Sustainable Synthesis of Superhydrophobic Perfluorinated Nanoporous Networks for Small Molecule Separation

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Ⓢ *Supporting Information*

ABSTRACT: Nanoporous polymers offer great promise in chemical capture and separations because of their versatility, scalability, and robust nature. Here, we report a general methodology for one-pot, metal-free, and room-temperature synthesis of nanoporous polymers by highly stable carbon−carbon bond formation. Three new polymers, namely, COP-177, COP-178, and COP-179, are derived from widely available perfluoroarenes and found to be superhydrophobic, microporous, and highly stable against heat, acid, base, and organic solvents. Nitrile, amine, and ether functionalities were successfully installed by S_NAr-type postfunctionalization and were shown to increase CO_2 uptake twice and CO_2/N_2 selectivity 4-fold. Due to its inherent superhydrophobicity, COP-177 showed high organic solvent uptake both in liquid and vapor form. Furthermore, in a first of its kind, by combining microporosity and hydrophobicity, COP-177 separated two small molecules with the same boiling point in a continuous column setting.
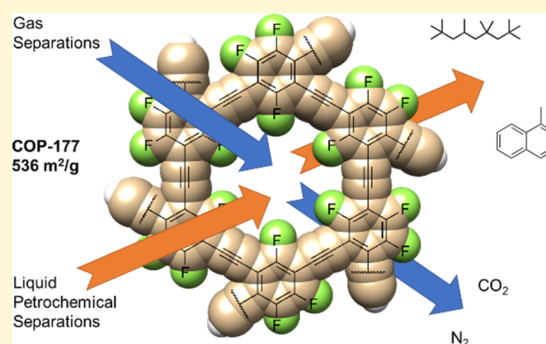
INTRODUCTION

Porous organic materials with strong covalent bonding have great potential for industrial applications such as carbon capture,[1,2] water treatment,[3] and catalysis.[4] To increase rigidity and therefore permanent porosity, multidentate bonding and heterocyclic linkages are often employed. For example, polymers of intrinsic microporosity (PIMs), which are unique porous polymers with the added property of solubility, use the dibenzodioxane ring as a linker.[5,6] We have recently introduced benzoxazoles to form porous networks that can withstand temperatures up to a record 600 °C.[4,7] Covalent triazine frameworks (CTFs) contain triazine building blocks, an unusual crystallinity, despite their high-temperature, ionothermal production.[8] We also showed that triazine-containing sulfur-covalent organic polymers (COPs) are shown to be highly porous and capable of effective CO_2 storage under high pressures.[9]

Carbon−carbon (C−C) bonded porous organic polymers, in particular, offer high stability against chemical, thermal, and mechanical impact.[2,10] For example, PAF-1, one of the most well-known porous polymers with a record high highest surface area, is formed through a Yamamoto-type cross-coupling reaction of tetrakis(4-bromophenyl)methane.[11] Other well-known C−C coupling reactions are also found to produce highly porous, stable networks including Suzuki coupling,[12,13] Sonogashira coupling,[14,15] or Heck reactions.[16,17] Our recent report describing a COP-220 structure followed Sonogashira

coupling of a commercial dye molecule with an available linker to synthesize a C−C bonded porous network, which was stable to thermal and chemical treatments.[18] The report by Jiang et al. introduces another porous polymer named CMP-0, which also showed high chemical and thermal stability.[19] In those reactions, however, costly catalysts such as Pd salts are used, which limits the application of the polymers to large-scale applications. CO_2 capture, for example, a well-publicized potential application of porous materials, demands microporous polymers without any metal involvement (either in the structure or even as a catalyst) since the scale of the sorbent needed is in the order of billions of tons.[1] This makes the cost efficient and easy synthetic ways to build porous polymers, particularly the C−C bonded ones, very important.

