



practical example, the Sweeney Water Treatment Plant in the impacted community of Wilmington, NC, installed a \$43 million system that removes PFECAs to low-ppt levels using 3 million pounds of GAC which is replaced every 270 days.<sup>16</sup> The annual operating costs for this water treatment system are estimated at approximately \$5 million.<sup>17</sup>

The expense of PFAS remediation by traditional granular sorbents and the impending scope of remediation motivates the development of materials that are selective for fluorinated chemicals. An effective PFAS sorbent would have high PFAS selectivity over natural organic matter and other co-constituents in water, resulting in higher-capacity sorbent beds, long operational lifetimes, and less material usage. Regenerability constitutes an additional attractive feature of an effective PFAS remediation sorbent that yields a longer usage life cycle and a concentrated PFAS waste that can be destroyed using emerging destruction technologies.<sup>18</sup> However, development of practical removal technologies relies on fundamental understanding of PFAS sorption processes. Taking inspiration from GAC, many materials leverage hydrophobic interactions to selectively partition PFAS from solution. Furthermore, molecular recognition<sup>19–23</sup> and supramolecular host-guest complexes<sup>24–26</sup> implemented *via* cationic crosslinked resins<sup>27–30</sup> and porous polymer sorbents<sup>31–36</sup> have demonstrated preliminary promise to remove PFAS from water. These materials often lack selectivity for a wide range of PFAS at environmentally relevant concentrations such as those in natural waters that serve as drinking water sources.<sup>37</sup>

To address this lack of selectivity in natural waters, we were inspired by the use of fluorophilicity to selectively partition PFAS from aqueous solution.<sup>29,38–44</sup> Previously, we reported Ionic Fluorogels (IFs), a selective class of PFAS remediation sorbents which leverage perfluoropolyethers (PFPEs) as fluorophilic matrices for PFAS removal. In a flow-through packed bed geometry, the IFs efficiently removed PFAS from natural waters spiked with part-per-trillion level PFAS, supporting our hypothesis that a synergistic combination of fluorophilic and electrostatic components enables high-performance PFAS remediation from natural waters (Fig. 1A).<sup>39</sup> However, PFPEs present some possible environmental hazards,<sup>45</sup> are expensive on scale, and suffer from hydrolytic degradation without chemical modification. Installation of aryl-ether linkages as PFPE end groups limited hydrolytic degradation (Fig. 1B),<sup>46</sup> but concerns regarding costs and potential environmental hazard remain. Given the need for a scalable and chemically-stable PFAS remediation technology, we hypothesized that a complementary class of partially fluorinated copolymers, fluoroolefin-vinyl ether copolymers (FVEs), could serve as low-cost, hydrolytically stable, high-performance fluorophilic matrices for PFAS removal (Fig. 1C).

FVEs are tunable, partially fluorinated polymers synthesized through the perfectly alternating radical copolymerization of a fluoroolefin monomer and one or more vinyl ether monomers (Fig. 2A).<sup>47–49</sup> The alternating character arises due to the difference in radical polarity<sup>50,51</sup> between the fluoroolefin (*e.g.* tetrafluoroethylene, hexafluoropropylene, chlorotrifluoroethylene) and the vinyl ether (*e.g.* isobutyl vinyl

### A. Previous work: IFs for PFAS remediation



- Synergistic combination of fluorophilicity & ion exchange
- Efficient PFAS sorption in complex matrices
- Hydrolytically degradable

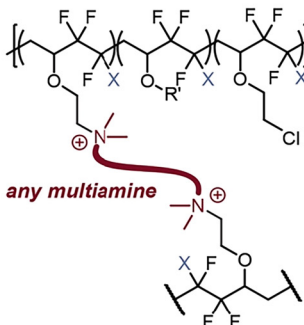
### B. Previous work: Stable IFs for PFAS remediation



- Selective PFAS removal from natural N.C. water
- Regenerable in green solvent
- Quantitative PFAS removal in column tests
- Poorly defined stoichiometry
- low-volume starting materials



### C. This Work: Fluoroolefin-Vinyl Ether IFs



- Selective for PFAS over non-fluorinated organic matter
- Regenerable in green solvent
- Highly tunable materials platform
- High-volume, low cost starting materials

**Fig. 1** (A) Perfluoropolyether Ionic Fluorogels (IFs) demonstrated the concept of using fluorophilicity and ion exchange for PFAS sorption. (B) Second generation IFs are hydrolytically stable but remain cost and scale prohibitive for water remediation applications. (C) This work demonstrates the use of widely available and chemically stable fluoroolefin-vinyl ether copolymers for the development of a library of materials for PFAS remediation.

