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Conjugated microporous polymers with the azide groups: A new strategy for postsynthetic fluoride functionalization en route for enhanced CO_2 adsorption properties

Di Cui,[a] Chan Yao[a] and Yanhong Xu*[a,b]

A series of conjugated microporous polymers (CMPs) has been synthesized based on zinc-porphyrin building block. Azide groups incorporated within the pores of the CMPs were subjected to alkyne click condition via a facile, one-step quantitative procedure, the resultant porous frameworks exhibited enhanced CO_2 sorption properties.

We face currently one of the greatest global problems is a rapid rise of CO_2 in the atmosphere due to anthropogenic activities. In the future, the situation could become worse because population expansion and industrial development will produce a continuous increase of carbon dioxide emissions after the combustion of carbon based energy resources.[1] It is a still challenging to develop effective techniques or strategies that can effectively capture CO_2 and alleviate the dilemma. Carbon capture and sequestration (CCS) technology has been proposed to solve this problem, which will play an important role in meeting the huge demand for social development.[2] In CCS technology, new materials can capture CO_2 with low-cost, efficient and durable manner is the breakthrough core of the success of CCS.[3]

Conjugated microporous polymers (CMPs) are a class of porous organic materials, possessing π-conjugation, a fine control of nanopores, and high chemical and thermal stability.[4] These merits of CMPs coupled with structural diversity, high mechanical robustness, and high surface areas make it an attractive platform for designing functional materials and have shown outstanding performance in various fields, including gas adsorption,[5] light emitters,[6] light-harvesting antennae,[7] heterogeneous catalyst,[8] supercapacitive energy storage,[9] and fluorescent sensors.[10] Since Cooper and co-workers reported the first CMPs in 2007,[11] over the past 10 years, more than hundreds CMPs have been constructed. In contrast with metal-organic frameworks (MOFs) and zeolites, a distinct feature of CMPs is that they have π-conjugation and permanent pores. In particular, CMPs based on metalloporphyrin building blocks not only are prone to be functionalized, but also have excellent thermal stability, which is ascribed to the hybrid properties of metalloporphyrin segments.[12] Furthermore, some activated sites of the metalloporphyrin, such as nitrogen atoms and built-in unsaturated metal sites, resulting in the metalloporphyrin-based CMPs can be an outstanding gas adsorption candidate.[13] However, in spite of the great progress achieved so far, the construction of CMPs that hold high performance in CO_2 capture at low pressure and humid condition still faces great challenges.

CMPs are quite promising porous materials due to their high porosity as well as high tunability of their pore surface functionality, which is important in enhancing interactions with CO_2. Given the highly modular nature of CMPs, the introduction of chemical functionality should be straightforward. Previous studies reported that surface modification of porous materials with polar groups, such as -COOH,[14a] -NO_2,[14b] -SO_3H,[14c] -OH,[14d] arylamines,[14e] and heterocyclic nitrogen atoms,[14f] which can significantly improve binding energy of CO_2 because of the high quadrupole momentand polarizability of CO_2, thereby increasing CO_2 uptake and/or CO_2 selectivity. It is well known that perfluorinated alkanes are known to be more hydrophobic than the corresponding hydrocarbons, so they can be tolerant to water and remain their excellent capture performance in the moisture condition, which is desirable in practical applications.[15a] More interestingly, the high electronegativity of fluoride would further promote CO_2 adsorption through electrostatic interactions.[15b] Recently, although MOF materials have emerged to show remarkable CO_2-uptake capacities, however, they are often very unstable toward moisture.

Consider above aspects, herein, we report access to fluoride

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[a] Key Laboratory of Preparation and Applications of Environmental Friendly Materials (Jilin Normal University), Ministry of Education, Changchun, 130103, China, Email: xuyh198@163.com
[b] Key Laboratory of Functional Materials Physics and Chemistry of the Ministry of Education, Jilin Normal University, Siping 136000, China

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: Details regarding the synthetic procedure, full methods, Nitrogen sorption curves, FT-IR spectra, TGA curves, PXRD profiles, TEM images, F1s XPS, UV-vis and corresponding data of gas adsorption properties. See DOI: 10.1039/x0xx00000x

