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Calix[4]pyrrole-Crosslinked Porous Polymeric Networks for Micropollutant Removal from Water

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Abstract: Three calix[4]pyrrole-based porous organic polymers (P1-P3) have been prepared with the goal of removing organic micropollutants from water. A bowl-shaped $\alpha, \alpha, \alpha, \alpha$ -tetraalkynyl calix[4]pyrrole and diketopyrrolopyrrole monomer were crosslinked via Sonogashira coupling to produce a three-dimensional network polymer P1. This polymer, which proved too hydrophobic for use as an adsorbent, was converted to the corresponding neutral polymer P2 (containing carboxylic acid groups) and its anionic derivative (polymer P3 containing carboxylate anion groups) through post-polymerization structural modification of the pendent tert-butyl esters. The anionic polymer P3 outperformed its precursor neutral polymer P2 as determined from screening studies involving a variety of model organic micropollutants of different charge, hydrophilicity and functionality, including dyes, simple aromatics, and two cationic pesticides. Polymer P3 proved particularly effective for cationic micropollutants. The theoretical maximum adsorption capacity $(q_{max,e})$ of P3 determined from the corresponding Langmuir isotherms reached 454 mg g⁻¹ for the dye methylene blue, 344 mg g⁻¹ for the pesticide paraguat, and 495 mg g⁻¹ for diquat, respectively. These uptake values are significantly higher than those of most synthetic adsorbent materials reported to date. The present findings thus lend support to the conclusion that calix[4]pyrrole-based porous organic polymers may have a role to play in water purification.

Introduction

Organic micropollutants, including industrial dyes, pesticides, hormones, and pharmaceuticals, are prime contributors to water pollution.^[1] Many of these organic micropollutants, in particular aromatic compounds, are not easily degraded yet can cause considerable harm to both the environment and human health due to their potential mutagenic and carcinogenic effects.^[2] Certain organic micropollutants are recognized endocrine disruptors while others can lead to aesthetic concerns. Not surprisingly, therefore, wastewater treatments targeting organic micropollutants have attracted increasing attention in the scientific and industrial communities in recent years.^[3] A variety of treatment options have either been adopted or are under consideration, including chemical oxidation, photodecomposition, filtration, coagulation, flocculation, and adsorption. Currently, the latter is generally viewed as the favored choice in terms of simplicity, efficiency, and versatility.^[4] However, the most commonly used adsorbent materials, various activated carbons (ACs), suffer from several drawbacks, such as slow adsorption rates, poor removal efficiencies in the case of many hydrophilic micropollutants, and regeneration protocols that are energy-intensive.^[5] Compared to ACs, organic adsorbents are emerging as promising alternatives due to their potential advantages, including potentially control over molecular structure, high thermal and chemical stability, absence of heavy elements, and ease of post-synthetic modification.^[6] Within the context of this effort, porous organic polymers (POPs), typically cross-linked systems containing small molecule supramolecular recognition motifs connected by covalent bonds, have attracted particular attention, including for applications beyond water purification.^[7] Here we report a new set of POPs wherein calix[4]pyrrole serves as the key macrocyclic constituent.

Recently, several macrocyclic molecules have been used as crosslinkers to generate macrocycle-containing POPs, several of which exhibited considerable promise for the removal of micropollutants from water.^[8] Typically, the constituent macrocycles endow the material with host-guest encapsulation capacity, which often translates into an ability to target micropollutant molecules with different sizes, shapes, and charges (i.e., positive, negative, or neutral). In a seminal 2016 study, Dichtel et al. reported the preparation of porous βcyclodextrin-containing polymers (P-CDPs) and demonstrated that they were considerably more effective in terms of adsorbing a variety of organic micropollutants from water than other adsorbents, including ACs.^[9] Subsequently, a number of other macrocycles, including calixarenes, pillararenes, and

