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By varying only one chemical bond of building blocks, the CMPs P-TPATCz and P-CzPTCz show sharp difference.

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# ARTICLE TYPE

# Topology-directed design and synthesis of carbazole-based conjugated microporous networks for gas storage

Shanlin Qiao,<sup>a</sup> Wei Huang,<sup>a</sup> Huan Wei,<sup>ab</sup> Ting Wang,<sup>a</sup> and Renqiang Yang<sup>\*a</sup>

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Two topological-directed conjugated microporous networks P-TPATCz and P-CzPTCz were synthesized. The two initial building blocks have similar chemical constitution but with different geometry configuration (TPATCz: quasi-tetrahedron 3D and CzPTCz: quasi-coplanar 2D structure). Scanning electron microscopy images and powder X-ray diffraction data indicate that the quasi-tetrahedron <sup>10</sup> structure monomer TPATCz is facile to form columnar crystalline aggregation, while the quasi-coplanar monomer of CzPTCz forms amorphous aggregation networks. Thermogravimetric analysis shows the thermal stability of two networks at high temperature may be affected by the stability of the core in the building blocks. Changing the triphenylamine core of monomer TPATCz with 9-phenyl-9H-carbazole in CzPTCz, the Brunauer-Emmett-Teller surface area of P-TPATCz (337 m<sup>2</sup> g<sup>-1</sup>) rises to 1315 m<sup>2</sup> g<sup>-1</sup> for P-<sup>15</sup> CzPTCz. Hydrogen isotherms of P-TPATCz and P-CzPTCz show the H<sub>2</sub> storage can be up to 0.85 and 1.90 wt% at 77 K/1.1 bar, respectively. At 273 K/1.1 bar, the CO<sub>2</sub> uptake capacity of P-CzPTCz can be up to 17.0 wt% which is 5.8 times than that of P-TPATCz. Fine designing and tailoring the steric configuration of building block could pre-determine the physicochemical property of the target networks and influence the gas uptake performance.

# 20 Introduction

Conjugated microporous polymers (CMPs) are networks constructed from conjugated building blocks with large surface areas, small pore sizes and low densities. The unique feature of CMPs is that they combine the stiff pore structure and conjugated <sup>25</sup> electron system in one bulk material. These materials have

- received an increasing level of research interest because their specific applications were proved to be as invaluable tools in the fields of gas storage and separation,<sup>[1]</sup> catalysts,<sup>[2]</sup> water treatment,<sup>[3]</sup> sensor<sup>[4]</sup> and photovoltaics.<sup>[5]</sup> Up to now, the main <sup>30</sup> strategy to enhance the performance of CMPs is to link together
- secondary building units with different topology structures to form extended networks.<sup>[6,7]</sup> To achieve a better gas storage performance, the porosity and morphology of the CMPs are two key factors that should be taken into account, because the
- <sup>35</sup> polymer rigidity,<sup>[8]</sup> free volume,<sup>[9]</sup> order<sup>[10]</sup> or amorphous<sup>[11]</sup> are pre-determined by the topology structures of secondary building units (SBUs).

The SBUs of porous organic materials can be classed as one, two and three dimensions structures which are the basic and necessary

- <sup>40</sup> components for the porosity networks. The created pores of lowdimensional (1D) networks originate from the quasi-regular chains which usually are built up from linear monomers via the covalent polymerization of small building units, such as the polymers of intrinsic microporosity (PIMs) which is first reported
- 45 by the group of McKeown and Budd<sup>[12]</sup>. Two-dimensional (2D)

networks are usually with defined crystalline extended topological structures, whose porosity are generated into periodic layer by linear, triangle and square building blocks. The special nature of 2D networks is that they exhibit well-ordered structures 50 with uniform pores and high specific surface areas. Yaghi group first made the crystalline 2D polymers COF with regular pore size, up to now the multifunctional COF-366 and COF-66 with high charge carrier mobility were reported.<sup>[13]</sup> The threedimensional (3D) networks are more complicated than 1D and 55 2D due to the polyhedral reaction sites which can possibly result in more intricate structures.<sup>[14]</sup> As stated above the final topology structure of target networks was pre-determined by the relative geometry of the starting building blocks, and we all know that the final porosity structure of the networks is the cornerstone of the 60 gas uptake application. Hydrogen is one of the alternative fuels to decrease both carbon dioxide emissions and dependency on oil related products. How to use hydrogen in safety state and design a storage material with a high specific surface area, narrow pore distribution and large isosteric enthalpies in physisorption field is 65 still a challenge.<sup>[15]</sup>

