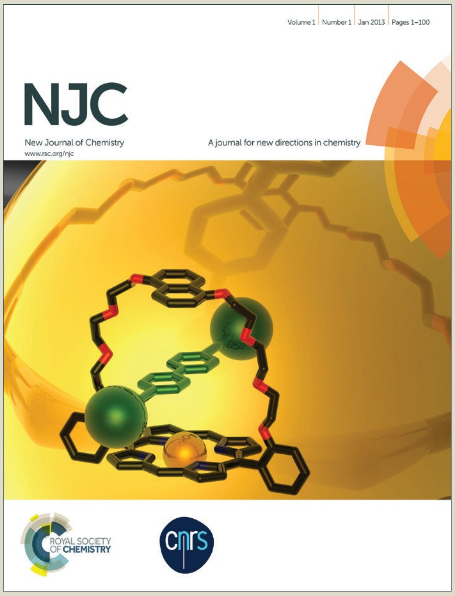
NJC

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. Qiao, H. Wei, T. Wang, W. Huang, C. Gu, R. Yang and L. xiaoyun, *New J. Chem.*, 2015, DOI: 10.1039/C5NJ02567B.



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/njc

View Article Online
DOI: 10.1039/C5NJ02567B

NJC

RSCPublishing

ARTICLE

Ribbon-like Ultramicroporous Conjugated Polycarbazole Network for Gas Storage and Separation

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2015,
Accepted 00th January 2015

DOI: 10.1039/x0xx00000x

www.rsc.org/

Shanlin Qiao‡[a,b], Huan Wei‡[a], Ting Wang[b], Wei Huang[b], Chunyang Gu,[b] Renqiang Yang[b]* and Xiaoyun Li[a]*

A new ultramicroporous conjugated network P-TCzTAT enriched with propeller-like configuration carbazole building block was designed and synthesized by $FeCl_3$ oxidative coupling polymerization at room temperature. The adsorption isotherm of N_2 reveals that the polymer features a high Brunauer-Emmett-Teller (BET) specific surface area of 1028 m^2g^{-1} and predominant narrow pore width at 0.54 nm. The ultramicroporous polymer has strong affinity for CO_2, with high sorption abilities of 18.15% and 10.69% at 273 K/1.1 bar and 298 K/1.1 bar, respectively, which can be ascribed to not only their optimal fraction of ultramicropores but also the high nitrogen-contents derived from carbazole components. P-TCzTAT also exhibited potential applications in gas storage and CO_2/CH_4 and CO_2/N_2 separation.

Introduction

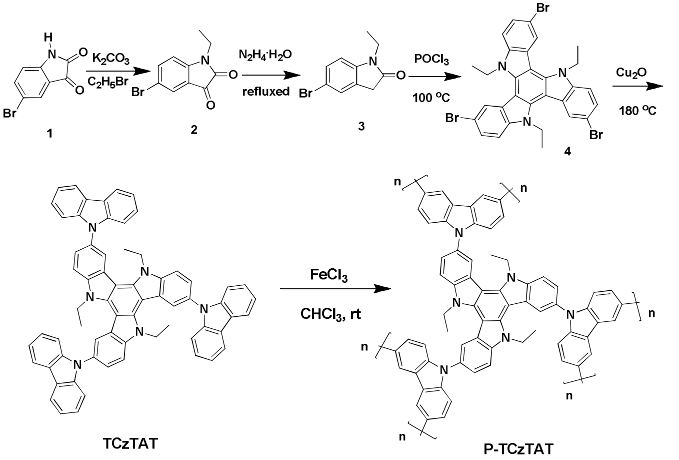
In recent years, global warming has been emerging as an international issue, which was attributed to the increasing emissions of greenhouse gas such as CO_2, CH_4 and so on, because of the rapid consumption of hydrocarbon fuels. The environmental agencies encourage the development of new cost-effective technologies to cope the climate-changing issues.[1] In particular, CO_2 capture and sequestration (CCS) in physical process cooperating with clean energy source such as hydrogen, are of interest to meet the energy and environmental demands.[2] To date, extensive efforts have been devoted to developing CO_2 capture and storage technologies and various adsorbents were prepared and employed for this purpose.[3] Among them, conjugated microporous polymers (CMPs) is a new series of porous materials with pore sizes comparable to traditional porous solid sorbents, such as metal-organic frameworks (MOFs),[4,5] covalent organic frameworks (COFs),[6-8] zeolites,[9,10] metal oxides[11,12] and porous carbons.[13-19] They are usually composed of light elements with large specific surface area and high chemical and thermal stability. The unique feature of CMPs is that they combine the stiff porous structure and conjugated electron system in one bulk material. Those properties made CMPs to be an invaluable tool for less energy penalty and cost associated with state-of-the-art gas uptake application.[20,21]

