

## “Clickable” SBA-15 Mesoporous Materials: Synthesis, Characterization and their reaction with alkynes

Bharmana Malvi<sup>1</sup>, Bibhas R. Sarkar<sup>1</sup>, Debasis Pati<sup>1</sup>, Renny Mathew<sup>2</sup>, T. G. Ajithkumar<sup>2</sup>,  
and Sayam Sen Gupta<sup>1\*</sup>

<sup>1</sup>CREST, Chemical Engineering Division and <sup>2</sup>Central NMR Facility, National Chemical  
Laboratory, Dr. Homi Bhabha Road, Pune 411008.

### Supporting Information

#### Synthesis

##### *Synthesis of methyl ester of pentynoic acid*

To a solution of 4-pentynoic acid (0.2 g, 2.04 mmol) in dry methanol (3 mL) was added p-toluenesulphonic acid (40 mg, 0.023 mmol) under nitrogen atmosphere. The reaction mixture was stirred under reflux for 6-7 h. After cooling, 15 mL of water was added and pH of the resulting mixture was brought to 10 by adding sodium bicarbonate solution. Then, it was extracted with three portions of 20 mL of ethyl acetate. The ethyl acetate layer was washed with water and brine solution respectively and then dried over anhydrous sodium sulphate. Finally, solvent was removed under reduced pressure to yield a colorless liquid. Yield: 205 mg, 90%

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 3.67 (s, 3H), 2.562-2.44 (m, 4H) and 1.97 (t, J=2.5Hz, 1H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 172.1, 82.4, 68.9, 51.7, 33.1, and 14.2.

##### *Synthesis of α-D-propargyl mannopyranoside*

α-D-propargyl mannopyranoside was synthesized by a procedure described before. A mixture of D-mannose(1) (1g, 5.56mmol) and propargyl alcohol (1.56ml, 27.80mmol) was taken in a two-necked round bottom flask and kept under nitrogen atmosphere. H<sub>2</sub>SO<sub>4</sub>-Silica was added from the side and the mixture was continuously stirred for 5 hours while maintaining a temperature of 65°C. α-D-propargyl mannopyranoside was finally purified by column chromatography (silica gel, eluent 95:5 EtOAc:MeOH). Yield: 0.864 g, 71%

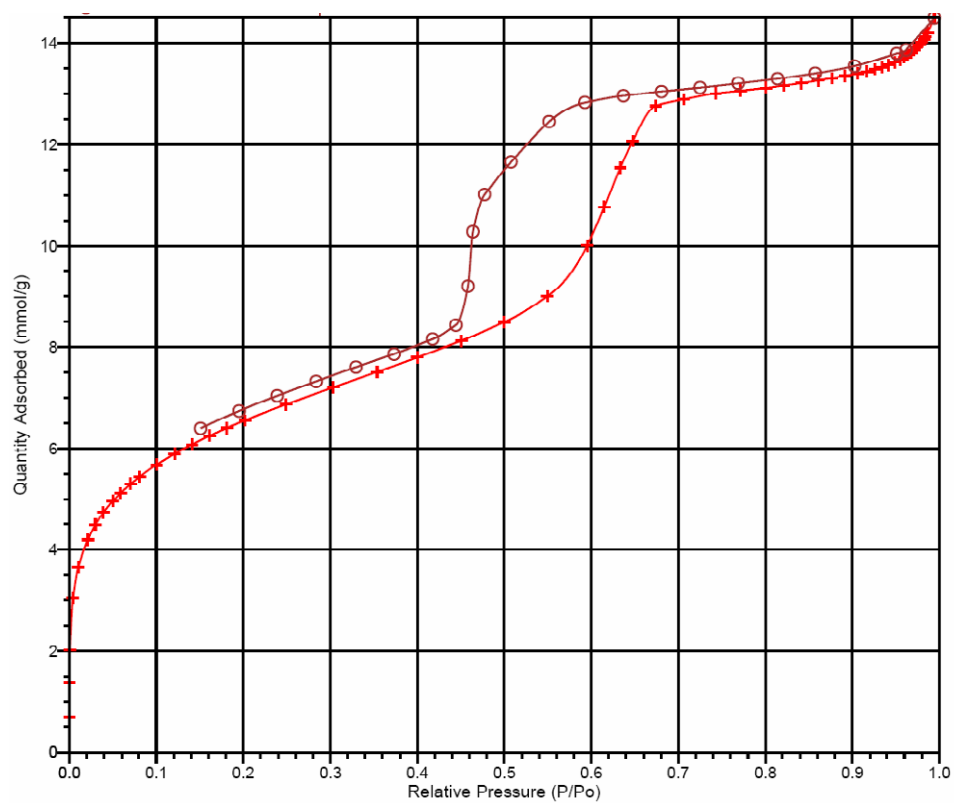
The  $\alpha$ -D-propargyl mannopyranoside was characterized as its  $\alpha$ -D-tetra-O-acetyl-propargyl mannopyranoside derivative.  $\alpha$ -D-propargyl mannopyranoside (0.10g, 0.5mmol) and pyridine (0.34ml, 4.14mmol) was stirred in a two-neck round bottom flask at 0-5°C. Acetic-anhydride (0.2ml, 2.07mmol) was then slowly added and the reaction mixture was stirred at 0-5 °C for 15-20 min. Finally catalytic amount of 4-dimethylaminopyridine (5-10mg) was added and the reaction was allowed to proceed for 10-12 hours. The reaction mixture was diluted with 15-20 mL of ethyl acetate and sequentially washed with 1(N) HCl, saturated NaHCO<sub>3</sub> solution, water and finally by brine solution. The ethyl acetate layer was dried using anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure to yield a white solid which was further purified by column-chromatography (eluent, light petroleum ether and ethyl acetate, 4:1) to yield pure  $\alpha$ -D-tetra-O-acetyl-propargyl mannopyranoside. Yield = 0.141 g, 80%

