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# Redox-responsive Covalent Organic Nanosheets from Viologens and Calix[4]arene for lodine and Toxic Dye Capture

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Abstract: Owing to their chemical and thermal stabilities, high uptake capacities, and easy recyclability, covalent organic polymers (COPs) have shown promise as pollutant sponges. Here, we describe the use of diazo coupling to synthesize two cationic COPs, COP1\*\* and COP2\*\*, that incorporate a viologen-based molecular switch and an organic macrocycle, calix[4]arene. Both COPs form nanosheets with height profiles of 6.00 and 8.00 nm, respectively, based on AFM measurements. The sheets remain morphologically intact upon one- or two-electron reductions of their viologen subunits. MD simulations of the dicationic COPs indicate that calix[4]arene adopts a partial cone conformation and that, in height, the individual 2D polymer layers are 5.48 Å in COP1\*\* and 5.65 Å in COP2\*\*, which, together with the AFM measurements, suggests that the nanosheets are composed of 11 and 14 layers, respectively. The COPs, in either dicationic, radical cationic, or neutral form exhibit high affinity for iodine, reaching up to 200% mass increase when exposed to iodine vapor at 70 °C, which makes the materials among the best-performing nanosheets for iodine capture reported in the literature. In addition, the COPs effectively remove Congo red from solution in the pH range of 2 - 10, reaching nearly 100% removal within 15 minutes at acidic pH.

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#### Introduction

Molecular switches are molecules that can reversibly switch between two or more stable states upon exposure to external stimuli such as light, temperature, specific pH, or a reducing environment.<sup>[1]</sup> Derivatives of 4,4'-bipyridine known as viologens, are a class of redox-active molecular switches that can exist in dicationic, radical cationic, or neutral states,<sup>[2]</sup> with each state characterized by unique physical and chemical properties. For example, dicationic viologens are aromatic and hydrophilic, whereas neutral ones are antiaromatic, hydrophobic, and Lewis basic. Because of their diverse properties that can be accessed in a single molecule by means of simple reduction or oxidation reactions, viologens have been incorporated into covalent organic polymers (COPs)<sup>[3-7]</sup> and covalent organic frameworks (COFs)<sup>[8]</sup> for the construction of robust stimuli-responsive materials. We recently showed, for instance, that changing the redox state of a viologen in a COP affected the material's selectivity for specific dyes.<sup>[9]</sup> Here, we describe the combination of a viologen with an organic macrocycle, calix[4]arene, for the synthesis of two redox-switchable, azo-bridged COPs.

Calix[n]arenes (n = 4, 6, 8) are well-known organic macrocycles with a hydrophobic cavity and easily functionalizable upper and lower rims for guest recognition.<sup>[10]</sup> Because of these structural characteristics, calix[n]arenes have been incorporated into polymers, but mostly as side-chain moieties.[11-13] Only a few polymers having calixarenes in their main chains have been reported in the literature.<sup>[14]</sup> We postulated that incorporating both positively charged viologens and calix[4]arenes within the backbone of COPs would produce multifunctional materials useful for pollutant adsorption. For instance, it is known that viologens<sup>[15]</sup> and other  $\pi$  electron-rich organic groups<sup>[16,17]</sup> have high affinities for iodine and iodides. For example, cationic viologens are known to bind negatively-charged polyiodides such as I<sub>3</sub><sup>-</sup>, I<sub>5</sub><sup>-</sup>, I<sub>7</sub><sup>-</sup> etc. through electrostatic interactions.<sup>[15]</sup> Furthermore, it has been reported that calix[n]arenes have the ability to bind toxic anionic azo dves such as Congo red.<sup>[14,18]</sup> Reactive Black<sup>[19]</sup> and Direct Blue,<sup>[20]</sup> among others.<sup>[21]</sup> This property is the result of noncovalent interactions including (i) hydrogen bonding involving the OH-rich lower rim of calix[4]arene; (ii)  $\pi$ - $\pi$  interactions between the phenyl rings of the macrocycles and the dyes; and (iii) in some cases, ionic interactions between positively-charged calix[n]arenes and negatively-charged dyes.

The azo-bridged viologen- and calix[4]arene-containing COPs reported here, **COP1**<sup>++</sup> and **COP2**<sup>++</sup>, serve as efficient Congo red sorbents in aqueous solution from pH 2 to 10. They are also

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potent iodine sorbents capable of adsorbing up to 200% of their weight in iodine vapor. Interestingly, these materials exhibit nanosheet morphology regardless of the redox state of their constituent viologens. According to AFM measurements, the dicationic sheets have height profiles of 6.00 and 8.00 nm, and molecular dynamics (MD) simulations indicate that single layers are 5.48 Å and 5.65 Å thick in **COP1**<sup>++</sup> and **COP2**<sup>++</sup>, respectively, which implies that the nanosheets observed by AFM are composed of 11 layers in **COP1**<sup>++</sup> and 14 layers in **COP2**<sup>++</sup>.

