

Fluorinated Conjugated Microporous Polymers Based on Pillar[*n*]arenes for Removal of Water Pollutants and Their Cation Selective Adsorption

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ABSTRACT: Organic dyes are widely used in many applications. However, the leaking of organic dyes into the natural environment has become a severe and worldwide problem owing to their high toxicity and non-biodegradability. Therefore, the development of effective removal technologies for organic dyes is required. In this paper, we report the synthesis and adsorption properties of highly fluorinated conjugated microporous polymers based on pillar[*n*]arenes. The polymers exhibited large Brunauer–Emmett–Teller surface areas of up to 1063 m² g⁻¹ and selective adsorptive removal of cationic organic dyes from aqueous solution. Comparison with the nonfluorinated polymers indicated that the adsorption mechanism mainly relies on the fluorine–cation electrostatic interaction. The maximum adsorption capacity reached 313 mg g⁻¹ for crystal violet, which is higher than those of common conventional adsorbents. Additionally, the fluorinated polymers could function as proton channel when it was embedded into lipid membranes.

KEYWORDS:

Porous Material, Pillar[*n*]arene, Network Polymer, Dye Adsorption, Water Pollutant, Ion Channel

INTRODUCTION

As outlined in Sustainable Development Goal 6, water resources are essential for our daily lives, and ensuring a clean and stable water supply is a critical issue.¹ However, water pollution has become a severe problem owing to the release of pollutants into rivers and other environments as a result of the recent development of the chemical industry.² Organic dyes, which are used in various industrial products including textiles, cosmetics, printings, paper, and pharmaceuticals, are one of the most common water pollutants. Organic dyes often block sunlight and inhibit plant growth, and some organic dyes have also been reported to be neurotoxic and carcinogenic, raising

1 concerns about their effect on ecosystems.^{3,4} Furthermore, in recent years, there have been
2 particular concerns about the adverse health effects associated with perfluoroalkyl substances
3 (PFASs). PFASs are widely used for surface treatments and other applications. However, the use
4 of PFASs is now strictly regulated in many countries owing to their damage to human health
5 resulting from PFAS contamination of water resources. Because they are extremely difficult to
6 decompose owing to their strong C–F bonds and remain in the environment for decades, they are
7 called “eternal chemical substances”.^{5–9} Therefore, the development of new technologies and
8 materials for removing these pollutants from water resources is required. To remove these
9 pollutants, extensive efforts have been devoted to oxidative degradation with ozone,¹⁰
10 photocatalytic degradation¹¹ and adsorptive removal using porous materials.¹² In particular,
11 adsorptive removal using porous materials is simple and efficient, and it is a reliable method for
12 water treatment.³

13 Many types of synthetic porous materials have been applied to remove harmful pollutants.
14 Metal–organic frameworks,¹³ covalent organic frameworks,¹⁴ and conjugated microporous
15 polymers (CMPs)¹⁵ are representative examples of porous functional materials. The rigid carbon–
16 carbon bonds of CMPs give them permanent porosity and much higher thermal and chemical
17 stability than metal–organic and covalent organic frameworks. Furthermore, CMPs offer
18 significant design flexibility, and thus a wide variety of porous materials with particular properties
19 can be synthesized from various types of building blocks.

20 Pillar[*n*]arenes^{16–19} are macrocyclic molecules composed of hydroquinone units connected by
21 methylene bridges at the para positions. They are currently attracting significant attention as
22 outstanding building blocks of CMPs because $2n$ functionalized linkers can be densely installed
23 per pillar[*n*]arene scaffold, and the functionalized pores can act as binding sites for specific

1 adsorbents.²⁰ Consequently, they have potential applications in gas separation,²¹ sensors,²² water
2 treatment,^{23,24} and heterogeneous catalysis.²⁵

3 The fluorine atom is the most electronegative element and sterically as small as the hydrogen
4 atom.^{26–29} These properties enable fluorine to show unusual noncovalent interactions.³⁰ Snyder and
5 co-workers³¹ first reported that the fluorine atoms incorporated in organic molecules interact with
6 cations through charge–dipole interactions. Furthermore, fluorine–fluorine interactions have also
7 been characterized both experimentally and theoretically.³² In recent years, highly fluorinated
8 porous materials have been found to show unconventional properties,^{5,33–35} and they are expected
9 to be useful materials for the adsorption of organic pollutants.

10 Herein, we report the synthesis of fluorinated pillar[*n*]arene-based CMPs and their application
11 to the removal of organic pollutants from aqueous solution. Owing to the densely decorated
12 pillar[*n*]arene scaffolds with fluorinated linkers, highly fluorinated micropores were readily
13 constructed. The fluorinated polymers showed efficient and cation-selective removal of organic
14 dyes, while the nonfluorinated polymers did not, indicating that the selectivity arises from the
15 charge–dipole interactions. Moreover, the fluorinated polymers exhibited higher capacity for
16 adsorbing perfluorooctanoic acid (PFOA) than the nonfluorinated polymers owing to the fluorine–
17 fluorine interactions. Additionally, the CMPs could function as proton channel under biologically
18 relevant conditions, which demonstrates that fluorinated polymers can be used in a wide range of
19 applications.

20 **EXPERIMENTAL SECTION**

21 **General Synthetic Procedure.** Pertriflated pillar[*n*]arene, linker and CuI (15 mg, 0.079 mmol)
22 were added into a 200 mL of round-bottom flask under N₂ atmosphere and dissolved in a 50 mL

of anhydrous degassed solvent mixture (toluene/triethylamine = 1/1). $\text{PdCl}_2(\text{PPh}_3)_2$ (25 mg, 0.036 mmol) was added and the mixture was refluxed at 110 °C for 72 h. The resulting precipitate was collected with filtration and washed thoroughly with THF, acetonitrile, water, acetone, DMF and dichloromethane. The solid was further purified by Soxhlet extraction (methanol) for 24 h to remove any remaining impurities. The product was dried under vacuo at 100 °C for 1 day. **P5-FP**: Pertriflated pillar[5]arene (200 mg, 0.10 mmol) and 1,4-diethynyl-2,3,5,6-tetrafluorobenzene (110 mg, 0.56 mmol), yield: quant. (137 mg). **P5-FBP**: Pertriflated pillar[5]arene (200 mg, 0.10 mmol) and 4,4'-diethynyl-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl (190 mg, 0.55 mmol), yield: quant. (250 mg). **P6-FP**: Pertriflated pillar[6]arene (200 mg, 0.083 mmol) and 1,4-diethynyl-2,3,5,6-tetrafluorobenzene (110 mg, 0.56 mmol), yield: quant. (176 mg). **P6-FBP**: Pertriflated pillar[6]arene (200 mg, 0.083 mmol) and 4,4'-diethynyl-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl (190 mg, 0.55 mmol), yield: quant. (240 mg). **P5-P**: Pertriflated pillar[5]arene (200 mg, 0.10 mmol) and 1,4-diethynylbenzene (70 mg, 0.55 mmol), yield: 91% (96 mg). **P5-BP**: Pertriflated pillar[5]arene (200 mg, 0.10 mmol) and 4,4'-diethynyl-1,1'-biphenyl (110 mg, 0.54 mmol), yield: quant. (230 mg). **P6-P**: Pertriflated pillar[6]arene (200 mg, 0.083 mmol) and 1,4-diethynylbenzene (70 mg, 0.55 mmol), yield: 94% (100 mg). **P6-BP**: Pertriflated pillar[6]arene (200 mg, 0.083 mmol) and 4,4'-diethynyl-1,1'-biphenyl (110 mg, 0.54 mmol), yield: quant. (200 mg).

