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Fast and Efficient Removal of Paraquat in Water by Porous Polycalix[n]arenes (n = 4, 6, and 8)

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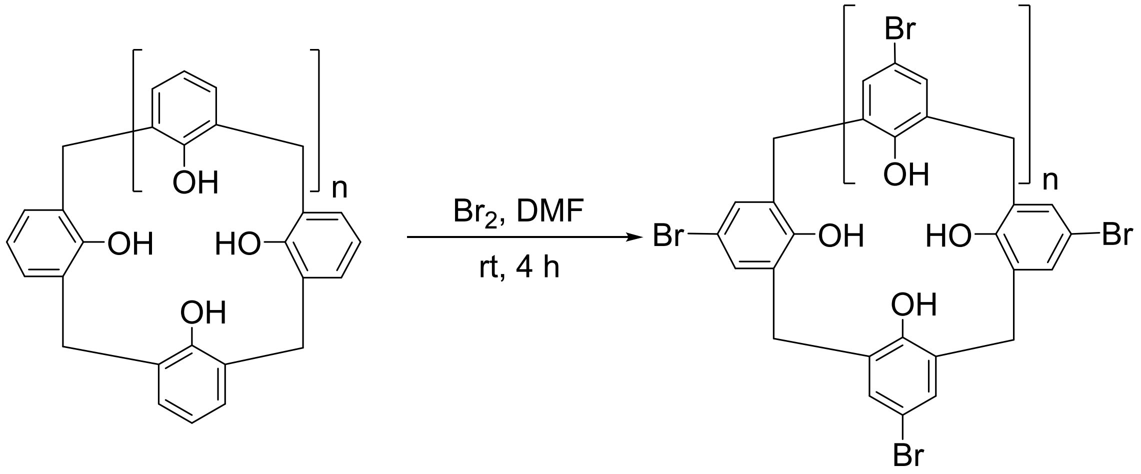
Supporting Information

General. All chemicals and solvents were purchased from Sigma-Aldrich and used without further purification. Deionized water was used from Millipore Gradient Milli-Q water purification system. Thin-layer chromatography (TLC) was performed on silica gel 60 F254 (E. Merck). The plates were inspected with UV light. Column chromatography was performed on silica gel 60F (Merck 9385, 0.040–0.063 mm). Routine nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on a Bruker Avance spectrometer, with working frequencies of 500 MHz for ^{1}H, and 125.7 MHz for ^{13}C nuclei, respectively. All chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvent (DMSO-d6: $\delta = 2.50$ ppm, $CDCl_3$: $\delta = 7.26$ ppm). Norit RO 0.8 activated carbon (AC) was purchased from Sigma Aldrich.

Material Characterization. FTIR studies were carried out on Agilent 670 IR spectrometer in the attenuated total reflectance (ATR) mode. SEM images were obtained from FEI Quanta 450FEG. TEM images were obtained from a FEI-Titan 300 operating at 200 kV. TGA experiments were performed on a TA SDT Q600 with a heating rate of 10 °C min^{-1} over a temperature range of 25–1000 °C. Powder X-ray diffraction (PXRD) measurements were carried out on Bruker D8 Advance X-ray diffractometer with Cu K_α ($\lambda = 1.5405$ Å) radiation source operating at 40 kV and 30 mA. The patterns were recorded with divergent slit of 1/16° over the 2θ range of 1–50° with step size = 0.01°. Solid-state magic angle spinning NMR spectra of the polymers were recorded on a Bruker Avance-I (300 MHz) NMR spectrometer at resonance frequency 107.7 MHz. We used a MAS double resonance probe designed for 4 mm o.d. zirconia spinners, and all samples were spun at 10 kHz, at room temperature. Surface area measurements were conducted on a Micromeritics 3Flex gas sorption analyzer. Samples (~30 mg) were degassed at 85 °C for 20 h and then backfilled with N_2. Adsorption isotherms were generated by incremental exposure to ultrahigh-purity nitrogen up to 1 atm in a liquid nitrogen bath, and surface parameters were determined using BET adsorption models included in the instrument software (Micromeritics ASAP 2020 V4.00). UV-Vis studies were carried out on Cary 5000 UV-Vis-NIR spectrophotometer. All UV-Vis spectra were recorded at room temperature using a quartz cell with 10 mm path length over the range 200–800 nm and corrected against an appropriate background spectrum.

Synthetic Procedures.

Synthesis of brominated CX[n]-Br derivatives.



