

**Supporting Information**

**Nanosponges based on self-assembled starfish-shaped cucurbit[6]urils**

**functionalized with imidazolium arms**

Vincenzo Patamia,<sup>a</sup> Davide Gentile,<sup>a</sup> Roberto Fiorenza,<sup>b</sup> Vera Muccilli,<sup>b</sup> Placido G. Mineo,<sup>b</sup> Salvatore Scirè<sup>b</sup>  
and Antonio Rescifina<sup>\*a,c</sup>

<sup>a</sup> *Dipartimento di Scienze del Farmaco e della Salute, Università di Catania, V.le A. Doria, 95125 – Catania, Italy. E-mail: [arescifina@unict.it](mailto:arescifina@unict.it)*

<sup>b</sup> *Dipartimento di Scienze Chimiche, Università di Catania, V.le A. Doria, 95125 – Catania, Italy*

<sup>c</sup> *Consorzio Interuniversitario Nazionale di ricerca in Metodologie e Processi Innovativi di Sintesi (CINMPS), Via E. Orabona, 4, Bari 70125, Italy*

## Table of contents

General information .....	S3
Synthesis of CB[6]-Funct <sub>12</sub> .....	S3
Synthesis of phenylpropionic acid .....	S4
<b>Table S1</b> Optimization of the reaction conditions for the carboxylation of phenylacetylene .....	S4
<b>Figure S1.</b> <sup>1</sup> H NMR spectrum of CB[6]-Funct <sub>12</sub> .....	S5
<b>Figure S2.</b> <sup>13</sup> C NMR spectrum of CB[6]-Funct <sub>12</sub> .....	S5
<b>Figure S3.</b> FTIR spectra of CB[6] (left) and CB[6]-Funct <sub>12</sub> (right) .....	S6
<b>Figure S4.</b> Enlarged FTIR spectra of CB[6] (black line) and CB[6]-Funct <sub>12</sub> (red line).....	S6
<b>Figure S5.</b> FTIR spectra of CB[6] (black line), CB[6]-(OH) <sub>12</sub> (red line) and CB[6]-Funct <sub>12</sub> after the CO <sub>2</sub> adsorption .....	S6
<b>Figure S6.</b> Full scan ESI mass spectrum of a CB[6]-Funct <sub>12</sub> solution.....	S7
<b>Figure S7.</b> TGA (red line, left axis) and DTG (blue line, right axis) of CB[6]-Funct <sub>12</sub> .....	S7
<b>References</b> .....	S7

## General information

All the required chemicals were purchased from Merck and Aldrich Chemical Company. The synthesis of CB[6],<sup>1</sup> CB[6]-OH<sub>12</sub>,<sup>2</sup> and 1-(2-bromoethyl)-3-methyl-1*H*-imidazol-3-ium bromide<sup>3</sup> were carried out as reported in the literature and subsequently characterized by NMR and IR spectroscopy.

Pre-coated aluminium sheets (silica gel 60 F254, Merck) were used for thin-layer chromatography (TLC), and spots were visualized under UV light. Silica gel column chromatography was performed using silica gel 60–120 mesh size. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded, at 300 K, on Varian UNITY Inova using CD<sub>3</sub>OD as a solvent, at 500 MHz for <sup>1</sup>H NMR and 125 MHz for <sup>13</sup>C NMR. <sup>13</sup>C spectra were <sup>1</sup>H-decoupled, and the APT pulse sequence determined multiplicities. Chemical shift ( $\delta$ ) values are given in ppm.

The CO<sub>2</sub> adsorption experiments were carried out in a quartz U-shape reactor, utilizing 150 mg of the investigated sample and a CO<sub>2</sub> (99.999%) flow of 30 mL/min. The CO<sub>2</sub> was detected by a quadrupole mass spectrometer (Sensorlab VG Quadrupoles) following the  $m/z = 44$  signal. The breakthrough curves of CO<sub>2</sub> were determined by measuring the ratio between the concentration of CO<sub>2</sub> after the achievement of saturation in the sample and the initial carbon dioxide concentration (*i.e.*, without the sample). Before the measurements, the materials were pretreated in He flow (50 mL/min) at 150 °C for 2 h to remove eventual impurities from the sample's surface.

