

ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Ultra-Micro Porous Organic Polymer for High Performance Carbon Dioxide Capture and Separation

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

Ali K. Sekizkardes,^{*a} Jeffrey T. Culp,^{a,d} Timur Islamoglu,^b Anne Marti,^a David Hopkinson,^a Christina Myers,^a Hani M El-Kaderi,^b and Hunaid B. Nulwala^{a,c}

DOI: 10.1039/x0xx00000x

www.rsc.org/

Rational design concepts were used to prepare a novel porous benzimidazole-linked polymer (BILP-101) in a simple one-pot reaction. BILP-101 has ultra-microporosity (0.54 nm), very high CO₂ uptake (~1 mmol/g, 4 wt%, 0.15 bar/298 K) and exceptional CO₂/N₂ selectivity of 80 (298 K), which results in remarkable working capacity and regenerability for CO₂ capture applications.

Carbon dioxide (CO₂) capture using solid sorbents has deemed high potential to remove CO₂ from power plant flue gas to mitigate problems associated with greenhouse gas emissions. Sorbents including zeolites, porous carbon, organic molecular crystals, and metal organic frameworks (MOFs) have been advent materials to the current solvent-based CO₂ capture.¹⁻² The ultimate goal is to capture CO₂ from the flue gas and release it for a long time storage without a high-energy penalty. Porous organic polymers (POPs) have been suggested as strong candidate for achieving these goals. Given their highly porous structures with tunable textural and chemical properties, and inherent lightweight, an increasing amount of research effort has been dedicated to the design and synthesis of versatile type of POPs.³⁻⁴

Ability to access targeted properties in a given material using simple and robust chemistry is vitally important to achieve CO₂ capture and separation goals.⁵⁻⁷ Textural properties such as pore size and surface area of polymers have a complimentary role with functional groups in CO₂ uptake performance of sorbents.⁸ The selection of certain properties is prominent for a polymer to be at the 'sweet spot' of gas interactions i.e. at the cusp of chemisorption-physorption.⁹ This would minimize the energy penalty to

regenerate the sorbent while maintaining high CO₂ uptake and selectivity properties. Strong interaction between CO₂ and framework of the sorbent is needed due to low partial pressure of CO₂ in gas separation systems such as those for flue gas. Studies have shown that pore size plays a more significant role than surface area in the CO₂ uptake at low CO₂ concentrations (~15% CO₂).¹⁰⁻¹¹ Therefore it is necessary to construct highly stable porous sorbent exhibiting narrow pore size distribution and high percentage functional sites for target CO₂ capture and separation systems. Accordingly, benzimidazole-linked polymers (BILPs) recently reported by El-Kaderi and co-workers showed promising performances for selective CO₂ capture.¹²

Herein, we report a new sorbent, benzimidazole-linked polymer (BILP-101), synthesized from commercially available building blocks. BILP-101 yields four distinct properties: (i) enhanced Lewis basic nitrogen /carbon ratio to ensure high CO₂ uptake, (ii) smaller pore size and high micro porosity rather than high surface area, (iii) optimal interaction energy within physisorption limits and (iv) high physicochemical stability. BILP-101 was synthesized by a facile, efficient and template-free polycondensation reaction,¹³ between aryl-*o*-diamine and aryl-aldehyde; 1,2,4,5-benzenetetramine tetrahydrochloride (TBA) and 1,3,5-triformylbenzene, respectively.

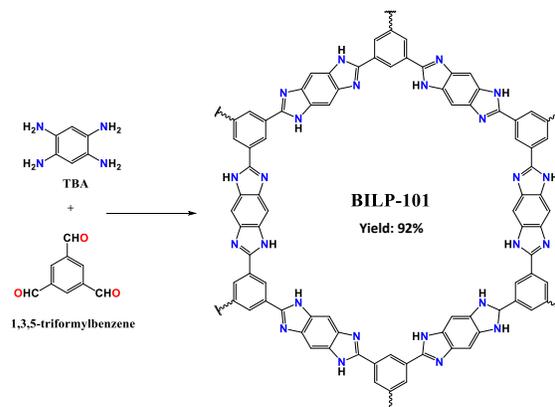


Figure 1. Illustrative scheme of BILP-101 synthesis, (i) DMF, -30 °C, 1 hr, (ii) DMF, RT, 12 hr under N₂, (iii) DMF, at 130 °C for two days under O₂.