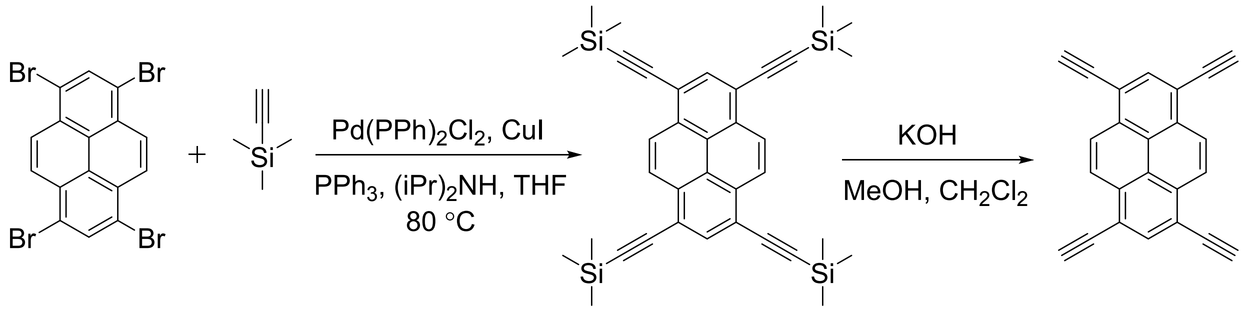
n = 1 CX4
n = 3 CX6
n = 5 CX8

n = 1 CX4-Br
n = 3 CX6-Br
n = 5 CX8-Br

5,11,17,23-Tetrabromo-25,26,27,28-tetrahydroxycalix[4]arene (1). Bromine (0.4 mL, 7.84 mol) in DMF (5 mL) was added dropwise with stirring to a solution of calix[4]arene (0.5 g, 1.18 mmol) in DMF (20 mL). The solution was stirred for 4 h. A precipitate began to form after about 0.5 h. After 4 h of reaction, methanol (20 mL) was added, and the mixture was left to stir for an additional 0.5 h. The precipitate was filtered off and washed with methanol to yield the brominated product, **1** (0.75 g, 87%) as a white solid. ^{1}H NMR ([D$_6$]DMSO, 25 °C, 500 MHz): δ = 7.34 (s, 8H), 3.81 ppm (br s, 8H). ^{13}C NMR ([D$_6$]DMSO, 25 °C, 125.7 MHz): δ$_c$ = 151.8, 131.98, 131.08, 110.89, 30.94.

CX[6]-Br (**2**) and CX[8]-Br (**3**) were synthesized in procedures analogous to that for CX[4]-Br. For CX[6]-Br: ^{1}H NMR ([D$_6$]DMSO, 25 ˚C, 500 MHz): δ = 7.12 (s, 12H), 3.78 ppm (br s, 12H). ^{13}C NMR ([D$_6$]DMSO, 25 °C, 125.7 MHz): δ$_c$ = 152.4, 131.1, 130.7, 111.1, 30.8 ppm. For CX[8]-Br: ^{1}H NMR ([D$_6$]DMSO, 25 °C, 500 MHz): δ = 7.01 (s, 16H), 3.87 ppm (br s, 16H). ^{13}C NMR ([D$_6$]DMSO, 25 ˚C, 125.7 MHz): δ$_c$ = 152.3, 130.8, 130.4, 111.4, 30.7 ppm.

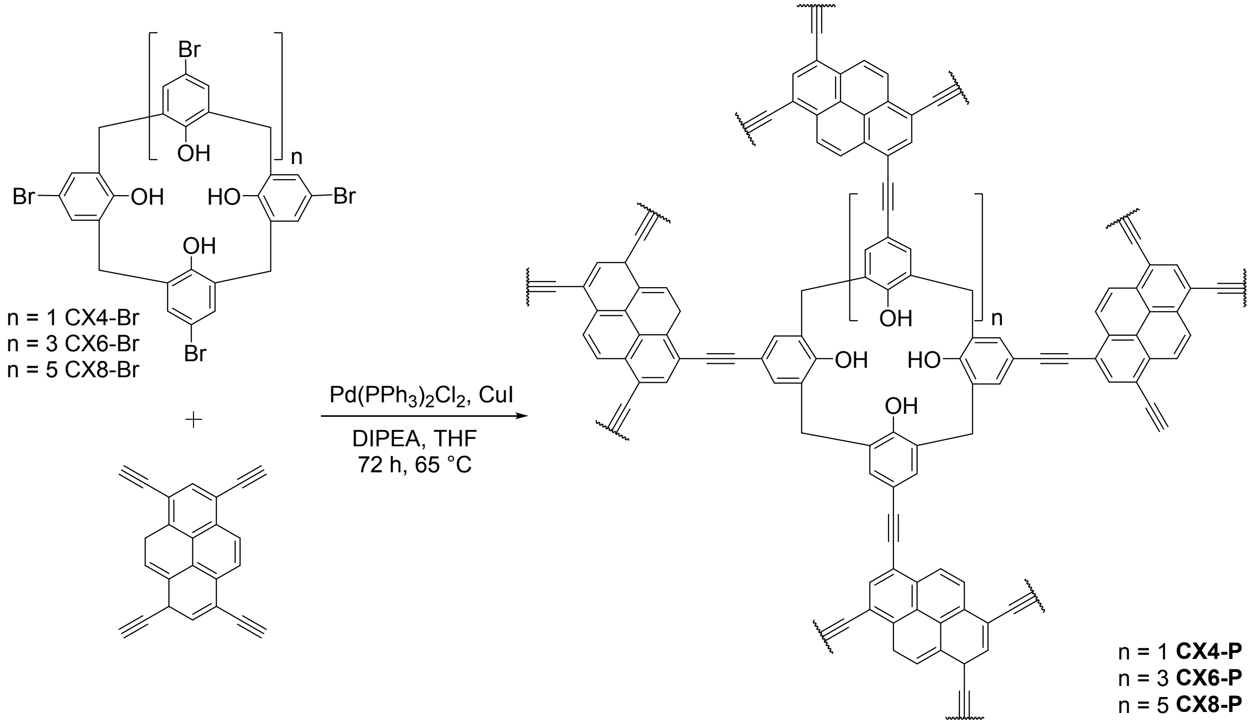
Synthesis of tetraalkyne linker.



1,3,6,8-Tetrakis(trimethylsilylethynyl)pyrene. Compound 1,3,6,8-tetrabromopyrene (1.0 g, 1.93 mmol), [$PdCl_2(PPh_3)_2$] (67 mg, 0.096 mmol), CuI (18 mg, 0.096 mmol), PPh_3 (50 mg, 0.193 mmol), and the trimethylsilylacetylene (11.6 mmol) were added to a degassed solution of diisopropylamine (20 mL) and THF (20 mL) under argon. The resulting mixture was stirred at 70 °C for 48 h. The reaction mixture was then cooled to room temperature and solvent was removed to give the crude product. Column chromatographic purification of the crude product on silica gel with hexane as the eluent yielded a red-orange solid (0.72 g, 66%). ^1H NMR ($CDCl_3$, 25 °C, 500 MHz): δ = 8.51 (s, 4 H), 8.26 (s, 2 H), 0.37 (s, 36 H) ppm. ^{13}C NMR ($CDCl_3$, 25 °C, 125.7 MHz): δ = 134.5, 131.9, 126.8, 123.4, 118.5, 102.8, 101.3, 0.1 ppm.