Micropores are classified into ultramicropores (pore widths < 0.7 nm) and supermicroporous (0.7 nm <pore widths<2 nm).[22] However, the wide pore size distribution is the typical property of most pore organic polymers (POPs) such as hyper-crosslinked polymers (HCPs),[23] polymers of intrinsic microporosity (PIMs),[24] and it is hard to get a pore with unique distribution like inorganic porous materials. For example, most CMP materials with superior surface areas exhibit broad pore width distribution from microporous to 10 nm,[25,26] suggesting the presence of both micropores and mesopores.[26] Efficient gas adsorption and separation of the CMPs depend on the high surface areas, narrow pore distribution and chemical functionality.[27] Both the initial building blocks and the polymerization approaches show great influence on the above three parameters. Among various starting materials, the unique structure of carbazole-containing block is a superior candidate for polymerization as their potential active sites. It is well-known that the 3- and 6-positions of carbazole are oxidation sites to construct conjugated microporous materials through $FeCl_3$ oxidative coupling.[28,29] And it is worth pointing out that besides the easy synthesis strategies, the carbazole-based CMPs displayed remarkable CO_2 capture and sequestration ability because of their high nitrogen-contents.[30,31]

In this work, we report a ribbon-like conjugated polymer P-TCzTAT straightforward synthesized by $FeCl_3$ oxidative coupling polymerization at room temperature (Scheme 1). This facile polymerization approach, using single building block without any expensive catalysts and just requiring mild conditions, is an economical and easier approach towards the synthesis of conjugated pore networks in high yield. In addition, both the flank part and the centre part of the starting

View Article Online
DOI: 10.1039/C5NJ02567B

block were consisted with carbazoles. The result will provide us insight about the effect of the propeller-type carbazole enriched system on the gas adsorption ability. The obtained polymer P-TCzTAT exhibits high surface area (1028 m^2 g^{-1}), narrow ultramicropore width (0.54 nm), and excellent gas storage and separation capability.



Scheme 1 Synthetic route of the carbazole-enriched network P-TCzTAT.

Results and discussion

The synthesis of the network P-TCzTAT is depicted in Scheme 1. Monomer TCzTAT with propeller-like geometrical configuration was prepared from carbazole by Ullmann reaction catalyzed by cuprous. The rigid fused ring of carbazole is beneficial for formation of polymers with permanent porosity stability, and the *N*-containing structure can increase CO$_2$-framework interactions by means of the dipole-quadrupole interactions.[32] Inarching the short-chain ethyl groups on the core will ensure the solubility of monomer to obtain a large skeleton structure, and meanwhile, short and soft chains can avoid the blocking of the micropores. TCzTAT, the core of monomer, features a fused triazatruxene unit of asteroid structure, which is a typical two-dimensional (2D) planar configuration.[33] The polymerization of TCzTAT extends the discotics core with three flanked carbazoles, which will change the configuration of the polymer from 2D to 3D.

