaks at 3.87, 3.69 ppm appeared, which is assigned to the methylene group (Ha', CH₂-NH). Meanwhile, the methine signal in cyclohexane shifted to higher field (Hb to Hb') and turned sharper, which is attributed to the shielding effect of the neighboring amine groups (Figure S14). Infrared spectra (IR) also indicated this imine-to-amine conversion, as evidenced by the depression of C=N vibration at 1639 cm⁻¹ and the enhancement of C-N band at 1450, 1337 cm⁻¹ (Figure S15). These amine groups in ReTTFcage could help to form hydrogen bonds and electrostatic attractions with the carboxyl group of PFOA, in combination with the charge-transfer between TTF unit and fluorocarbon tail, which would improve its affinity for PFOA and thus obtain superior abilities in adsorption and sensing.

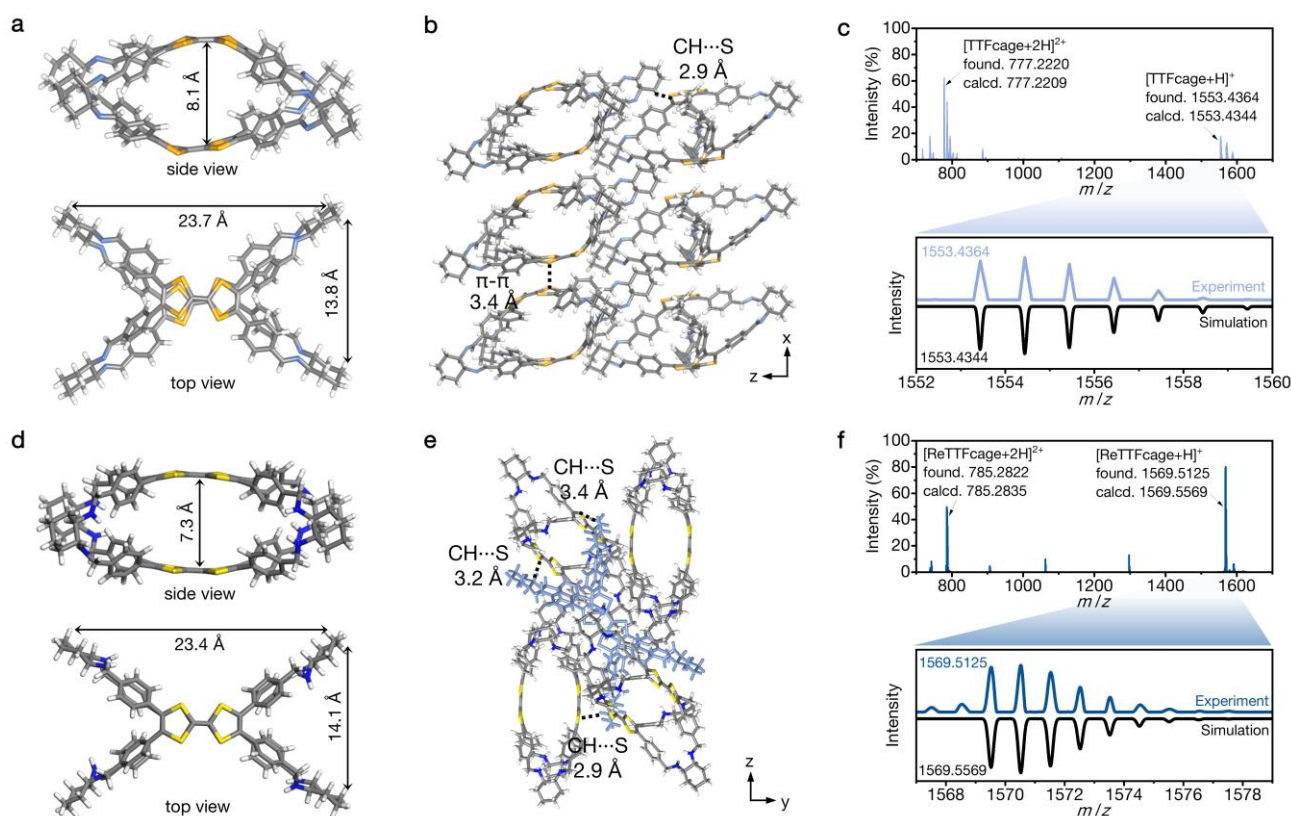


Figure 2. (a) Single crystal structure of TTFcage in side and top view. (b) The molecular packing fashion of TTFcage along the y-axis. (c) HR-ESI mass spectra of TTFcage for its m/z peaks (1⁺ and 2⁺ species) with the zoom-in isotope series (1⁺ species). (d) Single crystal structure of ReTTFcage in side and top view. (e) The packing mode of ReTTFcage along the x-axis. (f) HR-ESI mass spectra of ReTTFcage for its m/z peaks (1⁺ and 2⁺ species) with the zoom-in isotope series (1⁺ species).

Static uptake of PFOA by ReTTFcage. After identifying the cage structures, we preliminarily studied their performance as adsorbents to extract PFOA from aqueous media. The as-designed materials (2.0 mg) were immersed into a 50 mL of PFOA solution ($C_0 = 1000 \text{ ng L}^{-1}$) and employing LC-MS method to probe the residual PFOA content after treatment. As shown in Figure 3a, ReTTFcage exhibited an impressive uptake capacity, a rapid PFOA falling below 79 pg L^{-1} within just 4 min, with a 99.99% removal efficiency. When attaining in saturation around 20 min, only 14 pg L^{-1} of PFOA remained.

