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Supporting Information for

Anionic Porous Organic Frameworks as Advanced Functional Adsorbents of CO₂ and

Organic Micropollutants in Water

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Section 1. Methods and Materials

All the materials were used as received without further purification, unless otherwise noted.

Bis(1,5-cyclooctadiene) nickel (0), 1,5-Cyclooctadiene, anhydrous N,N-dimethylformamide (DMF, 99.0%), anhydrous toluene were purchased from Acros Organics. 4-bromocatechol, 2,2'bipyridyl, tetrakis(4-bromophenyl) methane, 2,2-bis(4-hydroxyphenol) propane. 1naphthylamine, bis(4-hydroxyphenol) sulfone, 2-naphthol, 2,4-dichlorophenol and propranolol hydrochloride were purchased from TCI. Phosphorus pentachloride, N-butyl lithium solution (1.6 M in hexanes), ethinyl oestradiol, and metolachlor were purchased from Sigma Aldrich. Methanol and acetone were purchased from Pharmco-Aaper. Concentrated hydrochloric acid was purchased from EMD Millipore. Triethylamine was purchased from Fisher Scientific and distilled before use. Deuterated solvents for NMR measurements were purchased from Cambridge Isotope Laboratories, Inc. Brita activated carbon was obtained from a Brita on tap faucet water filter and was ground into fine powder before use.

The scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDX) spectra were taken using a Hitachi S-4300 SEM. Samples were dispersed over a sticky carbon surface adhered to a flat aluminum platform sample holder. Samples were coated with 5 nm thick iridium for SEM imaging. Samples analyzed by EDX were not coated with any material for a better understanding of element analysis. X-ray diffraction data were recorded using a Rigaku Rotaflex diffractometer with a Cu K α radiation source ($\lambda = 0.15405$ nm). The thermogravimetric analysis (TGA) experiments were carried out both in air and nitrogen using a TA instrument Q-500 series thermal gravimetric analyzer, with a heating rate of 10 °C min⁻¹. Solution phase ¹H, ¹³C, ³¹P and ⁷Li NMR spectra were obtained on a Bruker Avance 500 MHz instrument. ³¹P solid state

NMR spectra were obtained on a Bruker Avance III HD 400 MHz instrument with the spin rate range from 8 k to 15 k. Samples were packed into 4 mm outer diameter zirconia rotors and inserted into a Bruker magic angle spinning (MAS) probe. Standard pulse sequences were employed with a 20 s relaxation delay. The ³¹P chemical shift of NH₄H₂PO₄ was set to zero using external reference standard. Ultraviolet-visible (UV-Vis) spectroscopy was performed on a Shimadzu UV-2101PC UV-Vis scanning spectrometer. UV-vis spectra were recorded at RT over the range of 200-400 nm, and normalized to zero absorbance at 400 nm. Nitrogen and carbon dioxide sorption measurements were collected using a Quantachrome Autosorb-1 instrument. Before analysis, all the samples were outgassed 5 hours at 200 °C in vacuum. The Brunauer-Emmett-Teller (BET) surface area analysis was carried out using 9 data points in the pressure range between 0.02 and 0.12 P/P₀. Pore size distribution of PA-POF materials are calculated by the CO₂ adsorption isotherms collected at 273 K (ice water bath) using non-local density functional theory (NLDFT) method (carbon slit pore model). The elemental analysis was performed by Midwest Microlab.

Ion Exchange Experiments

Ion exchange experiments were carried out by stirring 10 mg PA-POF material in 20 mL 1 M NaCl aqueous solution overnight. The material was then separated from aqueous phase by centrifugation. The resulting solid was washed by deionized water (20 mL x 3) and methanol (10 mL x 3), and dried in vacuo.

Pollutant Removal Kinetic Studies

In a typical BPA removal experiment, 0.1 mM BPA solution was prepared using deionized water. A glass vial was charged with 1 mg of PA-POF material and 10 mL 0.1 mM BPA aqueous solution. This procedure will be called hereafter "the removal of BPA from a 10 mL mg⁻¹ 0.1 mM BPA solution". The vial was closed and placed on a stirring plate with a 300 r.p.m stirring rate for a certain amount of time. The aqueous suspension obtained during the adsorption experiment was filtered through a VWR 0.45 μ m PTFE syringe filter. The filtrate was collected for UV-vis analysis.