The structure of P-TCzTAT network was confirmed by FT-IR spectra (Fig. 1a) and solid state magic angle spinning ^{13}C CP/MAS NMR spectra with assignments of the resonances as shown in Fig. 1b. The broad peaks in FTIR spectrum indicated the high crosslinking of the polymer and 744 cm^{-1}, 1224 cm^{-1}, and 1469 cm^{-1} are the characteristics vibration mode of carbazole unit. The NMR spectra shows a signal at 14 ppm which corresponds to the carbon atoms of the ethyl group. Thermogravimetric analysis (TGA, Fig. S1) trace shows that the thermal decomposition temperature (T_d 5 wt%) is up to ca. 280 °C. Powder X ray diffraction (P-XRD, Fig. 1c) revealed P-TCzTAT was amorphous aggregation without any crystalline phase. Scanning electron microscopy image (SEM, Fig. 1d) showed P-TCzTAT has ribbon-like network which is different from other reported porous organic polymers.[34]

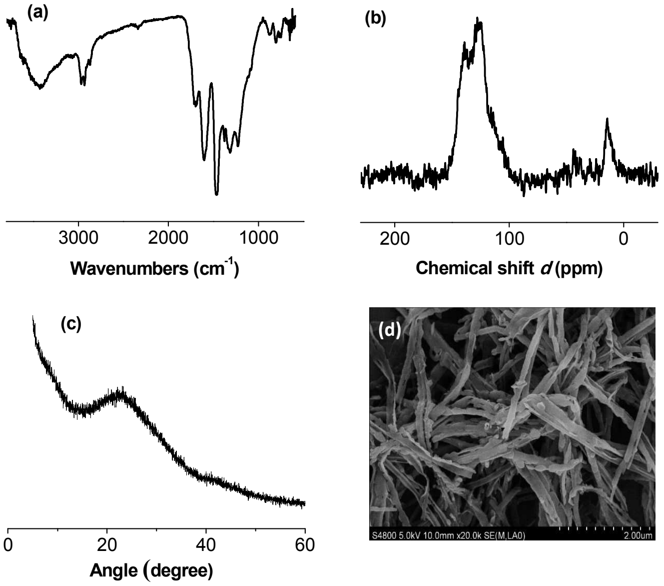


Fig. 1 (a) FT-IR spectra, (b) ^{13}C CP/MAS NMR spectra, (c) Powder X ray diffraction and (d) Scanning electron microscopy image.

The porosity properties of P-TCzTAT were measured by adsorption analysis using nitrogen as the probe molecule at 77 K shown in Fig. 2a. The isotherms demonstrate steep rise in nitrogen uptake at the relative pressure (P/P$_0$) less than 0.01, indicating significant microporosity in the obtained network. The result was evidenced by the pore size distribution derived from quenched solid density functional theory (QSDFT) in Fig. 2b. QSDFT is a multicomponent DFT, in which the network is treated as one of the components of the adsorbate-adsorbent system and this model has been demonstrated that it can significantly improve the accuracy of pore distribution compared to nonlinear density functional theory NL-DFT.[35]

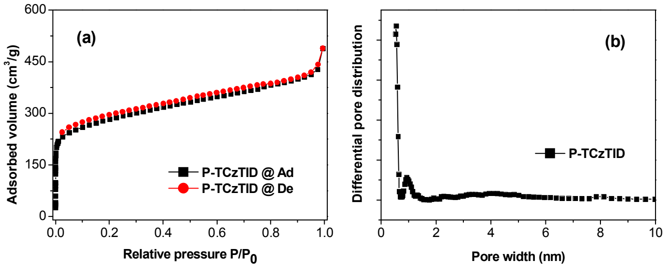


Fig. 2 (a) N$_2$ adsorption-desorption isotherm of the carbazole based network P-TCzTAT at 77 K, and (b) pore size distribution obtained by the QSDFT method.