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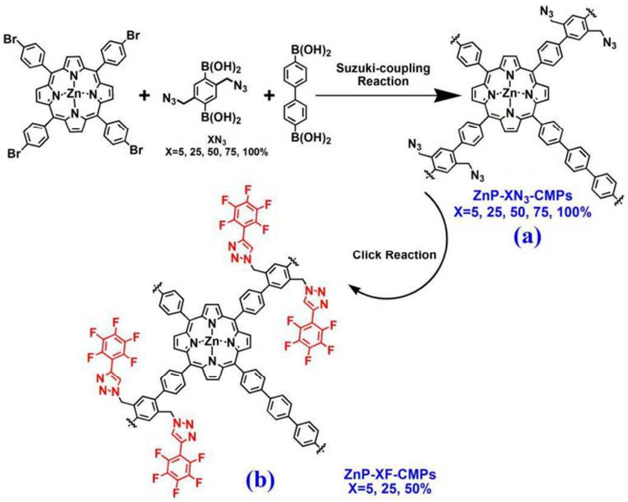
functionalized CMPs using a novel one-step fluoride "clicking post-synthetic modification procedure", performed under relatively mild synthetic condition (Scheme 1). The fluoride contents in the CMP skeletons can be tunable by controlling the percent of azide groups. We demonstrated this strategy by controlling integration of fluoride sites into the pore to synthesize CMPs containing different percentages of fluoride that exhibited enhanced capture capacity in adsorption. ZnP-XN_3-CMPs (X = 5, 25, 50, 75 and 100%) were synthesized by the Suzuki-coupling reaction (ESI†). A three-component reaction system consisting of 5,10,15,20-tetrakis(4-tetraphenylbromo)zinc porphyrin as the core and a mixture of 4,4′-biphenyldiboronic acid (A) and (2,5-bis(azidomethyl)-1,4-phenylene)diboronic acid (B) at varying molar ratios (X = [B]/([A] + [B])×100 = 5, 25, 50, 75 and 100%) as the linkage units were developed to construct the fluoride functionalized-CMPs, by allowing the integration of azide units of varying contents into the edges (Scheme 1, [ZnP-XN_3-CMPs, X = 5, 25, 50, 75 and 100%). Fluoride functionalized-CMPs were synthesized via a mild one-step copper-catalyzed alkyne–azide coupling reaction. In a typical experiment, ZnP-XN_3-CMPs (X = 5, 25, 50, 75 and 100%) is soaked in DMF at 50 °C for three days to obtain ZnP-XF-CMPs (X = 5, 25, 50, 75 and 100%), respectively (see ESI†).



Scheme 1. Schematic representation of (a) ZnP-XN_3-CMPs (X = 5, 25, 50, 75 and 100%), (b) ZnP-XF-CMPs (X = 5, 25 and 50%).

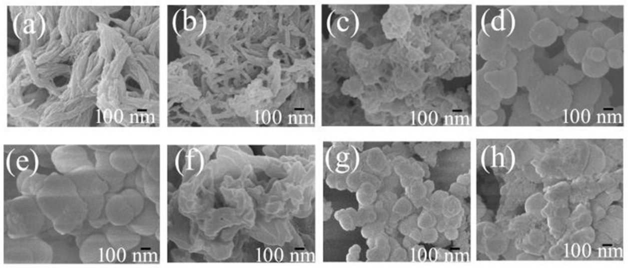


Fig. 1 FE-SEM images of (a) ZnP-5%N_3-CMPs, (b) ZnP-25%N_3-CMPs, (c) ZnP-50%N_3-CMPs, (d) ZnP-75%N_3-CMPs, (e) ZnP-100%N_3-CMPs, (f) ZnP-5%F-CMPs, (g) ZnP-25%F-CMPs, and (h) ZnP-50%F-CMPs, respectively.

