Electronic Supplementary Material (ESI) for ChemComm.

Crystalline nanotubular framework constructed by cucurbit[8]uril for selective CO_2 adsorption

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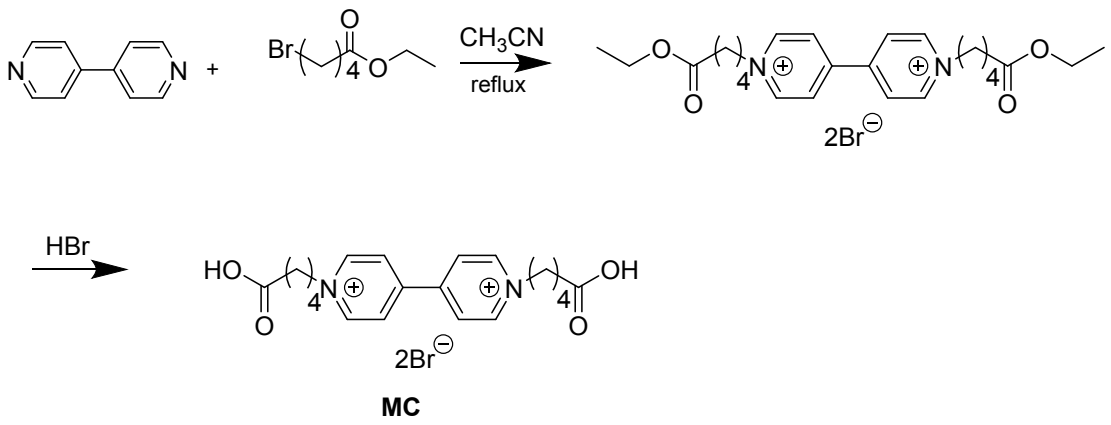
Table of Contents **Pages**

General Experimental Details.

Starting materials were purchased from commercial suppliers were used without further purification. CB[8][1] and **MC**[2-4] was prepared according to the published procedure. Melting points were determined using XT-4 apparatus. IR spectra were recorded on a Bruker IFS 120HR spectrometer and were reported in cm^{-1}. ^{1}H and ^{13}C NMR spectra were done on a Bruker ascend spectrometer at 400MHz. Electron Spray Ionization (ESI) mass spectra were acquired by using a UltiMate3000 electrospray instrument. Thermal gravimetric analysis (TGA) experiments were performed on NETZSCH STA 449C Simultaneous Thermal Analyzer over the temperature 30–800°C in a nitrogen-gas atmosphere. X-ray powder diffraction (XRD) experiments were recorded on Bruker D8 ADVAHCL. The Scanning Electron Microscope (SEM) images were obtained on Hitachi SU8010microscope. Sorption isotherms were measured by a Micrometrics Tristar 3020 instrument. UV-Vis spectra were done on Agilent Cary-100.

Synthetic Procedures and Characterization Data.



MC

*Compound **MC***. 4,4'-bipyridine (2.0 g, 12.8 mmol) and ethyl 5-bromovalerate (10.7 g，51.2 mmol) were refluxed in acetonitrile (50 mL) for 28 hours. A precipitate produced was appeared and then filtered. The filter cake was washed with ethyl ether and then recrystallized from MeOH–Et_2O provided to afford the yellow product. The yellow product was dissolved in 2 M aqueous HBr solution (15 mL) and left

standing for 2 days. Then the mixture was poured into 50 mL acetone and filtered. The precipitate was washed with acetone (3 × 35 mL) and dried in high vacuum. The ^{1}H NMR spectrum matches that reported in the literature.[2-4]

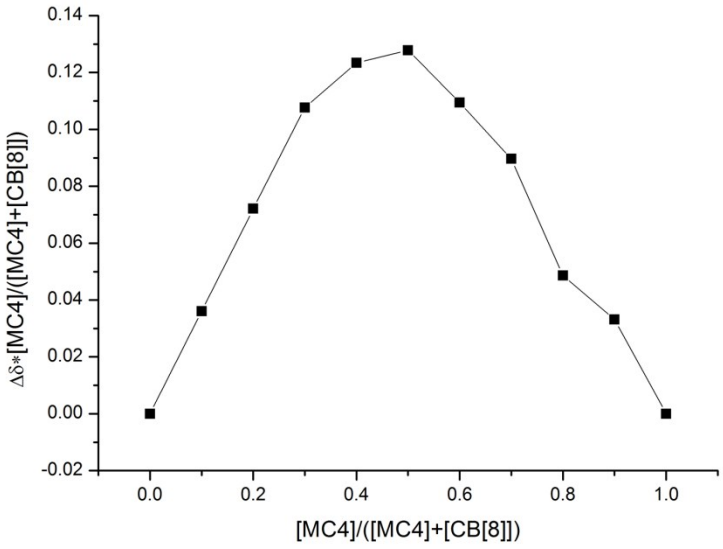


Figure S1. Job's plot obtained by recording ^{1}H NMR spectra for the solution of **MC** and CB[8] in D_2O ([**MC**] + [CB[8]] = 1.0 × 10^{-3} M), confirming the 1:1 stoichiometry of their complex.