P-TCzTAT has the dominant ultramicropores width centered at 0.54 nm which is beneficial for gas storage and separation. When the Brunauer–Emmett–Teller (BET) model is adopted to calculate the apparent surface area, the value of P-TCzTAT is 1028 m^2 g^{-1}. Its total pore volume and micropore volume calculated at P/P$_0$ = 0.99 and 0.1 are 0.76 cm^{3}g^{-1} and 0.4 cm^3 g^{-1},

View Article Online
DOI: 10.1039/C5NJ02567B

respectively. It is important to note the limitation of the N_2 with a kinetic diameter of 3.64 Å, which is difficult to probe the ultramicropore less than 5 Å,[36] so we believe that the actual surface area of P-TCzTAT is higher than the value calculated here. P-TCzTAT, featuring with high BET surface area, ultramicropores and electron-rich system, will be a good candidate for gas sorption and storage.

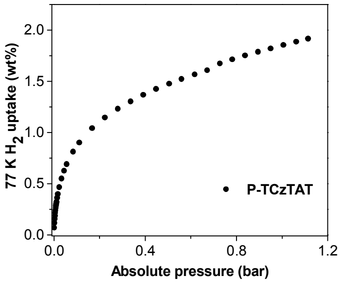


Fig. 3 H_2 adsorption isotherm of network P-TCzTAT at 77 K.

Hydrogen physisorption by porous materials is an immensely important topic in the clean energy application. The H_2 sorption isotherm of P-TCzTAT was measured at 77 K (Fig. 3), which shows a 1.92 wt% H_2 uptake at 77 K and 1.1 bar. This value is attractive compared to most of pore materials under the similar condition, for example, polyaniline is 0.85 wt%,[37] CMP-2 is 0.91 wt%,[38] COF-103 is 1.25 wt%,[39] PPN-3 is 1.58 wt%.[40] The adsorption curve shows that no saturation is achieved, indicating that a larger H_2 capacity can be obtained at higher pressure condition.

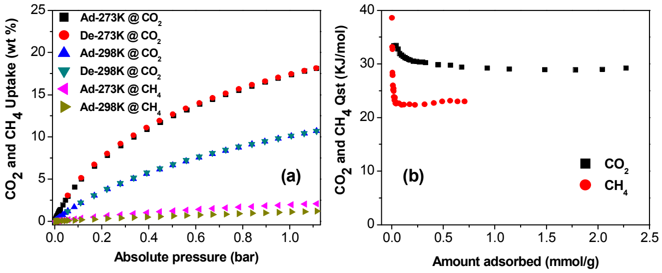


Fig. 4 (a) Adsorption isotherms of CO_2 and CH_4, (b) variations of isosteric enthalpies with the adsorbed amount of CO_2 and CH_4.

The CO_2 and CH_4 adsorption isotherms were collected at 273 K/0~1.1 bar and 298 K/0~1.1 bar, respectively, as shown in Fig 4a. CO_2 physisorption process is reversible as the desorption branches are very close to those of adsorptions. The CO_2 uptake capacity of P-TCzTAT can be up to 18.15 wt% and 10.69 wt% at 273 K/1.1 bar and 298 K/1.1 bar, respectively. The isosteric enthalpy (Qst) of P-TCzTAT for CO_2 uptake is calculated to be 33.42 KJ mol^{-1} at zero loading based on Clausius-Clapeyron equation shown in Fig. 4b. It can also retain the heats of adsorption at 29 KJ mol^{-1} as the increasing adsorption quantities, which indicated a superior CO_2 capture capacity despite the relatively modest surface area. The high CO_2 uptake may be ascribed to the ultramicropores and nitrogen-rich surfaces. CO_2 is an acidic adsorbate with a quadrupole moment, which influences the adsorption behavior inside the ultramicropores structure and on the alkaline surface. The performance of the carbazole-enriched polymer P-TCzTAT is competitive to the reported MOPs under the similar condition, such as BLP-1H of 7.4 wt%,[41] COF-103 of 7.6 wt%,[39] MCTFs of 13.9 wt%,[42] CMP-1 of 9.02 wt%,[43] etc.