The concentrations of the pollutants were characterized by UV-vis spectroscopy, based on their molar extinction coefficients using Beer's Law: bisphenol A (3,343 M⁻¹ cm⁻¹ at $\lambda_{max} = 276$ nm), bisphenol S (20,700 M⁻¹ cm⁻¹ at $\lambda_{max} = 259$ nm), 2-naphthol (4,639 M⁻¹ cm⁻¹ at $\lambda_{max} = 273$ nm), 1-naphthyl amine (5,185 M⁻¹ cm⁻¹ at $\lambda_{max} = 305$ nm), 2,4-dichlorophenol (2,255 M⁻¹ cm⁻¹ at $\lambda_{max} = 284$ nm), ethinyl oestradiol (8,430 M⁻¹ cm⁻¹ at $\lambda_{max} = 220$ nm), propranolol hydrochloride (5,310 M⁻¹ cm⁻¹ at $\lambda_{max} = 290$ nm) and metolachlor (213 M⁻¹ cm⁻¹ at $\lambda_{max} = 15,330$ nm). ^[1]

The efficiency of pollutant removal by the sorbent was determined by the following equation:

Pollutant Removal Efficiency =
$$\frac{C_0 - C_t}{C_0} \times 100\%$$

where C_0 (mmol l⁻¹) and C_t (mmol l⁻¹) are the initial and residual concentration of pollutant in the stock solution and the filtrate, respectively.

The amount of pollutant adsorbed by the adsorbent was determined by the following equation:

$$Q_t = \frac{\left(C_0 - C_t\right)M_w V}{m}$$

where where C_0 (mmol l⁻¹) and C_t (mmol l⁻¹) are the initial and residual concentration of pollutant in the stock solution and the filtrate, respectively. Q_t (mg g⁻¹) is the amount of the pollutant adsorbed. Mw (g mol⁻¹) is the molar mass of the pollutant. V (l) is the volume of the pollutant solution. m (g) is the mass of adsorbent used in the experiment.

The uptake rate of BPA was determined by a simple and popular model, pseudo-second-order model,^[2] showing in the following equation:

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_{obs}Q_e^2}$$

where Q_t (mg g⁻¹) and Q_e (mg g⁻¹) are the adsorbate uptakes at time *t* (min) and at equilibrium, respectively. k_{obs} (g mg⁻¹ min⁻¹) is the second-order rate constant.

BPA Adsorption Isotherms

Sorption isotherms were generated as follows. 1 mg of PA-POF-2 [0.8:1] was stirred in a closed bottle with 40 mL (for 40 mL mg⁻¹ study), 50 mL (for 50 mL mg⁻¹ study), ..., 140 mL (for 140 mL mg⁻¹ study) 0.1 mM BPA solution at RT for one hour to reach equilibrium. The suspension was filtered through a VWR 0.45 µm PTFE syringe filter. The filtrate was collected and measured by UV-vis spectroscopy.

Two classic sorption isothermal models, Langmuir and Freundlich isotherms were fitted to the experiment data. The Langmuir isotherm model assumes that the adsorption occurred in a monolayer.^[3] The Freundlich model was shown to be in accord with an exponential distribution of active sites which hypothesis that a multilayer adsorption takes place on the heterogeneous surface. ^[4] Two models are expressed in the following equations:

$$\frac{1}{Q_e} = \frac{1}{K_L Q_m C_e} + \frac{1}{Q_m}$$

 $Q_e = K_F C_e^{1/n}$

where $Ce \ (mg L^{-1})$ and $Qe \ (mg g^{-1})$ are the concentration of the pollutant in the solution after the adsorption and the adsorbate uptake at equilibrium, respectively. Ce and Qe were calculated based on the UV-vis spectrum for each study. $K_L \ (L \ mg^{-1})$ describes the intensity of the adsorption process, and $Q_m \ (mg \ g^{-1})$ reflects maximum adsorption capacity. $K_F \ (mg \ (L \ mg^{-1})^{1/n} \ g^{-1})$ is a constant related to bonding energy, and represents the general capacity of adsorbate adsorbed onto adsorbents for a unit equilibrium concentration. I/n gives an indication of the favorability of adsorption. Values of n > 1 represent favorable adsorption condition.^[5]

Regeneration Experiments.