1,3,6,8-Tetraethynylpyrene (4). To remove the silyl-protection groups, the filtrate was dissolved in ethanol (500 mL) in the presence of KOH (5 g), and stirred overnight. Two-thirds of the solvent was removed by evaporation, and gradual addition of water gave a pale brownish precipitate that was extracted several times with methylene chloride. Removal of the solvent gave the product **4**. ^1H NMR ([D_8]THF, 25 °C, 500 MHz): δ = 8.68 (s, 4 H), 8.34 (s, 2 H), 4.28 (s, 4 H) ppm. ^{13}C NMR ([D_8]THF, 25 °C, 125.7 MHz): δ = 135.7, 132.6, 127.3, 123.5, 119.1, 86.3, 81.9 ppm.

General procedure for the synthesis of polymers.



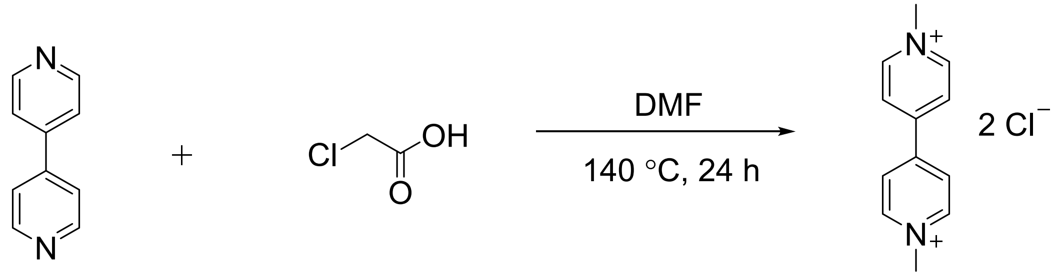
A solution of 5,11,17,23-tetrabromo-25,26,27,28-tetrahydroxycalix[4]arene, bis(triphenylphosphine) palladium(II) chloride and copper (I) iodide in anhydrous THF were placed in a 250 mL two-neck round-bottom flask equipped with a condenser. Diisopropylamine and 1,3,6,8-tetraethynylpyrene linker were loaded into a separate 50 mL flask. Both solutions were purged with argon for at least 15 min. The solution containing the ethylnyl linker was then added dropwise over 5 min to the solution containing the calixarene with stirring to afford a dark brown reaction mixture after 5 min. The reaction was heated at 65 °C under argon for 60 h. After cooling to room temperature, the solid product was centrifuged and washed with excess (cold and hot) tetrahydrofuran, dimethyl acetamide, chloroform, ethanol, and (cold and hot) water to remove any unreacted monomers and metal catalyst residues. The final product was dried under a vacuum for 16 h at 60 °C.

CX[4]P: 5,11,17,23-tetrabromo-25,26,27,28-tetrahydroxycalix[4]arene (1.0 g, 1.36 mmol), 1,3,6,8-tetraethynylpyrene (0.405 g, 1.36 mmol), bis(triphenylphosphine)palladium(II) chloride (0.285 g, 0.45 mmol), copper(I) iodide (0.13 g, 0.68 mmol), diisopropylamine (1 mL), and tetrahydrofuran (160 mL).

CX[6]P: 5,11,17,23,29,35-hexabromo-25,26,27,28,29,30-hexahydroxycalix[6]arene (1.0 g, 0.91 mmol), 1,3,6,8-tetraethynylpyrene (0.405 g, 1.36 mmol), bis(triphenylphosphine)palladium(II) chloride (0.190 g, 0.27 mmol), copper(I) iodide (0.068 g, 0.45 mmol), diisopropylamine (1 mL), and tetrahydrofuran (160 mL).

CX[8]P: 5,11,17,23,29,35,41,47-octaabromo-25,26,27,28,29,30,31,32-octahydroxycalix[8]arene (1.0 g, 0.68 mmol), 1,3,6,8-tetraethynylpyrene (0.405 g, 1.36 mmol), bis(triphenylphosphine) palladium(II) chloride (0.143 g, 0.21 mmol), copper(I) iodide (0.051 g, 0.34 mmol), diisopropylamine (1 mL), and tetrahydrofuran (160 mL).

Synthesis of paraquat (N,N'-dimethyl-4,4'-bipyridinium dichloride)



4,4'-bipyridine (2.0 g, 0.0128 mol) was dissolved in DMF (20 mL) before chloroacetic acid (3.0 g, 0.031746 mol) was added. The temperature of the mixture was increased gradually from 100 °C to 140 °C and the mixture was refluxed for 24 hours. The product obtained was filtered, washed with DMF and chloroform, and was left to dry. Yield: 90 %. ^{1}H NMR (MeOD, 25 °C, 500 MHz): δ = 9.22 (d, 4H), 8.68 (d, 4H), 4.56 (s, 6H). ^{13}C NMR (D_2O, 25 °C, 125.7 MHz): δ = 149.9, 146.3, 126.6, 48.3 ppm.