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calix[4]resorcinarenes, were incorporated into POPs frameworks and shown effective at removing a range of micropollutants, including *inter alia* radioactive iodine, per- and polyfluorinated alkyl substances, and halomethanes.^[8,10] However, calix[4]pyrroles, a well-studied class of non-aromatic tetrapyrrolic macrocycles,^[11] have yet to be used to create macrocycle-based POPs.^[12] In previous work, we showed that certain calix[4]pyrrole derivatives could be used to extract surrogate micropollutants from water. In such cases, two phase liquid-liquid extraction approaches were employed.^[13-15] However, the requirement for an organic receiving phase raises concerns that a potential secondary pollutant (the nonaqueous solvent) might be introduced into the environment when applied in non-specialty applications (e.g., radioactive waste remediation). We thus sought to prepare calix[4]pyrrole-based POPs that would achieve effective adsorption of micropollutants under solid-liquid conditions, thereby obviating the need for a secondary organic phase.



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Scheme 1. (a) Synthesis of porous organic polymers **P1-P3** based on α , α , α , α -tetraalkynyl calix[4]pyrrole and diketopyrrolopyrrole (DPP) monomers. Also shown is a cartoon representation of the polymer structure. (b) Photographs of the polymer products. (c) Chemical structures of organic micropollutants studied in this work. Cationic pollutants, anionic pollutants, and neutral pollutants are shown in blue, red, and purple, respectively.

Calix[4]pyrroles are readily accessible by simple acid-catalyzed condensation of pyrrole with various ketones. This allows calix[4]pyrrole to be functionalized readily at either the meso- or β -pyrrolic positions with a variety of functional groups, including those that facilitate polymerization or endow analyte selectivity.^[16] When pyrrole is reacted with 4'-iodoacetophenone, the calix[4]pyrrole reaction product is obtained as a mixture of four configurational isomers, including the tetra- α -isomer, which provides a bowl-shaped cavity in its cone conformation.^[17] In an

effort to create calix[4]pyrrole-based POPs, the α, α, α tetraalkynyl calix[4]pyrrole 5^[17] was chosen as the crosslinker and reacted with the diketopyrrolopyrrole (DPP) monomer 2^[18] under conditions of Sonogashira coupling to give polymer **P1** (Scheme 1a). Post-synthetic modification then gave **P2** and **P3**. The presence of the alkyne linkers was expected to endow the putative POP materials with high surface areas and enhanced adsorption capacities.^[10a,19] We further hypothesized that immobilizing the bowl-shaped calix[4]pyrroles within the polymer

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backbones would provide materials with locally defined spatial features, as well as recognition sites that might facilitate interactions with organic micropollutants. This design expectation was realized in the case of **P2** and **P3** with the latter proving particular effective as an adsorbent for cationic micropollutants. In fact, to our knowledge the maximum adsorption capacity of **P3** for the cationic test micropollutants, methylene blue and paraquat, is the highest among reported POP adsorbent materials, while that for diquat exceeds by a factor of 2.5 the capacity any other absorbent system of which we are aware.

Results and Discussion

Synthesis and Structural Characterization. The DPP monomer 2 and $\alpha, \alpha, \alpha, \alpha$ -tetra(4-[ethynylphenyl])calix[4]pyrrole (monomer 5) were synthesized according to previously reported procedures (Scheme S1 and Figures S1-S7).^[17,18] As depicted in Scheme 1a,

polymer P1 was prepared by subjecting monomers 2 and 5 to Pd(PPh₃)₄/Cul catalyzed Sonogashira coupling in a mixture of toluene and Et₃N (1 : 1) at 90 °C for 72 h. During the polymerization, a red solid gradually precipitated out. At the completion of the reaction, this precipitate was collected by filtration and washed successively with 1 M aqueous HCl, methanol, tetrahydrofuran, and acetone. The resulting solid was further purified by Soxhlet extraction with dichloromethane for 24 h to remove unreacted monomers and oligomers. Treating polymer P1 with trifluoroacetic acid served to remove the tert-butyl ester groups and give polymer P2 with free carboxylic acid groups. Subsequent treatment with aqueous sodium hydroxide at room temperature gave the anionic polymer P3 as a brown powder. Polymers P1-P3 proved completely insoluble in all solvents tested, including CHCl₃, THF, 1,4-dioxane, acetone, acetonitrile, MeOH, DMF, DMSO, and water. This insolubility was taken as initial evidence that covalently cross-linked porous materials were being formed.