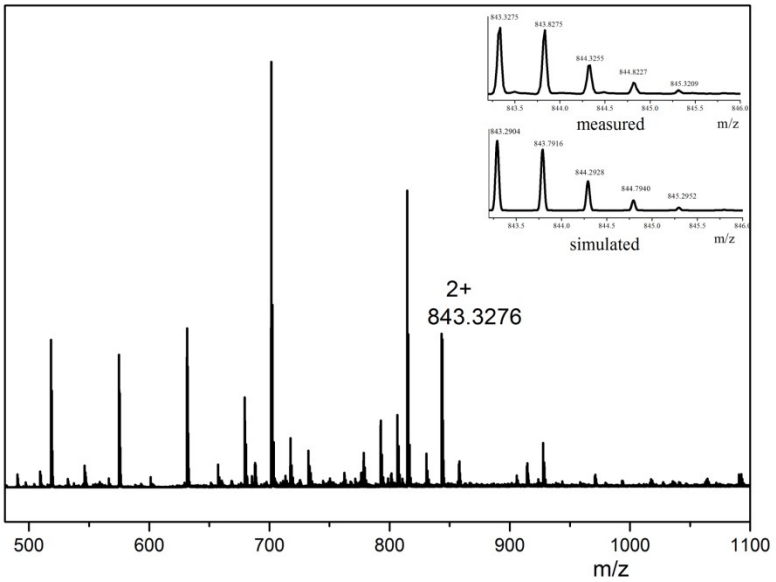


Figure S9. ESI-MS spectrum of **CB[8]** and **MC** in H_2O. Expansions confirm the expect m/z spacing of 0.5 for the 2^+ ion.

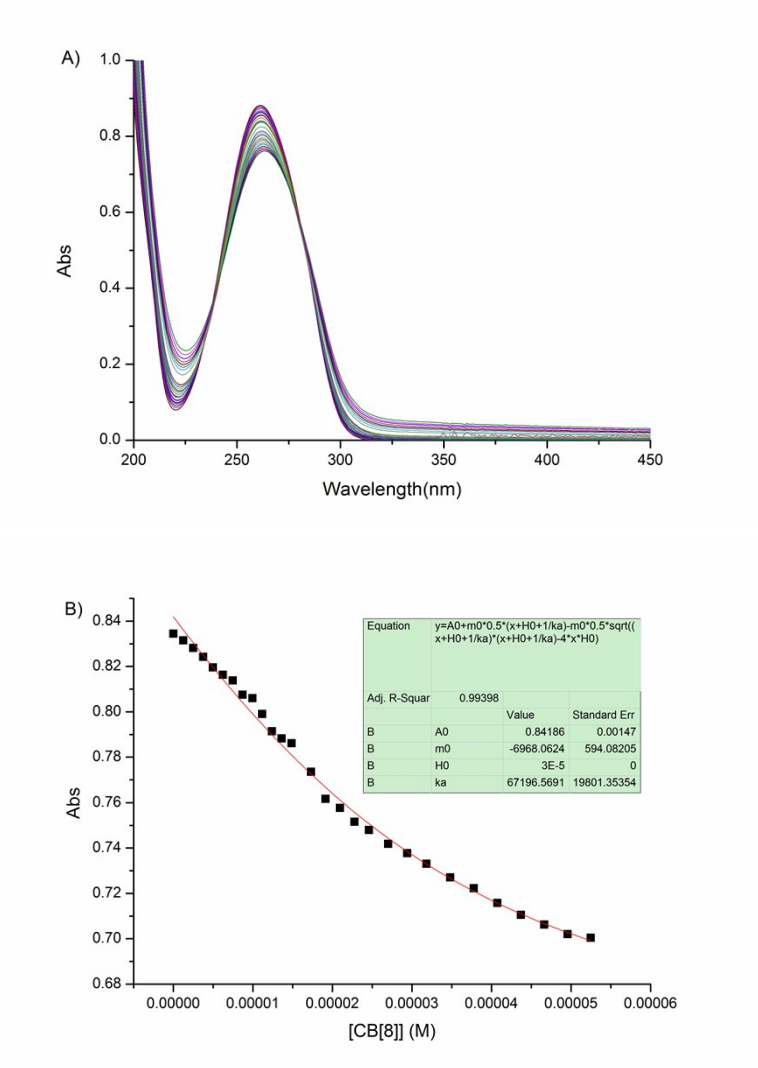


Figure S10.a. UV-vis titration absorption spectra of CB[8] and **MC**; b) Non-linear fitting curve of the intensity of absorbance changes of **MC** versus the concentration of CB[8].

Theassociation constant Ka was calculated according to the following equation:
$Abs = (Abs_{max}/[G]_0)(0.5[H] + 0.5([G]_0 + 1/K_a) - (0.5([H]^2 + (2[H](1/K_a - [G]_0)) + (1/Ka + [G]_0)^2)^{0.5}))$

Where Abs is the intensity of absorbance of **MC** upon titration, Abs_{max} is the intensity of absorbance of **MC**, $[G]_0$ is the fixed concentration of **MC** (0.00003 M), [H] is the concentration of added CB[8] (0.0015 M). Based on the above equation, the association constant (K_a) of CB[8]·**MC** was calculated to be $(6.7 \pm 1.9) \times 10^4$ M^{-1}.

