

## Supporting information

### A facile approach for the synthesis of hydroxyl-rich microporous organic networks for efficient CO<sub>2</sub> capture and H<sub>2</sub> storage

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#### Materials & Characterization:

Triphenylamine, benzene-1, 4-dialdehyde and 1, 4-bis(bromomethyl) benzene were purchased for Sigma-Aldrich. 1, 2-dichloro benzene, *p*-toluene sulphonic acid (PTSA) and thionyl chloride were obtained from Merck, India. Carbazole was supplied by Spectrochem, India. All the reagents were used without any further purification.

Powder X-ray diffraction patterns were recorded on a Bruker AXS D8 Advanced SWAX diffractometer using Cu K $\alpha$  ( $\lambda = 0.15406$  nm) radiation. Nitrogen adsorption/desorption experiments were performed with a Quantachrome Instruments Autosorb 1C, surface area analyser at 77 K. Fourier transform infrared (FT IR) spectra of the materials were recorded using Nicolet MAGNA-FT IR 750 spectrometer series-II by the KBr sample holder method. Elemental analyses (C, H and N) were performed using a CHN analyzer Perkin-Elmer 2400 series-II. NMR spectrum was recorded on Bruker 400 MHz spectrometer using tetramethylsilane as an internal reference. To examine the morphology of powder samples field-emission scanning electron microscopy (FE-SEM) experiments were performed on JEOL JEM 6700F. Thermogravimetry measurement (TG) was performed thermal analyzer TA-SDT Q-600 under the nitrogen atmosphere with heating rate 10 °C/min. Solid-state <sup>13</sup>C CP/MAS (cross-polarization with magic angle spinning) spectra were obtained from a Bruker Advanced II spectrometer at 500 MHz with a MAS frequency of 8

kHz. The CO<sub>2</sub> adsorption isotherms were measured at 273, 298 K on a Bel Japan Inc. BELSORP-HP apparatus. H<sub>2</sub> adsorption isotherms were measured at 77 K and 87 K on Micromeritics ASAP 2020 surface area and porosity analyzer.

### **Experimental Procedure:**

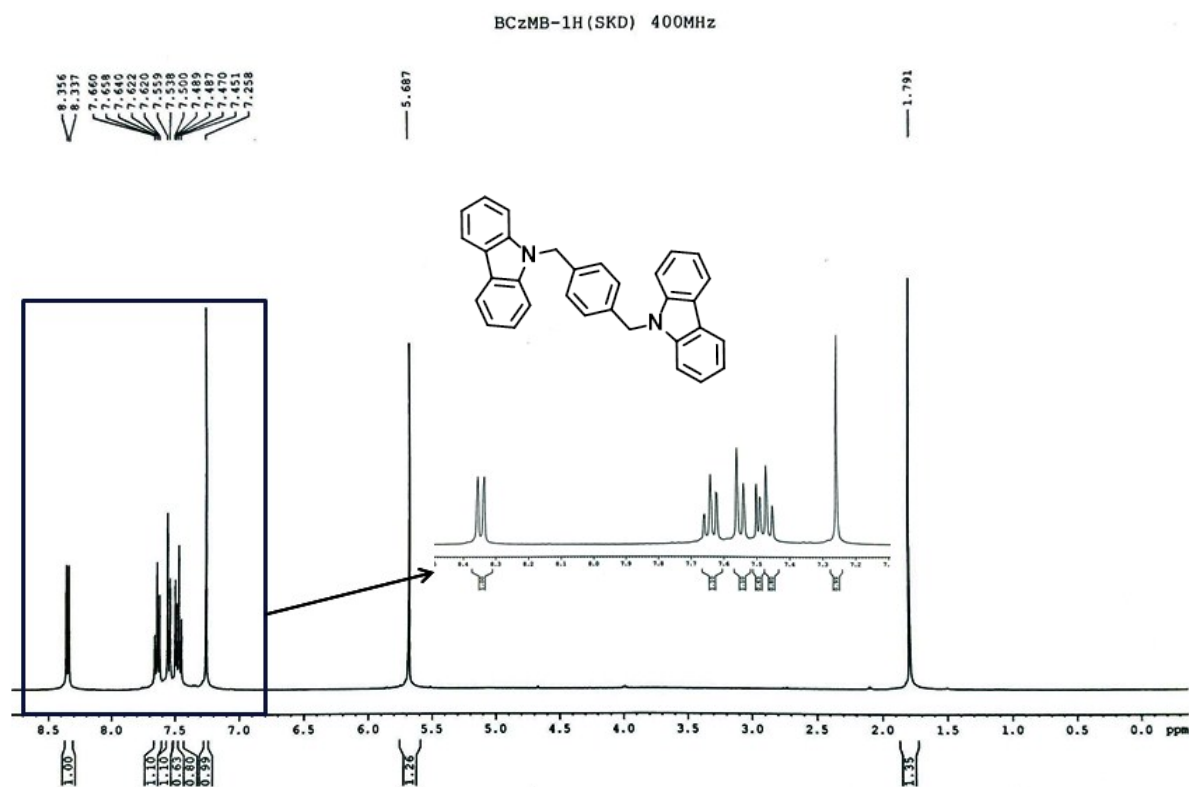
**BCzMB:** To prepare 1, 2-bis[(carbazole-9-yl)methyl]benzene we have followed the reported procedure of Bloxham et al.<sup>1</sup> In a typical synthesis procedure of BCzMB, carbazole (502 mg, 3.0 mmol) was added to a suspended potassium hydroxide (504 mg, 9.0 mmol) in 15 ml DMSO under nitrogen atmosphere and stirred for 1 h. After that 1, 4-bis(bromomethyl)benzene (396 mg, 1.50 mmol) was added to the reaction mixture and stirred was continued for overnight. After cooling to room temperature addition of 100 ml water caused instant precipitate of crude product which was filtered off and washed with excess water. Finally the product was purified by column chromatography using DCM/petroleum ether as eluent. Yield: 472 mg, 72% as a colourless solid. <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>) δ: 8.35 (d, 4H, J=8.0 Hz), 7.64 (t, 4H, J=7.6 Hz), 7.55 (d, 4H, J=8.0 Hz), 7.50 (s, 4H), 7.47 (t, 4H, J=7.6 Hz), 5.69 (s, 4H).