^a U.S. Department of Energy National Energy and Technology Laboratory, Pittsburgh, Pennsylvania 15236, US. Email; ali.sekizkardes@netl.doe.gov Phone: 1 (412) 386-7255.

^b Department of Chemistry, Virginia Commonwealth University, 1001 W. Main St., Richmond, VA 23284-2006.

^c Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213.

^d AECOM PO Box 618 South Park, PA 15219.

Electronic Supplementary Information (ESI) available: Experimental Procedure, Elemental Analysis, Gas uptake isotherms, working capacity and selectivity calculations See DOI: 10.1039/x0xx00000x

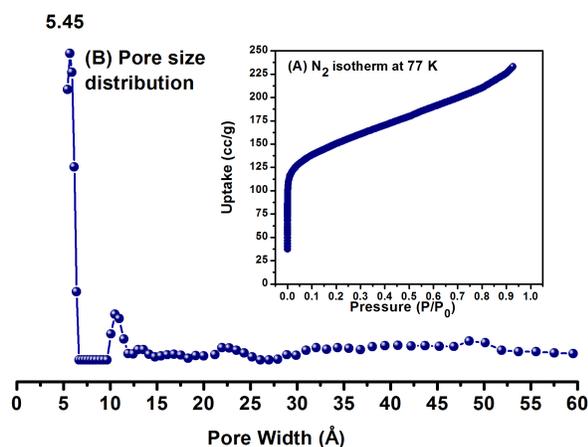


Figure 2. Pore size distribution (PSD) (A) and N_2 uptake isotherm of BILP-101 at 77 K (B).

The chemical connectivity of BILP-101 was investigated by FT-IR while chemical composition was confirmed by microelemental analysis. The characteristic stretching bands from the imidazole ring (free N-H and hydrogen-bonded N-H) were observed in FT-IR (Fig. S4).¹² The absence of the strong peak located at 1700 cm^{-1} , corresponding to the aldehyde carbonyl, indicates a complete consumption of aldehyde functional groups. The chemical connectivity of BILP-101 remained intact after washing with 1 M HCl and 1 M NaOH. The thermal stability of BILP-101 was confirmed by thermogravimetric analysis (TGA) which shows thermal stability up to $\sim 600\text{ }^\circ\text{C}$ (Fig. S1).

Porosity measurements were performed via low-pressure nitrogen sorption measurements at 77 K on the activated sample of the BILP-101 (Fig. 2B). The typical Type I isotherm showed a rapid N_2 uptake at low relative pressures ($P/P_0 < 0.1$ bar) as an indication of the microporous nature of BILP-101.¹³ The calculation of the specific BET surface area (SA_{BET}) using a BET consistency plot (Fig. S6) showed that BILP-101 possesses $SA_{\text{BET}} = 536\text{ m}^2\text{ g}^{-1}$ similar to reported POPs such as BILP-5,¹² and SNW-1¹⁴ which share similar polymer structure with BILP-101. Pore size distribution (PSD) of BILP-101 calculated by fitting the adsorption branch of the N_2 isotherm with none local density functional theory (NLDFT), revealed a pore width maxima of 0.54 nm. Pore volume was calculated to be 0.41 cc g^{-1} at $P/P_0 = 0.90$ (Fig. S7). Narrower micropores, compared to similar

porous polymers can be attributed to relatively small and rigid building blocks employed in the synthesis of BILP-101. In addition, the selection of a smaller aldehyde unit resulted in a higher Lewis basic N/C ratio, which is necessary to reach high CO_2 uptakes at low pressures as it provides more adsorption sites for CO_2 .