1 mg of PA-POF-2 [0.8:1] was placed in a glass vial equipped with a magnetic stirring bar, to which 80 mL 0.1 mM BPA solution was added. The mixture was stirred at RT for 1 hour, and then filtered through a VWR 0.45 μm PTFE syringe filter. The filtrate was collected and measured by UV-vis spectroscopy. PA-POF-2 [0.8:1] was regenerated by washing with MeOH (10 mL x 3) and recovered by filtration. PA-POF-2 [0.8:1] was then dried in vacuo and collected for the next cycle. This adsorption-desorption cycle was performed five times as shown in Fig. 5. The data shown are the average of triplicate experiments.

Solid Phase Extraction Experiments.

1 mg of PA-POF-2 [0.8:1] was placed in a glass vial equipped with a magnetic stirring bar, to which 10 mL 0.1 mM BPA solution was added. The mixture was stirred at RT for 10 min, and

then filtered through a VWR 0.45 µm PTFE syringe filter. The filtrate was collected and measured by UV-vis spectroscopy. PA-POF-2 [0.8:1] was regenerated by washing with MeOH (5 mL x 3) and recovered by filtration. PA-POF-2 [0.8:1] was dried in vacuo and collected for the next cycle. The methanol washing filtrate was evaporated, and the residual solid was dissolved in 10 mL DI water and measured by UV-vis spectroscopy to determine whether BPA that had been adsorbed by PA-POF-2 [0.8:1] could be fully extracted by MeOH. This adsorption-desorption-recovery cycle was performed three times as shown in Fig. 5.

Section 2. Synthetic Procedures

Triethylammonium [tris(4-bromocatecholate)] Phosphate (V) (TTBP)



Triethylammonium [tris(4-bromocatecholate)] Phosphate (V)

A solution of phosphorus pentachloride (4.4 mmol, 918 mg) in anhydrous toluene (30 mL) was added into a three neck flask with nitrogen gas flowing. The flask was heated and stirred in an oil bath at 50 °C. 4-Bromocatechol (13.2 mmol, 2.5 g) was added into the flask while nitrogen flushing. The resulting mixture was kept refluxing and stirring for 24 hours before being cooled gradually to RT. Triethylamine (0.5 mL) was then added dropwise into the reaction mixture via a syringe. Upon adding trimethylamine, the clear orange solution turned white cloudy immediately. The reaction mixture was stirred for 24 hours after which the mixture was vacuum filtered. The solid was washed several times with toluene. The product was obtained as a white solid powder in 92% yield (2.8 g). ¹H NMR (acetone-d6): δ (ppm) = 1.41 (triplet, 9H), 2.90 (singlet,1H), 3.46 (quartet, 6H), 6.51 (doublet, 3H), 6.74 (doublet, 3H), 6.76 (singlet, 3H). ¹³C NMR (acetone-d6): δ (ppm) = 8.1, 46.8, 109.2, 109.8, 111.8, 120.7, 145.0, 146.9. ³¹P NMR (acetone-d6): δ (ppm) = -80.5.



Lithium [tris(4-bromocatecholate)] Phosphate (V)

A solution of phosphorus pentachloride (4.4 mmol, 918 mg) in anhydrous toluene (30 mL) was added into a three neck flask with nitrogen gas flowing. The flask was heated and stirred in an oil bath at 50 °C. 4-Bromocatechol (13.2 mmol, 2.5 g) was added into the flask while nitrogen flushing. The resulting mixture was kept refluxing and stirring for 24 hours before being cooled gradually to RT. n-Butyl lithium (1.6 M in hexanes) (4.4 mmol, 2.75 mL) was then added dropwise into the reaction mixture via a syringe. Upon adding n-Butyl lithium, the clear orange solution turned grey cloudy immediately. The reaction mixture was stirred for 24 hours after which the mixture was vacuum filtered. The solid was washed several times with toluene. The product was obtained as a silver grey solid powder in 87% yield (2.3 g). ¹H NMR (acetone-d6): δ (ppm) = 6.50 (doublet, 3H), 6.73 (doublet, 3H), 6.76 (singlet, 3H). ¹³C NMR (acetone-d6): δ (ppm) = 109.2, 109.8, 111.8, 120.7, 145.1, 147.0. ³¹P NMR (acetone-d6): δ (ppm) = -80.3. ⁷Li NMR (acetone-d6): δ (ppm) = 0.67.