**TPA@PON:** 245 mg (1.0 mmol) of triphenylamine, 201 mg (1.5 mmol) of terephthalaldehyde and 290 mg *p*-toluene sulphonic acid were first taken in a glass tube followed by addition of 5 ml of 1, 2-dichlorobenzene into it. Then the reaction mixture was dispersed for half an hour by ultra-sonication and degassed by freeze-pump-thaw cycles for three times at 77 K (liquid nitrogen bath). Finally the high vacuum glass tube was flame sealed and putted into an oven at 180 °C for 8 h. After cooling at room temperature, the resulting bluish black solid was collected and thoroughly washed with methanol, acetone, dichloromethane and THF respectively. The product was dried under vacuum at 120 °C for overnight.

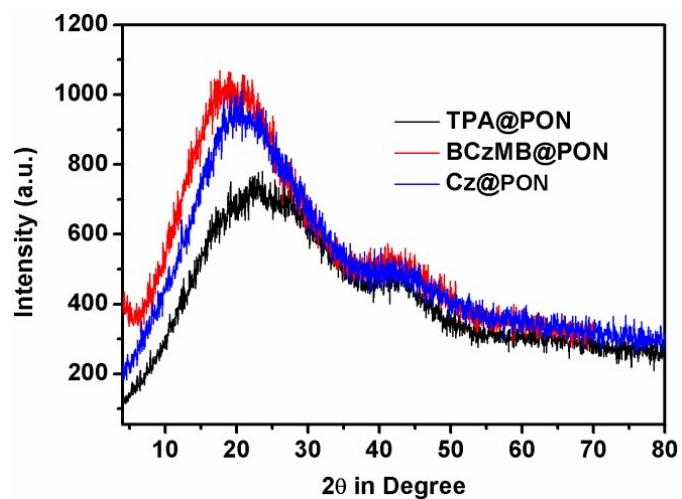
**BCzMB@PON:** For the synthesis of BCzMB@PON, similar procedure was followed as TPA@PON. A mixture of BCzMB (218 mg, 0.5 mmol), 101 mg (0.75 mmol) of

terephthalaldehyde and 145 mg *p*-toluene sulphonic acid were first taken in a glass tube with 5 ml of 1, 2-dichlorobenzene solvent. After sonication and degassing the high vacuum glass tube was flame sealed and kept for 8 h into an oven at 180 °C. After cooling to room temperature the final black product was thoroughly washed with methanol, acetone, dichloromethane and THF respectively and dried under vacuum at 120 °C for overnight.

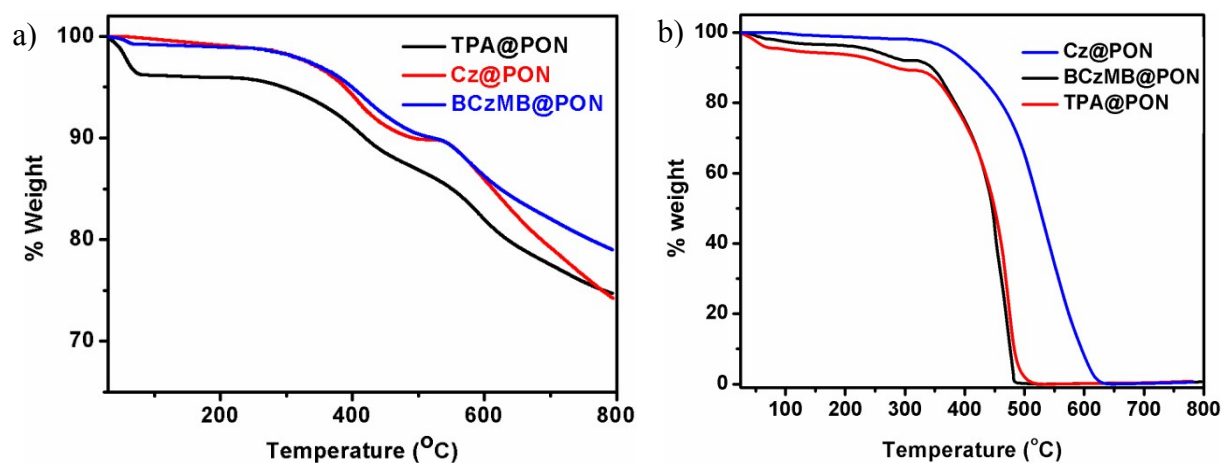
**Cz@PON:** For the synthesis of Cz@PON similar procedure was followed as mention above. A mixture of carbazole (251 mg, 1.5mmol), terephthalaldehyde (302 mg, 2.25 mmol) and *p*-toluene sulphonic acid were taken in a sealed tube along with 5 ml of 1, 2-dichlorobenzene solvent. After degassing and sealing of glass tube the mixture was kept to react for 8 h at 180 °C. After cooling at room temperature the solid was thoroughly washed with methanol, acetone, dichloromethane and THF respectively. The final product was dried under vacuum at 120 °C for 12 h.