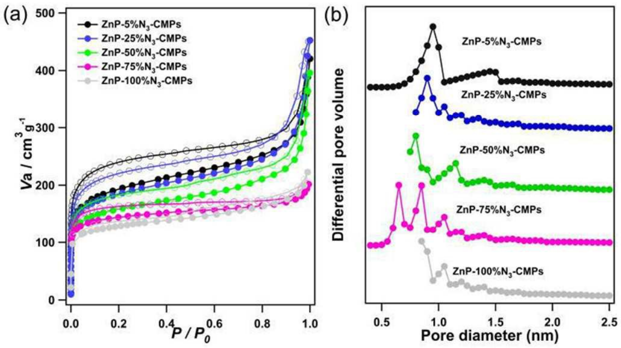


Fig. 2 Nitrogen adsorption (filled circle) and desorption (open circle) isotherm profiles of (a) ZnP-XN_3-CMPs (X= 5, 25, 50, 75 and 100%) measured at 77 k. Pore size distribution profiles of (b) ZnP-XN_3-CMPs (X= 5, 25, 50, 75 and 100%).

Elemental analysis confirmed that the weight percentages of C, H, and N contents were close to the theoretical values of their infinite 2D polymers. In the FT-IR spectra, a strong -N_3 stretch can be observed at about 2160 cm^{-1} in the ZnP-XN_3-CMPs (X = 5, 25, 50, 75 and 100%) (Fig. S1 and Fig. S2, ESI†), and the intensities of the bands increased with increasing azide contents, indicating the successful integration of azide units at different contents in the pores of ZnP-XN_3-CMPs (X = 5, 25, 50, 75 and 100%). After the click reaction, the disappearance of the vibration bands at around 2120 cm^{-1}, implying that all the -N_3 units in the CMPs are clicked to bear the reactive sites (Fig. S2, ESI†). However, IR stretches from unreacted azide groups could still be observed at about 2114 cm^{-1} in ZnP-75%N_3-CMPs and ZnP-100%N_3-CMPs, suggesting that the azide–alkyne coupling is incomplete. Field-emission scanning electron microscopy (FE-SEM) displayed that the original ZnP-XN_3-CMPs (X = 5 and 25%) adopt ribbon-like shape with the size of 10-100 nm (Fig. 1a and 1b). Interestingly, ZnP-XN_3-CMPs (X = 50, 75 and 100%) adopt spherical shape, and the size increased along with increase of azide contents in the skeletons (Fig. 1c-1e). In addition, the clicking ZnP-XF-CMPs (X = 5, 25 and 50%) adopt also spherical shape with the size of 200-300 nm (Fig. 1f-h). High-resolution transmission electron microscopy (HR-TEM) revealed ZnP-XN_3-CMPs (X = 5, 25, 50, 75 and 100%) and ZnP-XF-CMPs (X = 5, 25 and 50%) displayed the homogeneous distribution of nanometer-scale pores in the textures (Fig. S3, ESI†). X-ray diffraction profiles also showed that ZnP-XN_3-CMPs (X = 5, 25, 50, 75 and 100%) and ZnP-XF-CMPs (X = 5, 25 and 50%) are amorphous (Fig. S4, ESI†). And ZnP-XN_3-CMPs (X = 5, 25, 50, 75 and 100%) are stable up to 220 °C as revealed by thermal gravimetric analysis (Fig. S5, ESI†). Furthermore, X-ray photoelectron spectroscopy (XPS) results displayed fluoride element still existed in ZnP-XF-CMPs (X = 5, 25 and 50%) after clicking, and the peak intensity increased with the fluoride content increased (ESI, Fig.S6). UV-vis spectra of the CMPs networks were recorded in the solid state (ESI, Fig. S7). ZnP-XN_3-CMPs (X = 5, 25 and 50%) polymers showed a broad

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absorption across the wavelength range 300-800 nm, however, the polymer networks ZnP-XF-CMPs (X = 5, 25 and 50%) exhibited a little bathochromic shift of around 5-42 nm (Fig. S7). These results indicated clearly that the electronic states of the CMPs systems can be adjusted and tuned by increasing the fluoride contents.