$[\alpha]_D^{+38}$  (C=1.6, CHCl<sub>3</sub>); <sup>1</sup>H NMR(200 MHz, TMS in CDCl<sub>3</sub>): $\delta$  5.35-5.25 (m, 3H), 5.04(d,  $J$  =1.4Hz, 1H), 4.35-4.26 (m, 3H), 4.11 (dd,  $J$  =12.3 Hz, 1H), 4.06-3.99 (m, 1H), 2.48 (t,  $J$  =2.5 Hz, 1H), 2.17 (s, 3H), 2.12 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H) ppm

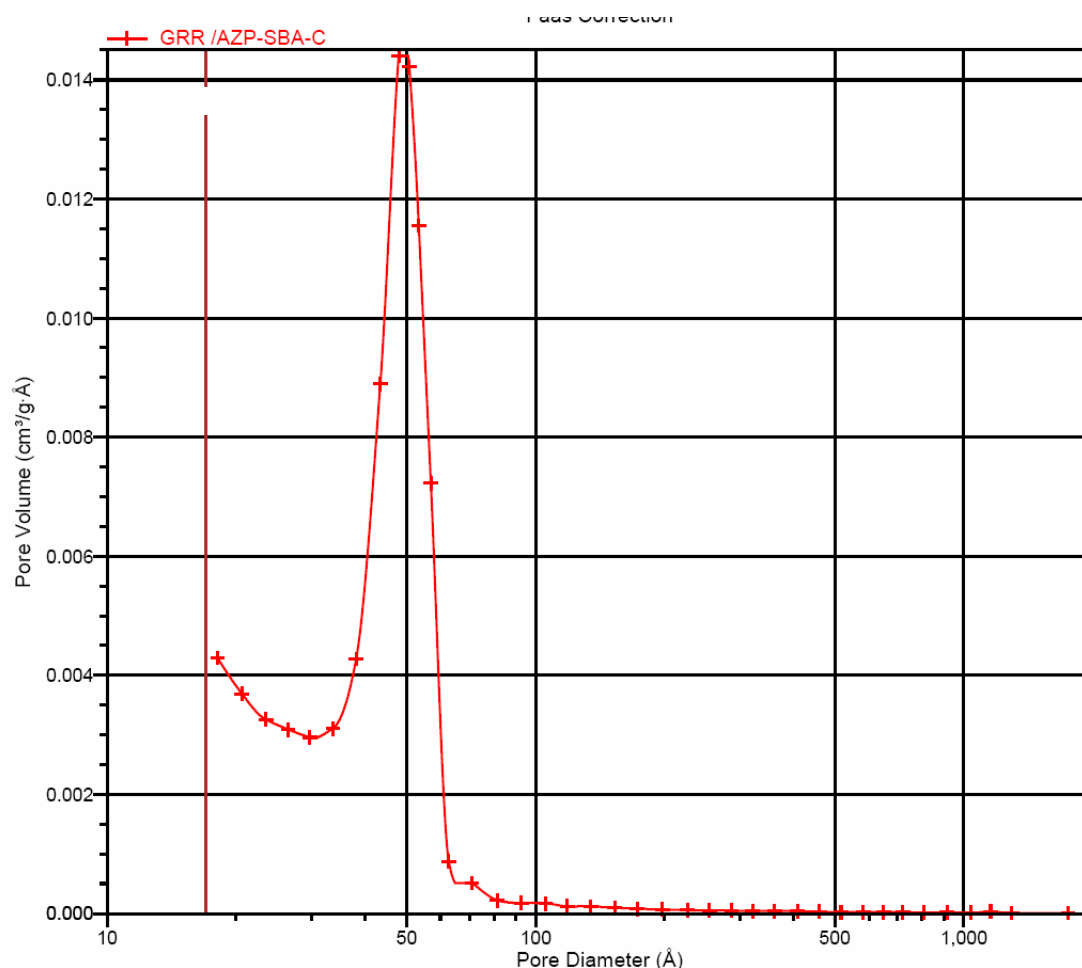
<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): $\delta$  170.6, 170.0, 169.8, 169.7, 96.2, 77.9, 75.6, 69.3, 68.9 (2C), 65.9, 62.3, 54.9, 20.8, 20.7, 20.6(2C) ppm