In this work, two carbazole based conjugated networks P-TPATCz and P-CzPTCz were topology-directed designed and synthesized shown in Scheme 1. This idea would provide an available way for detailed understanding the relationship of 70 geometry configuration of building block with the performance of materials in gas uptake application. FeCl<sub>3</sub> oxidative approach uses the single carbazole based building block without any other spacer inserted, which could avoid the unnecessary impact of other spacer on the morphology of the target polymer. This work demonstrates that, changing the geometry configuration of the initial building block directed by topology, can make a distinct difference in the polymer thermostability, aggregated <sup>5</sup> morphology, porosity structure parameters and the gas storage performance.

# **Experimental section**

# Materials

All reagents and solvents, unless otherwise specified, were <sup>10</sup> obtained from J&K, Aldrich and Acros Chemical Co. and used without additional purification. Anhydrous tetrahydrofuran (THF) and chloroform were distilled over sodium/benzophenone and calcium hydride under N<sub>2</sub> prior to use, respectively.

Synthesis of P-TPATCz<sup>[16]</sup>. The solution of monomer TPATCz <sup>15</sup> (200 mg, 0.37 mmol) dissolved in 30 mL of anhydrous chloroform was dropwise transferred to a suspension of ferric chloride (786 mg, 2.94 mmol) in 20 mL of anhydrous chloroform. The solution mixture was stirred for 24 h at room temperature under nitrogen protection, and then 100 mL of methanol was <sup>20</sup> added to the above reaction mixture. The resulting precipitate was collected by filtration and washed with methanol and concentrated hydrochloric acid solution. After extracted in a Soxhlet extractor with methanol for 24 h, and then with tetrahydrofuran for another 24 h, the desired polymer was <sup>25</sup> collected and dried in vacuum oven at 80 °C overnight. Yellowish powder, yield in 95%. Anal. Calcd. for C<sub>54</sub>H<sub>36</sub>N<sub>4</sub>: C,

87.54; N, 7.56; H, 4.90. Found: C, 84.20; N, 7.12; H, 3.94.

Synthesis of P-CzPTCz. This polymer was synthesized following the same method described above for P-TPATCz and using

 $_{30}$  CzPTCz as initial monomer. Yellowish powder, yield in 98%. Anal. Calcd. for  $C_{54}H_{34}N_4$ : C, 87.78; N, 7.58; H, 4.64. Found: C, 84.34; N, 7.28; H, 3.92.

# Methods

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<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV 600M <sup>35</sup> spectrometer with tetramethylsilane (TMS) as the internal reference. FT-IR spectra were collected in attenuated total reflection (ATR) mode on a Thermo Nicolet 6700 FT-IR Spectrometer. Scanning electron microscopy (SEM) was recorded using a Hitachi S-4800 with acceleration voltage 3.0 kV <sup>40</sup> and working distance 8.5 mm. Samples were coated on a thin

- layer of Au before investigation. Thermogravimetric analysis (TGA) were carried out using a TA Instruments Q-5000IR series thermal gravimetric analyzer with samples held in 50 µL platinum pans under an atmosphere of nitrogen (heating rate
- <sup>45</sup> 5 °C/min). Powder X-ray diffraction data were collected on a Bruker D8 ADVANCE. Samples were mounted on a sample holder and measured using Cu K $\alpha$  radiation with a 2 $\theta$  range of 5–50. Solid-state <sup>13</sup>C cross-polarization magic angle spinning (CP-MAS) NMR spectra for solid samples were taken at Bruker
- <sup>50</sup> AVANCE-III. Gas adsorption test: all the gas adsorption isotherms were tested on a Quantachrome instruments AutosorbiQ-MP-VP volumetric adsorption analyzer with the same degassing procedure. In a typical experiment, both two networks were degassed at 120 °C for 800 min under vacuum before
- <sup>55</sup> analysis. BET surface areas and pore size distributions were measured by nitrogen adsorption-desorption at 77 K. H<sub>2</sub> isotherms were measured at 77 K, 87 K up to 1.1 bar. CO<sub>2</sub>, CH<sub>4</sub>

and  $N_{\rm 2}$  isotherms were measured at 273 K and 298 K up to 1.1 bar.