To the best of our knowledge, there are only a few examples for one-pot synthesis of metal-free C−C bonded porous polymers. In 2015, Schute and Rose reported the synthesis of a hyper-cross-linked polymer (HCP) based on the 4,4′-bis-(chloromethyl)-1,1′-biphenyl monomer.[20] Only using Brønsted acids such as sulfuric acid or trifluoromethanesulfonic acid as a catalyst, HCP could be produced in a gram scale. Wang et al. reported the application of Knoevenagel condensation to make a porous conjugated polymer
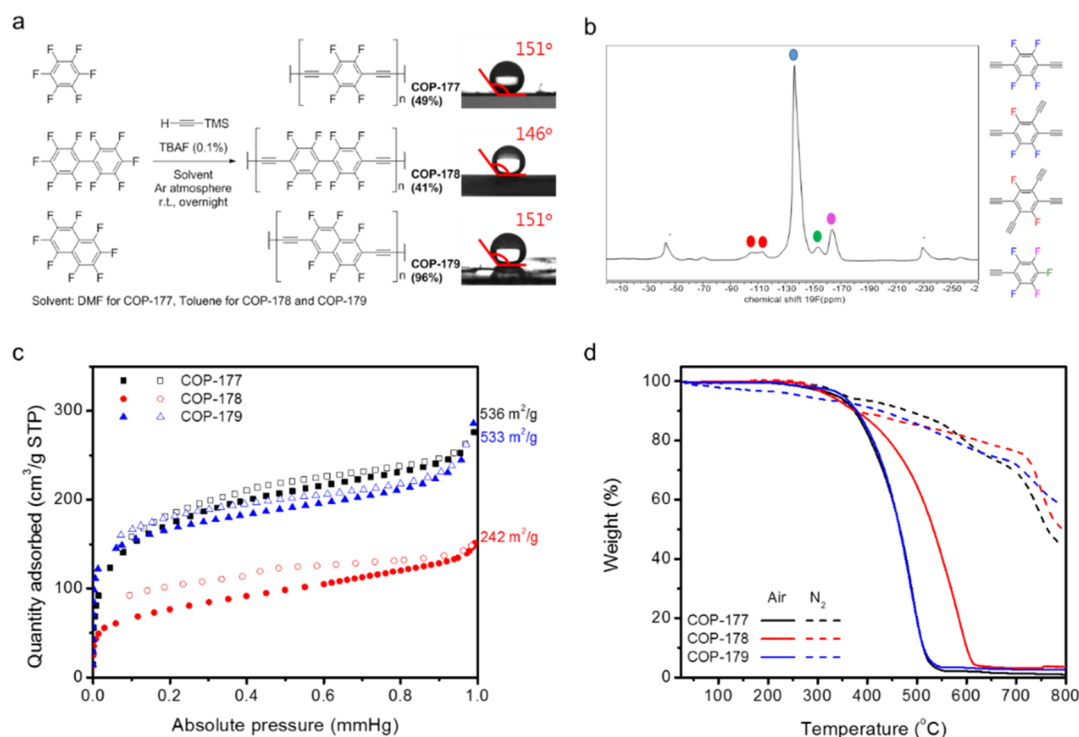
Figure 1. Synthesis and characterization of COP-177, 178, and 179. (a) Synthetic scheme and water contact angle measurement. (b) ^{19}F solid-state NMR of COP-177. (c) Argon physisorption isotherm at 87 K. (d) TGA analysis under air and N_2 flow.

(PCP).[21] Because of the rigid backbone exclusively composed of C−C bonds, PCP was stable enough for photocatalytic hydroxylation of arylboronic acids. Condensation reactions were further applied in the synthesis of 2D-CAP (conjugated aromatic polymer) reported by Liu et al.[10] There, a stable crystalline two-dimensional polymer was synthesized, which was also applicable as an organic anode in a sodium cell. We also reported condensation-based porous polymers that showed potential in ion detection[22] and CO_2 capture.[23] More recently, Lee et al. have suggested a new strategy for metal-free synthesis of conjugated microporous polymers (CMPs) with various acids.[24] In their report, CMP was synthesized via two steps: (1) formation of the imine bond followed by (2) in situ cyclization to get the C−C bond. Despite all these efforts, metal-free cross-coupling reactions that provide rigid aromatic backbones are still not adequately studied.

Our investigations for a robust, metal-free C−C bonding methodology that would yield rigid aromatic building blocks led to a selective S_NAr chemistry.[25] We showed that a perfluorinated core could react with a silylated alkyne under catalytic amounts of fluoride. This was a significant departure from precious-metal-catalyzed systems and offered a one-pot access to the versatile, microporous polymeric networks. An additional benefit was the easy functionalization of the porous polymer after synthesis. Our previous study, however, required the use of the tetraphenylmethane core and therefore was not quite promising for its wide-scale implementation and overall sustainability.[26]

One particular advantage of making C−C bonded porous networks from perfluorinated monomers is to have high coverage of fluoride in the super structure. This renders them superhydrophobic, arising from the low surface energy.[27] Some examples include PFCMP-0 by Yang et al.,[28] FCTF-1 by Zhao

et al.,[29] and COP-99 previously reported by us.[3] Although superhydrophobicity in porous materials has great promise in oil uptake,[30−33] to the best of our knowledge, the effective use of their inherent oleophilicity is scarce. More importantly, none of the fluorinated porous materials are used to couple superhydrophobicity with size-exclusion properties of micropores.