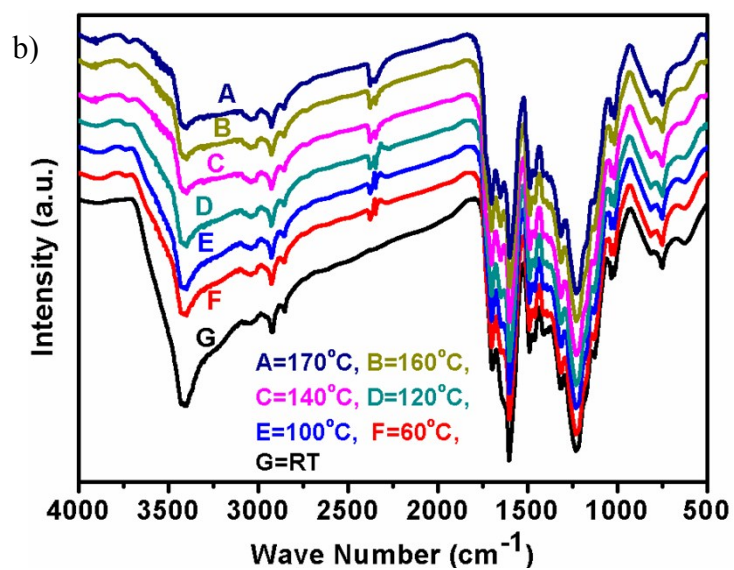
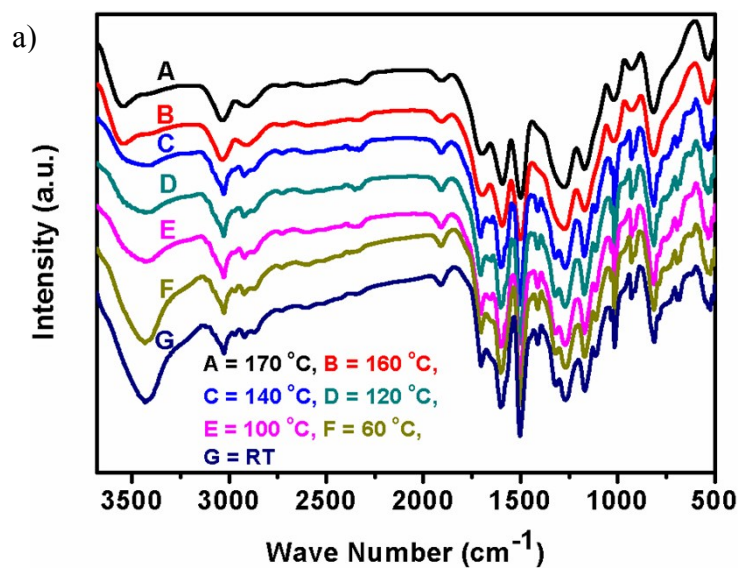
**Figure S1:** NMR spectrum of BCzMB



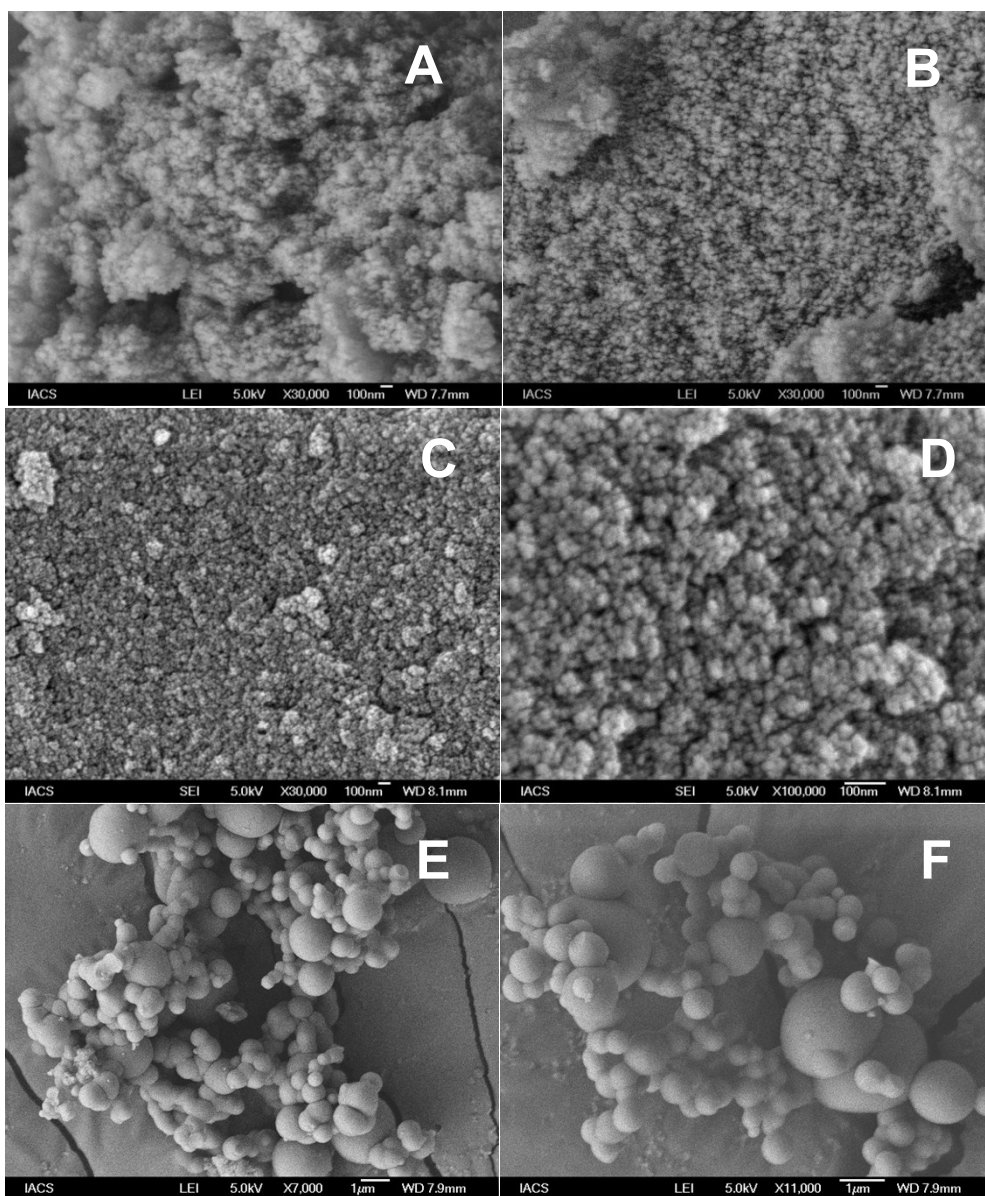
**Figure S2:** Wide angle powder x-ray diffraction patterns of PONs material.