Figure 1. (a) FT-IR spectra of monomers and P1-P3. (b) Solid-state ¹³C NMR spectra of polymer P1-P3. (c) N₂ adsorption curves of P1-P3. (d) TGA curves of P1-P3 recorded under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹.

Support for the proposed chemical structures of polymers **P1-P3** came from FT-IR and solid-state ¹³C NMR spectroscopic studies (Figure 1). The FT-IR spectrum of $\alpha, \alpha, \alpha, \alpha$ -tetra(4-[ethynylphenyl])calix[4]pyrrole (monomer **5**) shows stretching vibrations characteristic of a terminal alkyne at about 2108 cm⁻¹ (-C=C-) and 3285 cm⁻¹ (terminal alkyne -C-H). After polymerization (to give **P1**), neither terminal alkyne stretching vibration is visible in the corresponding IR spectrum. Meanwhile a new signal near 2210 cm⁻¹, ascribed to an asymmetric -C=C- stretching mode, appears. Additionally, a signal readily assigned to the

calix[4]pyrrole N-H stretch at 3400 cm⁻¹ is seen, as is one corresponding to the *tert*-butoxycarbonyl C=O stretch at 1733 cm⁻¹ in the FT-IR spectrum of **P1**. Such observations are consistent with the incorporation of the DPP and calix[4]pyrrole moieties into the POP material. After TFA treatment, the strong *tert*-butoxycarbonyl C=O stretching signal is almost absent from the FT-IR spectrum of **P2**. This is consistent with the expectation that this treatment promotes the elimination of isobutylene giving rise to the corresponding free carboxylic acid polymer.^[20]

The ¹³C NMR spectrum of **P1** exhibits broadened signals with chemical shift values in the range of 150-120 ppm and 120-110

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ppm corresponding to the carbons of the aromatic phenyl and pyrrole rings in the polymer frameworks, respectively. A broad peak near 180 ppm attributed to the carbonyl carbons of the DPP moiety is also seen, as is a broad peak near 95 ppm ascribed to the acetylene resonances (-C=C-) of the linkers.^[10a] Signals at about 50 ppm corresponding to the methylene carbon resonances of the calix[4]pyrrole are found in the ¹³C NMR spectra of **P1**, as they are in **P2** and **P3**. These observations provide support for the contention that the DPP and calix[4]pyrrole moieties are present in all three polymers. The peak at about 30 ppm in the ¹³C NMR spectrum of **P1**, corresponding to the methyl carbons of the *tert*butyl groups, is not found in the spectra of **P2** and **P3**, an observation taken as evidence that the *tert*-butyl ester groups were successfully cleaved during the conversion of **P1** to **P2**.

The porosity of these polymers was characterized by N₂ gas adsorption/desorption measurements. The nitrogen adsorption isotherms of the polymers can be categorized as type II, consistent with the existence of micropores and mesopores in the polymers. The polymers have an inferred pore size distribution mainly in the mesopore region, and non-local density functional theory calculations indicate the average pore diameters are 63 Å for P1, 34 Å for P2, and 24 Å for P3, respectively (Figure S8, Table S1). The Brunauer-Emmett-Teller (BET) surface areas are calculated to be 110 m² g⁻¹ for P1, 89 m² g⁻¹ for P2, and 32 m² g⁻¹ for P3, respectively. Both the surface area and pore width values decreased after subjecting P1 and then P2 to post-synthetic modifications, which may be due to partial filling of the pores or to the collapse of some of them during the ester hydrolysis and deprotonation reactions.^[10a]