We performed a set of CO_2 sorption measurements to evaluate BILP-101 in the target gas separation application: CO_2 separation from post-combustion flue gas. The CO_2 isotherm of BILP-101 showed an uptake of nearly 1 mmol g^{-1} at 0.15 bar and 298 K, competing with the best performing polymer, BILP-4 ($\sim 1\text{ mmol g}^{-1}$) in all reported polybenzimidazoles (Fig. 3A).^{12,15} In a typical gas separation study, CO_2 uptake performances of polymers are evaluated at 1 bar.^{16,17} However, major gas separation systems (flue gas, natural gas and shale gas) are designed for the gas composition where partial pressure of CO_2 does not exceed 10-30%. Nevertheless, we studied CO_2 uptake performances of BILP-101 at 273, 288, 298, 313 K and up to 10 bar to ensure fair comparison with similar porous organic polymers recognized as CO_2 sorbents (Fig. 3A, 4A, S8 and Table S2). Volumetric gas sorption analysis showed that CO_2 uptake of BILP-101 (2.43 mmol/g at 298 K and 1 bar) competes with porous organic sorbents such as SNW-1,¹⁴ CPOP-1,¹⁸ PPN-101,¹⁹ PPF-1,²⁰ Oz-COP,²¹ ALP-1,²² PAF-5,²³ PSNs,²⁴ MPIs²⁴ and functionalized NPOFs,²⁴ as well as other porous sorbents including Zeolite 13X,¹¹ UiO-66,²⁶ and ZIF-82.¹¹ We also conducted gravimetric gas sorption analysis on BILP-101 using gravimetric gas uptake isotherms. The CO_2 uptake of BILP-101 at 0.15 and 1 bar, and at 298 K showed virtually identical results (~ 4 and $\sim 10\text{ wt}\%$, respectively) compared to isotherms collected by volumetric gas analysis. Moreover, sorbent regenerability studies showed that BILP-101 preserves its CO_2 adsorption properties after five subsequent adsorption/desorption cycles without applying any thermal activation in the desorption cycle (Fig. 4B).

High CO_2 uptake properties of BILP-101 can be explained by two key parameters; ultra-micropores and high concentration of functional groups.^{27,28} While the former parameter endows higher surface energy, the latter parameter dictates interacting behaviour of the sorbent with CO_2 molecules.²⁹ For example: CO_2 uptake capacity of BILP-101 particularly outperforms SNW-1 polymer despite very similar textural properties (surface area, pore size, pore volume) between these two polymers.¹⁴

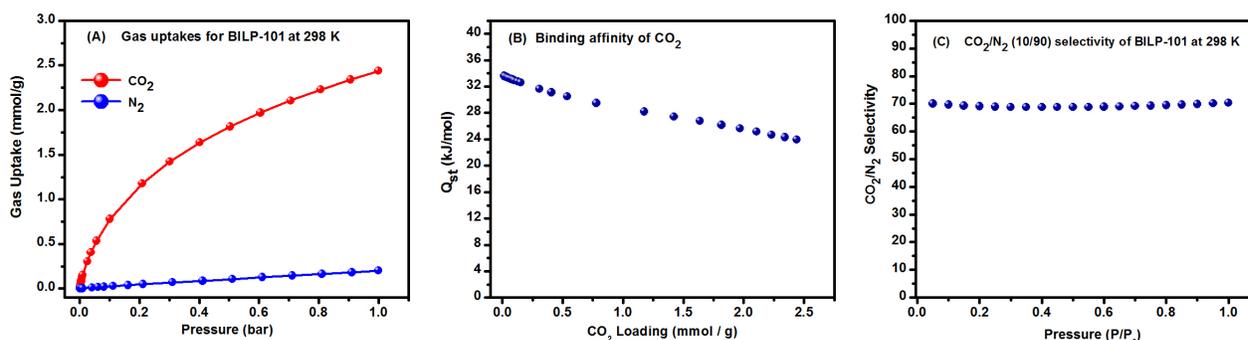


Figure 3. (A) Low-pressure (0-1 bar) volumetric CO_2 and N_2 uptake isotherms at 298 K, (B) CO_2 isosteric heats of adsorption (Q_{st}) and (C) IAST selectivity calculations ($\text{CO}_2:\text{N}_2 = 10:90$) for BILP-101.

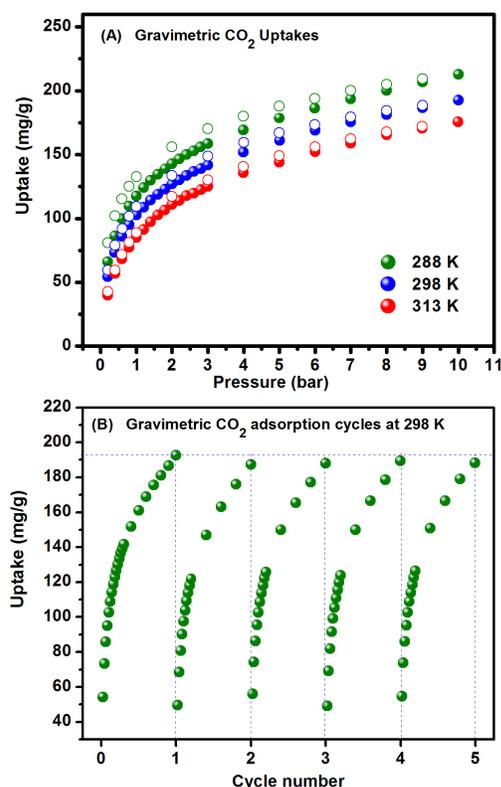


Figure 4. (A) High-pressure (0.2–10 bar) CO₂ adsorption/desorption isotherm at 288, 298 and 313 K (B) Five subsequent CO₂ adsorption cycles at 298 K.