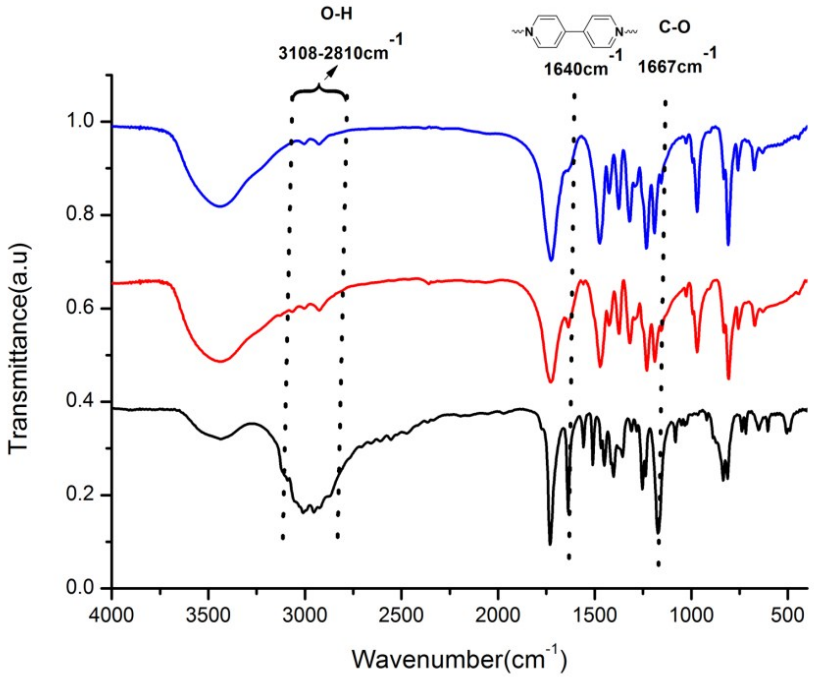


Figure S4. FTIR spectra of **MC** (black), crystal **1** (red) and amorphous of CB[8] (blue) obtained using KBr pellets.

X-ray Crystal Structure Determination.

Data collections for 1 was performed on a Bruker SMART APEX II diffractometer at 153 K with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). SADABS[5] absorption correction was applied for the data. The structure was solved by direct methods using SHELXS-2014,while the refinements were done by the use of the SHELXL-2014 program.[6]

A mixture of CB[8] (66 mg, 0.05 mmol), **MC** (78 mg, 0.15 mmol) and 40 ml H_2O was stirred for 30 seconds. After being filtered, supernate was transferred in tube. The colorless crystal **1** (25 mg, 38% yield) was got by slow evaporation after several days. $C_{96}H_{128}Br_6N_{64}O_{61,}$ M = 3634.08, Orthorhombic, *Pccn*, a = 25.909(5) Å, b = 26.983(5) Å, c=13.028(2) Å, α = 90°, β = 90°, γ = 90°, V = 9108(3) $Å^3$,Z = 2, $\rho_{calcd.}$ = 1.325 $g \cdot cm^{-3}$, final R_1 = 0.1198 and wR_2 = 0.2610 (R_{int}= 0.0463) for 54602 independent reflections [I >2σ(I)]. There are several alert level B induced by some disordered solvent molecules.A severely disordered solvent H_2O with 140 electrons were removed from the asymmetric unit by the SQUEEZE command,[7] which could correspond with the removal of 7.0 molecules of H_2O per formula unit. CCDC 1534775 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request /cif.

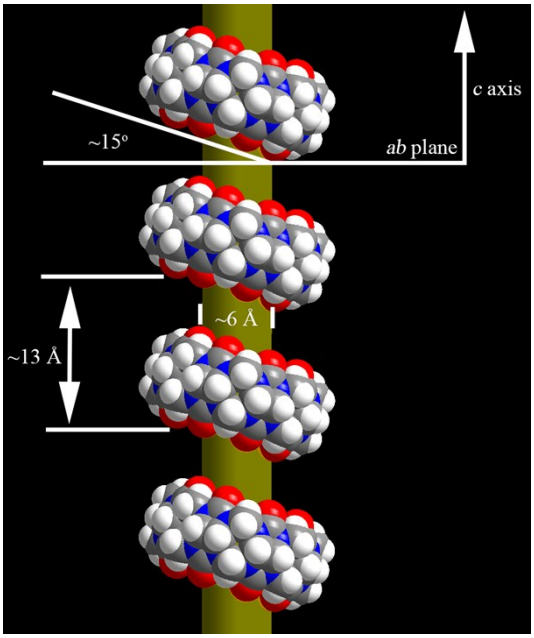


Figure S5. Side view of 1D nanotube in **1**. Color code: N, blue; O, red; C, gray. Water molecules and bromide ions are omitted.

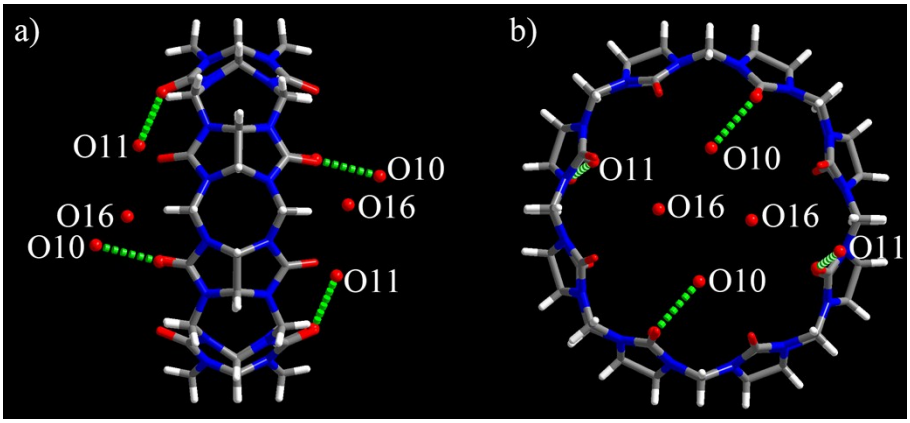


Figure S6. a) Side view and b) top view of CB[8] with isolated waters. Color code: N, blue; O, red; C, gray. H-bonds, green dotted line. Water molecules and bromide ions are omitted.

