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# Interaction of Short-Chain PFAS with Polycationic Gels: How Much Fluorination is Necessary for Efficient Adsorption?

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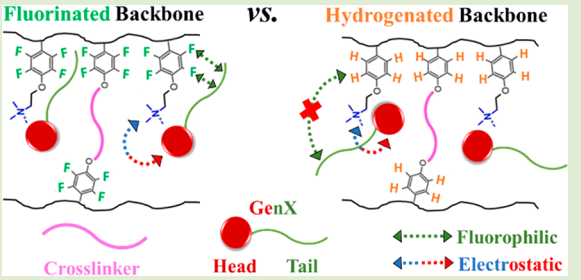
**ABSTRACT:** The short-chain per- and polyfluorinated alkyl substances (PFAS), introduced to replace the legacy PFAS compounds, turned out to be as toxic and harmful as their longer-chain predecessors and even harder to sequester from contaminated water sources. In this work, molecular dynamics (MD) simulations are employed to investigate the adsorption mechanism of GenX, a representative compound for short-chain PFAS, on a polycationic hydrogel with various extents of fluorination in its backbone and cross-linkers. Simulations indicate that the presence of fluorinated segments next to cationic groups in the polymer gel structure provides the most efficient environment for GenX adsorption. The combination of electrostatic and hydrophobic interactions offered by the cationic-fluorophilic segments amplifies the binding of GenX molecules compared to polymer segments with nonfluorinated cationic or noncationic fluorinated segments. Moreover, such a gel demonstrates high selectivity toward GenX against its hydrogenated analogue.






Per- and polyfluorinated alkyl substances (PFAS) are extensively used in the manufacturing of fluoropolymers,[1] aqueous fire-fighting foams,[2] and water and stain-repellent coatings.[3] The manufacturers of these products have continuously released PFAS into water bodies for years. The high toxicity, chemical resistance, and bioaccumulative nature of PFAS have caused adverse health effects on humans and wildlife.[4−6] As a result, the United States Environmental Protection Agency (EPA)[7] and European Chemicals Agency[8] have set the drinking water health advisory of 70 ng/L and 0.5 $\mu$g/L, respectively. Between 1950 and 2000, the eight-carbon long PFAS, specifically perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), were the dominant contaminants until 2015 when major fluorochemical manufacturers agreed to phase out the production of these pollutants. A short-chain compound, called GenX (ammonium perfluoro-2-propoxypropionate) was proposed as an alternative and sustainable replacement.[9] It was assumed to be biologically safe until a recent toxicology report published by the EPA asserts that it is hazardous in nature and can cause serious health problems even at lower exposure levels than PFOA.[10] The presence of GenX in elevated amounts across different parts of the world[11−13] has raised concerns as it has been linked to various serious health problems.[14] Despite the enormous shift in the industry and associated health problems with the usage of GenX and other short-chain PFAS, the efforts on sequestration and development of absorbent materials were primarily focused on long-chain PFAS.[15−18] The conventional technological filtration systems, for example, based on granular activated carbon (GAC) adsorbent, proved to show poor affinity toward short-chain PFAS.[15,19,20] A handful of studies have been done in the exploration of alternative adsorbents for GenX and other short-chain PFAS.[21−24] The polymer-based materials such as ion-exchange resins[25] and hydrogels[23,26] have primarily attained the interest because of the relative ease in tuning their chemical affinity, high water uptake capacity, and low-cost synthesis. The ion-exchange resins are considered as one of the conventional sorbents, but their nonselective behavior suppresses the PFAS removal efficiency in the presence of background anions.[27] Therefore, many novel hydrogels of different architecture and chemical structure discussed in the literature incorporate a high fraction of fluorinated segments to introduce selectivity.[26,28] Because of limited attention to short-chain PFAS, the fundamental understanding of GenX self-assembly in water and molecular interactions with the adsorbent material are mainly missing.

