From an equilibrium based MOF adsorbent to a kinetic selective carbon molecular sieve for paraffin/iso-paraffin separation†

Baiyan Li,‡[a] Youssef Belmabkhout,‡[b] Yiming Zhang,‡[a] Prashant M. Bhatt,[b] Hongming He,[a] Daliang Zhang,[b] Yu Han,[b] Mohamed Eddaoudi,*[b] Jason A. Perman[a] and Shengqian Ma*[a]

We unveil a unique kinetic driven separation material for selectively removing linear paraffins from iso-paraffins *via* a molecular sieving mechanism. Subsequent carbonization and thermal treatment of CD-MOF-2, the cyclodextrin metal–organic framework, afforded a carbon molecular sieve with a uniform and reduced pore size of *ca.* 5.0 Å, and it exhibited highly selective kinetic separation of *n*-butane and *n*-pentane from iso-butane and iso-pentane, respectively.

Engineering of the pore size in materials for various industrial processes is an area of extreme importance.[1] In particular, the development of advanced materials with precise pore aperture dimensions close to the molecular sizes of commodities, such as hydrocarbons,[2] has continued to attract attention in academia and industry. It is motivated by the challenge of the high degree of complexity involved in separation of hydrocarbon mixtures and their isomers only by their physical properties. In fact, the molecules in these hydrocarbon mixtures have similar boiling points, which makes the separation process energy and cost intensive. Therefore, the separation and purification of high purity isobutane/isopentane from a mixture currently depends on large-scale distillation technology. Consequently, there is a constant search for innovative solutions to develop advanced materials able to achieve the efficient size selective separation of molecules with similar vaporization/condensation transitions such as *n*-butane/isobutane and *n*-pentane/isopentane.

In spite of the lack of full uniformity, porous carbon materials, such as activated carbons (ACs), have achieved remarkable success

in many separation applications.[3] ACs possess pores ranging in size from sub-nano to macrometer dimensions. In specific cases, ACs with a high degree of pore uniformity matching the molecular dimensions of particular fluids are commonly classified as carbon molecular sieves (CMSs).[4] This subclass of ACs has attracted attention for the separation of small or isomeric molecules.[5] Multiple methods for synthesizing CMS materials exist in the literature, which are primarily formed after carbonization of organic molecules or polymers, at different temperatures and soaking times. Recently, metal organic frameworks (MOFs)[6] have been utilized as a new carbon source for porous carbonaceous materials which are finding application in the fields of gas adsorption and separation, electrocatalysis, and electrical conductivity and as supercapacitors.[7]

Formerly, many MOF based porous carbon materials ranged from micropores to mesopores with a wide pore size distribution. Broad or large pore size distributions are not advantageous for small molecule separation. Therefore, developing MOF materials as the carbon sources for CMS is still challenging and there are no previous reports in the literature showing the use of CMS for linear paraffin/monobranched paraffin separation in a single step. Herein, we report for the first time a CMS, derived from a MOF, which exhibits a narrow pore size centered at *ca.* 5 Å, effective for highly selective, kinetic based separation of *n*-butane and *n*-pentane from their monobranched isomers.

We selected CD-MOF-2 (γ-cyclodextrin-MOF-2)[8] for the synthesis of CMSs based on the following considerations. Cyclodextrins have been proven to be a good carbon source for porous carbon materials and the metal rubidium and its metallic oxide are easily removed after washing with dilute hydrochloric acid.[9] The CMS, **CMS-PMOF-1**, was obtained by heating CD-MOF-2 at 600 °C for five hours and then at 900 °C for one hour under a nitrogen atmosphere, followed by washing two times with 2 M HCl (ESI†). The powder X-ray diffraction (PXRD) patterns of **CMS-PMOF-1** (ESI,† Fig. S1) displayed two broad peaks, indicating the amorphous feature of **CMS-PMOF-1**. Scanning electron microscopy (SEM) images showed that the samples of **CMS-PMOF-1** are composed of irregular plate-like

[a] *Department of Chemistry, University of South Florida, 4202 E. Fowler Avenue, Tampa, FL 33620, USA. E-mail: sqma@usf.edu; Fax: +1-813-974-3203; Tel: +1-813-974-5217*