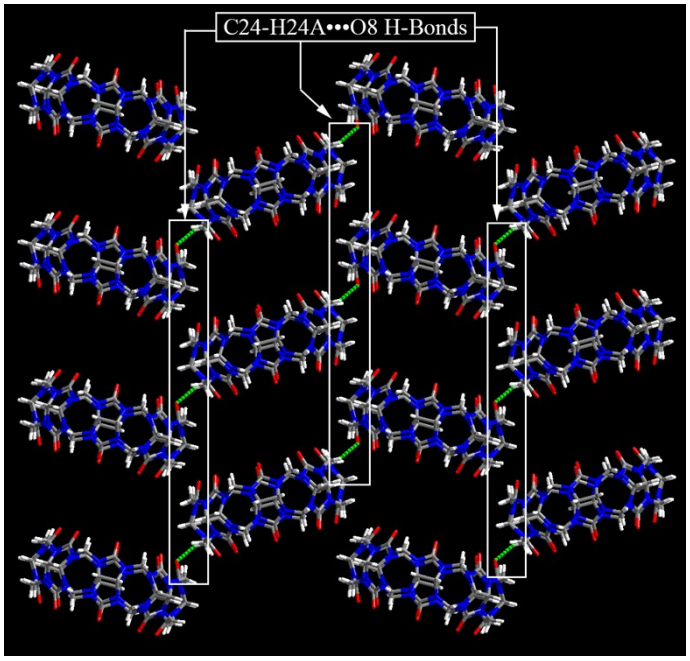


Figure S7. A 2D nanotubular layer formed by 1D nanotubes through non-classical hydrogen bonds. Color code: N, blue; O, red; C, gray. H-bonds, green dotted line. Water molecules and bromide ions are omitted.

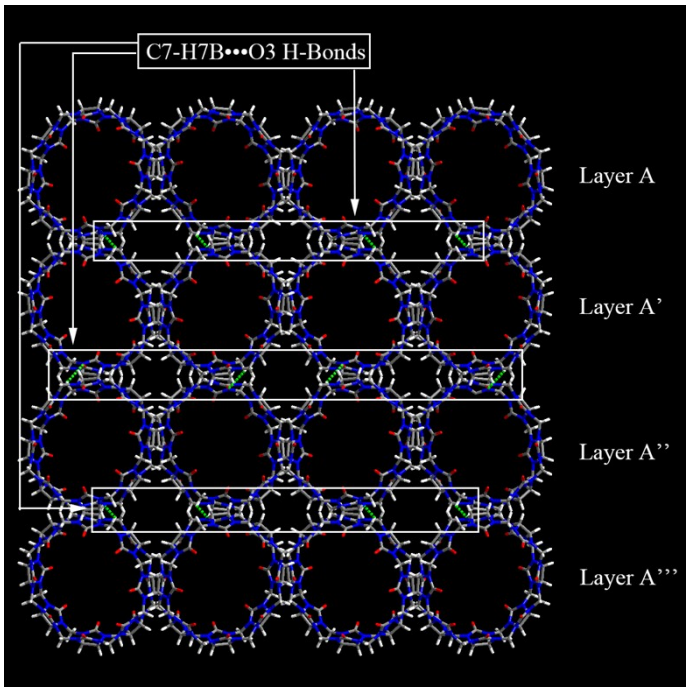


Figure S8. 2D nanotubular layers linked by through non-classical hydrogen bonds. Color code: N, blue; O, red; C, gray. H-bonds, green dotted line. Water molecules and bromide ions are omitted.

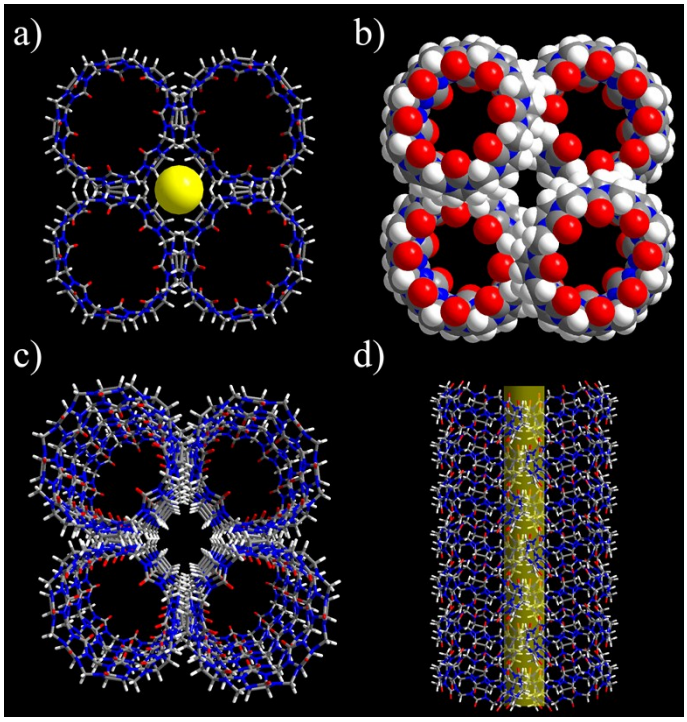


Figure S9. a) Top view, b) space-filling view, c) perspective view, and d) side view of 1D extrinsic nanochannel formed by the outer-surfaces of CB[8]. Color code: N, blue; O, red; C, gray. Water molecules and bromide ions are omitted.

Table S1. Parameters from O•••O hydrogen bonds observed in **1**.