In this work, we employed atomistic molecular dynamics (MD) simulations to probe the adsorption mechanisms of GenX on polycationic hydrogels. The smaller fluorocarbon chain length makes GenX less hydrophobic, and thus, providing just a fluorophilic environment in the polymer gel is insufficient to make the material an appropriate GenX adsorbent.[23,26] Therefore, we explored a set of polycationic gels, enabling us to exploit the importance of both electrostatic

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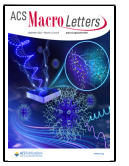





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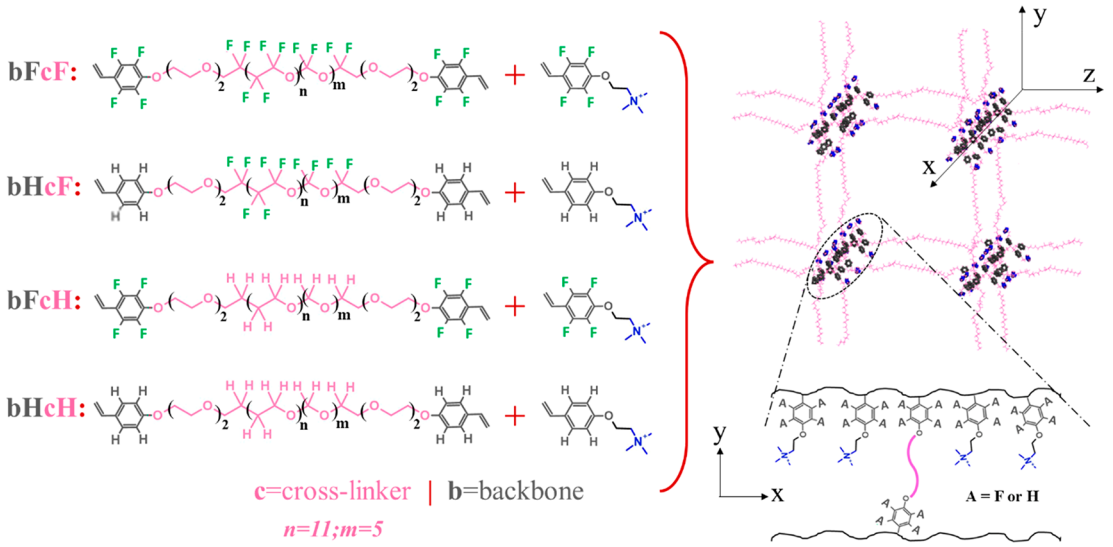
**Scheme 1. Chemical Structures of Investigated Combinations of Gel Backbones and Cross-Linkers**