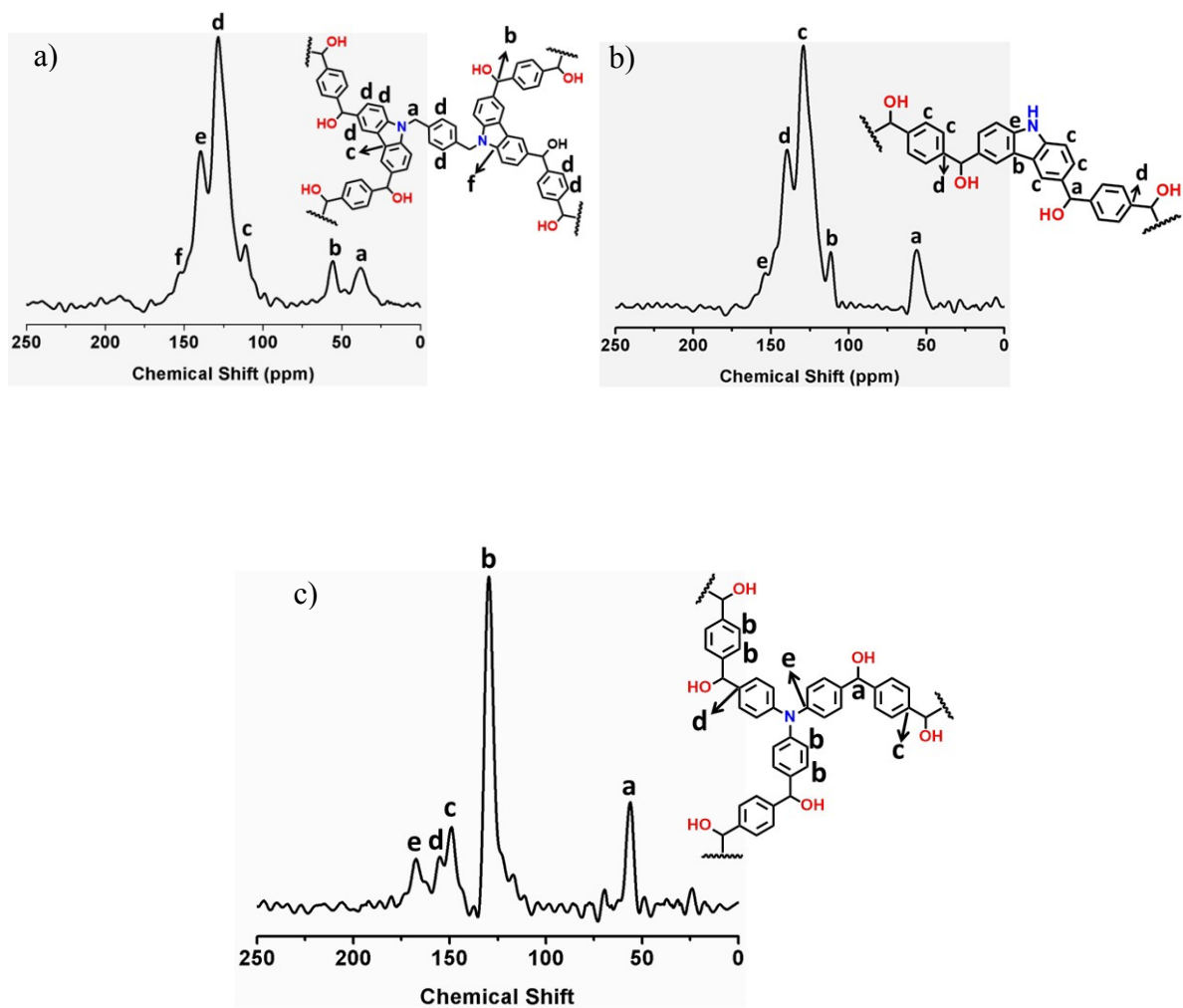
**Figure S3:** Thermogravimetric analysis for the PONs material under nitrogen atmosphere (a) and air (b) respectively.