However, TTFcage gave a slower uptake (94.57% removal in 4 min) and a higher final residue (1.13 ng L^{-1}) under the same conditions. This highlights the synergistic effect of multiple binding in ReTTFcage. In contrast, only 74.8% removal of PFOA was seen for the activated carbon (AC) benchmark adsorbent, because it relies solely on surface sorption without specific noncovalent recognition. According to the adsorption curves, we further assess the kinetics of PFOA uptake and fit with the pseudo first- and second-order kinetic models (Figure S16 and Table S3). The higher correlation coefficient was obtained via linear pseudo second order kinetics using Eq.(1),⁴¹

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_{obs}Q_e^2} \dots \dots \dots (1)$$

Where Q_t and Q_e are respectively the amount of PFOA absorbed at any time t and equilibrium, and k_{obs} is the apparent rate constant. A remarkably high k_{obs} up to $60500 \text{ g mg}^{-1} \text{ h}^{-1}$ was obtained for ReTTFcage (deep blue diamonds in Figure 3b and inset). This value not only far surpasses its cage counterpart (TTFcage, $639 \text{ g mg}^{-1} \text{ h}^{-1}$, light blue circles in Figure 3b) and commercial AC ($20.7 \text{ g mg}^{-1} \text{ h}^{-1}$, grey squares in Figure 3b), and also ranks among the top 3 of all reported porous materials (Table S4), such as 19 times of the best POC material (CDcage, $3189 \text{ g mg}^{-1} \text{ h}^{-1}$),³⁸ 47-74 times of those nitrogen-rich COFs (MELEM-COF, $1263 \text{ g mg}^{-1} \text{ h}^{-1}$; COF-1, $943 \text{ g mg}^{-1} \text{ h}^{-1}$; VZ-COF, $807 \text{ g mg}^{-1} \text{ h}^{-1}$),³⁰⁻³² 2.5 times of multisite porous polymers (PAF-1-NDMB, $24000 \text{ g mg}^{-1} \text{ h}^{-1}$),¹⁶ and over 10^4 -fold to most known MOFs (typical In(tcpp), $4.82 \text{ g mg}^{-1} \text{ h}^{-1}$) and macrocycle-based hydrogels (QFgel, $1.23 \text{ g mg}^{-1} \text{ h}^{-1}$).^{18-26,33} As far as we know, the kinetics is only lower than guanidium-containing cationic COF (TG-PD COF, $152100 \text{ g mg}^{-1} \text{ h}^{-1}$) and fluorinated NAC (F-cage2, $441000 \text{ g mg}^{-1} \text{ h}^{-1}$).^{29,36} On the other hand, their maximum uptake capacity (Q_m) was also evaluated.⁴¹ Adsorption isotherms of PFOA by ReTTFcage were measured across a wide range of initial PFOA concentrations (0.2 to 5000 mg L^{-1}). Using both Freundlich and Langmuir models to fit the experimental data disclosed that the plots

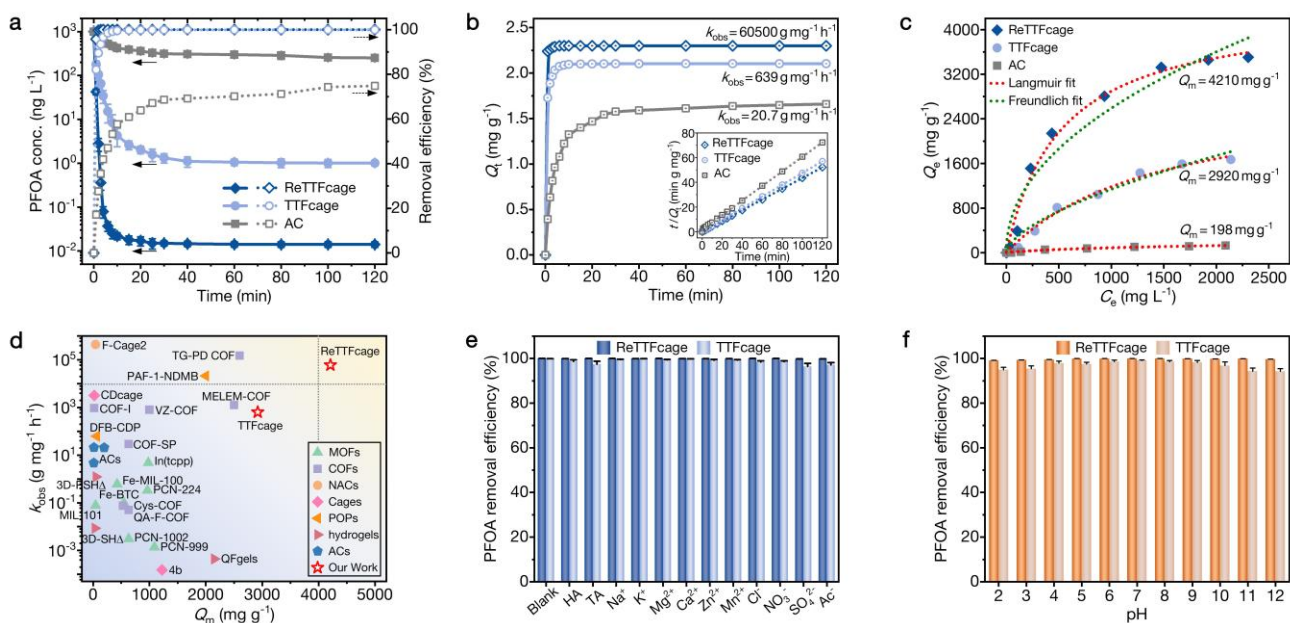


Figure 3. (a) Static adsorption and removal percentage of PFOA by ReTTFcage, TTFcage and AC. Adsorbent is 2.0 mg and the initial PFOA concentration is 1000 ng L⁻¹. (b) Adsorption kinetics of PFOA by different adsorbents. Inset, the pseudo second order kinetic plots and fitting curves. (c) Adsorption isotherms of PFOA by different adsorbents. (d) Comparison of the maximum uptake capacities (Q_m , x-axis) and uptake rate constants (k_{obs} , y-axis) by two cages and other reported PFOA adsorption materials. (e) Anti-interference abilities of the two cages to interfering substances, such as dissolved organic acids (HA and TA), metal cations (Na⁺, K⁺, Mg²⁺, Ca²⁺, Zn²⁺ and Mn²⁺), and anions (Cl⁻, NO₃⁻, SO₄²⁻ and Ac⁻) at 0.1 mM. (f) PFOA removal efficiency of two cages at different pH of 2-12.

match better with the Langmuir one as Eq.(2),

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \dots \dots \dots (2)$$

Where C_e is the equilibrium concentration of PFOA and K_L is the Langmuir adsorption affinity.⁴¹ It was found that ReTTFcage led to an uptake capacity of 4210 mg g⁻¹ (Figure 3c, Figure S17 and Table S5), whereas unreduced TTFcage and AC reference had only 69% (2920 mg g⁻¹) and 5% (198 mg g⁻¹) to that of ReTTFcage. Compared to other kinds of PFOA adsorbents, our cage offers twin advantages in Q_m and k_{obs} performance, excelling the state-of-art COFs (TG-PD COF and MELEM-COF)^{29,30} and

POP (PAF-1-NDMB),¹⁶ as well as NAC (F-cage2)³⁶, as depicted by Figure 3d and Table S4. These results mean that the cooperative effect of diverse supramolecular interactions within the molecular cage enables simultaneous enhancement on binding affinity and binding rate to PFOA, thereby defeating the inevitable trade-off between adsorption capacity and adsorption kinetics.