#### **Results and Discussion**

# Synthesis and characterization of azo-bridged **COP1**<sup>++</sup> and **COP2**<sup>++</sup>

The synthesis of **COP1**<sup>++</sup> and **COP2**<sup>++</sup> was accomplished by diazo bond formation<sup>[22]</sup> between a nitro derivative of calix[4]arene (*p***TNC4A**)<sup>[23]</sup> and two different viologen-based diamines (1 and 2) in presence of a strong base (Scheme 1, synthetic procedure in Experimental Section). The reaction was carried out in a Schlenk tube using dimethylformamide (DMF) as a solvent for 24 h at 150 °C. The resulting polymers were purified by Soxhlet extraction with DMF, tetrahydrofuran (THF), water and ethanol. Both materials were obtained as dark brown powders, which were stable at highly acidic and highly basic pH (Figure S1), and insoluble in DMF, THF, ethanol, acetone, diethyl ether and DMSO.

Molecular-level characterization of COP1\*\* and COP2\*\* was accomplished with Fourier transform infrared (FTIR) spectroscopy and cross polarization magic angle spinning (CP-MAS) <sup>13</sup>C solid state nuclear magnetic resonance (NMR). Peaks corresponding to NO<sub>2</sub> groups, which appear at 1336 cm<sup>-1</sup> and 1516 cm<sup>-1</sup> in the FTIR spectrum of **pTNC4A**, are absent in spectra of the polymers (Figure S2), indicating successful coupling. A weak peak at 1550 cm<sup>-1</sup> that corresponds to N=N bond vibration is also present in the spectra of both COPs. CP-MAS spectra show peaks in the range of 140 - 180 ppm that are consistent with aromatic carbons as well as peaks near 37 ppm that correspond to the aliphatic methylene bridges of calix[4]arene (Figure S3). Peaks at 163 and 162 ppm are due to the aromatic carbons directly bonded to the N of viologen in COP1\*\* and COP2\*\*, respectively. Peaks at 127 and 129 ppm

are consistent with other aromatic carbons of the linkers, and peaks at 138 and 140 ppm correspond to aromatic carbons of calixarenes in **COP1**<sup>++</sup> and **COP2**<sup>++</sup>, respectively. A peak at 63 ppm in the spectrum of **COP2**<sup>++</sup> corresponds to the methyl bridge in the linker. FTIR and NMR analyses both confirm the formation of **COP1**<sup>++</sup> and **COP2**<sup>++</sup> as shown in Scheme 1.

The powder X-ray diffraction (PXRD) patterns of **COP1**<sup>++</sup> and **COP2**<sup>++</sup> exhibit broad signals corresponding to the amorphous nature of the materials (Figure S4). Thermogravimetric analysis (TGA) demonstrates that the polymers have enhanced thermal stability up to 400 °C (Figure S5). Gas adsorption experiments demonstrate that **COP1**<sup>++</sup> and **COP2**<sup>++</sup> have modest Brunauer-Emmett-Teller (BET) surface areas of 17.9 and 51.8 m<sup>2</sup> g<sup>-1</sup> (Figure S6). Average pore diameters as determined by the Barrett-Joyner-Halenda (BJH) analysis are 192.7 Å and 148.7 Å, respectively (Figure S6).

Taking advantage of the viologen subunits in COP1++ and COP2\*\*, we performed one- or two-electron reductions to obtain radical cationic polymers COP1\*\* and COP2\*\*, and neutral polymers COP1º and COP2º, respectively. One-electron reductions were achieved with sodium dithionate (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) in degassed water under N<sub>2</sub> atmosphere. Although no color change was observed for either COP, due to their dark color in the dicationic state, electron paramagnetic resonance (EPR) spectra show a peak at 338 mT, confirming the formation of radical species in both COP1\* and COP2\* (Figure S7). We also analyzed solid state UV-Vis spectra of the as-synthesized and reduced polymers (Figure S8). The spectrum of COP1\* exhibits a strong peak at ~420 nm, analogous to that seen in spectra of monomeric viologen radicals.<sup>[24]</sup> A peak at ~600 nm also confirms the formation of viologen radicals.<sup>[15]</sup> On the contrary, the spectrum of COP2+ does not contain a strong reflectance band at 420 nm, which suggests that the radicals do not exist as monomers but rather as dimers. In addition, the Raman spectrum of COP1+ shows a peak at 1560 cm-1, which is characteristic of radical monomers (Figure S9).[25] This peak is absent in COP2\*\*, which further confirms radical dimerization in **COP2**<sup>+•</sup> that is likely due to flexibility of the viologen linker. EPR, solid state UV-Vis and Raman spectroscopy confirmed that both COP1\* and COP2\* radical cations were successfully formed. Upon prolonged exposure to air for several days, the radical character of the materials disappeared.



