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Rim-Differentiated Pillar[5]arene Based Nonporous Adaptive Crystals

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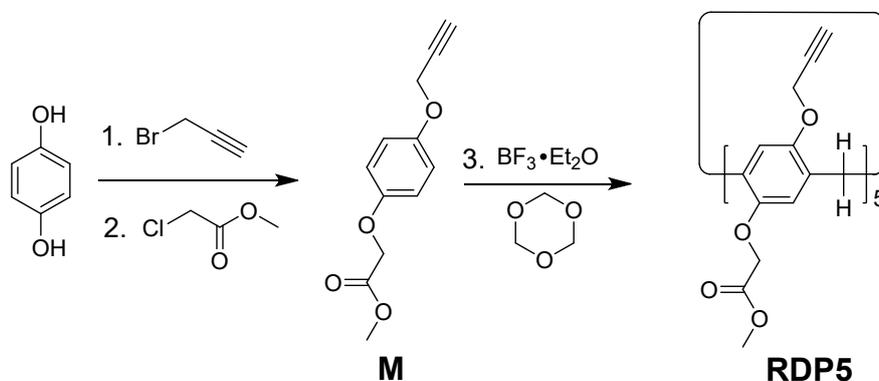
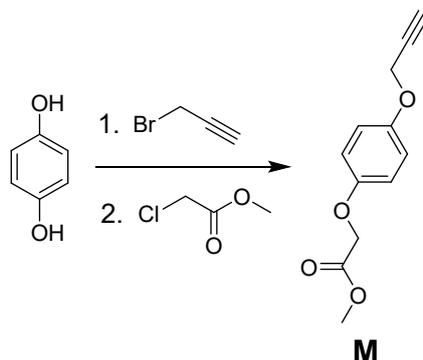
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1. Materials and methods

Hydroquinone, propargyl bromide, methyl chloroacetate, boron trifluoride etherate, and triformol were reagent grade and used as received. The rim-differential pillar[5]arene was prepared by the method called “Asymmetrical monomer direct cyclocondensation” we developed previously^{S1}. ¹H NMR spectra were collected on a Varian Unity INOVA-400 spectrometer with internal standard TMS. ¹³C NMR spectra were recorded on a Varian Unity INOVA-400 spectrometry at 100 MHz. Mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. HRMS were obtained on a Bruker 7-Tesla FT-ICRMS equipped with an electrospray source (Billerica, MA, USA). UV–Vis spectroscopy was measured on a Shimadzu UV-2501 PC UV–Vis spectrometer. XRD data were obtained with a graphite monochromatic device and Cu K α radiation ($\lambda = 0.15406$ nm) on the D8 Advance superspeed powder diffractometer (Bruker), operated in the $\theta:2\theta$ mode primarily in the 2–85° (2θ) range, with the tube voltage of 80 kV. Single crystal X-ray data sets were measured on a Rigaku MicroMax-007 HF rotating anode diffractometer (Mo-K α radiation, $\lambda = 0.71073$ Å, Kappa 4-circle goniometer, Rigaku Saturn724+ detector). Unless stated, solvated single crystals, isolated from the crystallization solvent, were immersed in a protective oil, mounted on a MiTeGen loop, and flash cooled under a dry nitrogen gas flow. Empirical absorption corrections, using the multi-scan method, were performed with the program SADABS. Gas Chromatographic (GC) Analysis: GC measurements were carried out using an Agilent 7890B instrument configured with an FID detector and a DB-624 column (30m \times 0.53 mm \times 3.0 μ m). Low-pressure gas adsorption measurements were performed on a Micromeritics Accelerated Surface Area and Porosimetry System (ASAP) 2020 surface area analyzer. Linear pentene and n-pentane adsorption isotherms were measured via Micromeritics 3Flex.

2. Synthesis of rim-differentiated pillar[5]arene **RDP[5]**.**Scheme S1.** Synthetic route to **RDP[5]**2.1 Synthesis of monomer **M****Scheme S2.** Synthetic route to monomer **M**

Anhydrous potassium carbonate (55.2 g, 400 mmol) was added to a solution of hydroquinone (44.0 g, 400 mmol) and propargyl bromide (47.6 g, 400 mmol) in dry acetonitrile (500 mL). The mixture was stirred at 80 °C for 24 hours under nitrogen atmosphere. Then methyl chloroacetate (43.2 g, 400 mmol) and additional anhydrous potassium carbonate (55.2 g, 400 mmol) were added into the reaction mixture and reacted for another 24 hours. After removal of the inorganic salts by filtration, the solvent was evaporated and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, *v/v* 10:1) to give **M** as a white solid (51.0 g, 58%). Mp: 83.4–85.1 °C. The proton NMR spectrum of **M** is shown in Figure S1. ¹H NMR (400 MHz, CDCl₃, 293K) δ (ppm): 6.94–6.86 (m, 4H), 4.65 (d, *J* = 2 Hz, 2H), 4.60 (s, 2H), 3.81 (s, 3H), 2.52 (t, *J* = 2 Hz, 1H). The ¹³C NMR spectrum of **M** is shown in Figure S2. ¹³C NMR (100 MHz, CDCl₃, 293K) δ (ppm): 169.5, 152.6, 152.4, 116.0, 115.7, 78.8, 75.5, 65.9, 56.4, 52.2. LR-ESI-MS is

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shown in Figure S3: m/z 243.3 $[M + Na]^+$ (100%). HR-ESI-MS: m/z calcd for $[M + Na]^+ C_{12}H_{12}NaO_4$, 243.0628; found, 243.0628; error 0 ppm.

