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Supramolecular Chemistry

Rim-Based Binding of Perfluorinated Acids to Pillararenes Purifies Water

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Abstract: Per- and polyfluoroalkyl substances (PFAS) pose a rapidly increasing global problem as their widespread use and high stability lead worldwide to water contamination, with significant detrimental health effects.[1] Supramolecular chemistry has been invoked to develop materials geared towards the specific capture of PFAS from water,[2] to reduce the concentration below advisory safety limits (e.g., 70 ng/L for the sum of perfluorooctane sulfonic acid, PFOS and perfluorooctanoic acid, PFOA). Scale-up and use in natural waters with high PFAS concentrations has hitherto posed a problem. Here we report a new type of host–guest interaction between deca-ammonium-functionalized pillar[5]arenes (DAF–P5s) and perfluoroalkyl acids. DAF–P5 complexes show an unprecedented 1:10 stoichiometry, as confirmed by isothermal calorimetry and X-ray crystallographic studies, and high binding constants (up to $10^6\,M^{-1}$) to various polyfluoroalkyl acids. In addition, non-fluorinated acids do not hamper this process significantly. Immobilization of DAF–P5s allows a simple single-time filtration of PFAS-contaminated water to reduce the PFOS/PFOA concentration 10^6 times to 15–50 ng/L level. The effective and fast (<5 min) orthogonal binding to organic molecules without involvement of fluorinated supramolecular hosts, high breakthrough capacity (90 mg/g), and robust performance (> 10 regeneration cycles without decrease in performance) set a new benchmark in PFAS-absorbing materials.

Per- and polyfluoroalkyl substances (PFAS) are broadly used chemicals for a wide range of consumer and industrial applications, such as in stain-repellent sprays, non-stick pans, firefighting foams and food paper coatings. However, the extremely high stability of these materials also turns out to be one of their drawbacks, e.g., leading to increasing water pollution. Dangerous contamination levels of soils and surface waters with PFAS have already reached many parts of the world, frequently exceeding the US Environmental Protection Agency (EPA)'s advisory limit for perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) (70 ng/L) by several orders of magnitude.[1a–d] Toxicity research has demonstrated that this will cause developmental toxicity, immune function disorder, immunotoxicity, and a range of chronic diseases.[1e–i] The ideal material for PFAS removal combines the following features: 1) a high affinity for PFAS; 2) high capacity; 3) fast absorption and desorption kinetics; 4) high specificity, as water also contains many other natural acids at much higher concentrations; 5) easy and robust regeneration; 6) scalable and

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eco-friendly synthesis. Efforts to develop PFAS-absorbing materials focused e.g. on high surface-area materials, like activated carbon, covalent organic frameworks (COFs), metal–organic frameworks (MOFs) and porous aromatic frameworks, or on advanced organic materials with tailor-made macrocycle-based cavities, such as cyclodextrin- or calixarene-based polymers and networks.[2f–h,3] Activated carbon, zeolite, COFs, MOFs and porous aromatic frameworks represent porous materials that use defined channel structures and tailored binding sites to absorb PFAS. Porous materials show a high affinity and capacity towards PFAS, but the specificity toward PFAS is low, as these materials suffer from competitive binding with other organic co-contaminants or natural organic matter, which is detrimental for practical applications (Figure 1).[4] In addition, the rates of PFAS absorption for this class of materials are relatively slow, typically taking 2–20 h to reach equilibrium. On the other side, supramolecular host–guest interactions can add to or replace such pore-based interactions, using the specific fluorophilic properties of PFAS or their negative charge.[5] Fluorophilicity refers to the specific aggregation of fluorinated compounds with themselves or with other fluorinated compounds.[6] This property has been used in supramolecular host–guest complexes to bind e.g. PFOA to a fluorinated β-cyclodextrin polymer with high affinity ($K=7\times10^4\,M^{-1}$), which was ca. 100 times higher than for similar non-perfluorinated cyclodextrins.[2a–d] Such polymer can effectively remove PFAS, but the absorption rates are also slow (1–2 days to reach equilibrium). Furthermore, the production of such highly fluorinated polymers would again involve poly- and per-fluorinated materials, which is not sustainable. Alternatively, charge-based interactions were invoked in the 1:1 complex formation of calix[5]arenes bearing five guanidinium groups with PFAS binding constants up to $4.8\times10^6\,M^{-1}$; efficient PFAS sensing was obtained, but water clean-up only reached μg/L levels.[2e] This category of materials shows a high specificity towards PFAS, but suffers from a low capacity. Among all the reported host–guest complexes with PFOA/PFOS, there is maximally one guest per host molecule, and reports that directly take natural river water or tap water are scarce. Until now, there are no materials that would feature all six properties required for efficient PFAS removal. Herein, we report an approach invoking fluorine-free pillararenes that overcomes all these reported limitations.

