ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2014, **50**, 8507

Received 26th May 2014,
Accepted 11th June 2014

DOI: 10.1039/c4cc04012k

www.rsc.org/chemcomm

Dual functionalization of porous aromatic frameworks as a new platform for heterogeneous cascade catalysis†

Yiming Zhang,‡ Baiyan Li‡ and Shengqian Ma*

Dual functionalization of porous aromatic frameworks (PAFs) has been illustrated in the context of incorporating two antagonistic sites of strong acid and strong base into the highly porous and highly robust PAF-1 *via* stepwise post-synthetic modification. The resulting bifunctionalized PAF-1 exhibits excellent performances in catalyzing a series of cascade reactions and demonstrates superior chemical stability compared to the counterparts of mesoporous silica and MOFs, thereby opening the door for dual functionalization of PAFs as a new platform for heterogeneous cascade catalysis.

The capability of enzymes to immobilize different catalytically active sites or mutually incompatible catalytic groups on a single molecule in a site-isolation manner maintaining their independent function yet acting cooperatively to catalyze one step in a multistep reaction sequence[1] has spurred intense interest in developing catalysts containing multiple types of active centers for cascade reactions.[2] The driving force for the keen pursuit of cascade catalysts lies in that cascade reactions can allow a consecutive series of reactions to proceed in a concurrent fashion without isolation of intermediates and self-quenching of catalysts, thus offering enormous economical advantages.[3] Given the important role in chemical industries, great attention has been paid to the development of bi/multi-functional solid catalysts for heterogeneous cascade catalysis, which however is challenged by the controlled spatial arrangement of a high-density yet continuous range of different active sites.[4] Extensive efforts have been devoted to grafting bi/multi-functional groups onto the surfaces of mesoporous silica materials.[5] However, the limited amount of silanol groups on the surface inevitably dilutes the density of active sites for mesoporous silica-based bi/multi-functional catalysts,[5f,6] and the instability of mesoporous silica in basic solutions also represents a potential limitation for their application in a wide range of catalytic systems.[7] Albeit bi/multi-functionalization has been demonstrated in metal–organic frameworks (MOFs)[8] with some investigated for cascade catalysis,[9] the issue of water/chemical stability[10] remains to be addressed for the majority of MOFs before MOF-based bi/multi-functional catalysts could meet the stringent industrial requirements. A bifunctional porous polymer incorporated with strong acidic sites and weak basic sites was reported recently,[11] but the weak basicity together with low surface area thereby exterior surface catalysis limits its performance in tandem reactions, particularly those that require the co-existence of both a strong acidic site and a strong basic site.

Therefore, there is still a need to search for new types of platforms for heterogeneous cascade catalysis. Several attributes have been delineated for an ideal platform to afford bi/multifunctional solid catalysts: (i) a high surface area with a high-density and continuous range of spatially arranged different active sites to afford high catalytic efficiency, (ii) a robust framework structure with high water/chemical stability to sustain framework integrity under typical reaction conditions, (iii) ease of functionalization to facilitate the tailoring of active sites.

It has been well documented that the phenyl ring can be functionalized with different groups through various established organic reactions.[12] Porous aromatic frameworks (PAFs),[13] a subclass of porous organic polymers[14] that are constructed from phenyl ring-derived building blocks, feature high surface area and robust structure with high water/chemical stability. These features make them a promising platform to afford bifunctionality for heterogeneous cascade catalysis.

