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Article

Polymerized Molecular Receptors as Adsorbents to Remove Micropollutants from Water

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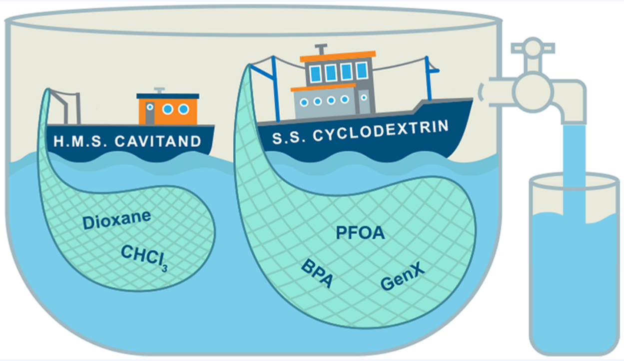

CONSPECTUS: Organic micropollutants (MPs) are increasing in number and concentration in water systems as a result of human activities. Often from human origin, these micropollutants build up in the environment because organisms lack the mechanisms to metabolize these substances, which cause negative health, ecological, and economic effects. Adsorption-based remediation processes for these compounds often rely on activated carbon materials. However, activated carbons are ineffective against certain MPs, exhibit low removal efficiencies in the presence of common aqueous matrix constituents, and require energy-intensive activation and regeneration processes. To overcome the deficiencies of traditional technologies, novel adsorbents based on molecular receptors offer promising alternative solutions. This Account describes the recent development of polymer adsorbents based on molecular receptors for removing trace organic chemicals from water. Polymer networks based on molecular receptors have high binding affinities for many MPs but, unlike activated carbons, have a specific molecule-binding mechanism that prevents these polymers from being fouled by matrix constituents such as natural organic matter. The size and hydrophobic pocket of the β-cyclodextrin receptor preferentially adsorbs target molecules such as organic micropollutants in the presence of matrix constituents, and the nature of the cross-linker tunes the binding affinity and selectivity of the adsorbent for specific classes of MPs, including those of varying charge and hydrophobicity. β-cyclodextrin polymers also exhibit rapid adsorption kinetics and are easily regenerated. This Account details β-cyclodextrin polymers made with three different cross-linkers, including a polymer that is postsynthetically transformed from a negatively charged polymer to a positively charged polymer to invert the polymer's micropollutant adsorption profile. Morphological constraints have so far limited these cross-linked polymers' ability to be used in commercial applications, but two methods to create larger and more uniformly sized particles for use in flow-through applications are described here. β-Cyclodextrin polymers are useful for trapping organic micropollutants such as bisphenol A, perfluorooctanoic acid, and many kinds of pharmaceuticals and pesticides, but their binding pockets are too large to capture micropollutants that are small or of high polarity. Other molecular receptors such as resorcinarene cavitands can target lower-molecular-weight MPs, including halomethane disinfection byproducts and industrial solvents, that are not bound strongly by β-cyclodextrins. These materials demonstrate the potential of expanding the library of polymers based on molecular receptors. Overall, these emerging adsorbents show promise for the removal of legacy and emerging MPs from water, as well as the ability to rationally tune the adsorbent's structure to target the most persistent and toxic MPs.

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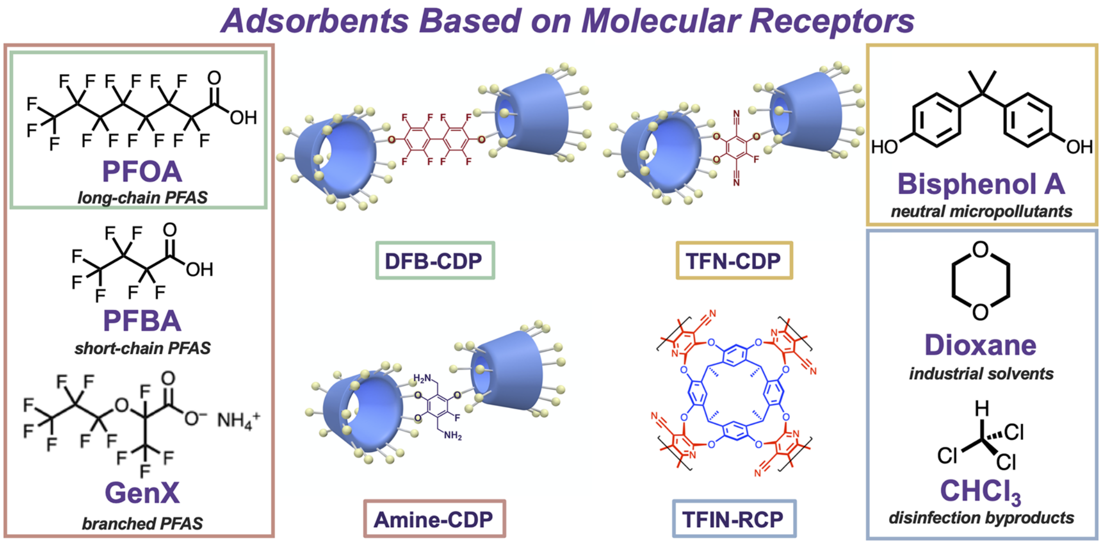

Figure 1. Representative micropollutants and the adsorbents developed to target them (β-CD polymer networks are represented as two blue cups linked by a representative substituted cross-linker). **TFN-CDP** targets a wide variety of micropollutants including bisphenol A and other neutral and cationic micropollutants. **DFB-CDP** targets long-chain PFAS like PFOA. **Amine-CDP** targets many types of anionic micropollutants including anionic PFAS like PFOA, PFBA, and GenX. **TFIN-RCP** targets the industrial solvent 1,4-dioxane and regulated trihalomethane disinfection byproducts (e.g., $CHCl_3$, $CHCl_2Br$, etc.).