FTIR analyses in the 4000–400 cm<sup>-1</sup> region were attained using FTIR System 2000 (Perkin-Elmer, Waltham, MA, USA) and using KBr as media.

The mass spectrometric analysis was performed on an ion trap mass spectrometer equipped with an electrospray ion source ESI (LCQ-DECA, Thermo Fischer Scientific, San Jose, CA, USA). The sample was dissolved in a mixture of CH<sub>3</sub>OH/H<sub>2</sub>O (50:50 v/v) at 1×10<sup>-5</sup> M and infused at 5μL/min. Full scan mass spectrum was acquired in positive ion mode in the  $m/z$  range 200–2000. ESI ion source operated with 220 °C capillary temperature, 25 a.u. sheath gas, +5 kV source voltage, and +26 V capillary voltage. Mass calibration was achieved with a standard mixture of caffeine (Mr 194.1 Da), MRFA peptide (Mr 524.6 Da), and Ultramark (Mr 1621 Da). Data analysis was performed with the Xcalibur v. 1.3 Software.

TGA was performed employing Pyris TGA7 (Perkin Elmer, Waltham, US) in the temperature range between 50 and 950 °C, under air N<sub>2</sub> (60 mL/min) and heating rate of 10 °C/min.

The N<sub>2</sub> adsorption-desorption measurements were performed utilizing a Sorptomatic series 1990 instrument. The samples were pretreated with an outgassing step at 150 °C for 12 h. The surface area was calculated with the BET (Brunauer-Emmett-Teller) method, whereas the pore size distribution with the BJH (Barrett, Joyner, and Halenda) method.

## Synthesis of CB[6]-Funct<sub>12</sub>

To a solution of NaH (306 mg, 7.657 mmol, 13 eq, 60% dispersion in mineral oil) in anhydrous DMSO (17 mL) was added CB[6]-(OH)<sub>12</sub><sup>2</sup> (700 mg, 0.589 mmol, 1 eq) at 0 °C and stirred at r.t. for 1 h. 1-(2-bromoethyl)-3-

methyl-1*H*-imidazol-3-ium bromide (2.23 g, 8.246 mmol, 14 eq.) was added to this reaction mixture and stirred for 12 h. The reaction mixture was poured into chloroform (150 mL), resulting in a pale-yellow solid precipitate that was collected by filtration, washed with chloroform, and finally dried in the oven at 60 °C to give the CB[6]-Funct<sub>12</sub> (770 mg, 38%). <sup>1</sup>H NMR (500 MHz, Methanol-*d*): δ = 3.88 (24 H, t, *J* = 5.9 Hz), 3.98 (36 H, s, *N*-Me), 4.68 (24 H, t, *J* = 5.9 Hz), 4.73 (12 H, d, *J* = 15.3), 5.52 (12 H, d, *J* = 15.3), 7.62 (12 H, d, *J* = 2.0 Hz), 7.67 (12 H, d, *J* = 2.0 Hz), 9.10 (12 H, s); <sup>13</sup>C NMR (125 MHz, Methanol-*d*): δ = 36.95, 49.99, 52.08, 66.57, 109.90, 123.76, 125.59, 137.51, 154.80.

### Synthesis of phenylpropionic acid (optimized procedure)

Into a pressure tube containing CB[6]-Funct<sub>12</sub> (715 mg, 0.206 mmol, 1.0 eq), phenylacetylene (21.0 mg, 0.206 mmol, 1.0 eq), Cs<sub>2</sub>CO<sub>3</sub> (100.7 mg, 0.309 mmol, 1.5 eq), and DMF (2 mL), gaseous CO<sub>2</sub> was blown for half an hour. Subsequently, the tube was sealed and the mixture was heated at 80 °C for 12 h. After this time, the mixture was processed as reported in the literature,<sup>4</sup> obtaining the phenylpropionic acid in 93% yield, based on phenylacetylene.