Additionally, the dissolved organic acids (humic acid, HA; tannic acid, TA), metal ions, or salts that usually coexisted in environmental water bodies may affect the adsorption of cage materials. To rule out their influence, we surveyed the PFOA decontamination effects in the presence of some competing acids (HA and TA), cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Zn^{2+} , and Mn^{2+}), and anions (Cl^- , NO_3^- , SO_4^{2-} , and Ac^-). From Figure 3e, it can be seen that ReTTFcage reflected good resistance to the above interfering species, with nearly unchanged removal efficiency (>99.9%), while ReTTFcage showed small drops (96.4% to 99.7%). In the same way, the adsorption tests were conducted in different pH of 2-12 (Figure 3f) and temperature of 5-65 °C (Figure S18). No appreciable alterations in PFOA uptake indicate their robust chemical and environmental tolerance.

Dynamic uptake of PFOA by ReTTFcage. In contrast to capture pollutants in still water, practical scenarios prefer materials capable of efficiently adsorbing PFAS in flowing water like contaminated rivers and groundwaters. Building on the favorable performance in static uptake, we attempted to evaluate their potential in continuous treatment system. Dynamic breakthrough tests were performed using a lab-scale fixed-bed equipment, in which the adsorbents were placed at the column and PFOA-spiked solution was pumped through the column in flowing mode (Figure 4a and Table S6). For high concentration PFOA ($100\ \mu\text{g L}^{-1}$), 20 mg of ReTTFcage can treat 4180 mL solution to reach the breakthrough point at a flow rate of $50\ \text{mL min}^{-1}$ (deep blue circles in Figure 4b). The residual PFOA was determined to be $2.73\ \text{ng L}^{-1}$ (deep blue column in sample S1, Figure 4d), lower than the threshold set by USEPA ($4\ \text{ng L}^{-1}$). However, TTFcage could reduce PFOA concentration to $36.31\ \text{ng L}^{-1}$ (3080 mL) under the same conditions (light blue in Figure 4b,d), only attaining the advisory level of China ($80\ \text{ng L}^{-1}$).⁵⁴ In contrast, AC benchmark material gave a poor exhibition with PFOA residue of $7820\ \text{ng L}^{-1}$ (grey in Figure 4b,d). Dynamic adsorptions at PFOA concentration gradients (1 to $10^4\ \text{ng L}^{-1}$) were further examined. It is evident that ReTTFcage maintained efficient performance even at lower PFOA contents (sample S2-S6 in Figure 4d). It is known that PFOA in heavily polluted water typically ranges $\sim 1000\ \text{ng L}^{-1}$, and ReTTFcage can decontaminate it to $82\ \text{pg L}^{-1}$ after treatment. This value is

not only one-fiftieth of USEPA standard, and also superior to the current best PFOA adsorbents (MELEM-COF, VZ-COF and F-cage2, 1000 ng L⁻¹ to 4 ng L⁻¹).^{30,32,36} Moreover, even when the flowing rate of PFOA-spiked solution was escalated from 50 to 1000 mL min⁻¹, ReTTFcage still retained a gratifying dynamic adsorption amount (1000 ng L⁻¹ to 0.67 ng L⁻¹, Figure 4c and Table S7), validating its high-efficient capture of PFOA from real water body.

