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Hyper-crosslinked cyclodextrin porous polymer: An efficient CO_2 capturing material with tunable porosity

Bo Meng,[a#] Haiying Li,[b,c#] Shannon M. Mahurin,[c*] Honglai Liu[b*] and Sheng Dai[a,c*]

[a] *Department of Chemistry, University of Tennessee, Knoxville, TN 37996, United States*

[b] *State Key Laboratory of Chemical Engineering and Department of Chemistry, East China University of Science and Technology, Shanghai, 200237, China. Email: hlliu@ecust.edu.cn*

[c] *Chemical Science Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, United States. Email: mahurinsm@ornl.gov, dais@ornl.gov*

[#] *These authors contributed equally to this work.*

General experimental procedure:

All chemicals were purchased as reagent grade and used without further purification, unless otherwise noted. Reagent grade dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), methanol (MeOH) and *N*,*N*-dimethylformamide (DMF) were obtained from the Pure-Solv (Innovation Technologies) solvent system that uses alumina columns except for DMF, which was dried over a column of 5 Å molecular sieves. All reactions were performed under anhydrous conditions unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) on silica gel precoated aluminum plates. Zones were detected by UV irradiation using a 254 nm lamp and/or by heat/charring with *p*-anisaldehyde–sulfuric acid development reagent. Column chromatography was performed on silica gel (40−63 μm). ^1H and ^{13}C NMR spectra were recorded at room temperature with a Varian VNMRS 600 instrument. Chemical shifts are reported in δ-units (ppm) relative to the residual ^1H $CDCl_3$ at δ 7.26 ppm and ^{13}C at δ 77.16 ppm. The solid-state ^{13}C NMR cross-polarization magic angle spinning nuclear magnetic resonance (CP-MAS NMR) spectroscopy was performed on Varian INOVA 400 instrument with spinning rate of 7k. Mass spectrometric analysis was performed on a QSTAR Elite quadrupole time-of-flight (QTOF) mass spectrometer with an ESI source. MALDI-TOF mass spectra were obtained on a Voyager-DE PRO BioSpectrometry workstation.

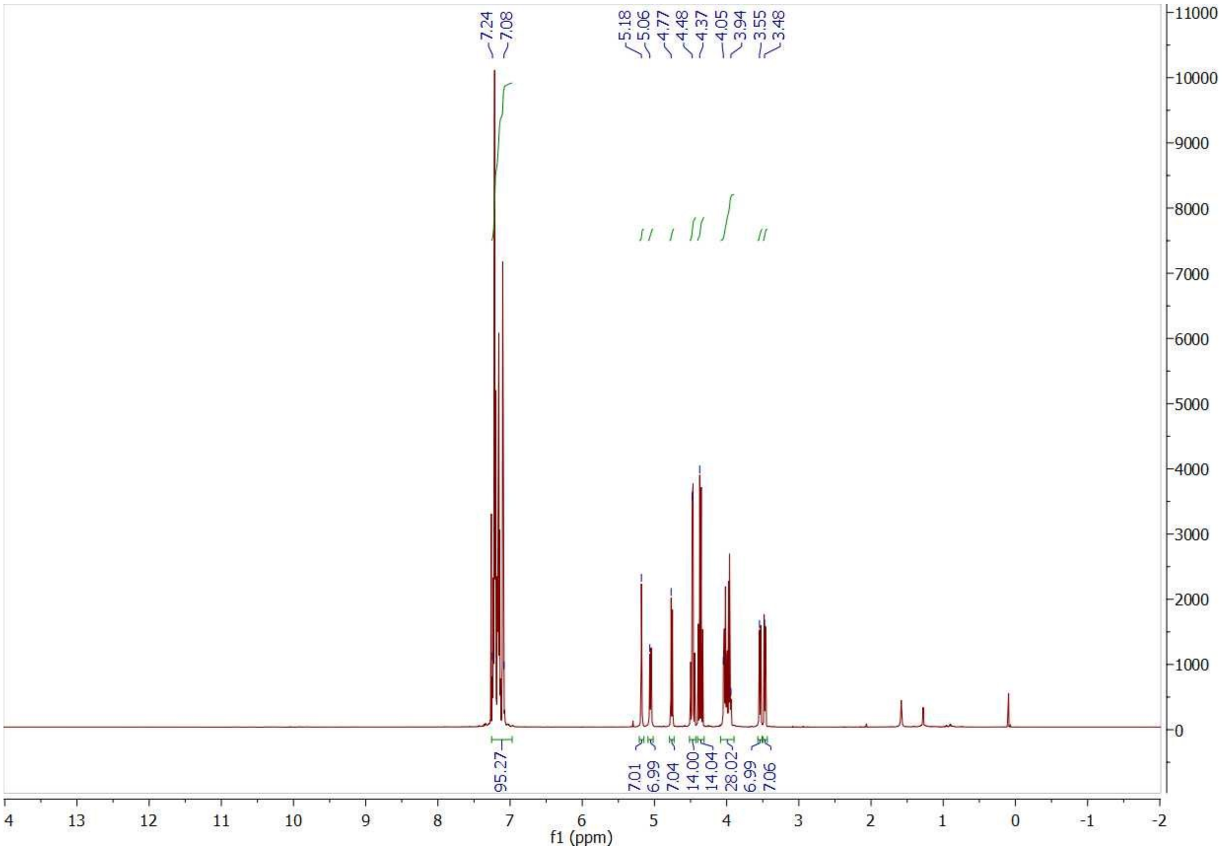
Per-2,3,6-tri-*O*-benzyl-β-cyclodextrin (βBnCD): β-Cyclodextrin (500 mg, 0.44 mmol) was dissolved in dry DMF (10 mL). The solution was cooled to 0 °C and added NaH (60%, 740 mg, 18.48 mmol) portionwise. After stirring for 15 min, benzyl bromide (2.20 mL, 18.48 mmol) was slowly added and the reaction mixture was warmed to room temperature. After stirring overnight, the reaction mixture was quenched by adding methanol (5 mL) and concentrated *in* *vacuo*. The resulting residue was mixed with water (100 mL) and extracted with methylene chloride (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by silica gel chromatography (Hexanes:EtOAc=8:1) to yield **βBnCD** (1.10 g, 83%) as colorless oil. ^1H NMR ($CDCl_3$, 600 MHz) δ 7.24 – 7.08 (m, 105H), 5.18 (d, *J* = 3.5 Hz, 7H), 5.06 (d, *J* = 10.9 Hz, 7H), 4.77 (d, *J* = 10.9 Hz, 7H), 4.48 (q, *J* = 12.1 Hz, 14H), 4.37 (q, *J* = 12.1 Hz, 14H), 4.05 – 3.94 (m, 28H), 3.55 (m, 7H), 3.48 (dd, *J* = 9.5, 3.5 Hz, 7H). ^{13}C NMR ($CDCl_3$, 151 MHz) δ 139.39, 138.46, 138.31, 128.41, 128.27, 128.10, 127.94, 127.65, 127.63, 127.55, 127.40, 127.04, 98.57, 81.02, 78.91, 78.80, 75.54, 73.39, 72.79, 71.62, 69.41. MALDI-TOFMS: calcd for $C_{189}H_{196}O_{35}\cdot Na^+$: 3050.3514; found: *m/z* 3050.3516.

