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DOI: 10.1039/C7CC01063J

Journal Name

COMMUNICATION

A Highly Porous Metal-Organic Framework for Large Organic Molecule Capture and Chromatographic Separation

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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A highly porous metal-organic framework (MOF) with large pores was successfully achieved *via* solvothermal assembly of a "click"-extended tricarboxylate ligand and Zn(II) ions. Inherent feature of large-molecule accessible pores endows the MOF with unique property for the utilization toward large guest molecules.

Metal–organic frameworks (MOFs) as a class of promising porous materials have attracted tremendous attention over the past decade owing to their intriguing architectures and high porosity as well as wide application potential.[1,2] Distinct from other inorganic porous materials such as zeolites, porous silica and activated porous carbons, MOFs are typically built by the self-assembly of polytopic bridging ligands with metal ions/clusters under solvothermal conditions.[1,2] Inherent structural feature with organic moieties endows MOFs with chemical tenability, such as adjustable composition, tunable pore size and modifiable pore surface.[3,4] As a unique group of porous materials, the pores in constructed MOFs play a crucial role toward the target applications.[5,6] Abundant MOF structures with different pore size and pore shape have been fabricated by judicious combination of organic ligands and metal ions/clusters, with which great efforts have been dedicated to the exploitation for gas or small molecule capture and storage.[2] However, developing efficient MOFs with suitable accessible pores for large-molecule-based applications such as heterogeneous catalysis, bioimaging and drug delivery, organic pollutant removal as well as organic molecule separation is also highly desired.[6-9] Extending the length of organic backbones should be a simple and feasible strategy for developing MOFs with large-molecule accessible pores, although other strategies have been also investigated such as mixed-ligand combination or template-directing syntheses.[10.11] Herein, we present the successful demonstration on the construction of a MOF, $[Zn_6(C_{33}H_{18}N_9O_6)_4(H_2O)_3]_n$ (**1**),[12] with large-molecule accessible pores assembled from click-extended tricarboxylate ligand and Zn(II) ions, and its remarkable capabilities for large molecule capture and chromatographic separation probed by organic dye molecules.

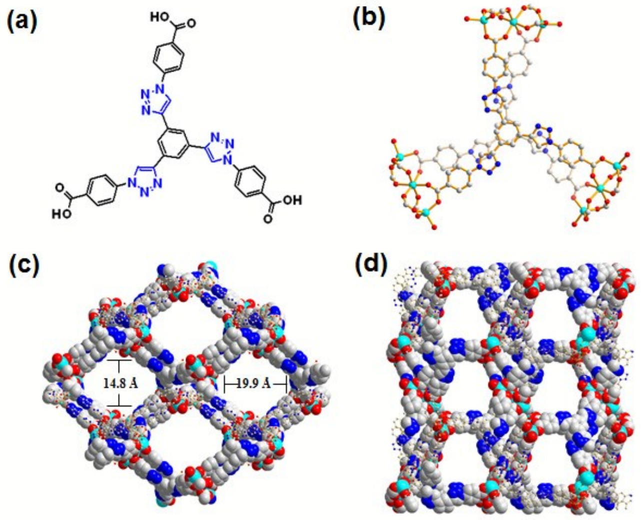

Fig. 1 (a) Schematic illustration of click-extended tricarboxylate ligand, **H_3L1**; (b) **L1** connected three Zn_3 units; (c) 1D porous channels along *c*-axis in 3D framework of crystal **1,** and (d) 1D porous channels against (110) plane in crystal **1**.