Interactions	Distance (Å)	Interactions	Distance (Å)
O6•••O9	2.88	O15•••O14	2.66
O9•••O12	2.91	O14•••O13	2.76
O12•••O5	2.82	O13•••O1	2.90
O12•••O15	2.94	O13•••O2	3.03
O15•••O4	2.98	O7•••O11	2.76
O4•••O10	2.88		

Table S2. Parameters from C–H•••O H-bonds observed in **1**.

Interactions	**H…O (Å)**	**C…O (Å)**	**∠C–H…O (º)**
C24–H24A•••O8	2.54	3.07	113.8
C7–H7B•••O3	2.60	3.10	111.3

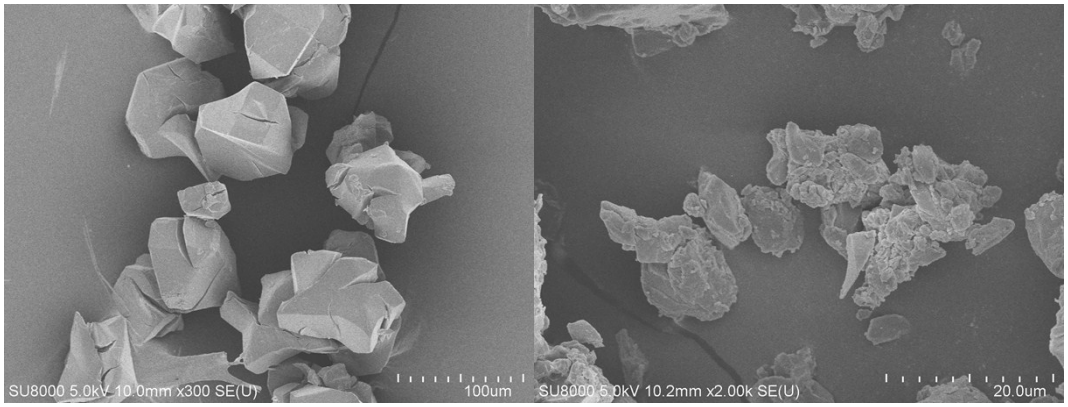


Figure S10. SEM images of **1** (left) and amorphous CB[8] (right).

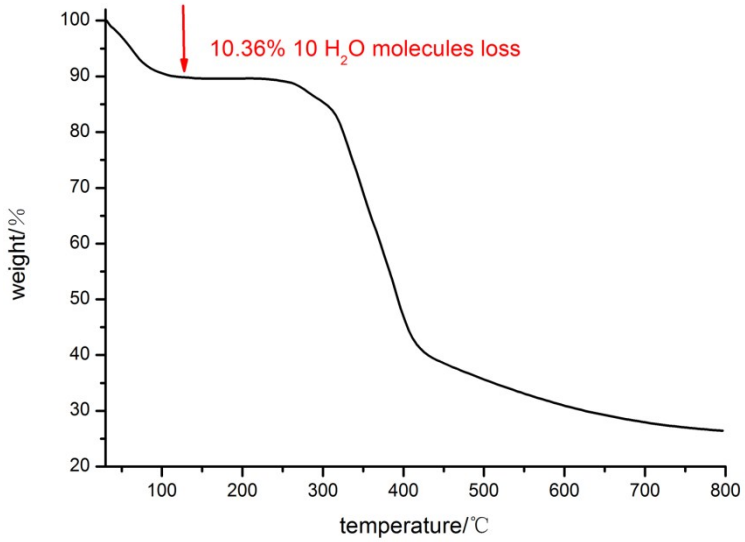


Figure S11. Thermal gravimetric analysis (TGA) curve for the crystal of **1**.

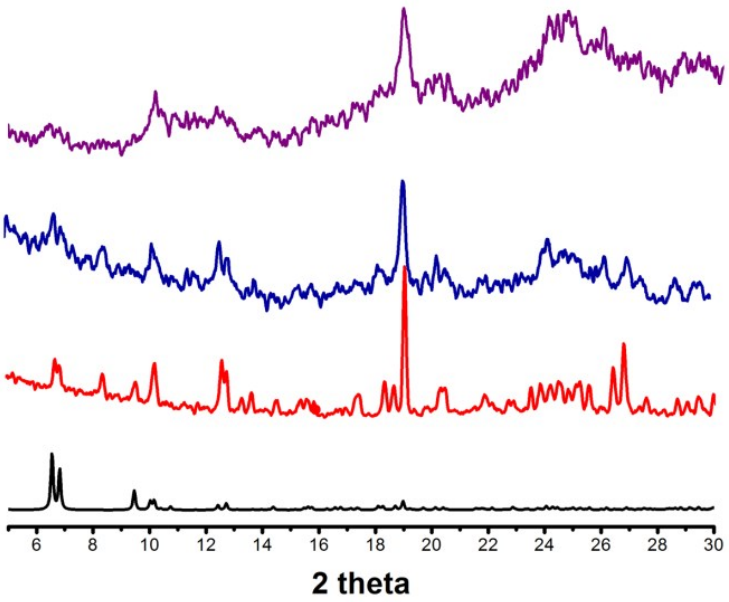


Figure S12. X-ray powder diffraction patterns of simulated (black), synthesized (red) , activated (blue), after adsorbed (violet) **1**.