Scheme 1. Schematic illustration of the synthetic route to COP1++ and COP2++.

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Figure 1. Characterization of the morphology of COP1<sup>++</sup> by SEM (A), TEM (B) and AFM (C, D); and that of COP2<sup>++</sup> by SEM (E), TEM (F) and AFM (G, H). The measured height profiles are 6.00 and 8.00 nm for COP1<sup>++</sup> and COP2<sup>++</sup>, respectively.

To synthesize the fully reduced COP1º and COP2º, COP1++ and COP2++ were reacted with an excess of bis(cyclopentadienyl)cobalt(II) (cobaltocene) in degassed acetonitrile under N2 atmosphere. As expected, solid state EPR spectra of COP1º and COP2º show no signal. FTIR spectra of the COPs after one- or two-electron reductions (Figure S10) are similar to those of the corresponding COP1\*\* and COP2\*\* with minor differences, including a small additional peak near 860 cm<sup>-</sup> <sup>1</sup> in the spectrum of **COP1**<sup>0</sup> and a change in the shape of the peak at 1265 cm<sup>-1</sup> in the spectra of both COP1+ and COP1<sup>0</sup>, which can be attributed to previously described changes in the geometry of the viologen subunit upon reduction.<sup>[26]</sup> No peak appears in the EPR spectrum of the materials even after a week of exposure to air. This suggests that neutral COP1º and COP2º are stable species which do not get spontaneously oxidized into radical cationic and afterwards to dicationic materials when exposed to air.

# Experimental and theoretical investigation of nanosheet morphology

The morphology of **COP1**<sup>++</sup> and **COP2**<sup>++</sup> was investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) (Figure 1). SEM images hint at the nanosheets which are rolled on top of one another (Figures 1A and 1E). TEM images clearly show thin individual nanosheets in both COPs (Figures 1B and 1F). Neither of the reductions (one and two electron) changed the nanosheet morphology, as demonstrated by SEM and TEM images recorded after reductions (Figure S11). Observations by TEM were further confirmed by AFM (Figures 1C and 1G), which shows individual stacks of nanosheets. A typical stack is about 1 – 3  $\mu$ m in width and length and has a height profile well under 10 nm, as illustrated by Figures 1D and 1H.

To further investigate the formation of the nanosheets, we performed MD simulations of **COP1**<sup>++</sup> and **COP2**<sup>++</sup>. Although monomeric and dimeric calixarene derivatives have been studied extensively using both quantum mechanical<sup>[27-30]</sup> and

classical molecular mechanics approaches,<sup>[31-34]</sup> MD simulations of covalent calixarene-based polymeric systems are still rare.<sup>[35]</sup> Initial structures of the repeating units of COP1\*\* and COP2\*\* were constructed in primitive unit cells such that parallel layers of sheets were stacked on top of each other in the first set (Figure S12). Chloride ions were added to neutralize the simulation box. These models were denoted as AA stacking sheets. In the second set of simulations, we varied the unit cell geometry in the initial models such that the interlayers are slid by half of the repeating unit in one of the directions. These constructs were denoted as AB stacking (Figure S13 and Table S1). A rapid transformation from the planar structure to a partial cone was observed for calix[4]arenes in both COP1\*\* and COP2\*\* in all stacking conditions, suggesting that the partial cone structure is dictated by the molecular topology. The partial cone<sup>[36]</sup> conformation has three OH groups pointing downward and one OH group pointing upward (Figure S14). The flexibility of the calix[4]arene rings resulted in rapid exchanges of the linker positions (up and down), which led to nanoscale undulations of the sheets during thermal motion (Supplementary movie SM1). However, despite the unit cell shape changes that were allowed in simulations, we did not observe any intra-sheet structural transitions (AA↔ AB) in the time scale of 100 ns, suggesting that such transitions are not accessible at room temperature due to high energy barriers. As our objective was to find the stable intra-sheet structure and not the transitions, we compared the stabilities of each intra-sheet state energetically. We estimated the free energies in the basin of attraction of each stacking condition by computing enthalpy and free energy (Table 1).