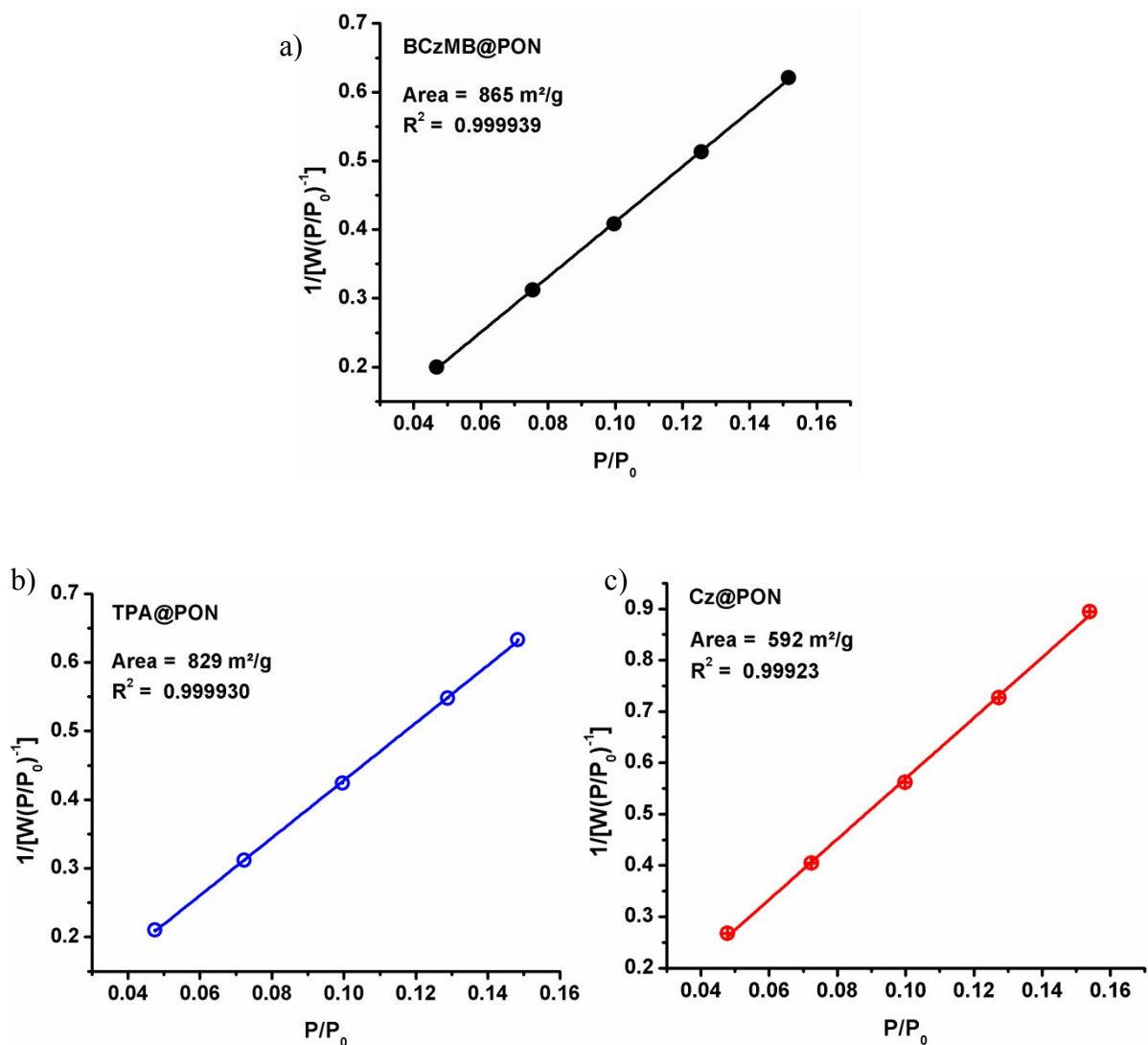
**Figure S4:** Effect of temperature on the FTIR spectra of TPA@PON (a) and Cz@PON (b).