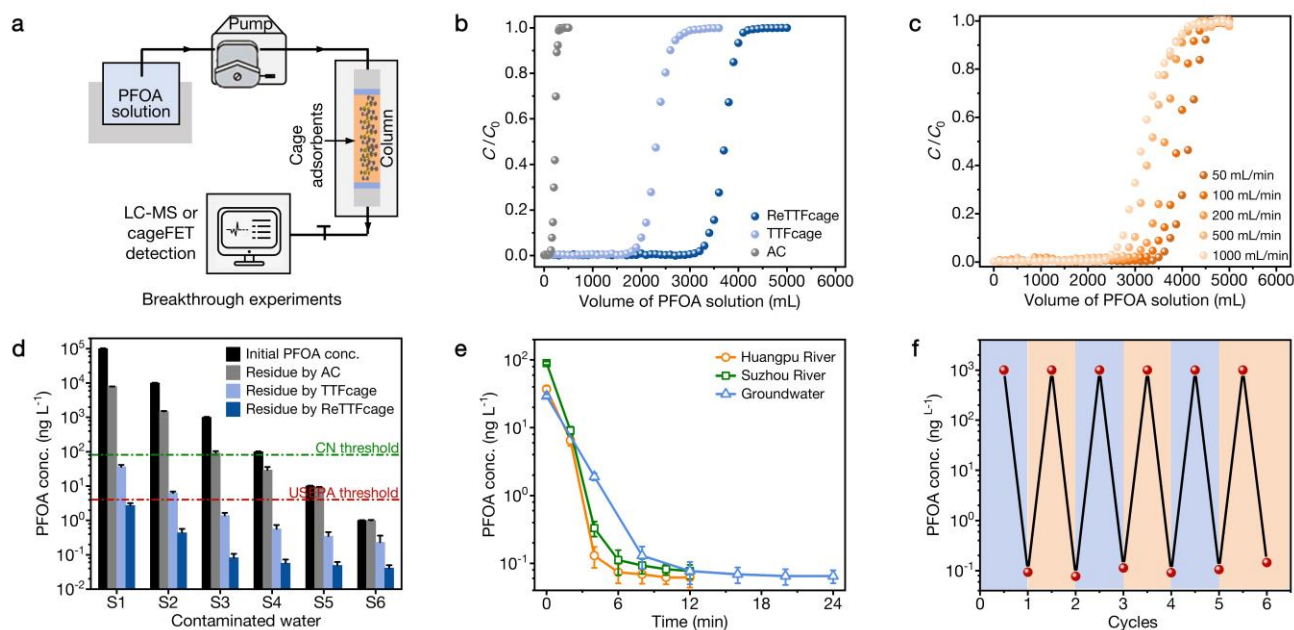


Figure 4. (a) Schematic diagram of the dynamic breakthrough experiment. (b) Breakthrough curves of PFOA-spiked solution (initial 100 µg L⁻¹) using ReTTFcage as column adsorbent in comparison to TTFcage counterpart and AC benchmark. (c) Breakthrough experiments using ReTTFcage as adsorbent under different flowing rate (50 to 1000 mL min⁻¹). (d) PFOA concentrations before (black columns) and after flow-through adsorption by AC (grey), TTFcage (light blue), and ReTTFcage (deep blue) at different PFOA initial levels (S1, 100 µg L⁻¹; S2, 10 µg L⁻¹; S3, 1000 ng L⁻¹; S4, 100 ng L⁻¹; S5, 10 ng L⁻¹; S6, 1 ng L⁻¹). Green and red dash lines represent PFOA advisory thresholds of China and U.S. Environmental Protection Agency (USEPA). (e) Dynamic adsorption performance of ReTTFcage for practical contaminated water samples in Shanghai from Huangpu River (orange), Suzhou River (green), and groundwater (blue). (f) Dynamic adsorption capacities of the regenerated ReTTFcage material within 6 reuse cycles.

To further verify that the cage could be applied to the practical environment, we carried out the

adsorption experiments to dispose the water samples taken from real rivers (Huangpu River and Suzhou River) and groundwater in Shanghai, which contain 37.2, 89.6, and 29.2 ng L⁻¹ of PFOA calibrated by LC-MS method. Upon uptake, ReTTFcage reduced the PFOA content below 0.1 ng L⁻¹ (Figure 4e). Notably, even after being loaded with different concentrations of PFOA, the crystallinity of ReTTFcage remained high (Figure S19). The cage material could be regenerated by washing the solid with a mixed solution of methanol and saturated sodium chloride. This enabled the cage to be reused at least 6 times, with no significant loss in capacity (Figure 4f), while maintaining its crystalline form and porosity (Figure S19,S21). Furthermore, the quantitative analysis conducted on the ReTTFcage after adsorbing PFOA revealed that Q_m in the solid material reached 3679 mg g⁻¹ (Figure S20), which was significantly lower than the value of 4210 mg g⁻¹ obtained in the residual supernatant (Figure S17). This result indicates that a small portion of PFOA does not bind firmly to ReTTFcage. It is speculated that during the adsorption process, the local concentration of PFOA near the surface of ReTTFcage significantly increases. The PFOA molecules form aggregates through the hydrophobic interaction between their tails.⁴⁶ Therefore, this portion of PFOA does not directly bind to ReTTFcage but stabilizes each other externally through the formation of aggregates and triggers the cooperative adsorption process.²⁹

ppq-Level Detection of PFOA by ReTTFcage-based transistor sensor. In addition to high-efficient PFOA removal, precise, rapid and real-time probing of trace PFOA is also significant. Presently, LC-MS technique is acknowledged as the gold standard for PFAS detection, because it has the lowest LoD (~0.1 ppt) and broadest detection range (10⁻¹⁰-10⁻³ g L⁻¹) among all the methods. However, LC-MS requires a costly and large equipment (~1 m) and time-consuming step (~1 h), impeding its on-site measurement. To overcome this issue, spectrometric detection techniques have been developed in recent years, since they offer merits on simple operation and fast response. However, their LoD and sensitivity are insufficient (at ppb level, 0.1-1 µg L⁻¹) and potentially result in false negative.⁴⁶ Hence, new PFOA sensors harboring rapid response, ultrasensitive detection and small volume are highly desired.

In this regard, field-effect transistor (FET) has become a promising candidate as high-performance sensor because it not only features small scale and user-friendliness, but also converts information on the concentration of analytes into detectable electrical signals, which originate from conductivity

changes relating to specific interactions between channel materials and analytes.⁵⁵ However, common graphene- or 2D inorganics-based FETs are difficult to detect PFAS due to the lack of recognition labels. Post-modification of channel materials with active labels adds steps for device fabrication and reduces detecting sensitivity.⁵⁶ A possible solution is to use materials to construct FET device that boast conductive and molecular recognition functions. Given that ReTTFcage can capture PFOA and TTF units are electroactive, it is anticipated that such cage could function as a cage-based FET (cageFET) to detect PFOA through changeable electrical properties upon PFOA binding. Given the single crystal structure of ReTTFcage combined with hexafluorobenzene (HFB), the guest molecule may facilitate the charge transfer process, thereby improving the conductivity of ReTTFcage. Current-voltage test shows that the ReTTFcage without the guest molecules has weak conductivity in the dual-electrode system (Figure S22). However, once the guest molecules (HFB or PFOA) are incorporated, the conductivity of the cage significantly increases. Further investigation revealed that the concentration of PFOA significantly affects the enhancement of conductivity. To this end, a bottom-gate top-contact FET device was prepared as Figure 5a, in which Au interdigitated electrodes (25 nm) were deposited on the SiO₂/Si substrate as the source and drain electrodes and connected by a 50 nm ReTTFcage thin-film (Figure 5b). An Ag/AgCl electrode was set to exert the gate voltage (V_{gs}) through the analyte solution in a polydimethylsiloxane (PDMS) well. The whole cageFET device was fabricated into the size of 1 × 1 cm (detailed process in Supporting Information, Section S5 and Figure S23).

Prior to PFOA addition, the pristine cageFET exhibited a typical gate modulation. The drain-source current (I_{ds}) increased with the drop of V_{gs} from 10 to −20 V, indicating a p-type transistor with hole carriers (blue solid line in Figure 5c). From transfer curve, the threshold voltage (V_{th}) is −2 V and the current on-off ratio is 2190. The calculated hole mobility is $\mu_h = 1.62 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (blue dot line in Figure 5c). Additionally, the output curves showed good linearity in the low drain-source voltage (V_{ds}) region, suggesting the Ohmic contact between the ReTTFcage film and Au electrode (Figure 5d). Interestingly, the transistor conductivity gave a large change after uptake of PFOA, where its I_{on}/I_{off} value increased by tenfold to 27000 while μ_h attained $0.57 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (orange solid and dot lines in Figure 5c). Such a large elevation in hole mobility (~350 times) before and after PFOA treatment points out that this cageFET could serve as a sensor to quantitatively probe PFOA content. By applying different PFOA concentrations (10^{-13} to 10^{-4} g L^{-1}), the current responses of devices versus time were