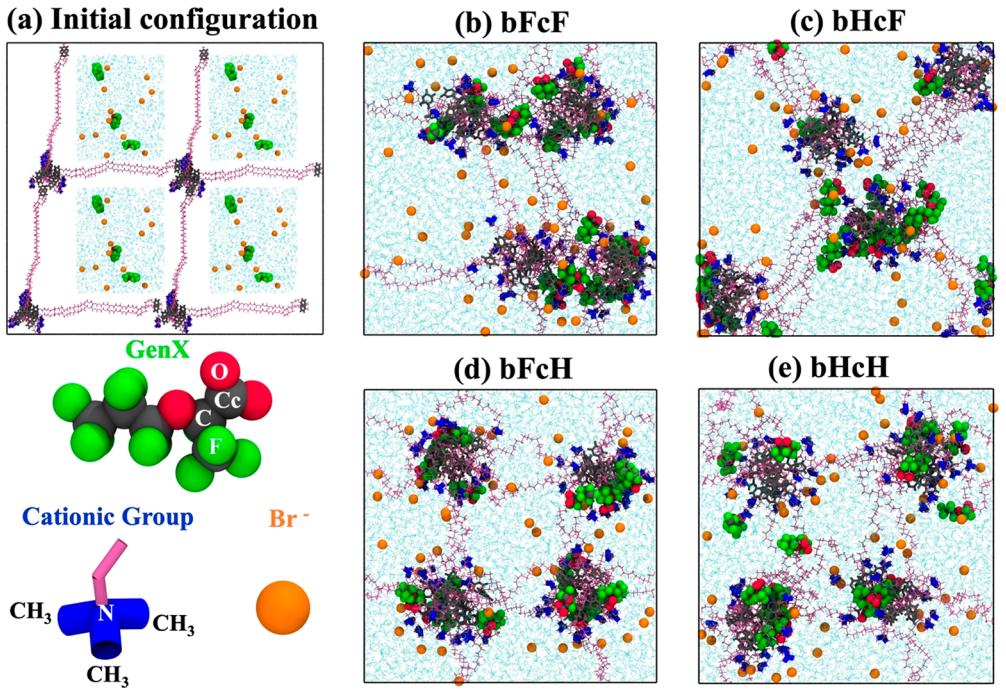




**Figure 1.** (a) Initial configuration of a polymer network and the GenX-containing aqueous solution. (b–e) Representative snapshots of equilibrated bFcF, bHcF, bFcH, and bHcH polymer gels, respectively. Dark blue: quaternary ammonium; Gray: styrene group; Pink: cross-linker; Green: F atoms of GenX; Red: O atoms of GenX; Gray: C atoms of GenX; Orange: bromide ion; Light Blue: water.

and fluorophilic interactions between gel and GenX pollutants by varying the extent of fluorination of the cationic backbone and cross-linkers. The analysis of MD simulations provides molecular-scale insight into pairwise interactions between different components of the polymer gel and GenX and the strength and stability of these interactions, and assesses gel selectivity toward GenX compared to other anionic compounds. To the best of our knowledge, this is the first MD simulation study that investigates adsorption of GenX on polymer gels. The mechanisms presented in this Letter should be applicable to a broader range of cationic polymer gels and short-chain PFAS and can facilitate the design of novel materials for efficient and selective adsorption.

A three-dimensional periodic simulation box contained a polymer gel immersed in the solution of GenX, $Br^-$ anions, and $H_2O$. The schematic structures of polymer gels investigated are given in Scheme 1. Four polymer gels were considered, namely, bFcF, bHcF, bFcH, and bHcH representing different combinations of fluorinated and hydrogenated segments in cationic backbone and ether cross-linkers (b, backbone; c, cross-linker; F, fluorinated; H, hydrogenated). The backbone chains consist of polystyrene or perfluorostyrene monomers with quaternary ammonium cations attached, as illustrated in Scheme 1. These backbone chains are cross-linked through polyether (PE) or perfluoropolyether (PFPE: Fluorolink E10H) chains, which are random copolymers of 11 ethylene oxide (or perfluoroethylene oxide) and 5 oxymethylene ether



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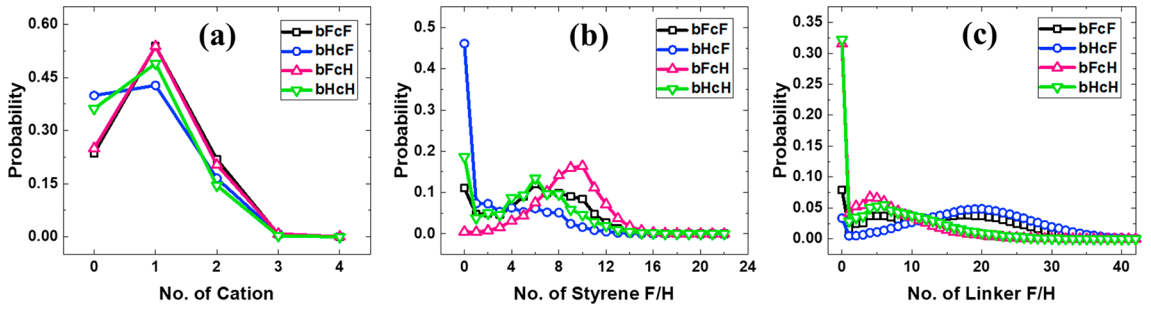


**Figure 2.** Probability distribution of (a) the number of cationic groups (defined by N atom) within 6.5 Å radius from GenX headgroup (defined by *Cc*), (b) the number of styrene F (in case of bFcF and bFcH) or styrene H (in case of bHcF and bHcH) atoms within 5.0 or 4.5 Å of any F atom of GenX molecule, and (c) the number of cross-linker F (in case of bFcF and bHcF) or cross-linker H (in case of bFcH and bHcH) atoms within 5.0 or 4.5 Å of any F atom of GenX molecule.