**Table S1** Optimization of the reaction conditions for the carboxylation of phenylacetylene<sup>a</sup>

Entry	Solvent	CB[6]-Funct <sub>12</sub> (eq.)	Adsorbed CO <sub>2</sub> (eq.) <sup>b</sup>	Temp (°C)	Isolated yield (%)
1	DMF	0.2	1.30	80	23
2	DMF	0.5	3.25	80	57
3	DMF	0.8	5.20	80	76
4	DMF	1.0	6.50	80	81
5	DMF	1.0	6.50 <sup>c</sup>	80	89
6	DMF	1.0	6.50 <sup>c</sup>	50	34
7	DMF	1.0	6.50 <sup>c</sup>	100	83
8	DMF	—	6.50 <sup>c</sup>	80	—
9	DMF	Only 1.0 of BEA	6.50 <sup>c</sup>	80	—
10	DMSO	1.0	6.50 <sup>c</sup>	80	81
11	ACN	1.0	6.50 <sup>c</sup>	80	79

<sup>a</sup> In all the cases were used 1.0 eq. of phenylacetylene, 1.5 eq. of cesium carbonate, 2 mL of solvent, and a reaction time of 12 h. <sup>b</sup> Based on the amount adsorbed by the 150 mg of CB[6]-Funct<sub>12</sub> sample (Fig. 3, 82.5 mg/g); the excess of CO<sub>2</sub> was removed, with the exception of entries 5–9. <sup>c</sup> Under CO<sub>2</sub> atmosphere.