In this research, we report a one-pot, metal-free synthetic strategy for perfluorinated porous polymers with C−C linkages from commercial building blocks. The resulting polymers, indexed as COP-177, 178, and 179, were highly stable to heat, acid or base, or organic materials. Their C−F bonds were activated under reflux conditions with strong nucleophiles. Some of these modifications increased CO_2 uptake and CO_2/N_2 selectivity dramatically. Due to the superhydrophobicity, high solvent affinity was observed for liquid and vapor phases. Furthermore, in accordance with the pore size distribution, we showed that microporous COP-177 could be used to separate small molecules with the same boiling point and different molecular weights in a continuous column setting. This also marks the first such example of petrochemical separations of liquids without the need for energy-intensive distillation.

■ EXPERIMENTAL SECTION

Materials and Characterization. The chemicals were purchased from Sigma-Aldrich, TCI, or Alfa Aesar. Silica gel 60 (catalog number 107734) as a control for the small molecule separation test was purchased from Merck Millipore. Chemicals and products were verified with ^{1}H NMR spectra obtained with a Bruker AVANCE 400. Contact angle measurements were performed with a SEO Phoenix 300 Plus contact angle analyzer. The polymer powder was finely ground using mortar and pestle. On a glass slide, ground powder (about 100 mg) was loaded, and another glass slide was pressed against the powder to form a thin film. The contact angle was measured by dropping water on the film and analyzing with a
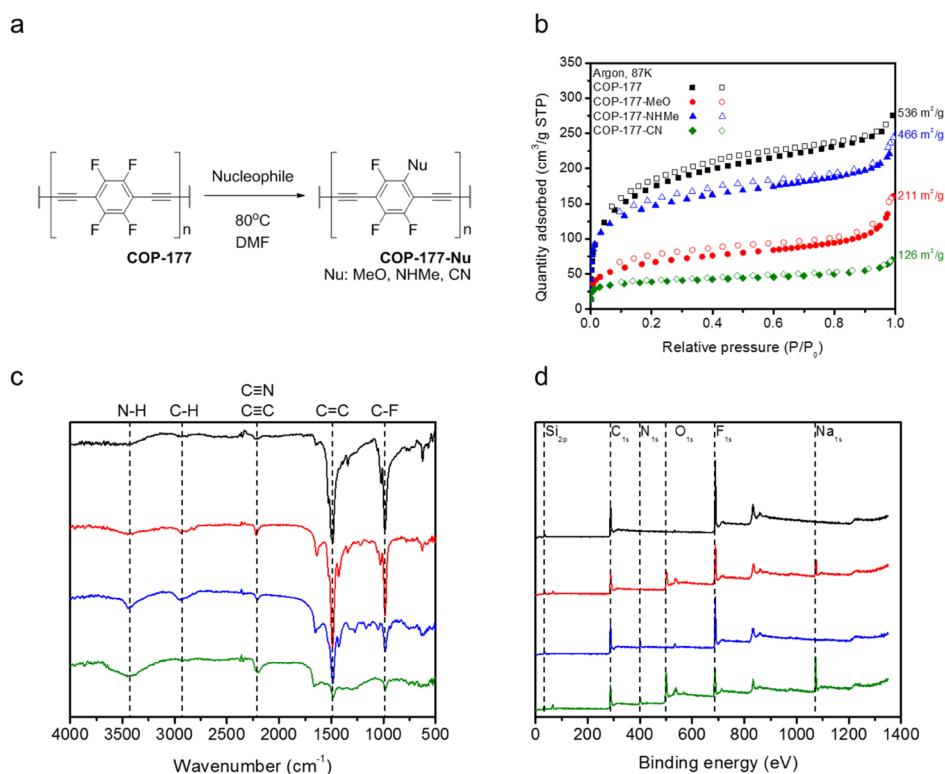
Figure 2. Synthesis and characterization of postfunctionalized COP-177. (a) Synthetic scheme for the reaction. (b) Argon physisorption isotherm at 87 K. (c) FTIR spectra. (d) XPS spectra. Unassigned peaks are from Na Auger (497 eV) and F Auger (832 and 858 eV).