We postulated that this is due to the higher Lewis basicity of the imidazole functionalities in BILP-101 compared to triazine functional groups of SNW-1,¹⁴ which play a key role in facilitating stronger interactions with polarizable CO₂.¹⁹ Such interactions should be maintained in the physisorption regime to accomplish adsorbent regeneration with a minimal energy input. To ascertain this point, the isosteric heats of CO₂ adsorption (Q_{st}) of BILP-101 was calculated by the two most common methods; virial equation (Fig. 3) and Clausius-Clapeyron equations (Fig. S13). BILP-101 showed a Q_{st} value of 33 kJ mol⁻¹ for CO₂ which falls in the optimal binding affinity region proposed by Wilmer *et al.* for CO₂ capture from flue gas.³⁰ This binding affinity endows a high CO₂ uptake in the low pressure region, yet it still yields minimal hysteresis in isotherms which is indicative of complete materials regeneration without heating (Fig. 4b and S9). In addition, the CO₂ binding affinity calculated by the Clausius-Clapeyron equation reveals an increase in Q_{st} with increased loading up to 40 mg/g and then it starts decreasing (Fig. S13). This increase in binding affinity with increased CO₂ loading has been attributed in recent literature to the cooperative binding of different adsorption sites.³¹

We investigated other gas (N₂ and CH₄) uptake performances of BILP-101 to characterize preferential binding of CO₂ over N₂ and CH₄. Compared to CO₂, BILP-101 shows much lower uptake for CH₄ and almost negligible adsorption of N₂ (Fig. S8). Using the initial slope method, BILP-101 revealed CO₂/N₂ selectivity of 80,

outperforming all reported selectivity values for BILPs (Fig. S10).¹⁵ This outstanding selectivity value of BILP-101 compared to other POPs can be attributed to higher imidazole concentration of BILP-101 coupled with its narrower pore size property. Recent studies conclude that the narrow pore size distribution (<1nm) dictates the selective CO₂ capture performance of sorbents when low CO₂ concentration (<0.5 bar) mixtures are considered, while high surface area materials are needed as CO₂ concentration increases.^{30,32} Still, the trade-off between high CO₂ selectivity and uptake remains as great hurdle to subsume these two properties in a porous sorbent with the desired performance. At this point, the systematically designed sorbent structure of BILP-101 challenges this ongoing problem by merging high CO₂ selectivity with high CO₂ uptake properties in a sorbent media.

Motivated by these high CO₂ uptake, selectivity and regenerability properties, we evaluated the CO₂ capture of BILP-101 in post combustion flue gas settings using the set of criteria collected from the chemical engineering literature.¹¹ Because this approach requires the selectivity calculations of BILP-101 using Ideal Adsorbed Solution Theory (IAST),¹⁵ it gives us a chance to validate our selectivity calculations from the initial slope method. The pure CO₂ isotherm and N₂ isotherms at 298 K were fitted to the dual site and single site Langmuir isotherm models, respectively (Fig. 11s). IAST selectivity for CO₂/N₂ (CO₂:N₂=10:90) values was calculated to be 71 at 298 K and 1 bar. In general, selectivity should decrease with increasing pressure (loading) as active sites are saturated and remaining sites are not that selective towards CO₂, however CO₂/N₂ selectivity in BILP-101 remains near unity at least up to 1 bar due to high density of strong adsorption sites (N atoms) in BILP-101. We used the same CO₂/N₂ composition to calculate sorbent selection parameters as depicted in Table 1 and S2 for BILP-101 under Vacuum Swing Adsorption (VSA) settings at 298K. Working capacity of BILP-101 was calculated to be 0.80 mol/kg which exceeds reported sorbents such as ZIF-82, HKUST-1, and MOF-4b (Table 1).¹¹ BILP-101 showed an exceptional sorbent selection parameter, S , (factor of 556.4) which is the comprehensive criteria to evaluate CO₂ capture properties of sorbents as it combines the working capacity, selectivity and regenerability criteria (Eq. S2), and therefore it gives a better insight into the trade-off between selectivity and uptake.¹¹

Table 1. Top performing sorbents for flue gas (CO₂/N₂:10/90) separation using VSA at 298K, $P_{ads} = 1$ bar and $P_{des} = 0.1$ bar.