P-WCA-POF-1 [1:1]

The ratios in the brackets represent moles of bromine in TTBP to moles of bromine in TBPM as reactants. The same rule applies for naming all other materials.



1,5-cyclooctadiene (cod, 0.7 mL, 5.55 mmol) was added to a solution of bis(1,5-cyclooctadiene) nickel (0) ([Ni(cod)₂], 1.125 g, 4.09 mmol), and 2,2'-bipyridyl (640 mg, 4.09 mmol) in anhydrous DMF (30 mL). To the purple solution, TTBP (312 mg, 0.449 mmol) and TBPM (213 mg, 0.336 mmol) were added. The reaction mixture was stirred and heated at 90 °C for 3 days to obtain a deep purple suspension. After cooling to RT, the suspension was vacuum filtered. The residue solid was washed with acetone and methanol, and dried in vacuo to give P-WCA-POF-1 [1:1] as a deep green powder (612 mg, 197%).



1,5-cyclooctadiene (cod, 0.7 mL, 5.55 mmol) was added to a solution of bis(1,5-cyclooctadiene) nickel (0) ([Ni(cod)₂], 1.125 g, 4.09 mmol), and 2,2'-bipyridyl (640 mg, 4.09 mmol) in anhydrous DMF (30 mL). To the purple solution, LTBP (269 mg, 0.449 mmol) and TBPM (213 mg, 0.336 mmol) were added. The reaction mixture was stirred and heated at 90 °C for 3 days to obtain a deep purple suspension. After cooling to RT, the suspension was vacuum filtered. The residue solid was washed with acetone and methanol, and dried in vacuo to give P-WCA-POF-3 [1:1] as a deep greyish green powder (379 mg, 142%).

The yield of P-WCA-POF was more than 100% because the material included substantial amounts of Ni as shown by EDX. The Ni impurities cannot be removed by washing with common organic solvents or by vigorous Soxhlet extraction using THF, chloroform, hexanes, acetone, methanol, acetonitrile and water. Chelating agents like EDTA were also tried, resulting in the breaking of P-O bonds and failure of full removal of Ni. Acids (concentrated HCl, 5 M HCl, 2 M HCl, 1 M HCl, 0.2 M HCl, glacial acetic acid, 10 M acetic acid, 2 M acetic acid, 1 M acetic acid) were also tried, and proved that acid treatment was effective in removing Ni, but the PO₆ octahedra structure did not remain intact.

PA-POF-1 [1:1]

1,5-cyclooctadiene (cod, 0.7 mL, 5.55 mmol) was added to a solution of bis(1,5-cyclooctadiene) nickel (0) ([Ni(cod)₂], 1.125 g, 4.09 mmol), and 2,2'-bipyridyl (640 mg, 4.09 mmol) in anhydrous DMF (30 mL). To the purple solution, TTBP (312 mg, 0.449 mmol) and TBPM (213 mg, 0.336 mmol) were added. The reaction mixture was stirred and heated at 90 °C for 3 days to obtain a deep purple suspension. To this purple suspension, concentrated HCl (10 mL x 2) was added and stirred for about 15 min. The reaction mixture got hot and a lot of bubbles were released. The purple color of the reaction mixture faded to green, and a lot of light yellow precipitates formed. This yellow precipitate was then vacuum filtered. The residue solid was washed with H₂O, acetone and methanol, and dried in vacuo to give PA-POF-1 [1:1] as a light yellow powder (106 mg). Elemental analysis (%) found: C (80.55), H (4.90), N (1.05), P (1.66).

PA-POF-1 [2:0], [2:1], [0.6:1], [0.3:1] were also synthesized using the same method except the amounts of TTBP and TBPM were added as below.

