Supporting Information for *Chemical Communications*

Cucurbit[7]uril: an Amorphous Molecular Material for Highly Selective Carbon Dioxide Uptake

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Experimental procedures:

1. Material synthesis and preparation. Cucurbit[7]uril and cucurbit[6]uril were synthesized according to the classical procedure reported by Day and Co-workers.[1] CB[7] was precipitated by pouring its hot solution of glycerol into methanol, followed by filtration and washing several times with methanol. The obtained solid was dried under vacuum at 150 °C for 48 hrs to remove included solvent molecules. The purity of CB[7] has been checked by ^{1}H NMR and mass spectrometry studies which are identical to the reported values. CB[7] solid is harvested in amorphous state which is confirmed by powder X-ray diffraction and selected area electron diffraction (SAED) studies. CB[6] is obtained in a semi-crystalline state and transformed into amorphous state by grinding.

2. CO_2 sorption isotherms and enthalpy of adsorption for CB[7] solid. Gas sorption isotherms were acquired from activated samples of CB[7] and CB[6] with an Autosorb-IQ (volumetric method) outfitted with the micropore option by Quantachrome Instruments (Boynton Beach, Florida, USA) running version 1.55 of the ASWin software package. CO_2 isotherms were collected at various temperatures (273 K, 297 K and 196 K) in the range 1.00×10^{-4} bar $\leq P \leq$ 1.00 bar using bone dry CO_2. The CO_2 adsorption enthalpy of CB[7] was calculated from the isotherms at 273 K and 297 K using the "heat of sorption" function enclosed in the software. The BET sure area is decided using the isotherm at 196 K.

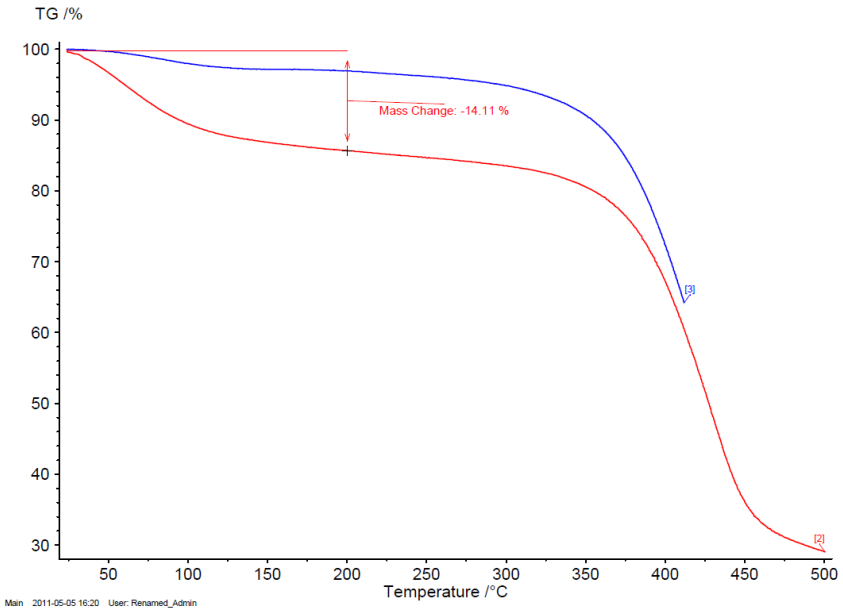

Figure S1. TGA profile of freshly synthesized CB[7] solid (red) and activated CB[7] solid after exposure to air for 24 hrs (blue).

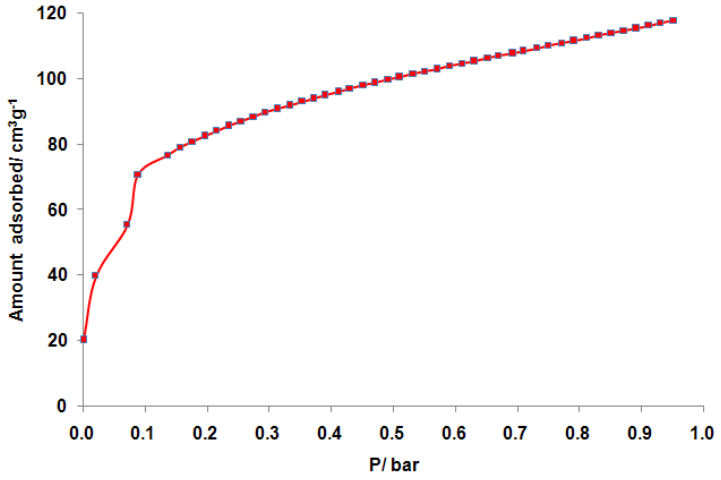

Figure S2. The CO_2 sorption isotherm of CB[7] solid at 196 K.