Among versatile click chemistry, copper(I)-catalyzed azide-alkyne cycloaddition is a typical reaction and could usually be carried out under mild conditions with a high yield, which has been intensively utilized in fabricating/modifying various functional materials and also in the design and synthesis of organic ligands for MOF constructions.[13-15] Taking advantage of click reaction, an tricarboxylate ligand, 4,4',4''-benzene-1,3,5-tryl-tri(1H-1,2,3-triazol-1-yl)benzoic acid (**H_3L1**, Fig. 1a), was designed and successfully synthesized. Literature reports show

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Electronic Supplementary Information (ESI) available: Experimental procedures, PXRD, TGA, gas physisorption, and CCDC No. 1502165. See DOI: 10.1039/x0xx00000x

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DOI: 10.1039/C7CC01063J

that Zn-based MOF crystals usually are transparent and also present various architectures with interesting pores.[9f,16] Thus, Zn(II) ion was selected for the coordination with **H_3L1** in N,N′-dimethylformamide (DMF) through solvothermal reaction, and subsequently block colorless crystals of MOF **1** were obtained (see the experimental section and Fig. S1 in ESI).

Single-crystal structural analysis reveals that **1** has a porous network with a framework formula of $[Zn_6(\mathbf{L1})_4(H_2O)_3]_n$ (Fig. 1 and S2). As illustrated in Fig. 1b, three neighbouring Zn(II) ions are bridged by six distributed carboxylate groups from six different **L1** ligands, giving the formation of a linear Zn_3 cluster.[16] In the linear Zn_3 cluster, the middle Zn(II) is coordinated by six oxygen atoms forming a typical octahedral geometry. The other two terminal Zn(II) ions showing the same tetrahedral geometry are coordinated by four oxygen atoms, three of which are from three carboxylates and one from the capped water molecule. Two superimposed **L1** ligands then bridge three linear Zn_3 clusters to form a $(Zn_3)_3(\mathbf{L1})_2$ subunit (Fig. 1b), which subsequently connects by each other to construct an uninodal (10,3)-net with intrinsically chiral $SrSi_2$ topology in a “srs” symbol.[16b] The same two networks sharing a capped water molecule coordinated with terminal Zn(II) ions finally give the formation of the porous framework of **1**. Having click-extended long organic backbone of the tricarboxylate ligand, large pores with opening windows of 14.8 × 19.9 Å^2 along *a*-axis and opening diameters of approximate 10.2 Å perpendicular to the (110) plane are successfully achieved in **1** (Fig. 1c,d). After removing the discrete solvents in the pores of **1**, the MOF structure was calculated using PLATON/VOID program.[17] The total solvent-accessible volume of **1** was estimated to be 76.1% and the density of the desolvated framework was calculated to be only 0.468 g cm^{-3}, further indicating that **1** possesses a high porosity. The structural analysis and calculations clearly reveal that **1** has a highly porous framework with large pores.

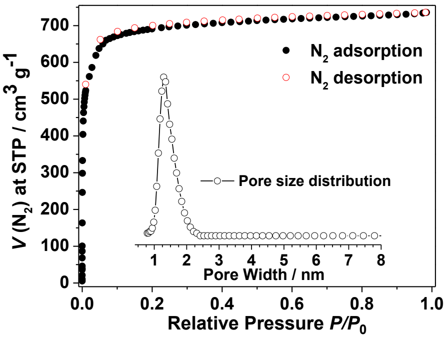

Fig. 2 N_2 adsorption/desorption isotherms at 77 K and pore-size distribution of activated **1**.

Gas adsorption measurements were then performed to further confirm its porosity. After the activation process (Fig. S3), N_2 sorption measurement for the activated **1** was carried out at 77 K. As illustrated in Fig. 2a, **1** exhibits reversible type I sorption isotherm starting from a quickly increased step at low pressure and ending to a plateau at relatively high pressure, demonstrating that it possesses a dominated microporous feature.[18] At 1 atm, **1** shows an overall N_2 uptake of 655 cm^3 g^{-1} and its Brunauer-Emmett-Teller (BET) surface area was calculated to be 2819 m^2 g^{-1}, which is comparable with our previously reported Zn-based MOF having tricarboxylate components.[19] The pore size distribution was further calculated based on the N_2 sorption isotherms at 77 K with the non-local density functional theory. The result reveals that the pore size distribution of **1** shows a broad peak ranging from ~10 to ~20 Å with a focused peak at 13.5 Å (Fig. 2b), which is consistent well with the observation from its crystal structure. Gas adsorption analyses further confirm that MOF **1** has a high porosity with large pore size.