Per-6-*O*-acetyl-2,3-di-*O*-benzyl-β-cyclodextrin (βBnCD-1): βBnCD (900 mg, 0.30 mmol) in acetic anhydride (15 mL) was cooled to -40 °C, followed by adding TMSOTf (0.38 mL, 2.10 mmol) in anhydrous dichloromethane (0.75 mL) dropwise. The reaction mixture was stirred at -40 °C for 1.5 hrs, and quenched by saturated $NaHCO_3$ (25 mL) at 0 °C. The reaction mixture was then diluted with water (25 mL) and extracted with EtOAc (40 mL). The organic solution was washed with saturated $NaHCO_3$ (40 mL), H_2O (40 mL), saturated brine (40 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by silica gel chromatography (Hexanes:EtOAc=4:3 to 5:4) to yield **βBnCD-1** (646 mg, 80%) as white solid. ^1H NMR ($CDCl_3$, 600 MHz) *δ* 7.23 – 7.14 (m, 70H), 5.02 (d, *J* = 11.0 Hz, 7H), 4.94 (d, *J* = 3.6 Hz, 7H), 4.75 (d, *J* = 11.0 Hz, 7H), 4.57 (d, *J* = 12.4 Hz, 7H), 4.46 – 4.40 (m, 14H), 4.38 (dd, *J* = 12.4, 4.9 Hz, 7H), 4.07 (m, 7H), 4.01 (d, *J* = 9.4, 8.1 Hz, 7H), 3.68 (dd, *J* = 9.6, 8.1 Hz, 7H), 3.47 (dd, *J* = 9.4, 3.6 Hz, 7H), 2.03 (s, 21H). ^{13}C NMR ($CDCl_3$, 151 MHz) *δ* 170.59, 139.20, 138.44, 128.38, 128.21, 128.08, 127.80, 127.30, 127.23, 99.12, 80.57, 79.92, 78.80, 75.51, 73.20, 70.06, 63.63, 20.97. MALDI-TOFMS: calcd for $C_{154}H_{168}O_{42}\cdot Na^+$: 2713.0937; found: *m/z* 2713.0935. The data of **βBnCD-1** are consistent with those previously reported.**[S1]**