General Procedure of Adsorption Experiments. The polymers were vacuum-dried, ground into a fine powder and transferred into a 20 mL of glass vial. Then, the solution of organic dyes was (10 mg L^{-1}) added to make 100 mg L^{-1} suspended solution and the mixture was stirred for 24 h at room temperature. The suspension was filtered with a membrane filter and the residual concentration of filtrate was calculated by UV-vis absorption spectroscopy. The detection

wavelengths were based on each of the absorption maxima; MO: 465 nm, MY: 465nm, MB: 664 nm, CV: 590 nm and 586 nm (methanol), LCV: 265 nm (methanol), RhB: 554 nm.

Removal of Perfluorooctanoic Acid. The polymer was vacuum-dried, ground into a fine powder and transferred into a 20 mL of glass vial. Then, the solution of perfluorooctanoic acid (10 mg L^{-1}) was added to make 100 mg L^{-1} suspended solution, and the mixture was stirred for 24 h at room temperature. The suspension was filtered with a membrane filter and the residual concentration of filtrate was calculated by liquid chromatography-tandem mass spectrometry (LC-MS/MS); LCMS-8030 (Shimadzu, Japan). The LC-MS/MS condition is as follows; mobile phase, mobile phase A, 10 mM ammonium acetate in water, mobile phase B, acetonitrile; flow rate, 0.2 mL min^{-1} ; column, ChemcoPak ODS ($2.1 \text{ mm i.d.} \times 150 \text{ mm}$) (Chemco Plus Co. Japan); temperature, 40°C ; detection; gradient condition, B 25% (0–1 min) –75% (10–12 min) –25% (12–14 min); ESI negative; injection, $5.0 \mu\text{L}$; $m/z = 413.0 > 169.0$; probe voltage, -3.5 kV ; nebulizing gas flow, 1.5 L/min ; heating gas flow, 10 L/min , DL temperature, 250°C ; BH temperature, 400°C .

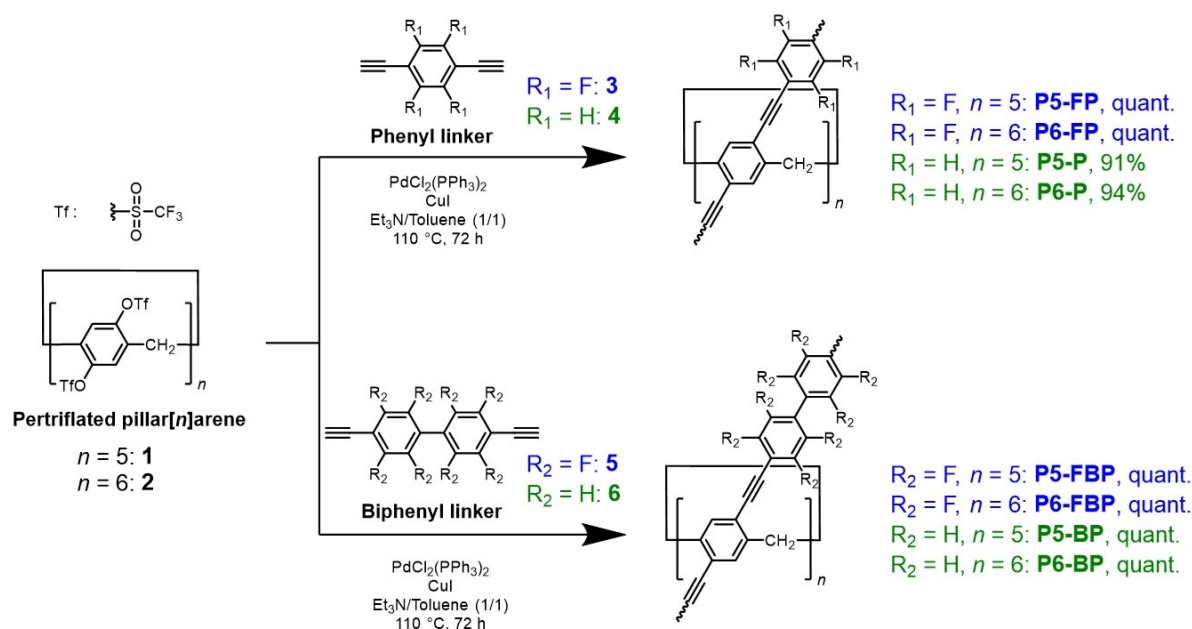
Ion Channels. (a) Preparation of giant unilamellar vesicles for phase-contrast and fluorescence microscopy. A $\text{CH}_3\text{Cl}/\text{CH}_3\text{OH}$ solution (2/1, v/v, $40 \mu\text{L}$) of 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC) ($[\text{DOPC}] = 1.0 \text{ mM}$) and D-glucose ($[\text{D-glucose}] = 1.0 \text{ mM}$) in a test tube was slowly evaporated to dryness under the N_2 gas flow at room temperature, and the resulting film was further dried under vacuum for 3 h. A lipid thin film developed on the interior surface of the test tube was hydrated with distilled water ($5.0 \mu\text{L}$) for 10 min at 55°C . Then, distilled water ($195 \mu\text{L}$) was added to the test tube and the mixture was further incubated for 16 h at 55°C to obtain a dispersion of giant unilamellar vesicles (GUVs) ($[\text{DOPC}] = 200 \mu\text{M}$, $[\text{D-glucose}] = 200 \mu\text{M}$). A THF dispersion of **P5-FP** or **P5-FBP** ($5.0 \mu\text{L}$, 0.50 mg mL^{-1}), which was sonicated for 3