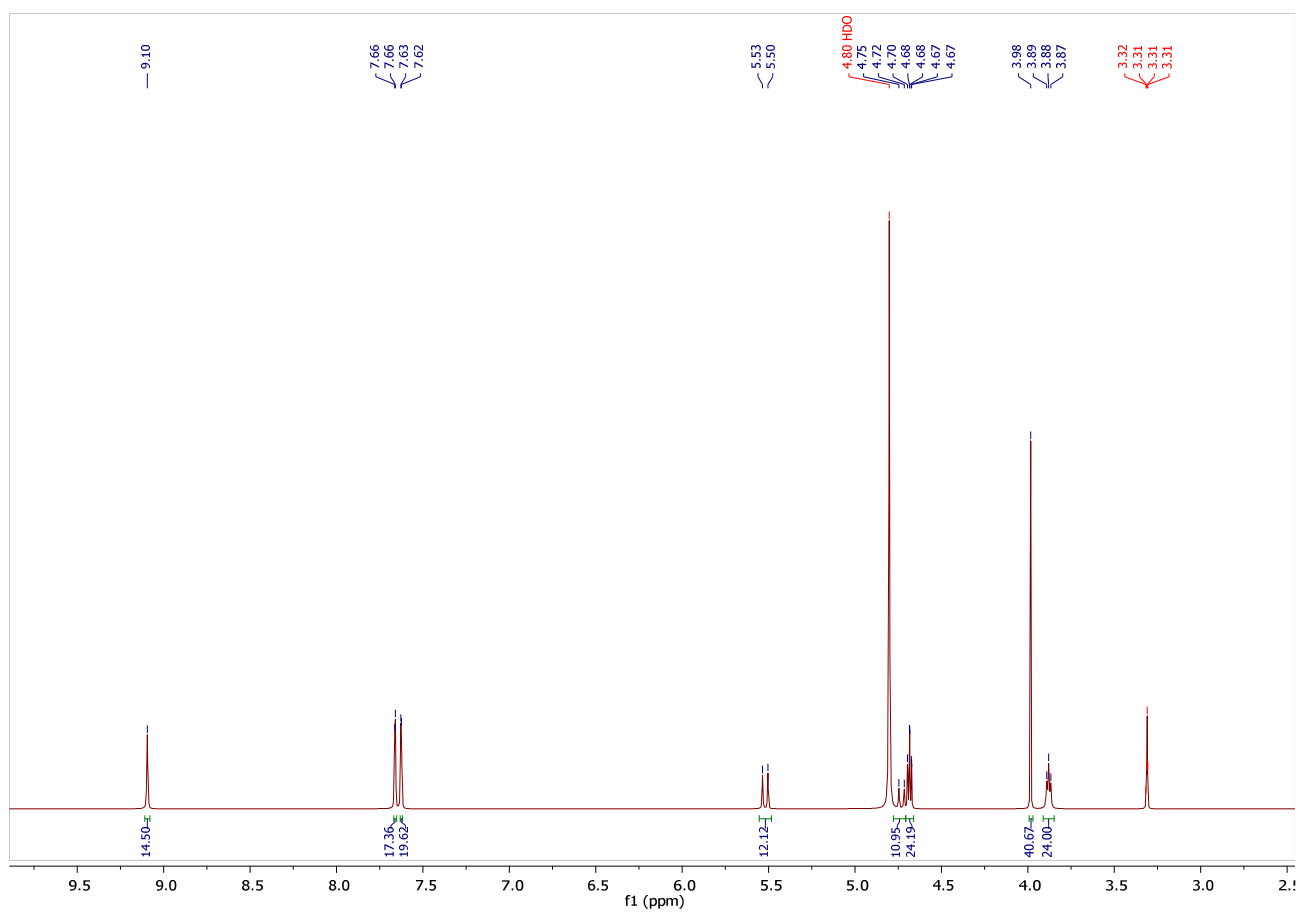


Figure S1. <sup>1</sup>H NMR spectrum of CB[6]-Funct<sub>12</sub>.