Despite the structural similarity of their components, the two polymers differ in their preference for stacking structure. **COP1**<sup>++</sup> is more stable in the AB stacking arrangement, whereas **COP2**<sup>++</sup> exhibits greater stability in the AA orientation (Table 1). These observations can be explained in terms of non-bonded interactions, in particular, the average van der Waals and Coulomb interactions. **COP1**<sup>++</sup> is greatly stabilized by van der

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**Figure 2.** Structures of calixarene-based polymers deduced from Molecular Dynamics simulations. (A) AB stacking orientation in **COP1**, with  $\pi$ - $\pi$  interactions between the linker molecules spaced 3.89 Å apart and 2.57 Å hydrogen bonds between calixarene OH groups. (B) AA stacking orientation in **COP2**, with  $\pi$ - $\pi$  interactions between linkers spaced 5.58 Å apart and 2.94 Å hydrogen bonding between calixarene OH groups.

Waals interactions in the AB form (55.89 kcal mol-1 compared to 313.73 kcal mol<sup>-1</sup> in AA stacking). The reason for this difference can be attributed to the formation of  $\pi$ - $\pi$  stacking in AB, and its absence in AA. In AA conformation, the distance between the two adjacent aromatic rings is 3.89 Å, allowing strong  $\pi$ - $\pi$ stacking interactions between the viologen linkers (Figure 2A). In contrast, parallel viologen linkers are about 8.06 Å away from each other in the AA conformation, which prevents intramolecular attraction between the linkers (Figure S15A). In addition, the conformation of calix[4]arene appears to be somewhat distorted in the AA stacking with distances between OH groups of adjacent calixarenes being too large for hydrogen bond formation (4.24 Å). The same distances in the AB stacking mode are only 2.57 Å, allowing hydrogen bond formation. Finally, stabilization in COP1\*\* is also supported by electrostatic interactions. AB stacking mode shows an average Coulomb energy of -115.76 kcal mol<sup>-1</sup> whereas AA stacking results in a higher electrostatic energy of -72.80 kcal mol<sup>-1</sup>. Interestingly, unlike COP1++, AA stacking is more stable in COP2++. Between the two non-bonded energy terms the electrostatic energy of AA and AB stacking modes are similar in COP2++. van der Waals interactions on the other hand, show a drastic difference that amounts to 30.23 kcal mol<sup>-1</sup> for AA and to 212.69 kcal mol<sup>-1</sup> in AB. A major stabilization of the AA stacking arises from favorable orientation, small enough distances between linkers in adjacent layers (5.58 Å), and hydrogen bond formation between adjacent calix[4]arene moieties (2.94 Å; Figure 2B). Linker moieties in AB stacking are not well aligned across viologen rings. Also, they are too far apart (> 6.32 Å) to form  $\pi$ - $\pi$ interactions (Figure S15B).

Our results show how interplay between hydrogen bonding and  $\pi$ - $\pi$  stacking governs the overall topology of nanosheet formation in calix[4]arene-based COPs. These two forces favor the AB super-structure in **COP1**<sup>++</sup> and disfavor the AB configuration in **COP2**<sup>++</sup>. Our molecular modeling results for **COP1**<sup>++</sup> and **COP2**<sup>++</sup> are in good agreement with our AFM measurements. The height profiles of **COP1**<sup>++</sup> and **COP2**<sup>++</sup>

measured by AFM are 6.00 and 8.00 nm, respectively. To relate simulation results to experiments, we defined  $\Delta z$  as the average distance between the highest and lowest atoms in a unit cell with respect to the z coordinate in a unit cell. Height profiles from AFM ( $\Delta h$ ) were divided by  $\Delta z$  to calculate the number of 2D polymer layers per nanosheet:  $n = \Delta h/\Delta z$ . Remarkably, we found n = 10.97 for COP1<sup>++</sup> and n = 13.94 for COP2<sup>++</sup>, values very close to integers, which demonstrates that the computational models are consistent with our physical observations. In contrast, n = 7.42 for COP1<sup>++</sup> in its disfavored AA stacking, and n = 13.79 for COP2<sup>++</sup> in its disfavored AB stacking. Given that n must be an integer, AA stacking in COP1<sup>++</sup> and AB stacking in COP2<sup>++</sup> are inconsistent with our experimental results.

 Table 1. Thermodynamic parameters obtained in MD simulations of COP1++

 and COP2++ in both AA and AB stacking configurations.