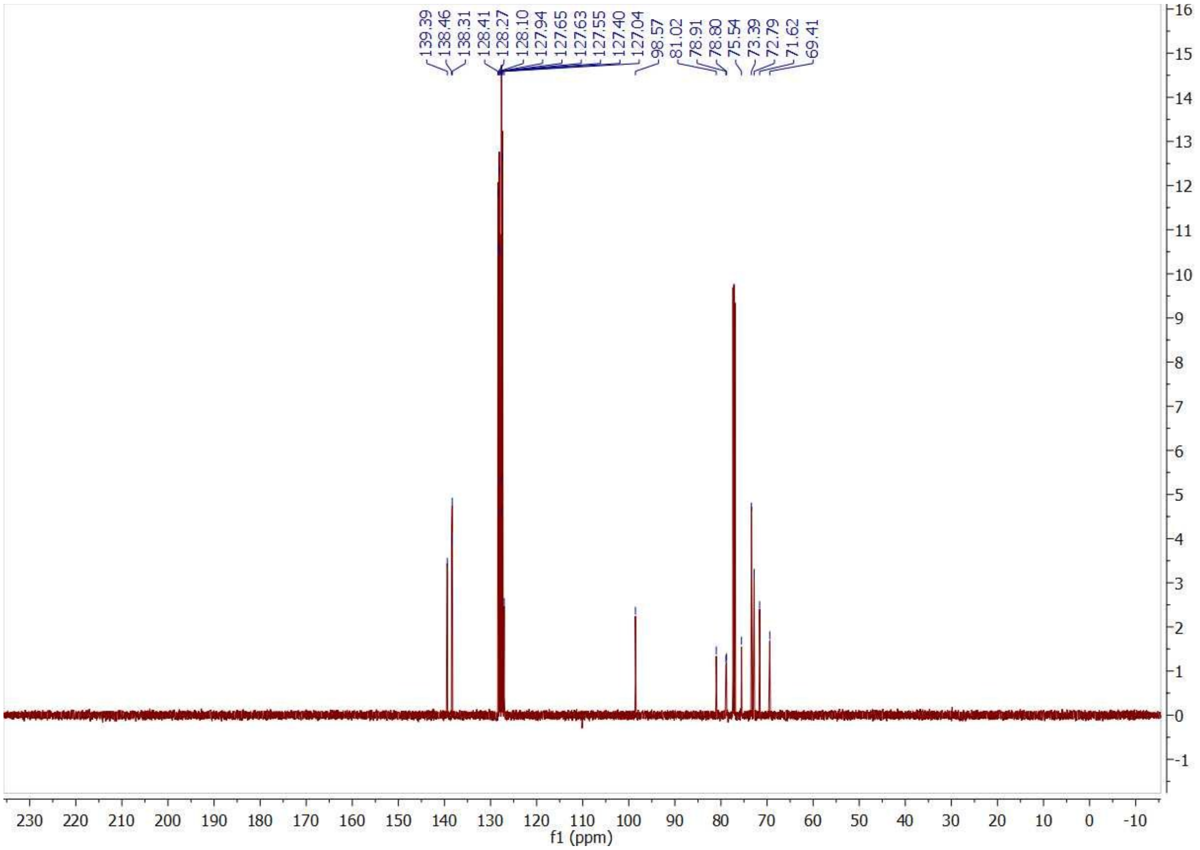
Per-2,3-di-*O*-benzyl-β-cyclodextrin (βBnCD6OH): βBnCD-1 (600 mg, 0.22 mmol) was dissolved in MeOH (4 mL) and anhydrous THF (1 mL), followed by adding NaOMe in small portion to afford pH 9. After overnight stirring, the solution was quenched by Amberlite® IR 120 (H^+). The resin was filtered off and the solvent was removed in vacuo to give **βBnCD6OH** (485 mg, 92%) as white solid. ^1H NMR ($CDCl_3$, 600 MHz) *δ* 7.19 – 7.12 (m, 70H), 5.02 (d, *J* = 3.7 Hz, 7H), 4.88 (d, *J* = 11.2 Hz, 7H), 4.69 (d, *J* = 11.2 Hz, 7H), 4.54 (d, *J* = 12.4 Hz, 7H), 4.46 (d, *J* = 12.3 Hz, 7H), 3.94 (m, 21H), 3.79 (m, 7H), 3.64 (t, *J* = 8.5 Hz, 7H) 3.48 (dd, *J* = 9.0, 3.8 Hz, 7H^{13}C NMR ($CDCl_3$, 151 MHz) *δ* 139.13, 138.40, 128.32, 128.15, 127.92, 127.60, 127.39, 127.16, 98.48, 80.58, 78.94, 78.53, 75.06, 73.09, 72.88, 61.69. MALDI-TOFMS: calcd for $C_{140}H_{154}O_{35}\cdot Na^+$: 2419.0197; found: *m/z* 2419.0198. The data of **βBnCD6OH** are consistent with those previously reported.[S2]