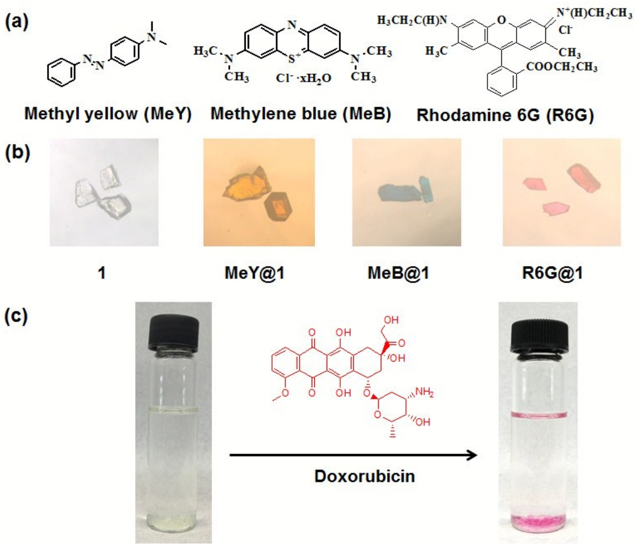

Fig. 3 (a) Structural illustration of the dye molecules, (b) comparison of the crystal colors before and after the dye soaking and (c) color change of the crystals after soaking in Dox/DMF solution, clearly showing that the dye and Dox molecules were adsorbed by **1**.

Inspired by the high porosity and large pores of **1**, investigations on large molecule based applications were subsequently carried out. Organic dyes, as a big group of organic molecules frequently used as biological markers for bioimaging, have variety of colors and sizes.[20] Given visible color feature of some organic dyes and transparent colorless nature of the crystal **1**, organic dyes should be ideal probes to investigate large-molecule uptake. Therefore, several organic dyes with different molecular sizes were selected for such investigation. The activated crystals of **1** were soaked in the DMF solution of methyl yellow (MeY, yellow), methylene blue (MeB, blue), and rhodamine 6G (R6G, red), respectively (Fig. 3a). For all three samples, color changes of the crystals of **1** were clearly observed by naked eyes after soaking for about two hours (Fig. 3b). The uniform distribution of dye colors throughout the crystals of **1** suggests that the organic dye molecules deeply penetrate into the large pores instead of only adsorbing on the external surface of the crystals. The dye-probed visible large-molecule soaking experiments demonstrate that large-porous MOF **1** constructed *via* click-extension of organic backbones can be used in large-molecule uptake applications, such as dye-based bioimaging. Keeping these positive results in mind, the investigations were then extended not only to others dyes (toluylene Red and

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rhodamine B in Fig. S7), but also to a large drug molecule for checking the generality of the large-molecule uptake. An anticancer drug, doxorubicin (Dox), with red color was selected for intuitively visible demonstration. As shown in Fig. 3c, after immersing the activated crystals of **1** into the DMF solution of Dox, the color change of the crystals from colorless to red was clearly observed, indicating that the Dox molecule penetrates into the pores of **1** and this large-pore MOF could be promising porous materials for drug uptake in potential drug delivery application.