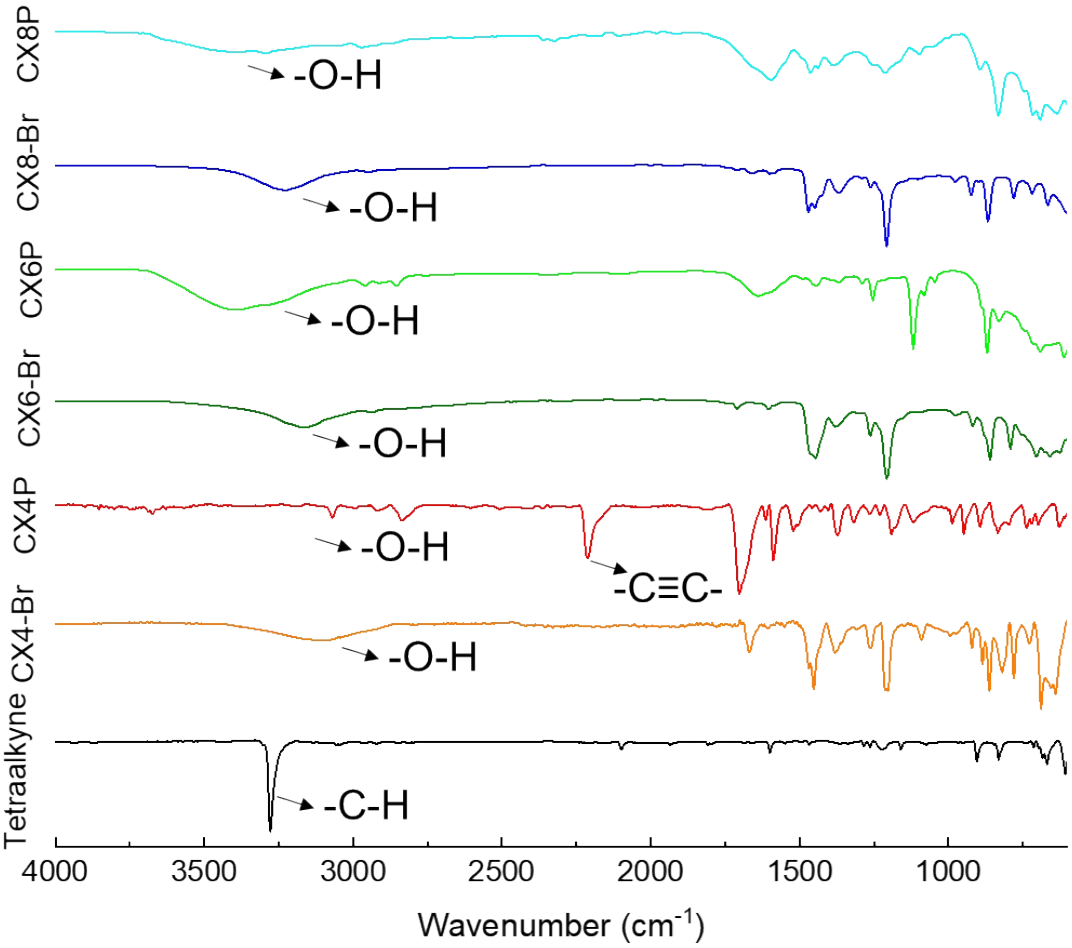


Figure S1. Fourier-transform infrared spectroscopy spectra of **CX4P**, **CX6P** and **CX8P** along with the spectra of the corresponding starting materials.

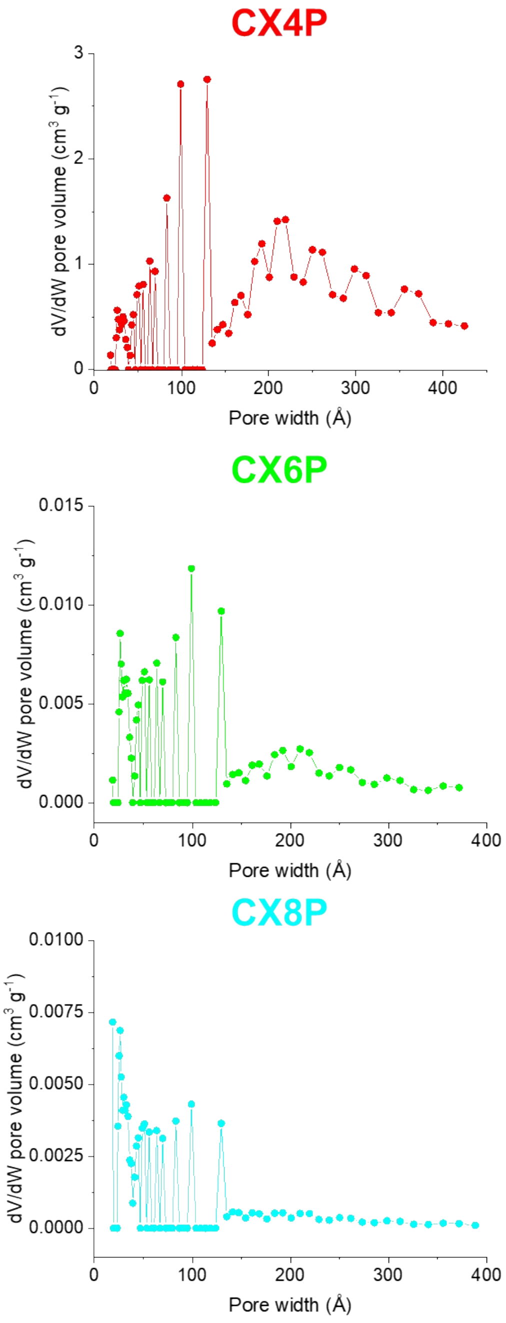


Figure S2. NLDFT pore size distributions of **CX4P**, **CX6P** and **CX8P**.