Porous structures were investigated by nitrogen sorption isotherm measurements at 77 K. In light of IUPAC classification, ZnP-XN_3-CMPs (X= 5, 25 and 50%) exhibit a combination of types I and IV; the other two polymers (ZnP-XN_3-CMPs (X= 75 and 100%)) show type I isotherm curves (Fig. 2a). From all isotherms, we can see all the networks show an evident hysteresis loop, which is partly attributed to the swelling in a flexible polymer network, as well as mesopore contribution.[16] The presence and magnitude of this hysteresis may be an indication of the softness of the materials. Moreover, a sharp rise in the high pressure region (P/P_0 > 0.8) is also observed in the sorption isotherms of ZnP-XN_3-CMPs (X= 5, 25 and 50%), respectively, suggesting that the three materials possess some macropores, which is attributed to the nitrogen condensation in interparticular voids formed by the aggregation of polymer microspheres, which is similar to the previous reports.[16] Surprisingly, the Brunauer–Emmett–Teller (BET) surface areas of CMPs decreased along with increasing amount of azide groups in the reaction system. For example, the BET surface areas of ZnP-5%N_3-CMPs, ZnP-25%N_3-CMPs, ZnP-50%N_3-CMPs, ZnP-75%N_3-CMPs and ZnP-100%N_3-CMPs are 711, 685, 654, 565 and 477 m^2 g^{-1}, and their corresponding pore volumes are 0.7659, 0.7029, 0.6812, 0.4383, and 0.3446 cm^3 g^{-1}, respectively (Table S1, ESI†). Pore size distributions were calculated by the Saito-Foley (SF) method, which revealed pore sizes centered at 0.6-1.5 nm (Fig. 2b), and main pores exhibited a decrease trend with the increasing azide content in the pores (Fig. 2b). After the click reaction, the BET surface areas of fluoride functionalized-CMPs are 430, 362, 240, 148, and 37 m^2 g^{-1} for ZnP-5%F-CMPs, ZnP-25%F-CMPs, ZnP-50%F-CMPs, ZnP-75%F-CMPs, and ZnP-100%F-CMPs, respectively (Fig. S8, Table S1, ESI†). The pore volumes are 0.6767, 0.5211, 0.3762, 0.1790 and 0.1187 cm^3 g^{-1} for ZnP-5%F-CMPs, ZnP-25%F-CMPs, ZnP-50%F-CMPs, ZnP-75%F-CMPs, and ZnP-100%F-CMPs, respectively.

In order to clarify whether the azide groups affect the BET surface areas and pore volumes in the CMPs skeletons. We synthesized a series of CMPs (ZnP-XC-CMPs (X = 5, 25, 50, 75 and 100%, C= benzene-1,4-diboronic acid) without azide groups under the same reaction condition (Scheme S1, ESI†). A three-component reaction system consisting of 5,10,15,20-tetrakis(4-tetraphenylbromo)zinc porphyrin as the core and a mixture of 4,4'-biphenyldiboronic acid (A) and benzene-1,4-diboronic acid (C) at varying molar ratios (X = [C]/([A] + [C])×100 = 5, 25, 50, 75 and 100%) as the linkage units were developed to construct the CMPs (ZnP-XC-CMPs (X = 5, 25, 50, 75 and 100%)). These CMPs also exhibited type I and IV isotherm curves, which are similar to those of ZnP-XN_3-CMPs (X= 5, 25 and 50%) (Fig. S9 and Table S2, ESI†). However, they showed very similar BET surface areas of 430-483 m^2 g^{-1}, main pore sizes of 0.70-0.85 nm and pore volumes of 0.4675-0.5333 cm^3 g^{-1} (Table S2, ESI†). These results demonstrated the azide groups really affect the pore diameters when we tuned the azide content in the pores of CMPs skeletons.