PA-POF-1 [2:0] (0 mg): TTBP (312 mg, 0.449 mmol)

PA-POF-1 [2:1] (0 mg): TTBP (312 mg, 0.449 mmol), TBPM (106 mg, 0.168 mmol)

PA-POF-1 [0.6:1] (98 mg): TTBP (187 mg, 0.269 mmol), TBPM (213 mg, 0.336 mmol). Elemental analysis (%) found: C (82.20), H (5.17), N (1.25), P (1.22).

PA-POF-1 [0.3:1] (103 mg): TTBP (94 mg, 0.135 mmol), TBPM (213 mg, 0.336 mmol). Elemental analysis (%) found: C (91.58), H (6.09), N (0.90), P (< 0.4). PA-POF-2 [1:1]

1,5-cyclooctadiene (cod, 0.7 mL, 5.55 mmol) was added to a solution of bis(1,5-cyclooctadiene) nickel (0) ([Ni(cod)₂], 1.125 g, 4.09 mmol), and 2,2'-bipyridyl (640 mg, 4.09 mmol) in anhydrous DMF (30 mL). To the purple solution, LTBP (269 mg, 0.449 mmol) and TBPM (213 mg, 0.336 mmol) were added. The reaction mixture was stirred and heated at 90 °C for 3 days to obtain a deep purple suspension. To this purple suspension, concentrated HCl (10 mL x 2) was added and stirred for about 15 min. The reaction mixture got hot and a lot of bubbles were released. The purple color of the reaction mixture faded to green, and a lot of light yellow precipitates formed. This yellow precipitate was then vacuum filtered. The residue solid was washed with H₂O, acetone and methanol, and dried in vacuo to give PA-POF-2 [1:1] as a light yellow powder (92 mg). Elemental analysis (%) found: C (83.14), H (5.18), N (1.09), P (0.93).

PA-POF-2 [2:0], [2:1], [0.8:1], [0.6:1], [0.4:1], [0.2:1] were also synthesized using the same method except the amounts of TTBP and TBPM were added as below.

PA-POF-2 [2:0] (0 mg): LTBP (269 mg, 0.449 mmol)

PA-POF-2 [2:1] (43 mg): LTBP (269 mg, 0.449 mmol), TBPM (106 mg, 0.168 mmol). Elemental analysis (%) found: C (84.14), H (4.92), N (1.04), P (1.44).

PA-POF-2 [0.8:1] (101 mg): LTBP (215 mg, 0.359 mmol), TBPM (213 mg, 0.336 mmol). Elemental analysis (%) found: C (87.01), H (4.88), N (0.85), P (<0.4).

PA-POF-2 [0.6:1] (90 mg): LTBP (161 mg, 0.269 mmol), TBPM (213 mg, 0.336 mmol). Elemental analysis (%) found: C (87.23), H (5.46), N (0.63), P (<0.4). PA-POF-2 [0.4:1] (97 mg): LTBP (108 mg, 0.180 mmol), TBPM (213 mg, 0.336 mmol). Elemental analysis (%) found: C (88.26), H (5.15), N (0.91), P (<0.4).

PA-POF-2 [0.2:1] (97 mg): LTBP (54 mg, 0.0898 mmol), TBPM (213 mg, 0.336 mmol). Elemental analysis (%) found: C (88.91), H (5.34), N (0.84), P (<0.4).

Elemental analysis was performed by Midwest Microlab, LLC. P (<0.4) means the phosphorus content was under the detection limit. Oxygen content cannot be analyzed when phosphorus is present in the sample.

It is worthwhile to mention that no product was collected after the hydrochloric acid treatment in the synthesis of PA-POF-1 [2:0], PA-POF-1 [2:1], PA-POF-2 [2:0]. This can be explained by the fact that the acid treatment breaks P-O bonds and leaves only terminal PO₄. If too much TTBP or LTBP is used as the starting monomer, the framework is linked by a large number of PO₆ nodes. The breakage of these nodes by acid depolymerizes the framework to give smaller, soluble molecules.