# 60 Results and discussion

# Synthesis and Characterization of P-TPATCz and P-CzPTCz networks

Two carbazole based conjugated networks P-TPATCz and P-CzPTCz were straightforward synthesized by  $\mbox{FeCl}_3$  oxidative

- <sup>65</sup> coupling polymerization at room temperature shown in Scheme 1. FeCl<sub>3</sub> oxidative coupling polymerization was firstly reported to synthesize microporous polycarbazole by Bao-Hang Han's group, which is quite a facile and effective way to prepare CMPs.<sup>[16]</sup> Monomer TPATCz and CzPTCz were prepared by cuprous oxide <sup>70</sup> catalytic Ullmann reaction.<sup>[17,18]</sup> The two initial building blocks have the different geometrical configurations, the core of TPATCz is triphenylamine unit which is a typical quasitetrahedron and the core of CzPTCz is a planar unit 9-phenyl-9Hcarbazole. The outside of the two secondary building units
- 75 TPATCz and CzPTCz was constructed by three carbazole molecules to form six polymeric binding sites. Rigid conjugated backbone of carbazole is beneficial for formation of porous networks with permanent porosity stability, and the well-known highly reactive oxidation coupling in the 3, 6-position of so carbazole made this backbone a potential building block to construct conjugated networks.<sup>[19]</sup> The building blocks constitute rigid cores and outside carbazole topology configurations could avoid the pore structure collapsing at dry state. P-TPATCz and P-CzPTCz networks have the identical chemical constitution which
- <sup>85</sup> provides a platform for fine investigating the relationship of the monomer structure with gas storage.
- Solid state magic angle spinning <sup>13</sup>C CP/MAS NMR spectra and the corresponding networks with assignment of the resonances are shown in Figure 1a. In networks P-TPATCz, the 90 characteristic resonance signal peaks at 141, 142 and 145 ppm correspond to the carbons binding with carbazole nitrogen atom and the core of triphenylamine nitrogen atom. The difference of networks P-TPATCz with P-CzPTCz is the resonance signal at 121 ppm assigned to the carbon signal of the core 9-phenyl-9H-95 carbazole. A more detailed analysis of the structures of the polymers was confirmed by FT-IR spectra collected in attenuated total reflection (ATR) mode shown in Figure S1, in which we can find the apparent carbazole characteristic peaks of P-TPATCz and P-CzPTCz. The signals at 744, 1224, 1469 and 1608 cm<sup>-1</sup> are 100 assigned to characteristic bands of carbazole. TGA traces show that both networks have high thermal stability, the thermal decomposition temperature (Td) is up to ca. 474 °C for P-TPATCz and 525 °C for P-CzPTCz at 5% weight loss shown in Figure 1b. The two polymers showed better stability than some 105 reported CMPs, such as PDCzBT which exhibited decomposition
- The reported CMPS, such as PDC2BT which exhibited decomposition at 350 °C, and O-TTPP and S-TTPP.<sup>[20, 21]</sup> When temperature raised more than 480 °C, the TGA curve of P-TPATCz exhibited sharp decrease and at 592 °C the loss weight reached to 50%, which can be ascribed to the decomposition of the core of 110 triphenylamine. Interestingly, during the whole temperature range (T <800 °C) the P-CzPTCz networks showed ideal thermal stability and no evidence for distinct glass transition below the thermal decomposition temperature due to the nature of its high cross-linking structure. The Powder X-ray Diffraction (PXRD)



Scheme 1. Synthetic routes of carbazole-based networks P-TPATCz and P-CzPTCz.

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- results for the two networks are shown in Figure 1c. P-CzPTCz 5 networks reveal a conventional amorphous nature of the polymer, as commonly observed in the literature for other materials.<sup>[22]</sup> However, there are many strong sharp peaks observed in the P-TPATCz networks, providing a sound proof that P-TPATCz was obtained in a quasi-crystalline phase.<sup>[23]</sup> Additionally, the 10 scanning electron microscopy (SEM) images confirmed again that P-TPATCz and P-CzPTCz (Figure 1d and 1e) have remarkably different aggregation morphologies, P-CzPTCz networks is consisted of regular spherical particles. However, P-
- 15 crystalline aggregation morphology which is corresponding to the result of P-XRD. Both building blocks were employed the same polymerization process, but the monomer TPATCz formed large long-range ordered 3D crystalline morphology which is similar to the COF networks (more SEM images of different magnification

TPATCz image appeared a certain number of the columnar

20 are shown in Figure S2). Based on the analysis above, it can be concluded that subtle change in the geometry configuration of the building blocks or starting monomers will not only alter the thermal stability of the target polymer but also determine the aggregation morphology, even though both polymers have the 25 same chemical composition.