ether, chloroethyl vinyl ether) during propagation.<sup>48,52,53</sup> Vinyl ethers are readily available, electron-rich monomers that do not homopolymerize through radical polymerization.<sup>54,55</sup> Fluoroolefins are electron-deficient monomers that are polymerized at an industrial scale using radical polymerization. The matching of radical polarity leads to a lower kinetic barrier ( $\Delta G^\ddagger$ ) toward crosspropagation, which results in an alternating polymer microstructure.<sup>53,56–71</sup> Incorporation of a functional comonomer such as chloroethylvinyl ether (CEVE) enables post-polymerization modification to form graft copolymers<sup>62,72</sup> or ionomers,<sup>49,61</sup> further diversifying the structural manifold provided by the FVE copolymer platform.

We leveraged functional CEVE to provide a platform for the generation of a library of polymer networks to evaluate for





**Fig. 2** Synthesis of fluoroolefin-vinyl ether copolymers (FVEs). (A) Synthesis of fluoroolefin copolymers (FVEs) with chloroethylvinyl ether (CEVE), and/or isobutylvinyl ether (iBVE), and either hexafluoropropylene (X = CF<sub>3</sub>) or chlorotrifluoroethylene (X = Cl). (B) Copolymers characterization. <sup>a</sup> kg mol<sup>-1</sup> as measured *via* SEC (THF, Refractive Index detector). Mol% = mole percent,  $M_n$  = number average molar mass,  $\bar{D}$  = dispersity.

PFAS remediation (Fig. 2B). Nucleophilic substitution of the alkyl chloride with tertiary amines results in formation of quaternary ammonium groups, installing both a covalent crosslink and permanent cationic character in a single synthetic step. We hypothesized that this new class of IFs would be efficient PFAS sorbents, as they would leverage both a fluorinated matrix and electrostatic interactions to remove PFAS from water.

Herein, we report FVE copolymer-based Ionic Fluorogels (FVE-IFs) as a library of granular resins for PFAS remediation. These modular materials demonstrate improved sorption of PFAS from simulated natural water relative to commercial ion exchange resins, high PFAS capacity, and facile regeneration. Competitive sorption experiments indicate that FVE-IFs show superior selectivity for PFAS over organic matter compared to a state-of-the-art ion exchange resin. The tunability and performance of FVE-IFs make them a promising platform for translationally relevant PFAS remediation technology.

## Results and discussion

A significant advantage of the FVE-IF materials platform is the tunability of the FVE copolymer structure to access varied degrees of ionic content and fluorophilicity. To understand the effect of fluoroolefin identity and functional comonomer density, we first synthesized a representative suite of FVE copolymers by radical copolymerization (Fig. 2A). Hexafluoropropylene (HFP) and chlorotrifluoroethylene (CTFE) were identified as fluoroolefin monomers to modulate fluorophilicity by changing the backbone fluorination of the polymer. CEVE was chosen as the functional comonomer through which post-polymerization nucleophilic substitution would occur.<sup>49</sup> Two FVEs with 1 : 1 feed ratios of fluoroolefin

and CEVE were synthesized with different fluoroolefins to yield poly(HFP-*alt*-CEVE) and poly(CTFE-*alt*-CEVE) (Fig. 2B, entries 1 and 2). To investigate the role of functional comonomer loading, a terpolymer with a 2 : 1 : 1 incorporation of HFP, CEVE, and isobutylvinyl ether (iBVE) (poly[(HFP-*alt*-CEVE)-*co*-(HFP-*alt*-iBVE)]) was also synthesized (Fig. 2B, entry 3). At a multi-gram scale, all three copolymers were isolated in yields consistent with literature precedent<sup>49</sup> and at appropriate number average molar masses ( $M_n$ ) for subsequent cross-linking reactions ( $M_n = 10\text{--}20\text{ kg mol}^{-1}$ ).