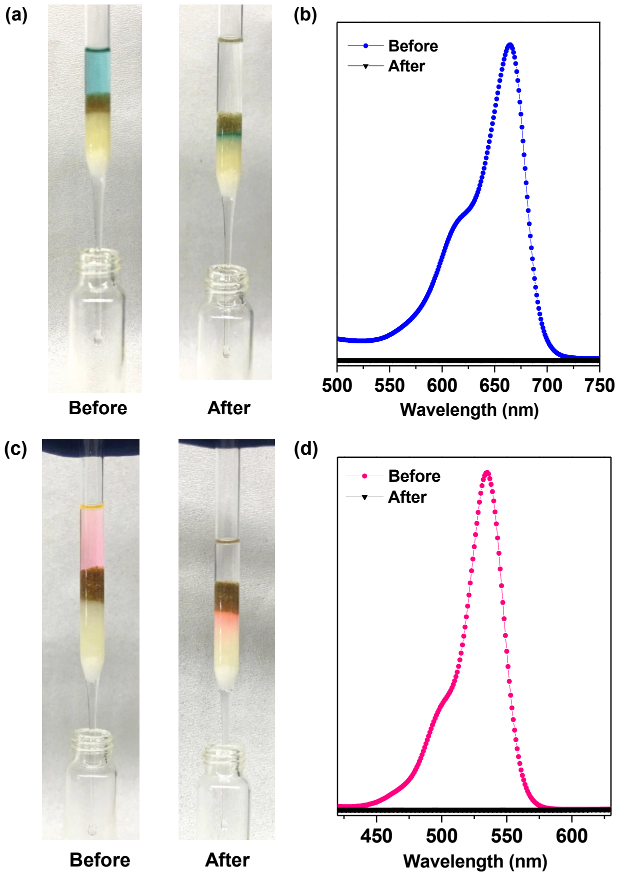

Fig. 4 (a) Images and (b) UV-Vis spectra of the DMF solution of MeB before and after passing through **1**-packed column; (c) Images and (d) UV-Vis spectra of the DMF solution of R6G before and after passing through **1**-packed column.

On the other hand, some organic dyes as organic pollutants can lead to environmental problems even at low concentrations.[21] Thus, organic dyes are also suitable probes for investigating organic pollutant removal. In this case, homemade columns were packed by crystals of **1** to examine its performance on such application (Fig. S8). As shown in Fig. 4a, when the DMF solution of MeB dye passed slowly through the **1**-packed column, a clarified effluent was observed, while the crystals in top part of the column became blue, indicating that the MeB molecules were captured by the crystals of **1**. To further detect the concentration of MeB in the effluent, UV-Vis spectrum was measured, clearly showing that MeB molecules were removed from the DMF solution and fully captured by crystals of **1** during the passing-through process (Fig. 4b). When changing to R6G dye instead of MeB, the same phenomenon was observed after passing through fresh **1**-packed column (Fig. 4c,d). Moreover, the packed MOF crystals could be regenerated after thoroughly soaking in fresh DMF solvent. The demonstration clearly shows that the constructed MOF is highly promising porous materials for large molecule capture and organic pollutant removal.

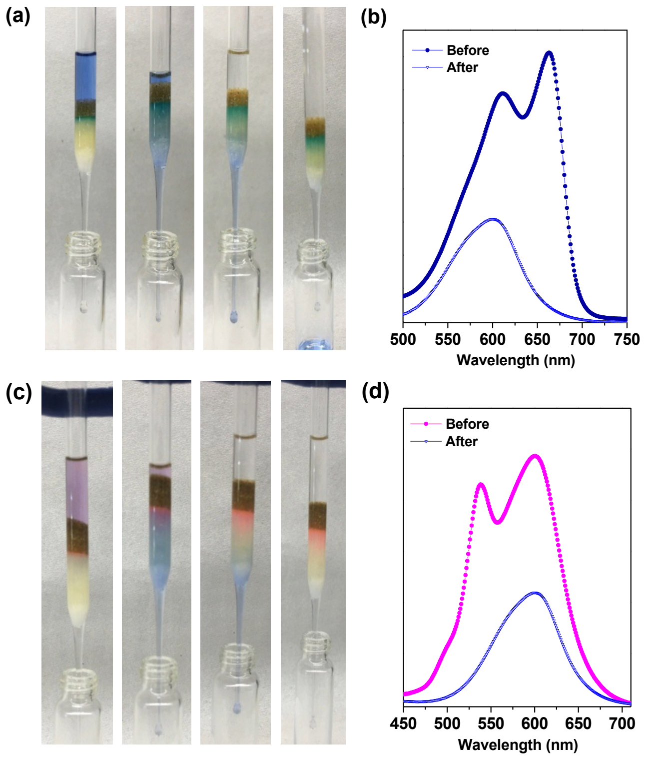

Fig. 5 (a) Images and (b) UV-Vis spectra of the DMF solution of MeB/BBR mixture before and after passing through **1**-packed column; (c) Images and (d) UV-Vis spectra of the DMF solution of R6G/BBR mixture before and after passing through **1**-packed column.