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Figure 1. (a) Solid state magic angle spinning <sup>13</sup> C CP/MAS NMR spectra. (b) Thermal decomposition temperature curves (Td). (c) Powder X-ray Diffraction. (d) P-TPATCz and (e) P-CzPTCz field-emission scanning electron microscopy.

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Figure 2. Nitrogen adsorption-desorption isotherms of the P-TPATCz and P-CzPTCz networks were measured at 77 K.

### 5 Nitrogen adsorption

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The porosity properties of networks P-TPATCz and P-CzPTCz were measured by adsorption analysis using nitrogen as the probe molecule at 77 K. Figure 2 shows the N<sub>2</sub> adsorption-desorption isotherms for the two networks. The sorption branch of P-10 CzPTCz exhibited a steep rise of uptake at the relative pressure  $(P/P_0)$  less than 0.01, indicating the presence of more substantial micropores structure than P-TPATCz. At high relative pressure both networks show a large increasing course due to the existence of macroporosity structure which caused by the collapse of the 15 loose nanoparticulate stockpiling yielded small and ill-defined interstitial voids in the obtained networks.<sup>[24]</sup> When the Brunauer-Emmett-Teller (BET) model is adopted to calculate the apparent surface area, the surface areas of P-TPATCz and P-CzPTCz are 337 and 1315 m<sup>2</sup> g<sup>-1</sup>, respectively. The BET area of P-CzPTCz 20 network is 3.9 times more than P-TPATCz. A comparison of pore size distribution (PSD) using the quenched solid density functional theory (QSDFT) is shown in Figure S3. QSDFT is a multicomponent DFT, in which the networks is treated as one of the components of the adsorbate-adsorbent system and this

- 25 model has been demonstrated that it can improve the accuracy of pore distribution significantly than NLDFT (nonlocal density functional theory).<sup>[25]</sup> The dominant pore widths of P-TPATCz and P-CzPTCz center at about 1.5-5.5 nm and 0.5 nm, 0.9 nm, respectively. The steric configuration of quasi-coplanar building
- 30 block CzPTCz could be more facile to form smaller porosity than quasi-tetrahedron monomer TPATCz. The pore total volume of both networks is 1.02 and 1.09 cm<sup>3</sup> g<sup>-1</sup> at relative pressure  $P/P_0 =$ 0.99 for P-TPATCz and P-CzPTCz, respectively. N2 adsorption analysis and pore size distribution show the relationships among
- 35 the initial building block, polymer aggregation morphology and the porosity structural parameters. The building block of TPATCz with quasi-tetrahedron geometrical configuration may be facile to yield long-range ordered crystalline aggregation during the solution polymerization process, which leads to low
- 40 appearance surface area and large pore width. In contrast, the quasi-planar structure of CzPTCz prefers to form amorphous spherical particles aggregation and this type of aggregation could be more effective to increase the BET areas and reduce the pore

width.

# Hydrogen storage

The hydrogen adsorption isotherms of P-TPATCz and P-CzPTCz networks are shown in Figure 3a, and the adsorption enthalpies which are calculated based on the isotherms of 77 K and 87 K are 50 shown in Figure 3b. In the low pressure range, P-CzPTCz