The resulting FVE copolymers were crosslinked *via* substitution with multi-functional nucleophiles (Fig. 3A and Table 1), leveraging the CEVE comonomer as a functional handle. The parent FVE copolymers are soluble in common organic solvents, therefore the reaction proceeded readily in acetone following an adapted literature procedure (see SI for a detailed procedure).<sup>49</sup> Upon network formation, the reaction solution formed an insoluble gel. After reaction completion, the material was ground into a powder and purified *via* Soxhlet extraction in ethanol, followed by drying *in vacuo* at 50 °C. The products were obtained in quantitative yield. The FVE-IFs were characterized *via* scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) (Fig. S2–S4). SEM revealed the expected morphology of granular resins; the particles were irregularly shaped with significant crevices and other surface features but no observable long-range order or porosity in the micrometer range (Fig. 3B).

The library of FVE-IFs synthesized is shown in Table 1. The nucleophilic crosslinker loading is described by mole percent (mol%) incorporation relative to fluoroolefin repeat unit. Poly(HFP-*alt*-CEVE) was used as the primary FVE for FVE-IF synthesis due to safety concerns regarding transport and storage of CTFE.<sup>73</sup> However, representative experiments using poly(CTFE-*alt*-CEVE) to form FVE-IF-3 and FVE-IF-5 were successful, demonstrating the ability to synthesize FVE-IFs with diverse fluoroolefin monomers. Using *N,N,N',N'*-tetramethylethylenediamine (TMEDA) as a model nucleophile resulted in quantitative conversion of the soluble polymer to a crosslinked network, even when only 10 mol% of TMEDA was used (FVE-IF-1), or when CEVE incorporation was decreased (FVE-IF-6). Because a tertiary amine-based crosslinker was used, the nucleophilic substitution resulted in quaternary ammonium ion formation, such that network formation and permanent charge installation are achieved in one step. This represents an advance over existing technologies, which typically require separate reactions for network formation and quaternary ammonium group formation.

To investigate the effect of multiamine molecular weight and architecture, 1,1,4,7,7-pentamethyldiethylenetriamine (PMDTA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), and tris[2-(dimethylamino)ethyl]amine (Me<sub>6</sub>TREN) were each used as multiamines for FVE-IF synthesis (FVE-IF-8, FVE-IF-9, FVE-IF-10, FVE-IF-11). Incorporation of fluorinated tetraethylene glycol (FTEG) as a secondary nucleophile also resulted in network formation (FVE-IF-4, FVE-IF-5). FTEG incorporation





**Fig. 3** Synthesis of FVE-IFs. (A) Synthesis of FVE-IFs *via* nucleophilic substitution crosslinking. (B) SEM images of ground FVE-IF-2.

**Table 1** Library of FVE-IFs

Ref.	FVE	Multiamine		mol% FTEG
		Identity	mol%	
<b>FVE-IF-1</b>	Poly(HFP- <i>alt</i> -CEVE)	TMEDA	10	0
<b>FVE-IF-2</b>	Poly(HFP- <i>alt</i> -CEVE)	TMEDA	40	0
<b>FVE-IF-3</b>	CTFE- <i>alt</i> -CEVE	TMEDA	40	0
<b>FVE-IF-4</b>	Poly(HFP- <i>alt</i> -CEVE)	TMEDA	40	20
<b>FVE-IF-5</b>	Poly(CTFE- <i>alt</i> -CEVE)	TMEDA	40	20
<b>FVE-IF-6</b>	Poly[(HFP- <i>alt</i> -CEVE)- <i>co</i> -(HFP- <i>alt</i> -iBVE)]	TMEDA	40	0
<b>FVE-IF-7</b>	Poly(HFP- <i>alt</i> -CEVE)	TMEDA	94	0
<b>FVE-IF-8</b>	Poly(HFP- <i>alt</i> -CEVE)	PMDTA	37	0
<b>FVE-IF-9</b>	Poly(HFP- <i>alt</i> -CEVE)	HMTETA	74	0
<b>FVE-IF-10</b>	Poly(HFP- <i>alt</i> -CEVE)	Me <sub>6</sub> TREN	20	0
<b>FVE-IF-11</b>	Poly(HFP- <i>alt</i> -CEVE)	Me <sub>6</sub> TREN	40	0

introduced an additional fluorous component to the FVE-IFs, which we hypothesized would further improve PFAS sorption.