[b] *Functional Materials Design, Discovery & Development Research Group (FMD3), Advanced Membranes & Porous Materials Centre (AMPMC), Division of Physical Sciences and Engineering (PSE), 4700 King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia. E-mail: mohamed.eddaoudi@kaust.edu.sa*
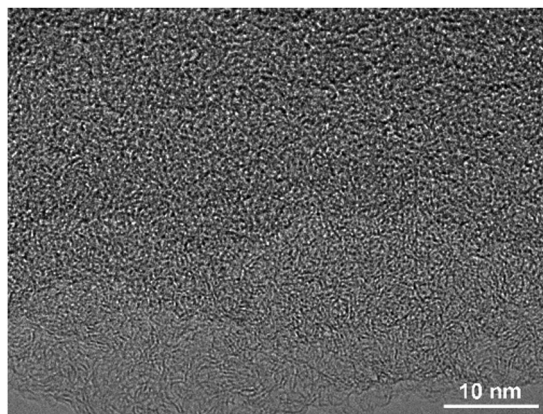
Fig. 1 TEM images of **CMS-PMOF-1**.

morphologies with micrometer dimensions (ESI,† Fig. S2), which are different from the morphology of the precursor of CD-MOF-2 with a block shape. Transmission electron microscopy (TEM) showed that these plates of **CMS-PMOF-1** exhibited sponge-like micropores (Fig. 1), thus confirming the amorphous features displayed by PXRD analysis.

CMS-PMOF-1 was activated by degassing the sample under a continuous vacuum at 150 °C for 10 hours prior to N_2 gas adsorption isotherms collected at 77 K (Fig. 2a). **CMS-PMOF-1** exhibited a type I isotherm with a sharp knee at low relative pressure and a lack of condensation at higher relative pressure. This is characteristic of narrow microporous carbonaceous materials with pores ≤0.7 nm. Its Brunauer–Emmett–Teller (BET) specific surface area was calculated to be 799 m^2 g^{-1} and its nitrogen uptake capacity at saturation ($P/P_0 = 0.95$) reached 213 (STP) cm^3 g^{-1}. The pore size distribution analysis of CMS commonly uses the Horvath–Kawazoe (HK) model.[10] As indicated in Fig. 2b, the pore size of **CMS-PMOF-1** is predominantly distributed around 5 Å *vs.* 17 Å for the parent material CD-MOF-2 (the CD-MOF-2 breakdown after pyrolysis), indicative of the relatively uniform and highly contracted microporosity in the ultra-microporous range for the carbonized material. To corroborate the surface analysis using N_2 as a probe, we measured CO_2 adsorption isotherms at 273 and 295 K (ESI,† Fig. S3). Uptake capacities of 119 and 95 (STP) cm^3 g^{-1} (5.3 or 4.2 mmol g^{-1} and 23.3 or 18.6 wt%), respectively were achieved under 1 atm pressure. These values are higher than that of the parent CD-MOF-2 (~60 cm^3 g^{-1} or 2.7 mmol g^{-1} or 11.8 wt%) under 800 Torr and 298 K.[11]
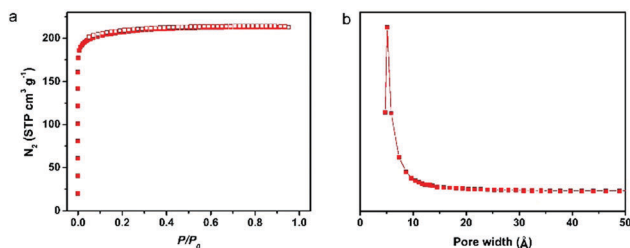
To achieve our ultimate objective in this work, we opted to explore the potential use of **CMS-PMOF-1** for gas/vapour separation where the involved molecules have a size close to the average pore size of **CMS-PMOF-1** (5 Å), such as *n*-butane/iso-butane and pentane/isopentane having kinetic diameters of *ca.* 4.3 and 5.0 Å, respectively.[12] These types of highly energy intensive separations are extremely important in energy and industry related applications. To begin with, we explored the adsorption properties of *n*-butane (*n*-C_4H_{10}) and isobutane (iso-C_4H_{10}) at 293 K and observed the differences in their respective uptakes (Fig. 3a) The adsorption of butane was characteristic of a type I isotherm and reached 1.9 mmol g^{-1} at 1 bar. On the other hand, the isobutane isotherm was not as distinct as *n*-C_4H_{10} with a less noticeable knee at lower pressure and an overall lower adsorption of 1.43 mmol g^{-1} at 1 bar. Interestingly, the adsorption and desorption branches in the case of iso-C_4H_{10} were not overlapping mainly due to the relatively slow adsorption–desorption kinetics, resulting in turn from the difficulty of iso-C_4H_{10} to adsorb/desorb from the porous material. This was further confirmed from the pressure decay measurements carried out at 14.94 Torr initial feed gas pressure (Fig. 3b) for more than 3500 s without reaching equilibrium. Delightfully, the corresponding pressure decay measurements in the case of *n*-C_4H_{10} (Fig. 3b) showed extremely fast adsorption kinetics with an