Sorbent	ΔN_1	R	α_{12}^{ads}	S
BILP-101 (POP)	0.80	84.8	70.3	556
SNU-Cl-va ³³ (POP)	0.41	87.3	38.0	262
Zeolite-13X ³⁴ (Zeolite)	1.35	54.2	86.2	128
ZIF-78 ³⁵ (MOF)	0.58	96.3	34.5	396
ZIF-82 ³⁵ (MOF)	0.38	92.5	22.7	101
MOF-4b ³⁶ (MOF)	0.06	83.8	154	104
HKUST-1 ³⁷ (MOF)	0.55	89.0	20.4	46.2
Ni-MOF-74 ³⁸ (MOF)	3.20	73.7	41.1	83.5
NoritR1 extra ³⁹ (Activated Carbon)	0.28	73.7	10.7	5.09

ΔN_1 : CO₂ working capacity (mol/kg), R= Regenerability, α_{12}^{ads} = IAST selectivity, S=Sorbent selection parameter (Eq. S3).¹¹

This S value is the highest in top performing sorbents considered for post-combustion flue gas separation including Zeolite 13X, Ni-MOF-74, and TBILP-2 which were evaluated under the same settings (temperature, pressure, method).^{11,16,33}

This study presents the rational design of a ultra-microporous organic polymer, BILP-101, which comprises cost-efficient preparation with high chemical (acid/base) and thermal stability (> 600 °C). BILP-101 challenges the trade-off between the CO₂ uptake and selectivity by scoring very high CO₂ uptake (~1 mmol/g) at 0.15 bar and 298 K and with an unprecedented CO₂/N₂ selectivity (80 at 298 K). Moreover, BILP-101 shows very promising sorbent selection parameter performance, S, (556) for practical CO₂ capture and flue gas separation.

Acknowledgements

This technical effort was performed in support of the U.S. Department of Energy's National Energy Technology Laboratory's ongoing research on CO₂ capture 2015 F.Y. F.W.P. The authors thank to Sittichai Natesakhawat for the porosity measurements and Adefemi Egbebi for running the TGA experiments.