Pillararenes,[7] and especially pillar[5]arenes, are characterized by a powerful three-facet combination of features: a pillar-like structure with well-defined cavity size (4.7 Å),[7b] easy functionalization with very wide range of functionalities,[8] and routes that allow multigram synthesis.[9] Herein we report a new host–guest interaction between fluorine-free, deca-ammonium-functionalized pillar[5]arenes (DAF–P5s) and polyfluoroalkyl acids with an unprecedented 1:10 host–guest ratio and high binding constants in water up to $10^6\,M^{-1}$ (Figure 1). We also demonstrate the ability to use this novel mode of interactions to develop robust and high-performing PFAS absorbents that allow for the one-step clean-up of natural, heavily polluted waters to current EPA-acceptable levels within 5 min.

To study the binding of perfluorinated acids to pillararene-based hosts, we synthesized a series of deca-ammonium and deca-trimethylammonium substituted P5 s with C_2 and C_4 alkyl chains (**1**–**3**, Figure 2) according to literature procedures.[10] Due to the ^{1}H NMR silent feature of PFAS, the binding constants were determined by isothermal titration calorimetry (ITC). The first striking observation

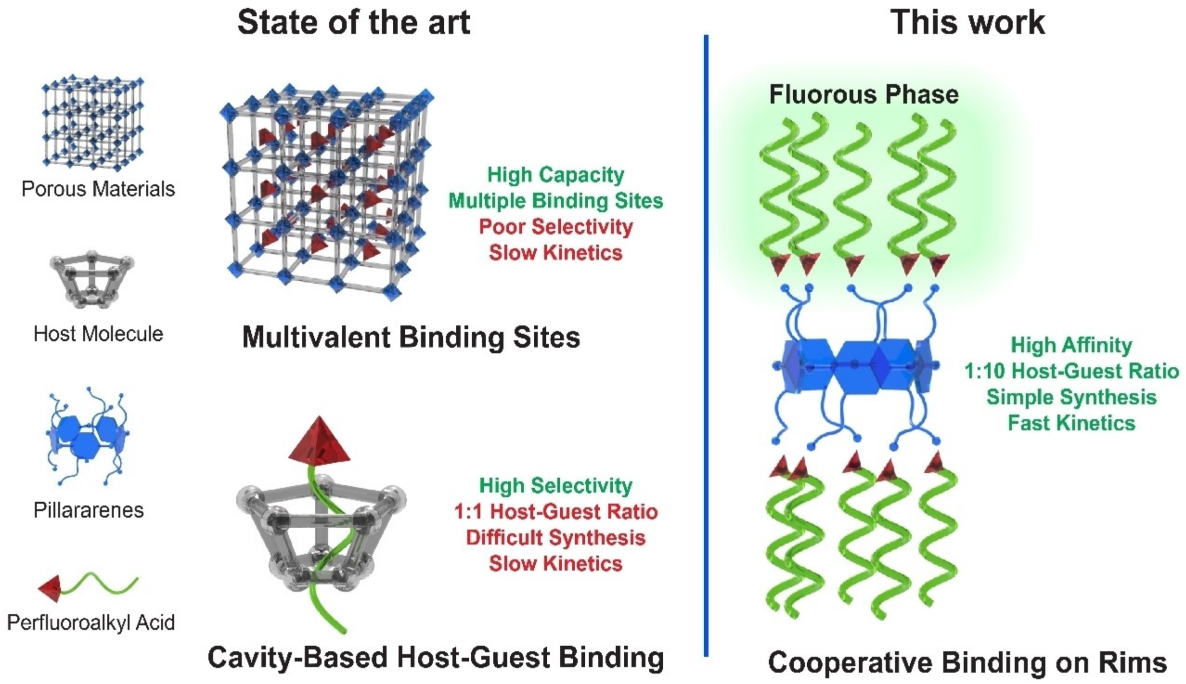

Figure 1. Materials for capture of polyfluoroalkyl acids: (left) state of the art, (right) current work.