General polymerization of benzylated carbohydrates

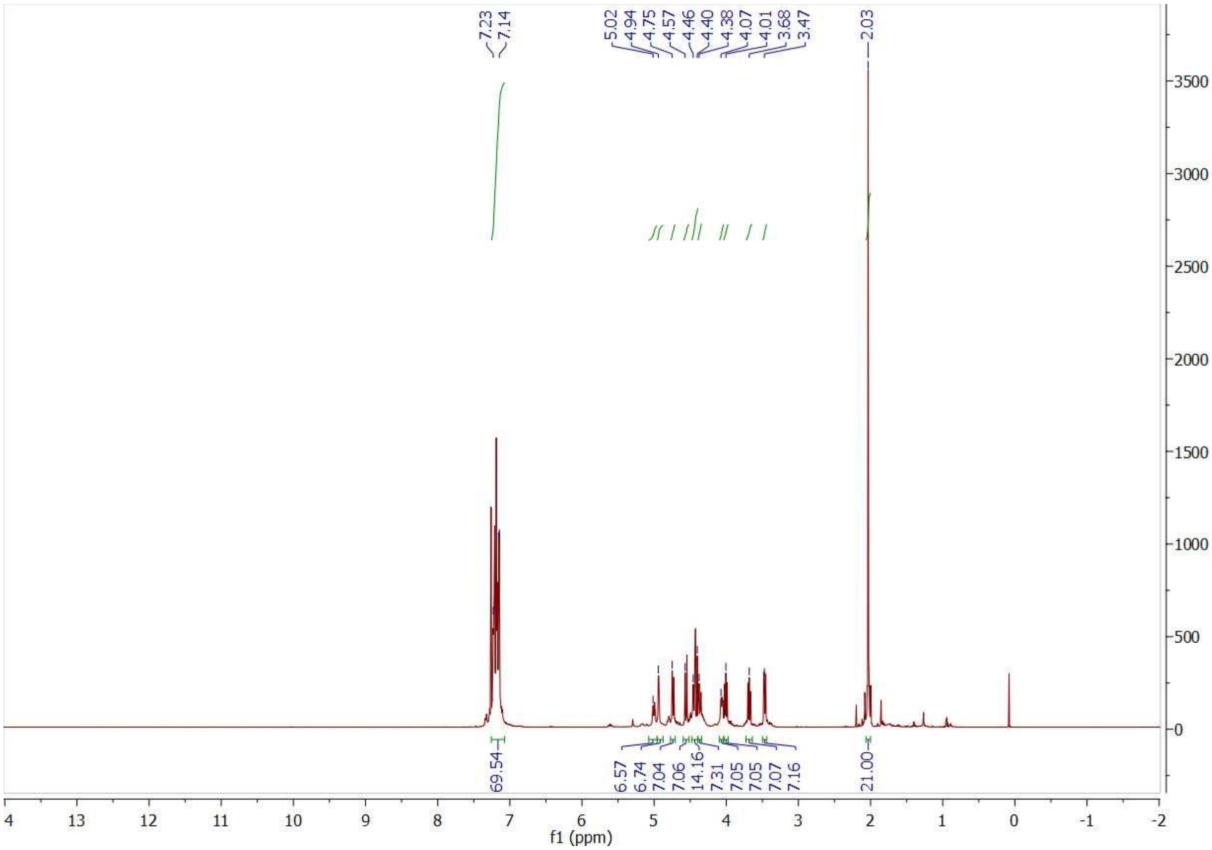
Typically, to a solution of the monomer and FDA in anhydrous 1,2-dichlorehane, $FeCl_3$ in DCE was slowly added under nitrogen atmosphere. The mixture was then heated to 45 °C for 5 h and 80°C for 19 h. The resulting brown precipitate was filtered and washed with methanol and water until the filtrate became colorless and further purified by Soxhlet Extraction with methanol for 24 h. The polymer was dried in vacuum oven for 24 h at 60 °C. For different monomers, the ratio of external cross-linker FDA and catalysis $FeCl_3$ was adjusted according to the numbers of benzyl rings: for βBnCD, the molar ratio was 1 βBnCD: 6 FDA: 6 $FeCl_3$; and for βBnCD6OH, it was 1 βBnCD6OH: 4 FDA: 4 $FeCl_3$.



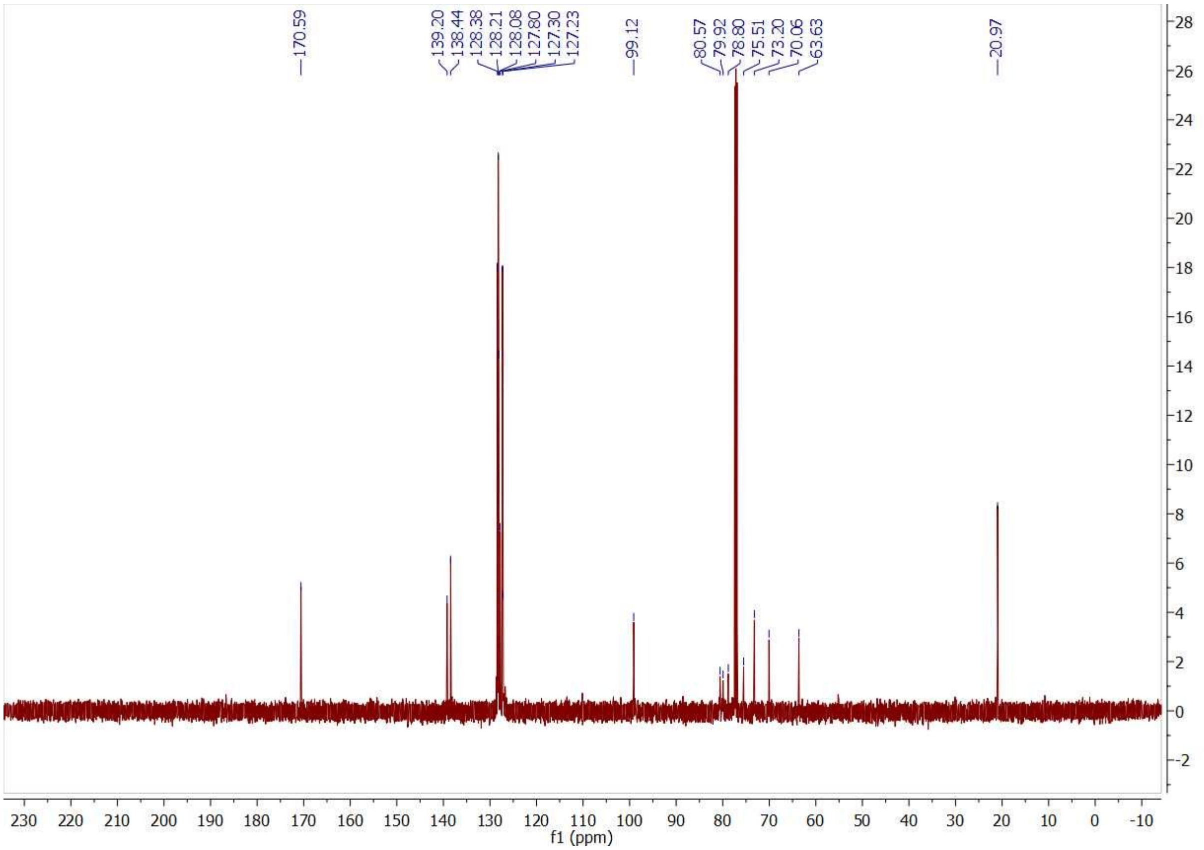
¹H NMR Per-2,3,6-tri-*O*-benzyl-β-cyclodextrin (**βBnCD**)