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■ INTRODUCTION

Nearly 100 000 anthropogenic organic chemicals are registered for commercial use in the United States under the Toxic Substances Control Act.[5] These substances improve our lives when used as intended, but many organic chemicals persist in the aquatic environment following industrial discharge or use and disposal.[6] Once in the environment, many of these substances have negative effects on aquatic ecosystems and human health.[7] The emerging paradigm for sustainable human development recognizes that the occurrence of these so-called micropollutants (MPs) in freshwater resources is a major contemporary environmental and human development problem.[8] As a result, technologies have been developed to remove MPs from water resources. For example, ion exchange resins, zeolites, and more recently metal organic frameworks have all shown preliminary promise as remediation technologies.[9,10] However, advanced oxidation processes (AOPs) and adsorption using activated carbon (AC) have emerged as perhaps the most viable technologies with respect to efficacy and scalability,[11,12] though both exhibit technical deficiencies that limit their widespread adoption. For example, AOPs rely on chemical and energy inputs and may form undesirable chemical byproducts.[13] Activated carbon (AC) and other adsorption processes do not consume reagents, introduce substances into water, or generate chemical byproducts; however, adsorption on AC is limited by relatively slow adsorption kinetics,[14] low affinity for more polar MPs,[15] and inhibition by water matrix constituents.[16] Novel adsorbents that address these deficiencies will advance adsorption-based water remediation.

To develop a new generation of novel adsorbents, we hypothesized that porous polymers with discrete molecular binding sites might be used to remove MPs from impacted water resources more effectively than conventional adsorbents.[17−20] Since the 1960s[21,22] countless molecular receptors have been studied for their ability to form host−guest complexes in dilute solution,[23] including in water.[24] A small number of these receptors, including β-cyclodextrin (β-CD), have been proposed as scalable alternatives for adsorption-based water remediation technologies,[25−30] yet historically, polymers containing these receptors have not outperformed traditional adsorbents such as AC.

Cyclodextrins (CDs) are notable receptors used to create adsorbents for MPs. They are cyclic oligosaccharides containing glucose units linked by α-1,4-glycosidic bonds[31] and are produced from cornstarch at the industrial scale. α-, β-, and γ-CDs, which are composed of six, seven, and eight glucose units per oligosaccharide macrocycle, respectively, are commercially available. β-CDs specifically bind many organic compounds in water,[32] and adsorbents based on CD both bind organic MPs and resist fouling from dissolved organic matter found in natural and engineered water systems.[3,33−36] Early CD-based adsorbents were cross-linked with epichlorohydrin,[25−27,37] diisocyanates,[38−40] and poly(carboxylic acid)s,[41−44] though clear performance advantages over ACs were not observed. Wilson and co-workers showed evidence for anionic surfactants such as octanoic acid and perfluorooctanoic acid (PFOA) binding on the polymer−solution interface, first at binding sites, and then at interstitial sites.[45] These findings may explain why many early, nonporous polymers suffered from slow kinetics and low affinity for micropollutants such as PFOA[46] even though the β-CD⊂PFOA complex has a high association constant.[47] We introduced rigid, aromatic cross-linkers into a CD-based polymer, first tetrafluoroterephthalonitrile (TFN) and later others, that provided permanently porous, high-surface-area CD-based adsorbents that outperformed ACs in removing MPs from water.[1] We later explored many variants of the cross-linkers and charged groups to improve the polymerization yield and removal performance, and to specifically target fluorous MPs known as per- and polyfluoroalkyl substances (PFAS).[3,35] We

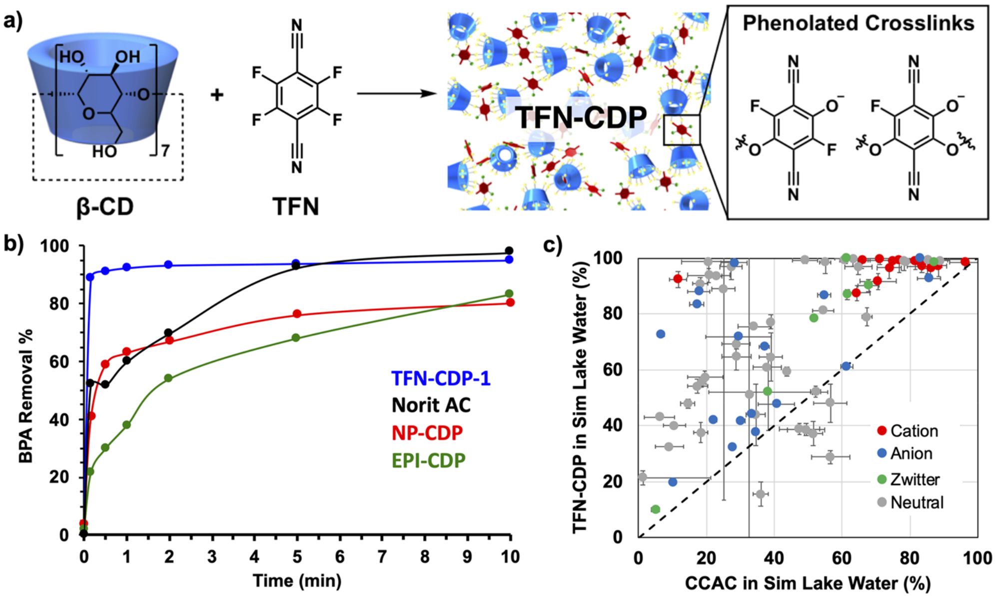


Figure 2. (a) **TFN-CDP-1** synthesis yields a high-surface-area cyclodextrin polymer, but there is a side reaction that leads to phenolated cross-links. (b) Bisphenol A removal kinetics show that the porous **TFN-CDP-1** has superior kinetics when compared to Norit activated carbon and nonporous cyclodextrin polymers cross-linked by TFN (**NP-CDP**) and epichlorohydrin (**EPI-CDP**) ($[\mathrm{BPA}]_0 = 22$ mg L^{-1}, [adsorbent] 1 mg mL^{-1}. (c) Flow-through removal of 83 different micropollutants in simulated surface water ($[\mathrm{MP}]_0 = 1$ μg L^{-1}, [adsorbent] = 1 mg loaded on to a membrane, [Humic acid] = 20 mg L^{-1}, [NaCl] = 200 mg L^{-1}, 8 mL total) shows that adsorption on **TFN-CDP-1** is not inhibited by matrix constituents, whereas adsorption on coconut shell activated carbon is inhibited.