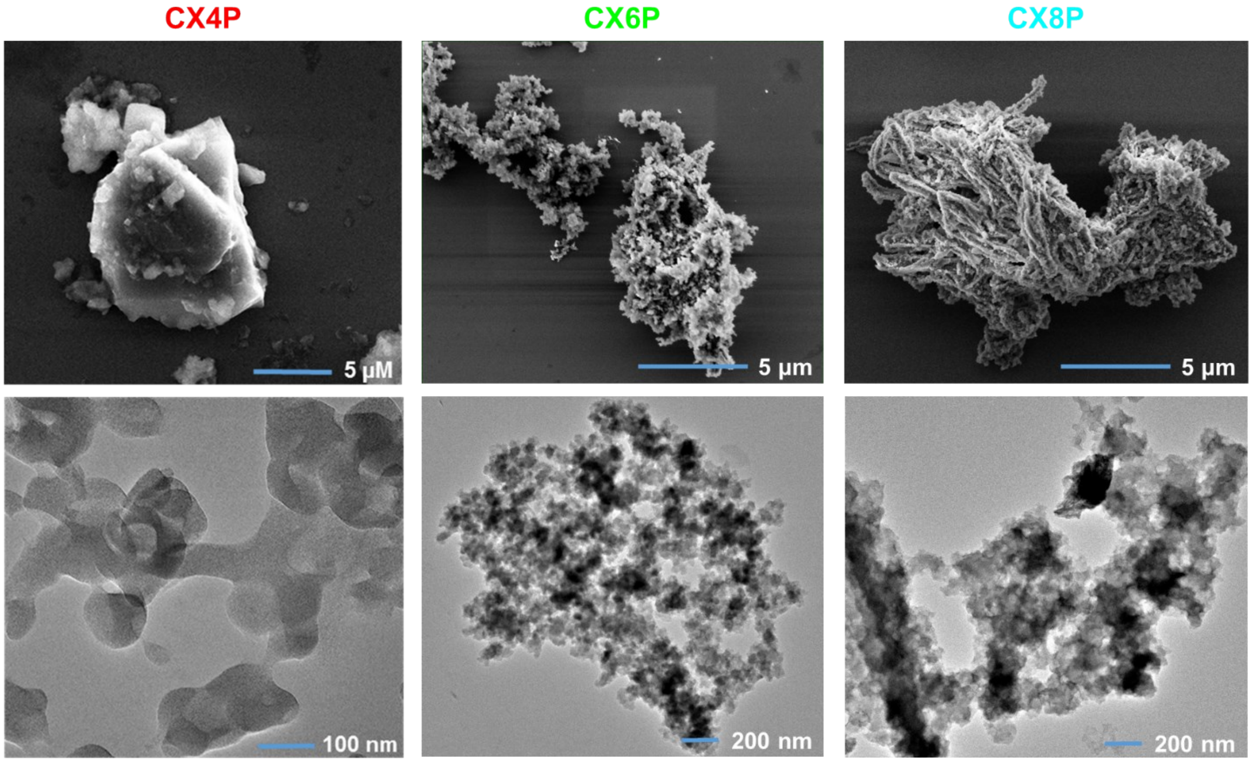


Figure S3. Scanning electron micrographs (top row) and transmission election micrographs (bottom row) of **CX4P**, **CX6P** and **CX8P**.

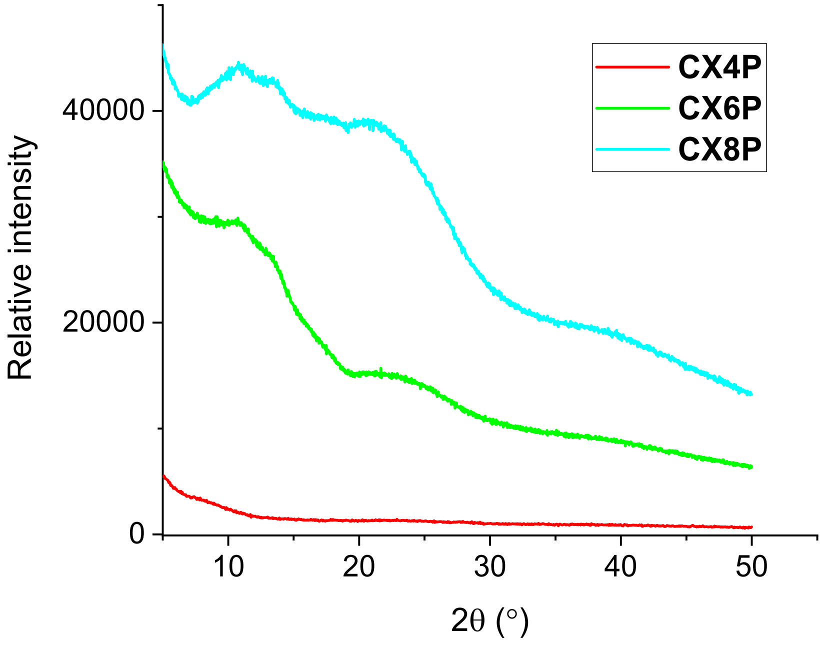


Figure S4. Powder XRD spectra of **CX4P**, **CX6P** and **CX8P**.

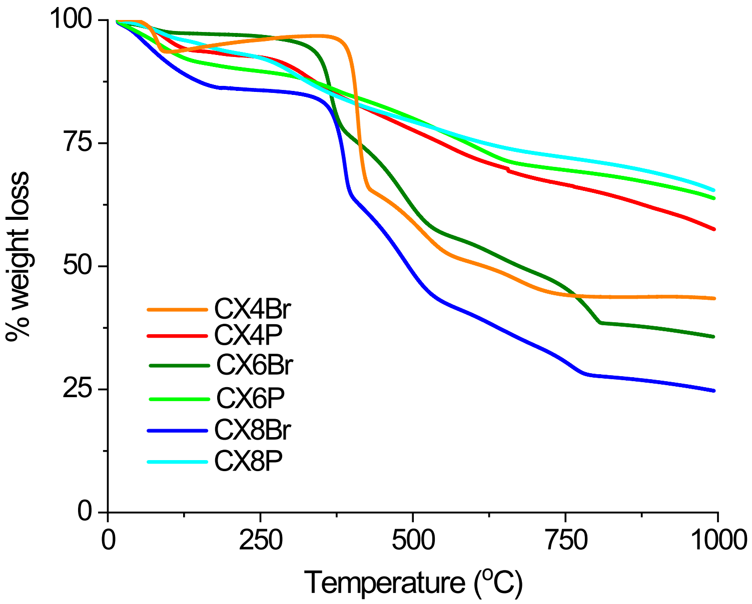


Figure S5. Thermogravimetric analysis profiles of **CX4P**, **CX6P** and **CX8P** along with corresponding calixarene starting materials.