- networks show much higher adsorption capacity than P-TPATCz suggesting the importance of higher achievable adsorption enthalpies. One can observe that the adsorption enthalpies of both networks can be up to 9.74 and 10.22 kJ mol<sup>-1</sup> at zero loading. 55 This can be ascribed to the structure of conjugated electron-rich backbone, and plenty of electric charges in the networks can
- promote strong interactions of H2 molecules with the surfaces.<sup>[26]</sup> It should be pointed out that P-TPATCz and P-CzPTCz have identical chemical constitution and prepared with same 60 polymerization process, the difference between the two enthalpies may be mainly caused by the different degree of  $\pi$ -conjugation and pore width. Increasing the surface charge density and
- reducing the pore width are useful strategies to increase adsorption enthalpies which has been predicted by theory<sup>[27]</sup> and 65 demonstrated by experiments.<sup>[28,29]</sup> At the medium and high
- pressure range, P-CzPTCz still exhibits larger H2 uptake capacity than P-TPATCz, and during this period the pore volume may be the dominant factor for hydrogen adsorption capacity. At 77 K and 1.1 bar, P-CzPTCz obtains a H<sub>2</sub> uptake of 1.90 wt%, which is 70 higher than P2 (1.36 wt%) [30] and PPN-3 (1.58 wt%)[31], and comparable to BILP-1 (1.90 wt%).<sup>[32]</sup> It is noticeable that the uptake of P-CzPTCz is 2.35 times of P-TPATCz (0.81 wt%) networks. No saturation is observed in the isotherms, suggesting that a higher H<sub>2</sub> capacity can be achieved at higher pressure 75 condition.

# Carbon dioxide and methane adsorption

The carbazole-based networks of P-TPATCz and P-CzPTCz show much difference in porosity structure and H<sub>2</sub> adsorption capacity. In order to understand deeper the relationship of <sup>80</sup> building blocks, topology structure and performance among the two networks, we further investigate the CO<sub>2</sub> and CH<sub>4</sub> uptake at 273 K and 298 K, up to 1.1 bar. The adsorption isotherms and gas isosteric enthalpies are shown in Figure 4. CO<sub>2</sub> physisorbed process is reversible in all cases because the desorption branches 85 are overlapped with the adsorption ones. At 273 K and 1.1 bar, the CO<sub>2</sub> uptake capacity of P-CzPTCz can be up to 17.0 wt%, which is 5.8 times of the networks of P-TPATCz (2.9 wt%). And the capacity of P-CzPTCz also exceeds other reported conjugated polymers, such as CMP Network 1-4 (7.59 wt%, 298 K, 1.13 90 bar ), [33] CMP-1-COOH (7.04 wt%). [34] At 298 K, the capacities of CO<sub>2</sub> uptake are 2.0 and 9.4 wt% for P-TPATCz and P-CzPTCz, respectively. The isosteric enthalpies Qst of the two networks were calculated from the adsorption isotherms based on Clausius-Clapeyron equation and the values for P-TPATCz and P-CzPTCz 95 are 40.3 and 30.7 kJ mol<sup>-1</sup> at zero loading shown in Figure 4b. As the load of CO<sub>2</sub> increasing, the Qst of P-TPATCz sharply drops to 25 kJ mol<sup>-1</sup> and then slowly decreases to 20 kJ mol<sup>-1</sup>. However, the networks of P-CzPTCz can retain the Qst around 28 kJ mol<sup>-1</sup> at the whole pressure range with adsorbed CO<sub>2</sub> increasing. The

100 stable Qst can enhance the CO<sub>2</sub> capture despite the low Qst at zero loading. The CH<sub>4</sub> adsorption isotherms of P-TPATCz and P-



Figure 3. (a)  $H_2$  adsorption isotherms of P-TPATCz and P-CzPTCz networks at 77 K and 87 K. (b) Variation of  $H_2$  isosteric enthalpies with the adsorbed amount.

- $_{5}$  CzPTCz were collected at 273 K, 298 K and 1.1 bar shown in Figure 4c. The CH<sub>4</sub> uptake of P-TPATCz is 0.5 wt% at 273 K and 0.3 wt% at 298 K; P-CzPTCz is 2.5 wt% at 273 K and 1.2 wt% at 298 K. At the whole pressure range (273 K and 298 K), P-CzPTCz networks exhibit steep adsorption isotherm and show no
- <sup>10</sup> saturation station, which means that it could absorb more  $CH_4$  at a higher pressure condition. It is noteworthy that its isosteric heat of  $CH_4$  uptake can be up to 38.2 kJ mol<sup>-1</sup> at zero loading which calculated from adsorption experiment at 273 K and 298 K (Figure 4d). The property of high isosteric heats is advantageous
- <sup>15</sup> because it allows the possibility of greater storage capacities for materials with comparable micropore size and volume. The lower BET surface area, larger pore width and rapidly decreasing adsorption enthalpies made P-TPATCz networks a poorer gas uptake capacity compared with P-CzPTCz. It can be concluded that the geometry application of the building blocks on starting
- <sup>20</sup> that the geometry configuration of the building blocks or starting monomers may be the dominant factor determining the gas uptake performance of CMPs with the similar chemical constitution.