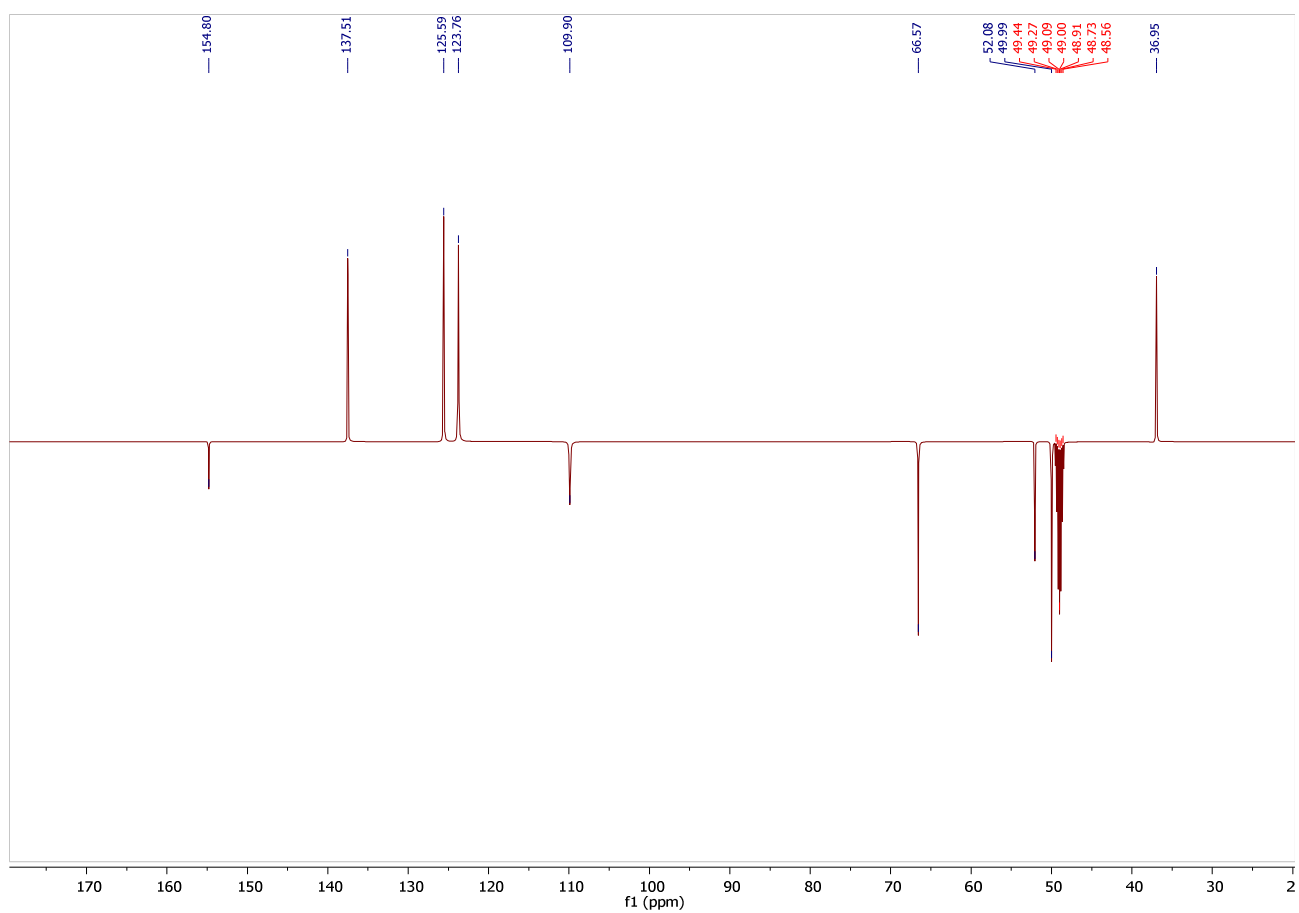
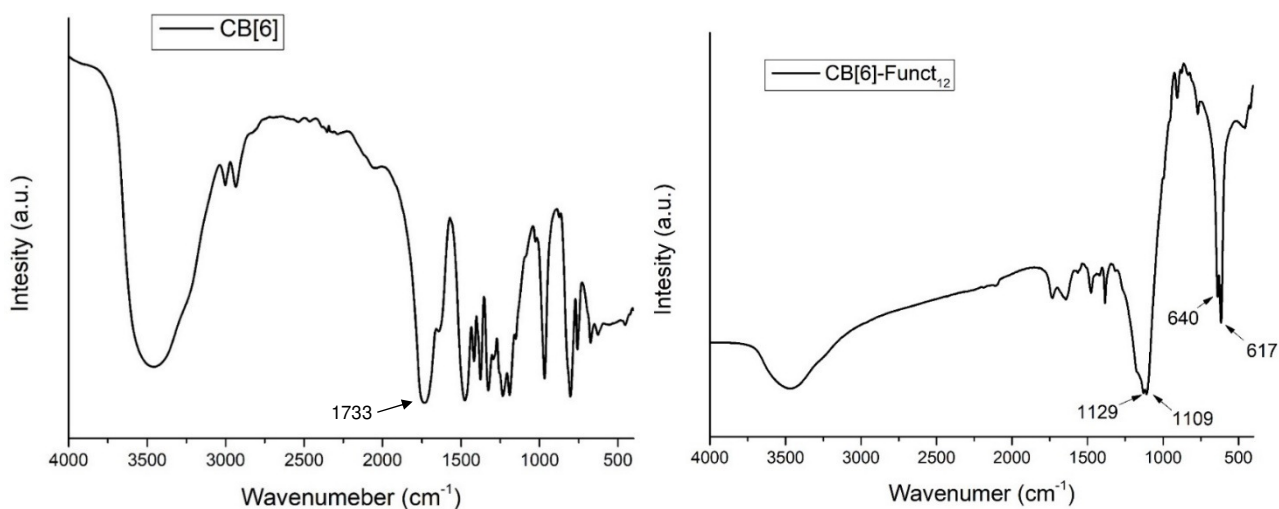
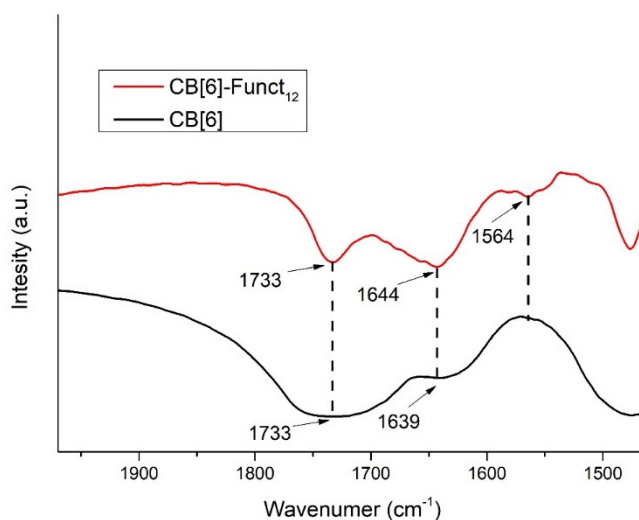