Super-large molecules with polarity are impossible or the last ones to pass through the traditional silica gel column, although in some cases they are the desired products. The high performance of the dye capture experiments *via* passing through **1**-based column inspired us to further investigate the possibility of reversed processes to obtain the super-large molecules firstly rather than small ones by the MOF capture effect. The dye soaking investigation showed that a super-large dye, Brilliant Blue R (BBR, blue), was too large to be encapsulated by the MOF pores (Fig. S7). Thus, a DMF solution of the MeB/BBR mixture was prepared for the investigation on molecule-size dependent separation. When the dye mixture MeB/BBR passed naturally through **1**-packed column under the gravity, it was clearly observed that small-sized MeB molecule was captured at top part of the column, while the large BBR molecule passed through the column (Fig. 5a). The comparison of the UV-Vis spectra before and after the separation process also reveals that a pure phase of BBR solution was obtained (Fig. 5b). This effective size-dependent separation capability was further confirmed by the separation process of another dye mixture R6G/BBR (Fig. 5c,d). The results clearly show that larger molecules can firstly pass through the column, while small ones can be captured by the

MOF crystals, confirming our hypothesis that MOF based column could be used for large molecule preparation *via* size-dependent separation. Such a demonstration makes MOF crystals with suitable pore sizes promising column-packing materials instead of traditional silica gel for size-dependent large molecule separation.

These successful experiments of dye-probed organic molecule uptake, capture and separation demonstrate that MOF **1** is a highly promising porous material for large-molecule based applications. Since the performance of porous materials on the large-molecule based applications is always influenced by the pore size, the demonstration of dye-probed large molecule uptake, capture and separation confirms that extending organic backbones of ligands to increase the pore size of MOFs *via* versatile click reaction is an efficient approach.

In summary, by artfully extending the backbones of tricarboxylate ligands *via* click chemistry, a highly porous MOF with large pores has been successfully assembled. The dye-probed investigations clearly indicate that the constructed MOF is a highly promising porous material for large-molecule based applications including imaging, delivery, pollutant removal as well as size-dependent separation. On account of the easy and efficient approach for the generation of porous frameworks with large pore sizes for large organic molecule based applications, the present method of constructing MOFs *via* click-extension of the organic backbones could serve as a general protocol for developing more MOFs with large pores for desired applications.

This research is financially supported by the Singapore Academic Research Fund (RG112/15 and RG19/16).

Notes and references

1 (*a*) C. Janiak and J. K. Vieth, *New J. Chem.*, 2010, **34**, 2366; (*b*) M. Li, D. Li, M. O'Keeffe and O. M. Yaghi, *Chem. Rev.*, 2014, **114**, 1343.

2 (*a*) B. Chen, S. Xiang, and G. Qian, *Acc. Chem. Res.*, 2010, **43**, 1115; (*b*) J.-R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P. B. Balbuen and H.-C. Zhou, *Coord. Chem. Rev.*, 2011, **255**, 1791; (*c*) H. Wu, Q. Gong, D. H. Olson, J. Li, *Chem. Rev.*, 2012, **112**, 836; (*d*) P.-Z. Li and Y. Zhao, *Chem. Asian J.*, 2013, **8**, 1680; (*e*) E. Barea, C. Montoro and J. A. R. Navarro, *Chem. Soc. Rev.*, 2014, **43**, 5419; (*f*) Y. Zhao, *Chem. Mater.*, 2016, **28**, 8079.