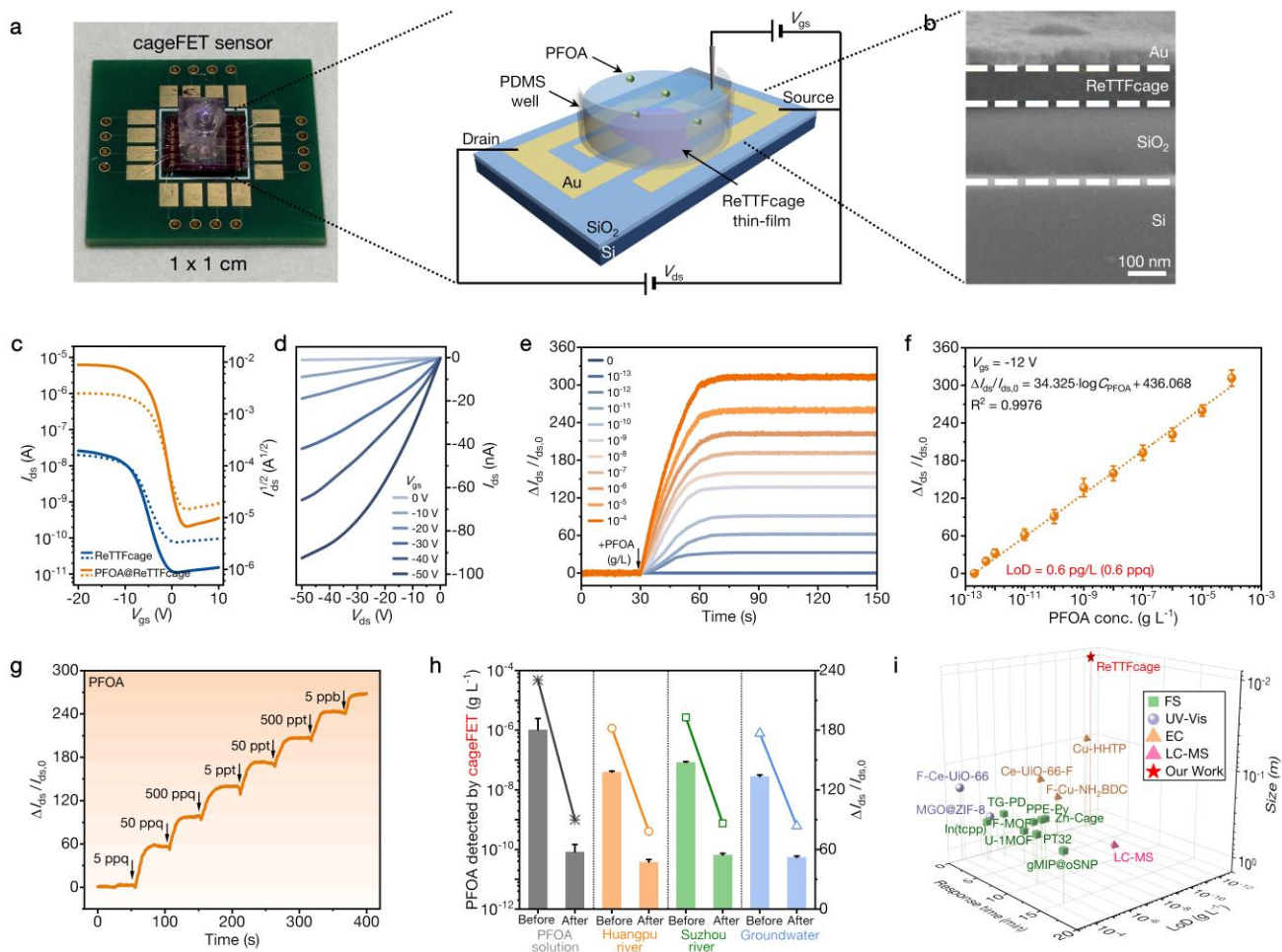


Figure 5. (a) Photograph (left) and schematic illustration (right) of the configuration of cageFET sensor. (b) SEM image for the cross-section structure of bottom-gate top-contact cageFET. (c) Transfer curves of cageFET before and after PFOA binding. (d) Output curves of bare cageFET at varied gate voltages (V_{gs} , 0 to -50 V). (e) The drain-source current response ($\Delta I_{ds}/I_{ds,0}$) as a function of time curves of the cageFET upon addition of PFOA concentration gradients (10^{-13} to 10^{-4} g L⁻¹). (f) The quantitative relationship between $\Delta I_{ds}/I_{ds,0}$ response and PFOA concentration. LoD was calculated from the interception of the noise level and the linear fitting curve. Error bars represent mean $\pm$ s.d., with $n = 3$ independent measurements. (g) Time-resolved current response of cageFET with continuous addition of PFOA at different levels (5 ppq, 50 ppq, 500 ppq, 5 ppt, 50 ppt, 500 ppt, and 5 ppb). (h) The variation of $\Delta I_{ds}/I_{ds,0}$ responses monitored by cageFET and corresponding PFOA contents of different water samples before and after adsorption. The water samples were taken from PFOA-spiked solution (1000 ng L⁻¹), Huangpu River, Suzhou River, and groundwater in Shanghai. i) Performance comparison of cageFET among various detecting techniques reported in terms of LoD, response time, and device size.

recorded (Figure 5e). The current response is defined as $\Delta I_{ds}/I_{ds,0}$, where $I_{ds,0}$ is the initial current without PFOA ($V_{gs} = -12$ V), while ΔI_{ds} representing the current change, $|I_{ds} - I_{ds,0}|$, upon PFOA addition. It can be seen that the $\Delta I_{ds}/I_{ds,0}$ signals were gradually enhanced (0.04 to 313.5) with PFOA dose, and the response times ranged 23-35 s. Repeated tests showed that the current response as a function of analyte concentration follows a linear relationship in logarithm scale, and a regression equation is obtained as $\Delta I_{ds}/I_{ds,0} = 34.325 \cdot \log C_{PFOA} + 436.068$, with a correlation coefficient (R^2) of 0.997 (Figure 5f). It is notable that this cageFET sensor has a high sensitivity (slope = 34.325), which outperforms other chemical transistors made by graphene or 2D materials (slope < 1).^{55,56} Moreover, the LoD of this sensor toward PFOA is determined to be 6×10^{-13} g L⁻¹ (equal to 0.6 ppq, Figure S24), 10^6 lower than the spectrometric assay (0.1~1 ppb) and also 100 times better than the LC-MS standard (0.1 ppt).