h at 40 °C, was then added to the dispersion of DOPC GUVs (45 μ L, [DOPC] = 200 μ M, [D-glucose] = 200 μ M) and the dispersion was mixed five times with a pipette before phase-contrast and fluorescence microscopy observations. (b) Current recording measurements. A *n*-octane solution of 1,2-diphytanoyl-*sn*-glycero-3-phosphocholine (DPhPC) (5.0 μ L, 5.0 mg mL⁻¹) was deposited onto an orifice (diameter: 100 μ m) placed on a microcavity filled with an aqueous HCl (100 mM, 150 μ L) to prepare black lipid membranes (BLMs). A THF dispersion of **P5-FP** or **P5-FBP** (5.0 μ L, 0.50 mg mL⁻¹) was then gently added to the BLMs. All current recording measurements were performed at 22 °C.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization. Pertriflated pillar[5]arene (**1**),³⁶ pertriflated pillar[6]arene (**2**),³⁷ 1,4-diethynyl-2,3,5,6-tetrafluorobenzene (**3**),⁵ 4,4'-diethynyl-2,2',3,3',5,5',6,6'-octafluoro-1,1'-biphenyl (**5**),⁵ and 4,4'-diethynyl-1,1'-biphenyl (**6**)⁵ were prepared according to previously reported procedures. Coskun and co-workers²¹ reported that pertriflated pillar[5]arene efficiently reacts with 1,4-diethynylbenzene and 4,4'-diethynyl-1,1'-biphenyl via Pd-catalyzed Sonogashira–Hagihara cross-coupling to synthesize porous network polymers. To obtain the fluorinated network polymers, pertriflated pillar[*n*]arenes **1** and **2** and perfluorinated linkers **3** and **5** were reacted with the aid of PdCl₂(PPh₃)₂ and CuI in a mixed solution of toluene and triethylamine at 110 °C for 72 h, resulting in the formation of four types of fluorinated network polymers: **P5-FP**, **P5-FBP**, **P6-FP**, and **P6-FBP** (Scheme 1). The nonfluorinated network polymers were used as control polymers. Using the same reaction procedures with nonfluorinated phenyl and biphenyl linkers (**4** and **6**), we synthesized the corresponding nonfluorinated network polymers: **P5-P**, **P5-BP**, **P6-P**, and **P6-BP** (Scheme 1). All

1 of the synthesized polymers were completely insoluble in common solvents, suggesting that they
 2 had highly cross-linked structures.



Scheme 1. Synthesis of fluorinated and nonfluorinated network polymers based on pillar[n]arenes.

The consumption of the monomers was confirmed by Fourier transform infrared spectroscopy (Figure 1a). The spectra of the fluorinated polymers exhibited absorption bands at 975 and 2200 cm^{-1} , which correspond to the C–F and $\text{C}\equiv\text{C}$ stretching vibrations, respectively. Furthermore, the peaks of the $-\text{SO}_3$ stretching vibration at 900 cm^{-1} and $\text{C}\equiv\text{CH}$ stretching vibration at 3300 cm^{-1} almost disappeared, indicating the successful formation of the fluorinated network polymers.³⁸ The formation of the nonfluorinated polymers was confirmed through the same measurements (Figure S1). Furthermore, we examined the long-term stability of the fluorinated polymers when they were stored at room temperature under air. The FT-IR spectra of them showed no change even after more than 6 months passed (Figures S12 and S13). This result clearly demonstrates the high chemical stability of the polymers. The structures of the fluorinated polymers were further

1 characterized by solid-state cross-polarization/magic angle spinning ^{13}C NMR spectroscopy
2 (Figure 1b). The peaks at 30 ppm correspond to the methylene bridge of pillar[n]arene, and the
3 peaks at 105 ppm were assigned to the acetylene moieties. The peaks between 115 and 150 ppm
4 were assigned to the sp^2 carbon atoms of the phenyl rings, with the peaks at 145 ppm indicating
5 the presence of sp^2 carbon atoms connected to fluorine atoms⁵ (see Supplementary Note 1 in
6 Supporting Information for discussion on the chirality of pillar[n]arene moieties in the network
7 polymers).

8 Morphological analysis of the fluorinated network polymers by scanning electron microscopy
9 revealed that the polymers were amorphous solids (Figure S2). The powder X-ray diffraction
10 patterns of the polymers showed broad peaks, confirming that they were amorphous (Figure S3).