(fluoro-oxymethylene ether) monomers, terminated with corresponding styrene end groups. Gels synthesized with similar segments as in bFcF have shown great performance for PFAS adsorption in experimental testing.[29] There are four backbone chains each containing 16 cationic groups and aligned parallel in the *X*-direction. The backbone chains are cross-linked in the *Y* and *Z* directions by 16 cross-linkers, resulting in each backbone participating in 8 cross-links. These gels are immersed in a solution containing 8000 $H_2O$ molecules, 16 GenX molecules, and 48 $Br^-$ anions. The effective concentration of GenX in water is 86 mM which is below the critical micelle concentration (CMC) of 175 mM.[30] Therefore, at this concertation, GenX molecules are not expected to form micelles or clusters in bulk water, which could interfere with the mechanism of their adsorption on the gel. The $Br^-$ is included to understand the impact on GenX adsorption in the presence of other anions as well as allowing a charge neutrality of the system. In the initial configuration, all polymer chains were in their stretched configuration and the interstitial space was filled with $H_2O$/GenX/$Br^-$ solution with no pollutant in close contact with polymer gel (Figure 1a). The initial simulation cells were shrunk to a reasonable density over 30 ps. Then equilibration runs over 15 ns were conducted followed by 25 ns of production runs in the NPT ensemble. A detailed description of simulation parameters is provided in the Supporting Information (SI).

Typical snapshots of equilibrated bFcF, bHcF, bFcH, and bHcH gels are given in Figure 1b−e, respectively. In gels with fluorinated cross-linkers, that is, bFcF and bHcF, the cross-linkers form bundles because of their strongly hydrophobic character and sufficiently long and flexible chains. Whereas, hydrogenated cross-linkers in bFcH and bHcH gels spread out in solution owing to their higher water solubility. The high density of quaternary ammonium ions in the backbone makes them soluble in water and prevents backbones from aggregating with each other because of strong intermolecular cationic−cationic electrostatic repulsion. From the snapshots it is evident that most GenX molecules prefer to adsorb near the backbone segments. To quantify which locations in the gel structure are the most favorable for GenX adsorption, we computed the radial distribution functions ($g(r)$) and coordination numbers (CN) between representative groups of GenX and gel segments (see Figure S1). The $g(r)$ between nitrogen atom (N) of the cationic group and the double-bonded carbon atom (*Cc*) of the GenX headgroup shows similar features in all four adsorbents, with the highest peak observed for the bFcF and bFcH gels followed by bHcF and the weakest interaction in case of bHcH. The CN of cationic N atoms within the first coordination shell of GenX *Cc* atoms (defined as 6.5 Å) is 1.0 for bFcF and bFcH, while 0.7 for bHcF and bHcH. For a better understanding of coordination environments of *Cc*, Figure 2a displays the distribution of probability to find a number of N atoms within 6.5 Å from a *Cc* atom. Although the most probable coordination number is 1.0 for all four systems, the probability of GenX to have no cationic groups in the first coordination shell is also significant and is the highest for the bHcF, followed by bHcH. Despite having the same charge on cationic groups across all gels, in systems with hydrogenated backbones, there is almost a twice higher probability of finding GenX molecules that do not interact with cationic groups of the backbone. This indicates that hydrophobic interactions between GenX molecules and styrene backbone segments also play an important role.

To further probe the role of fluorination of styrene units in the GenX adsorption we analyzed the interaction between F atoms of GenX and F (or H) atoms from the backbone styrene segments. Figure 2b compares the probability distribution of the number of styrene F (or H) atoms within 5.0 Å (or 4.5 Å) from the F atoms of GenX. The average values (Table S1) follow the trend: bFcH > bFcF > bHcH > bHcF. Owing to a highly hydrophobic perfluorostyrene group, bFcH and bFcF have on average 9 and 6 F atoms, respectively. As mentioned above these two gels also showed preferential N-*Cc* interaction and relatively high CN compared to the gels with hydrogenated backbones. The probability of having zero F (or H) styrene atoms in the first coordination is the highest for bHcF followed by bHcH, indicating that hydrogenated styrene groups do not provide sufficiently favorable environment for the hydrophobic GenX tail. This is consistent with the weaker coordination between N and *Cc* observed in these gels. These results clearly indicate that the presence of fluorinated environment (perfluorostyrene) in the vicinity of cationic group complements the electrostatic interaction with GenX molecule and their combined effect leads to a stronger overall interaction with the backbone.