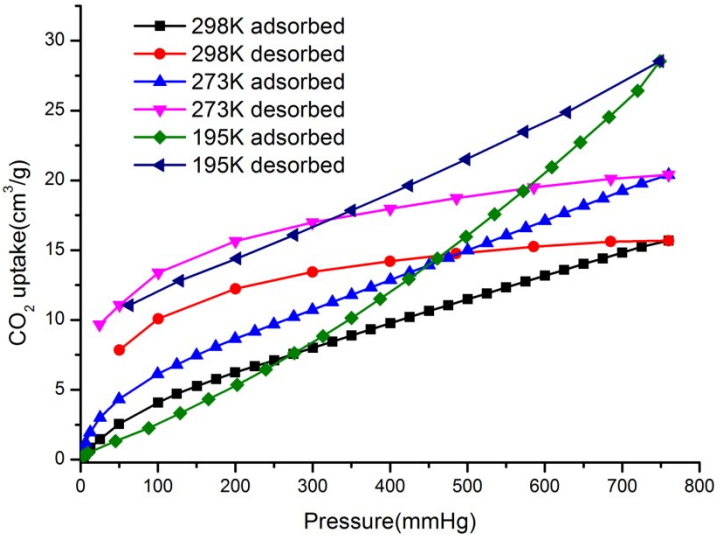


Figure S13. CO_2 adsorption and desorption isotherm of **1** at 195, 273 and 298 K.

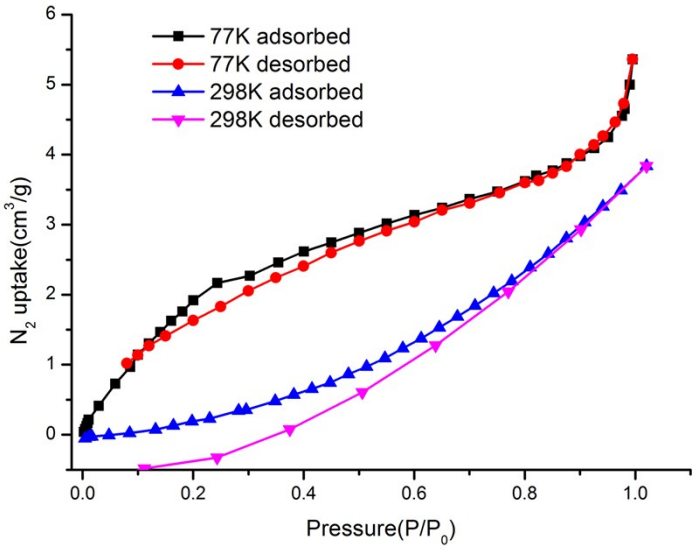


Figure S14. N_2 adsorption and desorption isotherm of **1** at 77 and 298 K.

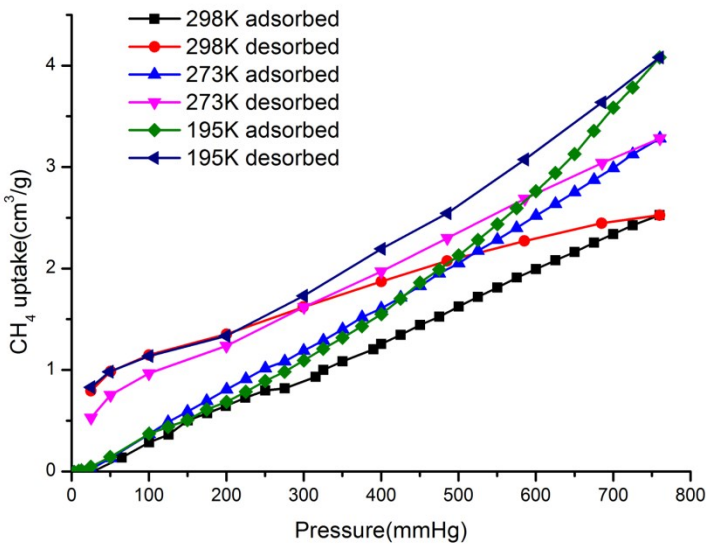


Figure S15. CH_4 adsorption and desorption isotherm of **1** at 195, 273 and 298 K.

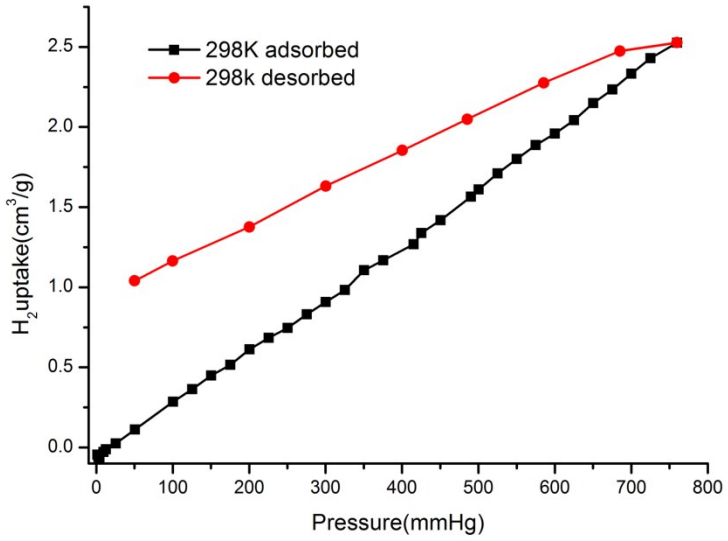


Figure S16. H_2 adsorption and desorption isotherm of **1** at 298K.