The resulting FVE-IFs were first subjected to PFAS remediation batch experiments under equilibrium conditions in simulated natural water. The parameters of this experiment are described in the SI and our previous work.<sup>39</sup> Briefly, simulated natural water was prepared by dissolving 200 mg L<sup>-1</sup> NaCl and 20 mg L<sup>-1</sup> humic acid in deionized water. The salt content mimicked the salt content of natural water; however, the humic acid loading was one to two orders of magnitude higher than what would be expected in a practical remediation scenario, making this a challenging experiment for non-selective sorbents. Next, the sorbent (10 mg L<sup>-1</sup>) was suspended in the solution, then stirred 3 hours to hydrate. Upon hydration,

the particles swelled marginally but retained the shape and structural integrity. For example, **FVE-IF-2** swelled ~50 wt% compared to its dry weight, which indicates that it is a loosely crosslinked polymer network (Table S2 and Fig. S5). Attempts to analyze their surface area through nitrogen adsorption were not successful, presumably because FVE-IFs behave like “gel” ion exchange resins with no permanent porosity. Finally, the solution was spiked with three representative PFAS at 1 μg L<sup>-1</sup> each, resulting in a 20 000 times excess of humic acid relative to each PFAS. After 21 hours of stirring, the solution was analyzed *via* Liquid Chromatography-Mass Spectrometry (LC-MS) to determine how much of each PFAS was removed by the sorbent. Control experiments without sorbent or with a commercial ion exchange resin were also performed. The figure of merit for this experiment is percent removal of each PFAS relative to a control with no sorbent present, where higher percent removals correlate to better sorbent performance (Fig. 4).

Batch equilibrium sorption results for the FVE-IFs revealed informative structure–property–performance relationships (Fig. 4). **FVE-IF-1**, with 10 mol% incorporation of TMEDA relative to repeat unit (equating to a maximum of 20 mol% incorporation of quaternary ammonium groups given TMEDA contains two tertiary amines), demonstrated poor PFAS removal. However, **FVE-IF-2**, with 40 mol% incorporation of TMEDA, demonstrated over 85% PFOA removal, 68% PFHxA removal, and 49% GenX removal. **FVE-IF-3**, synthesized using poly(CTFE-*co*-CEVE), demonstrated similar performance to **FVE-IF-2**, synthesized using poly(HFP-*alt*-CEVE), indicating there may be little to no effect on performance when replacing the HFP trifluoromethyl moiety with chloride. **FVE-IF-4** and







near-quantitative removal of PFOA and GenX, as measured by  $^{19}\text{F}$  NMR, and no removal of OA or HxA, demonstrating significant selectivity for fluorinated analytes. Meanwhile, the IX removed all PFOA and GenX, as well as 43% of OA and 36% of HxA. In a mixed solution of PFOA and OA, **FVE-IF-2** removed all detectable PFOA and 31% of OA, while IX removed 100% of both PFOA and OA. Likewise, in a mixed solution of GenX and HxA, **FVE-IF-2** removed 98% of GenX and 31% of HxA, while IX removed 100% of GenX and 46% of HxA. Therefore, in a mixed solution of fluorinated and non-fluorinated organic matter, both **FVE-IF-2** and IX are more selective for fluorinated molecules. However, **FVE-IF-2** demonstrated significantly higher PFAS selectivity than IX, as evidenced by the results with mixed PFAS and non-fluorinated organic matter, in particular the PFOA and OA solution, and as supported by the superior **FVE-IF-2** performance in the batch tests with simulated natural water depicted in Fig. 4. Coupled with the high GenX binding capacity, the selectivity of FVE-IFs for PFAS makes them a promising class of materials for translational application to water remediation systems.

## Conclusion

FVE copolymers are an underexplored class of functional materials. Here, we demonstrated a new class of Ionic Fluorogels that synergistically combine an FVE copolymer fluorinated matrix with ion exchange *via* cationic quaternary ammonium groups for selective PFAS remediation from simulated natural water. The resulting polymer networks are high-performing sorbents with excellent binding capacity for GenX as well as facile regenerability in a green solvent. Finally, when compared to commercial ion exchange resins under identical conditions, FVE-IFs outperform IX under both simulated natural conditions, and in high-concentration NMR studies. These FVE-IFs represent a significant advance in the development of translationally relevant PFAS sorbents, as the principles of Ionic Fluorogels have been demonstrated to be general across multiple classes of fluorinated polymers.

## Conflicts of interest

Two international patent applications have been filed by the University of North Carolina at Chapel Hill on technology related to ionic fluorogels, including PCT/US2020/047365 and PCT/US2022/013249. F. A. L., O. C. and I. M. H. have a financial interest in Sorbenta Inc.

## Data availability

The data that supports the findings of this study, including chemical and materials characterization, methods, and procedures, can be found in the supplementary information (SI). See DOI: <https://doi.org/10.1039/d5py00795j>.

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