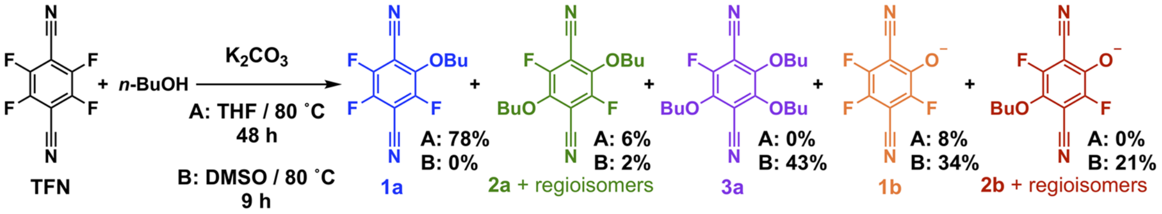
also changed the morphology of the polymer from a fine powder to granular, polymer-coated cellulose microcrystals to allow their use in both batch adsorption contactors and packed-bed filtration processes for water treatment.[36,48] Most recently, we leveraged a new receptor, a resorcinarene derivative, to remove industrial solvents and halomethane disinfection byproducts (DBPs) from drinking water.[4] This Account describes the synthesis, optimization, and use of supramolecular adsorbents for the removal of a wide variety of MPs from natural and engineered water systems and demonstrates the utility and modularity of using supramolecular adsorbents for advanced water treatment (Figure 1).

■ β-CD POLYMERS CROSS-LINKED BY TETRAFLUOROTEREPHTHALONITRILE

In 2016, we reported **TFN-CDP-1** (Figure 2A), a porous polymer composed of β-CD cross-linked by TFN.[1] **TFN-CDP-1** removed the MP bisphenol A (BPA)—a widely used chemical in the production of polycarbonates, epoxy resins, and other plastics—from water faster than two nonporous CDPs and three grades of AC, reaching equilibrium in seconds rather than minutes. The selection of the TFN cross-linker was in part inspired from polymers of intrinsic microporosity (PIMs), which achieve permanent porosity in the solid state by using rigid or contorted monomers.[49] These subunits frustrate efficient packing during drying of a PIM solution, providing voids in the resulting film. Although PIMs are soluble, linear polymers, we hypothesized that cross-linking β-CD with a rigid monomer such as TFN could create a network with frustrated packing and permanent porosity. Furthermore, we speculated that this permanent mesoporosity would provide rapid access to the β-CDs, resulting in rapid adsorption kinetics. **TFN-CDP-1** was prepared via a nucleophilic aromatic substitution reaction ($\mathrm{S_NAr}$), yielding a mesoporous powder with Brunauer−Emmett−Teller surface areas (S_{BET}) of 260 $\mathrm{m^2\ g^{-1}}$. The porous structure of **TFN-CDP-1** confers rapid MP adsorption. In these preliminary experiments, **TFN-CDP-1** reached equilibrium in seconds rather than minutes (Figure 2b). **TFN-CDP-1** was regenerated by washing with methanol at room temperature, which restored at least 98% of the polymer's original capacity over five regeneration cycles. It is important to note that these preliminary experiments were conducted at a high adsorbent dose and high MP concentrations ([adsorbent] = 1000 mg L^{-1}, $[\mathrm{BPA}]_0$ = 22 mg L^{-1}) that are neither economically nor environmentally relevant. Nevertheless, the fast kinetics and facile regeneration of **TFN-CDP-1** were sufficiently promising to prompt further investigations into the properties of this novel adsorbent at environmentally relevant conditions.

MP removal studies conducted under environmentally relevant conditions demonstrated that **TFN-CDP-1** exhibits high selectivity for cationic MPs over anionic MPs. Experiments were conducted with a mixture of 83 structurally diverse MPs at an initial concentration of 1 μg L^{-1} per MP in both batch and flow-through experiments. A set of batch experiments were conducted in Milli-Q-purified water (MQ) at an adsorbent loading of 10 mg L^{-1} of either **TFN-CDP-1** or coconut shell activated carbon (CCAC). Flow-through experiments where adsorbent was loaded on a membrane (1 mg for each adsorbent) were conducted in both MQ and simulated surface water ([NaCl] = 200 mg L^{-1}, [humic acid] = 20 mg L^{-1}). In kinetic batch experiments, **TFN-CDP-1** initially outperformed AC for the majority of the MPs tested, but after 5 min of contact time, the performance was comparable. As a general trend, **TFN-CDP-1** had a high affinity for cationic MPs and variable affinity for anionic and neutral MPs. In flow-through experiments where the matrix was MQ, **TFN-CDP-1** and AC exhibited characteristic selectivities, with neither material outperforming the other across all MPs. When simulated surface water was used as the matrix, **TFN-CDP-1** outperformed AC for 76 of the 83 MPs (Figure 2c). These data demonstrate that **TFN-CDP-1** exhibits

Scheme 1. Soluble Model Reaction in Which *n*-Butanol Was Used in Place of *β*-CD



a higher selectivity for binding MPs in preference to humic acid, which was used as a surrogate for natural organic matter (NOM). In real-world water treatment, NOM is omnipresent and often can inhibit the performance of AC, decreasing lifetime and performance. **TFN-CDP-1** does not suffer results inhibition from NOM because the uniformly sized CD binding pocket will not interact strongly with high-molecular-weight NOM (>1000 Da). In subsequent studies, we concluded that NOM of moderate molecular weight (600−1000 Da) and high-molecular-weight NOM do not inhibit adsorption of MPs on **TFN-CDPs**. However, low-molecular-weight NOM (<600 Da) does inhibit adsorption of MPs, further supporting the conclusion that **TFN-CDP-1** exhibits size-selective adsorption.[34] To learn more about cationic selectivity and deconvolute the mechanism of adsorption, further quantitative analysis of the MP affinity as a function of chemical descriptors was needed.

We achieved further understanding of the adsorption mechanisms of CDPs by developing quantitative structure−activity relationships (QSARs) that relate experimentally derived distribution coefficients (K_d) to a set of molecular descriptors.[50] This study further confirmed our understanding of the primary adsorption mechanisms and introduced a tool for predicting the adsorption affinity of large sets of untested MPs for **TFN-CDP-1**. The molecular descriptors related to electrostatic interactions, molecular size, and hydrophobic interactions carried the most predictive power for describing affinity of MPs for **TFN-CDP-1**. The electrostatic descriptors predict that cationic MPs will have a high affinity for **TFN-CDP-1**, which agrees with our findings of relatively rapid and complete removal of cationic MPs in our previous experimental studies.[33,36] Another significant descriptor represented the van der Waals volume of the MPs. The van der Waals volume descriptor had a positive correlation with affinity, indicating that larger MPs have a higher affinity for **TFN-CDP-1**. This predictor agrees with conventional wisdom that MPs below a certain size do not interact strongly with the interior cavity of the *β*-CD, though the increasing hydrophobicity of MPs of increasing van der Waals volume may also play a role in this predictor being selected into the QSAR. This QSAR workflow was also used to predict the affinity between AC and MPs, demonstrating the possibilities of using this method to accurately predict the affinity between other MP and adsorbent pairs.