microscope. ^{19}F solid-state NMR spectra were acquired from an Agilent 400 MHz 54 mm NMR DD2. Argon gas physisorption and CO_2, N_2, or organic vapor physisorption isotherms were obtained using a Micromeritics 3-Flex surface characterization analyzer. For organic vapor physisorption, adsorptive properties were imported from the Micromeritics database. Port 3 of the instrument was used as the vapor source. The quantity of adsorption was recorded from the instrument as mmol/g unit up to a relative pressure of 0.8 to prevent solvent condensation in the measurement system. The unit was directly converted to mg/g based on the molecular weight of each adsorptive. Powder X-ray diffraction (PXRD) patterns were acquired on a Rigaku SmartLab with Cu Kα radiation. Thermogravimetric analysis (TGA) was carried out with a Shimadzu Model DTG-60A. FTIR spectra on KBr pellets were measured with a Jasco FTIR-4100 type-A spectrometer. X-ray photoelectron spectroscopy (XPS) spectra were obtained using a Thermo VG Scientific Sigma Probe system equipped with an Al Kα X-ray source with an energy resolution of 0.47 eV FWHM under UHV conditions of 10^{-10} torr.

Synthesis of COP-177, 178, and 179. Perfluoroarene (10 mmol) and trimethylsilylacetylene (20 mmol, 2.82 mL) were dissolved in a desired reaction solvent (20 mL) at room temperature under nitrogen. 0.1 M tetrabutylammonium fluoride (100 μL, 0.01 mmol) was added dropwise to the transparent solution, which instantly darkened. The mixture was left to stir at room temperature overnight. Methanol (20 mL) was added, and the polymer was filtered out and Soxhlet-extracted for 24 h with THF and a further 24 h with chloroform. The polymer was dried at 100 °C for 18 h and obtained as a dark brown solid.

Postfunctionalization of COP-177. COP-177 (150 mg) was dispersed in DMF (10 mL). A nucleophile (sodium methoxide 150 mg, methylamine 0.8 mL, or sodium cyanide 150 mL) was added, and the mixture was stirred at 80 °C for 24 h. Water was added, and the solid was filtered off. The solid was washed extensively with dilute HCl, MeOH, and THF until the filtrate becomes neutral.

The resulting polymer was dried at 120 °C for 18 h and obtained as a dark brown powder.

Organic Solvent Uptake Test. In a 2 mL syringe, cotton wool (10 mg) was used to block the tip. One of the syringes was used as a control. To the other syringes, COP-177 (10 mg) was added. After that, 1 mL of solvent was added so that it flowed out through the tip of the syringe. Once the flow ceased, the increased weight of the syringe was measured. Subtracting the amount absorbed by the cotton wool (control) resulted in the actual uptake of solvents by COP-177.

Petrochemical Separation Test. In a 1 mL syringe, 250 mg of COP-177 powder was packed. Deuterated chloroform (CDCl$_3$) was used to equilibrate the column. Then 0.1 mL of an equimolar mixture of 2,2,4,6,8,8-heptamethylnonane and 1-methylnaphthalene was loaded. The resulting fractions every 0.05 mL was gathered by continued elution with CDCl$_3$. Each fraction was diluted with fresh CDCl$_3$ and directly analyzed using ^{1}H NMR. The amounts of molecules were quantified by tetramethylsilane as an internal reference. For the control, the same procedure was performed except the use of silica gel of the same amount to COP-177 as a column packing material.