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	COP1++	COP1++	COP2++	COP2++	
	AA	AB	AA	AB	
Enthalpy [kcal mol-1]	577.96	189.37	79.42	345.94	
Free energy [kcal mol-1]	579.91	191.26	81.33	347.79	
van der Waals int.	313.73	55.89	30.23	212.69	
[kcal mol-1]					
Coulomb int.	-72.80	-115.76	-96.99	-102.49	
[kcal mol <sup>-1</sup> ]					

#### lodine capture with COP1 and COP2

Knowing that viologen species,<sup>[15]</sup> azo bonds<sup>[37,38]</sup> and phenyl rings<sup>[16]</sup> interact strongly with iodine, we decided to test our polymers as iodine sorbents. Significant amounts of iodine radionuclides (1<sup>129</sup> and 1<sup>131</sup>) with half-lives of up to 15.7 million years are generated in nuclear power plants,<sup>[39]</sup> and these pose a great danger to the environment and human health if released. Although inorganic materials<sup>[40]</sup> and metal organic frameworks (MOFs)<sup>[41]</sup> have been used for iodine capture, these classes of material suffer from low uptake capacity and poor thermal and water stability, respectively. COPs, in contrast, display excellent

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thermal and chemical stability, can be synthesized on large scale and are recyclable.  $\ensuremath{^{[42]}}$ 

Considering the importance of developing materials for I2 removal, we utilized our viologen-based materials for iodine capture, and investigated the effect of viologen redox state on the uptake capacities. In vapor phase experiments, COPs were exposed to iodine vapors in a closed chamber at 70 °C and ambient pressure, and iodine uptake was measured gravimetrically after 24 h (Figure 3A). The particularly high uptake capacity observed for COP1+, up to 200 wt %, can be explained by a mechanism that involves an interaction between **COP1**<sup>++</sup> and the polymerized  $I_3^-$  species and that ultimately yields oxidized COP1\*\* and I- ions (Figure S16), as supported by the EPR-silent spectrum of the polymer after iodine adsorption (Figure S17). Radical stabilization through conjugation is less effective in COP2\*\* because of the methylene bridges present in the linker molecule and the presence of radical dimers rather than monomers. The effects of Lewis basicity in COP2<sup>0</sup> are more prominent, so the neutral polymer is the most effective iodine capturer among the three redox states in COP2, reaching up to a 180% weight increase. In most forms, our COPs performed better than previously reported organic or inorganic nanosheet materials used for iodine capture (Table S2). X-ray photoelectron spectroscopy (XPS) of the COPs suggest that the adsorbed iodine exists as I<sub>2</sub>, with signals at 619 (3d 5/2) and 630 (3d 3/2) eV appearing in the spectra of all iodine-exposed COPs (Figure S18) except COP1+, where peaks appear at 617 eV (I2 3d 5/2), 618 eV (I3- 3d 5/2), 628 eV (I2 3d 3/2) and 631 eV ( $I_3^-$  3d 3/2). This can be explained by the electron transfer from COP1+ to iodine (Figures S16). Adsorption of iodine in all COPs results in an additional weight loss in a TGA profile between 150 and 300 °C (Figure S19), which can be attributed to iodine evaporation. COP1\*\* and COP2<sup>++</sup> were also tested for their recyclability (Figure S20). A loss of iodine uptake capacity was observed in the 2<sup>nd</sup> cycle. This phenomenon, which we have observed previously during the testing of similar COPs, is likely caused by residual iodine that remains in the material due to strong intermolecular attractions.[15]

Because the counter ion of viologen has been shown to significantly influence the gas adsorption capacity of COPs,[43] we studied the effects that changing the counter ion had on the uptake capacities of COP1 and COP2 for iodine vapor. By soaking the materials in saturated aqueous solutions of KI or NH<sub>4</sub>PF<sub>6</sub> followed by several washes with water, Cl<sup>-</sup> counter ions in as-synthesized polymers were successfully replaced by I- or PF<sub>6</sub>-, as demonstrated by energy dispersive X-ray (EDAX) spectroscopy (Figure S21). COP1++(I-) and COP2++(I-) adsorbed about 10 and 20% more of vapor iodine than COP1++(CI-) and COP2++(CI<sup>-</sup>), respectively (Figure 3B). This can be attributed to I<sup>-</sup> counter ions being able to catalyze the formation of polyiodide species on the surface of the polymer.[44] In contrast, substituting Cl<sup>-</sup> with bulky PF<sub>6</sub><sup>-</sup> reduced iodine uptake capacity by about 30% in both COP1<sup>++</sup> and COP2<sup>++</sup>. Due to its size, PF<sub>6</sub><sup>-</sup> occupies a larger area of the polymer's surface, so fewer intermolecular forces can develop with vapor iodine and the uptake capacity drops significantly.