Figure 2b also shows that there are fewer styrene F atoms interacting with GenX tail group in bFcF than in bFcH (or in bHcF than in bHcH). These variations arise because of the third component of the gel, the cross-linkers, that can be categorized into two categories: (i) gels with fluorinated linkers (bFcF and bHcF) and (ii) gels with hydrogenated linkers (bFcH and bHcH). Figure 2c provides the probability distribution of a number of cross-linker F (or H) atoms within 5.0 Å (or 4.5 Å) of a F atom of GenX molecule. The


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average values for CN (Table S1) show the following trend: bHcF > bFcF > bHcH > bFcH. The gels with fluorinated linkers strongly interact with the fluorinated tail of GenX. Within this category, the bHcF gel has a higher number of cross-linker F atoms interacting with GenX, as there are no other sources of fluorinated environments present in this system, whereas in bFcF, the hydrophobic/fluorophilic environments are also provided by the fluorinated styrene units. On the other hand, gels with hydrogenated linkers (bHcH and bFcH) have the highest probability at zero, which confirms a very weak interaction between the hydrophilic polyethers and GenX tail group.

The binding strength between GenX and a specified function group/segment can be quantified by computing the residence time from the first coordination shell neighbor autocorrelation function (ACF), see SI for methodology details. The residence times ($\tau$) of GenX near different segments of gels are shown in Figure 3. The headgroup of

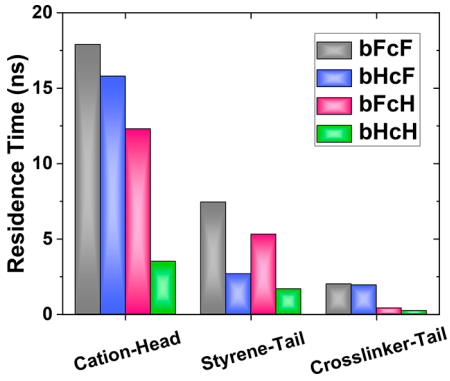


**Figure 3.** Residence times between GenX headgroup (defined by *Cc*) and quaternary ammonium (defined by N), GenX tail group (defined by F) and styrene (defined by F in bFcF and bFcH or H in bHcF and bHcH), and GenX tail group (defined by F) and cross-linkers (defined by F in bFcF and bHcF or H in bFcH and bHcH).

GenX molecule spends most of the time near cations with the highest residence time ($\tau_{\text{cation-head}}$) for bFcF gel and the shortest for bHcH. The $\tau_{\text{cation-head}}$ for bFcF is ∼13.5% longer than bHcF gel, while for bFcH it is about 250% longer than bHcH. These comparisons confirm a considerable impact of fluorinated styrene units in improving the GenX-quaternary ammonium affinity and strength of binding. Notably, fluorinated styrene units near the cationic sites simultaneously provide electrostatic interaction for the headgroup and a highly hydrophobic surrounding for GenX tail group. Comparing $\tau_{\text{cation-head}}$ for bFcF with bFcH and bHcF suggests that replacement of perfluoropolyether cross-linkers with polyethers only marginally impairs the GenX−cation binding. Whereas $\tau_{\text{cation-head}}$ decreases drastically for bHcH versus bHcF, as no other fluorinated units are present in the gel. To support this argument, the residence time of GenX tails with styrene backbone ($\tau_{\text{styrene-tail}}$) and cross-linker ($\tau_{\text{cross-linker-tail}}$) were also calculated. We observed that $\tau_{\text{cation-head}} \gg \tau_{\text{styrene-tail}} > \tau_{\text{cross-linker-tail}}$ for all gels, as the electrostatic interactions are stronger than the hydrophobic interactions. As expected, gels with fluorinated styrene groups have a longer $\tau_{\text{styrene-tail}}$ because of a stronger hydrophobic interaction. Similar behavior is observed for the $\tau_{\text{cross-linker-tail}}$. Along with the residence time comparison, we also computed the Helmholtz free energy as a function of distance for the GenX headgroup and the cationic group (*Cc*-N pair correlation) and for GenX tail and styrene units (F (GenX) − F or H (styrene) pair correlations). The obtained binding energies (Figure S2) for the [*Cc*-N] pair show similar values as the cationic group and GenX's headgroup have similar electrostatic interactions in all gels, the difference in binding strength is less than 2 kJ/mol. On the other hand, binding energies for GenX tail with the styrene units show more significant difference with the strongest binding energy is for bFcH gel and the weakest for bHcF gel.