All three polymers were subject to thermogravimteric analysis (TGA) (Figure 1d). The gradual weight loss of polymers at approximate 100 °C is attributed to the loss of adsorbed water. For **P1** evidence of apparent decomposition is seen starting at about 170 °C and ending at about 230 °C. This is correlated with a weight loss of about 10%, which corresponds to the theoretical weight reduction (~12%) expected for the elimination of isobutylene from the side chains of the DPP moiety. Such a weight loss is not seen for **P2** and **P3**. These analyses thus

provide support for the conclusion that both **P2** and **P3** are quite stable under nitrogen.^[20]

Polymer **P1** was found to be superhydrophobic and to float on water. The hydrophobicity of **P1** is consistent with the hydrophobic character of its constituents, including the *tert*-butyl ester groups. "Water regain" analyses reflected increased hydrophilicity when **P1** was subject to post-synthetic modification (Table S2). In particular , polymer **P3** was found to take up 27.5% of its own weight when dispersed in H₂O. The corresponding values are 15.7% and 5.9% for **P2** and **P1**, respectively.

The powder X-ray diffraction (PXRD) patterns of polymers **P1-P3** are characterized by the broad peaks seen for most POPs (Figure S9). This was taken as support for their proposed amorphous nature. The bulk morphology of the polymers was further characterized by scanning electron microscopy (SEM). All three polymers of this study act as dense amorphous monoliths with **P2** and **P3** showing features consistent with higher relative surface porosity as inferred from the SEM images (Figure S10).

Micropollutant Uptake and Separations Tests. Due to the poor hydrophilicity of P1, only P2 and P3 were evaluated as potential adsorbent materials for micropollutants. For these tests, a range of surrogate organic pollutants of different charges, hydrophilicity and functionality were used. As shown in Scheme 1c. our test series included both cationic (methylene blue) and anionic (methyl orange and Congo red) dyes, paraguat and diquat (dicationic, non-selective herbicides), the typical triazine herbicide atrazine, the plasticizer bisphenol A, and several neutral aromatic species (1-naphthyl amine and 2-naphthol). For each analysis, 5.0 mg of the polymer sample (P2 or P3) was suspended into an aqueous solution of the micropollutant (0.10 mM, 5.0 mL). After constructing appropriate calibration curves, the removal efficiency and the pollutant uptake could be calculated for each polymermicropollutant combination by monitoring the change in the UV-Vis absorbance intensity of the aqueous phase (Figures S11-S19, Table S3).



Figure 2. UV-Vis absorption spectra of aqueous solutions of methylene blue (a and e), paraquat (b and f) and diquat (c and g) (0.1 mM in all cases) in the presence of polymers P2 and P3 (1.0 mg mL⁻¹), respectively, recorded as a function of increasing adsorption times. Insets show the color change of the methylene blue solutions before and after the corresponding adsorption study. Time-dependence of the adsorption efficiencies for the adsorptive removal of various test micropollutants (0.1 mM in each) by POPs P2 (d) and P3 (h) (1.0 mg mL⁻¹).

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A first qualitative screening study revealed that polymer P2 was moderately effective at removing neutral micropollutants, such as bisphenol A, atrazine, and 2-naphthol, from an aqueous source phase under the above test conditions. However, it proved relatively ineffective as an adsorbent for cationic micropollutants, such as methylene blue, paraquat, and diquat (cf. Figures 2d and S20 and discussion below). A similar screening study carried out with the anionic polymer P3 revealed adsorption efficiencies that could be correlated closely with the micropollutant charge (Figures 2h and S21). In the case of the cationic micropollutants, almost complete removal from the aqueous source phase was seen when P3 was tested under the standard assay conditions given above, i.e., methylene blue (99.8%), paraquat (98.4%), and diquat (94.3%). In contrast, P3 proved much less effective as an adsorbent material for the neutral and anionic test species considered in the present study, with efficiencies of about 20%~50% and 15~40% being seen for these classes of micropollutants, respectively,