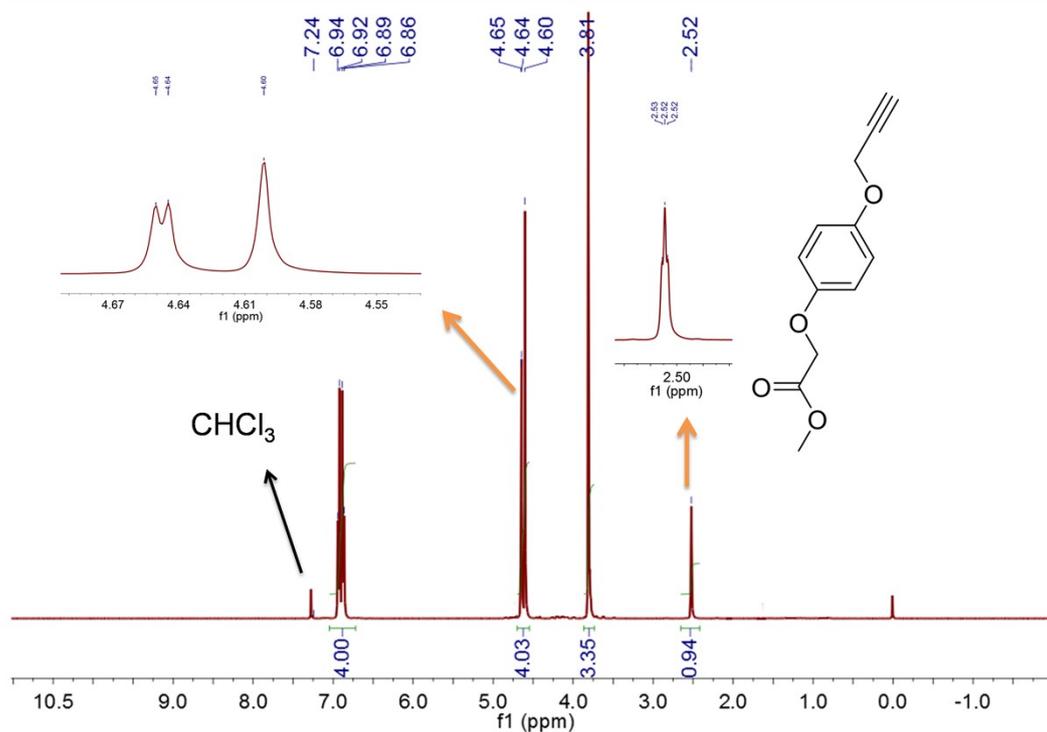


Figure S1. 1H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of monomer **M**.

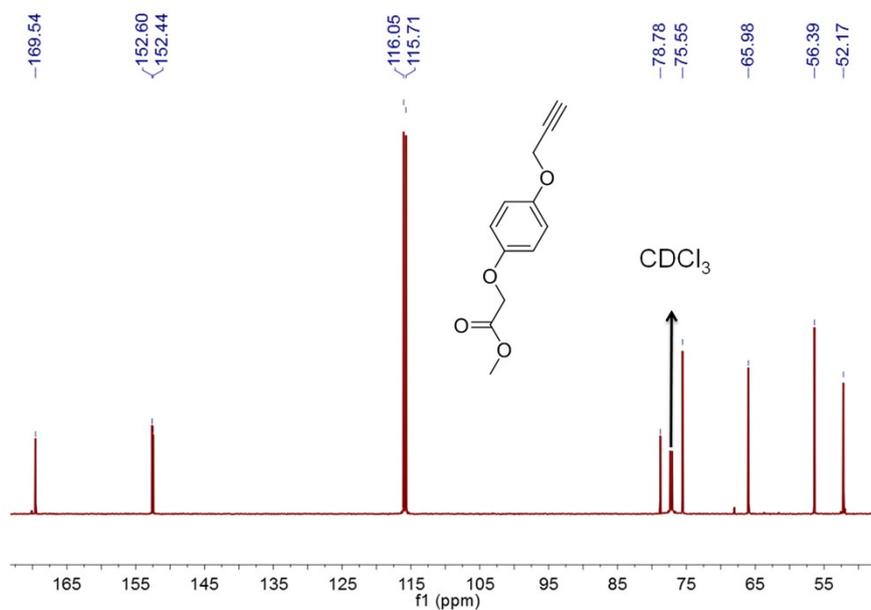


Figure S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 293 K) of monomer **M**.

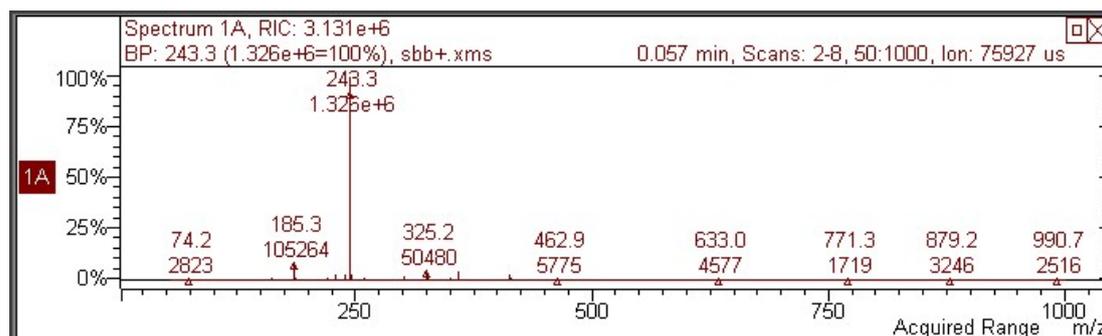
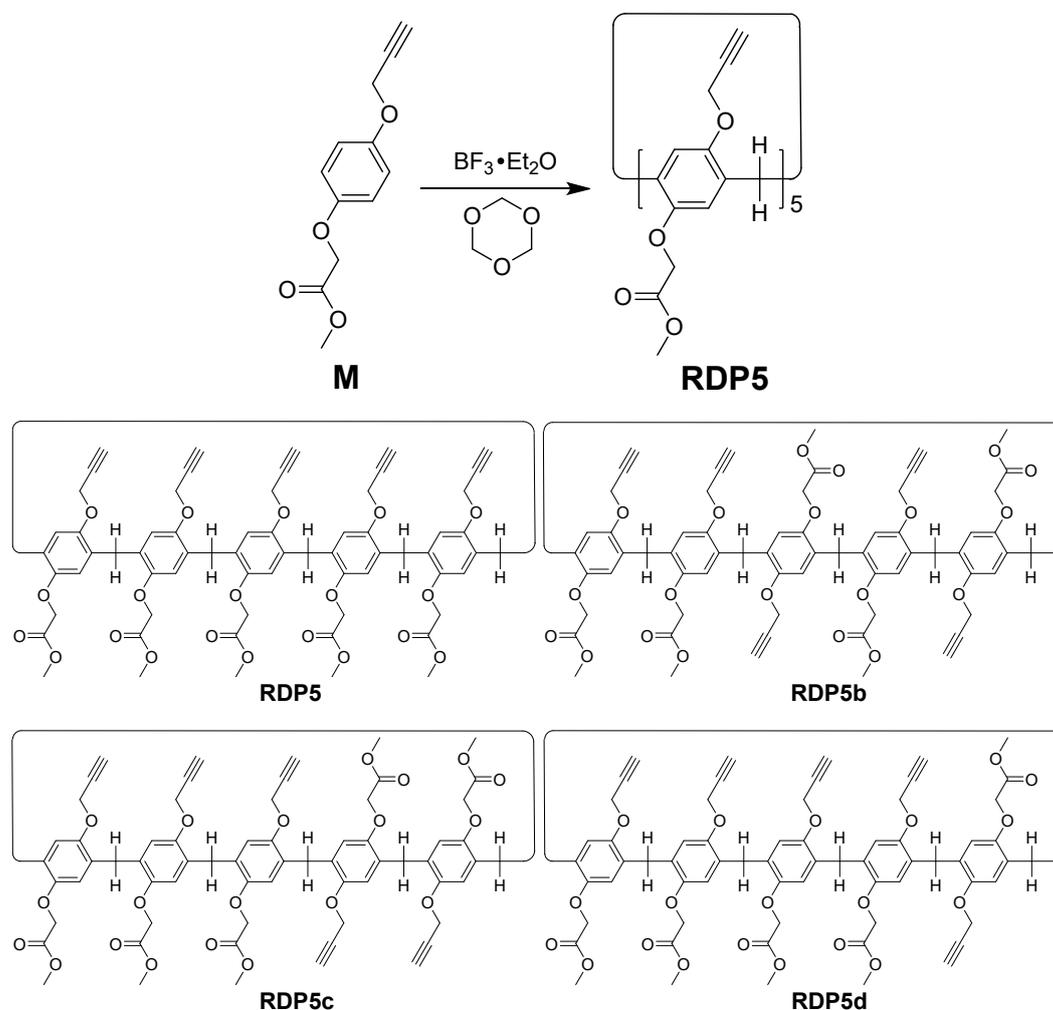