Overall, the analysis of trends in $\tau_{\text{cation-head}}$, $\tau_{\text{styrene-tail}}$, and $\tau_{\text{cross-linker-tail}}$ indicates that bHcH gel exhibits poor affinity toward GenX. While among other gels, the bFcF has the most stable adsorbate−adsorbent complex, followed by bHcF and bFcH. Despite having vastly different extents of fluorination (Table S2), surprisingly, the difference in binding is minimal. Thus, replacing the PFPE cross-linker in bFcF with hydrogenated oligomers to form bFcH does not reduce the gel's efficacy to adsorb GenX. But from the technological point of view, such a replacement can be advantageous as it minimizes the use of fluorinated materials whose degradation during the water treatment process can potentially generate fluorinated compounds of unknown toxicity.[31,32] Verduzco et al. emphasize the success of fluorine-containing hydrogels but concurrently express concerns over the usage of fluoropolymers.[33] Manning et al. found that one of the fluoropolymer-based ionic gels (IF-20+) lost about 38% mass over 56 days in basic solution (pH = 8.7) at 50 ° C. Considering these concerns about the leaching of fluoropolymers in solution, we believe that gels with fluorinated backbone and hydrogenated cross-linkers (like the bFcH) would be a better design model for adsorbent materials as they minimize the use of fluoropolymers without compromising the performance.

Finally, all simulations were conducted in the presence of $Br^-$ ions in the solution, which allows us to examine GenX adsorption in the presence of other anions that compete for electrostatic interactions with the cationic gel. We did not observe any hindrance in the cation−GenX headgroup interaction due to presence of $Br^-$. In the bFcH gel, only 45% of $Br^-$ ions interact with quaternary ammonium groups, while 78% of GenX molecules interact with them (Figure S3). Even then, the gel has not reached saturation as 45−50% of cationic sites are still free from any of the anions and are available for further absorption. Additionally, a relatively short residence time of 0.2 ns for the N−$Br^-$ complex indicates a weaker binding of cationic groups toward $Br^-$ ions, which can be easily replaced by stronger interacting PFAS anions. To check how selective the bFcH gel toward PFAS compared to other hydrocarbons that can be present in contaminated waters, we compared the affinity of the GenX molecule with its hydrogenated form (HyGenX), that is, 2-propoxypropanoate. The number of HyGenX molecules interacting with the ammonium group is significantly lower than the GenX molecule (Figure S4), which is also evident from the final snapshot of such a system (Figure S5), clearly showing that majority of HyGenX molecules are in the solution and are not adsorbed on the gel. Also, the residence time $\tau^{\text{HyGenX}}_{\text{cation-head}}$ is almost 70 times shorter than $\tau^{\text{GenX}}_{\text{cation-head}}$. This drastic difference is attributed to the higher water solubility of HyGenX and the absence of strong hydrophobic interactions between fluorinated styrene groups and HyGenX tail. This preferential interaction makes the bFcH gel highly selective toward short-chain anionic PFAS compared to anionic hydrocarbons.


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In conclusion, we elucidated the adsorption mechanisms of GenX, a short-chain anionic PFAS, on cationic polymer gels with various degrees of fluorination. While electrostatic interactions between GenX headgroup and cationic groups in the gel are the same in all gels, the presence or absence of fluorine atoms in the backbone and cross-linker dramatically affects the binding affinity and strength. The positioning of fluorinated atoms near the cationic site provides the most efficient environment for GenX binding as it allows the hydrophobic and electrostatic interaction to complement each other. This design principle also facilitates minimizing the content of fluoroethers (or other fluorinated segments) in the PFAS adsorbents.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.2c00383.

Additional experimental details and supporting figures, tables, and references (PDF)

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### Notes

The authors declare no competing financial interest.

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