In a typical solution-phase iodine adsorption experiment, 5.0 mg of polymer was added to 5 mL of cyclohexane having an iodine concentration of 1 mM. The progress of iodine uptake was

monitored by UV-Vis spectrophotometry (Figure S21). Regardless of redox state, COP2 performed better than COP1 (Figure 3C): **COP2** removed > 97% of  $I_2$  in all redox states, while the performance of COP1 varied between 57% and 95% depending on the redox state. The flexibility of COP2 likely allows the material to adjust its structure in solution so as to maximize interactions with the small molecule. Furthermore, both radical-containing polymers, COP1+ and COP2+, performed worse (57% and 96%, respectively) than the corresponding dicationic polymers (95% and 100% for COP1++ and COP2\*\*, respectively) and neutral polymers (91% and 98% for COP1º and COP2º, respectively). Although COP1++, COP1º, COP2\*\* and COP2º all removed nearly 100% of iodine in 210 min, COP2<sup>o</sup> showed a particularly quick uptake, as 100% was removed after only 15 min (Figure S22). Upon two-electron reduction of viologen, the counter ion is no longer bound to the COP, so some additional surface area is available for interaction with iodine. In addition, viologen gains the character of a Lewis base, which further enhances interactions with I<sub>2</sub>.

#### pH dependence of dye adsorption by COP1++ and COP2++

Congo red, an anionic azo-based dye known to cause allergic reactions as well as cytotoxicity, genotoxicity, hematotoxicity and neurotoxicity,<sup>[46]</sup> interacts with the hydroxyl portal of calix[*n*]arenes.<sup>[18]</sup> Knowledge of this favorable interaction prompted us to test our COPs as Congo red adsorbents. Congo red-containing effluents from textile, printing, dyeing, paper, and other industries<sup>[46]</sup> are often acidic<sup>[47,48]</sup> but generally range in pH depending on the source of pollution. We therefore investigated the abilities of **COP1** and **COP2** in their various redox states to remove Congo red from aqueous solutions of different pH (Figure S23).

Since our materials were found to be stable from pH 2 to pH 10 (Figure S1), Congo red solutions at pH 2.0, 4.0, 6.0, 8.0 and 10.0 were prepared, and a fixed amount of the polymer was added to each. Both COP1\*\* and COP2\*\* were effective at removing the dye over the whole pH range after 375 min (Figures 4A and S24). At all tested pH, COP1\*\* adsorbed the same or a lower percentage of the dye than COP2++ (pH 2: 97% each; pH 4: 80% and 91%; pH 6: 87% and 97%; pH 8: 73% and 97%; pH 10: 84% and 97%, respectively), likely, again, because of flexible structure of COP2\*\* which allows for maximum interaction with the guest molecule. Both COP1\*\* and COP2\*\* performed best at pH 2.0 (97% removal in both cases). At higher pH, the carboxylic acid groups of the dye molecule are deprotonated, making the dye anionic. At basic pH, the phenolic (OH) groups of calix[4]arene become deprotonated, as well, to form phenoxides (Ph-O<sup>-</sup>), which makes interaction between the dye and the polymer less favorable due to electrostatic repulsion.<sup>[18]</sup> Adsorption by the as-synthesized COPs at pH 2.0 was investigated in greater detail in terms of kinetics. COP1\*\* and COP2\*\* adsorb Congo red with a pseudo second-order rate constants of 0.0116 g/mg·min and 0.0239 g/mg·min, respectively (Figure S24). Maximum quantity of Congo red adsorbed by COP1\*\* as determined from a Langmuir isotherm was 928 mg  $g^{-1}$  (Figure S25).

Also, adsorption experiments involving **COP1**<sup>++</sup>, **COP1**<sup>0</sup>, **COP2**<sup>++</sup> and **COP2**<sup>0</sup> were conducted at pH 2.0, the optimal pH for adsorption. In these, 17%, 95%, 86% and 96% of the dye was absorbed after 15 minutes, respectively. **COP1**<sup>++</sup> and **COP2**<sup>++</sup>

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Figure 3. Histograms illustrating iodine adsorption by COP1 and COP2. (A) Vapor phase iodine adsorption by the three redox states of COP1 and COP2; (B) Effect of counter ion in COP1<sup>++</sup> and COP2<sup>++</sup> on iodine sorption, and (C) solution phase iodine adsorption by the three redox states of COP1 and COP2.

thus performed significantly worse than the corresponding dicationic and neutral COPs (Figure 4B). However, it is known that viologens are oxidized under acidic conditions,<sup>[49,50]</sup> so after longer incubation times, **COP1**<sup>++</sup> and **COP2**<sup>++</sup> are oxidized to **COP1**<sup>++</sup> and **COP2**<sup>++</sup>, respectively. Also, **COP2**<sup>++</sup> is oxidized much more rapidly because the polymer is less conjugated and therefore stabilizes the radical form of its viologens lesseffectively. Due to oxidation, the uptake capacity of both radical cationic polymers becomes comparable to that of dicationic and neutral COPs after longer incubation times (Figure S26).