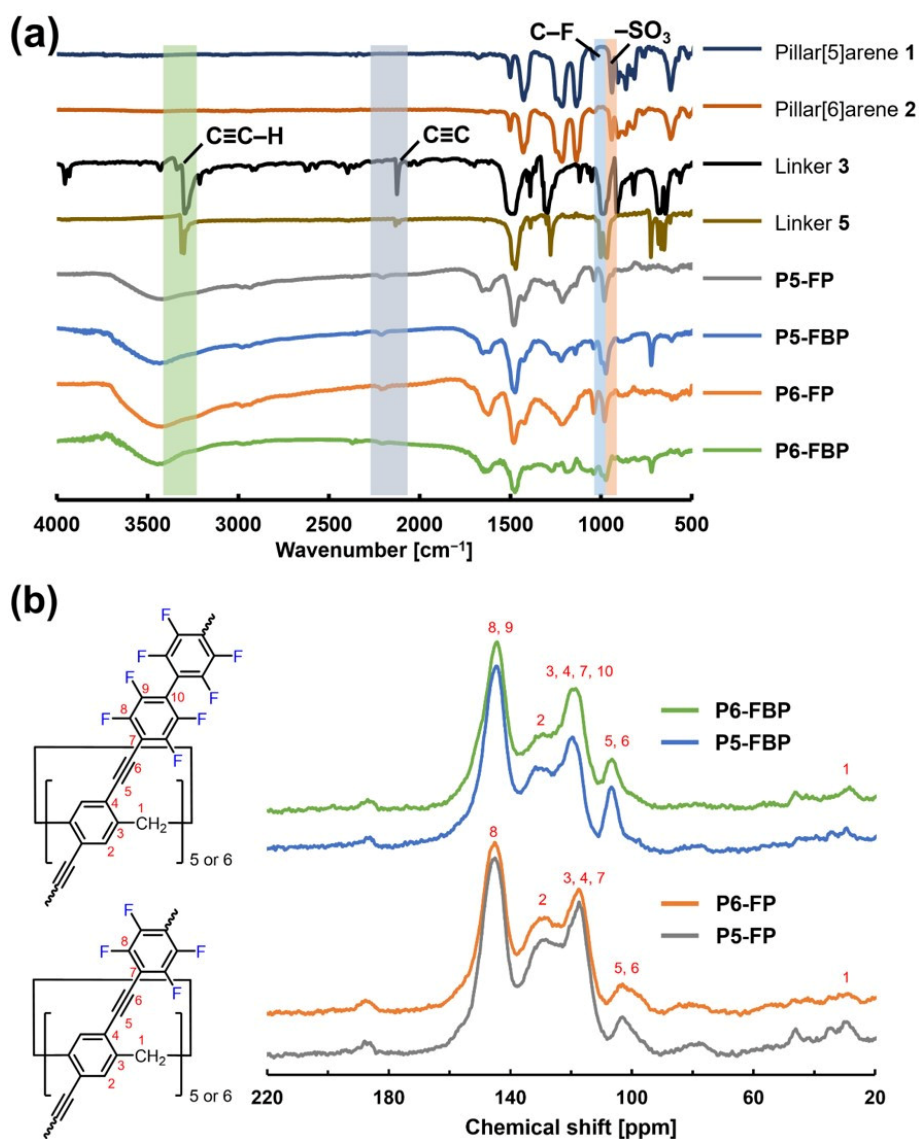


Figure 1. (a) Fourier transform infrared spectra of the pertriflated pillar[*n*]arenes, perfluorinated linkers, and fluorinated polymers. (b) Solid-state cross-polarization/magic angle spinning ¹³C NMR spectra of the fluorinated polymers.

To further investigate the internal structures of the polymers, their porosities were analyzed by N₂ gas adsorption/desorption measurements at 77 K (Figure 2a). The isotherms of the fluorinated polymers, except for that of **P5-FP**, showed rapid nitrogen adsorption in the low pressure range,

indicating the presence of micropores (~ 2 nm). The Brunauer–Emmet–Teller (BET) surface areas of **P5-FP**, **P5-FBP**, **P6-FP**, and **P6-FBP** were determined to be 300, 766, 1063, and 629 $\text{m}^2 \text{g}^{-1}$, respectively. Notably, **P6-FP** exhibited the highest surface area among reported pillar[n]arene-based CMPs (Table S1). The BET surface areas of the nonfluorinated polymers **P5-P**, **P5-BP**, **P6-P**, and **P6-BP** were determined to be 138, 458, 30, and 503 $\text{m}^2 \text{g}^{-1}$, respectively (Figure 2b). Previous literature which reports on partially fluorinated covalent organic frameworks (COFs)^{39,40} indicated that fluorinated COFs tend to exhibit higher surface areas compared to the non-fluorinated counterparts, which is the same trend with our case. These studies suggest that the electrostatic arene–perfluoroarene interactions can enhance crystallinity, which was beneficial for the formation of well-defined pore structures. However, our fluorinated polymers were still amorphous as suggested by PXRD patterns (Figure S3), therefore, we guess that electrostatic repulsion between electron-negative fluorine atoms disturbs the π -stackings between fluorinated linkers in contrast to the fluorinated COFs, which should be advantageous for the pore formation in the network polymers.

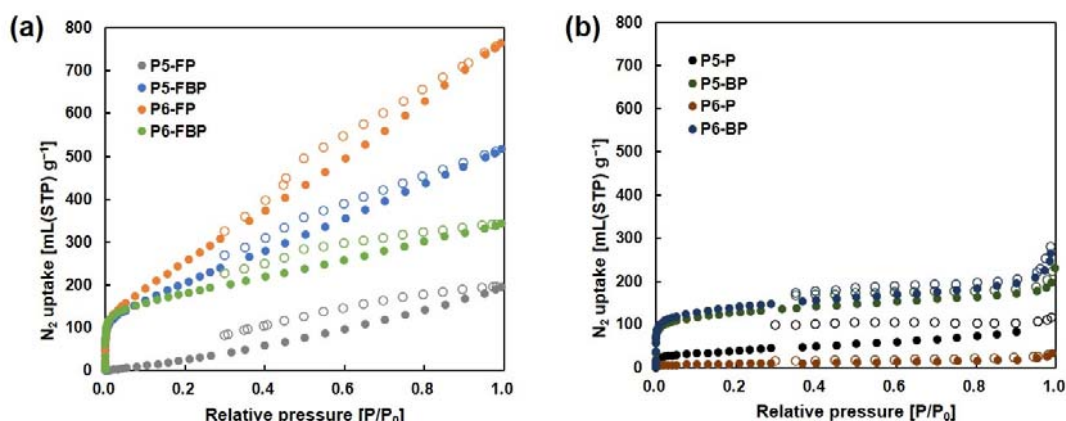


Figure 2. N₂ sorption isotherms of the (a) fluorinated and (b) nonfluorinated polymers at 77 K. Solid symbols = adsorption; open symbols = desorption.

The pore size distributions (PSDs) of the fluorinated polymers were calculated by nonlocal density functional theory. The micropore size peaked at 1.3, 1.5, and 1.3 nm for **P5-FBP**, **P6-FP**, and **P6-FBP**, respectively (Figure 3b–d). Considering that the cavity sizes of pillar[*n*]arenes are approximately 0.47 (*n* = 5) to 0.67 nm (*n* = 6),⁴¹ the micropores in these polymers should be derived from the highly cross-linked structures rather than the pillar[*n*]arene cavities. The PSDs of the nonfluorinated polymers were also calculated to discuss the structural differences arising from the introduction of fluorine into the polymers. The PSDs of the fluorinated and nonfluorinated polymers synthesized with phenyl linkers were significantly different (Figure 3a and b), while those synthesized with biphenyl linkers exhibited comparable porosity (Figure 3c and d). Because the polymers exhibited similar porous structures regardless of fluorination, the adsorptive performance of the biphenyl-linked polymers was then compared to investigate the fluorination effect.