RESULTS AND DISCUSSION

Synthesis and Characterization of Porous Polymers. To synthesize perfluorinated porous polymers, perfluoroarenes were reacted with trimethylsilylacetylene and a catalytic amount of organic fluoride salt under an argon atmosphere (Figure 1a). This one-pot reaction did not require the use of a metal catalyst or elevated temperature. Three network polymers were produced depending on the type of perfluoroarene used: hexafluorobenzene for COP-177, decafluorobiphenyl for COP-178, and octafluoronaphthalene for COP-179. Reaction condition optimizations and the detailed proposed mechanism are shown in Table S1 and Figure S1, respectively. Contact angle measurement with water was performed to analyze hydrophobicity. All three polymers were highly hydrophobic; especially for COP-177 and COP-179, their water contact angle was 151°, showing super-
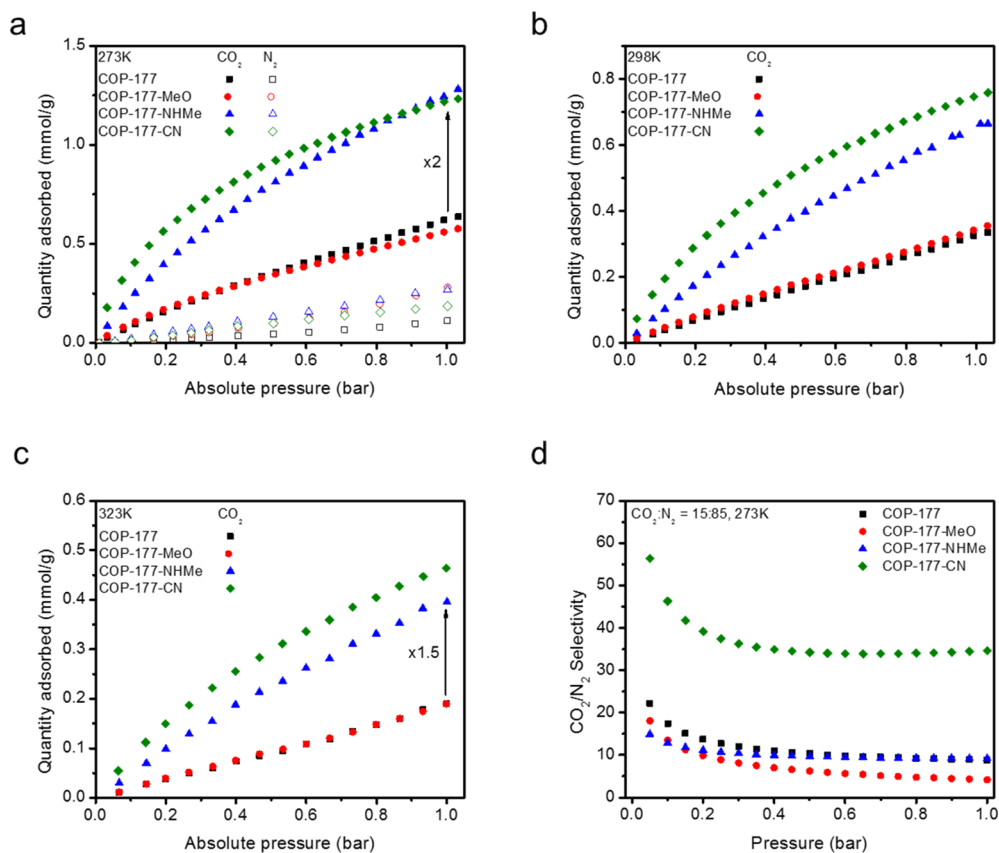
Figure 3. CO_2 adsorption and CO_2/N_2 selectivity for COP-177 and functionalized polymers. (a) CO_2 and N_2 adsorption at 273 K. (b) CO_2 adsorption at 298 K. (c) CO_2 adsorption at 323 K. (d) CO_2/N_2 selectivity at 273 K calculated by IAST.

hydrophobicity. To get insight into material conformation, ^{19}F solid-state NMR spectra were acquired for COP-177 (Figure 1b). Interestingly, it showed several different peaks for fluorine atoms. Although the fluorine between another fluorine and $C\equiv C$ bond (blue in Figure 1b) dominates, peaks for the fluorines between two alkynes (red in Figure 1b) or between two other fluorines (purple or green in Figure 1b) could be observed. These diverse types of new C−C bonds enabled COP-177 to form a porous network. Based on the integral value of each peak, terminal fluorines (green in Figure 1b) correspond to 5.6% of total fluorines. The low ratio of terminal fluorines shows cross-linked structures that feature permanent porosity and high reproducibility. To evaluate the crystallinity of the material, PXRD data were acquired for COP-177 (Figure S2). When COP-177 was made in toluene, it showed a complete amorphous nature, as is common for most porous polymers. However, when DMF was used in the synthesis, two major peaks were observed at 2θ values of 19.1 and 30.7°, corresponding to d values of 4.636 and 2.915 Å, respectively. The degree of crystallinity was calculated as 52.2%, reflecting the half-crystalline property of COP-177 that is made in DMF. Pore properties of the three polymers were analyzed by argon physisorption measurements at 87 K (Figure 1c). All three polymers showed a type I isotherm, showing the microporous properties of the three materials. Brunauer−Emmett−Teller (BET) surface areas were 536, 242, and 533 m^2/g for COP-177, 178, and 179, respectively. Because of high electronegativity, the fluorine atom has a small van der Waals radius of 1.32 Å and strong C−F bond (bond dissociation energy of 485 kJ/mol).[34] The formation of the rigid C−F bond allows

the fluoropolymer to have high thermal stability. In TGA, all the three polymers showed exceptionally high stability at 300 °C and above (Figure 1d). In addition to the thermal stability, they were also stable under acid or base, water, and organic solvents.