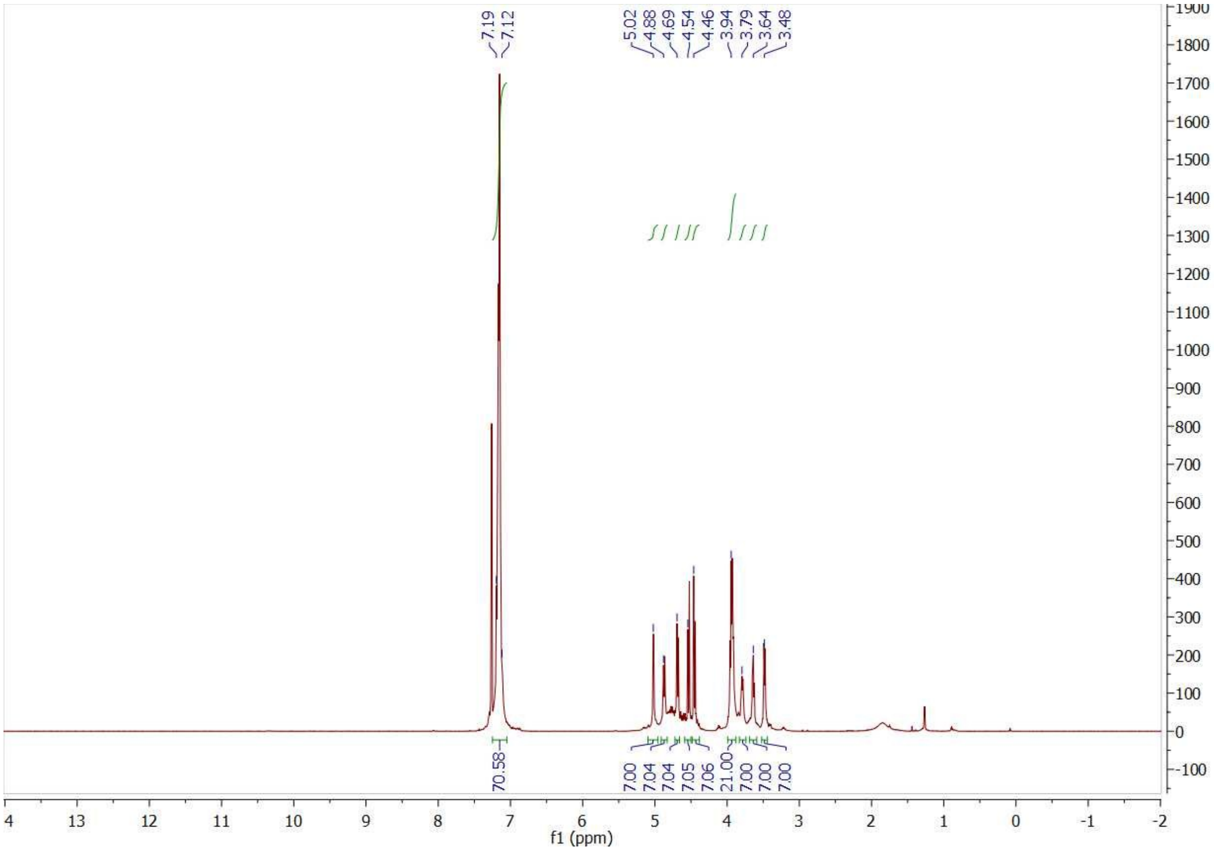
^{13}C NMR Per-2,3,6-tri-*O*-benzyl-β-cyclodextrin (**βBnCD**)