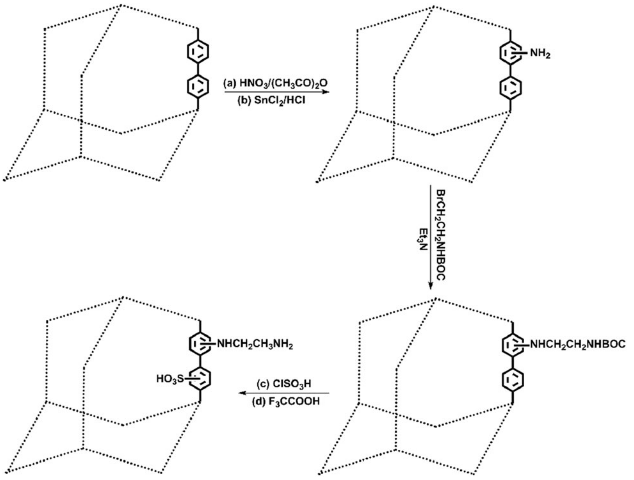
We selected PAF-1,[15] which possesses a hypothetical diamondoid-topology structure with very high surface area and exceptional stability in water and acidic–basic media, for "proof-of-concept" studies. To achieve dual functionality in PAF-1, two different types of functional groups can be readily grafted to the phenyl rings *via* stepwise post-synthetic modification[16] using selected organic reactions (Scheme S1, ESI†). In this contribution, we demonstrate how two antagonistic sites of strong acid and strong base can be incorporated into PAF-1 to afford a highly effective and highly stable bifunctional solid catalyst for acid–base catalyzed tandem reaction, thereby paving a way

---

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

† Electronic supplementary information (ESI) available: Experimental details, procedures for catalytic reactions, and the TGA plot. See DOI: 10.1039/c4cc04012k

‡ These authors contributed equally to this work.



Scheme 1 Illustration of stepwise post-synthetic modification of PAF-1 to graft the two antagonistic functional groups of a strong acid and a strong base to afford PAF-1-$NHCH_2CH_2NH_2$–SO_3H.

for dual functionalization of PAFs as a new platform for heterogeneous cascade catalysis.

In order to graft the two antagonistic functional groups of strong acid and strong base onto PAF-1 (Scheme 1), the freshly prepared PAF-1 was first nitrated and then reduced to PAF-1-NH_2, which was further modified by *N*-BOC-bromoethylamine to afford PAF-1-$NHCH_2CH_2NHBOC$. Sulfonation of PAF-1-$NHCH_2CH_2NHBOC$ followed by deprotection gave rise to the desired bifunctional catalyst PAF-1-$NHCH_2CH_2NH_2$–SO_3H in which the aliphatic amine group can serve as the strong basic catalytic site and the sulfonic group can act as the strong acidic catalytic site.

Elemental analysis suggested that PAF-1-$NHCH_2CH_2NH_2$–SO_3H contains ~1.66 mmol g^{-1} of aliphatic amine groups and 0.79 mmol g^{-1} of –SO_3H groups. The FT-IR spectra (Fig. 1) of PAF-1-NO_2 show two asymmetric and symmetric stretching vibrations of the nitro group at 1528 cm^{-1} and 1344 cm^{-1},[17] indicating the successful modification of nitro groups onto the framework of PAF-1. The disappearance of the nitro group bands in PAF-1-NH_2 can be attributed to the reduction of the nitro group to the amino group. The existence of sulfonic groups in PAF-1-$NHCH_2CH_2NHBOC$–SO_3H and PAF-1-$NHCH_2CH_2$ NH_2–SO_3H is confirmed by the appearance of absorption peaks at 1229 cm^{-1} and 1033 cm^{-1}, the characteristic bands of SO_3H.[18]

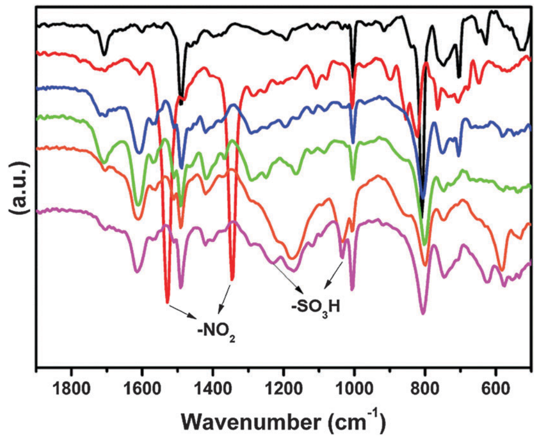


Fig. 1 FT-IR spectra of PAF-1 (black), PAF-1-NO_2 (red), PAF-1-NH_2 (blue), PAF-1-$NHCH_2CH_2NHBOC$ (green), PAF-1-$NHCH_2CH_2NHBOC$–SO_3H (orange), and PAF-1-$NHCH_2CH_2NH_2$–SO_3H (magenta).