<sup>25</sup> Figure 4. (a)  $CO_2$  and c)  $CH_4$  adsorption isotherms of P-TPATCz and P-CzPTCz networks at 273 K and 298 K. (b)  $CO_2$  and d)  $CH_4$ variation of gas isosteric enthalpies with the adsorbed amount.

# Conclusions

Two carbazole based building blocks TPATCz and CzPTCz were 30 designed and prepared as conjugated networks P-TPATCz and P-CzPTCz through FeCl<sub>3</sub> oxidative polymerization. SEM, P-XRD and TGA data indicate that the geometry configuration of the monomer could pre-determine the morphology and influence the thermal stability of the networks. Gas adsorption investigation 35 shows that subtle change of the building block core can make great difference in pore structures and gas capacities of CMPs. The BET surface areas of the two networks are raised from 337 to 1315 m<sup>2</sup> g<sup>-1</sup>, and the H<sub>2</sub> (77 K), CO<sub>2</sub> (273 K), CH<sub>4</sub> (273 K) storage of P-CzPTCz can be up to 1.9, 17.0 and 2.5 wt% at 1.1 40 bar, respectively. The results provide us an approach to further understand the relationship of topological structure design with the gas uptake performance in clean energy applications and environmental field, and the findings would be helpful to design new efficient materials for the relative community.

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## Notes and references

- <sup>50</sup> <sup>a</sup> CAS Key Laboratory of Bio-based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China. Fax: +86 532 80662778; Tel: +86 532 80662700; E-mail: <u>yangrq@qibebt.ac.cn</u>
- <sup>b</sup> School of Chemical and Pharmaceutical Engineering, Hebei University 55 of Science and Technology, Shijiazhuang 050018, China
- † Electronic Supplementary Information (ESI) available: [Details of Synthesis, IR spectrum, additional SEM images and pore size distribution, Fig.S1, S2 and S3]. See DOI: 10.1039/b000000x/
- 60 1. F. Vilela, K. Zhang and M. Antonietti. *Energ. Environ. Sci.* 2012, 5, 7819-7832.
  - Y. Xie, T. T. Wang, X. H. Liu, K. Zou and W. Q. Deng, *Nat. Commun.* 2013, 4, 1960-1966.