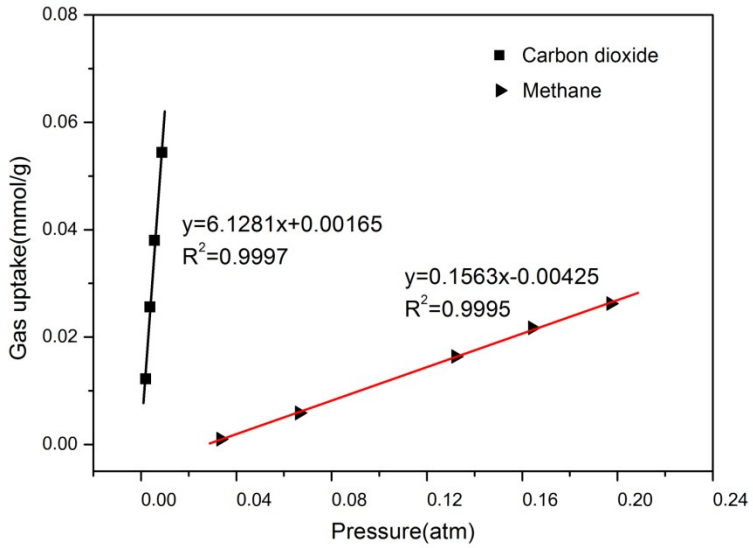


Figure S17. Initial slope calculation for CO_2 and CH_4 isotherms collected at 273K (CO_2: black squares; CH_4: red triangles).

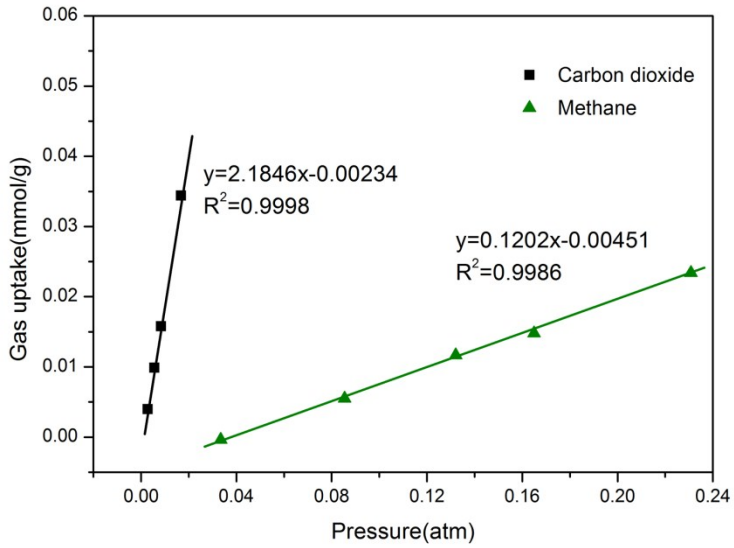


Figure S18. Initial slope calculation for CO_2 and CH_4 isotherms collected at 298K (CO_2: black squares; CH_4: green triangles).

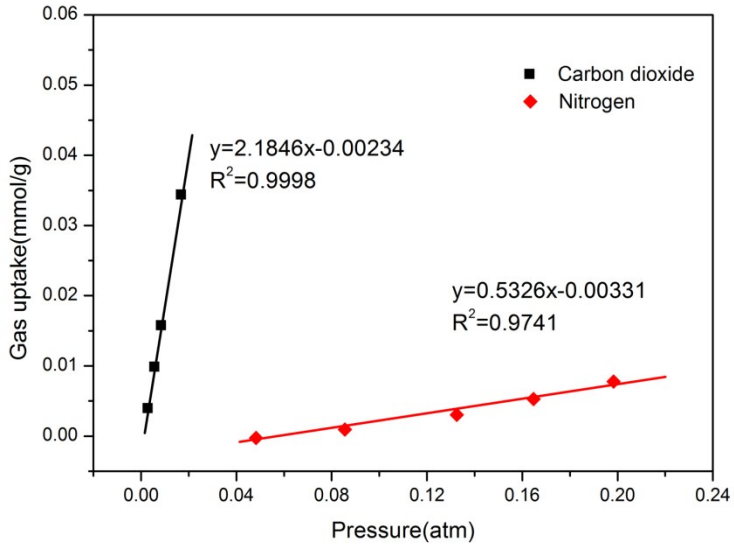


Figure S19. Initial slope calculation for CO_2 and N_2 isotherms collected at 298K (CO_2: black squares; N_2: red squares).

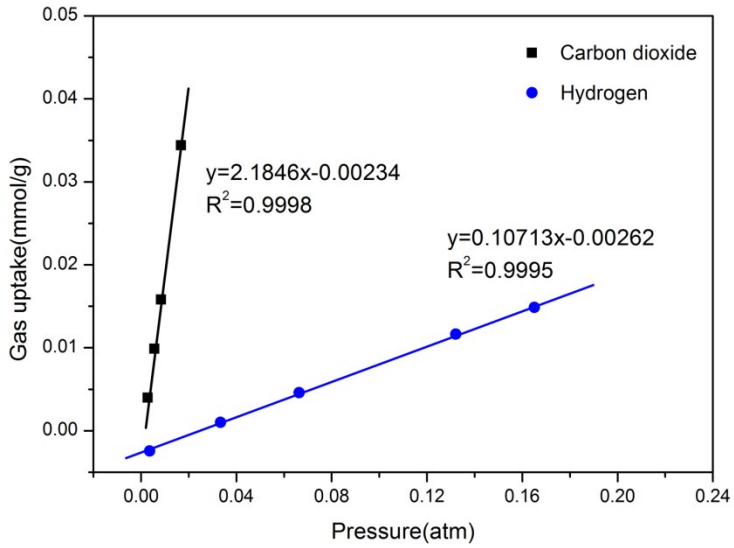


Figure S20. Initial slope calculation for CO_2 and H_2 isotherms collected at 298K (CO_2: black squares; H_2: blue circulars).