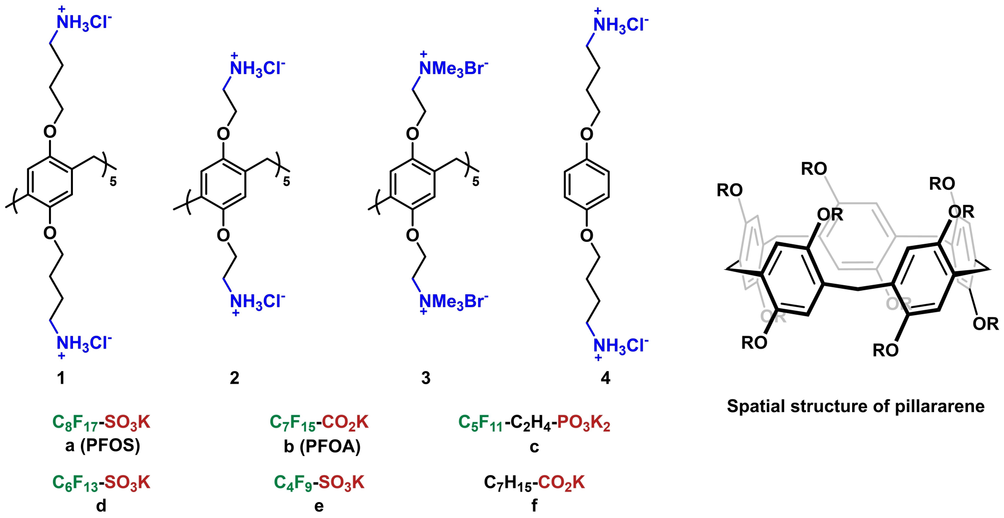

Figure 2. Structures of investigated DAF–P5s **1**–**3** with positively charged rims, monomer **4**, polyfluorinated anions **a**–**e** and anion of octanoic acid **f**.

was an extremely high ca. 1:10 pillararene - PFAS binding stoichiometry, suggesting that host–guest interactions occur on the rim rather than in the cavity of the pillararenes. For a range of perfluoroalkyl acids guests (**a**–**d**), including PFOS (**a**) and PFOA (**b**), with 11 to 17 fluorine atoms and varying negatively charged end groups (carboxylate, sulfonate, phosphonate; see Figure 2 and Table 1), pillararene hosts **1**–**3** show an excellent affinity, with a 1:10 stoichiometry and binding constants in the 10^4–$10^6\ M^{-1}$ range, up to $5\times10^6\ M^{-1}$. Blank titrations of **1** and water, and **b** with water confirmed that the ITC signal originates from the binding between pillararenes and PFAS instead of PFAS micelle formation (Figures S42–43).

The consistently high stoichiometry ratio was further confirmed by isolation of adducts **1a** and **1b** and their characterization by quantitative ^{1}H and ^{19}F NMR with an internal standard (Figures S16–19).

Table 1: Results of ITC titration of pillararenes **1**–**3** with guests **a**–**f**. Top value is a host–guest binding ratio; bottom value is a binding constant M^{-1}.[a]

	1	2	3
a	1:10±1 $(1.3\pm0.1)\times10^6$	1:10±1 $(5.1\pm0.4)\times10^6$	1:13±1 $(3.4\pm0.7)\times10^6$
b	1:10±1 $(1.7\pm0.5)\times10^5$	1:10±1 $(1.9\pm0.5)\times10^5$	1:11±1 $(5.52\pm0.9)\times10^5$
c	1:10±1 $(6.6\pm0.2)\times10^5$	1:12±1 $(1.9\pm0.4)\times10^5$	n.d.[b]
d	1:8±1 $(1.2\pm0.1)\times10^5$	1:12±2 $(1.4\pm0.1)\times10^5$	1:10±1 $(3.9\pm0.9)\times10^6$
e	n.d.[b]	n.d.[b]	n.d.[b]
f	1:1 $(1.4\pm0.1)\times10^4$	n.d.[b]	1:1 $(2.7\pm0.1)\times10^4$

[a] All values are average of triplicate experiments, see Supporting Information for the full details; [b] n.d. = not detected.