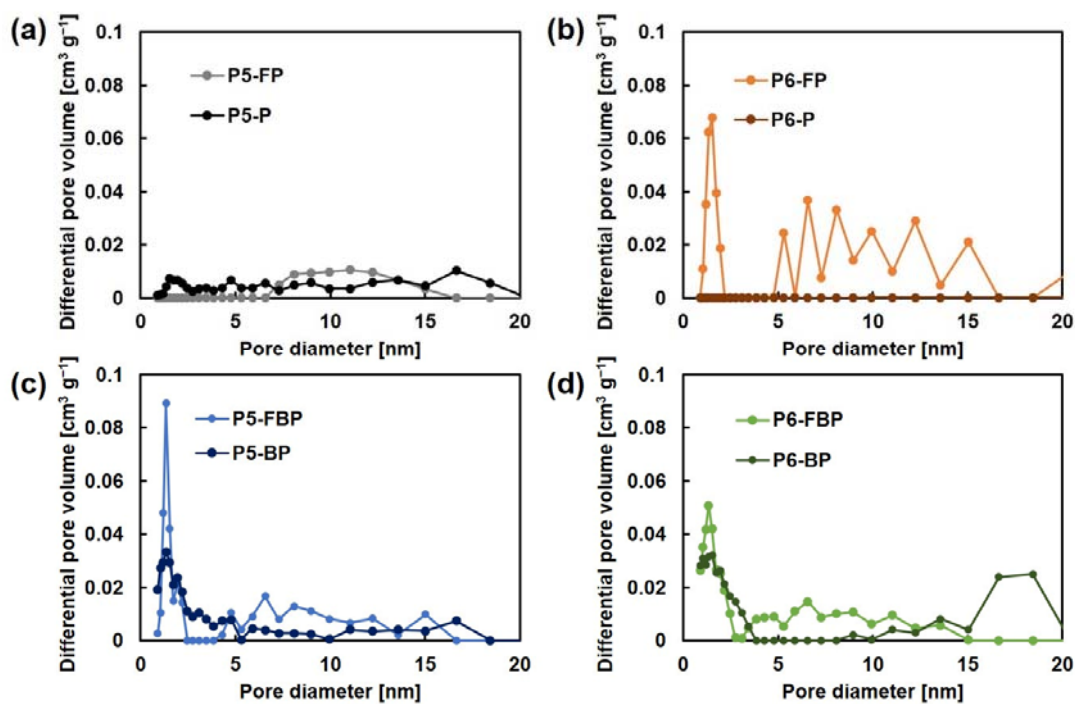


Figure 3. Nonlocal density functional theory pore size distributions of (a) **P5-FP** and **P5-P**, (b) **P6-FP** and **P6-P**, (c) **P5-FBP** and **P5-BP**, and (d) **P6-FBP** and **P6-BP**.

Selective Adsorption of Cationic Organic Dyes. The synthesized fluorinated network polymers are potential adsorptive materials for organic dyes owing to their high surface areas, microporosity, thermal stability, and insolubility in common solvents. Therefore, we investigated the adsorptive performance of the organic dyes and the fluorination effect using the biphenyl-linked polymers (**P5-FBP**, **P6-FBP**, **P5-BP**, and **P6-BP**). Anionic dyes (methyl orange (MO) and metanil yellow (MY)) and cationic dyes (methylene blue (MB) and crystal violet (CV)) were selected as adsorbates and dissolved in deionized water. Each polymer (1 mg) was added to 10 mL of 10 mg L⁻¹ organic dye solution, and the mixture was stirred for 24 h. The UV–vis absorption spectra were recorded to determine the remaining concentrations after the adsorption experiments. The removal efficiency (%removal) was calculated by the following equation (1):

$$\% \text{ removal} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 (mg L⁻¹) and C_t (mg L⁻¹) are the initial and residual concentration of the dye, respectively. **P5-FBP** and **P6-FBP** exhibited low removal efficiencies for the anionic dyes MO and MY (Figure 4a and b), while the removal efficiencies for the cationic dyes MB and CV were higher (Figure 4c and d). Considering the size of MB and CV (12–14 Å), they are not taken up into the cavity of pillar[*n*]arenes (4.7–6.7 Å), but rather into the voids among the pillar[*n*]arene moieties and fluorinated linkers. The control polymers **P5-BP** and **P6-BP** showed relatively poor removal performance for all of the dyes tested. These results reveal the highly selective adsorption of cationic dyes to the fluorinated polymers

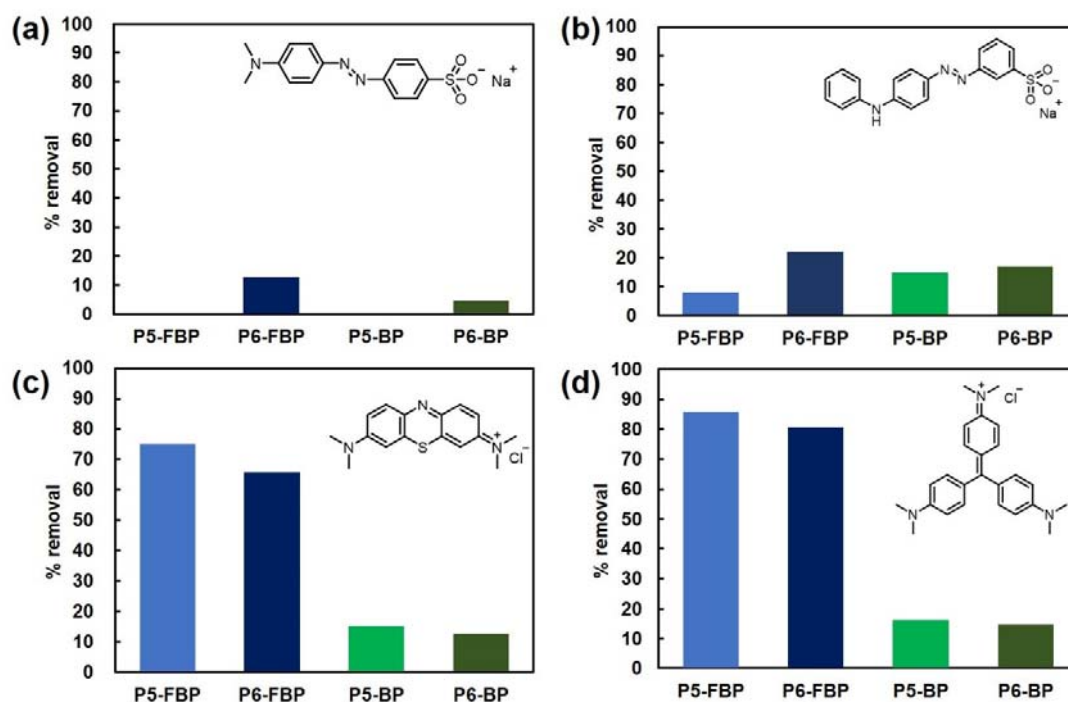


Figure 4. Removal efficiencies of (a) methyl orange, (b) metanil yellow, (c) methylene blue, and (d) crystal violet (CV) (10 mg L^{-1}) by the pillar[*n*]arene polymers (100 mg L^{-1}).