We next conducted time-resolved sensing tests to evaluate the reliability of cageFET devices in continuous operation. A $\Delta I_{ds}/I_{ds,0}$ response of 48.7 was observed upon 5 ppq PFOA, and it grew to 255.8 as PFOA reached 5 ppb (Figure 5g). A small current drift exists in the measurement, which is attributed to the environmental disturbances such as temperature.⁵⁷ The drifts accounting for the total current response were 0.5%, 0.7%, 0.9%, 0.2%, 0.2%, 1.1%, and 0.8% for 5 ppq, 50 ppq, 500 ppq, 5 ppt, 50 ppt, 500 ppt, and 5 ppb PFOA, respectively (Figure S25). This negligible signal drift ensures the stability and accuracy of the sensor during real-time detection. As control, no signal change appeared in bare cageFET, confirming that the electrical response comes from the specific binding to PFOA (Figure S26).

The long-term stability assessment under ambient temperature (25 °C) for 28 days showed that the response value of cageFET had nearly no change (Figure S27). This phenomenon can be attributed to the high stability of the secondary amine structure under room temperature. Additionally, the impacts of interfering ions (Na^+ , Mg^{2+} , Cl^- and SO_4^{2-}) and dissolved organic acids (HA and TA) on the sensing ability were evaluated. The results showed that the response of cageFET remained almost unaltered, confirming that the binding effect between the ReTTFcage and PFOA is unaffected by these interferents (Figure S28).

With this sensor in hand, we re-assessed the PFOA removal efficiency of cage materials. After dynamic adsorption (containing 1000 ng L⁻¹ PFOA) by ReTTFcage, the filtrate was introduced into the cageFET

chamber for in-situ measurement. The $\Delta I_{ds}/I_{ds,0}$ decreased from 230.4 to 89.9, exactly corresponding to 82.1 pg L⁻¹ PFOA residue (Figure 5h, grey column and lines) according to the standard curve (Figure 5f). In the case of real water samples from rivers, the residual contents after uptake were determined to be 37.4 pg L⁻¹ for Huangpu River, 64.6 pg L⁻¹ for Suzhou River, and 53.9 pg L⁻¹ for groundwater (Figure 5h, orange, green, and blue columns). In comparison, we also monitored the decontamination efficiency of commercial adsorbent (AC) using cageFET, but for three river samples the PFOA residues were 24.2, 59.5, and 19.1 ng L⁻¹ (Figure S29), not matching the criteria of USEPA. On the other hand, the long-term stability tests of the device were performed. There is no evident response deviation under identical conditions after 42 h, indicating its reliable detecting ability towards real environment (Figure S30). Up to now, there have been many new assays and techniques for PFOA detection, such as fluorescent monitoring (FS),^{29,25,58-62} colorimetric methods (UV-Vis),^{63,64} and electrochemical sensing (EC).⁶⁵⁻⁶⁷ Compared to these reported methods, the cageFET sensor offers the best performance. Not only can it reach a lowest LoD to ppq level (0.6×10^{-13} g L⁻¹) to surpass the LC-MS gold standard, but it features short detection time (~30 s) and miniaturized size (1 cm), which simultaneously fulfil the goals of high sensitivity, fast response, and portable utility (Figure 5i and Table S8). This would permit us to establish a cage-based sensing platform for on-site PFOA monitoring and assessment.

Mechanistic insight on PFOA Binding by ReTTFcage. In principle, such an excellent PFOA uptake and detection could arise from the synergistic binding effect of cage. To verify this mechanism, Fourier infrared (IR), X-ray photoelectron spectroscopy (XPS), UV-Vis diffuse reflectance spectroscopy (UV-Vis-DRS) and ¹⁹F NMR were carried out. IR spectra exhibited that PFOA had typical carboxyl (C=O) and fluorocarbon (C-F) stretching bands at 1767 cm⁻¹ and 1143 cm⁻¹, but ReTTFcage did not have (Figure S34). However, these two vibrations gave large downfield shifts to 1667 cm⁻¹ and 1123 cm⁻¹ in PFOA@ReTTFcage, attesting strong interactions between the two groups of PFOA and the cage (Figure S34).²⁶ XPS analysis further clarified the specific binding sites on cage. From Figure 6b, the S 2p XPS result of pristine cage had a sole binding energy at 163.8 eV, whereas a new peak emerged at 165.5 eV when adding PFOA. This should result from the charge-transfer (TTF···CF₂) between TTF units and fluorocarbon chain. Similarly, for N 1s XPS spectra, a new peak at 401.1 eV was found, which means that the amine groups on the cage form hydrogen bonding with the carboxyl head of PFOA (Figure 6c).³⁰ The UV-Vis diffuse reflectance spectrum of the PFOA@ReTTFcage complex

exhibits a distinct broad absorption band in the visible region (Figure S31). This low-energy absorption shoulder is characteristic of a charge-transfer transition from the electron-rich TTF-based cage to the electron-deficient PFOA. The solution color changing from pale yellow to deep red corroborated the formation of such donor-acceptor complex. To further clarify the charge-transfer, the molecular orbitals (HOMO/LUMO) were calculated by DFT. The results disclosed that the HOMO and LUMO of the complex were located on ReTTFcage and PFOA, respectively (Figure S32), which indicates the existence of charge-transfer interactions. Moreover, ^{19}F NMR spectra displayed a discernible change upon addition of PFOA to ReTTFcage. The $-\text{CF}_2$ signals close to carboxyl group underwent substantial downfield shifts (-119.2 to -117.3 ppm), supporting the hydrogen bonds formed (Figure S35,S37),³⁶ ^1H NMR titration between PFOA and ReTTFcage also provided additional evidence to support this conclusion (Figure S36). Energy-dispersive X-ray spectroscopy (EDS) mapping also revealed a uniform distribution of PFOA within ReTTFcage (Figure S33). These findings together demonstrate that the synergy of multiple noncovalent interactions plays a crucial role in enhancing the binding capacity between the cage host and PFOA guest.

As well, we studied the association mechanism of the unreduced TTFcage counterpart to PFOA. By contrast, almost no changes were observed in their IR and NMR spectra (Figure S34-S35), and XPS only gave an S2p peak shift due to the charge transfer but without change on N1s peak (Figure S38). This means the lack of hydrogen bonding between the two molecules, thus explaining why TTFcage has a weaker adsorption capacity (2920 mg g^{-1}) than ReTTFcage (4210 mg g^{-1}).