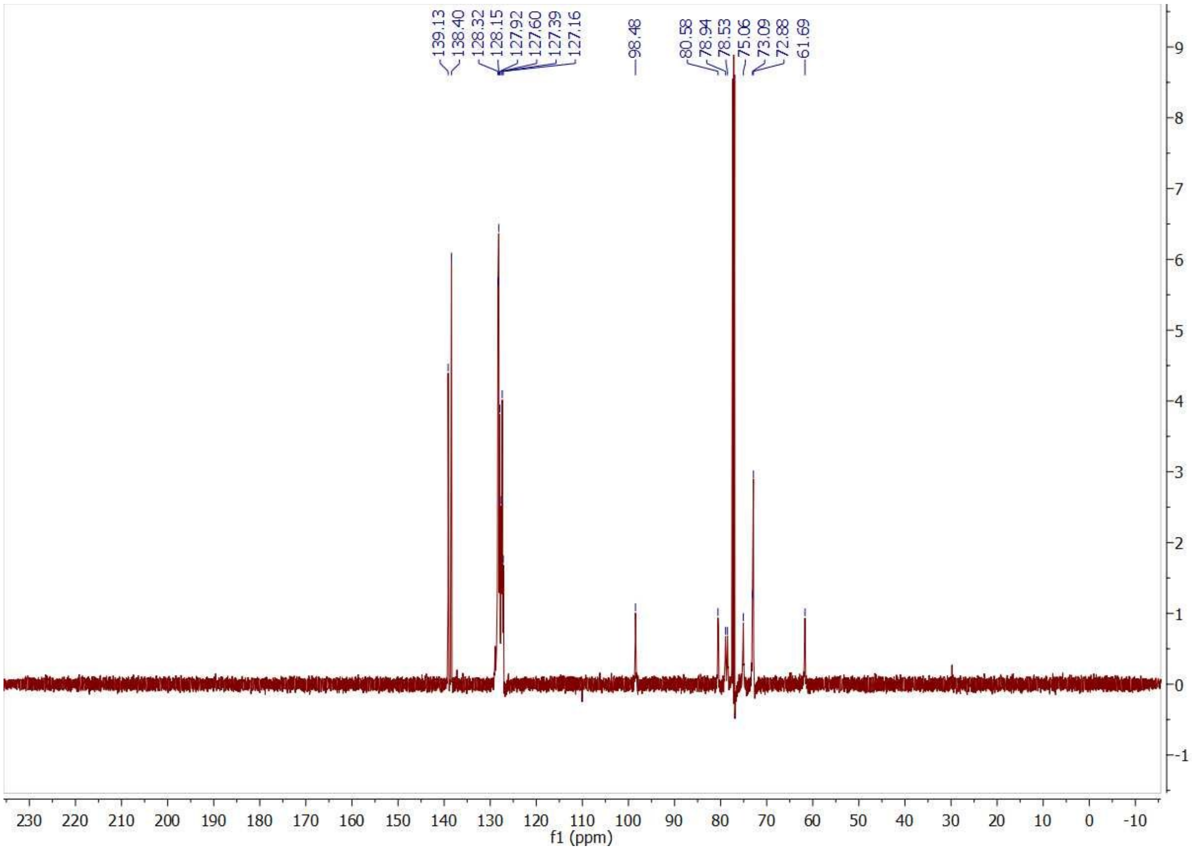
¹H NMR Per-6-*O*-acetyl-2,3-di-*O*-benzyl-β-cyclodextrin (**βBnCD-1**)



^{13}C NMR Per-6-*O*-acetyl-2,3-di-*O*-benzyl-β-cyclodextrin (**βBnCD-1**)



¹H NMR Per-2,3-di-*O*-benzyl-β-cyclodextrin (**βBnCD6OH**)



^{13}C NMR Per-2,3-di-*O*-benzyl-β-cyclodextrin (**βBnCD6OH**)

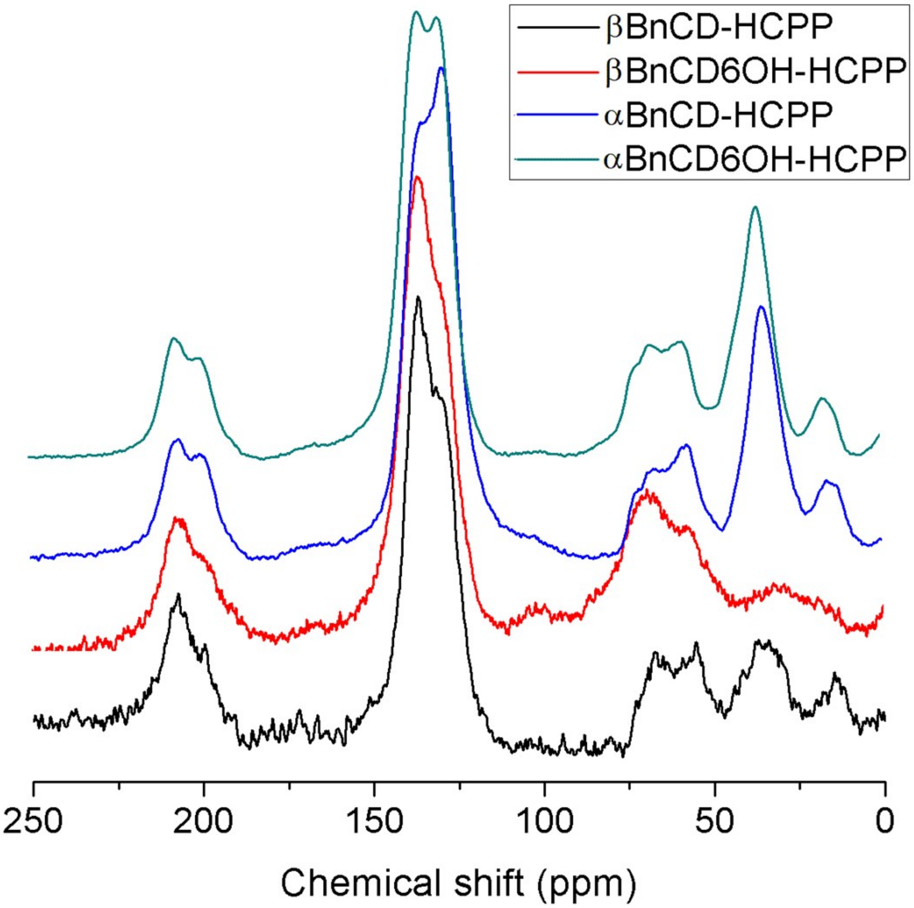


Figure S1 Solid State ^{13}C NMR of four CD-based polymers.