Fig. 2 (a) N_2 sorption isotherm and (b) pore size distribution (HK model) for **CMS-PMOF-1**.
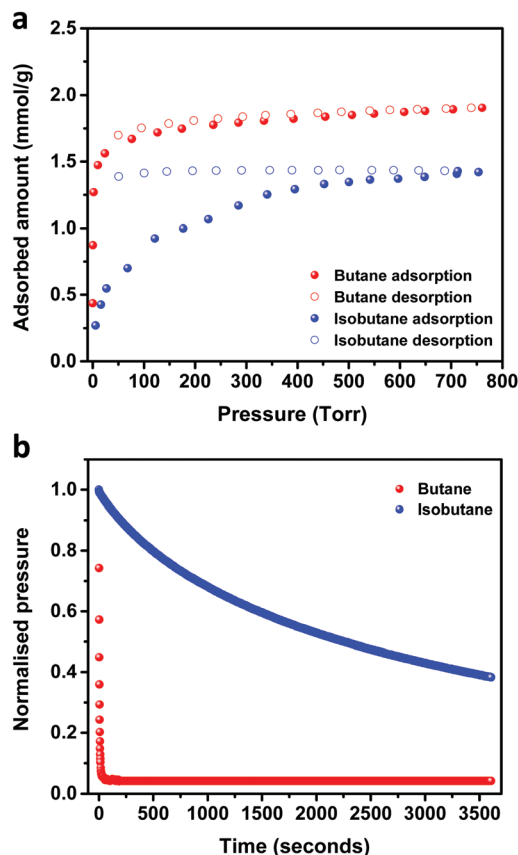

Fig. 3 (a) Comparison of *n*-butane and isobutane adsorption isotherms for **CMS-PMOF-1** with the absolute pressure scale at 293 K, (b) comparison of pressure decay for *n*-butane and isobutane during adsorption measurements at 3.16 and 14.94 Torr, respectively, on **CMS-PMOF-1**. The pressure is normalized for comparison purpose.

equilibration time of 60 s. This prompted us to explore the opportunity to exploit this outstanding kinetic driving force and investigate further the use of **CMS-PMOF-1** for real separation of n-C_4H_{10} from iso-C_4H_{10}. To evaluate the applicability of the kinetic driven separation feature of **CMS-PMOF-1** compared with other isomeric hydrocarbons, pentane (n-C_5H_{12}) and iso-pentane (iso-C_5H_{12}) adsorption experiments were performed. Remarkably, while the adsorption of n-C_5H_{12} (Fig. 4) showed optimal thermodynamics (closed type I isotherm) and kinetics (fast rate of adsorption), iso-C_5H_{12} adsorption on **CMS-PMOF-1** showed similar slow kinetic behaviour to iso-C_4H_{10} (Fig. 4). From the relatively much lower uptake of iso-C_5H_{12} as compared to iso-C_4H_{10} and the less visible hysteresis in the case of the iso-C_5H_{12} adsorption–desorption isotherm, we tentatively attributed this behaviour to the non-accessibility of iso-C_5H_{12} to a certain portion of the ultramicropores, while **CMS-PMOF-1** was found to adsorb almost the same amount of n-C_4H_{10} and n-C_5H_{12}.