Figure S3. Electrospray ionization mass spectrum of the noncyclic monomer **M**. Assignment of main peak: m/z 243.3 [$M + Na$]⁺ (100%).

2.2 Synthesis of nonsymmetric pillar[5]arene **RDP[5]**

Scheme S3. Synthetic route to **RDP[5]**



A solution of **M** (3.37 g, 11.5 mmol) and triformol (0.349 g, 11.5 mmol) in 1,2-dichloroethane (50 mL) was cooled with ice bath. Boron trifluoride etherate (3.26 g,

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23.0 mmol) was added to the solution and the mixture was stirred at room temperature for 1 hour. The reaction mixture was then washed with water (50 mL \times 2) and dried with Na₂SO₄. The solvent was evaporated to provide a crude product, which was purified by column chromatography (eluent: petroleum ether/ethyl acetate, 5:1) to give **RDP5** isomers as white solids (total weight 0.80 g, total yield 40%). **RDP5** has 4 constitutional isomers **RDP5**, **RDP5b**, **RDP5c**, and **RDP5d**, which is similar to our previous reported nonsymmetric pillar[5]arenes.^{S1} Isomer **RDP5** (0.020 g, 1%) was got by recrystallization in a mixture of dichloromethane and methanol (v:v, 1:4). The proton NMR spectrum of **RDP5** (Mp: 113.1–113.8 °C) is shown in Figure S4. ¹H NMR (400 MHz, chloroform-*d*, 293K) δ (ppm): 6.91 (s, 5H), 6.88 (s, 5H), 4.59 (d, $J = 2$ Hz, 10H), 4.53 (s, 10H), 3.83 (s, 10H), 3.49 (s, 15H), 2.33 (t, $J = 2$ Hz, 5H). The ¹³C NMR spectrum of **RDP5** is shown in Figure S5. ¹³C NMR (100 MHz, chloroform-*d*, 293K) δ (ppm): 170.2, 150.7, 132.9, 116.9, 80.0, 78.8, 69.1, 59.7, 51.8, 31.6. LR-ESI-MS is shown in Figure S6: m/z 1183.9 [**RDP5** + Na]⁺ (100%). HR-ESI-MS: m/z calcd for [**RDP5** + Na]⁺ C₆₅H₆₀NaO₂₀, 1183.3570; found, 1183.3564; error –0.5 ppm.

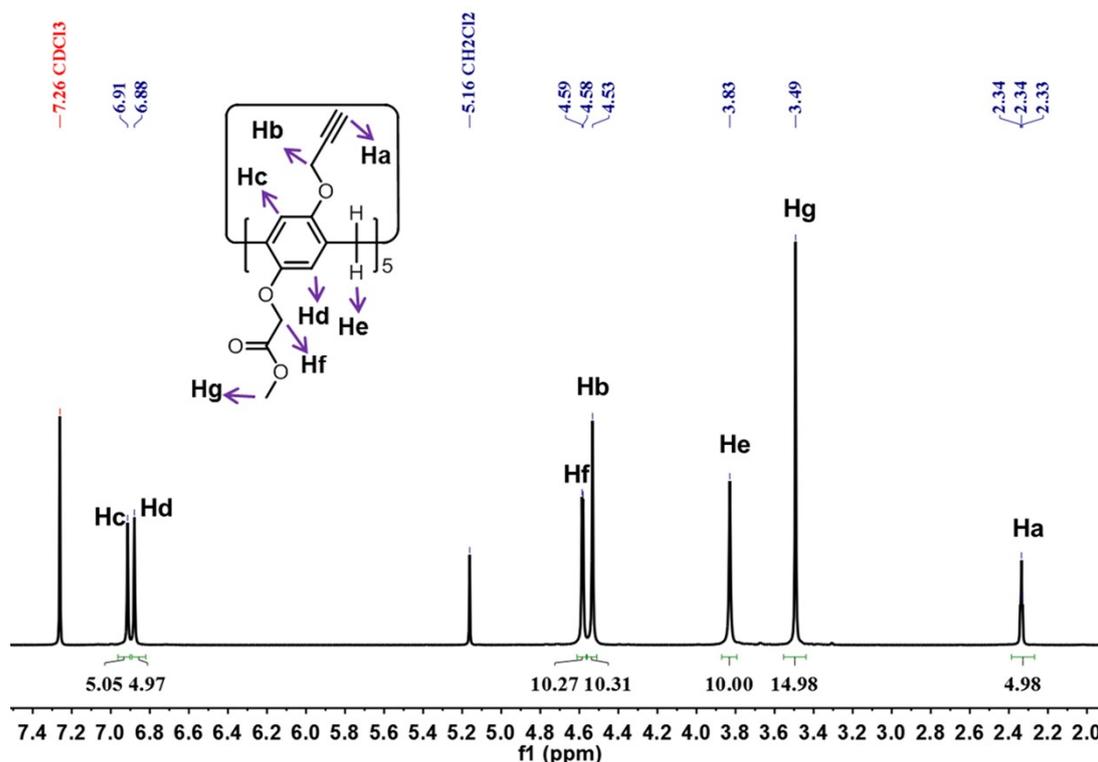


Figure S4. ¹H NMR spectrum (400 MHz, CDCl₃, 293 K) of **RDP5**.