Physisorption of methane in principle can provide a safe and economical approach for energy densities storage comparable to compressed gas at much lower pressures. The CH_4 uptake for P-TCzTAT was measured up to 1.1 bar (Fig 4a). The CH_4 uptake of P-TCzTAT is 2.09 wt% at 273 K/1.1 bar and 1.19 wt% at 298 K/1.1bar, respectively. It is noteworthy that the isosteric heat of P-TCzTAT can be up to 38.55 KJ mol^{-1} at zero loading and keep almost stable at 22 KJ mol^{-1} on the whole loading range (Fig 4b), which is higher than the Qst of non-conjugated pore networks.[44] The high isosteric heat allows the possibility of greater storage capacities at lower pressures for materials with appropriate microporous size and volume.

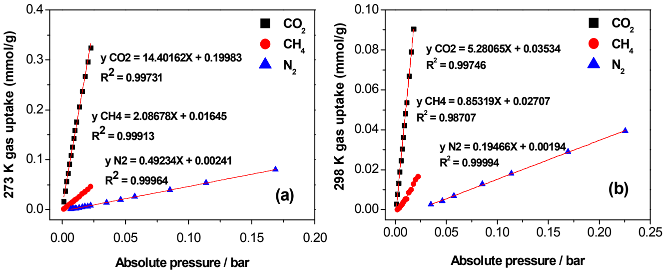


Fig. 5 Initial gas uptake slopes of the network at (a) 273 K and (b) 298 K.

To further investigate the separation ability of polycarbazole P-TCzTAT, the gas selectivity of the polymer for CO_2/CH_4 and CO_2/N_2 were estimated using the ratios of the Henry law constants calculated from the initial slopes of the pure component isotherms at low pressure range,[45] as shown in Fig. 5. The calculated CO_2/CH_4 selectivity of P-TCzTAT at 273 K/1.1 bar and 298 K/1.1 bar is 6.9 and 6.4, respectively. The selectivity of CO_2/N_2 at 273 K/1.1 bar and 298 K/1.1 bar is 29.3 and 27.1, respectively. One can observe that P-TCzTAT show stabile CO_2/CH_4 and CO_2/N_2 selectivity even if the temperature rises from 273 K to 298 K. It could be concluded that the ultramicropores (pore width < 0.7 nm) is advantageous for gas separation.

Conclusions

In summary, a new carbazole-enriched polymer was designed and synthesized with a facile method. The polymer features unique ultramicroporous structure. Extending the planar core of triazatruxene with three carbazoles increases the torsion angle and forms a propeller-like building block. The obtained network P-TCzTAT exhibits narrow pore distribution with the domain pore centerd at 0.54 nm. Gas (H_2, CO_2 and CH_4) adsorption isotherms show that the H_2 storage can reach 1.92 wt % (1.1 bar and 77 K) and uptake capacity for CO_2 and CH_4

View Article Online
DOI: 10.1039/C5NJ02567B

is up to 18.15 wt % and 2.09 wt% (1.1 bar and 273 K), respectively. The obtained network and the excellent adsorption ability provide us an approach to further understand the topological structure design, polymerization method with gas uptake performance in clean energy and environmental protection fields.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21274161, 51173199, 51303197 and 51573205), Ministry of Science and Technology of China (2010DFA52310).

Notes and references

[a] *Institute of Chemical Industry and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang 050000, China*
[b] *CAS Key Laboratory of Bio-based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China.*
‡ *These authors contributed equally to this work.*

Experimental section

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 600M 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 5 kV and working distance 10.0 mm. Samples were coated on a thin layer of Au before investigation. For gas adsorption test, P-TCzTAT network was degassed at 120 °C for 800 min under vacuum before analysis. BET surface areas and pore size distributions were measured by nitrogen adsorption-desorption at 77 K. H_2 isotherms were measured at 77 K up to 1.1 bar. CO_2, CH_4 and N_2 isotherms were measured at 273 K and 298 K up to 1.1 bar. All the gas adsorption isotherms were tested on a Quantachrome Instruments Autosorb-iQ-MP-VP volumetric adsorption analyzer.