Although we gained an improved understanding of the important adsorption mechanisms for one particular CDP, the QSAR results did not readily explain the molecular basis for the affinity of **TFN-CDP-1** for cationic MPs. Additionally, the low yield of the **TFN-CDP-1** synthesis complicated its scale-up for larger-volume testing. Therefore, we launched a mechanistic investigation into the **TFN-CDP-1** synthesis pathway to better understand the monomer reactivity and polymer structure. We investigated the S_NAr reaction pathway of the TFN-cross-linked CDP (**TFN-CDP**) using model studies and uncovered a previously unreported side reaction, the phenolation of TFN, that occurs under the polymerization conditions.[51] By controlling this side reaction, we increased polymerization yields and characterized the presence of phenolate groups in the polymer structure (Figure 2a). These negatively charged phenolate functional groups impart the unexpected selectivity for binding cationic MPs, and their prevalence in several **TFN-CDP-1** variants was positively correlated with their ability to simultaneously remove Pb^{2+} from water. Our original polymerization conditions provided **TFN-CDP-1** samples as insoluble powders in 18−40% mass recovery.[52] Mass recovery refers to the mass of the isolated polymer divided by the mass of the monomers used in the reaction. This calculation will inherently provide values below 100% because each ether bond formed in the polymerization corresponds to the formal loss of HF.

Nevertheless, mass recovery is the most logical metric for evaluating yield for different polymerization conditions, under which each polymer can differ in its cross-linking density. Prior to this work, polycondensation of TFN with catechols was used to access high-molecular-weight polymers, indicating efficient and selective reactions,[53] but there was only one report of an S_NAr reaction between TFN and an aliphatic alcohol.[54] We probed the S_NAr reaction through a soluble model reaction in which *n*-butanol was used in place of *β*-CD (Scheme 1). The reaction was relatively slow in THF with a major product of only one butyl ether per TFN (1a) after 48 h (Scheme 1, reaction A). This slow reactivity compounded with the low solubility of *β*-CD in THF likely contributed to the low polymerization yield of **TFN-CDP-1**. We also observed a side reaction in which one of the fluorines was replaced by a phenolate, likely due to potassium carbonate reacting with TFN (1b). We obtained higher polymer mass recovery (64%) by changing the reaction solvent to DMSO, producing the formulation **TFN-CDP-2**. When the model reaction was carried out in DMSO, the major product contained three butyl ether substitutions per TFN (3a) in less than 9 h (Scheme 1, reaction B), suggesting that DMSO increases polymerization yields by increasing the S_NAr reaction rate. This model reaction in DMSO also contained a significant quantity of products containing one butyl ether and one phenolate per TFN (2b + regioisomers). This side product indicated that there were likely phenolates introduced into the polymer during the polymerization (Figure 2a). New formulations of **TFN-CDP** were produced with decreasing phenolate concentration by decreasing the rate of base addition and increasing the reaction concentration, producing three additional **TFN-CDP** variants. **TFN-CDPs** with higher phenolation levels exhibited higher Pb^{2+} capacity and higher affinity for cationic MPs. Surprisingly, more-phenolated polymers also provided slightly higher affinity to neutral and anionic MPs, although none of the **TFN-CDPs** bind anionic substances strongly enough to be technologically useful. In fact, we observed that all **TFN-CDPs** had low affinity for the important class of anionic MPs known as PFAS.

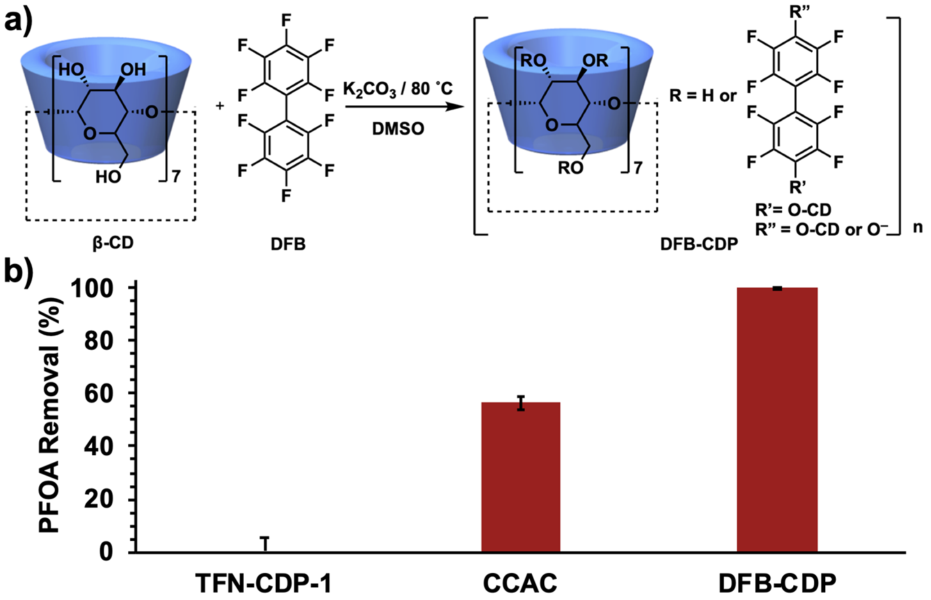


Figure 3. (a) Synthesis of **DFB-CDP**. (b) Equilibrium PFOA removal efficiency ($[\text{PFOA}]_0 = 1\ \mu\text{g L}^{-1}$) by equal mass concentrations of **TFN-CDP-1**, AC, and **DFB-CDP** ($[\text{adsorbent}] = 10\ \text{mg L}^{-1}$).

STRATEGIES FOR TARGETING PFAS

PFAS removal from water is of interest due to the compounds' prevalence, environmental persistence, and association with negative human health effects.[55,56] We targeted anionic PFAS removal through two approaches: first, using CDP cross-linkers with higher fluorine content to target long-alkyl-chain PFAS and later by using a postpolymerization modification of **TFN-CDP** to introduce cationic functional groups into the adsorbent to target a wide spectrum of long- and short-chain anionic PFAS.