Paraquat adsorption experiments

Paraquat solutions of desired concentrations were obtained by dissolving appropriate amount of synthesized paraquat in distilled water. The concentration of the solutions was tracked via UV-Vis spectroscopy during the sorption experiments. The experiments reported below were performed for each polymer (**CX4P**, **CX6P**, **CX8P**).

Paraquat sorption isotherm

The polymer (2.5 mg) was added into 5 mL solutions of paraquat of different initial concentrations (0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.5, 2.0 mM). The suspension obtained after sonication was stirred overnight at room temperature until it reached equilibrium. The solutions were filtered through a 0.45 μm membrane filter and the new concentration of paraquat was determined using UV-Vis spectroscopy by measuring absorbance at 257 nm.

The amount of paraquat adsorbed at equilibrium q_e was determined by:

$$q_e = \frac{(C_i - C_f) \cdot V \cdot M_w}{m}$$

where C_i and C_f are the initial and final paraquat concentrations (mM), respectively, V is the volume of the paraquat solution (L), M_w is the molecular weight of paraquat, and m is the mass of polymer (g).

The data was fitted to Langmuir isotherm model using the following equation:

$$q_e = \frac{Q_{max} \cdot b \cdot C_e}{1 + b \cdot Ce},$$

where q_e (mg g^{-1}) is the amount of paraquat adsorbed at equilibrium, C_e (mg L^{-1}) is the equilibrium solute concentration remaining in solution when q_e is achieved, Q_{max} is the maximum adsorption capacity corresponding to complete monolayer coverage, and b is a constant (L mg^{-1}).

Paraquat adsorption kinetics

The adsorbent (10 mg) was added into a paraquat solution (20 mL, 0.05 mM). The obtained mixture was sonicated for the first 15 seconds before being stirred at room temperature. At different time intervals, 2 mL were extracted from the solution and filtrated through a 0.45 μm membrane filter. The remaining amount of paraquat was determined with UV-Vis spectroscopy analysis at 257 nm.

The amount of paraquat at time t, q_t, was calculated by:

$$q_t = \frac{(C_i - C_t) \cdot V \cdot M_w}{m},$$

where q_t (mg g^{-1}) is the quantity of paraquat adsorbed at time t (min), C_i and C_t are the initial and paraquat concentration at time t, M_w is the molecular weight of paraquat and m (g) is the mass of polymer used for adsorption.

The obtained data was fitted to a pseudo-second-order kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_{obs} q_e^2} + \frac{t}{q_e},$$

where q_t and q_e are the adsorbate uptake per g of adsorbent at time *t* and equilibrium, respectively, (mg g ^{1}) and k_{obs} is the pseudo-second-order rate constant (mg g ^{1} min ^{1}).

Polymer regeneration

CX4P, **CX6P** or **CX8P** (20 mg) was added to a 15 mL paraquat solution (0.05 mM) and stirred for 15 minutes. The mixture was centrifuged at 14 000 rpm for 15 minutes and the supernatant was discarded. Methanol (15 mL) was added to the polymer remaining in the pellet and the mixture was stirred for 15 minutes before it was once again centrifuged. The polymer was washed 4 times with methanol, left to dry and used for paraquat adsorption in the next adsorption cycle.