On the other hand, theoretical simulations were performed to decipher the contribution of multiple sites in the cage for PFOA binding at molecular level. The molecular electrostatic potential (MESP) distribution disclosed that except the eight amine groups with negatively charged, the cage surface shows positive MESP value (Figure 6e). For PFOA, however, the electron-rich portion is only localized at the carboxyl group, while the entire fluorocarbon chain presents electron-deficient state (Figure 6f). This becomes the molecular basis to form multiple interactions, including the charge-transfer from TTF units to fluorocarbon tail, hydrogen bonds between NH- and $-\text{COOH}$, and especially electrostatic interactions between NH_2^+ and COO^- . Meanwhile, in the acidic condition, the surface of TTFcage carries positive charges, while ReTTFcage exhibits stronger positive charges (Figure S39). Their pH_{zp} values are 6.1 and 7.3, respectively. This indicated that the secondary amine group of

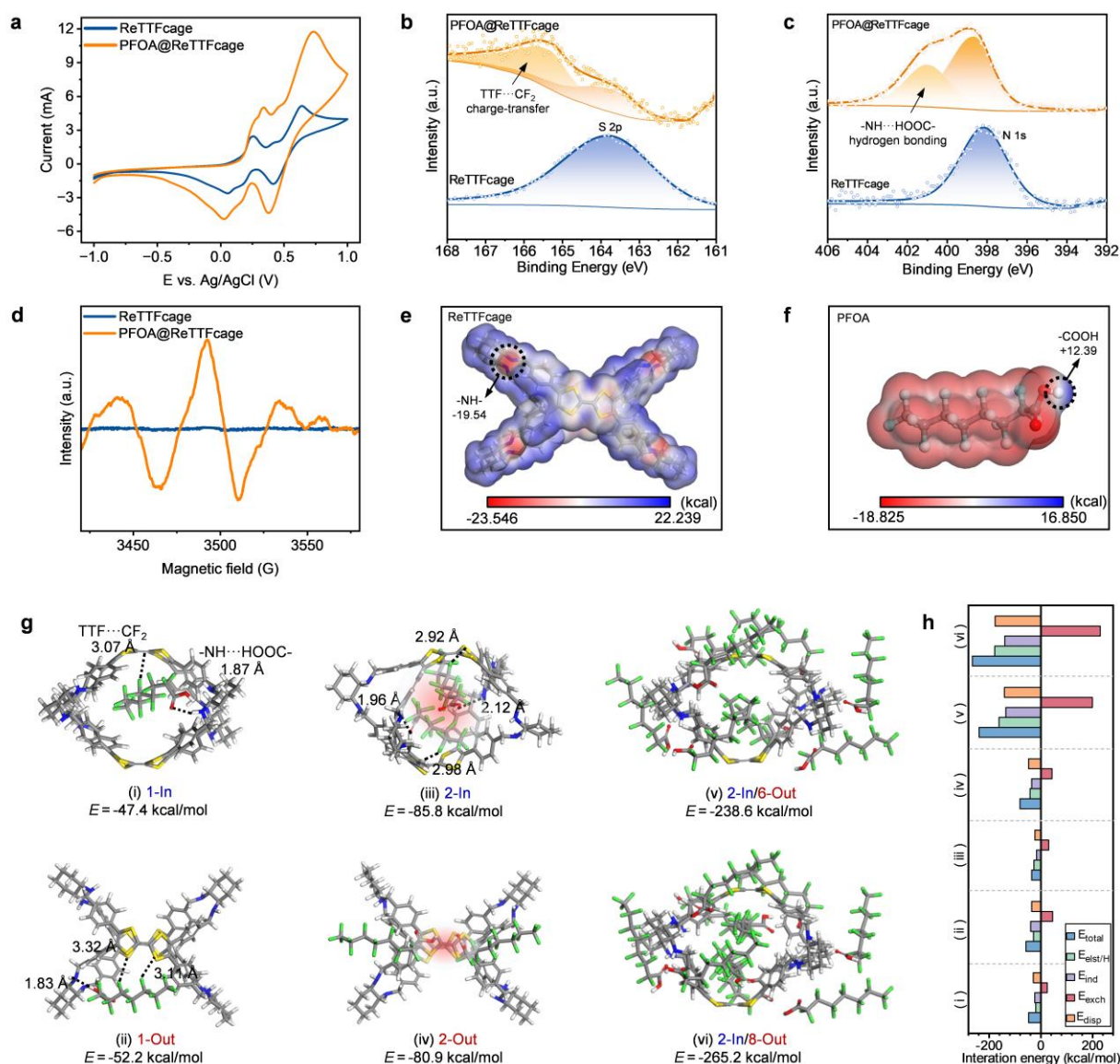


Figure 6. (a) Cyclic voltammograms of ReTTFcage before and after PFOA uptake. (b,c) XPS analysis of (b) S2p spectra and (c) N1s spectra of ReTTFcage before and after PFOA uptake. (d) Electron paramagnetic resonance spectra of ReTTFcage before and after PFOA uptake. (e,f) Molecular electrostatic potential (MESP) distributions of (e) ReTTFcage and (f) PFOA. (g) DFT-optimized structures of PFOA bound to ReTTFcage at different sites and binding numbers: (i)-(ii) one PFOA bound in and outside the cage, (iii)-(iv) two PFOAs bound in and outside the cage (red region indicating the F...F interactions and hydrogen-bonding dimer between two PFOAs), (v)-(vi) one cage holding 8 and 10 PFOAs. (h) Independent gradient model (IGM) analysis of the noncovalent interactions between ReTTFcage and PFOA in diverse binding motifs (i)-(vi)