Our first β-CD adsorbents to target PFAS removal from water were cross-linked with decafluorobiphenyl (**DFB-CDP**), which exhibited high affinity for perfluorooctanoic acid (PFOA).[35] We first focused on PFOA because of its links to ecological damage and negative human health effects including liver damage, thyroid disease, and cancer.[56] PFOA and unmodified β-CD have a high 1:1 association constant[47] on the order of $10^5\ \text{M}^{-1}$, so we attributed PFOA's low affinity for **TFN-CDPs** to the CDP's phenolated cross-linkers (Figure 2a). We screened several fluorinated aromatic cross-linkers under the hypothesis that a linker with increased fluorine content and decreased propensity to phenolation would increase the affinity of CDP absorbents. Polymers cross-linked by DFB emerged as adsorbents with the highest affinity for PFOA (Figure 3a). In a batch PFOA adsorption study at environmentally relevant concentrations ($[\text{PFOA}]_0 = 1\ \mu\text{g L}^{-1}$, $[\text{adsorbent}] = 10\ \text{mg L}^{-1}$), **DFB-CDP** removed PFOA to the limit of quantification (>99% removal) and outperformed both **TFN-CDP-1** (no detectable removal) and AC (modest removal, 54%, Figure 3b). **DFB-CDP** is much less prone to phenolation than TFN, but this side reaction does still occur under the polymerization conditions; a study of **DFB-CDP** samples with higher phenolate levels demonstrated their lower affinities for PFOA.[57] These experiments are consistent with the hypothesis that phenolation of CDPs lowers their affinity for anionic PFAS. Additionally, all **DFB-CDPs** tested had higher affinity for anionic PFAS and lower phenolate concentrations compared to **TFN-CDPs**.[57] We propose that a low negative surface charge allows anionic PFAS to better diffuse into the CD active sites. Although the **DFB-CDP** polymer has an excellent PFOA uptake ability, water systems contain a wide variety of PFAS of different alkyl chain lengths, functionalities, and 3D molecular shapes.[58,59] **DFB-CDPs** only show high affinity for anionic PFAS with alkyl chains of C7+, possibly due to the size-dependent hydrophobically driven binding mechanism of β-CD. To overcome this limitation, we designed a CDP that would operate on both hydrophobic and electrostatic binding mechanisms to remediate many PFAS and other anionic MPs.

To introduce a cationic functionality into a CDP, we performed a postpolymerization modification on a **TFN-CDP** to produce a new cationic CDP (**Amine-CDP**) that has high affinity for all anionic PFAS tested, including short-chain and branched PFAS.[3] Inspired by a similar transformation in a TFN-based PIM reported by Mason and co-workers,[60] we reduced the nitrile groups of a **TFN-CDP** to introduce amino groups, many of which will exist as cationic ammonium groups in neutral water. The nitrile groups in the TFN cross-linker are advantageous for the polymerization, as they pull electron density from the aromatic ring and increase its electrophilicity, which facilitates the $\text{S}_\text{N}\text{Ar}$ reaction. However, after the polymerization, the nitrile groups are unlikely to contribute strongly to MP adsorption. Upon reduction of the nitrile groups, we produced a benzyl amine-functionalized CDP (Figure 4a) with positive surface charge, as indicated by its ζ potential (+1.7 ± 0.8 mV). These values are more positive than those measured for the negatively charged parent **TFN-CDP** (−28.9 ± 0.7 mV) and the previous PFAS-targeting polymer **DFB-CDP**[57] (−14.5 ± 0.3 mV). Using combustion analysis, we estimated that at least 70% of the nitriles converted to amines.

The removal performance and adsorption kinetics of **Amine-CDP** were measured at environmentally relevant concentrations ($[\text{PFAS}]_0 = 1\ \mu\text{g L}^{-1}$; $[\text{CDP}] = 10\ \text{mg L}^{-1}$). **Amine-CDP** removes PFOA and perfluorooctanesulfonic acid (PFOS) rapidly, as the combined residual PFOA + PFOS concentration was 58 ng L^{-1} after 30 min (below the 2016 Environmental Protection Agency (EPA) health advisory level of 70 ng L^{-1} for PFOA and PFOS cocontamination) and reached an equilibrium aqueous phase concentration of approximately 25 ng L^{-1} after 9 h from an initial concentration of 2000 ng L^{-1}(Figure 4b). These