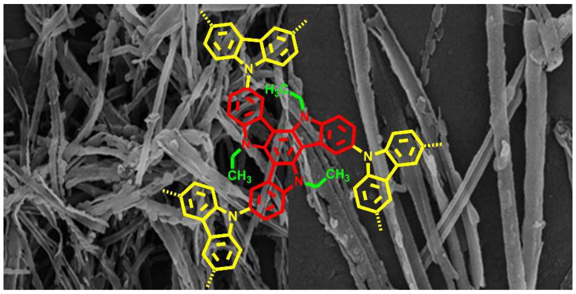
1. Z. Cao, H. Jiang, H. Luo, S. Baumann, W. A. Meulenberg, J. Assmann, L. Mleczko, Y. Liu and J. Caro, *Angew. Chem. Int. Ed.,* 2013, **52**, 13794-13797.
2. K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae and J. R. Long, *Chem. Rev.,* 2012, **112**, 724-781.
3. Y. Zhu, H. Long, W. Zhang, *Chem. Mater*., 2013, **25**, 1630-1635.
4. J.-R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, et al. *Coord. Chem. Rev.,* 2011, **255**, 1791–1823.
5. K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, et al. *Chem. Rev*., 2012, **112**, 724–781.
6. H. Furukawa, O. M. Yaghi, *J. Am. Chem. Soc*., 2009, **131**, 8875–8883.
7. X. Feng, X. Ding, D. Jiang, *Chem. Soc. Rev.,* 2012, **41**, 6010–6022.
8. Y.-F. Zhao, K.-X. Yao, B.-Y. Teng, T. Zhang, Y. Han, *Energ. Environ. Sci.,* 2013, **6**, 3684–3692.
9. D. Saha, Z.-B. Bao, F. Jia, S.-G. Deng, *Environ. Sci. Technol.,* 2010, **44**, 1820–1826.
10. F. Akhtar, Q.-L. Liu, N. Hedin, L. Bergstro¨m. *Energ. Environ. Sci.,* 2012, **5**, 7664–7673.
11. B.-J. Kim, K.-S. Cho, S.-J. Park, *Colloid Interface Sci.,* 2010, **342**, 575–578.
12. M. Bhagiyalakshmi, P. Hemalatha, M. Ganesh, P. M. Mei, H. T. Jang, *Fuel,* 2011, **90**, 1662–1667.
13. M. Sevilla, R. Mokaya, A. B. Fuertes, *Energ. Environ. Sci.,* 2011, **4**, 2930-2936.
14. G.-P. Hao, W.-C. Li, D. Qian, A.-H. Lu, *Adv. Mater.*, 2010, **22**, 853–857.
15. N. P. Wickramaratne, M. Jaroniec, *J. Mater. Chem. A,* 2013, **1**, 112–116.
16. Y. Jin, S. C. Hawkins, C. P. Huynh, S. Su, *Energ. Environ. Sci.,* 2013, **6**, 2591–2596.
17. H. Wei, S. Deng, B. Hu, Z. Chen, B. Wang, J. Huang, et al. *ChemSusChem.,* 2012, **5**, 2354–2360.
18. M. Sevilla, P. Valle-Vigo´n, A. B. Fuertes, *Adv. Funct. Mater.,* 2011, **21**, 2781–2787.
19. V. Presser, J. McDonough, S.-H. Yeon, Y. Gogotsi, *Energ. Environ. Sci.,* 2011, **4**, 3059–3066.
20. A. I. Cooper, *Adv. Mater.,* 2009, **21**, 1291-1295.
21. F. Vilela, K. Zhang and M. Antonietti, *Energ. Environ. Sci.,* 2012, **5,** 7819.
22. K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniewska, *Pure. Appl. Chem.,* 1985, **57**, 603-619.
23. Y. Luo, B. Li, W. Wang, K. Wu and B. Tan, *Adv. Mater.*, 2012, **24**, 5703-5707.
24. A. Del Regno, A. Gonciaruk, L. Leay, M. Carta, M. Croad, R. Malpass-Evans, N. B. McKeown and F. R. Siperstein, *Ind. Eng. Chem. Res.*, 2013, **52**, 16939-16950.
25. J.-X. Jiang, A. Laybourn, R. Clowes, Y. Z. Khimyak, J. Bacsa, S. J. Higgins, D. J. Adams and A. I. Cooper, *Macromolecules*, 2010, **43**, 7577-7582.
26. J.-X. Jiang, F. Su, H. Niu, C. D. Wood, N. L. Campbell, Y. Z. Khimyak and A. I. Cooper, *Chem. Commun.*, 2008, **4**, 486-488.
27. H. Frost, T. Duren and R. Q. Snurr, *J. Phys. Chem. B*, 2006, **110**, 9565-9570.
28. Q. Chen, M. Luo, P. Hammershøj, D. Zhou, Y. Han B. W. Laursen, C.-G. Yan and B.-H. Han, *J. Am. Chem. Soc.,* 2012, **134**, 6084–6087.
29. S. Qiao, Z. Du, C. Yang, Y. Zhou, D. Zhu, J. Wang, X. Chen and R. Yang, *Polymer,* 2014, **55,** 1177–1182.
30. X. Zhu, S. M. Mahurin, S.-H. An, C.-L. D-Thanh, C. Tian, Y. Li, L. W. Gilll, E. W. Hagaman, Z. Bian, J.-H. Zhou, J. Hu, H. Liu, and S. Dai, *Chem. Commum,* 2014, **50**, 7933-7936.
31. Q. Chen, D.-P. Liu, M. Luo, L.-J. Feng, Y.-C. Zhao, and B.-H. Han, *Small*, 2014, **10**, 308-315.
32. S. Qiao, Z. Du and R. Yang, *J. Mater. Chem. A*, 2014, **2,** 1877-1885.
33. B. Gomez-Lor, B. Alonso, A. Omenat and J. L. Serrano, *Chem. Commun.*, 2006, **48**, 5012-5014.
34. Q. Chen, M. Luo, P. Hammershøj, D. Zhou, Y. Han, B. W. Laursen, C.-G. Yan and B.-H. Han, *J. Am. Chem. Soc.*, 2012, **134**, 6084-6087.
35. A. V. Neimark, Y. Lin, P. I. Ravikovitch and M. Thommes, *Carbon*, 2009, **47**, 1617-1628.