ReTTFcage can exert a positive effect on the adsorption of PFOA anion via electrostatic force. Independent gradient model (IGM) analysis also supported this point. When the carboxyl group of PFOA approaches the secondary amine, PFOA@ ReTTFcage tends to form an ion pair consisting of protonated amine and the anion of PFOA (Figure S40). Furthermore, cyclic voltammetry (CV) was employed to probe the redox behavior of the TTF units upon PFOA binding (Figure 6a). After PFOA uptake, the CV curve of ReTTFcage exhibits significant asymmetric changes: the anodic peak current corresponding to TTF oxidation increases dramatically, while the cathodic peak current undergoes a substantial decrease. This irreversible redox behavior indicates that the strong donor-acceptor interaction between electron-rich TTF units and electron-deficient perfluorocarbon chain of PFOA facilitates a unidirectional charge transfer, where PFOA acts as an electron sink that intercepts charge from TTF oxidation, thereby hindering the re-reduction of TTF^+ .⁶⁸ Electron paramagnetic resonance (EPR) analysis further confirmed this. Compared with the ReTTFcage without PFOA loading, the cage loaded with PFOA exhibited a distinct EPR signal (Figure 6d), indicating that free radical species were generated when PFOA was absorbed. The Nyquist plots reveal a significant decrease in the charge transfer resistance from approximately 6000 Ω for the pristine ReTTFcage to around 4000 Ω after PFOA adsorption (Figure S41). This phenomenon can be attributed to the synergistic interplay between electrostatic attraction and charge transfer at the interface. The positively polarized -NH- sites within the ReTTFcage framework serve as electrostatic anchoring points for the deprotonated carboxylate (COO^-) of PFOA, consistent with the dominant electrostatic binding mechanism observed for PFOA with cationic molecular hosts⁶⁹. Concurrently, the electron-rich TTF units within ReTTFcage undergo partial charge transfer to the electron-accepting LUMO of PFOA, analogous to the established $\text{TTF} \rightarrow$ acceptor electron injection process that generates $\text{TTF}^{\bullet+}$ radical cations⁷⁰. The electrostatic pulling induced by $\text{NH}_2^+ \cdots \text{COO}^-$ interaction not only brings PFOA into close proximity with the TTF units but also establishes a preferential electron transfer pathway, thereby effectively lowering the kinetic barrier for interfacial charge transport. DFT further figured out the adsorption site and binding number (Figure 6g). By energy-optimized calculations, ReTTFcage offers two types of stable association for one PFOA, in-cage hosting and out-of-cage binding (Figure 6g, i-ii). Both modes depend upon the synergy of $\text{NH}_2^+ \cdots \text{COO}^-$ electrostatic forces and $\text{TTF} \cdots \text{CF}_2$ charge-transfer interactions, with near energy (-47.4 and -52.2 kcal/mol). Furthermore, we also surveyed the case of one cage holding two PFOAs. When the two PFOAs are inside the cage, they can be arranged on a side-by-side fashion with

tail overlapping and head outward. This stabilizes the complex (-85.8 kcal/mol) via the F $\cdots$ F interactions of fluorocarbon chains (red region; Figure 6g, iii).¹⁵ While the two PFOAs bind outside, they can pre-form head-to-head dimers to lower the energy (-80.9 kcal/mol; Figure 6g, iv). With the binding number increasing, it was found that the total energy can be further reduced and achieve an extreme minimum of -265.2 kcal/mol when each cage binding to 10 PFOA molecules, in which the cage interior houses two and exterior carries eight, stabilized by multiple charge-transfer, hydrogen bonds and electrostatic attractions (Figure 6g, v-vi). Such a large binding number theoretically interprets why ReTTFcage has an ultrahigh PFOA uptake capacity (based on Q_m , per cage binds with 13 PFOAs). In addition, we used IGM to analyze the energy components of the above binding motifs. Typically, the main energy components in (vi) are the electrostatic/hydrogen-bonding energy ($E_{\text{elst/H}} = -178.3$ kcal/mol) and induction energy ($E_{\text{ind}} = -139.9$ kcal/mol). Their sum is -318.2 kcal/mol, much larger than the dispersion energy ($E_{\text{disp}} = -176.9$ kcal/mol), demonstrating that the major forces involved in the complex are charge-transfer, hydrogen bonding and electrostatic interactions, and their contributions are similar (Figure 6h).^{39,71}

Conclusion

In conclusion, we have developed a conductive organic cage with electroactive TTF units via post-modification (ReTTFcage). This cage material seamlessly integrates the dual goals on exceptional capture and ultrasensitive sensing of trace PFOA contaminant in water. As a PFOA adsorbent, ReTTFcage can overcome the performance trade-off between the adsorption capacity and adsorption kinetics, culminating in a record equilibrium uptake of 4210 mg g⁻¹ and fast uptake rate of 60500 g mg⁻¹ h⁻¹, which surpasses industrial activated carbon (AC) adsorbent by 20 times and other benchmark porous materials by 2-10 times under the same conditions. Also, it achieves extraordinary dynamic adsorption capacity that can decontaminate PFOA-spiked water to an unprecedented picogram level (82 pg L⁻¹) in flowing state, below one-fiftieth of the current USEPA threshold (4 ng L⁻¹). More strikingly, benefiting from the enhanced conductivity and the electrical modulation properties of TTF units upon PFOA binding, the cage can be fabricated into a field-effect transistor (cageFET) to detect PFOA in ultrasensitive and fast manners. The cageFET sensor manifests a reporting LoD as low as 0.6 ppq (0.6 pg L⁻¹) and short response time (~30 s), superior to that of spectroscopic assays by 6 orders

of magnitude and excelling LC-MS gold standard by over 100 times. Moreover, the cage-based device has portable size (1×1 cm), suitable for on-site assessment and point-of-care monitoring of PFOA in environmental water bodies. Mechanistic studies reveal that the efficient PFOA adsorbing and detecting functions stem from its structural uniqueness, which synergizes charge-transfer, hydrogen bonding, and electrostatic attractions to enhance the preferential affinity toward PFOA. This molecular cage not only presents a new material platform to push the performance limits of PFOA in adsorption and detection beyond ppq level, but also suggests the potential of conductive cages in electronic devices. Future work will focus on installing various endohedral groups on the cages to achieve highly selective identification of different PFAS, thereby creating cage-based transistor sensor arrays for precise detection of all PFAS pollutants.

Supporting Information. Synthesis and characterization of cage compounds, supplementary characterization of cage adsorption of PFOA, and fabrication and performance of the cageFET device.

Author Information

Corresponding Author

* Yixin Wang, Email: 23110440027@m.fudan.edu.cn.

* Qiang Yan, Email: yanq@fudan.edu.cn

Author Contributions

Chao-Wang Tang and Yixin Wang proposed the research concept, designed and implemented the characterization, and analyzed the data. Wen-Wen Wang assisted in the transmission electron microscope (TEM) characterization. Jing-Yan Tang conducted the theoretical calculations. Yang-Yang Wang provided writing guidance. Qiang Yan was responsible for the research conception, research methods, fund raising, project management, writing - review and editing, and guidance. All authors jointly reviewed and discussed the results and provided comments on the manuscript.

Notes

The authors declare no competing financial interest.

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