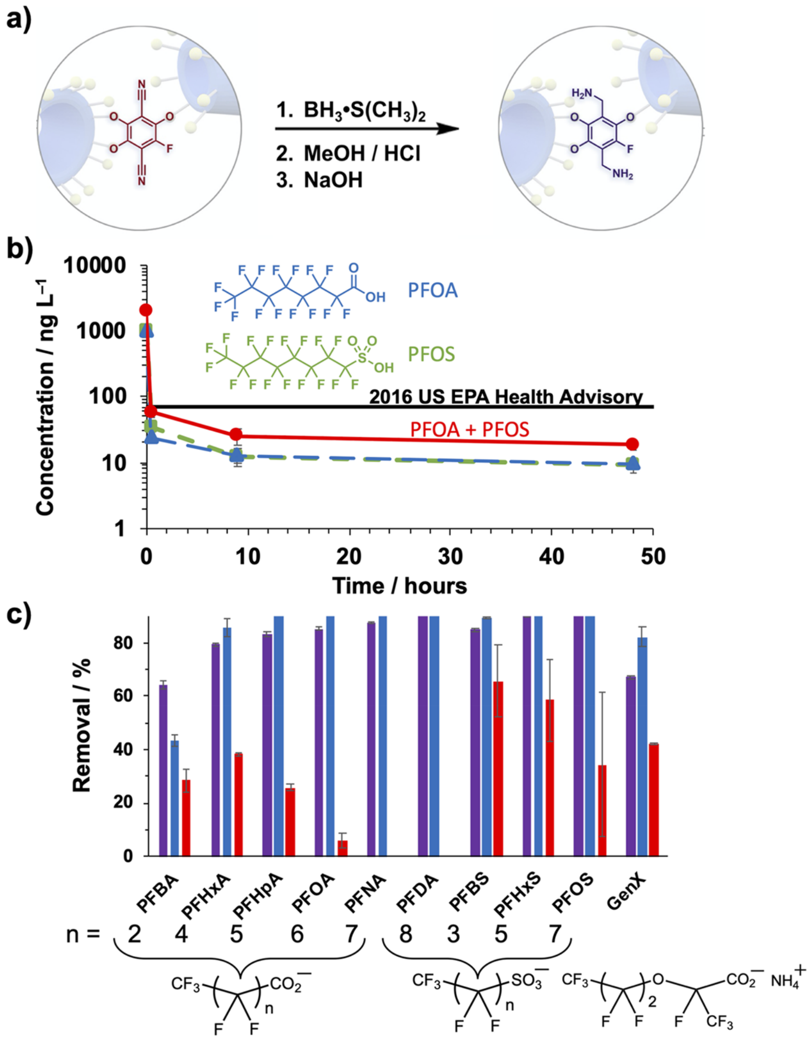


Figure 4. (a) Synthesis of **Amine-CDP** from **TFN-CDP**. (b) Removal of PFOA (green short dashed line), PFOS (blue long dashed line), and the combination of PFOA and PFOS (red solid line) as a function of time, demonstrating that the combined concentration of PFOA + PFOS is reduced from 2000 ng L^{-1} (1000 ng L^{-1} each) to below 70 ng L^{-1} within 30 min by 10 mg L^{-1} of **Amine-CDP**. (c) PFAS removal by **Amine-CDP** (purple), powdered AC (blue), and granular AC (red) with 30 min of contact time ($[\text{PFAS}]_0 = 0.5\ \mu g\ L^{-1}$; $[\text{CDP}] = 10$ mg L^{-1}).

observations agree with other recent studies suggesting that amine-containing polymers are effective for PFAS removal.[61−64] **Amine-CDP** also removed a wide spectrum of PFAS with different alkyl chain lengths and acidic head groups. In a batch removal study, **Amine-CDP** removed >60% of 10 structurally diverse anionic PFAS within 30 min, superior to granular AC and similar to powdered AC (which is typically not used for PFAS remediation because of problems with adsorption inhibition when in contact with matrix constituents) (Figure 4c). These findings demonstrate the tunability of CDP adsorbents available from a single polymerization.

CHANGING THE MORPHOLOGY OF CDPS FOR PACKED-BED FILTRATION APPLICATIONS

The adsorbents discussed above exhibit excellent adsorption performance, but their irregularly shaped powder morphology limits their applications to batch adsorption contactors, which are less practical for treating large volumes of contaminated water. In this section, we will discuss strategies used to change the morphology of CDPs and thereby expand their applicability to packed-bed filtration. We developed a preliminary granular formulation of **TFN-CDP-2** and later bonded the polymer onto the surface of cellulose microcrystals (CMCs). These developments enabled us to produce cartridges for solid phase extraction (SPE) and CDPs of uniform particle size for packed-bed filtration, respectively. The first solution was simply implementing a granular formulation of **TFN-CDP-2**.[36] The granularization of the material was achieved by forming the polymer as a solid gel and, after workup and drying, crushing the material into large chunks. This granular **TFN-CDP-2** was packed into solid phase extraction cartridges and benchmarked against commercially available hydrophobic lipophobic balance resin (HLB). The resulting **TFN-CDP** cartridge outperformed HLB in absolute recovery experiments in wastewater-impacted surface water samples, providing a superior and potentially more cost-effective alternative to common HLB resins. This report also demonstrated that **TFN-CDP** adsorbents could be regenerated from >90 different MPs using a simple wash with a solution of calcium chloride dissolved in methanol. However, this simple granulation approach produces a broad and uncontrolled distribution of particle sizes, which is sufficient for low-pressure applications like SPE but insufficient for high-pressure packed-bed filtration applications due to high back pressures and limited flow rate. To this end, we developed a

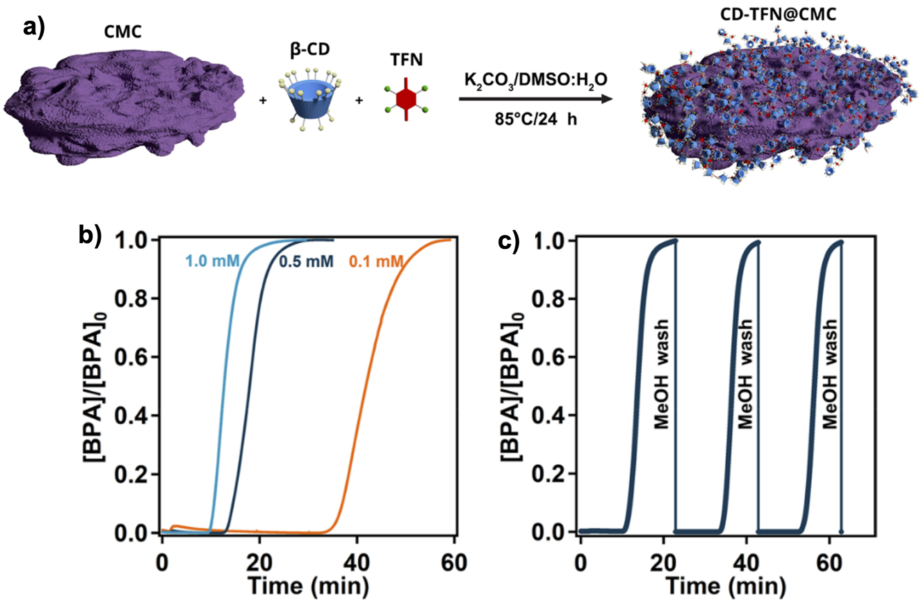


Figure 5. (a) Reaction scheme of the **CMC-CDP** synthesis. (b) Packed-bed uptake of BPA at three different BPA concentrations, measured as a function of time for **CMC-CDP** (200 mg) packed in a column. (c) Packed-bed regeneration of **CMC-CDP** (200 mg) packed in a column. Saturation was performed with a 1.0 mM BPA solution, and methanol was used for regeneration.

method for synthesizing the adsorbent polymer on low-dispersity CMC particles where the adsorbent particle size is controlled by the starting size of the CMC.