Figure 4. pH-dependence of Congo red adsorption by COP1++ and COP2++ after 375 min of incubation (A); the effect of redox state on Congo red adsorption at pH 2.0 after 15 minutes of incubation (B).

Cationic dye Rhodamine B and neutral dye Nile red were also removed from aqueous solution by **COP1**<sup>++</sup> and **COP2**<sup>++</sup>, demonstrating that our materials serve as versatile dye adsorbers (Figure S27).

#### Conclusions

In summary, we used diazo coupling to synthesize two viologenbased polymers that incorporate calix[4]arene in their backbones. Interestingly, both polymers were isolated as nanosheets, and the sheets remained intact upon chemical reduction of their viologen subunits. The materials adsorbed iodine vapor and iodine dissolved in cyclohexane, and removed Congo red from aqueous solutions of different pH. The flexible neutral polymer removed iodine from solution most efficiently, whereas the rigid radical polymer was the most efficient at removing iodine from the vapor phase. The cationic polymers effectively removed Congo red from water in the pH range of 2 -10. These studies have provided insight into the effects that backbone rigidity and redox state have on the uptake capacities of viologen-based polymers and will aid the design of materials that are even more effective at pollutant adsorption.

### **Experimental Section**

Synthesis of COP1<sup>++</sup> and COP2<sup>++</sup>. The polymers were synthesized under solvothermal conditions. A magnetic stir bar, *p*NC4A (0.200 g, 0.33 mmol), two equivalents of the appropriate viologen diamine (1 or 2), and KOH (0.186 g, 3.31 mmol) were placed into a Schlenk tube, and 15 mL of DMF was added under Ar atmosphere. The contents were degassed by three freeze-pump-thaw cycles. The tube was then placed in an oil bath and heated at 150 °C for 24 h. The reaction mixture was centrifuged and the solid was collected and partially dried. Impurities were removed by Soxhlet extraction with DMF, THF, water, and ethanol as solvents. Finally, the washed polymer was dried in a vacuum oven at 55 °C for 16 hours.

**MD** simulations of **COP1**<sup>++</sup> and **COP2**<sup>++</sup> nanosheets. The repeating units of **COP1** and **COP2** were drawn using GaussView<sup>[51]</sup> as shown in Figure S10. Initial geometries were assumed to be planar. These repeating units were imported into Materials and Process Simulation (MAPS)<sup>[52]</sup> to create unit cells of periodic systems in the Crystal Builder module as well as to prepare the input files and forcefield parameters for the molecular simulation set-ups. Two types of unit cells were created for



each polymer by adjusting the angle  $\alpha$  and the height c (Figure S12) so that layers of sheets directly on top of one another (AA) or offset by half of the repeating unit (AB) were created. Specific parameters used in each unit cell can be found in Table S1 and unit cells visualized in MAPS can be found in Figure S11. The net charge of COP1 and COP2 unit cell was +4. To neutralize the polymer, we added 4 CI<sup>-</sup> counter ions in random positions into the simulation box. Geometry optimization and MD simulations were conducted using LAMMPS<sup>[53]</sup> program with DreidingX6<sup>[54]</sup> force field. Equations of states were integrated using a velocity-Verlet<sup>[55]</sup> integrator with a timestep of 2 fs in the isothermalisobaric (NPT) ensemble for each model. A temperature of 298.15 K and a pressure of 101.325 kPa (1 atm) were maintained using a Nose-Hoover  $thermostat^{[56]}$  and barostat,  $^{[57]}$  respectively. Coulomb interactions were evaluated using an implementation of the Ewald summation algorithm<sup>[58]</sup> with a relative force accuracy of 1.0 × 10<sup>-4</sup>. Lennard-Jones and Coulomb interactions were cut off at a distance of 12 Å. Tail corrections were employed for accurate computation of the long-range interactions. Each structure was left to sample conformations for 100 ns to ascertain its stability and to visualize and analyze the equilibrium populations. Data were recorded with 1 ps intervals with the first 10 ns considered equilibration and discarded. All observables reported here were obtained by time series averaging of the snapshots.