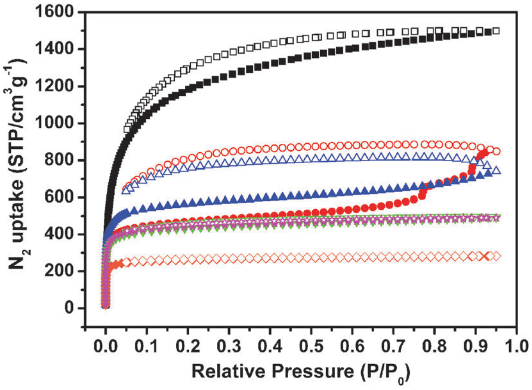
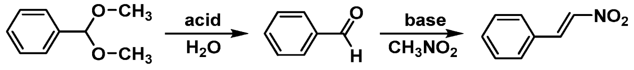


Fig. 2 The N_2 adsorption isotherms (solid symbols: adsorption; open symbols: desorption) at 77 K for: PAF-1 (black); PAF-1-NO_2 (red), PAF-1-NH_2 (blue), PAF-1-$NHCH_2CH_2NHBOC$ (green), PAF-1-$NHCH_2CH_2NHBOC$–SO_3H (orange), and PAF-1-$NHCH_2CH_2NH_2$–SO_3H (magenta).

N_2 sorption measurements at 77 K reveal the preservation of permanent porosity during the stepwise dual functionalization process of PAF-1 even under harsh conditions (Fig. 2). Nitration of PAF-1 leads to a significant decrease in the Brunauer–Emmett–Teller (BET) surface area from 4162 m^2 g^{-1} for PAF-1 to 1764 m^2 g^{-1} for PAF-1-NO_2, whereas the reduction of the NO_2 group to the NH_2 group results in an increase of the BET surface area to 2129 m^2 g^{-1} for PAF-1-NH_2. Steady reduction of the BET surface area was observed during the process of modifying PAF-1-NH_2 with *N*-BOC-bromoethylamine followed by sulfonation, as indicated by the values of 1637 m^2 g^{-1} and 1003 m^2 g^{-1} for PAF-1-$NHCH_2CH_2NHBOC$ and PAF-1-$NHCH_2CH_2NHBOC$–SO_3H respectively. Deprotection of PAF-1-$NHCH_2CH_2NHBOC$–SO_3H affords a BET surface area of 1672 m^2 g^{-1} for the bifunctional PAF-1-$NHCH_2CH_2NH_2$–SO_3H, which however is much higher than the BET surface areas of similar bifunctional mesoporous silica[5] and porous polymers[11] reported previously.

Given the high surface area together with the high density of strong basic and strong acidic sites, we evaluated the performances of PAF-1-$NHCH_2CH_2NH_2$–SO_3H as a bifunctional solid catalyst in the context of acid–base catalyzed tandem reaction involving the deacetalization and subsequent Henry reaction (Table 1). Remarkably, PAF-1-$NHCH_2CH_2NH_2$–SO_3H can effectively catalyze benzaldehyde dimethyl acetal (**1**) into 2-nitrovinyl benzene (**3**) in almost quantitative yield in 24 h (Table 1, entry 1). In contrast, the employment of the monofunctional PAF-1-SO_3H with strong acidity as a catalyst afforded only the product of benzaldehyde (**2**) (Table 1, entry 2) and a negligible amount of **3** was obtained when the reaction was catalyzed by the monofunctional PAF-1-CH_2NH_2 with strong basicity (Table 1, entry 3). In addition, a negligible amount of **3** was also observed when the bifunctional PAF-1-NH_2–SO_3H with a weak basic site was used (Table 1, entry 4). These results therefore suggest the requirement of co-existence of a strong