3 S. M. Cohen, *Chem. Rev.*, 2012, **112**, 970.

4 (*a*) Y. Goto, H. Sato, S. Shinkai and K. Sada, *J. Am. Chem. Soc.*, 2008, **130**, 14354; (*b*) C. Liu, T. Li and N. L. Rosi, *J. Am. Chem. Soc.*, 2012, **134**, 18886; (*c*) P.-Z. Li, X.-J. Wang, R. H. D. Tan, Q. Zhang, R. Zou and Y. Zhao, *RSC Adv.*, 2013, **3**, 15566.

5 (*a*) H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gándara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O'Keeffe, O. Terasaki, J. F. Stoddart and O. M. Yaghi, *Science*, 2012, **336**, 1018; (*b*) X. Cui, K. Chen, H. Xing, Q. Yang, R. Krishna, Z. Bao, H. Wu, W. Zhou, X. Dong, Y. Han, B. Li, Q. Ren, M. J. Zaworotko and B. Chen, *Science*, 2016, **353**, 141.

6 (*a*) W. Xuan, C. Zhu, Y. Liu and Y. Cui, *Chem. Soc. Rev.*, 2012, **41**, 1677; (*b*) L. Song, J. Zhang, L. Sun, F. Xu, F. Li, H. Zhang, X. Si, C. Jiao, Z. Li, S. Liu, Y. Liu, H. Zhou, D. Sun, Y. Du, Z. Cao and Z. Gabelica, *Energy Environ. Sci.*, 2012, **5**, 7508.

7 (*a*) T. Zhang and W. Lin, *Chem. Soc. Rev.*, 2014, **43**, 5982; (*b*) A. H. Chughtai, N. Ahmad, H. A. Younus, A. Laypkov and F. Verpoort, *Chem. Soc. Rev.*, 2015, **44**, 6804; (*c*) Z. Zhou, C. He, J. Xiu, L. Yang and C. Duan, *J. Am. Chem. Soc.*, 2015, **137**, 15066.

8 P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Ferey, R. E. Morris and C. Serre, *Chem. Rev.*, 2012, **112**, 1232.

9 (*a*) S. Han, Y. Wei, C. Valente, I. Lagzi, J. J. Gassensmith, A. Coskun, J. F. Stoddart and B. A. Grzybowski, *J. Am. Chem. Soc.*, 2010, **132**, 16358; (*b*) S. Pramanik, C. Zheng, X. Zhang, T. J. Emge and J. Li, *J. Am. Chem. Soc.*, 2011, **133**, 4153; (*c*) Y.-Q. Lan, H.-L. Jiang, S.-L. Li and Q. Xu, *Adv. Mater.*, 2011, **23**, 5015; (*d*) V. Bon, V. Senkovskyy, I. Senkovska and S. Kaskel, *Chem. Commun.*, **2012**, *48*, 8407; (*e*) T.-H. Chen, I. Popov, W. Kaveevivitchai, Y.-C. Chuang, Y.-S. Chen, A. J. Jacobson, O. S. Miljanic, *Angew. Chem. Int. Ed.*, **2015**, *54*, 13902; (*f*) P.-Z. Li, X.-J. Wang, S. Y. Tan, C. Y. Ang, H. Chen, J. Liu, R. Zou and Y. Zhao, *Angew. Chem. Int. Ed.*, **2015**, *54*, 12748.

10 (*a*) K. Koh, A. G. Wong-Foy and A. J. Matzger, *Angew. Chem. Int. Ed.*, 2008, **47**, 677; (*b*) K. Koh, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.*, 2009, **131**, 4184; (*c*) N. Klein, I. Senkovska, K. Gedrich, U. Stoeck, A. Henschel, U. Mueller and S. Kaskel, *Angew. Chem. Int. Ed.*, 2009, **48**, 9954; (*d*) H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. O. Yazaydin, R. Q. Snurr, M. O'Keeffe, J. Kim and O. M. Yaghi, *Science*, 2010, **329**, 424.

11 (*a*) Y. J. Zhao, J. L. Zhang, B. X. Han, J. L. Song, J. S. Li and Q. A. Wang, *Angew. Chem. Int. Ed.*, 2011, **50**, 636; (*b*) L. B. Sun, J. R. Li, J. Park and H. C. Zhou, *J. Am. Chem. Soc.*, 2012, **134**, 126.