Mechanism of Selective Adsorption of Cationic Dyes. To investigate the mechanism of the charge-selective adsorption of dyes, adsorption experiments were performed with leuco crystal violet (LCV). LCV is the reduced form of CV, and it has almost the same molecular size as CV. It can be used as a reference compound of uncharged CV to understand the interaction between fluorine and the cation. The experiments were performed in methanol solution owing to the insolubility of LCV in water. The adsorptive removal experiments of CV showed that **P5-FBP** exhibited significantly higher removal efficiencies than **P5-P** even in methanol (Figure 5a), which was the same trend as the adsorption experiments of CV in water (Figure 4d). In contrast, the removal efficiency of uncharged LCV by **P5-FBP** substantially decreased to almost 0% (Figure 5b), suggesting that the cationic moiety of CV is essential for the adsorption to the fluorinated

polymer. The results suggest that the fluorine–cation electrostatic interaction³⁵ is the major driving force for the cation-selective adsorption (see Supplementary Note 2 and Figures S7–S9 in Supporting Information for the adsorption experiments using a mixed solution of MO and CV). We further performed DFT calculation on model compounds for the fluorinated and non-fluorinated polymers (Figure S14). The electron potential map indicates that the fluorine atoms provides electron-negative binding sites due to the high electron-negativity of fluorine. Therefore, the electron negative sites are responsible for the capture of cationic organic dyes though the network polymers themselves are neutral. This is may be attributed to the presence of $2n$ fluorinated linkers densely installed on each pillar[n]arene scaffold (see Supplementary Note 3 and Table S5 in Supporting Information for the surface charge study of the fluorinated and control polymers).

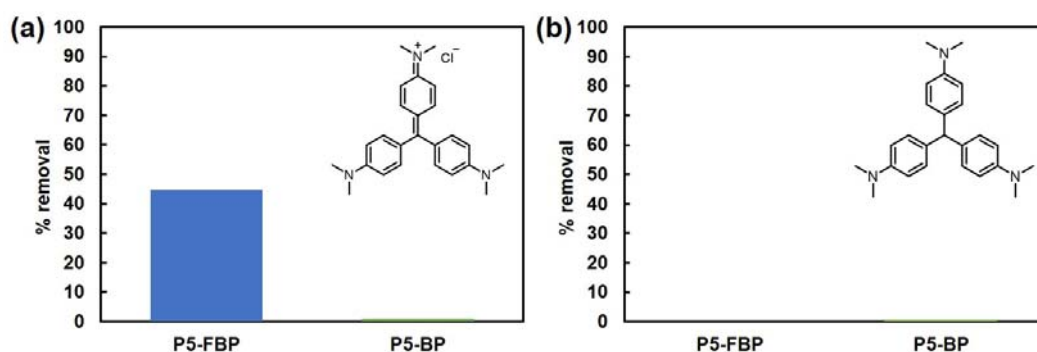


Figure 5. Removal efficiencies of (a) CV and (b) leuco crystal violet (10 mg L^{-1} in methanol) by the pillar[5]arene polymers (100 mg L^{-1}).

Because Rhodamine B (RhB) has a cationic moiety and a carboxy group in its molecular structure, it can adopt a cationic form ($\text{pH} < 4$) and a zwitterionic form ($\text{pH} > 4$) depending on the pH (Figure S5a).⁴² This characteristic of RhB makes it a suitable model compound to further

investigate the charge-selective adsorption behavior to **P5-FBP**. We evaluated the adsorptive performance with variation of the pH of the solution by addition of HCl or NaOH. The removal efficiency of **P5-FBP** decreased as the pH increased, and **P5-BP** showed no pH-dependent adsorption behavior (Figure S5b). This phenomenon can be explained by the charge repulsion of the anion–fluorine interaction. From these results, we experimentally elucidated the presence of two types of interactions: the attractive interaction between the cation and fluorine and the repulsive interaction between the anion and fluorine. The former is advantageous for the adsorption of cationic dyes.

In general, the surface area is an important factor for adsorption processes.³ Owing to the high removal efficiencies of CV by the fluorinated polymers, we selected CV as an adsorbate to investigate the effect of the surface area. The removal efficiencies of CV followed the order of **P6-FP** > **P5-FBP** > **P6-FBP** > **P5-FP**, which was in good agreement with the trend of the BET surface areas (Figures S4 and S6). This suggests that the surface area is an important factor for the adsorption performance of the fluorinated polymers.

Reusability is important for the economic efficiency of the purification of wastewater.⁴³ Simple ethanol ultrasonic washing was sufficient to regenerate **P6-FP** at least four times (Figures 6 and S10), in contrast to activated carbon which degrades during regeneration.⁴⁴ This indicates that the fluorinated polymers can be repeatedly used for long periods of time.

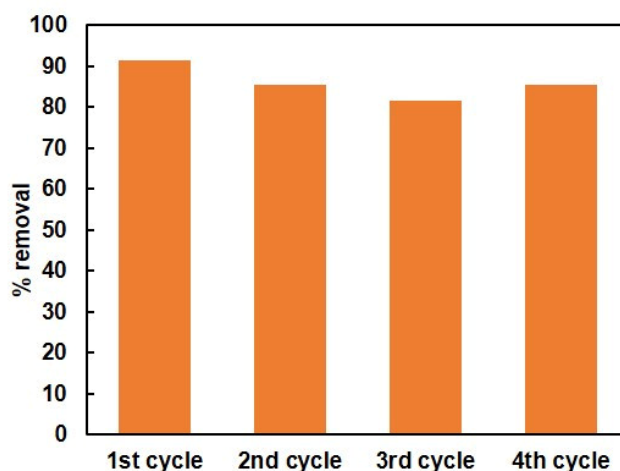


Figure 6. Removal efficiencies of CV (20 mg L⁻¹) by ethanol-washed **P6-FP** (100 mg L⁻¹) for four cycles.

Adsorption Kinetics and Isotherms. To investigate the adsorption kinetics of CV to the polymers, time-dependent adsorption experiments were performed with an initial CV concentration of 20 mg L⁻¹ (Figure 7a). **P5-FBP** and **P6-FP** exhibited faster adsorption rates than **P5-BP**, indicating that they have higher affinities for the adsorbate. The equilibrium time was approximately 24 h for all of the tested polymers (Figure S5). Furthermore, kinetic analyses were performed with pseudo-first-order and pseudo-second-order kinetics models.⁴⁵ The results showed that the pseudo-second-order model is more appropriate for describing the time-dependent adsorption process in this system than the pseudo-second-order model (Table S2).