**Figure S5:** FE SEM images of TPA@PON (A, B); BCzMB@PON (C, D) and Cz@PON (E, F) at different magnifications

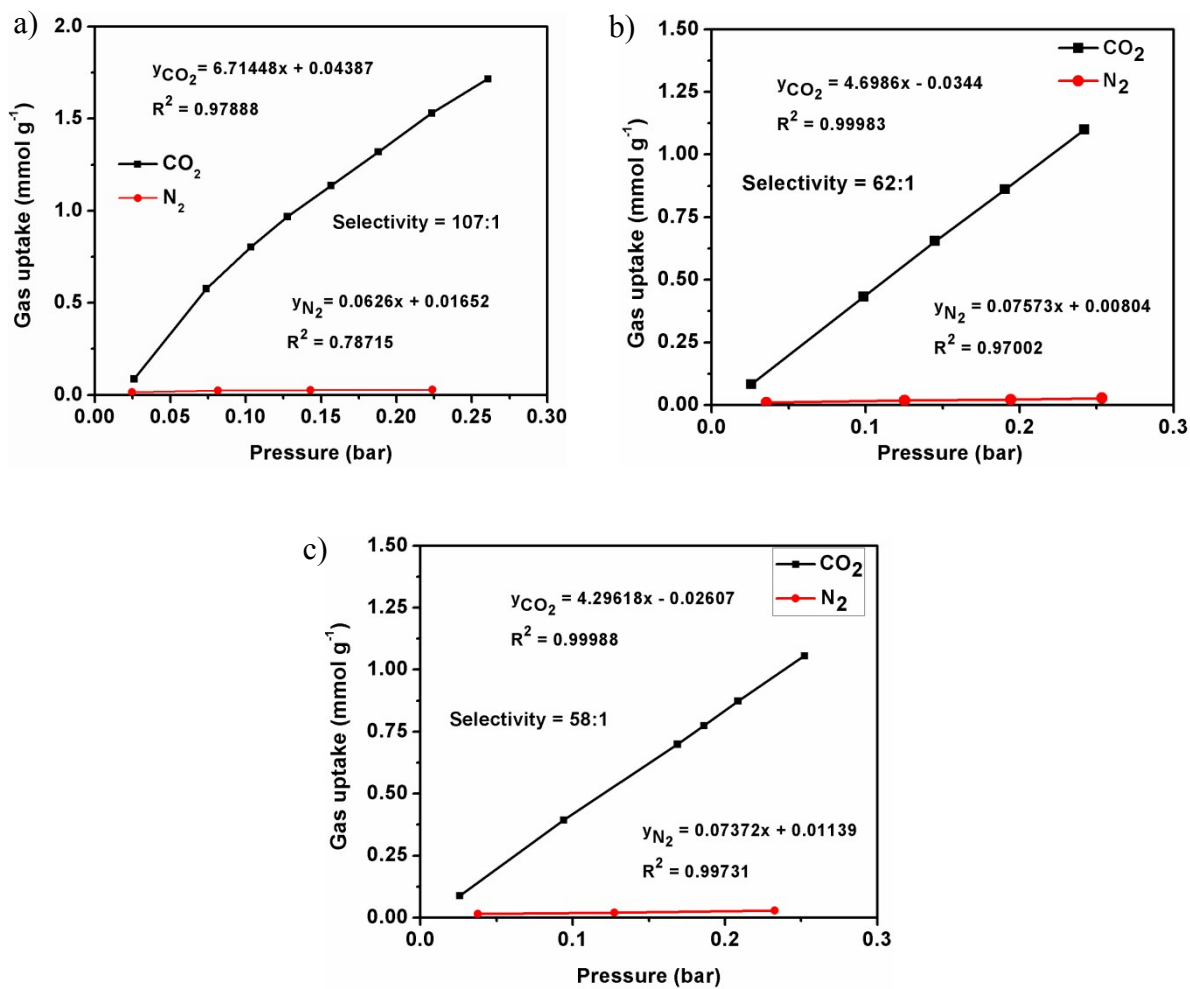


**Figure S6:**  $^{13}\text{C}$  CP-MAS NMR spectra of the PONs material BCzMB@PON (a), Cz@PON (b) and TPA@PON (c).

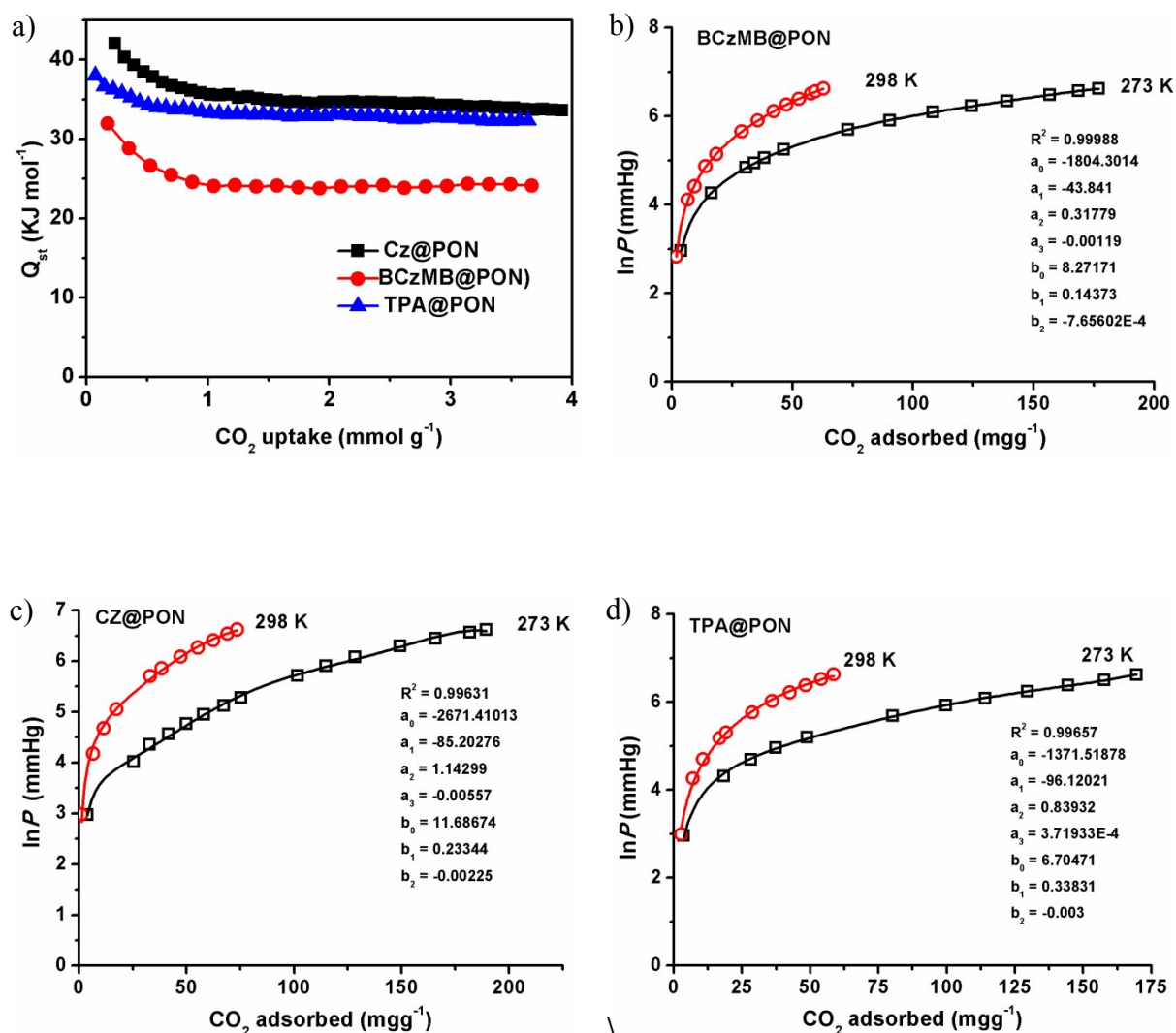


**Figure S7:** BET plot for PONs materials measured from the N<sub>2</sub> adsorption isotherm at 77 K. The model was applied in the lower pressure region  $P/P_0 = (0.047- 0.152)$ ,  $(0.047- 0.148)$  and  $(0.048-0.154)$  for BCzMB@PON, TPA@PON and Cz@PON respectively. The correlation coefficient ( $R^2$ ) is indicated. ( $W$ = weight of gas adsorbed at a relative pressure  $P/P_0$ )





**Figure S8:** CO<sub>2</sub>/N<sub>2</sub> selectivities of Cz@PON (a), TPA@PON (b) and BCzMB@PON (c) respectively.



**Figure S9.** a) Isosteric heat of adsorption for  $\text{CO}_2$  of three PON materials ;b), c) and d) are the  $\text{CO}_2$  adsorption isotherms at 273 K and 298 K (symbols) with the virial equation fits (lines) for BCz@PON, CzMB@PON and TPA@PON, respectively.