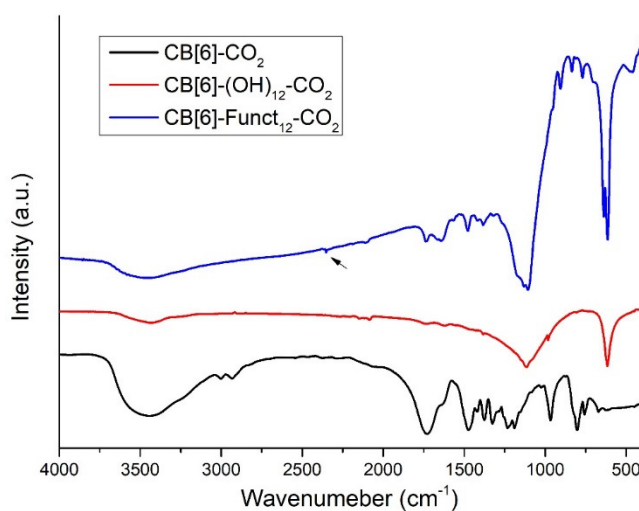
Figure S2. <sup>13</sup>C NMR spectrum of CB[6]-Funct<sub>12</sub>.



**Figure S3.** FTIR spectra of CB[6] (left) and CB[6]-Funct<sub>12</sub> (right). On the left, it is possible to see the typical vibrations of the carbonyl groups at 1733 cm<sup>-1</sup>, as previously reported in the literature.<sup>5</sup> On the right, it is possible to see the presence of the characteristics C–O–C stretching<sup>6</sup> at 1109 cm<sup>-1</sup> and 1129 cm<sup>-1</sup>, Me–N bending at 617 cm<sup>-1</sup>, and H–C=C bending at 640 cm<sup>-1</sup>.<sup>7</sup>