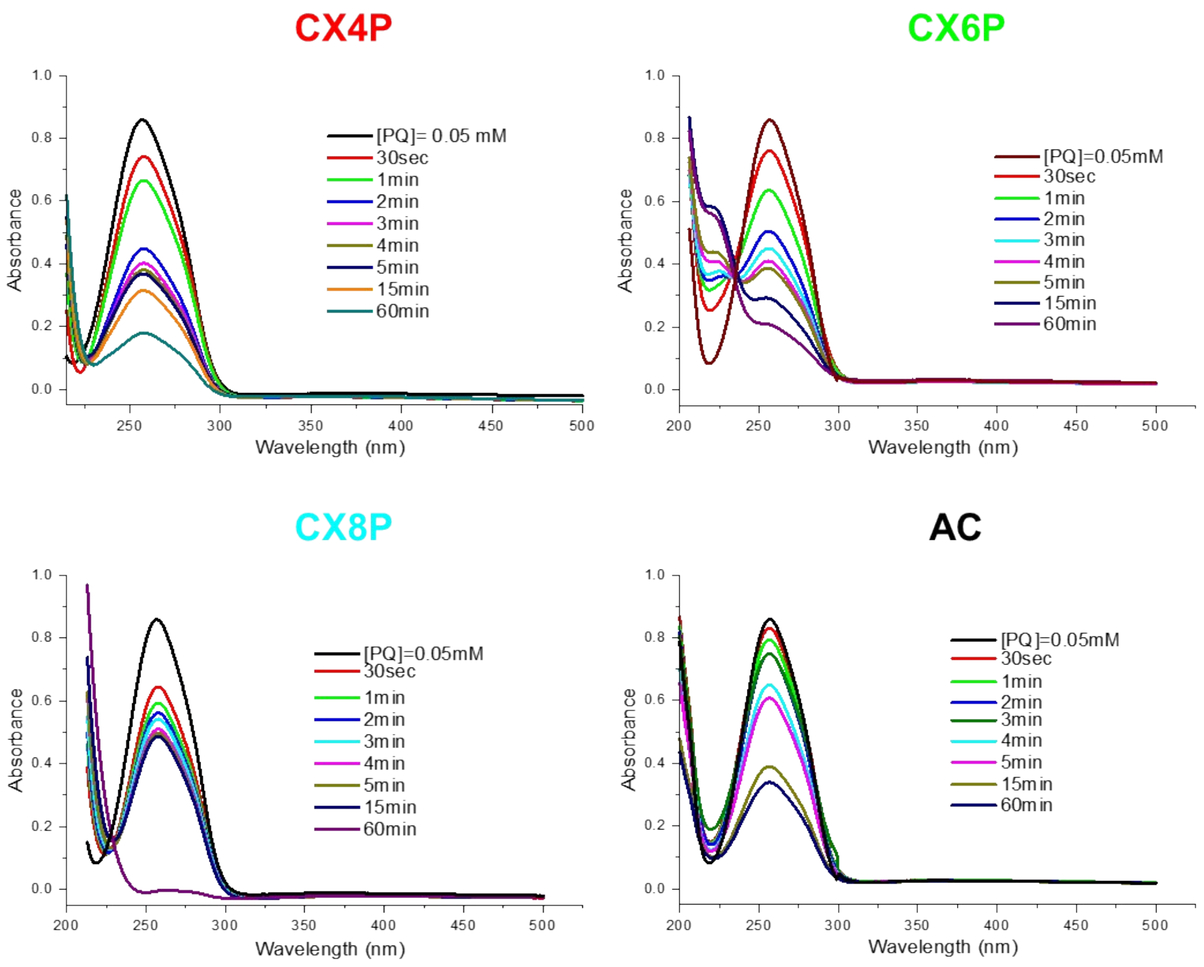


Figure S6. UV-Vis spectra of paraquat at different time points of incubation with **CX4P**, **CX6P**, **CX8P**, or activated carbon (**AC**).

Table S1. List of reported materials for paraquat adsorption and their corresponding Q_{max} and k_{obs} values.

Adsorbent	**Q_{max} (mg g^{-1})**	**k_{obs} (g mg^{-1} min^{-1})**	**Reference**
Calixarene-based porous polymers	411 – 419	0.020 – 0.179	This work
Carbon-coated electrospun fiber	438	0.0008 – 0.0019	[1]
Methacrylic acid-modified rice husk	318	n/a	[2]
Pillararene-based porous polymer	209	33.3	[3]
TEMPO-oxidized pulp	174	0.017 – 0.079	[4]
Zeolite LTL	166.7	n/a	[5]
Activated carbon	160	0.35 – 0.66	[6]
3D Zn-based metal organic framework	160	0.000181	[7]
3D graphene	119	0.00062 – 0.00073	[8]
Amino-acid modified mesoporous silica	115	0.0024 – 0.022	[9]
Algerian bentonite	111	n/a	[10]

Hexagonal mesoporous silica	107	0.32 – 1.13	[11]
Surfactant-functionalized montmorillonite	89	0.09 – 0.22	[12]
Activated carbon from used tires	76	0.08 – 6.45	[13]
Pillararene-functionalized silica	64	n/a	[14]
Activated clay	58	0.009 – 0.098	[15]
Cyclodextrin polymer	26.7	0.0017 – 0.0065	[16]
Regenerated spent bleaching earth	25	0.009 – 0.29	[17]
Anionic cyclodextrin polymer	24.2	0.0008 – 0.0095	[18]
Rice husk silica	18.9	n/a	[19]
Ayous sawdust	9	6.08	[20]
Phillipsite–faujasite tuff	7	n/a	[21]
Diatomaceous earth	3.5-17.5	0.036 – 0.108	[22]
Swine-manure-derived biochar	n/a	0.0031 – 0.0151	[23]

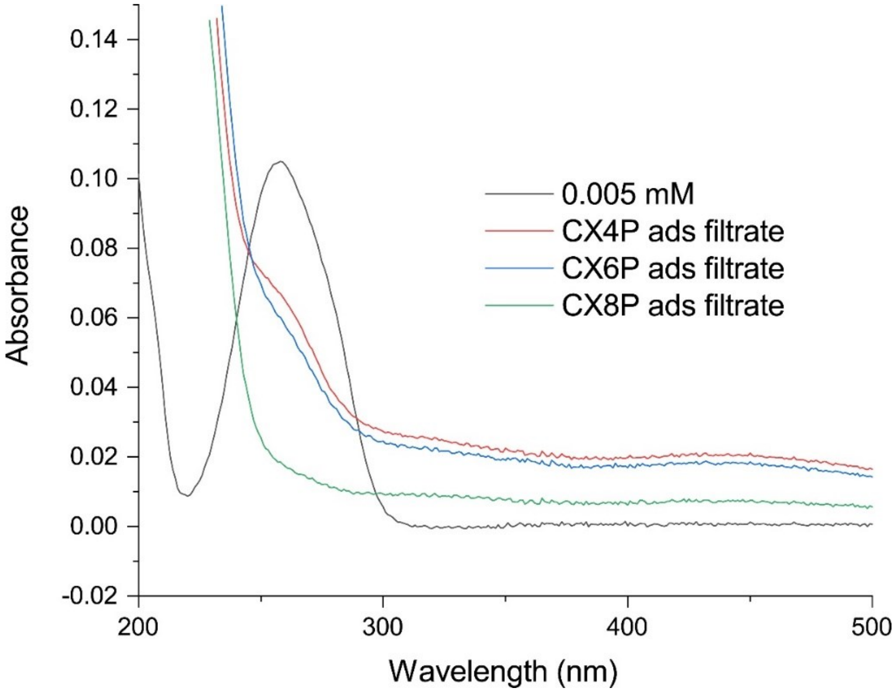


Figure S7. UV-vis spectra showing adsorption capacity of the polymers from ultra-trace concentration (5 μM) of paraquat.