12 MOF **1** in the main text can be cited as **NTU-130**.

13 (*a*) H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem. Int. Ed.*, 2001, **40**, 2004; (*b*) V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem. Int. Ed.*, 2002, **41**, 2596.

14 (*a*) X.-J. Wang, P.-Z. Li, Y. Chen, Q. Zhang, H. Zhang, X. X. Chan, R. Ganguly, Y. Li, J. Jiang and Y. Zhao, *Sci. Rep.*, 2013, **3**, 1149; (*b*) P.-Z. Li, X.-J. Wang, K. Zhang, A. Nalaparaju, R. Zou, R. Zou, J. Jiang and Y. Zhao, *Chem. Commun.*, 2014, **50**, 4683; (*c*) P.-Z. Li, X.-J. Wang, J. Liu, J. S. Lim, R. Zou and Y. Zhao, *J. Am. Chem. Soc.*, 2016, **138**, 2142.

15 (*a*) A. Nnagai, Z. Guo, X. Feng, S. Jin, X. Chen, X. Ding, D. Jiang, *Nat. Commun.*, 2011, **2**, 536; (*b*) L. Sun, Y. Li, Z. Liang, J. Yu and R. Xu, *Dalton Trans.*, 2012, **41**, 12790; (*c*) Y. Yan, M. Suyetin, E. Bichoutskaia, A. J. Blake, D. R. Allan, S. A. Barnett and M. Schroder, *Chem. Sci.*, 2013, **4**, 1731; (*d*) H. Xu, J. Gao and D. Jiang, *Nat. Chem.*, 2015, **7**, 905.

16 (*a*) H. Li, C. E. Davis, T. L. Groy, D. G. Kelley and O. M. Yaghi, *J. Am. Chem. Soc.*, 1998, **120**, 2186; (*b*) T.-H. Chen, I. Popov, Y.-C. Chuang, Y.-S. Chen and O. S. Miljanic, *Chem. Commun.*, 2015, **51**, 6340.

17 A. Spek, *Acta Crystallogr, Sect. D* 2009, **65**, 148.

18 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, P. A. Pierotti, J. Rouquerol and T. Siemieniewska, *Pure Appl. Chem.*, 1985, **57**, 603.

19 R. Zou, P.-Z. Li, Y.-F. Zeng, J. Liu, R. Zhao, H. Duan, Z. Luo, J.-G. Wang, R. Zou, Y. Zhao, *Small*, 2016, **12**, 2334.

20 (*a*) Q. Zhang, F. Liu, K. T. Nguyen, X. Ma, X. Wang, B. Xing and Y. Zhao, *Adv. Funct. Mater.*, 2012, **22**, 5144; (*b*) Q. Zhang, X. Wang, P.-Z. Li, K. T. Nguyen, X.-J. Wang, Z. Luo, H. Zhang, N. S. Tan and Y. Zhao, *Adv. Funct. Mater.*, 2014, **24**, 2450.

21 (*a*) C. Chen, W. Ma and J. Zhao, *Chem. Soc. Rev.*, 2010, **39**, 4206; (*b*) J. Gao, J. Miao, P.-Z. Li, W. Y. Teng, L. Yang, Y. Zhao, B. Liu and Q. Zhang, *Chem. Commun.*, 2014, **50**, 3786.

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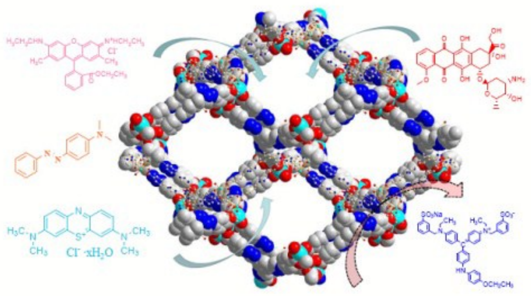

A highly porous metal-organic framework with large pores presents large molecule based applications probed by organic dye molecules.