Table 1 One pot deacetalization–Henry reaction[a]



1 2 3

Entry	Catalyst	Conv. of 1 [%]	Yield of 2 [%]	Yield of 3 [%]
1	PAF-1-$NHCH_2CH_2NH_2$–SO_3H	100	2	97.2
2	PAF-1-SO_3H	100	100	0
3	PAF-1-CH_2NH_2	Trace	Trace	Trace
4	PAF-1-NH_2–SO_3H	100	100	Trace
5	Ethylamine + *p*-toluene sulfonic acid	Trace	Trace	Trace
6	PAF-1-$NHCH_2CH_2NH_2$–SO_3H + ethylamine	Trace	Trace	Trace
7	PAF-1-$NHCH_2CH_2NH_2$–SO_3H + *p*-toluene sulfonic acid	100	100	Trace
8[b]	PAF-1-$NHCH_2CH_2NH_2$–SO_3H	100	5	94.7

[a] Reaction conditions: benzaldehyde dimethyl acetal (1.0 mmol), CH_3NO_2 (5.0 mL), 90 °C, 24 h. [b] Treatment with NaOH (2 M) and HCl (2 M).

acidic site and a strong basic site as in the bifunctional PAF-1-$NHCH_2CH_2NH_2$–SO_3H for effectively catalyzing the one-pot deacetalization–Henry reaction; and also indicate the tailorability of active sites in bifunctionalized PAF-1. Mixing equal amounts of free acid of *p*-toluene sulfonic acid with free base of ethylamine cannot drive the deacetalization–Henry reaction due to the rapid neutralization in the homogeneous system (Table 1, entry 5). Moreover, only a trace amount of **3** could be detected when a stoichiometric amount of ethylamine or *p*-toluene sulfonic acid was added to PAF-1-$NHCH_2CH_2NH_2$–SO_3H due to the formation of ion pairs thereby quenching the active acid or basic sites (Table 1, entries 6 and 7). These results highlight PAF-1 as an excellent solid support capable of fixing and spatially separating the two antagonistic sites of strong acid and strong base. The applicability of PAF-1-$NHCH_2CH_2NH_2$–SO_3H as a bifunctional catalyst to other types of cascade reactions has been illustrated in the tandem deacetalization–Knoevenagel reaction, which PAF-1-$NHCH_2CH_2NH_2$–SO_3H can catalyze with high efficiency (Scheme S2, Fig. S2, ESI†). It is noteworthy that the initial catalytic activity of PAF-1-$NHCH_2CH_2NH_2$–SO_3H was higher (∼2 times) than physical mixtures of PAF-1-SO_3H and PAF-1-CH_2NH_2 (Fig. S2, ESI†). We attribute this enhancement of activity to the lack of proximity of catalytic sites in a physical mixture. The accelerated reaction rate that results from a shortened mass transfer path underscores PAF-1 as a platform for imparting a continuous range of spatially arranged antagonistic active sites.

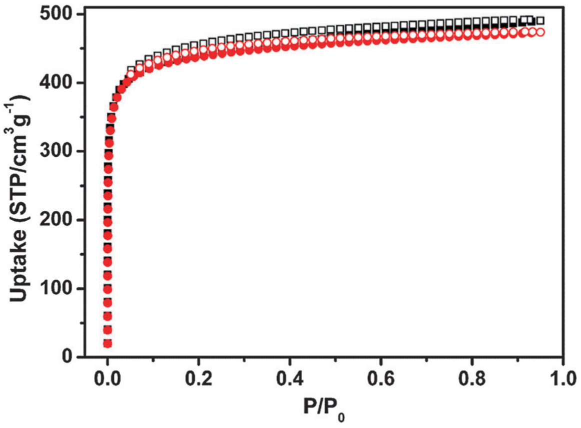


Fig. 3 N_2 sorption isotherms of PAF-1-$NHCH_2CH_2NH_2$–SO_3H (black) and PAF-1-$NHCH_2CH_2NH_2$–SO_3H after treatment with 2 M NaOH and then with 2 M HCl (red).