Analysis of pressure decay measurements showed that n-C_4H_{10} and n-C_5H_{12} reached high equilibrium uptakes of 0.437 mmol g^{-1} and 0.481 mmol g^{-1} in 20 s, respectively while iso-C_4H_{10} and iso-C_5H_{12} were observed to adsorb very little. This suggests that **CMS-PMOF-1** has potential for high selective
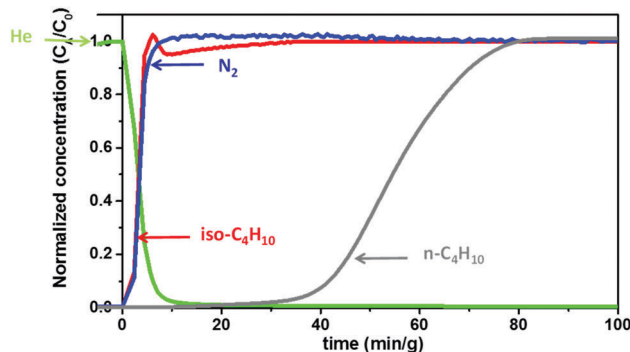
Fig. 5   Column breakthrough test for the adsorption of mixed n-butane (5%) and isobutane (5%) in balance with N_2 (n-C_4H_{10}/iso-C_4H_{10}/N_2: 5/5/90 mixture) with a flow rate of 8 cm^3 min^{-1} on **CMS-PMOF-1**.

kinetic separation of these isomers, which is better than a few reports in the literature.[12]

To further confirm the molecular sieving behaviour of **CMS-PMOF-1** for paraffin-isoparaffin separation, experiments using a gas mixture of n-C_4H_{10}/iso-C_4H_{10}/N_2 = 5/5/90 were carried out at 298 K and 1 bar total pressure with a flow rate of 8 cm^3 min^{-1} (Fig. 5). The choice of this specific mixture in balance with N_2 is motivated by the negligible N_2 uptake as compared to n-C_4H_{10} and its use as a reference non-absorbable gas. Surprisingly, in real mixed testing, iso-C_4H_{10} was not retained in the column similarly to the reference gas N_2, confirming that iso-C_4H_{10} is not adsorbed (Fig. 5) under these conditions while n-C_4H_{10} was retained in the column for *ca.* 35 minutes per gram with the n-C_4H_{10} adsorbed amount (0.62 mmol g^{-1}) in the bed, which is in good agreement with the n-C_4H_{10} single adsorption data (Fig. 3) at 35 Torr partial pressure. It is important to note that the breakthrough curves were normalized by taking into account the overlap of mass fragmentation intensities m_{29} and m_{39} associated with n-butane and isobutane, respectively, as was reported elsewhere[2b] (see also details in the ESI†).