Given that the CMPs have tuned functional azide groups pointing into the pores, we were naturally interested in evaluating their absorbent potential. First, we investigated the effect of the azide content on the CO_2 adsorption behaviors of ZnP-XN_3-CMPs (X= 5, 25, 50, 75 and 100%) at 298 K and 1.0 bar (Fig. 3a and Table S1). Interestingly, we observed an increased trend in the adsorption of CO_2 with the raise of azide contents in the skeletons. For instance, ZnP-5%N_3-CMPs at 298 K and 1.0 bar exhibited a capacity of 26 mg g^{-1} (blue circle), ZnP-25%N_3-CMPs (green circle) and ZnP-50%N_3-CMPs (red circle) displayed capacities 31 and 49 of mg g^{-1}, respectively. However, the CO_2 capacity of CMPs showed a decrease trend when the azide content is higher than 75%, such as ZnP-75%N_3-CMPs (cyanl circle) and ZnP-100%N_3-CMPs (gray circle) exhibited the CO_2 uptake of 43 and 40 mg g^{-1}. It is reasonable to assume that this remarkable enhancement of CO_2 adsorption capacity is due to the pore size of CMPs more suitable for CO_2 adsorption with the increase of azide contents in the pores. At 273 K, the capacity of CO_2 is 44, 54, 87, 72 and 69 for mg g^{-1} for ZnP-5%N_3-CMPs, ZnP-25%N_3-CMPs, ZnP-50%N_3-CMPs, ZnP-75%N_3-CMPs and ZnP-100%N_3-CMPs, respectively (Fig. 3b and Table S1). The result suggested that the pore properties (pore size, surface area and pore volume) of CMPs could be finely tuned by introducing proper edge units to porous polymer networks.

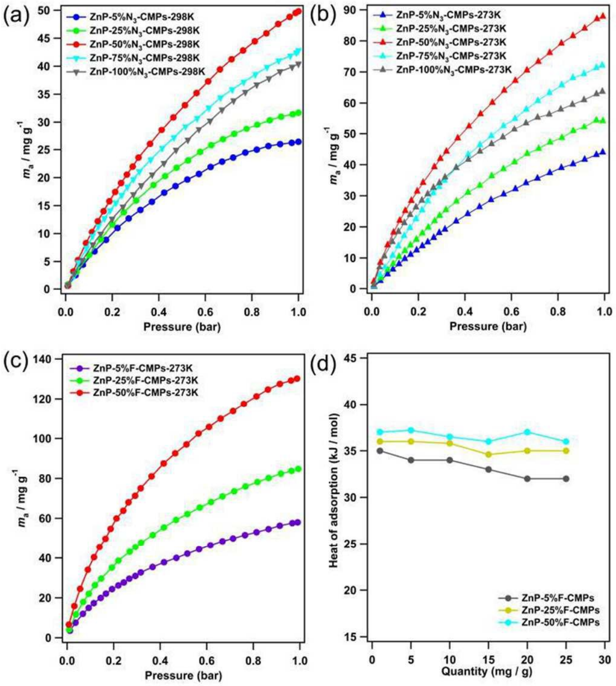

Fig. 3 CO_2 adsorption isotherms. (a) ZnP-XN_3-CMPs (X= 5, 25, 50, 75 and 100%) at 298 K and 1.0 bar; (b) ZnP-XN_3-CMPs (X= 5, 25, 50, 75 and 100%) at 273 K and 1.0 bar; (c) ZnP-XF-CMPs (X= 5, 25 and 50%) at 273 K and 1.0 bar; (d) the isosteric heat of CO_2 adsorption.

Then we investigated the capacity of CO_2 in the ZnP-XF-CMPs (X= 5, 25 and 50%). In contrast to original CMPs, the uptake of ZnP-XF-CMPs (X= 5, 25 and 50%) displayed an

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increased trend with the fluoride contents increased in the networks (Fig. S10, ESI†). For example, ZnP-5%F-CMPs at 298 K and 1.0 bar exhibited a capacity of 34 mg g^{-1}, which was 1.31-times of that of the original CMPs (ZnP-5%N_3-CMPs) (Fig. S10a, ESI†). The CO_2 uptake of ZnP-25%F-CMPs and ZnP-50%F-CMPs was 52 and 90 mg g^{-1} at 298 K, respectively, which was 1.68- and 1.84-times as high as original CMPs (ZnP-25%N_3-CMPs and ZnP-50%N_3-CMPs) (Fig. S10(b-d), ESI†). Then, we measured the CO_2 capacity of the CMPs from 298 K to 273 K to further investigate ultra-micropores in CMPs and to examine their potential application in post-combustion CO_2 capture. ZnP-5%F-CMPs, ZnP-25%F-CMPs and ZnP-50%F-CMPs displayed the CO_2 capacity of 58, 84 and 130 mg g^{-1} at 273 K and 1.0 bar, respectively (Fig. 3c and Fig. S10(b-d)). The CO_2 capture capacity of ZnP-XF-CMPs (X= 5, 25 and 50%) is 1.31-, 1.56- and 1.49-times of that of ZnP-XN_3-CMPs (X= 5, 25 and 50%) at the same conditions, respectively. These results indicated that the increase of fluoride contents in the skeletons could effectively improve the CO_2 adsorption capacity of the polymers at the same conditions.