To get a better understanding of the structure and host–guest arrangement we performed crystallization and single-crystal X-Ray diffraction studies.[11] We were able to grow a crystal of **1b** suitable for X-Ray analysis by slow evaporation of solvent from a methanol-water solution. The structure of the complex confirms that the binding happens exclusively on the rim, as no PFOA molecule was found in the host cavity. The crystal structure contains 19 molecules of PFOA per 2 molecules of **1**, confirming the overall ca. 1:10 stoichiometry observed in ITC and NMR experiments. Out of 19 perfluorinated chains, 18 are oriented along the pillararene axis, creating a well-distinct fluorous phase above and below the pillararene ring. Only one residual chain is oriented perpendicular to the pillararene axis and interacts with the perfluorinated phase of a neighboring pillararene group (Figure 3). In addition, multiple hydrogen bonding interactions between carboxylates, ammonium groups, methanol and water molecules were observed. These solid-phase data are thus in line with the solution-phase studies.

For a better understanding of the high binding constant, wB97M-V/QZVP calculations were performed (detailed information in ESI), as this level of density functional theory has recently been established to calculate the fluorous-phase interactions with a high accuracy.[12] To this aim, the top five fluorous chains were placed together as we found them in the crystal structure (so without the presence of the P5). Next, the charged carboxylate groups were replaced by H atoms to eliminate the charge effects without changing the position of any of the other atoms in the fluorinated chains. The energy of this fluorous chain cluster was then compared with the energy of five separated fluorous chains, and this yielded that this fluorous-phase cluster provides 24 kcal/mol "fluorous-phase" stabilization compared to the separated chains. It is worth mentioning that even this significant energy is an underestimation of the fluorophilic effect, because in e.g., DAF–P5-resin materials with a high density

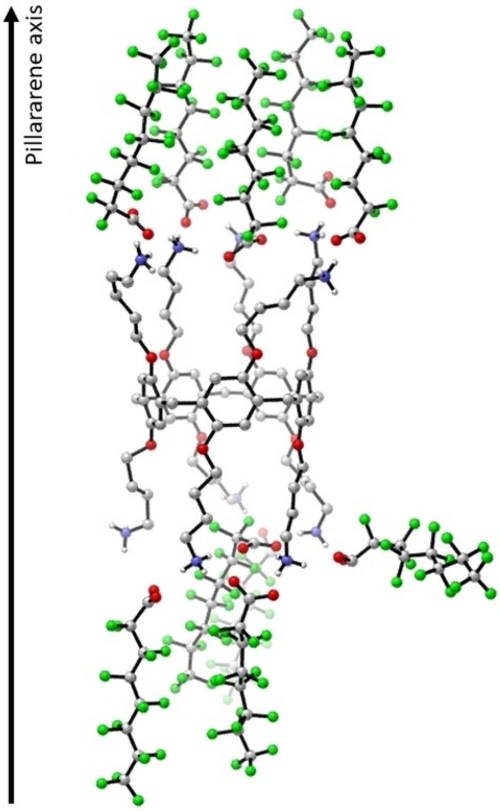

Figure 3. X-ray crystal structure of adduct 1b, all C–H bonds; MeOH, H2O solvent molecules; and disordered alkyl chains were omitted for clarity.

of pillararenes there will be fluorous-phase clusters that can also interact with other clusters. In addition, full optimization of a truncated structure (removal of the 5 PFOA molecules from one rim of the crystal structure and reduction of the alkoxyamines to H atoms on that same rim, for computational efficiency, on the hypothesis that both rims are interacting with PFOA independently from one another) showed that this mutual fluorophilic stabilization was maintained when the structure optimized without restraints. These computational data thus support a complexation mechanism that combines electrostatic interactions between the carboxylate moieties and the relatively densely packed amine moieties (either protonated in neutral water or permanently charged by quaternization) with the formation of the local fluorous phase, yielding the high affinity towards PFAS guests arranged on the rim.

This hypothesis was further confirmed by analysis of the difference in binding in various hosts **1**–**3** and guests **a**–**e**. The first important observation is that shortening the CF_2 chain from eight to six and then to four carbon atoms in perfluoroalkyl sulfonic acids (**a** vs **d** vs **e**) results first in a 10–50 fold decrease in the binding constant (**a** vs **d**) for both **1** and **2**, and then for **e** no interactions are even detectable anymore by ITC (i.e., binding constant $<10^3$ M^{-1}). This trend is in line with a decrease of fluorophilic interactions occurring due to the shorter length of the fluorinated chain. Perfluoroalkyl acids with longer CF_2 chains (e.g., perfluorodecanoic acid) were not measured due to their poor solubility in water. In addition to sulfonic acid PFOS (**a**) and carboxylic acid PFOA (**b**), the corresponding phosphoric acid (**c**) also forms 1:10 complexes with pillararenes with K values of 1.9–6.6×10^5 M^{-1}. This highlights that the nature of the anion does not significantly affect the resulting pillararene-PFAS assembly. Similarly, the nature of the ammonium cation group on the pillararene was not significant for the 1:10 adduct formation, as R-NH_3^+ (**1**, **2**) and R–NMe_3^+ (**3**) both showed a similar level of interaction. This latter example particularly suggests that hydrogen bonding interactions between P5 and PFAS are not crucial for the 1:10 adduct formation. In short: the rim-guest interaction is determined by fluorophilic and generic electrostatic attractions.