Section 3. Nitrogen Sorption Isotherms of P-WCA-POFs

Figure S1: Nitrogen adsorption (red squares) and desorption (black squares) isotherms of polymerized TTBP measured at 77K.



Figure S2: Nitrogen adsorption (red squares) and desorption (black squares) isotherms of P-WCA-POF-1 [1:1] measured at 77K.



Figure S3: Nitrogen adsorption (red squares) and desorption (black squares) isotherms of P-WCA-POF-2 [1:1] measured at 77K.



Section 4. ³¹P Solid State NMR Spectra of P-WCA-POFs and PAPOFs

Figure S4: ³¹P solid state NMR spectrum of polymerized TTBP. Asterisks (*) indicate peaks arising from spinning side bands.



Figure S5: ³¹P solid state NMR spectrum of P-WCA-POF-1 [1:1]. Asterisks (*) indicate peaks arising from spinning side bands.



Figure S6: ³¹P solid state NMR spectrum of P-WCA-POF-2 [1:1]. Asterisks (*) indicate peaks arising from spinning side bands.



Figure S7: ³¹P solid state NMR spectrum of PA-POF-1 [1:1]. Asterisks (*) indicate peaks arising from spinning side bands.



Figure S8: ³¹P solid state NMR spectrum of PA-POF-1 [0.6:1]. Asterisks (*) indicate peaks arising from spinning side bands.







Figure S10: ³¹P solid state NMR spectrum of PA-POF-2 [2:1]. Asterisks (*) indicate peaks arising from spinning side bands.



Figure S11: ³¹P solid state NMR spectrum of PA-POF-2 [1:1]. Asterisks (*) indicate peaks arising from spinning side bands.



Figure S12: ³¹P solid state NMR spectrum of PA-POF-2 [0.8:1]. Asterisks (*) indicate peaks arising from spinning side bands.







Figure S14: ³¹P solid state NMR spectrum of PA-POF-2 [0.4:1].



Figure S15: ³¹P solid state NMR spectrum of PA-POF-2 [0.2:1]. Asterisks (*) indicate peaks arising from spinning side bands.



Section 5. EDX spectra of P-WCA-POFs and PAPOFs





Figure S17: EDX spectrum of P-WCA-POF-1 [1:1] after treatment of concentrated HCl.





Figure S18: EDX spectrum of P-WCA-POF-2 [1:1].

Figure S19: EDX spectrum of P-WCA-POF-2 [1:1] (PA-POF-2 [1:1]) after treatment of concentrated HCl.



Figure S20: EDX spectrum of polymerized TTBP after ion exchange in NaCl solution. No Na can be found in the EDX spectrum shows that the cation was not exchangeable.





Figure S21: EDX spectrum of PA-POF-1 [1:1] after ion exchange in NaCl solution.

Figure S22: EDX spectrum of PA-POF-1 [0.6:1] after ion exchange in NaCl solution.





Figure S23: EDX spectrum of PA-POF-1 [0.3:1] after ion exchange in NaCl solution.



Figure S24: EDX spectrum of PA-POF-2 [2:1] after ion exchange in NaCl solution.

Figure S25: EDX spectrum of PA-POF-2 [1:1] after ion exchange in NaCl solution.





Figure S26: EDX spectrum of PA-POF-2 [0.8:1] after ion exchange in NaCl solution.

Figure S27: EDX spectrum of PA-POF-2 [0.6:1] after ion exchange in NaCl solution.





Figure S28: EDX spectrum of PA-POF-2 [0.4:1] after ion exchange in NaCl solution.

Figure S29: EDX spectrum of PA-POF-2 [0.2:1] after ion exchange in NaCl solution.



Section 6. Pore Size Distribution of PA-POFs

Figure S30. Pore size distribution of (a) PA-POF-1s and (b) PA-POF-2s calculated from CO_2 sorption isotherms collected at 273 K by NLDFT method (carbon slit pore model).



Section 7. FTIR Spectra of PA-POFs

Figure S31: FTIR spectra of (A) PA-POF-1s and (B) PA-POF-2s. The FTIR spectrum of PAF-1 was inserted in each figure for comparison. Spectra are labeled by compound names. Because of the low content of phosphorus, P-O stretching is not obvious in the spectra.