To investigate the binding affinity of the studied CMPs towards CO_2, we calculated the isosteric heats of adsorption from Clausius–Clapeyron equation using adsorption data collected at 273 K and 298 K. ZnP-XF-CMPs (X = 5, 25 and 50%) had relatively higher CO_2 uptake among the synthesized CMPs with the heat of adsorption of about 32-37 kJ mol^{-1} (Fig. 3d). The Q_{st} values for ZnP-XN_3-CMPs (X = 5, 25, 50, 75 and 100%) are about 18-25 kJ mol^{-1}, which are lower than those of their corresponding perfluoroalkyl counterparts (Fig. S11, ESI†). The result suggested that introducing fluoride element in the polymers can effectively enhance the adsorption enthalpy of the porous materials.

In summary, a new strategy for construction of porous polymer with CMPs architectures has been developed. Implementation of the strategy leads to the successful development of three novel fluoride functionalized-CMPs, which exhibit highly efficient uptake of CO_2 than those of original CMPs (ZnP-XN_3-CMPs (X = 5, 25 and 50%)) at the same conditions. Moreover, all of the fluoride functionalized-CMPs show high isosteric heats of CO_2 adsorption (32-37 kJ mol^{-1}). This work not only indicates that highly complicated three-dimensional polymeric structures can be facilely constructed from simple building blocks but also suggests a promising way to improve the isosteric heats and CO_2 uptake of porous materials. This provides a new idea for the development of new strategies for the construction of porous organic materials in the field of adsorption.

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Notes and references

1 P. Markewitz, W. Kuckshinrichs, W. Leitner, J. Linssen, P. Zapp, R. Bongartz, A. Schreiber and T. E. Muller, *Energy Environ. Sci.*, 2012, **5**, 7281.

2 R. Dawson, A. I. Cooper and D. J. Adams, *Polym. Int.*, 2012, **37**, 530.

3 K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. Bae, and J. R. Long, *Chem. Rev.*, 2012, **112**, 724.

4 (a) Y. Xu, S. Jin, H. Xu, A. Nagai and D. Jiang, *Chem. Soc. Rev.*, 2013, **42**, 8012; (b) A. I. Cooper, *Adv. Mater.*, 2009, **21**, 1291; (c) D. Wu, F. Xu, B. Sun, R. Fu, H. He and K. Matyjaszewski, *Chem. Rev.*, 2012, **112**, 3959; (d) R. Dawson, A. I. Cooper and D. J. dams, *Prog. Polym. Sci.*, 2012, **37**, 530; (e) B. C. Ma, S. Ghasimi, K. Landfester, F. Vilela and K. A. I. Zhang, *J. Mater. Chem. A*, 2015, **3**, 16064.

5 (a) 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; (b) R. Dawson, D. J. Adams, A. I. Cooper. *Chem. Sci.*, 2011, **2**, 1173.

6 (a) Y. Xu, Y.A. Nagai and D. Jiang, *Chem. Commun.*, 2013, **49**, 1591; (b) Y. Xu, L. Chen, Z. Guo, A. Nagai and D. Jiang, *J. Am. Chem. Soc.*, 2011, **133**, 17622.

7 K. Venkata Rao, R. Haldar, T. K. Maji and S. J.George, *Phys. Chem. Chem. Phys.*, 2016, **18**, 156.

8 (a) K. Zhang, D. Kopetzki, P. H. Seeberger, M. Antonietti and F. Vilela, *Angew. Chem., Int. Ed.*, 2013, **52**, 1432; (b) Q. Cao, Q. Yin, Q. Chen, Z. B. Dong, and B. H. Han, *Chem. Eur. J.*, 2017, **23**, 9831.