We tested the stability of PAF-1-$NHCH_2CH_2NH_2$–SO_3H under harsh chemical conditions (*i.e.* very high pH and very low pH media), which represents an issue for mesoporous silica and MOF-based bifunctional catalysts. Immersing PAF-1-$NHCH_2CH_2NH_2$–SO_3H into aqueous solutions of 2 M NaOH and 2 M HCl sequentially led to neither a substantial loss of catalytic activity (Table 1, entry 8) nor a significant decrease in surface area (Fig. 3), in striking contrast to MOF MIL-101-Cr[19] and the mesoporous silica MCM-41,[20] both of which have been widely employed for dual functionalization but would be decomposed under similar treatments. These observations thus highlight PAF as a robust and chemically stable platform superior to mesoporous silica and MOF-based platforms for applications in heterogeneous cascade catalysis in a broad range of reaction media.

To examine the potential of microporous dual functionalized PAF-1 for size/shape catalysis, PAF-1-$NHCH_2CH_2NH_2$–SO_3H was assessed in the context of catalyzing the Knoevenagel reaction using two substrates with different sizes/shapes (Scheme S3, ESI†). It was observed that PAF-1-$NHCH_2CH_2NH_2$–SO_3H can efficiently catalyze the small sized substrate of benzaldehyde with 99% yield; in contrast, only 8% yield was obtained for the large sized/shaped substrate of benzophenone under the same reaction conditions.

PAF-1-$NHCH_2CH_2NH_2$–SO_3H can be readily recycled after three runs without observable loss of catalytic activity (Fig. S3, ESI†), which could be attributed to the covalent anchoring of catalytically active sites as well as framework robustness. In addition, after removal of PAF-1-$NHCH_2CH_2NH_2$–SO_3H from the solutions, the reaction would stop immediately, indicating no leaching of catalytically active species. These results therefore confirm the heterogeneous nature of PAF-1-$NHCH_2CH_2NH_2$–SO_3H as a bifunctional catalyst for cascade reactions.

In summary, we have illustrated the incorporation of two antagonistic sites of strong acid and strong base into the high surface area and highly robust porous aromatic framework, PAF-1. The resulting bifunctional PAF-1-$NHCH_2CH_2NH_2$–SO_3H not only exhibits excellent performance in catalyzing a series of cascade reactions, but also demonstrates superior chemical stability compared to mesoporous silica and MOFs. Our studies therefore lay a solid foundation for dual functionalization of

PAFs as a new platform for heterogeneous cascade catalysis. Ongoing work in our laboratory includes introducing other types of functional groups into PAF-1 and bifunctionalizing other PAFs for cascade catalysis.

The authors acknowledge the University of South Florida and the National Science Foundation (DMR-1352065) for financial support of this work.

Notes and references

1 K. M. Koeller and C. H. Wong, *Chem. Rev.*, 2000, **100**, 4465.

2 J. C. Wasilke, S. J. Obrey, R. T. Baker and G. C. Bazan, *Chem. Rev.*, 2005, **105**, 1001.

3 (*a*) K. C. Nicolaou and J. S. Chen, *Chem. Soc. Rev.*, 2009, **38**, 2993; (*b*) C. Grondal, M. Jeanty and D. Enders, *Nat. Chem.*, 2010, **2**, 167.

4 (*a*) J. M. Notestein and A. Katz, *Chem. – Eur. J.*, 2006, **12**, 3954; (*b*) Y. Yang, X. Liu, X. Li, J. Zhao, S. Bai, J. Liu and Q. Yang, *Angew. Chem., Int. Ed.*, 2012, **51**, 9164; (*c*) C. Yu and J. He, *Chem. Commun.*, 2012, **48**, 4933; (*d*) W.-H. Peng, Y.-Y. Lee, C. Wu and K. C.-W. Wu, *J. Mater. Chem.*, 2012, **22**, 23181.