Section 8. SEM Images of PAPOFs

Figure S32: SEM images of PA-POF-1s. (A) PA-POF-1 [1:1]; (B) PA-POF-1 [0.6:1]; and (C) PA-POF-1 [0.3:1].



Figure S33: SEM images of PA-POF-2s. (A) PA-POF-2 [2:1]; (B) PA-POF-2 [1:1]; (C) PA-POF-2 [0.8:1]; (D) PA-POF-2 [0.6:1]; (E) PA-POF-2 [0.4:1]; and (F) PA-POF-2 [0.2:1].



Section 9. Powder XRD Patterns of PAPOFs





Figure S35: XRD patterns of PA-POF-2s. Patterns are offset for clarification.



Section 10. Thermograms of PAPOFs







Figure S37: (A) PA-POF-1s and (B) PA-POF-2s thermograms measured in nitrogen.

Section 11. BPA Removal Studies

Figure S38: (A) UV-vis spectra and (B) removal efficiencies of PA-POF materials and PAF-1 in 100 mL mg⁻¹ 0.1 mM BPA solution. In the studies, 1 mg of each material was stirred in 100 mL 0.1 mM BPA solution at RT for 1 hour, after which the resulting mixture was filtered through a VWR 0.45 μ m PTFE syringe filter. The filtrate was collected for UV-vis analysis.



Figure S39: UV-vis spectra recorded at different contact time and time dependent removal efficiency of 10 mL mg⁻¹ (A) 0.1 mM 2-naphthol, (B) 0.1 mM 1-naphthyl amine, and (C) 0.1 mM bisphenol S.



Figure S40: UV-vis spectra recorded at different contact time and time dependent removal efficiency of 10 mL mg⁻¹ (A) 0.09 mM propranolol hydrochloride, (B) 0.1 mM metolachlor, (C) 0.04 mM ethinyl oestradiol, and (D) 0.1 mM 2,4-dichlorophenol.



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Section 12. BET Plots of PA-POFs.

Figure S41. BET plot for PA-POF-1 [1:1] calculated from nitrogen adsorption data.



Figure S42. BET plot for PA-POF-1 [0.6:1] calculated from nitrogen adsorption data.



Figure S43. BET plot for PA-POF-1 [0.3:1] calculated from nitrogen adsorption data.



Figure S44. BET plot for PA-POF-2 [2:1] calculated from nitrogen adsorption data.



Figure S45. BET plot for PA-POF-2 [1:1] calculated from nitrogen adsorption data.



Figure S46. BET plot for PA-POF-2 [0.8:1] calculated from nitrogen adsorption data.



Figure S47. BET plot for PA-POF-2 [0.6:1] calculated from nitrogen adsorption data.



Figure S48. BET plot for PA-POF-2 [0.4:1] calculated from nitrogen adsorption data.



Figure S49. BET plot for PA-POF-2 [0.2:1] calculated from nitrogen adsorption data.



SAMPLE ID	BET SURFACE AREA (M2 G-1)	DFT & MONTE- CARLO CUMULATIVE PORE VOLUME (CM3 G-1)	CO ₂ UPTAKE AT 1 BAR (CC G-1)			ISOSTERIC HEAT OF CO2
			258 K	273 K	298 K	ADSORPTION (KJ MOL-1)
PA-POF-1 [1:1]	478	0.40	66	56	34	23.8
PA-POF-1 [0.6:1]	979	0.56	89	85	54	20.8
PA-POF-1 [0.3:1]	1548	0.75	101	88	64	15.7
PA-POF-2 [2:1]	1291	0.74	78	73	43	22.2
PA-POF-2 [1:1]	1536	0.86	132	98	57	21.4
PA-POF-2 [0.8:1]	1761	0.84	126	91	64	23.8
PA-POF-2 [0.6:1]	2084	1.03	135	103	66	19.8
PA-POF-2 [0.4:1]	2220	1.08	133	97	59	20.4
PA-POF-2 [0.2:1]	2408	1.09	107	94	53	20.3

Table S1. Summary of porosity, pore volume, N_2 and CO_2 uptake behavior, heats of CO_2 adsorption of PAPOFs.

Reference

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