Control experiments with monomer **4** (Figure 2, Table S4) showed no binding for both PFOS (**a**) and PFOA (**b**), supporting the necessity of multiple interactions to achieve appreciable binding. Similarly, no interactions were observed (with ITC) for polyethylenimine [$(CH_2–CH_2–NH–)_n$] in contact with either **a** or **b**. This showcases the importance of the pillararene structure for the host–guest interaction, pointing to multivalency effects as e.g., observed in macrocycle-protein based studies.[13] In addition, we observed that non-fluorinated alkyl anions display the well-known 1:1 in-cavity host–guest chemistry with these pillararene compounds. For example, ITC measurements revealed for octanoic acid **f** a typical 1:1 binding with pillararenes **1**–**3** (K = 1.4–2.7×10^4 M^{-1}), in line with previous literature.[14]

The high 1:10 host–guest ratio opens up intriguing possibilities for the development of efficient practical absorbents for PFAS, as PFAS pollution is an urgent environmental problem. Our reasoning was that these positively charged DAF–P5s would strongly bind to multiple units of PFAS, potentially enabling the cleanup of PFAS-polluted water through filtration using DAF–P5-loaded materials. Another advantage of our system is the straightforward synthesis of DAF–P5s **3**, which takes only 3 steps with a 33 % overall unoptimized yield from readily available, commercial materials. It can be easily performed on a multigram scale,[14b] and likely allows further scale up.

To demonstrate a proof-of-principle application, DAF–P5s were covalently bound to a commercial resin, TentaGel S (see Supporting Information for details). The DAF–P5-functionalized resin featured a 10 wt % loading of DAF–P5s, determined through weight change and XPS measurements. Subsequently, 100 mg of DAF–P5-resin was packed into a standard 1 mL solid phase extraction (SPE) cartridge. The SPE cartridge was connected to a peristaltic pump, and 1100 mL of PFOS solution (10 mg/L, i.e., corresponding to a heavily polluted water) was flushed through at a 1 mL/min flow rate. The residual PFOS concentration was determined by UPLC-MS. For the first 900 mL of purified water the residual concentration of PFOS was of only 19–42 ng/L, i.e., significantly lower than the EPA-advised limit of 70 ng/L (Figure 4a). Phrased differently, the one-time pass reduced the PFOS concentration from 10^6 ng/L to 19–42 ng/L. It is worth mentioning

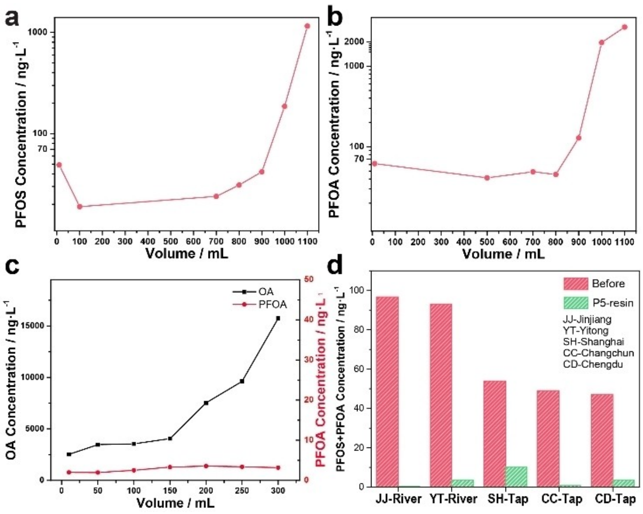

Figure 4. a. Residual concentration of PFOS after flushing heavily polluted water (10 mg/L PFOS) through a DAF–P5-functionalized resin. b. Residual concentration of PFOA after flushing heavily polluted water (10 mg/L PFOA) through a DAF–P5-functionalized resin. c. Residual concentration of PFOA and octanoic acid (OA) in mixture solution (original concentrations: PFOA = 1 μg/L; octanoic acid = 10 mg/L). d. Purification of environmental samples after 5 minutes treatment.

that in the very first fraction collected within the first 5 min, the residual concentration was already reduced to 49 ng/L, while upon further flushing with water up to 30 min an even better performance was reached. This is a big advantage in comparison with benchmark materials, such as activated carbon, which need at least hours to reach equilibrium.[15] The initial 5–30 min delay in optimal performance is also in line with the cooperative fluorophilic absorption mechanism we proposed. For comparison, analogous experiments with activated carbon resulted in residual PFOS concentration of 230–515 μg/L, i.e., four orders of magnitude higher than with the DAF–P5-functionalized resin (Figure S4).