Postmodification of the Fluorinated Porous Polymers. As we previously described,[25] aromatic fluorides could effectively be substituted by strong nucleophiles through S_NAr reactions. Here, three different types of nucleophiles were used to introduce new functional groups to COP-177: MeO, NHMe, and CN (Figure 2a). Pore property changes depending on the introduced functional group were analyzed by argon physisorption analysis (Figure 2b). Although all the functionalized polymers were still microporous, the BET surface area decreased from the original version due to the introduction of bulkier functional groups. For MeO, NHMe, and CN introduction, surface areas were 466, 211, and 126 m^2/g, respectively. They were also characterized by FTIR spectra (Figure 2c). Overall peak shapes are similar, but it is clear that the N−H bond is introduced to COP-177-NHMe and the triple bond signature peak got stronger in COP-177-CN. XPS spectra indicate the introduction of the nitrogen element by the N 1s peak at 400 eV for COP-177-NHMe and COP-177-CN (Figure 2d). The peaks for C 1s and F 1s were predominant in all structures.

CO_2 Uptake and Separations. COP-177 and postmodified polymers were tested for CO_2 adsorption (Figure 3a−c). At 273 K, COP-177 and its methoxy modification showed about 0.6−0.7 mmol/g uptake for CO_2. However, the introduction of methylamine or nitrile functional groups
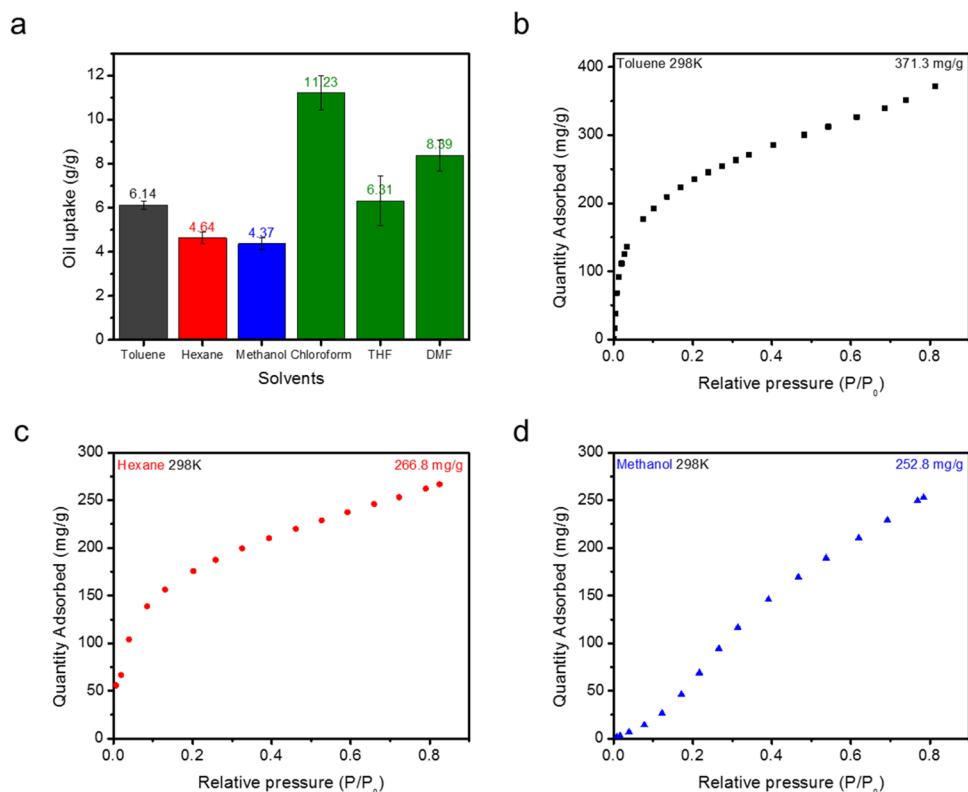
a

b

c

d

Figure 4. Organic solvent uptake capacity tests of COP-177. (a) Liquid phase uptake tests for toluene, *n*-hexane, methanol, chloroform, tetrahydrofuran, and *N,N*-dimethylformamide. Vapor adsorption isotherms at 298 K: toluene (b), *n*-hexane (c), and methanol (d).