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- H. Urakami, K. Zhang and F. Vilela, Chem. Commun. 2013, 49, 2353-2355.
- 4. X. Liu, Y. Xu and D. Jiang, J. Am. Chem. Soc. 2012, 134, 8738-41.
- C. Gu, Y. C. Chen, Z. B. Zhang, S. F. Xue, S. H. Sun, K. Zhang, C. M. Zhong, H. H. Zhang, Y. Y. Pan, Y. Lv, Y. Q. Yang, F. H. Li, S. B. Zhang, F. Huang and Y. G. Ma, *Adv. Mater.* 2013, 25, 3443-3448.
- R. Dawson, A. I. Cooper and D. J. Adams, *Prog. in Polym. Sci.* 2012, 37, 530-563.
- 7. J. X. Jiang and A. I. Cooper, Top. In Curr. Chem, 2010, 62, 1-33.
- 10 8. P. M. Budd, N. B. McKeown and D. Fritsch, J. Mater. Chem. 2005, 15, 1977-1986.
- 9. M. P. Tsyurupa and V. A Davankov, *React. Funct. Polym.* 2002, 53, 193-203.
- 10. A. P. Cote, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger <sup>5</sup> and O. M. Yaghi, *Science* 2005, **310**, 1166-1170.
- J. X. Jiang, F. Su, A. Trewin, C. D. Wood, H. Niu, J. T. A. Jones, Y. Z. Khimyak and A. I. Cooper, *J. Am. Chem. Soc.* 2008, **130**, 7710-7720.
- 12. P. M. Budd, B. S. Ghanem, S. Makhseed, N. B. McKeown, K. J. Msayib and C. E. Tattershall, *Chem. Commun.* 2004, **46**, 230-231.
- S. Wan, F. Gandara, A. Asano, H. Furukawa, A. Saeki, S. K. Dey, L. Liao, M. W. Ambrogio, Y. Y. Botros, X. F. Duan, S. Seki, J. F. Stoddart and O. M. Yaghi, *Chem. Mater.* 2011, 23, 4094-4097.
- T. Ben, H. Ren, S. Q. Ma, D. P. Cao, J. H. Lan, X. F. Jing, W. C.
  Wang, J. Xu, F. Deng, J. M. Simmons, S. L. Qiu and G. S. Zhu, *Angew. Chem. Int. Ed.* 2009, **48**, 9457-9460.
- 15. L. J. Murray, M. Dinca and J. R. Long, Chem. Soc. Rev. 2009, 38, 1294-1314.
- Q. Chen, M. Luo, P. Hammershoj, D. Zhou, Y. Han, B. W. Laursen,
  C. G. Yan and B. H. Han, *J. Am. Chem. Soc.* 2012, *134*, 6084-6087.
- 17. J. Q. Ding, B. H. Zhang, J. H. Lu, Z. Y. Xie, L. X. Wang, X. B. Jing and F. S. Wang, *Adv. Mater.* 2009, **21**, 4983-4986.
- Z. H. Zhao, H. Jin, Y. X. Zhang, Z. H. Shen, D. C. Zou and X. H. Fan, *Macromolecules* 2011, 44, 1405-1413.
- 35 19. E. Preis, C. Widling, G. Brunklaus, J. Schmidt, A. Thomas and U. Scherf, ACS. Macro. Lett. 2013, 2, 380-383.
- 20. S. L. Zhang, W. Huang, P. Hu, C. S. Huang, C. Q. Shang, C. J. Zhang, R. Q. Yang and G. L. Cui, *J. Mater. Chem. A* 2015, **3**, 1896–1901
- X. Chen, S. Qiao, Z. Du, Y. Zhou and R. Yang, Macromol. Rapid Commun. 2013, 34, 1181–1185.
- J. Chun, S. Kang, N. Kang, S. M. Lee, H. J. Kim and S. U. Son, J. Mater. Chem. A 2013, 1, 5517-5523.
- E. L. Spitler, B. T. Koo, J. L. Novotney, J. W. Colson, F. J. Uribe-Romo, G. D. Gutierrez, P. Clancy and W. R. Dichtel, *J. Am. Chem. Soc.* 2011, **133**, 19416-19421.
  - 24. B. Kiskan and J. Weber, ACS. Macro. Lett. 2012, 1, 37-40.
  - 25. A. V. Neimark, Y. Z. Lin, P. I. Ravikovitch and M. Thommes, *Carbon* 2009, **47**, 1617-1628.
- C. D. Wood, B. Tan, A. Trewin, H. J. Niu, D. Bradshaw, M. J.
  Rosseinsky, Y. Z. Khimyak, N. L. Campbell, R. Kirk, E. Stockel and A. I. Cooper, *Chem. Mater.* 2007, **19**, 2034-2048.
  - 27. P. Kowalczyk, H. Tanaka, R. Holyst, K. Kaneko, T. Ohmori and J. Miyamoto, *J. Phys. Chem. B* 2005, **109**, 17174-17183.
- 28. J. Germain, F. Svec and J. M. J. Frechet, *Chem. Mater.* 2008, **20**, 7069-7076.
  - 29. S. H. Jhung, H. K. Kim, J. W. Yoon and J. S. Chang, J. Phys. Chem. B 2006, 110, 9371-9374.
  - 30. W. Huang, C.T. Gu, T. Wang, C.Y. S. L. Qiao and R. Q. Yang, *RSC Adv.*, 2014, 4, 62525-62531
- <sup>60</sup> 31. W. Lu, D. Yuan, D. Zhao, C. I. Schilling, O. Plietzsch, T. Muller, S. Brase, J. Guenther, J. Blumel and R. Krishna, Chem. Mater., 2010, 22, 5964–5972.
- M. G. Rabbani and H. M. El-Kaderi, Chem. Mater., 2011, 23,1650– 1653.
- 65 33. J. R. Holst, E. Stockel, D. J. Adams and A. I. Cooper, *Macromolecules* 2010, **43**, 8531-8538.
- R. Dawson, D. J. Adams and A. I. Cooper, *Chem. Sci.* 2011, 2, 1173-1177.