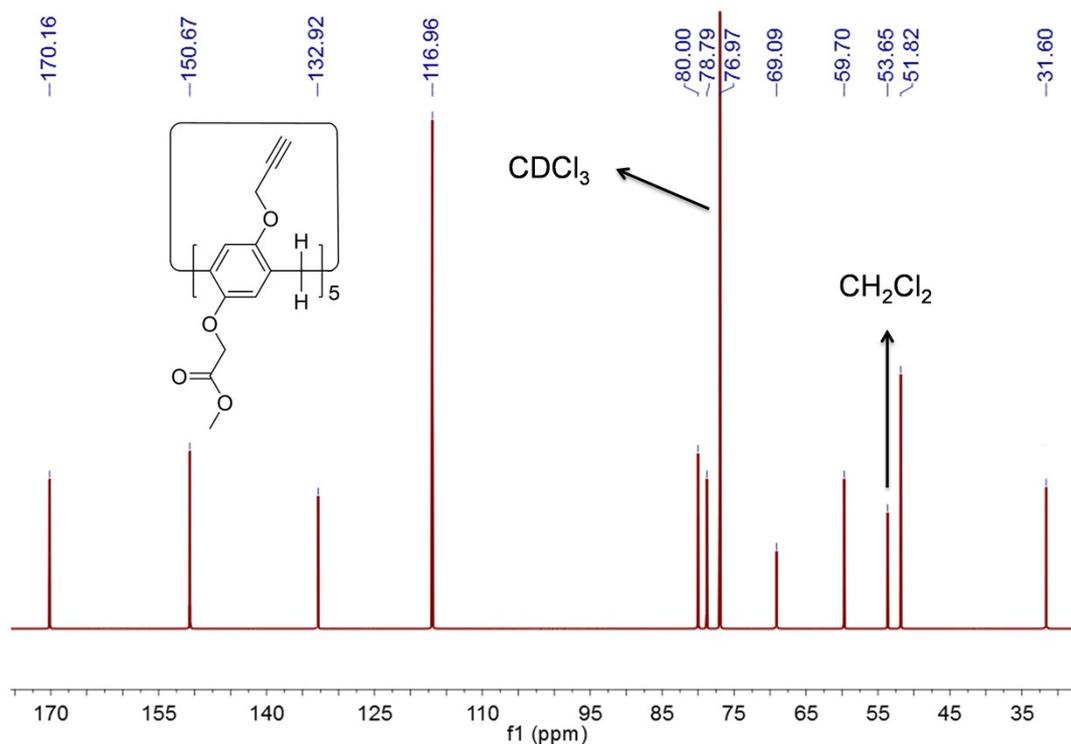


Figure S5. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 293 K) of **RDP5**.

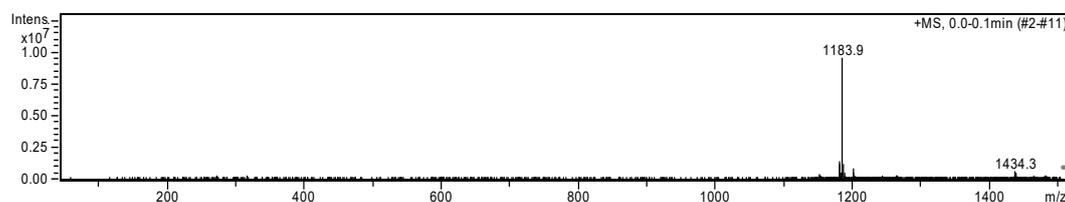


Figure S6. Electrospray ionization mass spectrum of **RDP5**. Assignment of main peak: m/z 1183.9 **RDP5** + $\text{Na}]^+$ (100%).

X-ray crystal data for RDP5

Crystallographic data: block, colorless, $0.48 \times 0.19 \times 0.16 \text{ mm}^3$, $\text{C}_{67}\text{H}_{64}\text{Cl}_4\text{O}_{20}$, FW 1330.98, monoclinic, space group $P2_1/n$, $a = 19.3459(7)$, $b = 15.9668(6)$, $c = 21.2957(8) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 95.564(3)^\circ$, $\gamma = 90^\circ$, $V = 6547.1(4) \text{ \AA}^3$, $Z = 4$, $D_c = 1.350 \text{ g cm}^{-3}$, $T = 140(2) \text{ K}$, $\mu = 2.267 \text{ mm}^{-1}$, 24304 measured reflections, 11115 independent reflections, 841 parameters, 0 restraints, $F(000) = 2776$, $R(\text{int}) = 0.0519$, $R_1 = 0.0985$, $wR_1 = 0.2049$ (all data), $R_2 = 0.0673$, $wR_2 = 0.1752$ [$I > 2\sigma(I)$], max. Residual density $1.160 \text{ e} \cdot \text{\AA}^{-3}$, and goodness-of-fit (F^2) = 1.026. CCDC number: 946658.

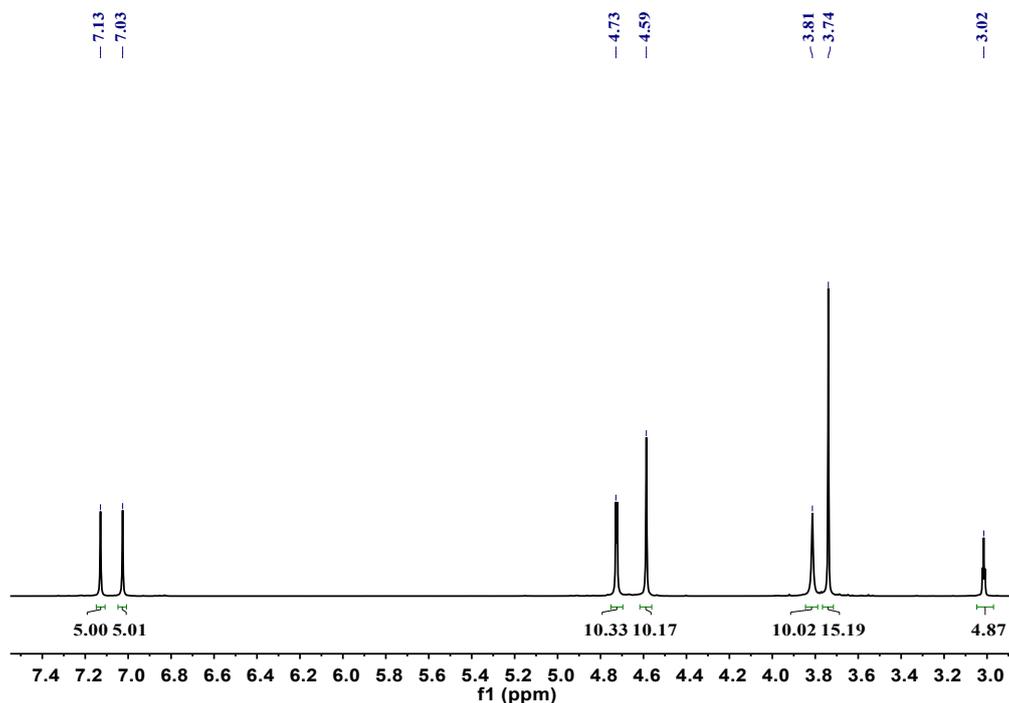
3. Characterization of Nonporous **RDP5** Crystals (**RDP5a**)

Figure S7. ^1H NMR spectrum (400 MHz, CD_3COCD_3 , 293 K) of **RDP5** which recrystallized from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ mixture and dried under vacuum at 150 °C overnight.