To compare the stability of alternative sheet configurations we computed the average enthalpy  $\Delta H = (1/t) \sum_{i=1}^{t} \Delta H_i$ , where  $\Delta H_i$  is the instantaneous enthalpy of snapshot *i*, and *t* is the total number of snapshots after equilibrium is reached. The entropy of inter-layer state is estimated from the trajectory using Gibbs Entropy  $\Delta S = -k_B \int P(E) ln(P(E)) dE$ , where  $k_B$  is the Boltzmann constant, and P(E) is the probability density of total energy, E sampled during the simulations. Using these two entities we compute the Gibbs free energy as  $\Delta G = \Delta H - T\Delta S$ .

**Iodine capture experiments.** For vapor phase experiments, ~10 mg of the polymer was placed on a small crystallization dish, which was placed in a closed chamber containing solid  $I_2$  and incubated at 70 °C. Gravimetric measurements of the polymer were recorded at regular time intervals up to 24 h, and the % mass increase was calculated as follows: % mass increase at [t=t<sub>1</sub>]= (mass at [t=t<sub>1</sub>]-mass at [t=0])/mass at [t=0]. For solution phase experiments, 5 mL of 1 mM stock solution of  $I_2$  was prepared in cyclohexane. 5.0 mg of polymer was added to the stock solution, and the mixture was continuously stirred. The progress of iodine capture was monitored by UV-Vis spectrophotometry at regular time intervals up to 210 min. % iodine uptake was calculated by dividing the absorbance at  $\lambda_{max}$  of the starting  $I_2$  solution.

**Congo red adsorption experiments.** To determine the effect of pH on Congo red uptake, 25  $\mu$ M aqueous dye solutions of various pH were prepared. Solution pH was adjusted with 1 M NaOH or 1 M HCl solutions. UV-Vis spectra of the starting solutions were measured. Then, 5.0 mg of polymer was added to 5 mL of each solution, and the mixture was continuously stirred. The progress of dye uptake was monitored by UV-Vis spectrophotometry at regular time intervals up to 375 min. Percent Congo red uptake was calculated by dividing the absorbance of the dye solution and multiplying by 100. Uptake was calculated for each polymer, and for each of the three redox states of its constituent viologens. To compare the different redox states of COPs in their ability to adsorb Congo red, the % uptake after 15 min was considered.

For investigation of the kinetics, the amount of pollutant adsorbed at each time point was determined using the equation  $q_t = [(C_0 - C_t) \cdot M_{W'} \cdot V]/m$ , where  $q_t$  (mg/g) is the quantity of adsorbed Congo red per 1 g of adsorbent at a given time t (min),  $C_0$  (mmol/L) is the initial concentration before polymer treatment,  $C_t$  (mmol/L) is the residual concentration of the dye after treatment with polymer, V is the volume of dye solution, m (g) is the amount of adsorbent used, and  $M_{W}$  (g/mol) is the molecular weight of

Congo red. The data were fitted to Ho and McKay's pseudo second-order adsorption model  $t/q_t = t/q_e + 1/(k_{obs}, q_e^2)$ , where  $q_t$  is the quantity of adsorbed Congo red at time *t* (min),  $q_e$  is the adsorbed amount at equilibrium, and  $k_{obs}$  is the second-order rate constant (g mg<sup>-1</sup> min<sup>-1</sup>).<sup>[59]</sup>

To determine maximum adsorption capacity, adsorption isotherms were obtained by varying the initial concentration of the dye from 0.1 mM to 1.5 mM. The adsorption isotherms were fitted (correlation coefficients, R<sup>2</sup> >0.96) by using the Langmuir adsorption model:  $q_e = q_m \cdot b \cdot C_e / (1+b \cdot C_e)$ , where  $q_e$  (mg g<sup>-1</sup>) is the amount of dye adsorbed at equilibrium,  $C_e$  (mg L<sup>-1</sup>) is the equilibrium solute concentration remaining in solution when  $q_e$  is achieved,  $q_m$  is the maximum adsorption capacity corresponding to complete monolayer coverage, and b is a constant (L mg<sup>-1</sup>).<sup>[14]</sup>

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Tunable sheets for the environment. Two cationic covalent organic polymers (COPs) are synthesized through diazo coupling of a calix[4]arene derivative and viologen-based, redox-responsive linkers. Interestingly, the COPs exhibit nanosheet morphology consistent with MD simulations. Because of their cationic and aromatic nature, these materials serve as efficient sponges for iodine and for organic dyes over a broad range of pH.

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Redox-responsive Covalent Organic Nanosheets from Viologens and Calix[4]arene for lodine and Toxic Dye Capture