Generally. P3 outperformed its precursor polymer P2 in terms of removal efficiency. For instance, whereas P3 effected almost complete adsorption of paraguat and methylene blue, P2 removed only 4.4% and 26.5% of these positively charged species, respectively, under the same test conditions (Figure 2). However, similar uptake efficiencies (approaching 50%) were seen for P2 and P3 in the case of bisphenol A, a neutral micropollutant for which P2 proved relatively effective as compared to its performance for the positively charged test species. In the case of the anionic dyes, Congo red and methyl orange, contacting aqueous solutions of these surrogate micropollutants with P2 resulted in an immediate color change of the mixture, a finding that was ascribed to charge transfer interactions between P2 and these two anionic dyes. Support for this latter contention came from the observation of a new adsorption peak at the longer wavelength region of UV-Vis spectrum that gradually increased as a function of contact time (Figure S22).

The greater ability of P3 to adsorb cationic surrogate micropollutants as compared to P2 is rationalized in structural terms. In general, the uptake of a pollutant by an adsorbent depends on both the affinity of the molecular components within the material for the targeted species, as well as the physical features of the bulk material, such as pore size, effective charge, and pore volume. In our polymers, a number of putative factors can regulate the attraction between the adsorbent and adsorbate, including: (1) electrostatic interactions (dipole-dipole and monopole-dipole interactions); (2) host-guest effects involving the (3) $\pi - \pi$ donor-acceptor calix[4]pyrrole macrocycle; and solvophobic interactions involving, e.g., the aromatic cores of the pollutants and the hydrophobic surfaces of the polymer. The strong uptake of methylene blue, paraquat, and diquat by P3 leads us to suggest that electrostatic interactions play a dominant role in the case of these positively charged species. However, that anionic dyes were adsorbed by both P2 and P3 provides evidence for the hypothesis that the anion recognition sites afforded by the calix[4]pyrrole subunits present in the polymer backbones play a role in mediating the adsorption characteristics of these two porous materials.

We also compared the uptake of cationic micropollutants by **P3** and activated carbon (Acros, NORIT[®] A SUPRA) (Figure S23). It was found that both **P3** and this AC (1 mg mL⁻¹ in both) eventually removed almost all the methylene blue from a 0.1 mM aqueous

source phase. In contrast, only 68% of paraquat, and 49.6% of diquat could be adsorbed by the activated carbon under the same conditions, whereas **P3** effected nearly complete removal.

Adsorption Kinetics and Isotherms. The time required to achieve maximum removal revealed trends that mirrored the adsorption efficiencies. In general, **P3** took less time to reach equilibrium in adsorbing cationic pollutants than was required in the case of the test neutral and anionic micropollutants. For example, about 90% of the methylene blue is removed by **P3** within 10 min under our test conditions with apparent equilibrium being reached in about 15 min. In contrast, roughly 2 and 4 h were required to reach equilibrium in the case of the neutral species bisphenol A and the anionic dye methyl orange, respectively.

To obtain more quantitative information, the adsorption kinetics were fit using Ho and McKay's pseudo-second-order model (Figures S24-S25 and Table S3a).^[21] The good fits (correlation coefficients $R^2 > 99\%$) to this pseudo-second order kinetic model is consistent with the adsorption of the dye following a chemisorption mechanism, likely driven by electrostatic attraction effects.^[22,23] The apparent rate constant (k_{obs}) for the adsorption of the cationic and neutral surrogate pollutants by **P3** are in the range of 0.01-0.06 g mg⁻¹ min⁻¹, while the k_{obs} value proved much lower in the case of the anionic test micropollutants.