Table S3. Selective CO_2 uptake for a series of selected macrocycle-based organic molecular porous material.

Material	BET/Langmuir surface area [m^2g^{-1}]	CO_2 sorption capacity [mg g^{-1}] 298K	$-\Delta H$ ads (kJ mol^{-1})	Selectivity[c]		
				CO_2/CH_4	CO_2/H_2	CO_2/N_2
CB[8] (**1**)	34.5[a]/47[b]	28.2	37	18/39[d]	20	41
CB[6][8]	210[a]	96.8	33	14.8	-	-
CB[6](II)[9]	140[a]	136.7	-	-	-	27
CB[7][10] (amorphous)	293[a]	101.2	40	-	-	-
CB[8] (amorphous)	-	5.86	-	-	-	-
P5-SOF[11]	97[a]	88	44	375	-	339
CalixMOM-1[12]	236[b]	~45	40	9	-	-
CalixMOM-2[12]	184[a]/208[b]	~36	33	6	-	-

a) BET surface area; b) Langmuir surface area; c) Data obtained at 298K; d) Data obtained at 273K.

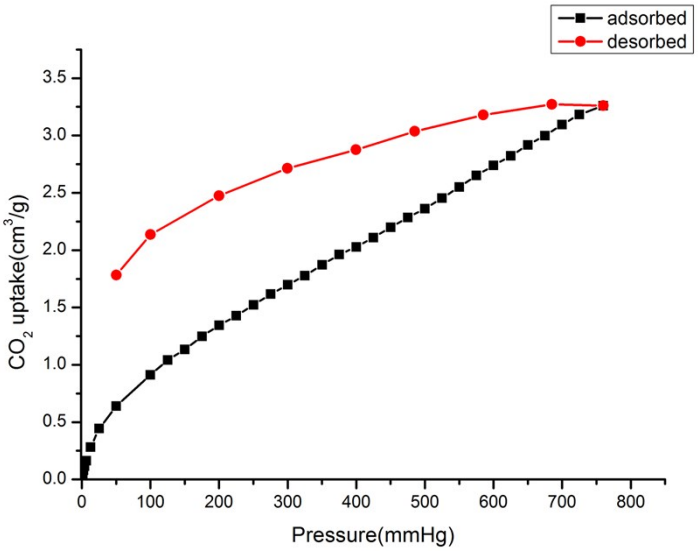


Figure S21. CO_2 adsorption and desorption for amorphous CB[8] at 298K.

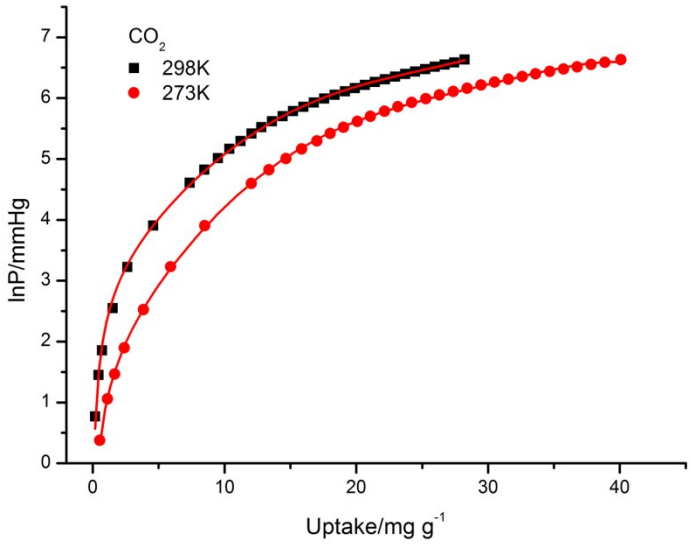


Figure S22. Virial analysis of the CO_2 adsorption data for **1** at 273 and 298 K. Fitting results: a0 = -4489.84, a1 = 170.24, a2 = 1.82, a3 = -0.32, Chi^2 = 0.00166, R^2 = 0.99939.

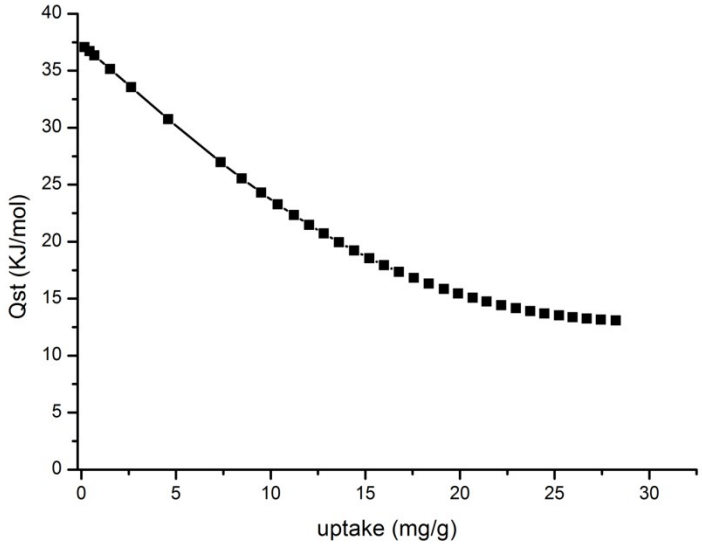


Figure S23. Isosteric heat of CO2 adsorption for **1** estimated by the virial equation from the adsorption isotherms at 273 and 298 K.

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