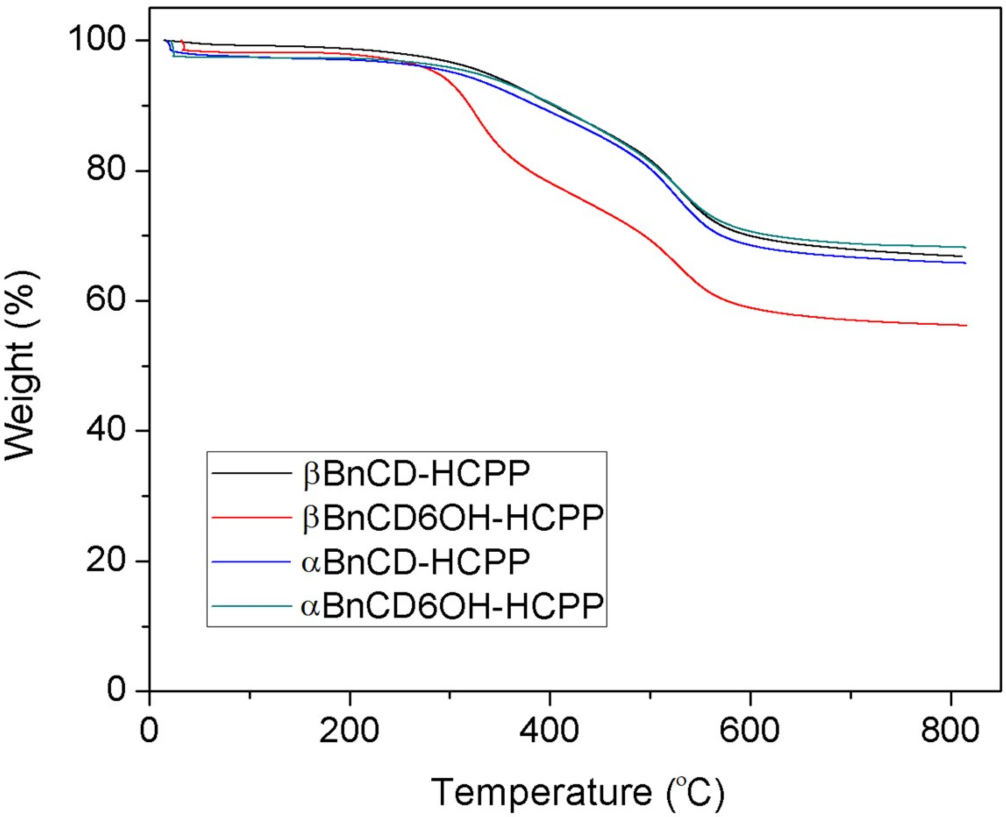


Figure S2 Thermal gravimetric analysis (TGA) of all carbohydrate polymers (heated with the rate of 10 °C/min up to 900 °C under nitrogen fluid)

While we have not fully explored the reason for this difference, one possible explanation is that the monomer of βBnCD6OH-HCPP, per-2,3-di-*O*-benzyl-β-cyclodextrin, consists of seven glucose in α(1,4) linkage. Two hydroxyl groups (2-OH and 3-OH) are benzylated while 6-OH is free. This structure property determines that only two benzyl groups are available for the hyper-crosslinking, and less binding sites and linkages in the polymer will result in lower thermal stability (compared with per-*O*-benzylated HCPP). Besides, the macro cyclic structure of β-cyclodextrin makes it easier to be stretched and twisted, which may also reduce its thermal stability (compared with α-cyclodextrin).