### BET Surface Area and Pore Size Analysis

**Figure S1:** Isotherm Linear Plot for *AZP-SBA-C*



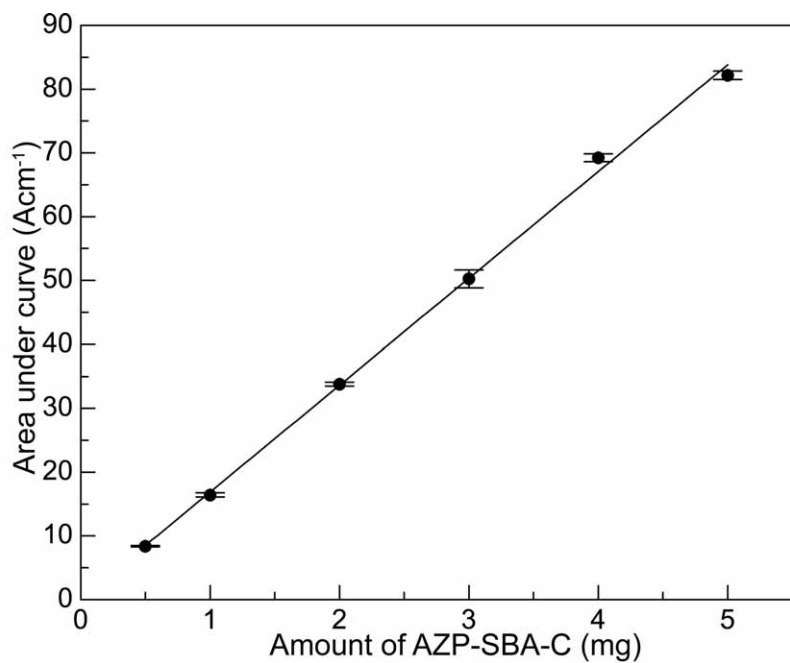
**Figure S2:** BJH Adsorption  $dV/dD$  Pore Volume of AZP-SBA-C



### Calibration Curve for semi-quantitative determination of Azide groups in SBA-15

To obtain a semi-quantitative estimation of the percentage of azide functionalized, a calibration curve was prepared using various quantities of AZP-SBA-C. Typically, various quantities of AZP-SBA-C and KBr were mixed such that the total weight was 100 mg. Pellets were prepared from this mixture and the IR spectrum was taken. Finally, the area under the 2100 cm<sup>-1</sup> peak (that is characteristic of the azide) was plotted against the concentration of AZP-SBA-C used. For all data points, an average of three values was used.

**Figure S3:** Calibration curve for estimation of azide in AZP-SBA-C



**Figure S4:** <sup>29</sup>Si MAS spectra of the different functionalized SBA-15 materials