In summary, we showed for the first time a shift from an open porous metal–organic framework to a promising carbon molecular sieve for paraffin–isoparaffin separation, *via* the well known carbonization methodology. The use of CD-MOF-2 as the carbon source led to the formation of **CMS-PMOF-1** with contracted and homogeneous pores of 5 Å, and it showed outstanding sieving properties for meeting the industrial challenge of n-C_4H_{10}/iso-C_4H_{10} and n-C_5H_{12}/iso-C_5H_{12} separation. Further research work will address the development of MOF derived membrane materials for hydrocarbon and biofuel separation.
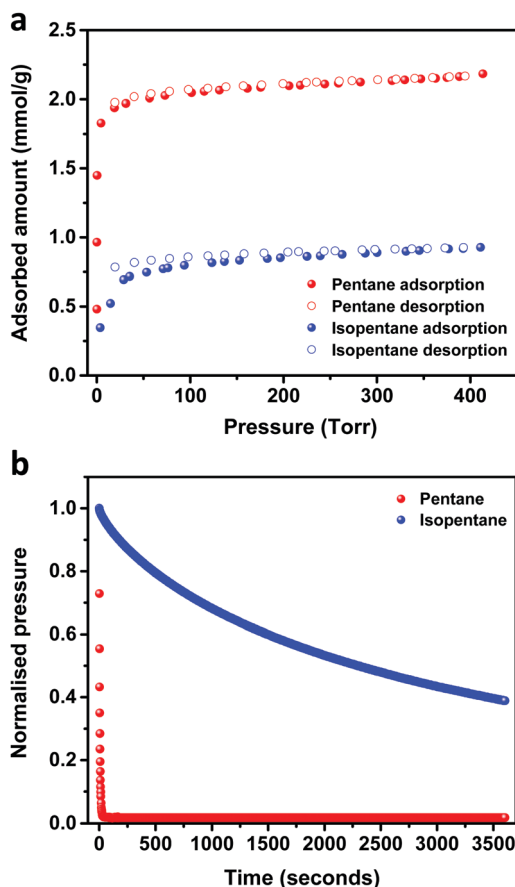
Fig. 4   (a) Comparison of n-pentane and isopentane adsorption isotherms for **CMS-PMOF-1** with absolute pressure scale at 293 K, (b) comparison of pressure decay for n-pentane and isopentane during adsorption measurement at 5.37 and 17.14 Torr, respectively on **CMS-PMOF-1**. The pressure is normalized for comparison purpose.

Notes and references

1 (*a*) Z. R. Herm, B. M. Wiers, J. A. Mason, J. M. van Baten, M. R. Hudson, P. Zajdel, C. M. Brown, N. Masciocchi, R. Krishna and J. R. Long, *Science*, 2013, **340**, 960–964; (*b*) S. Ma, X.-S. Wang,

C. D. Collier, E. S. Manis and H.-C. Zhou, *Inorg. Chem.*, 2007, **46**, 8499–8501; (*c*) Y. Yuan, F. Sun, L. Li, P. Cui and G. Zhu, *Nat. Commun.*, 2014, **5**, 4260; (*d*) 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**, 141–144; (*e*) Y. Belmabkhout, H. Mouttaki, J. F. Eubank, V. Guillerm and M. Eddaoudi, *RSC Adv.*, 2016, **4**, 63855–63859.

2 (*a*) A. Cadiau, K. Adil, P. M. Bhatt, Y. Belmabkhout and M. Eddaoudi, *Science*, 2016, **353**, 137–140; (*b*) A. H. Assen, Y. Belmabkhout, K. Adil, P. M. Bhatt, D.-X. Xue, H. Jiang and M. Eddaoudi, *Angew. Chem., Int. Ed.*, 2015, **54**, 14353–14358; (*c*) R. T. Yang and E. S. Kikkinides, *AIChE J.*, 1995, **41**, 509–517; (*d*) M. C. Campo, A. M. Ribeiro, A. Ferreira, J. C. Santos, C. Lutz, J. M. Loureiro and A. E. Rodrigues, *Sep. Purif. Technol.*, 2013, **103**, 60–70; (*e*) J. Liu, Y. Liu, D. K. Talay, E. Calverley, M. Brayden and M. Martinez, *Carbon*, 2015, **85**, 201–211; (*f*) C. A. Grandea, J. Gasconb, F. Kapteijnb and A. E. Rodrigues, *Chem. Eng. J.*, 2010, **160**, 207–214; (*g*) C. A. Grande and A. E. Rodrigues, *Ind. Eng. Chem. Res.*, 2005, **44**, 8815–8829; (*h*) D. Xue, Y. Belmabkhout, O. Shekhah, H. Jiang, K. Adil, A. J. Cairns and M. Eddaoudi, *J. Am. Chem. Soc.*, 2015, **137**, 2089–2092; (*i*) B. Li, Y. Zhang, R. Krishna, K. Yao, Y. Han, Z. Wu, D. Ma, Z. Shi, T. Pham, B. Space, J. Liu, P. K. Thallapally, J. Liu, M. Chrzanowski and S. Ma, *J. Am. Chem. Soc.*, 2014, **136**, 8654; (*j*) Y. Zhang, B. Li, R. Krishna, Z. Wu, D. Ma, Z. Shi, T. Pham, K. Forrest, B. Space and S. Ma, *Chem. Commun.*, 2015, **51**, 2714–2717.