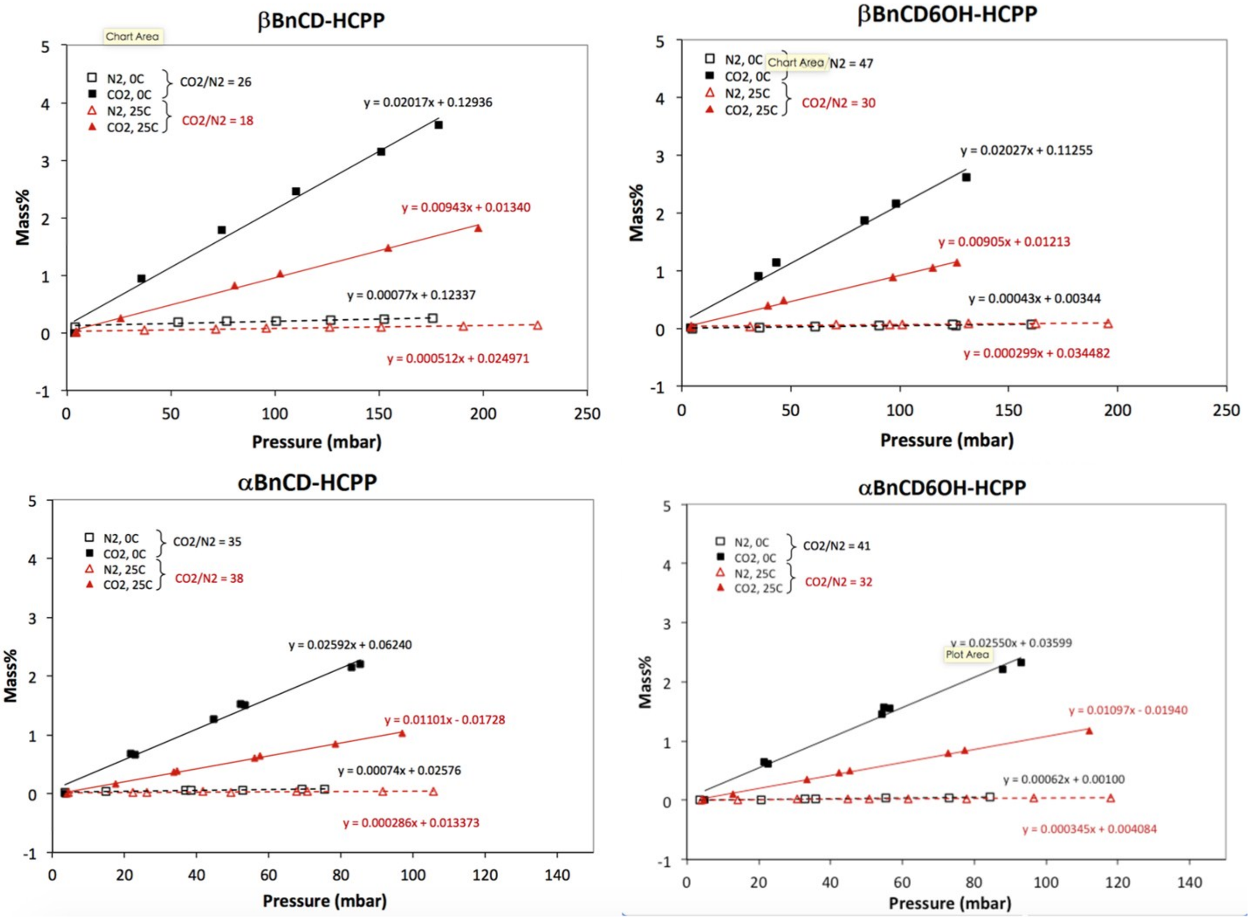


Figure S3 Initial slope calculations of CO_2 and N_2 isotherms for CO_2/N_2 selectivity collected at 273 K and 298 K respectively.

Calculation of Heat of Adsorption:

The CO_2 uptake curves were acquired at two different temperatures, 273 K and 298 K. The isotherms were acquired up to a maximum pressure of 1 bar and were initially fit to a Dual Langmuir Model. The results from the Dual Langmuir fitting were used in a variant of the Clausius-Clapeyron equation shown below to obtain the heats of adsorption:

$$\ln\left(\frac{P_1}{P_2}\right) = \Delta H_{ads}\left[\frac{T_2 - T_1}{R \cdot T_1 \cdot T_2}\right]$$

where *P* is the pressure, *T* is the temperature in Kelvin and R is the ideal gas constant.

Characterization of Morphology

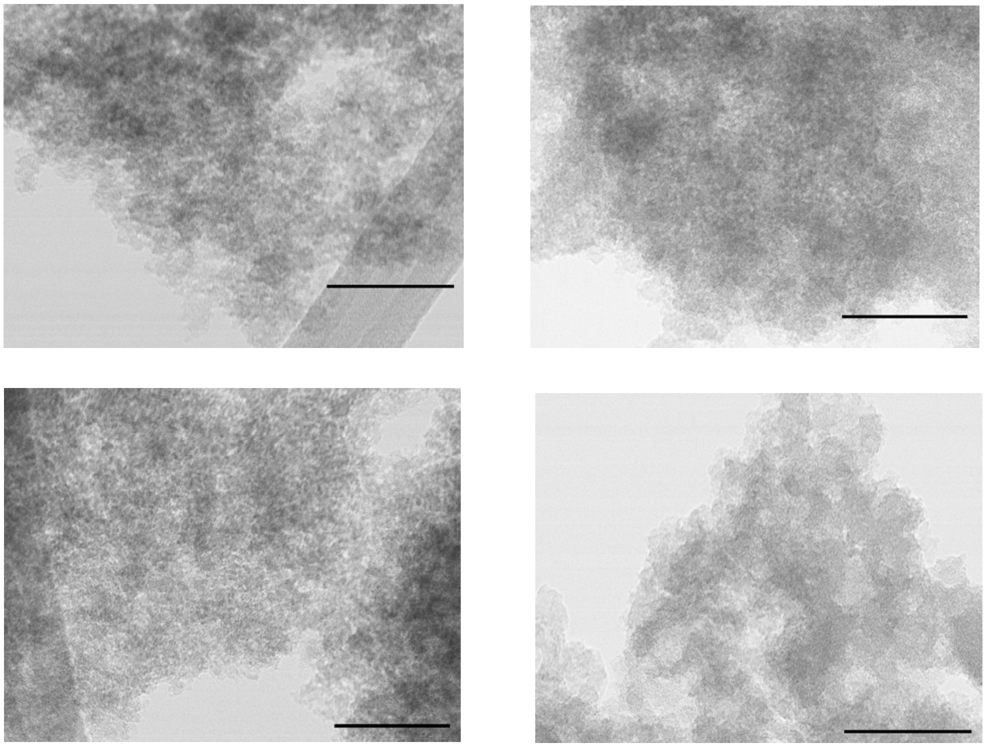


Figure S4. Transmission electron microscopy images of the cyclodextrin: a) αBnCD-HCPP, b) αBnCD6OH-HCPP, c) βBnCD-HCPP, d) βBnCD6OH-HCPP. Scale bars are 80 nm for all images.

The morphology of the different cyclodextrin materials shown in Figure S4 were acquired with a Hitachi HD-2000 scanning transmission electron microscope with an accelerating voltage of 200 kV. All four materials show an aggregated structure with nanoscale features. From BET measurements, structural variations are predominantly in the micropore range which is below the resolution of our instrument. However, the particle size of the βBnCD6OH-HCPP is slightly larger than the other CD materials.

References:

S1. S. Ward, O. Calderon, P. Zhang, M. Sobchuk, S. N. Keller, V. E. Williams, C.-C. Ling, *J. Mater. Chem. C,* **2014**, *2*, 4928-4936.