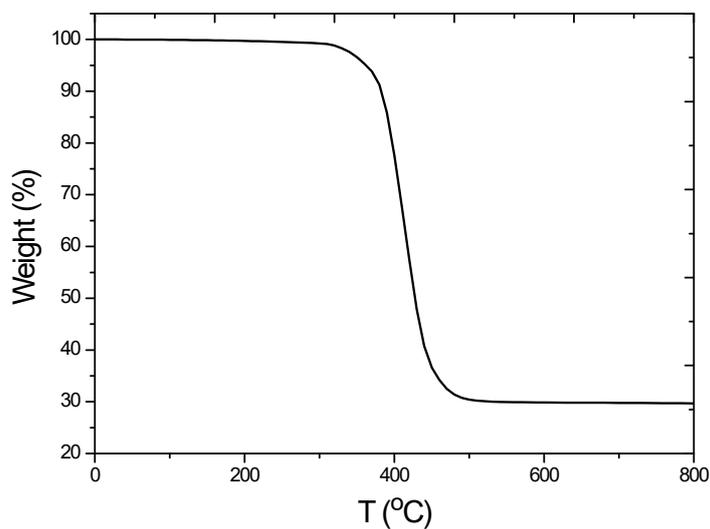


Figure S8. TGA experiment of **RDP[5]** dried under vacuum at 150 °C overnight (**RDP[5a]**).

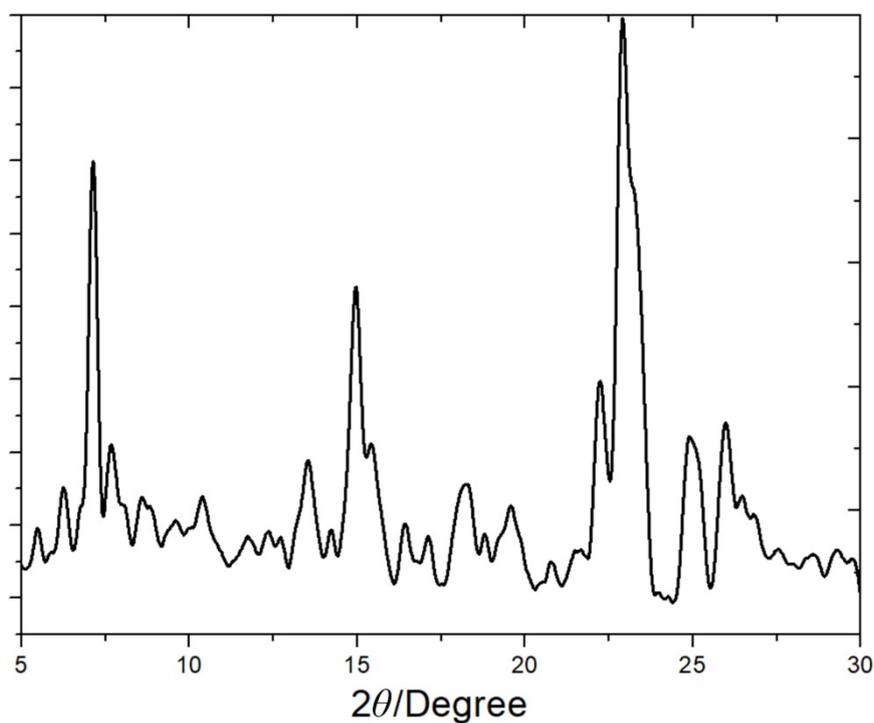


Fig. S9 PXRD pattern of **RDP[5]** dried under vacuum at 150 °C overnight (**RDP[5]α**).

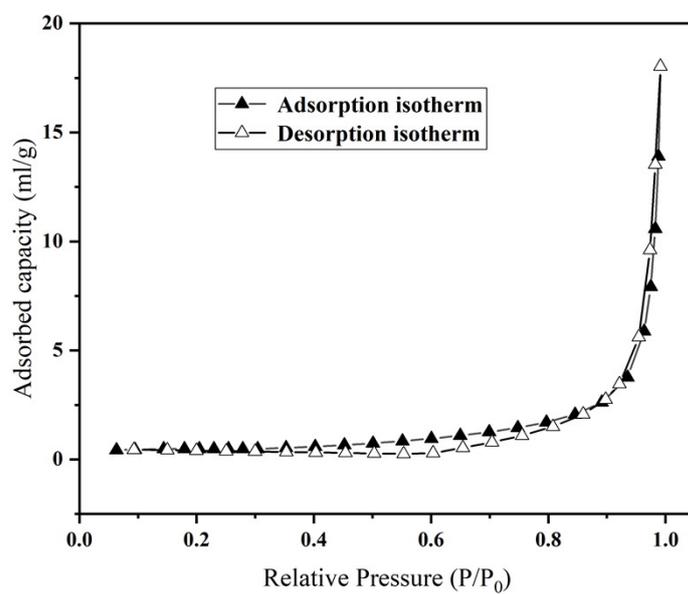


Fig. S10 N₂ adsorption isotherm of **RDP[5]α**. The BET surface area value is 1.49 m²/g, indicating it is barely porous, which is different from conventional adsorption materials.^{S2}

4. Vapor-Phase Adsorption Measurements

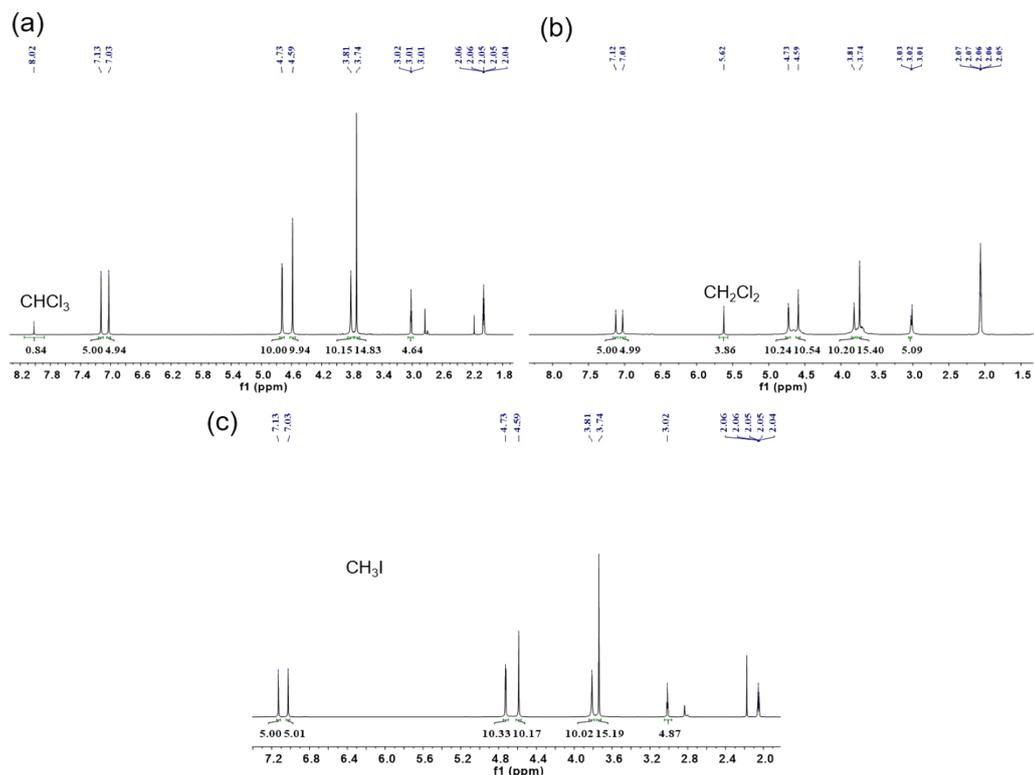


Fig. S11 ^1H NMR spectrum (400 MHz, CD_3COCD_3 , 293 K) of **RDP5a** after sorption of (a) CHCl_3 , (b) CH_2Cl_2 , (c) CH_3I vapor.