BET Surface Area Report
BET Surface Area: 293.3418 ±3.0144 m^2/g
Slope: 0.015688 ±0.000157 g/cm^3STP
Y-Intercept: -0.000116 ±0.000031 g/cm^3STP
C: -134.692837
Qm: 64.2143 cm^3/g STP
Correlation Coefficient: 0.9998498
Molecular Cross-Sectional Area: 0.1700 nm^2

Relative Pressure(P/Po)	Quantity Adsorbed(cm3/g STP)	1/[Q(Po/P - 1)]
0.156436232	79.0150	0.002347
0.175717463	80.8105	0.002638
0.196007035	82.6524	0.002950
0.214187911	84.1210	0.003240
0.234287276	85.7287	0.003569

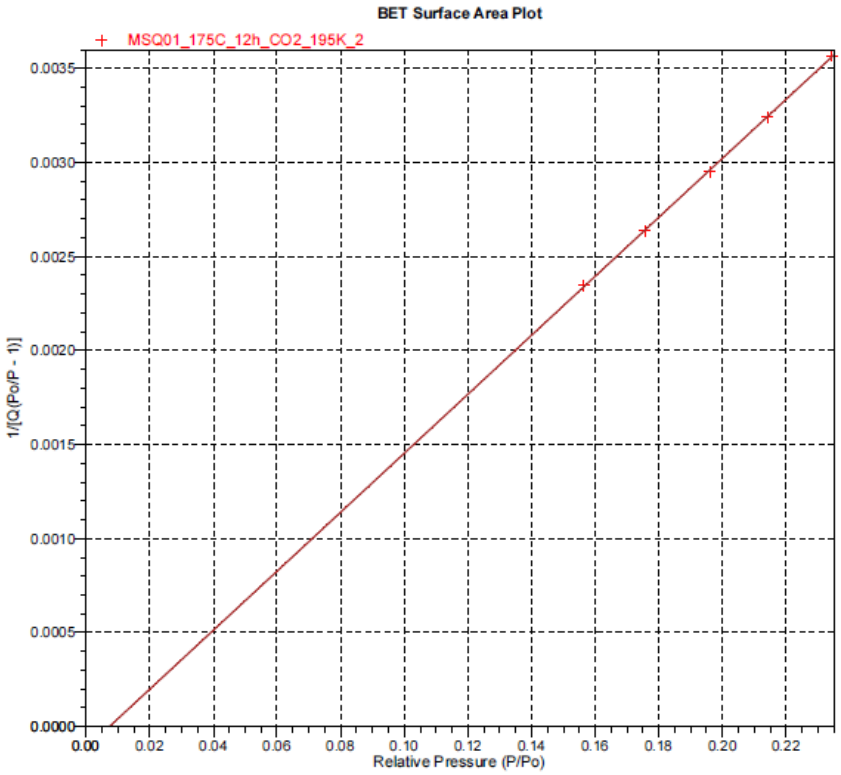

Figure S3. The measurement of multi-point surface area of CB[7] was based on sorption profile at $P/P^o = 0.15$-0.25.

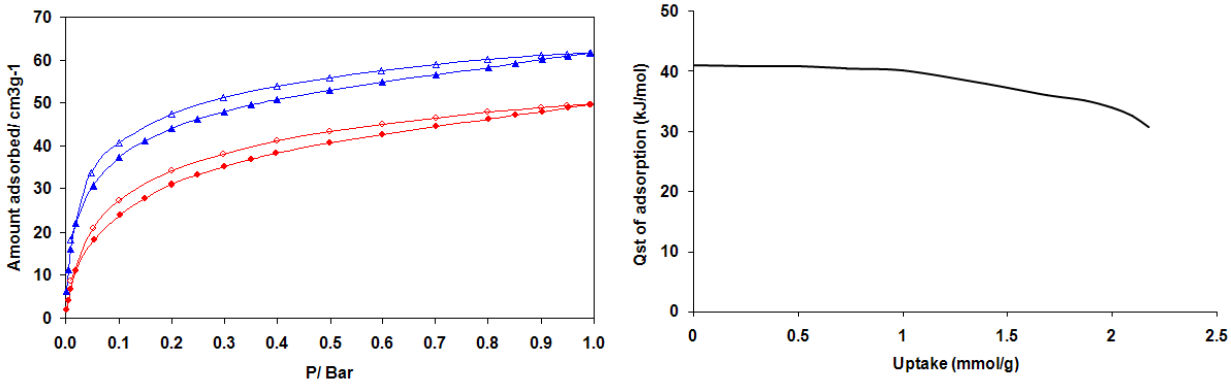

Figure S4. (left) CO_2 sorption isotherms of CB[7] solid at 297 K (red circle) and 273 K (blue triangle). (right) The CO_2 adsorption enthalpy of CB[7] calculated from the isotherms at 273 K and 297 K using the "heat of adsorption" function enclosed in the software.