The DAF–P5-functionalized resin also demonstrated a high capacity and robust performance. The PFOS breakthrough capacity of DAF–P5-resin is 90 mg/g calculated from the breakthrough volume. By calculating the ratio between P5-loading and PFOS-absorption, we realized the P5-PFOS ratio in the saturation state is ca. 1:4.3. This P5-PFOS ratio suggests that the DAF–P5s are immobilized vertically on the surface of the resin, with one rim bound to resin, while the other rim is used to absorb PFOS, resulting a ~1:5 ratio. The resin could be easily regenerated to 80 % of its initial capacity by washing with 0.1 g/L NaCl in neutral MeOH. From the second regeneration onward, the capacity remained stable for at least 10 cycles, importantly with maintaining the residual PFOS concentration continues to be below 50 ng/L. Similarly, DAF–P5-resin also shows excellent absorbing performance to PFOA. The residual concentration is 35–48 ng/L,_and the PFOA capacity of DAF–P5-resin is 80 mg/g (Figure 4b), which is two times higher compared with the top benchmark materials (40 mg/g for PAF).[3e] Notably, this is the capacity for a 10 wt % loading of DAF–P5, which thus still has 90 wt % of non-absorbing resin support; recalculating on the active P5 absorbent, the capacity reaches 800 mg/g.

One of the biggest challenges in the remediation of water from PFAS is the insufficient efficiency of absorbent in the presence of potentially competing, natural organic co-contaminants, such as carboxylic acids. Common organic molecules are known to interact with the cavity of pillararenes,[7c,14b] but it was not known to which degree this would interfere with the binding of PFAS to the rim. To demonstrate this property, we ran a competitive experiment, absorbing PFOA (1 μg/L) in the presence of a 10000-fold excess of its non-fluorinated counterpart—octanoic acid (OA, 10 mg/L). The residual concentration of OA increased dramatically after purifying 150 mL of solution, while the PFOA residual concentration stayed in range of 1–5 ng/L, order of magnitude lower than the safety advisory limit (Figure 4c).

For further proof of the effectiveness of our absorbent, we conducted experiments using environmental samples collected from various locations in China. Specifically, we obtained water samples from the Yitong River in Changchun, the Jin River in Chengdu, and tap water from Changchun, Chengdu, and Shanghai. In our experiments, we introduced 0.025 wt % of the DAF–P5-resin to each of these samples. After subjecting them to 5 minutes of sonication, we removed the absorbent from the samples through filtration, and measured the [PFOS + PFOA] concentrations (Figure 4d). Clearly, the DAF–P5 resin effectively removes the PFOA and PFOS from water, yielding a residual concentration of the total of [PFOS + PFOA] that is lower than 10 ng/L in all cases. The DAF–P5-resin is not affected by natural organic co-contaminants, allowing it to maintain its efficiency for complex environmental samples.

In conclusion, we report a new type of supramolecular binding between perfluoroalkyl acids to fluorine-free macrocyclic pillararene hosts, with an unprecedented 1:10 binding stoichiometry and high binding constants (up to $5\times10^{6}\ M^{-1}$). Crucial for these rim-based (rather than cavity-based) complexes is the combination of electrostatic host–guest attractions with strong fluorophilic interactions between PFAS molecules. This allows for the efficient removal of PFAS from water, in a fashion orthogonal to the in-cavity complexation of common organic molecules. DAF–P5-functionalized resin effectively reduces PFOA and PFOS concentrations also in natural river waters and tap water to safe levels via simple filtration. The easily scalable synthesis of DAF–P5-functionalized materials together with the demonstrated high capacity and robust performance are expected to strongly contribute to the remediation of PFAS-polluted water.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Pillar[n]arenes · Host-Guest Chemistry · Perfluoroalkyl Compounds · Macrocycles · Water Treatment

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