Adsorption isotherm analysis was performed with the Langmuir adsorption model to investigate the adsorption mechanisms and abilities of the polymers. The linear form of the Langmuir adsorption equation (2) is⁴⁶

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{K_L q_{\max}} \quad (2)$$

where C_e (mg L^{-1}) is the concentration of the organic dye at equilibrium, q_e (mg g^{-1}) is the adsorption capacity of the organic dye at equilibrium, q_{max} (mg g^{-1}) is the maximum adsorption capacity of the organic dye, and K_L (L mg^{-1}) is the constant of the Langmuir model. The fluorinated polymers were added to 10 mL of CV aqueous solutions with different initial concentrations and weights of the polymers (Table S3). The mixtures were stirred for 4 days, and the obtained C_e and q_e values were then fitted to the above equation (Figure 7). High correlation coefficients of 0.9913 and 0.9866 were obtained for **P5-FBP** and **P6-FP**, respectively, indicating that the adsorption process can be described as monolayer adsorption on the homogeneous surface of the adsorbent.⁴⁷ The maximum adsorption capacities of **P5-FBP** and **P6-FP** were calculated to be 112 and 313 mg g^{-1} , respectively, which are higher than those of previously reported adsorbents (Table S4). This suggests that the fluorinated polymers, especially **P6-FP**, shows great potential for the selective and efficient removal of CV and other cationic dyes from aqueous solution.

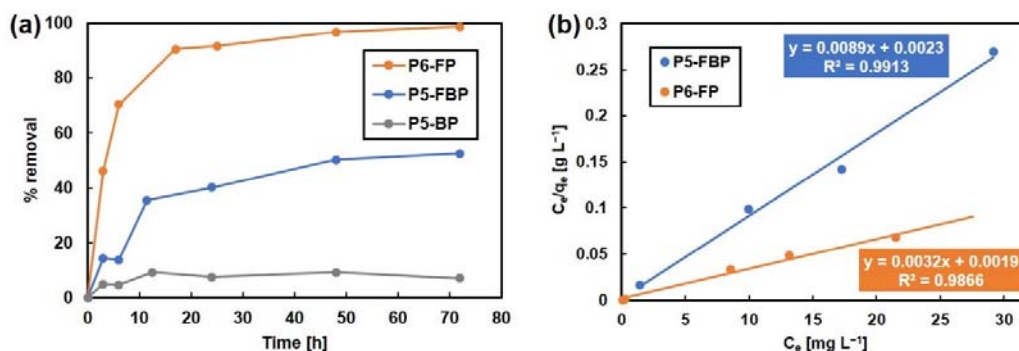


Figure 7. (a) Removal efficiencies of CV (20 mg L^{-1}) by the pillar[n]arene polymers (100 mg L^{-1}) with time and (b) Langmuir isotherm analysis of **P5-FBP** and **P6-FP**.

Removal of Perfluorooctanoic Acid from Water. The accumulation of PFOA (a type of PFAS) in the natural environment has become a severe and worldwide problem because breaking the

chemically robust C–F bond is difficult under mild conditions. Therefore, the development of effective separation technologies for PFOA is required. Recently, highly fluorinated porous polymers have been found to efficiently remove PFOA.^{5,6} Accordingly, we evaluated the adsorptive removal performance of PFOA by the fluorinated polymers synthesized in this study. Each polymer (1 mg) was added to 10 mL of 10 mg L⁻¹ PFOA solution, and the mixture was stirred for 24 h. The residual PFOA concentration was determined by LC-MS/MS. The fluorinated polymers showed superior removal efficiencies to the nonfluorinated polymers (Figure 8), indicating that the fluorine–fluorine interactions also contribute to the adsorption ability of these polymers (see Supplementary Notes 4 and 5, Figures S15–S17 and Tables S6–S9 in the Supporting Information for the regeneration, adsorption kinetic and isotherm).

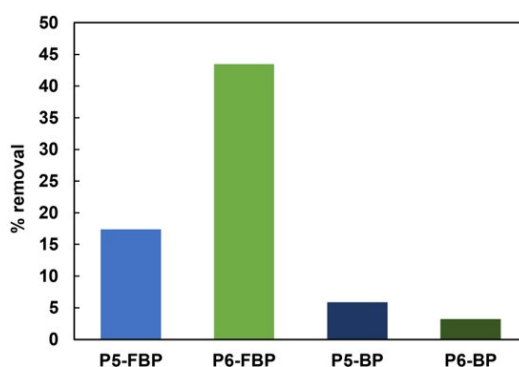


Figure 8. Removal efficiencies of perfluorooctanoic acid (10 mg L⁻¹) from water by the polymers (100 mg L⁻¹).

Application to Ion Channels. Finally, we investigated the functionality of **P5-FP** and **P5-FBP** under biologically relevant conditions. For this purpose, we prepared giant unilamellar vesicles (GUVs) from 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC) as a model cell membrane and added a dispersion of **P5-FP** or **P5-FBP**. Phase-contrast microscopy revealed the successful formation of micrometer-sized GUVs in the presence of **P5-FP** and **P5-FBP** (Figure 9).

1 Interestingly, the corresponding fluorescence micrograph of the DOPC GUVs with **P5-FP** showed
2 emission along the edge of the GUVs (Figure 9c), whereas such localization was hardly observed
3 in the case of **P5-FBP** (Figure 9d). These results indicate that **P5-FP** was localized to the
4 membranes in a preferential manner to **P5-FBP** under these conditions.⁴⁸ Next, we investigated
5 the possibility for **P5-FP** and **P5-FBP** to function as transmembrane nanochannels. We prepared
6 planer black lipid membranes (BLMs) from 1,2-diphytanoyl-*sn*-glycero-3-phosphocholine
7 (DPhPC) in aqueous HCl and added a dispersion of **P5-FP** or **P5-FBP**. We then applied voltage
8 across the DPhPC-based BLMs to monitor the currents generated by the transmembrane ion
9 permeation. The current profile obtained from the **P5-FP**-embedded DPhPC-based BLMs showed
10 clear spikes (Figure 9e), while that of **P5-FBP** did not (Figure 9f). These results suggest that **P5-**
11 **FP** functions as a proton channel. Previously, we demonstrated that perfluorinated
12 oligo(phenylene-ethynylene) is suitable for transmembrane ion permeation.⁴⁸ Owing to the
13 presence of the same building blocks, **P5-FP** would function as a transmembrane ion channel.
14 Conversely, the current profiles of the **P5-P**- and **P5-BP**-embedded DPhPC-based BLMs did not
15 exhibit spikes (Figure S11), suggesting that fluorination of the polymers is indispensable for them
16 to function as proton channels.