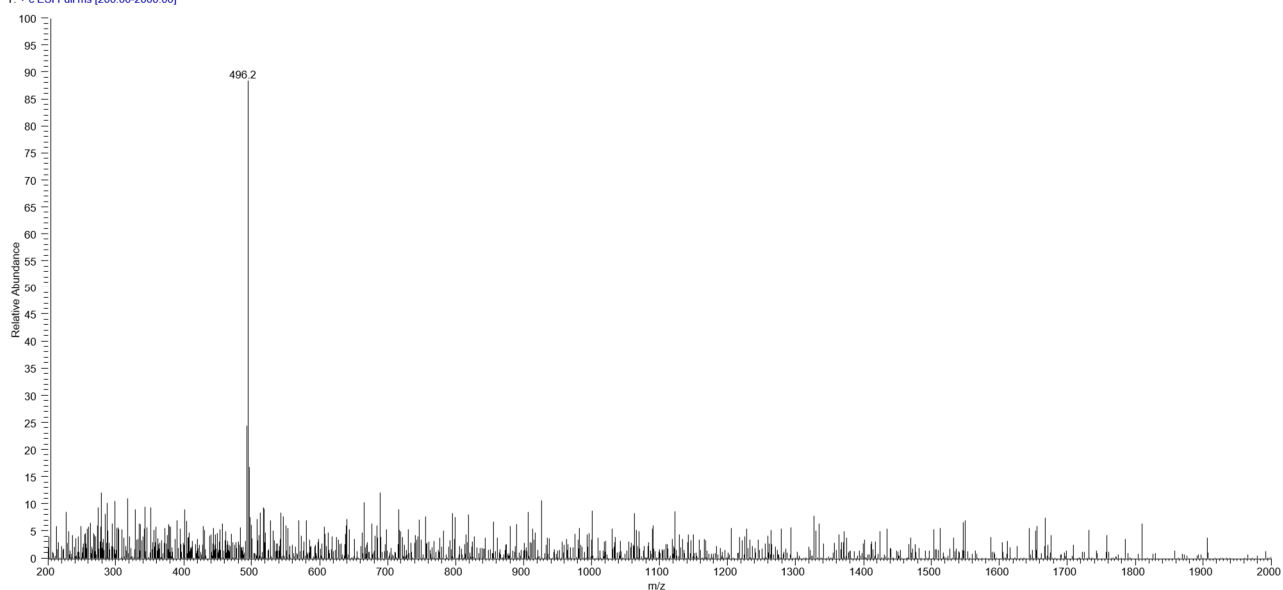


**Figure S4.** Enlarged FTIR spectra of CB[6] (black line) and CB[6]-Funct<sub>12</sub> (red line).

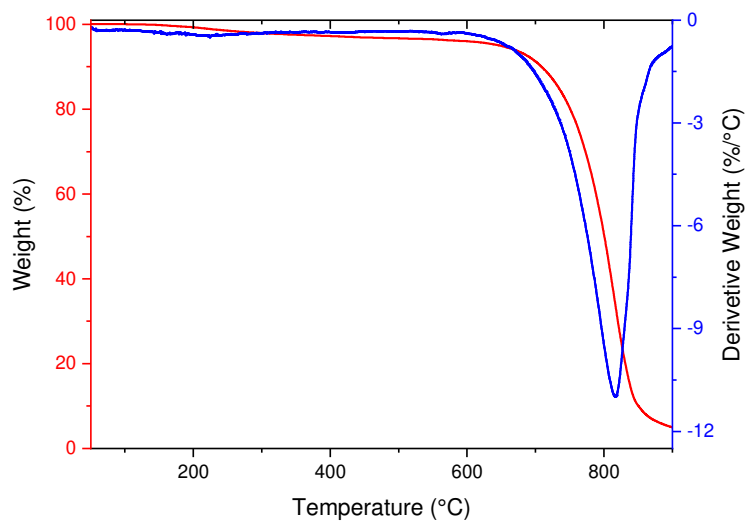


**Figure S5.** FTIR spectra of CB[6] (black line), CB[6]-(OH)<sub>12</sub> (red line) and CB[6]-Funct<sub>12</sub> after the CO<sub>2</sub> adsorption.

sample-1 #33 RT: 2.04-2.40 AV: 10 NL: 1.11\*6  
T: + c ESI Full ms [200.00-2000.00]



**Figure S6.** Full scan ESI mass spectrum of a CB[6]-Funct<sub>12</sub> solution. The spectrum shows a signal at  $m/z$  496.2, with  $z = 6$ . This  $m/z$  value corresponds to the average molecular mass of the multi charged ion of CB[6]-Funct<sub>12</sub> minus six bromides as originated during ESI ionization (calcd for  $[C_{108}H_{144}N_{48}O_{24}Br_6]^{6+}$ , 496.3).



**Figure S7.** TGA thermogram (red line, left axis) and DTG (blue line, right axis) of CB[6]-Funct<sub>12</sub>.

## References

1. A. Day, A. P. Arnold, R. J. Blanch and B. Snushall, *J Org Chem*, 2001, **66**, 8094-8100.
2. S. Y. Jon, N. Selvapalam, D. H. Oh, J. K. Kang, S. Y. Kim, Y. J. Jeon, J. W. Lee and K. Kim, *J Am Chem Soc*, 2003, **125**, 10186-10187.
3. J. Sun, J. Q. Wang, W. G. Cheng, J. X. Zhang, X. H. Li, S. J. Zhang and Y. B. She, *Green Chem*, 2012, **14**, 654-660.

4. S. Ghosh, A. Ghosh, S. Riyajuddin, S. Sarkar, A. H. Chowdhury, K. Ghosh and S. M. Islam, *Chemcatchem*, 2020, **12**, 1055-1067.
5. D. Meng, H. L. Liang, Q. D. Chen and X. H. Shen, *Chinese Chem Lett*, 2018, **29**, 447-450.
6. J. P. Coates, *Appl Spectrosc Rev*, 1996, **31**, 179-192.
7. S. A. Katsyuba, P. J. Dyson, E. E. Vandyukova, A. V. Chernova and A. Vidis, *Helv Chim Acta*, 2004, **87**, 2556-2565.