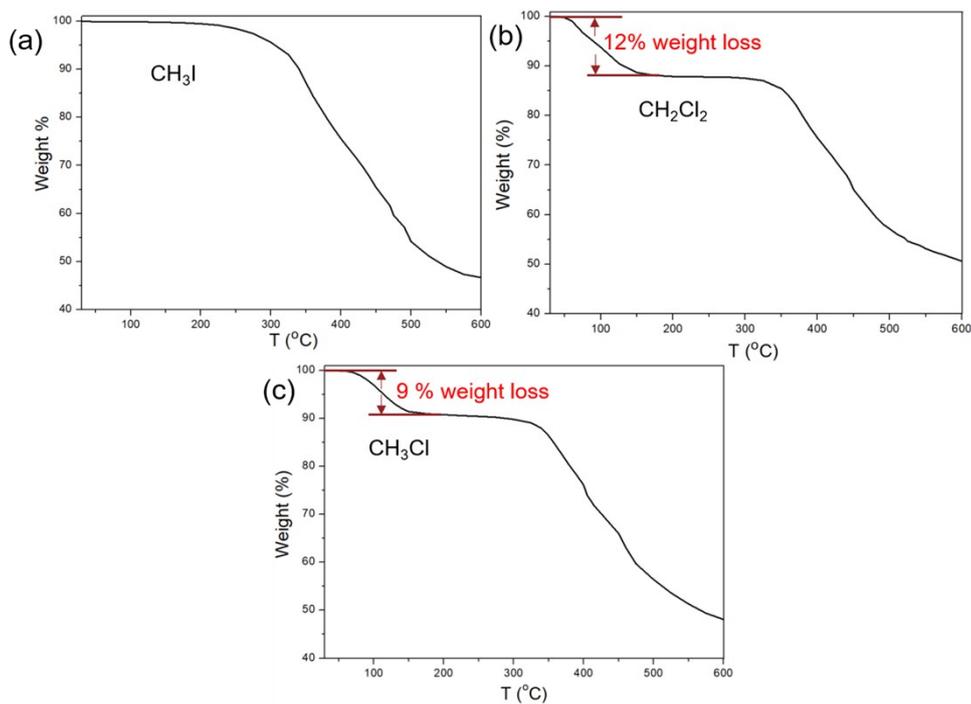


Fig. S12 TGA of **RDP5a** after sorption of (a) CH_3I , (b) CH_2Cl_2 , (c) CHCl_3 vapor.

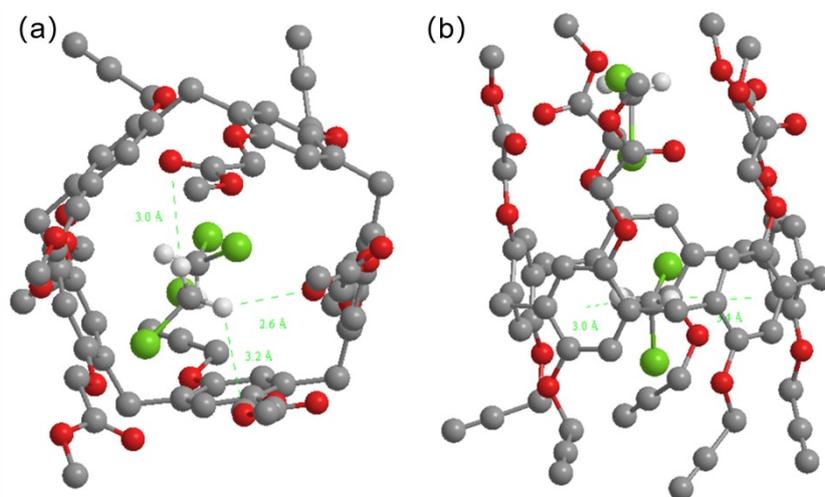


Fig. S13 Single crystal structure of DCM@RDP5.