9 (a) Y. Kou, Y. H. Xu, Z. Q. Guo and D. Jiang, Angew. *Chem., Int. Ed.*, 2011, **50**, 8753; (b) X. Zhuang, F. Zhang, D. Wu, N. Forler, H. Liang, M. Wagner, D. Gehrig, M. R. Hansen, F. Laquai and X. Feng, *Angew. Chem., Int. Ed.*, 2013, **52**, 9668.

10 (a) Q. Chen, J. X. Wang, F. Yang, D. Zhou, N. Bian, X. J. Zhang, C. G. Yan and B. H. Han, *J. Mater. Chem.*, 2011, **21**, 13554; (b) K. V. Rao, S. Mohapatra, T. K. Maji and S. J. George, *Chem. – Eur. J.*, 2012, **18**, 4505.

11 J. X. Jiang, F. Su, A. Trewin, C. D. Wood, N. L. Campbell, H. Niu, C. Dickinson, A. Y. Ganin, M. J. Rosseinsky, Y. Z. Khimyak and A. I. Cooper, *Angew. Chem., Int. Ed.*, 2007, **46**, 8574.

12 S. A, Y. Zhang, Z. Li, H. Xia, M. Xue, X. Liu and Y. Mu, *Chem. Commun.*, 2014, **50**, 8495.

13 (a) Z. Li, H. Li, H. Xia, X. Ding, X. Luo, X. Liu and Y. Mu, *Chem. Eur. J.*, 2015, **21**, 17355; (b) Y. Zhang, S. A, Y. Zou, X. Luo, Z. Li, H. Xia, X. Liu and Y. Mu, *J. Mater. Chem. A*, 2014, **2**, 13422; (c) X. Liu, H. Li, Y. Zhang, B. Xu, S. A, H. Xia and Ying Mu, *Polym. Chem.*, 2013, **4**, 2445.

14 (a) R. Dawson, D. J. Adams and A. I. Cooper, *Chem. Sci.*, 2011, **2**, 1173; (b) R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 3875; (c) W. Lu, D. Yuan, J. Sculley, D. Zhao, R. Krishna and H. C. Zhou, *J. Am. Chem. Soc.*, 2011, **133**, 18126; (d) S. Chen, J. Zhang, T. Wu, P. Feng and X. Bu, *J. Am. Chem. Soc.*, 2009, **131**, 16027; (e) R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi and T. K. Woo, *Science*, 2010, **330**, 650; (f) L. H. Xie and M. P. Suh, *Chem. – Eur. J.*, 2013, **19**, 11590.

15 (a) M. P. Krafft and J. G. Riess, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 1185; (b) Y. Zhao, K. X. Yao, B. Teng, T. Zhang and Y. Han, *Energy Environ. Sci.*, 2013, **6**, 3684.

16 (a) S. Bandyopadhyay, A. G. Anil, A. James and A. Patra, A*CS Appl. Mater. Interfaces*, 2016, **8**, 27669; (b) S. Qiao, T. Wang, W. Huang, J. Jiang, Z. Du, F. Shieh and R. Yang, *Polym. Chem.*, 2016, **7**, 1281; (c) Z. Tang, S. Liu, Z. Lu, X. Lin, B. Zheng, R. Liu, D. Wu and R. Fu, *Chem. Commun.*, 2017, **53**, 6764; (d) M. Trunk, A. Herrmann, H. Bildirir, A. Yassin, J. Schmidt and A. Thomas, *Chem. – Eur. J.*, 2016, **22**, 7179.

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Conjugated microporous polymers with the azide groups: A new strategy for postsynthetic fluorine functionalization en route for enhanced CO_2 adsorption properties

Di Cui,[a] Chan Yao[a] and Yan-hong Xu*[a,b]

Corresponding Author:

Professor Yan-Hong Xu

[a]*Key Laboratory of Preparation and Applications of Environmental Friendly Materials (Jilin Normal University), Ministry of Education, Changchun, 130103, China*

[b]*Key Laboratory of Functional Materials Physics and Chemistry of the Ministry of Education, Jilin Normal University, Siping 136000, China*

The different azide group contents incorporated within the pore of the zinc-porphyrin CMPs were subjected to alkyne click condition via a facile, one-step quantitative procedure, the route can effectively enhance the CO_2 sorption and the adsorption enthalpy of porous materials.

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