increased the CO_2 uptake to 1.28−1.35 mmol/g, which is about twice that of the original version. This increase of CO_2 uptake originates from the increased chemical interaction between introduced functional groups and amine or nitrile.[1,35,36] CO_2/N_2 selectivities for flue gas conditions (CO_2/N_2 = 15:85) were calculated according to the ideal adsorbed solution theory (IAST) (Figure 3d). COP-177-CN showed higher CO_2/N_2 selectivity of minimum 35 at 1 bar, which was about 4 times higher than the other polymers. Since the argon adsorption for COP-177-CN was the lowest among the derivatives of COP-177, the exceptionally high CO_2-philicity of the nitrile functional group might be at play. Calculation of the ratio between surface area by argon adsorption to CO_2/N_2 selectivity resulted in 0.275 (=34.6/126), which is about 17 times higher than COP-177 (0.016 = 8.8/536). High affinity of the COP-177-CN to CO_2 is thought to be originated from the partial negative character of the nitrogen atom in the nitrile group. In methylamine modification, nitrogen is directly connected to the aromatic ring, and the free electron pair is both more delocalized and shielded by the methyl substituent.

Solvent Uptake Properties of the Superhydrophobic Porous Polymers. Inspired by the hydrophobicity of COP-177, its chemical affinity to several organic solvents was investigated (Figure 4a). Solvents were added to a COP-177 powder inside a syringe so that they are absorbed by the polymer and excess amounts are released out of the syringe. All the six solvents tested (toluene, hexane, methanol, chloroform, THF, and DMF) showed high affinity to COP-177, with especially high uptake for chloroform to 11 times of COP-177 weight (11.23 g/g) by mass. Based on the molar calculation and volumetric calculation, uptake values of methanol and

DMF were the highest (Figure S3). Water was also tested for uptake by COP-177, but there was not enough contact between water and COP-177, showing its superhydrophobicity. Although liquid phase oil uptake is quite common in the porous polymer field,[33] to the best of our knowledge, there are only a few reports applying hydrophobic porous polymers for organic vapor uptake.[13,37−39] Here, we report the vapor adsorption properties of COP-177 for three solvents: toluene, *n*-hexane, and methanol (Figure 4b−d). The density difference between liquid and gas reduced the scale of vapor adsorption to mg/g. The general trend for vapor adsorption capacity matched to that for liquid absorption capacity. Based on the adsorption at a relative pressure of 0.8, toluene was adsorbed as 37.1 wt % to COP-177. For *n*-hexane and methanol, this value was 26.7 and 25.3 wt %, respectively. One interesting point is the isotherm-type dependence on solvents. For toluene and hexane, type I isotherm was observed in which the vapor molecules fill the micropore structure in relatively low pressures. However, for methanol, the isotherm curve was concave to the P/P_0 axis in the low-pressure region, resembling a type V isotherm. This indicates that the interaction between methanol molecule and COP-177 network is weaker than the interaction between methanol molecules. Considering that methanol is much more hydrophilic than toluene or hexane, we suggest that vapor isotherm measurement is also a clear way to observe hydrophobicity.