By introducing CMCs into the **TFN-CDP** synthesis, we produced adsorbent polymers grafted on the surface of uniform CMC particles, **CMC-CDP** (Figure 5a). When packed into a column for flow separation, **CMC-CDP** has a much lower back pressure than powdered **TFN-CDP** formulations and provides interpretable MP breakthrough curves at many flow rates. Characterization of these materials was achieved by cross-sectional transmission electron microscopy (TEM) of the CMC obtained before and after functionalization.[48] These TEM images show a polymer phase attached to the surface of the CMC particle after the polymerization. BPA column removal tests were carried out with **CMC-CDP** (200 mg) with various concentrations of BPA (1.0, 0.5, and 0.1 mM). These data showed rapid breakthrough curves, which indicate that **CMC-CDP** retains the fast MP removal kinetics observed in the **TFN-CDP** powder (Figure 5b). Flow regeneration of the column was carried out by saturating the column with a BPA solution (1 mM) and regenerating the column *in situ* by washing with methanol and equilibrating with clean water. After multiple adsorption−regeneration cycles, the capacity and breakthrough times were virtually unchanged (Figure 5c). These innovations in CDP morphology highlight the potential of CD-based adsorbent technologies in packed-bed filtration water remediation strategies. Furthermore, there are many alternative granulation strategies practiced in industry that can provide independent control of particle size and adsorbent composition as CD-based adsorbents are engineered for specific separation processes.

NEXT-GENERATION SUPRAMOLECULAR ADSORBENTS BASED ON RESORCINARENE CAVITANDS

DBPs like chloroform ($CHCl_3$) and water-soluble organic solvents like dioxane do not bind well to CDs due to their small size. Finding new ways to target these MP classes is of the utmost importance due to their known health effects.[65] Moreover, these contaminants have been shown to be pervasive in drinking water where utilities use free chlorine for water disinfection. For example, drinking water sampled from a fountain at Northwestern University in late 2018 contained $CHCl_3$ concentrations of ~30 μg L^{-1} (in compliance with the 80 μg L^{-1} EPA limit[66]). Additionally, 1,4-dioxane, an emerging contaminant and industrial solvent, has been detected in 22% of public water systems.[67,68] To target these smaller MPs, we explored resorcinarene cavitand (RC) receptors, whose synthesis and affinity for halomethanes were first explored by Cram and coworkers[69−72] (Figure 6a). We targeted smaller MPs by developing new adsorbents based on the RC supramolecular receptor. These adsorbents showed high affinity for halomethanes and 1,4-dioxane compared to commercially available adsorbents.

To embed cavitand structures in a polymer network, we developed a one-step cavitand formation/polymerization between two commercially available monomers, tetrafluoroisonicotinonitrile (TFIN) and resorcinarene (Figure 6a). This process yielded a porous yellow powder, **TFIN-RCP**, with S_{BET} of 1190 m^2 g^{-1}. We benchmarked this polymer against Filtrasorb 600 (FA600), an AC marketed for $CHCl_3$ removal. To simulate contaminated drinking water treatment, we challenged the **TFIN-RCP** to remove $CHCl_3$ from water taken from a fountain next to our laboratories (Figure 6b) ($[CHCl_3]_0$ = 32 μg L^{-1}, [adsorbent] = 30 mg L^{-1}) and benchmarked it against FA600. **TFIN-RCP** removed 84% of the $CHCl_3$ from the tap water, outperforming FA600, which removed 52%. Additionally, **TFIN-RCP** outperformed FA600 for the removal of other halomethanes such as CH_2Cl2, $CHBrCl_2$, $CHBr_2Cl$, and CCl_4 ($[DBP]_0$ = 80 μg L^{-1}, $[CCl_4]_0$ = 200 μg L^{-1}, [adsorbent] = 30 mg L^{-1}) in MQ water. **TFIN-RCP** was exploited further for dioxane removal from MQ ($[dioxane]_0$ = 100 μg L^{-1}, [adsorbent] = 500 mg L^{-1}) and was benchmarked against FA600 and Ambersorb 560, a commercial resin marketed for dioxane adsorption. **TFIN-RCP** removed 86% of the dioxane while both FA600 and Ambersorb 560 only removed 47% and

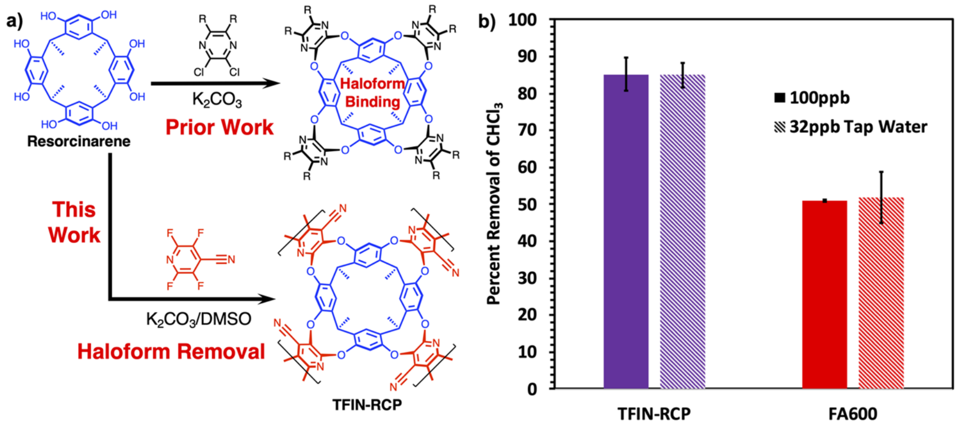


Figure 6. (a) Design of porous cavitand polymers. (b) Solid bars: removal of $CHCl_3$ (100 μg L^{-1}) from nanopure water by **TFIN-RCP** and FA600 (30 mg L^{-1}) after 24 h. Striped bars: removal of $CHCl_3$ (32 μg L^{-1}) from drinking water by **TFIN-RCP** and FA600 (30 mg L^{-1}). The residual $CHCl_3$ concentrations were determined using headspace-GCMS.

51% of the dioxane, respectively. The success of cavitand-based polymers further suggests that supramolecular chemistry can be used as a source of inspiration for the design of new adsorbents that remediate persistent and difficult-to-remove MPs.