## Estimation of the Isostatic heats of H<sub>2</sub> gas adsorption

The virial method<sup>2</sup> was employed to calculate the enthalpies of adsorption for H<sub>2</sub> (77 and 87 K) on CzPON, BCzMB@PON and TPA@PON materials. In each case, the data were fitted using the equation:

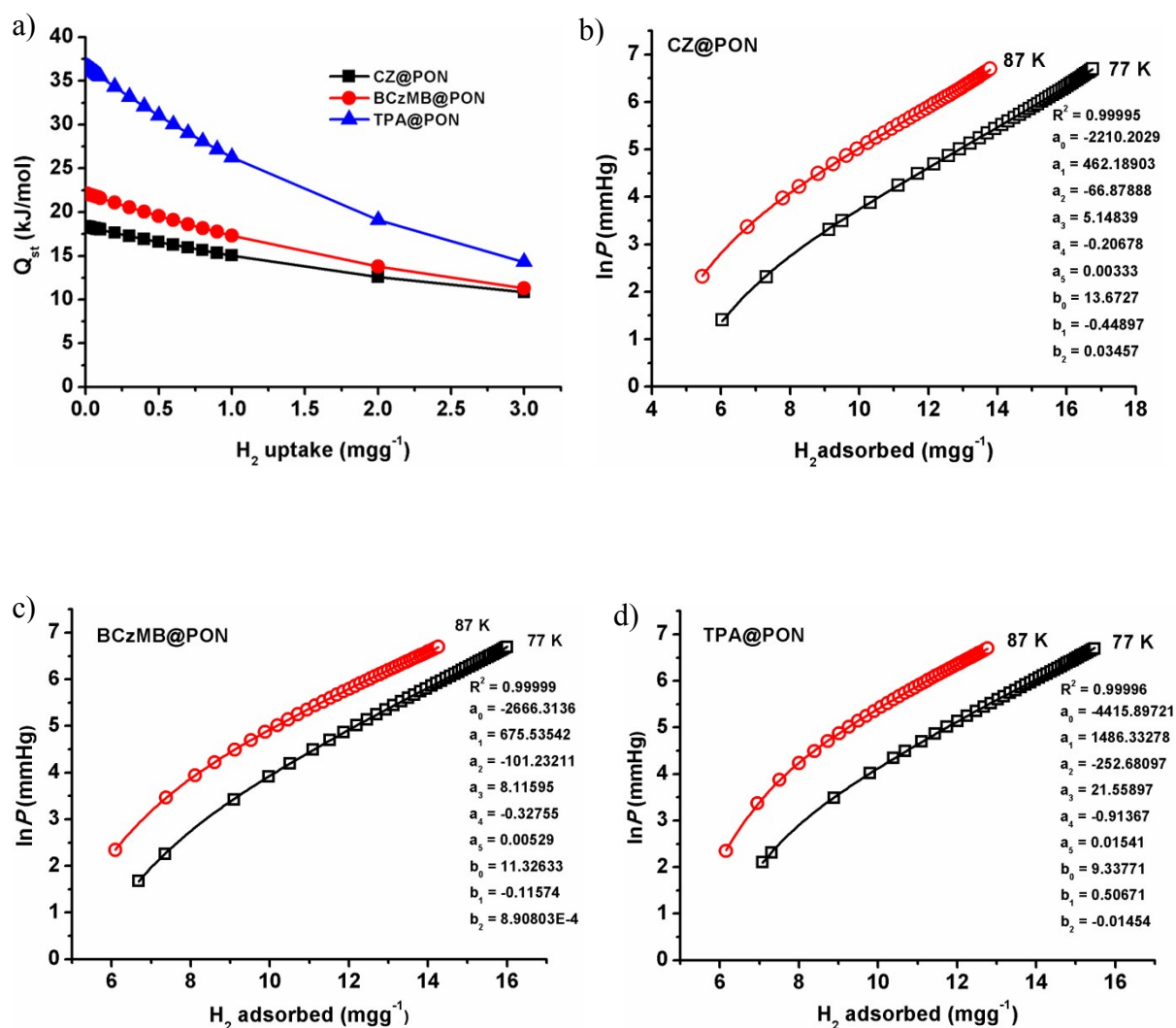
$$\ln (P) = \ln (N) + 1/T \sum_{i=0}^m a_i N^i + \sum_{i=0}^n b_i N^i \quad (\text{I})$$

Here,  $P$  is the pressure expressed in mmHg,  $N$  is the quantity adsorbed in mg/g,  $T$  is the temperature in K,  $a_i$  and  $b_i$  are virial coefficients,  $m$  and  $n$  represent the number of coefficients required to adequately describe the isotherms ( $m$  and  $n$  were gradually increased until the contribution of extra added  $a$  and  $b$  coefficients was deemed to be statistically insignificant towards the overall fit, and the average value of the squared deviations from the experimental values was minimized). The values of the virial coefficients  $a_0$  through  $a_m$  were then used to calculate the isosteric heat of adsorption using the following expression

$$Q_{st} = -R \sum_{i=0}^m a_i N^i \quad (\text{II})$$

Where  $R$  is the universal gas constant (8.314 J K<sup>-1</sup> Mol<sup>-1</sup>)

$Q_{st}$  is the coverage-dependent isosteric heat of adsorption and  $R$  is the universal gas constant.



**Figure S10.** a) Isosteric heat of adsorption for H<sub>2</sub> of the PON materials; b), c) and d) are the H<sub>2</sub> isotherms at 77 K and 87 K (symbols) with the virial equation fits (lines) for CZ@PON, BCzMB@PON and TPA@PON respectively.

**Table S1:** Comparison of CO<sub>2</sub>, H<sub>2</sub> and N<sub>2</sub> storage aptitudes of different types of porous adsorbent reported in the literature with our synthesized PONs materials.