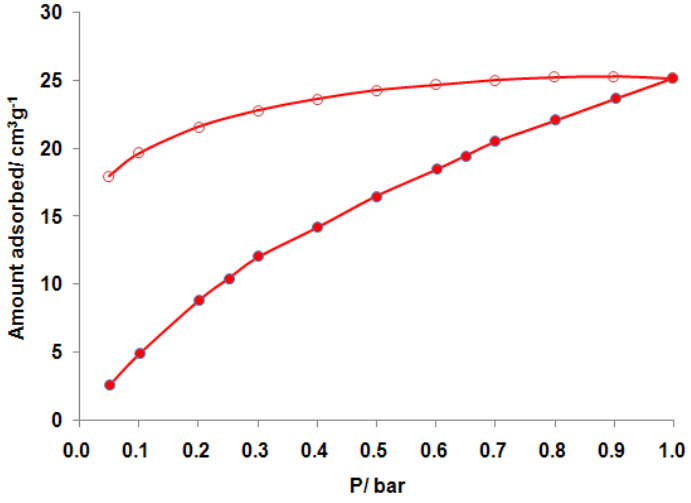

Figure S5. The CO_2 sorption isotherm of amorphous CB[6] solid at 297 K. (filled symbols: adsorption; open symbols: desorption).

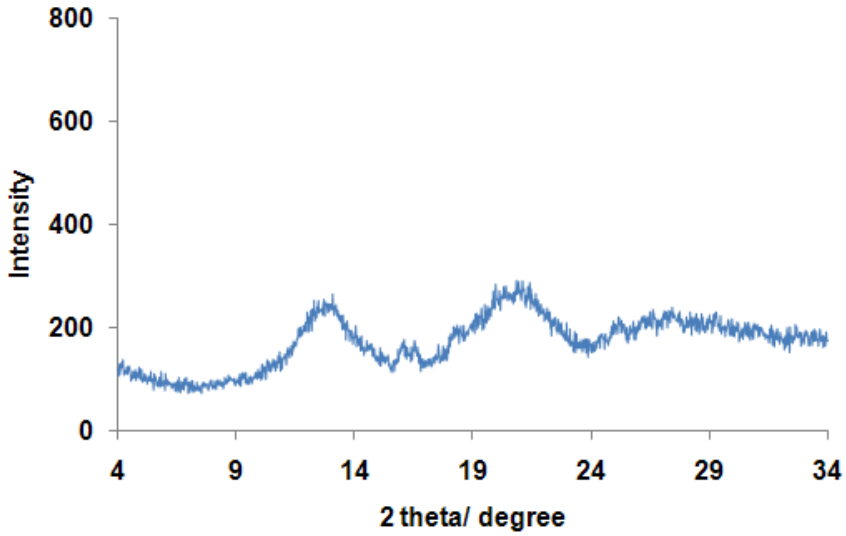

Figure S6. The PXRD pattern of activated CB[7] solid shows two broad peaks.

Table S1. CO_2 uptake and enthalpy of adsorption for selected MOFs and organic molecular solids.

Material	BET surface area $[m^2g^{-1}]$	$V_p[cm^3g^{-1}]$	$V(CO_2)$ [mg/g], RT 0. 1 bar	$V(CO_2)$ [mg/g], RT 1 bar	$-\Delta H_{ads}$ (kJ/mol)
CB[7]	293	0.21	48.0	100	40
CB[6](Hexagonal)[2]	210	0.13	32.0	90	33
CC3[3]	624		30.0*	100*	
TPP[4]	240		13	43	
SOF-1a[5]	474	0.23	10.0	32	27.5
MOF-5[6]	3563	1.319	3.5	36.5	15.9
HKUST-1[6]	2134	0.801	27.3	123.5	23.3
Mg-DOBDC[6]	1495		261.6	352	47

Reference:

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* At 273 K.