3 H. Marsh and F. Rodríguez-Reinoso, *Activated Carbon*, Taylor & Francis, 2006.

4 H. C. Foley, *Microporous Mater.*, 1995, **4**, 407–433.

5 (*a*) B. C. Bai, S. Cho, H.-R. Yu, K. B. Yi, K.-D. Kim and Y.-S. Lee, *J. Ind. Eng. Chem.*, 2013, **19**, 776–783; (*b*) P. S. Tin, T.-S. Chung, Y. Liu and R. Wang, *Carbon*, 2004, **42**, 3123–3131; (*c*) T.-H. Weng, H.-H. Tseng and M.-Y. Wey, *Int. J. Hydrogen Energy*, 2010, **35**, 6971–6983; (*d*) K. Briceño, A. Iulianelli, D. Montané, R. Garcia-Valls and A. Basile, *Int. J. Hydrogen Energy*, 2012, **37**, 13536–13544.

6 (*a*) B. Li, M. Chrzanowski, Y. Zhang and S. Ma, *Coord. Chem. Rev.*, 2016, **307**, 106–129; (*b*) S. R. Caskey, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.*, 2008, **130**, 10870–10871; (*c*) A. Demessence, D. M. D'Alessandro, M. L. Foo and J. R. Long, *J. Am. Chem. Soc.*, 2009, **131**, 8784–8786; (*d*) J. An, S. J. Geib and N. L. Rosi, *J. Am. Chem. Soc.*, 2010, **132**, 38–39; (*e*) B. Li, Z. Zhang, Y. Li, K. Yao, Y. Zhu, Z. Deng, F. Yang, X. Zhou, G. Li, H. Wu, N. Nijem, Y. J. Chabal, Z. Lai, Y. Han, Z. Shi, S. Feng and J. Li, *Angew. Chem., Int. Ed.*, 2012, **51**, 1412–1415; (*f*) F. Wang, Y.-X. Tan, H. Yang, Y. Kang and J. Zhang, *Chem. Commun.*, 2012, **48**, 4842–4844; (*g*) S. Xiang, Y. He, Z. Zhang, H. Wu, W. Zhou, R. Krishnaand and B. Chen, *Nat. Commun.*, 2012, **3**, 954; (*h*) P. Cui, Y.-G. Ma, H.-H. Li, B. Zhao, J.-R. Li, P. Cheng, P. Balbuena and H.-C. Zhou, *J. Am. Chem. Soc.*, 2012, **134**, 18892–18895; (*i*) W.-Y. Gao, W. Yan, R. Cai, K. Williams, A. Salas, L. Wojtas, X. Shi and S. Ma, *Chem. Commun.*, 2012, **48**, 8898–8900; (*j*) L. Du, Z. Lu, K. Zheng, J. Wang, X. Zheng, Y. Pan, X. You and J. Bai,

J. Am. Chem. Soc., 2013, **135**, 562–565; (*k*) J.-R. Li, J. Yu, W. Lu, J. Sculley, P. B. Balbuena and H.-C. Zhou, *Nat. Commun.*, 2013, **4**, 1538; (*l*) P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *Nature*, 2013, **495**, 80–84; (*m*) S. Osama, Y. Belmabkhout, Z. Chen, V. Guillerm, A. Cairns, K. Adil and M. Eddaoudi, *Nat. Commun.*, 2014, **5**, 4228; (*n*) P. M. Bhatt, Y. Belmabkhout, A. Cadiau, K. Adil, O. Shekhah, A. Shkurenko, L. J. Barbour and M. Eddaoudi, *J. Am. Chem. Soc.*, 2016, **138**, 9301–9307; (*o*) Y. Belmabkhout, V. Guillerm and M. Eddaoudi, *Chem. Eng. J.*, 2016, **296**, 386–397.