OUTLOOK

Adsorbents based on supramolecular receptors are promising for MP remediation technologies, but challenges still remain. The challenges include cross-linker cost, morphological control, and targeting difficult-to-remove pollutants (those with low molecular weight and/or high water solubility). The occurrence of MPs at orders of magnitude lower concentrations than other background water constituents (e.g., NOM and anions) mandates the evaluation of adsorption inhibition in aquatic matrices. Although CDs and RCs are relatively inexpensive starting materials, the cross-linkers used, including TFN, DFB, and TFIN, are comparatively expensive. For many applications, these materials' costs will be offset by the need to use less adsorbents to achieve acceptable MP removal, contributing also to reduced infrastructure costs and less-frequent materials replacement, as well as multiple reuse cycles enabled by regeneration. Nevertheless, producing high-performance porous supramolecular adsorbents from inexpensive feedstocks remains desirable.

Morphological control is also important in increasing the utility of adsorbents; chemists developing novel adsorbents should carefully consider morphology and particle size when evaluating novel adsorbents. In early batch studies, these parameters will strongly affect kinetics and may lead to optimistic conclusions if the new adsorbent has a much smaller particle size than benchmarked materials. Promising materials eventually need to be produced with control of particle size, shape, and distribution to enable packed-bed separations or other removal experiments in flow. We have first addressed these challenges pragmatically using chemistry specific to CD polymers. However, there are many industrial methods available to control the particle sizes of new adsorbents that might eventually be used to transition promising new materials into legitimate separation technologies.

Difficult-to-remove pollutants include the myriad PFAS of varying charge and structural classification,[73] other organic MPs that resist removal from water by means of conventional treatment technologies,[74] inorganic chemicals of anthropogenic and geogenic origin,[75] and chemicals produced as byproducts of water treatment or water reclamation such as emerging types of DBPs[76] and other chemical or biological transformation products.[77,78] In our lab, we have explored CD- and RC-based adsorbents, but there are hundreds of supramolecular receptors that could be leveraged to remove a wide range of micropollutants with different properties (i.e., molecular size, geometrical configuration, hydrophobicity, aromaticity, polarity, and substituent groups).[19,79,80] Supramolecular receptors can even be designed to extract high-value commodities like lithium or gold from seawater.

As humans continue to produce products that improve our quality of life, we also increase the negative impact on the water resources upon which we depend. Although we do not fully understand the full implications of consuming MP contaminated water, remediation of MPs by molecular receptor-containing adsorbents is a good general strategy because of the rational design that can lead to selectivity, rapid MP uptake, and high affinities. Once design criteria for the removal of one or more MPs have been established in laboratory-scale systems, many factors will influence the relevance of a novel sorbent for these applications, including the ability to scale up a material and control important parameters such as particle size, as well as technoeconomic analysis of the use of the new polymer in engineered separation processes. Nevertheless, adsorbents that do not transition from the benchtop to commercialization remain valuable systems from which a deeper understanding of sorbent performance emerges. As depletion of freshwater resources continues, and wastewater reclamation is needed to supplement drinking and agricultural water, we believe that adsorbents based on molecular receptors have the potential to aid in the reclamation effort to provide clean water to the world.

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Notes

The authors declare the following competing financial interest(s): Northwestern University and Cornell University have filed a patent application based on the results described in this article. D.E.H. and W.R.D. serve on the scientific advisory board and own equity and/or stock options in CycloPure, Inc., which is commercializing related cyclodextrin polymers.

Biographies

Max Klemes graduated with a B.S. degree in Chemistry in 2014 from Ithaca College where he conducted his undergraduate thesis research on rhodium complex catalysis under the supervision of Prof. Anna Larsen. He received his Ph.D. in 2020 from Northwestern University focusing on the development of cyclodextrin-based adsorbents for water purification under the mentorship of Prof. William Dichtel. After completion of his Ph.D., he joined Intel, where he is currently a process engineer.

Luke Skala obtained his B.S. degree in Chemistry from the University of Maryland where he studied supramolecular assemblies under Prof. Jeffery T. Davis. In 2015 he moved to the National Institutes of Health where he worked under Dr. John Tisdale as an IRTA research fellow. In 2017 he moved to Northwestern's chemistry department to pursue his Ph.D. in chemistry with Prof. William Dichtel. His research is focused on bridging the gap between host-guest chemistry and functional materials.

Mohamed Ateia is a Research Associate in Department of Chemistry, Northwestern University. He received his B.S. degree (2009) from Alexandria University, Egypt, and his M.S. degree (2014) and Ph.D. (2017) from Tokyo Institute of Technology, Japan. Then, he moved to Clemson University as a postdoc before joining the Dichtel Group at Northwestern University. His research focus is on the development of new solutions for abatement of micropollutants in water by means of separation using novel adsorbents and composites and/or destruction using photocatalytic and electrochemical techniques.

Brittany Trang is a Ph.D. candidate in Prof. William Dichtel's group in the Department of Chemistry at Northwestern University. She has conducted research with Dr. Anne Staubitz at Christian-Albrechts Universität in Kiel, Germany, and with Dr. J. Nathan Hohman at the Molecular Foundry at Lawrence Berkeley National Lab. In 2017, she earned her B.S. degree in chemistry and English at the Ohio State University, where she studied the synthesis of new organic dyes for *p*-type dye-sensitized solar cells with Dr. Yiying Wu. At Northwestern, her Ph.D. research interests include developing new materials and methods for PFAS remediation.

Damian E. Helbling received his Ph.D. in civil and environmental engineering from Carnegie Mellon University in 2008. He was a postdoctoral research fellow at the Swiss Federal Institute of Aquatic Science and Technology (Eawag) from 2008 to 2013. He joined the faculty of the School of Civil and Environmental Engineering at Cornell University as an assistant professor in 2014 and was promoted to associate professor in 2019. His research group focuses on the inextricable link between human social mobility and technological development and the quality of freshwater resources. He is particularly interested in the occurrence and fate of anthropogenic organic chemicals in natural and engineered water systems.

William Dichtel is the Robert L. Letsinger Professor of Chemistry at Northwestern University. He holds a B.S. degree and Ph.D. in Chemistry from MIT and UC-Berkeley, respectively, the latter under the mentorship of Prof. Jean M. J. Fréchet. After a joint postdoctoral position at UCLA and Caltech with Profs. Fraser Stoddart and James Heath, prior to his current appointment at Northwestern (2016–present), he was on the faculty of Cornell University (2008–2016). His research interests span the synthesis, properties, and applications of novel polymer architectures. He is particularly interested in topics in multidimensional polymerization, polymer reprocessing, sustainability, and water purification.

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