Entry	Materials	Uptake (mmol g <sup>-1</sup> ) at 1 bar					CO <sub>2</sub> /N <sub>2</sub> Selectivity at 1 bar, 273 K	Q <sub>st</sub> (kJ mol <sup>-1</sup> )	Q <sub>st</sub> (kJ mol <sup>-1</sup> )	Reference
		CO <sub>2</sub>		N <sub>2</sub>	H <sub>2</sub>					
		273 K	298 K	273 K	77 K	87K				
1	OMC	3.0	2.0	0.47	-	-	12.8*	22	-	3
2	PECONF-1	1.86	1.34	-	-	-	109*	29	-	4
3	PECONF-3	3.49	2.47	-	-	-	77*	26	-	4
4	PECONF-4	2.95	1.96	-	-	-	83*	34	-	4
5	CTF-1	2.47	1.41	-	-	-	20*	27.5	-	5
6	FCTF-1	4.67	3.21	-	-	-	31*	35.0	-	5
7	Azo-COP-2	2.55	1.53	0.06	-	-	110*	24.8	-	6
8	Azo-POF-1	2.98	1.88	0.19	-	-	69	27.5	-	7
9	BILP-1	4.27	2.98	0.18	9.50	7.0	70	26.7	7.9	8
10	BILP-2	3.39	2.36	0.12	6.50	5.0	113	28.6	8.0	9
11	C1M3-Al	4.11	-	-	9.55	-	24*	20.9	7.9	10
12	C2M3-Al	2.91	-	-	7.30	-	24.9*	20.1	8.1	10
13	[EtNH <sub>2</sub> ] <sub>50</sub> -H <sub>2</sub> P-COF	3.02	1.52	0.18	-	-	-	20.9	-	11
14	BPOP-1	3.48	-	-	5.45	-	-	-	-	12
15	BPOP-2	2.03	-	-	7.10	-	-	-	-	12
16	KPOP-3	2.52	-	-	9.80	-	-	-	-	13
17	KPOP-4	1.89	-	-	6.80	-	-	-	-	13
18	BDT1b	1.57	-	0.78	10	-	2	20.0	-	14
19	BDT2	2.37	-	0.39	1.50	-	11	26.8	-	14
20	BDT3	3.75	-	1.64	2.20	-	3	30.6	-	14
21	BILP-5	2.91	1.98	-	-	-	36	29.0	-	15
22	BILP-7	4.38	2.77	-	-	-	34	28.0	-	15
23	PBI-Ad-1	3.93	-	-	8.00	-	71	-	-	16
24	PBI-Ad-2	3.11	-	-	6.50	-	70	-	-	16
25	p-PDM-DVB	2.55	-	-	4.10	-	51.02	-	-	17
<b>26</b>	<b>BCzMB@PON</b>	<b>4.02</b>	<b>1.43</b>	<b>0.19</b>	<b>7.86</b>	<b>6.97</b>	<b>58</b>	<b>31.96</b>	<b>22.16</b>	<b>This Work</b>
<b>27</b>	<b>TPA@PON</b>	<b>3.85</b>	<b>1.33</b>	<b>0.18</b>	<b>7.59</b>	<b>6.25</b>	<b>62</b>	<b>37.98</b>	<b>36.70</b>	<b>This Work</b>
<b>28</b>	<b>Cz@PON</b>	<b>4.31</b>	<b>1.67</b>	<b>0.19</b>	<b>8.23</b>	<b>6.76</b>	<b>107</b>	<b>42.01</b>	<b>18.37</b>	<b>This Work</b>

\* Selectivity calculated by IAST method.

## Reference:

1. J. Bloxham, C. J. Moody and A. M. Z. Slawin, *Tetrahedron*, 2002, **58**, 3709.
2. J. L. C. Rowsell, and O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 1304.
3. B. Yuan, X. Wu, Y. Chen, J. Huang, H. Luo and S. Deng, *Environ. Sci. Technol.* 2013, **47**, 5474-5480.
4. P. Mohanty, L. D. Kull and K. Landskron, *Nat. Commun.* 2011, **2**, 401.
5. Y. Zhao, K. X. Yao, B. Teng, T. Zhang and Y. Han, *Energy Environ. Sci.* 2013, **6**, 3684-3692.
6. H. A. Patel, S. H. Je, J. Park, Y. Jung, A. Coskun and C. T. Yavuz, *Chem. Eur. J.* 2014, **20**, 772-780.
7. J. Lu and J. Zhang, *J. Mater. Chem. A*, 2014, **2**, 13831-13834.
8. M. G. Rabbani, H. M. El-Kaderi, *Chem. Mater.*, 2011, **23**, 1650-1653
9. M. G. Rabbani and H.M. El-Kaderi, *Chem. Mater.* 2012, **24**, 1511-1517.
10. G. Liu, Y. Wang, C. Shen, Z. Ju and D. Yuan, *J. Mater. Chem. A*, 2015, **3**, 3051-3058.
11. N. Huang, R. Krishna and D. Jiang, *J. Am. Chem. Soc.* 2015, **137**, 7079-7082.
12. Y. C. Zhao, T. Wang, L. M. Zhang, Y. Cui and B. H. Han, *ACS Appl. Mater. Interfaces*, 2012, **4**, 6975-6981.
13. Y. Han, L. M. Zhang, Y. C. Zhao, T. Wang and B. H. Han, *ACS Appl. Mater. Interfaces*, 2013, **5**, 4166-4172.
14. S. Bandyopadhyay, A. G. Anil, A. James and A. Patra, *ACS Appl. Mater. Interfaces*, 2016, **8**, 27669-27678.
15. A. K. Sekizkardes, S. Altarawneh, Z. Kahveci, T. İslamoğlu, and H. M. El-Kaderi, *Macromolecules*, 2014, **47**, 8328-8334.
16. B. Zhang, G. Li, J. Yan and Z. Wang, *J. Phys. Chem. C*, 2015, **119**, 13080-13087.
17. H. Gao, L. Ding, W. Li, G. Ma, H. Bai and L. Li, *ACS Macro Lett.* 2016, **5**, 377-381.