7 (*a*) B. Liu, H. Shioyama, T. Akita and Q. Xu, *J. Am. Chem. Soc.*, 2008, **130**, 5390–5391; (*b*) B. Liu, H. Shioyama, H. Jiang, X. Zhang and Q. Xu, *Carbon*, 2010, **48**, 456–463; (*c*) L. Radhakrishnan, J. Reboul, S. Furukawa, P. Srinivasu, S. Kitagawa and Y. Yamauchi, *Chem. Mater.*, 2011, **23**, 1225–1231; (*d*) S. J. Yang, T. Kim, J. H. Im, Y. S. Kim, K. Lee, H. Jung and C. R. Park, *Chem. Mater.*, 2012, **24**, 464–470; (*e*) G.-P. Hao, D. Mondin, Z. Zheng, T. Biemelt, S. Klosz, R. Schubel, A. Eychmüller and S. Kaskel, *Angew. Chem., Int. Ed.*, 2015, **54**, 1941–1945; (*f*) M. Hu, J. Reboul, S. Furukawa, N. L. Torad, Q. Ji, P. Srinivasu, K. Ariga, S. Kitagawa and Y. Yamauchi, *J. Am. Chem. Soc.*, 2012, **134**, 2864–2867; (*g*) S. J. Yang, S. Nam, T. Kim, J. H. Im, H. Jung, J. H. Kang, S. Wi, B. Park and C. R. Park, *J. Am. Chem. Soc.*, 2013, **135**, 7394–7397; (*h*) H.-L. Jiang, B. Liu, Y.-Q. Lan, K. Kuratani, T. Akita, H. Shioyama, F. Zong and Q. Xu, *J. Am. Chem. Soc.*, 2011, **133**, 11854–11857; (*i*) J. Tang, R. R. Salunkhe, J. Liu, N. L. Torad, M. Imura, S. Furukawa and Y. Yamauchi, *J. Am. Chem. Soc.*, 2015, **137**, 1572–1580; (*j*) W. Zhang, Z.-Y. Wu, H.-L. Jiang and S.-H. Yu, *J. Am. Chem. Soc.*, 2014, **136**, 14385–14388; (*k*) A. Aijaz, N. Fujiwara and Q. Xu, *J. Am. Chem. Soc.*, 2014, **136**, 6790–6793; (*l*) Q. Lin, X. Bu, A. Kong, C. Mao, X. Zhao, F. Bu and P. Feng, *J. Am. Chem. Soc.*, 2015, **137**, 2235–2238; (*m*) Y.-H. Shih, C.-P. Fu, W.-L. Liu, C.-H. Lin, H.-Y. Huang and S. Ma, *Small*, 2016, **12**, 2057–2066; (*n*) L. Lux, K. Williams and S. Ma, *CrystEngComm*, 2015, **17**, 10–22.

8 R. A. Smaldone, R. S. Forgan, H. Furukawa, J. J. Gassensmith, A. M. Z. Slawin, O. M. Yaghi and J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2010, **49**, 8630–8634.

9 (*a*) B.-H. Han, W. Zhou and A. Sayari, *J. Am. Chem. Soc.*, 2003, **125**, 3444–3445; (*b*) S. Polarz, B. Smarsly, L. Bronstein and M. Antonietti, *Angew. Chem., Int. Ed.*, 2001, **40**, 4417–4421.

10 (*a*) G. Horváth and K. Kawazoe, *J. Chem. Eng. Jpn.*, 1983, **16**, 470–475; (*b*) Y. Zhang, B. Li, K. Williams, W.-Y. Gao and S. Ma, *Chem. Commun.*, 2013, **49**, 10269–10271; (*c*) B. Li, Y. Zhang, D. Ma, L. Zhu, D. Zhang, M. Chrzanowski, Z. Shi and S. Ma, *Chem. Commun.*, 2015, **51**, 8683–8686.

11 J. J. Gassensmith, H. Furukawa, R. A. Smaldone, R. S. Forgan, Y. Y. Botros, O. M. Yaghi and J. F. Stoddart, *J. Am. Chem. Soc.*, 2011, **133**, 15312–15315.

12 J. Coronas, R. D. Noble and J. L. Falconer, *Ind. Eng. Chem. Res.*, 1998, **37**, 166–176.