In order to gain insight into the rate determining step involved in the adsorption of the three cationic substrates, methylene blue, paraquat, and diquat, by P3, the uptake data were analyzed in terms of Weber's intra-particle diffusion model (Figure 3b).[24] Generally, the adsorption of micropollutant from solution into an adsorbent includes three consecutive steps: External diffusion, pore diffusion (intraparticle diffusion), and adsorption on the pore surface.^[25] In the case of P3, a double linear pattern is seen for each cationic pollutant, and the two straight lines do not pass through the origin. Such a finding is taken as evidence that intraparticle diffusion is not the sole rate-limiting step, and the overall adsorption process may be controlled by multiple-diffusion steps.^[26] The first fitting line in this diffusion model may be attributed to the transfer of the adsorbate molecule from the solution to the adsorbent surface, while the second fitting line likely reflects intraparticle diffusion within P3 (Figure 3d). For the cationic pollutants, k_{i1} is larger than k_{i2} , indicating external diffusion is rapid while intraparticle diffusion is more gradual.

The effect of different initial pollutant concentrations on the adsorption process was studied in the case of P3. The higher the initial concentration of the pollutant, the higher the adsorption. This finding is rationalized in terms of a greater driving force for mass transfer. As shown in Figure 3c, the equilibrium uptake by P3 as a function of residual pollutant concentration after adsorption could be fit well to the Langmuir model as expected for a system where the adsorption sites are identical.^[27] The maximum adsorption capacity $(q_{\max,e})$ of P3 determined from the Langmuir isotherm was estimated to be 454 mg g⁻¹ for methylene blue ($R^2 = 0.9841$), 344 mg g⁻¹ for paraquat ($R^2 = 0.9907$), and 495 mg g⁻¹ for diquat ($R^2 = 0.9906$). These results provide support for the conclusion that the adsorption capacities of P3 for these test cationic micropollutants are superior to those of most recently reported adsorbents. Particularly, the maximum adsorption capacity of P3 for paraquat and diquat is the highest among the reported POPs;^[10d] that for diquat by P3 exceeds that of any other adsorbent of which we are aware. Comparisons between the adsorption capacity of P3 and other adsorbents are provided in Tables S4-S6.

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Figure 3. Fits to a pseudo-second-order model (a) and intra-particle diffusion model (b). Langmuir adsorption isotherms (c) for the adsorption of cationic pollutants by P3. Calculated parameters for the indicated kinetic and adsorption isotherm models of cationic pollutant uptake by P3 (d).

Binary-Component Adsorption Studies. The ability of P3 to adsorb cationic micropollutants effectively in single substrate tests led us to explore how this adsorbent material system (1 mg mL⁻¹) would function when exposed to an aqueous binary dye mixture consisting of methylene blue and methyl orange (0.1 mM in each). As can be seen from an inspection of Figure 4, under these experimental conditions, roughly 70% of the methylene blue is adsorbed in the first 10 minutes, a quantity that gradually increased to an apparent equilibrium value of 92% within 1 h. Simultaneously, only 3 minutes were required to reach the maximum removal value for methyl orange (44%). This latter value then gradually decreased with time before an apparent equilibrium efficiency of 24% is reached after approximately 30 minutes. The color of the mixed methylene blue-methyl orange aqueous solution (Figure 4a inset) changed during the course of this adsorption experiment from an initial deep green to orange reflecting the dominant residual presence of non-adsorbed methyl orange at equilibrium. Relative to the corresponding monocomponent experiments, the removal efficiency of methylene blue in the binary dye study was decreased by ca. 8%, while that for methyl orange increased by 9%. Similarly, for methylene blue and congo red binary aqueous solutions, the removal efficiencies of