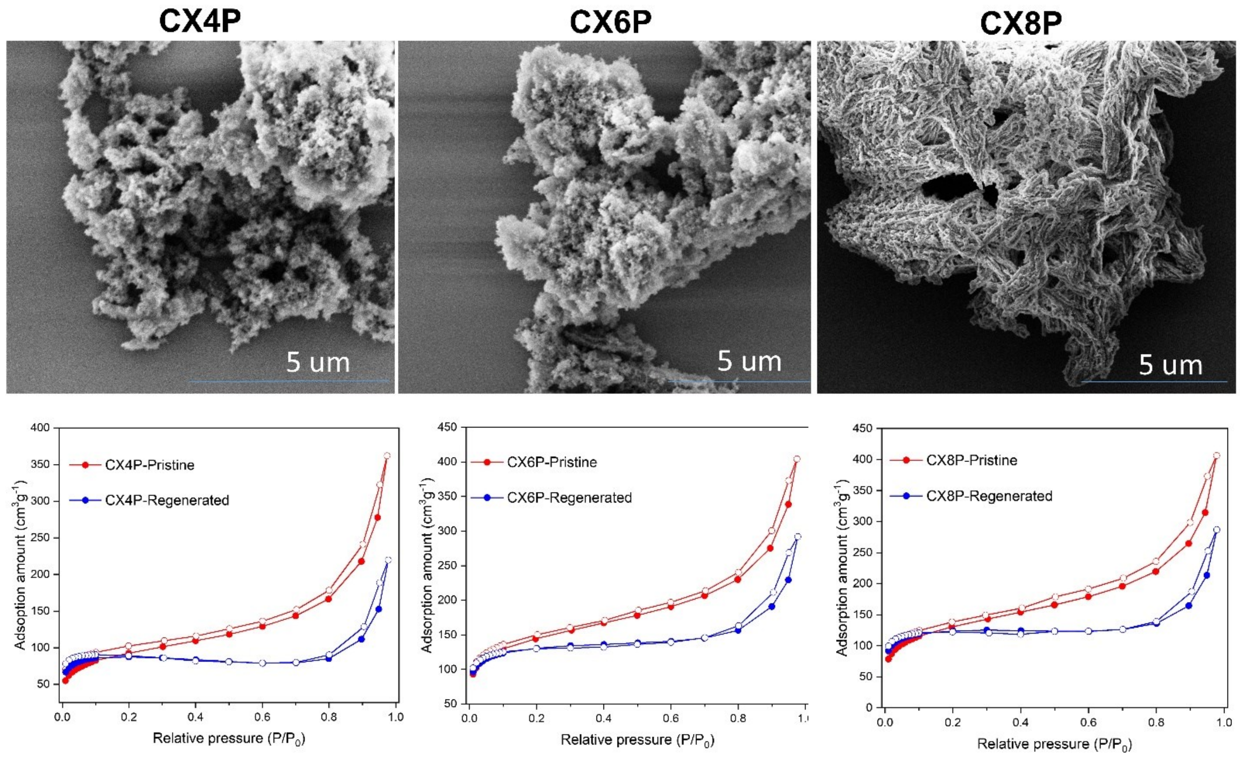


Figure S8. The SEM images of the regenerated polymers and N_2 adsorption results for regenerated polymers in comparison with their corresponding pristine polymers.

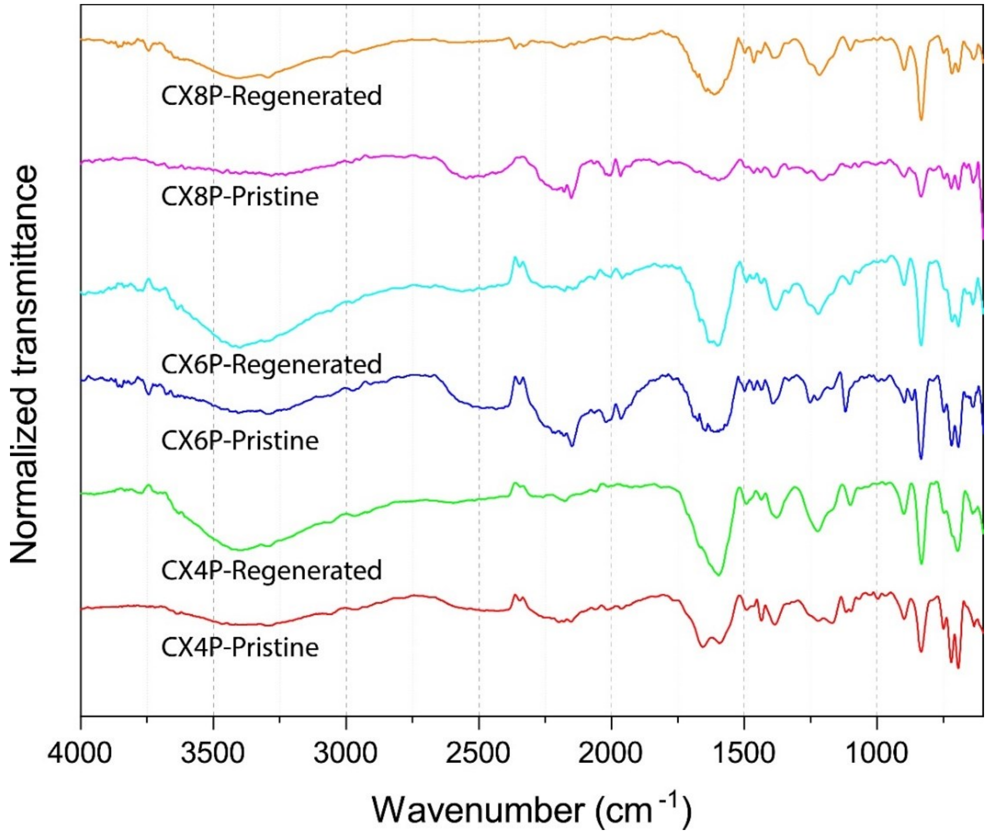


Figure S9. FTIR spectra comparing the structural features of CXnP polymers in their pristine form and after regeneration.

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