Notes and references

- S. Chu, *Science*, 2009, **325**, 1599.
- (a) A. G. Slater and A. I. Cooper, *Science*, 2015, **348**, 8075. (b) D. Wu, F. Xu, B. Sun, R. Fu, H. He and K. Matyjaszewski, *Chem. Rev.*, 2012, **112**, 3959.
- Y. Zhang and S. N. Riduan, *Chem. Soc. Rev.*, 2012, **41**, 2083.
- R. Dawson, E. Stockel, J. R. Holst, D. J. Adams and A. I. Cooper, *Energy Environ. Sci.*, 2011, **4**, 4239.
- (a) W. Lu, Z. Wei, D. Yuan, J. Tian, S. Fordham and H.-C. Zhou, *Chem. Mater.*, 2014, **26**, 4589. (b) C. J. Hawker and K. L. Wooley, *Science*, 2015, **309**, 1200.
- S. Wu, S. Gu, A. Zhang, G. Yu, Z. Wang, J. Jian and C. Pan, *J. Mater. Chem. A*, 2015, **3**, 878.
- 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.
- R. Dawson, A. I. Cooper and D. J. Adams, *Polym. Int.*, 2013, **62**, 345.
- P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Q. Ma, B. Space, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *Nature*, 2013, **495**, 80-84.
- T. C. Drage, C. E. Snape, L. A. Stevens, J. Wood, J. W. Wang, A. I. Cooper, R. Dawson, X. Guo, C. Satterley and R. Irons, *J. Mater. Chem.*, 2012, **22**, 2815.
- Y. S. Bae and R. Q. Snurr, *Angew. Chem., Int. Edit.*, 2011, **50**, 11586.
- M. G. Rabbani and H. M. El-Kaderi, *Chem. Mater.*, 2012, **24**, 1511.
- M. G. Rabbani and H. M. El-Kaderi, *Chem. Mater.*, 2011, **23**, 1650.
- X. Gao, X.-Q. Zou, H.-P. Ma, S. Meng and G.-S. Zhu, *Adv. Mater.*, 2014, **26**, 3644.
- (a) A. K. Sekizkardes, T. Islamoglu, Z. Kahveci and H. M. El-Kaderi, *J. Mater. Chem. A*, 2014, **2**, 12492. (b) A. K. Sekizkardes, S. Altarawneh, Z. Kahveci, T. Islamoglu and H. M. El-Kaderi, *Macromolecules*, 2014, **47**, 8328. (c) J. Weber, M. Antonietti, A. Thomas, *Macromolecules*, 2007, **40**, 1299. (d) Y.-C. Zhao, T. Wang, L.-M. Zhang, Y. Cui, B.-H. Han, *Poly. Chem.*, 2015, **6**, 748.
- (a) D. M. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem., Int. Ed.*, 2010, **49**, 6058. (b) V. Guillermin, L. J. Weselinski, M. Alkordi, M. I. Mohideen, Y. Belmabkhout, A. J. Cairns and M. Eddaoudi, *Chem. Commun.*, 2014, **50**, 1937.
- 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.
- 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.
- M. Zhang, Z. Perry, J. Park, and H.-C. Zhou, *Polymer*, 2014, **55**, 335.
- Y. Zhu, H. Long, and W. Zhang, *Chem. Mater.* 2013, **25**, 1630.
- D. Ko, H. A. Patel and C. T. Yavuz, *Chem. Commun.*, 2015, **51**, 2915.
- P. Arab, M. G. Rabbani, A. K. Sekizkardes, T. Islamoglu and H. M. El-Kaderi, *Chem. Mater.*, 2014, **26**, 1385.
- H. Ren, T. Ben, F. Sun, M. Guo, X. Jing, H. Ma, K. Cai, S. Qiu and G. Zhu, *J. Mater. Chem.*, 2011, **21**, 10348.
- (a) G. Li, B. Zhang, J. Yan, Z. Wang, *Chem. Commun.*, 2014, **50**, 1897. (b) G. Li and Z. Wang, *Macromolecules*, 2013, **46** (8), 3058. (c) T. Islamoglu, M. G. Rabbani and H. M. El-Kaderi, *J. Mater. Chem. A*, 2013, **1**, 10259.
- G. E. Cmarik, M. Kim, S. M. Cohen and K. S. Walton, *Langmuir*, 2012, **28**, 15606.
- H. A. Patel, S. H. Je, J. Park, D. P. Chen, Y. Jung, C. T. Yavuz and A. Coskun, *Nat. Commun.*, 2013, **4**, 1357.
- X. Zhu, S. M. Mahurin, S.-H. An, C.-L. Do-Thanh, C. Tian, Y. Li, L. W. Gill, E. W. Hagaman, Z. Bian, J.-H. Zhou, J. Hu, H. Liu and S. Dai, *Chem. Commun.*, 2014, **50**, 7933.
- Y. H. Xu, S. B. Jin, H. Xu, A. Nagai and D. L. Jiang, *Chem. Soc. Rev.*, 2013, **42**, 8012.
- G. Li, B. Zhang, J. Yan and Z. Wang, *Macromolecules*, 2014, **47**, 6664.
- C. E. Wilmer, O. K. Farha, Y. S. Bae, J. T. Hupp and R. Q. Snurr, *Energy Environ. Sci.*, 2012, **5**, 9849.
- R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi and T. K. Woo, *Science*, 2010, **330**, 650.
- A. O. Yazaydin, R. Q. Snurr, T. H. Park, K. Koh, J. Liu, M. D. LeVan, A. I. Benin, P. Jakubczak, M. Lanuza, D. B. Galloway, J. J. Low and R. R. Willis, *J. Am. Chem. Soc.*, 2009, **131**, 18198.
- L. H. Xie and M. P. Suh, *Chem-Eur. J.*, 2013, **19**, 11590.
- R. Cavenati, C. A. Grande, A. E. Rodrigues, *J. Chem. Eng. Data*, 2004, **49**, 1095.
- R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keefe, and O. M. Yaghi, *J. Am. Chem. Soc.* 2009, **131**, 3875.
- Y.-S. Bae, O. K. Farha, A. M. Spokoynny, C. A. Mirkin, J. T. Hupp, R. Q. and C. A. Mirkin, *Chem. Commun.* 2010, **46**, 3478.
- P. D. C. Dietzel, V. Besikiotis, and R. Blom, *J. Mater. Chem.* 2009, **19**, 7362.
- Z. J. Liang, M. Marshall, and A. L. Chaffee, *Energy & Fuels*, 2009, **23**, 2785.
- F. Dreisbach, R. Staudt, and J. U. Keller, *Adsorption*, 1999, **5**, 215.