methylene blue and congo red were ca. 96% and 56%, respectively. These values are decreased by roughly 4%, and increased by approximately 14% compared to the corresponding mono-component experiments. However, for binary mixtures consisting of diquat and methyl orange, the removal efficiencies decreased to about 64% and 2.3%, respectively. As noted above, we postulate that cationic and anionic micropollutants largely occupy different sites within the polymer. Specifically, we suggest that the cationic micropollutant is bound predominantly to the carboxylate anions of polymer P3 through electrostatic attraction effects, whereas the anionic dye is accommodated via host-quest interactions involving the calix[4]pyrrole subunits or via less specific π - π donor-acceptor interactions involving the POP structure as a whole. As a result, appreciable competitive adsorption involving the anionic and cationic micropollutant surrogates is not expected. However, this is an oversimplification since interactions between the micropollutant and the POPs, as well as between the two species in question are expected. Such effects, which are expected to be a complex function of size, charge density, solvation effects, and possibly ion pairing, could account for the generally modest (but readily discernible) difference in adsorption behavior seen on moving from the singlecomponent to the two-component source mixtures.

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Figure 4. Simultaneous adsorption of cationic and anionic micropollutants by P3 (1 mg mL⁻¹) seen upon exposure to binary aqueous solutions consisting of the indicated two surrogate micropollutants (0.1 mM in each). UV-Vis absorbance spectra of respective methylene blue-methyl orange (a), methylene blue-congo red (b), and diquat-methyl orange (c) binary aqueous solutions in contact with P3 recorded at different time points. Inset shows the color of the aqueous solution before and after contact with P3 and presumed differential adsorption of the two test dyes. Time-dependent adsorption efficiency of methylene blue-methyl orange (d), methylene blue-methyl orange (f) binary aqueous solutions.

We studied the desorption of methylene blue from P3 in an effort to assess its potential reusability. Simply rinsing with polar solvents (DMF or ethanol) or dilute protic acid (1 M H₂SO₄) at room temperature failed to release appreciable quantities of the bound methylene blue dye as inferred from UV-Vis spectral studies. This finding was taken as further evidence that this organic cationic dye was adsorbed effectively, presumably as the result of strong electrostatic interactions. However, effective dye release and regeneration of the POP system could be achieved by physically removing the polymer (ca. 5 mg) from the initial aqueous solution, stirring in 1 M H₂SO₄ solution (5 mL) for about 10 h at 80 °C and then treating with aqueous NaOH (0.5 M) to convert the adsorbent back to its carboxylate anion form. Three consecutive methylene blue adsorption/desorption cycles were performed (cf. Figure S26). It was found that the methylene blue removal efficiency decreased about 10% after the three recycling/regeneration cycles.

Conclusion

In summary, we report here the first calix[4]pyrrole-based porous organic polymers and tests of their potential for water purification. The structure of the present porous polymers could be easily modified by converting the pendent *tert*-butyl esters to carboxylic acid and carboxylate groups. The anionic polymer **P3** was found to out-perform its neutral polymer precursor **P2** in terms of removing the majority of the surrogate micropollutants considered in this study from an aqueous source phase. In particular, polymer

P3 exhibited excellent adsorption capacity for cationic micropollutants. This ability is ascribed to dipolar interactions between the carboxylate anions of the DPP moieties, as well as nonpolar interactions involving the constituent aromatic rings and alkynes of the polymers. Furthermore, polymer **P3** could be treated with strongly acidic aqueous media to release the bound micropollutant methylene blue. It could then be regenerated by treating with aqueous NaOH and reused with only modest loss in function. The results reported here illustrate the structural tunability of calix[4]pyrrole-based POPs, and provide support for the contention that systems such as **P2** and **P3** may have potential utility in the area of water purification.

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RESEARCH ARTICLE

Entry for the Table of Contents



The calix[4]pyrrole-based porous organic polymers have been prepared for water purification. The structure of the polymer **P1** could be easily modified by converting the pendent *tert*-butyl esters to carboxylic acid and carboxylate groups. The anionic polymer **P3** showed particularly effective adsorption for cationic micropollutants. And the theoretical maximum adsorption capacity ($q_{max,e}$) of **P3** determined from the corresponding Langmuir isotherms reached 454 mg g⁻¹ for the dye methylene blue, 344 mg g⁻¹ for the pesticide paraquat, and 495 mg g⁻¹ for diquat, respectively.