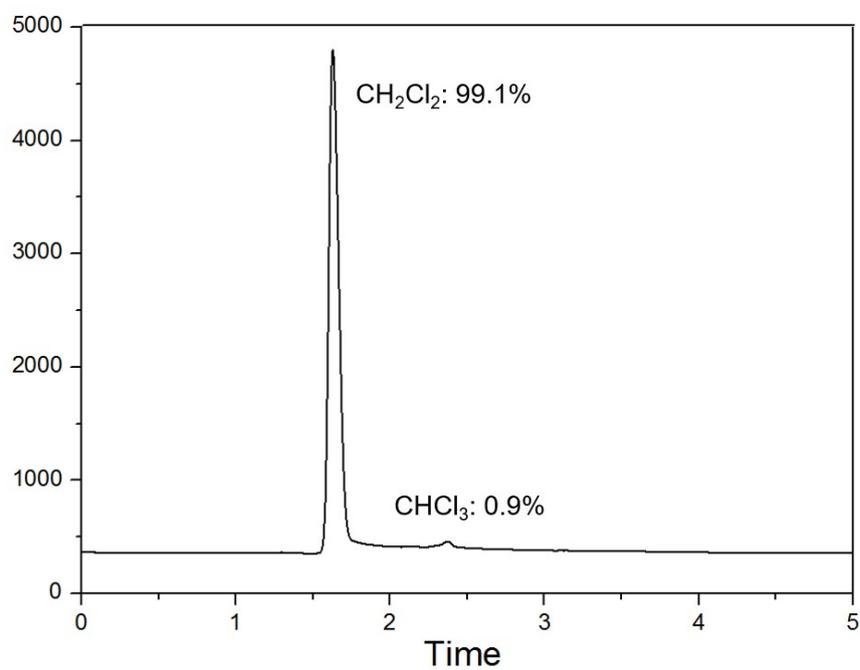
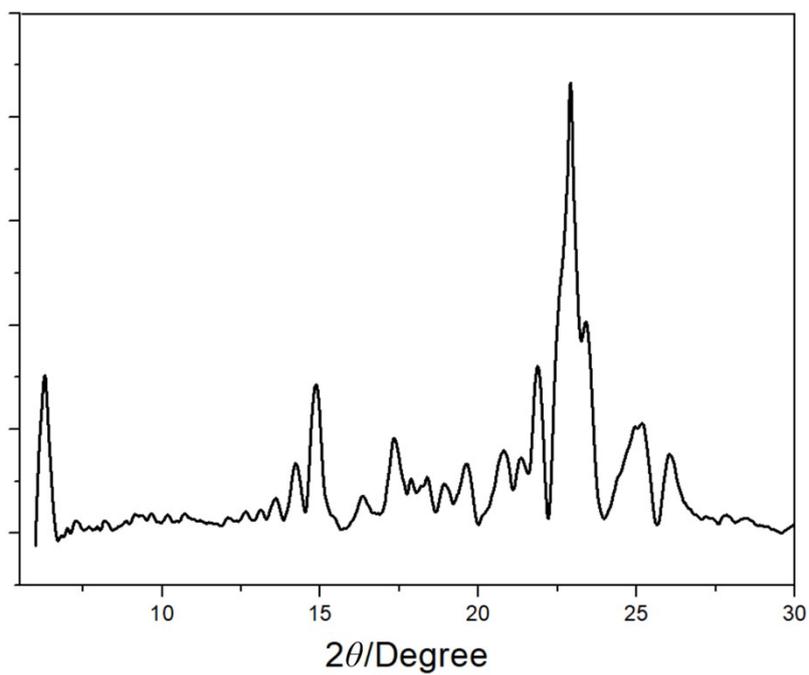
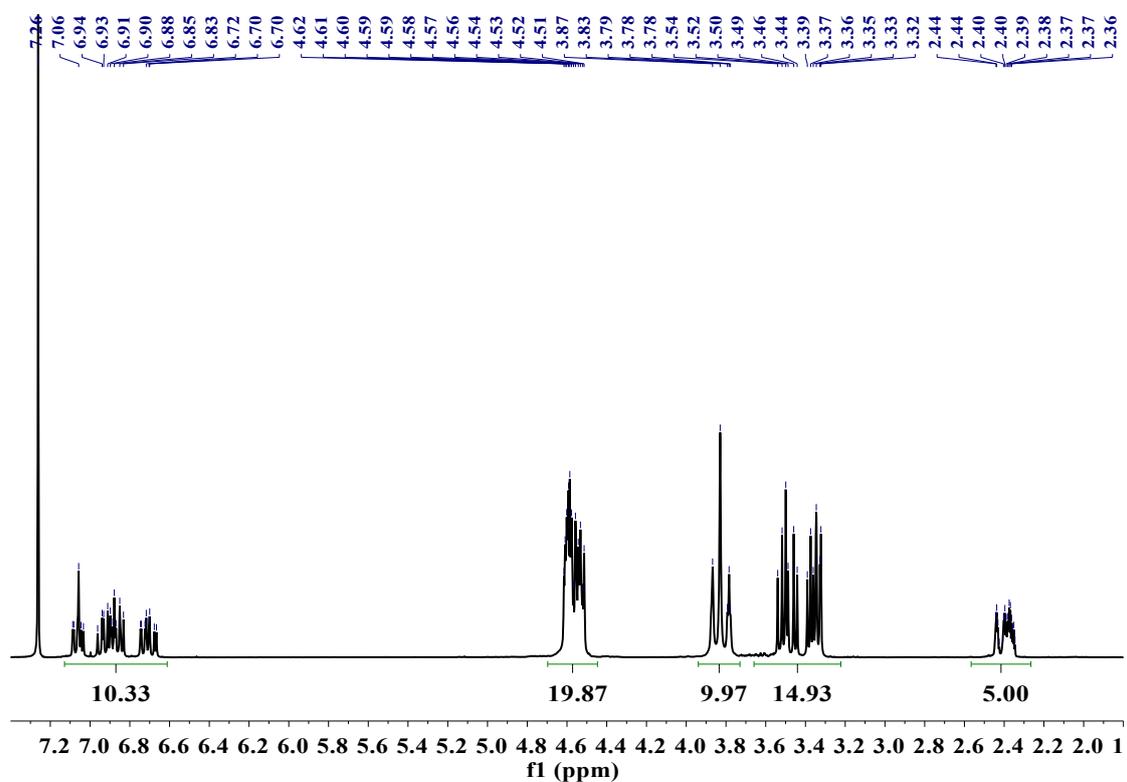


Fig S14 Relative CF/DCM/IM uptake in RDP5 after 8 hours measured by a headspace method using gas chromatography.

5. Recyclability of **RDP[5] α** CrystalsFig S15 PXRD pattern of renewed **RDP[5] α** .Figure S16. ^1H NMR spectrum (400 MHz, CDCl_3 , 293 K) of **P5b**.

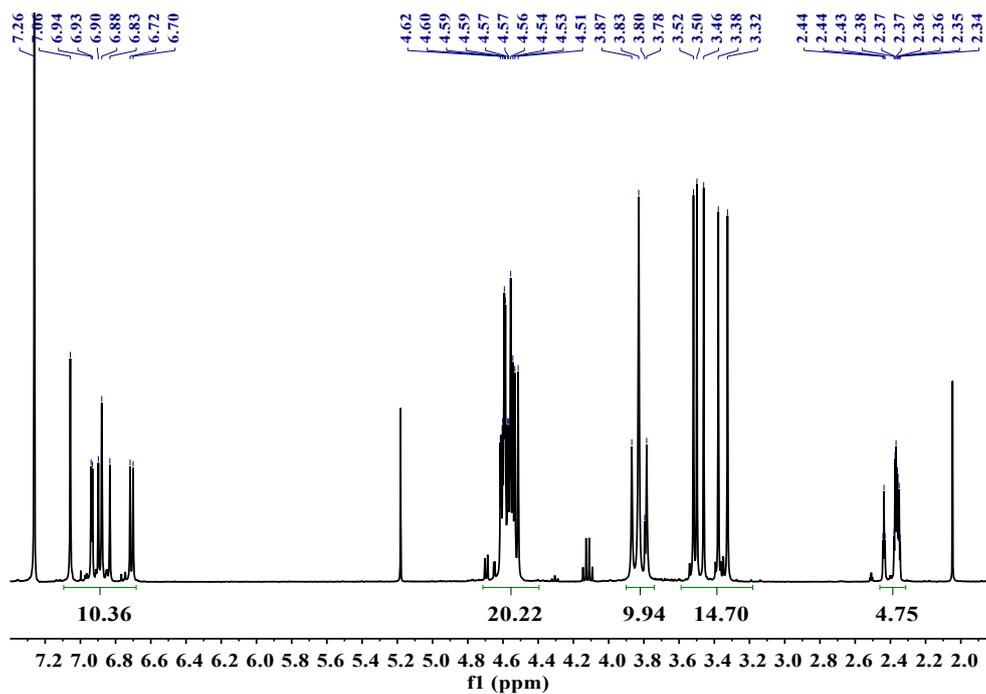


Figure S17. ¹H NMR spectrum (400 MHz, CDCl₃, 293 K) of P5c.