Separation of Same Boiling Point Petrochemicals. Petrochemical separation by distillation is one of the most energy intensive of the chemical technologies and therefore was selected among the "seven chemical separations to change the world".[40] As particles of micrometer scales are used to separate macromolecules such as polymers or proteins by gel
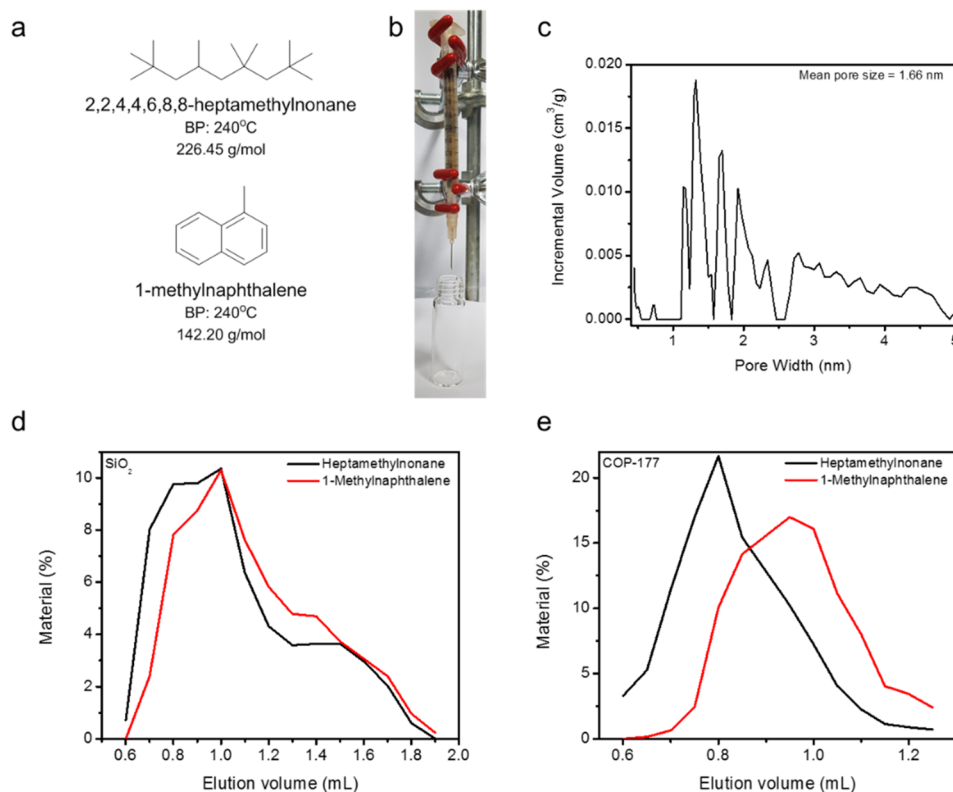
Figure 5. Small molecule separation tests with COP-177. (a) Two target molecules to be separated and their properties. (b) Column setup with COP-177. (c) Pore size distribution of COP-177 calculated by NLDFT from argon physisorption isotherms. (d) Separation with silica gel as a control. (e) Separation with COP-177.

permeation chromatography, we expected that COP-177 with nanosized pores would be suitable for small molecule separation. Two petrochemical molecules, namely, 2,2,4,4,6,8,8-heptamethylnonane and 1-methylnaphthalene, that are industrially used for determination of the cetane number, an indicator for kerosene quality, were chosen. Although their sizes and molecular weights are different, they have the same boiling point, which makes their separation difficult (Figure 5a). Here, we show that COP-177 could separate them in a rough setting of a column filled with its microporous powder (Figure 5b). The molecular mixture was loaded, eluted with deuterated chloroform, and directly analyzed by ^{1}H NMR to get relative ratios between two molecules at varying collection times. In the pore size distribution of COP-177, the median pore width was calculated by the nonlocal density functional theory (NLDFT) to be 1.66 nm and total pore volume was calculated to be 0.485 cm^3/g (Figure 5c). Since 2,2,4,4,6,8,8-heptamethylnonane is bulkier than 1-methylnaphthalene, it was expected for 1-methylnaphthalene to be trapped inside the pores so that its elution would be slower. As a control column packing, silica gel with particle sizes between 63 to 200 μm was used. Separation trial from the silica column resulted in almost simultaneous elution of both molecules together (Figure 5d) because of very small sizes of target molecules compared to the particle size. However, when the COP-177-packed column was used, 1-methylnaphthalene was eluted slower than 2,2,4,4,6,8,8-heptamethylnonane (Figure 5e). Considering the small size differences of less than 100 Da, this experimental demonstration gives an insight into the promising application of microporous structures for small molecule separation.

CONCLUSIONS

In summary, we presented a synthetic strategy for three novel porous polymers that feature C−C bond linkages. The reaction is one-pot, metal free, and takes place at room temperature. The polymers from different perfluoroarenes were shown to be superhydrophobic and highly stable. COP-177 was further modified with three kinds of nucleophiles. The introduction of the nitrile group increased CO$_2$/N$_2$ selectivity 4 times from the original COP-177. Superhydrophobicity of COP-177 was further studied for organic solvent adsorption in both liquid and vapor phases. Especially, the vapor adsorption isotherm for methanol showed a type V isotherm, which is an indicator for the methanol-phobic property of COP-177. Finally, two small molecules were shown to be separated by a COP-177-filled column. This suggests a general concept that the synergistic effect of microporosity and superhydrophobicity of a porous polymer can be applied for size-exclusion molecular separations.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.9b01447.

Reaction conditions optimization, suggested mechanism for polymer synthesis, powder XRD patterns and solvent uptake properties of COP-177 in liquid pase (PDF)

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