DOI: 10.1039/C5NJ02567B

36. S. Ma, D. Sun, X.-S. Wang and H.-C. Zhou, *Angew. Chem. Int. Ed.*, 2007, **46**, 2458-2462.
37. J. Germain, F. Svec and J. M. J. Frechet, *Chem. Mater.*, 2008, **20**, 7069-7076.
38. 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.
39. H. Furukawa and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 8875-8883.
40. W. Lu, D. Yuan, D. Zhao, C. I. Schilling, O. Plietzsch, T. Muller, S. Bräse, J. Guenther, J. Blümel, R. Krishna, Z. Li and H.-C. Zhou, *Chem. Mater.*, 2010, **22**, 5964-5972.
41. K. T. Jackson, M. G. Rabbani, T. E. Reich and H. M. El-Kaderi, *Polym. Chem.,* 2011, **2**, 2775-2777.
42. X. Liu, H. Li, Y. Zhang, B. Xu, S. A, H. Xia and Y. Mu, *Polym. Chem.*, 2013, **4**, 2445-2448.
43. R. Dawson, D. J. Adams and A. I. Cooper, *Chem. Sci.*, 2011, **2**, 1173-1177.
44. C. D. Wood, B. Tan, A. Trewin, F. Su, M. J. Rosseinsky, D. Bradshaw, Y. Sun, L. Zhou and A. I. Cooper, *Adv. Mater.*, 2008, **20**, 1916-1921.
45. G. Li and Z. Wang, *J. Phys. Chem. C*, 2013, **117**, 24428-24437.

View Article Online
DOI: 10.1039/C5NJ02567B

Graphical abstract



Ribbon-like ultramicroporous conjugated polycarbazole network P-TCzTAT have high BET surface area and narrow pore width distribution was synthesized.