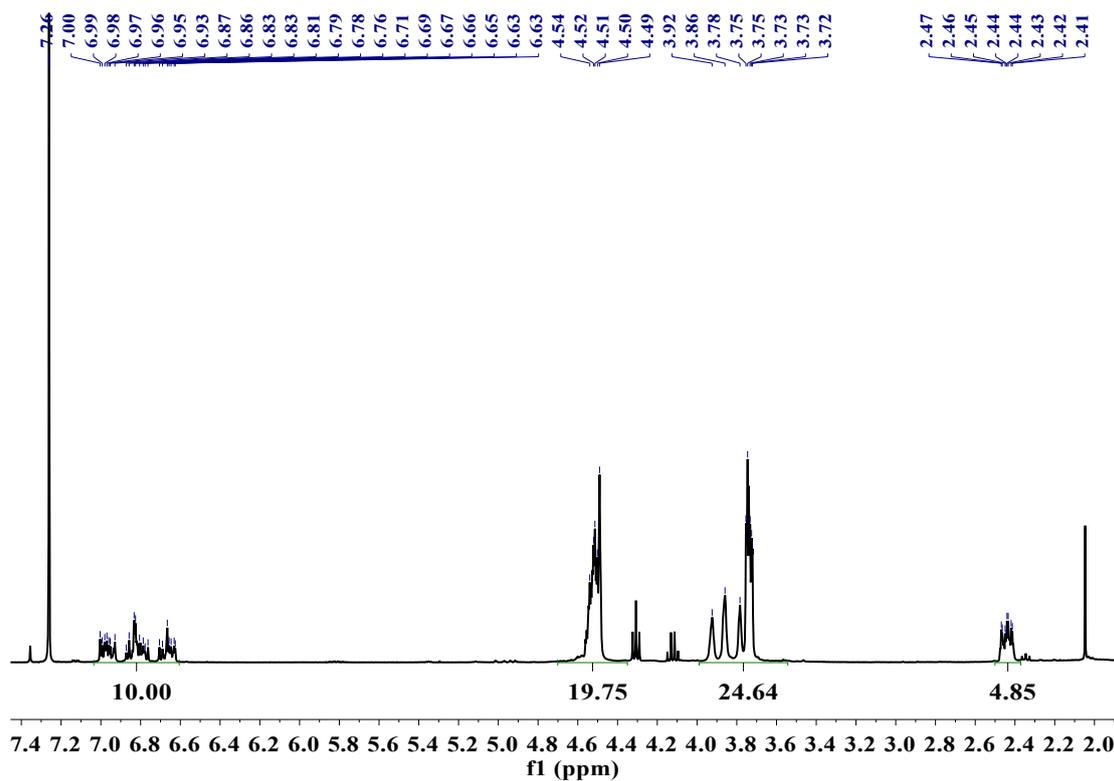


Figure S18. ¹H NMR spectrum (400 MHz, CDCl₃, 293 K) of P5d.

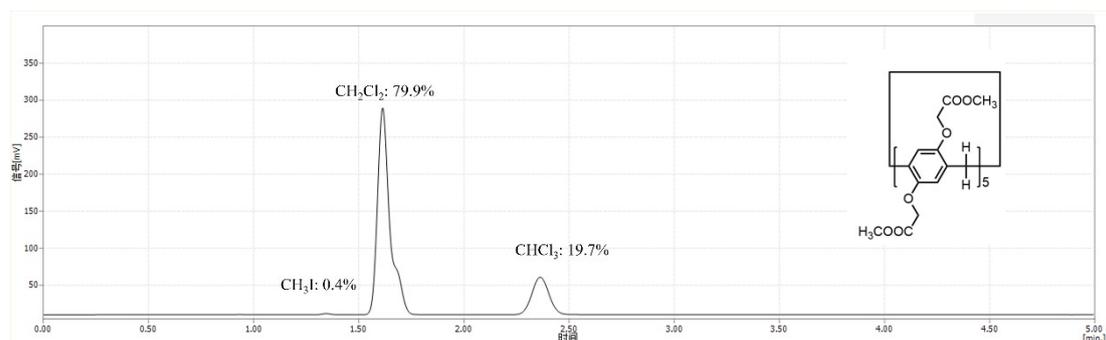


Figure S19. Relative CF/DCM/IM uptake in PP5 after 8 hours measured by a headspace method using gas chromatography.

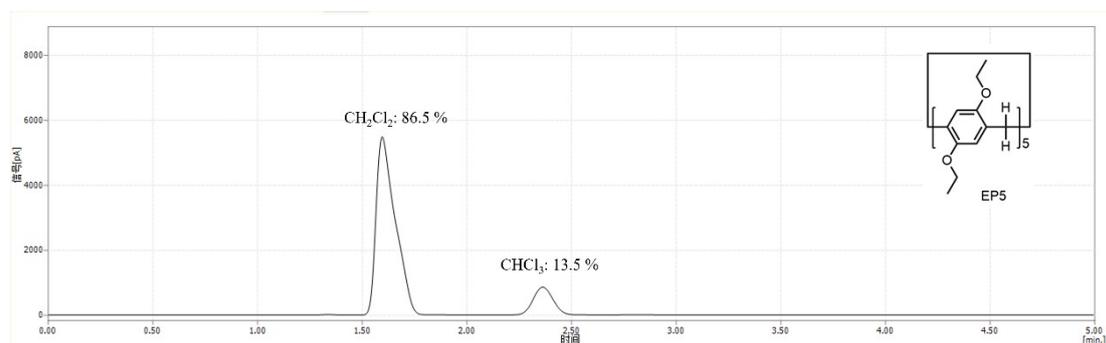


Figure S20. Relative CF/DCM/IM uptake in EP5 after 8 hours measured by a headspace method using gas chromatography.

Reference

- S1. (a) Yao, Y.; Xue, M.; Chen, J.; Zhang, M.; Huang, F. "An Amphiphilic Pillar[5]arene: Synthesis, Controllable Self-Assembly in Water, and Application in Calcein Release and TNT Adsorption". *J. Am. Chem. Soc.*, **2012**, *134*, 15712–15715.
 (b) Zhang, Z.; Luo, Y.; Xia, B.; Han, C.; Yu, Y.; Chen X.; Huang, F. "Four constitutional isomers of Bmpillar[5]arene: synthesis, crystal structures and complexation with n-octyltrimethyl ammonium hexafluorophosphate" *Chem. Commun.*, **2011**, *47*, 2417-2419.
- S2. Jie, K.; Zhou, Y.; Li, E.; Huang, F. "Nonporous Adaptive Crystals of Pillararenes". *Acc. Chem. Res.*, **2018**, *51*, 2064–2072.