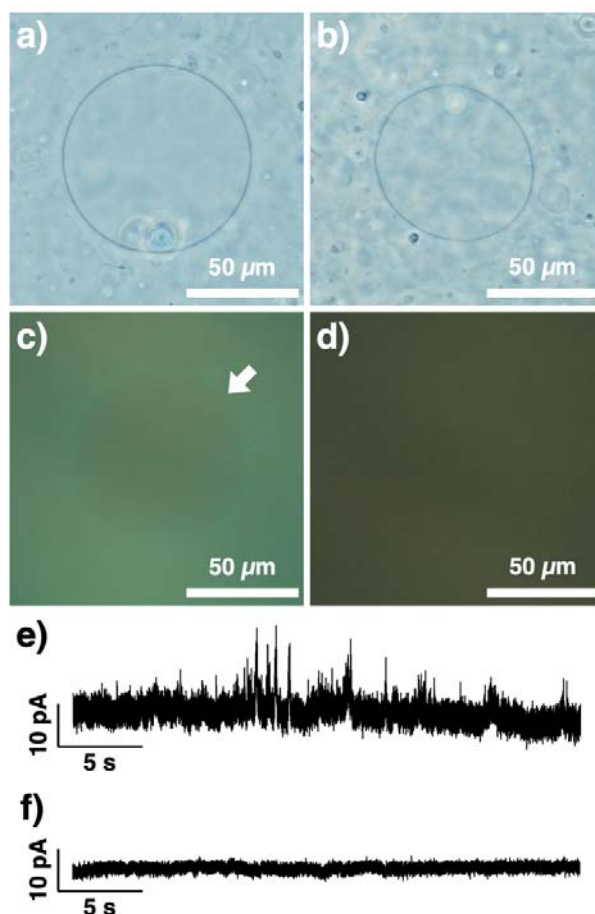


Figure 9. (a) and (b) Phase-contrast and (c) and (d) fluorescence microscopy ($\lambda_{\text{ex}} = 340\text{--}390\text{ nm}$, $\lambda_{\text{em}} > 420\text{ nm}$) images of the 1,2-dioleoyl-*sn*-glycero-3-phosphocholine giant unilamellar vesicles ([1,2-dioleoyl-*sn*-glycero-3-phosphocholine] = 200 μM) in aqueous D-glucose ([D-glucose] = 200 μM) in the presence of **P5-FP** ((a) and (c)) and **P5-FBP** ((b) and (d)) at 22 $^{\circ}\text{C}$. Current versus time plots of the 1,2-diphytanoyl-*sn*-glycero-3-phosphocholine-based black lipid membranes in the presence of (e) **P5-FP** and (f) **P5-FBP** in aqueous HCl (100 mM) at an applied voltage of 100 mV at 22 $^{\circ}\text{C}$.

CONCLUSION

Four types of highly fluorinated conjugated microporous polymers based on pillar[*n*]arenes have been successfully synthesized by the cross-coupling reaction using pertriflated pillar[*n*]arenes and perfluorinated alkyne linkers. The fluorinated polymers exhibited high surface areas of up to 1063 m² g⁻¹, which is a largest value among those of reported pillar[*n*]arene-based CMPs, and selectively removed cationic organic dyes from aqueous solution. Detailed control experiments with the nonfluorinated polymers revealed that the cation–fluorine electrostatic interaction is the major driving force for the adsorptive removal of cationic organic dyes. The **P6-FP** polymer possessed the highest maximum adsorption capacity (313 mg g⁻¹) for CV among the tested polymers, indicating that this polymer has great potential for the efficient removal of cationic organic dyes. From an industrial aspect, such selective adsorption of organic dyes is highly demanded because the simultaneous adsorption of multiple dye components requires a large adsorption capacity, and thus a large amount of adsorbent. In particular, the toxicities of cationic dyes are higher than those of anionic dyes.⁴⁹ They can readily bind to surfaces bearing negatively charge, facilitating their entry into cells and subsequent concentration in the cytoplasm. Therefore, this study provides practical adsorptive materials with great potential for the selective and efficient removal of CV and other cationic dyes from aqueous solution. Moreover, we demonstrated further applications of the polymers for PFOA removal and as proton channels, suggesting that these fluorinated polymers can potentially be used in a wide range of applications. Fluorination of pillar[*n*]arene-based CMPs develops a large surface area and generates more functions compared with the non-fluorinated CMPs, such as selective cationic dye uptake, PFOA removal, and proton channels. Therefore, the molecular designability of pillar[*n*]arene-based CMPs will facilitate further development of diverse functional porous materials.

ASSOCIATED CONTENT

The Supporting Information is available free of charge at <http://pubs.acs.org>. Synthetic procedures, structural characterizations, general procedure for the adsorption experiments, adsorption isotherms, purification of the dye mixtures, procedure for polymer regeneration, gas and vapor adsorption, procedure for the removal of PFOA, preparation of giant unilamellar vesicles for phase-contrast and fluorescence microscopy, and current recording measurements (PDF).

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by JSPS KAKENHI (grant number JP22K14725, Early-Career Scientists, S.O.; grant number JP21K14611, Early-Career Scientists, K.K.; grant number JP22K19063,

Challenging Research (Exploratory), T.O.; and grant number JP22H00334, Scientific Research (A), T.O.), JST CREST (grant number JPMJCR18R3, T.O.), and the MEXT World Premier International Research Center Initiative (WPI), Japan. S.O. acknowledges financial support from a Toyota Physical and Chemical Research Institute Scholarship. The authors thank Dr. Takeshi Yamamoto and Prof. Michinori Suginome (Kyoto University, Japan) for the powder X-ray diffraction measurements. We thank Edanz (<https://jp.edanz.com/ac>) for editing a draft of this manuscript.

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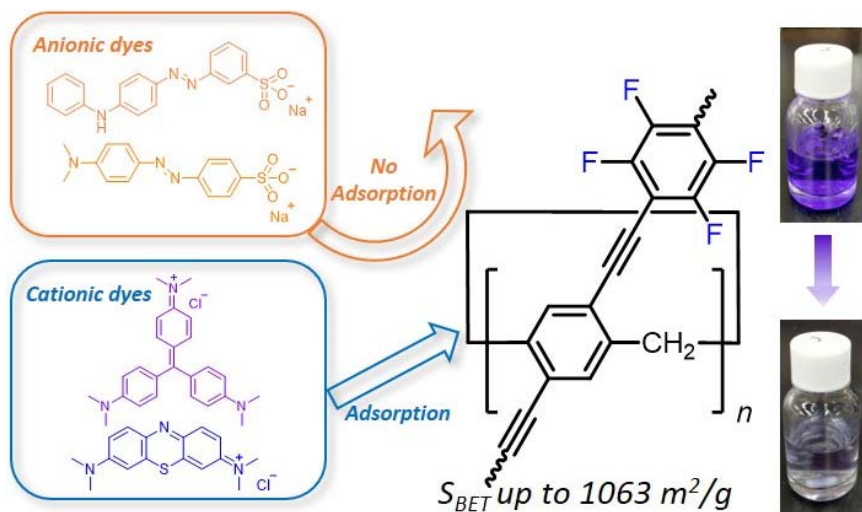
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1

TOC Image



- Fluorinated polymers with high surface areas
- Selective removal of cationic organic dyes

2