5 (*a*) S. Huh, H.-T. Chen, J. W. Wiench, M. Pruski and V. S.-Y. Lin, *J. Am. Chem. Soc.*, 2004, **126**, 1010; (*b*) H. Seong, H.-T. Chen, J. W. Wiench, M. Pruski and V. S.-Y. Lin, *Angew. Chem., Int. Ed.*, 2005, **44**, 1826; (*c*) R. K. Zeidan, S.-J. Hwang and M. E. Davis, *Angew. Chem., Int. Ed.*, 2006, **45**, 6332; (*d*) K. K. Sharma and T. Asefa, *Angew. Chem., Int. Ed.*, 2007, **46**, 2879; (*e*) E. L. Margelefsky, R. K. Zeidan, V. Dufaud and M. E. Davis, *J. Am. Chem. Soc.*, 2007, **129**, 13691; (*f*) E. L. Margelefsky, R. K. Zeidan and M. E. Davis, *Chem. Soc. Rev.*, 2008, **37**, 1118; (*g*) S. Shylesh, A. Wagener, A. Seifert, S. Ernst and W. R. Thiel, *Chem. – Eur. J.*, 2009, **15**, 7052; (*h*) S. Shylesh, A. Wagener, A. Seifert, S. Ernst and W. R. Thiel, *Angew. Chem., Int. Ed.*, 2010, **49**, 184; (*i*) N. R. Shiju, A. H. Alberts, S. Khalid, D. R. Brown and G. Rothenberg, *Angew. Chem., Int. Ed.*, 2011, **50**, 9615; (*j*) Y. Huang, S. Xu and V. S.-Y. Lin, *Angew. Chem., Int. Ed.*, 2011, **50**, 661.

6 (*a*) W. Li and D. Zhao, *Chem. Commun.*, 2013, **49**, 943; (*b*) N. Linares, E. Serrano, M. Rico, A. M. Balu, E. Losada, R. Luque and J. García-Martínez, *Chem. Commun.*, 2011, **47**, 9024; (*c*) D. Brühwiler, *Nanoscale*, 2010, **2**, 887; (*d*) C. Gérardin, J. Reboul, M. Bonne and B. Lebeau, *Chem. Soc. Rev.*, 2013, **42**, 4217.

7 (*a*) X. Fang, X. Zhao, W. Fang, C. Chen and N. Zheng, *Nanoscale*, 2013, **5**, 2205; (*b*) R. Luque, A. M. Balu, J. M. Campelo, M. D. Gracia, E. Losada, A. Pineda, A. A. Romero and J. C. Serrano-Ruiz, *Catalysis*, 2012, **24**, 253; (*c*) F.-S. Xiao, *Top. Catal.*, 2005, **35**, 9.

8 (*a*) D.-Y. Hong, Y. K. Hwang, C. Serre, G. Férey and J.-S. Chang, *Adv. Funct. Mater.*, 2009, **19**, 1537; (*b*) S. Kitagawa, R. Kitaura and S.-I. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (*c*) H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 673; (*d*) M. Yoon, R. Srirambalaji and K. Kim, *Chem. Rev.*, 2012, **112**, 1196; (*e*) A. Corma, H. García and F. X. Llabrés i Xamena, *Chem. Rev.*, 2010, **110**, 4606; (*f*) R.-Q. Zou, H. Sakurai and Q. Xu, *Angew. Chem., Int. Ed.*, 2006, **45**, 2542; (*g*) K. Mo, Y. Yang and Y. Cui, *J. Am. Chem. Soc.*, 2014, **136**, 1746.

9 (*a*) R. Srirambalaji, S. Hong, R. Natarajan, M. Yoon, R. Hota, Y. Kim, Y. H. Ko and K. Kim, *Chem. Commun.*, 2012, **48**, 11650; (*b*) J. Park, J.-R. Li, Y.-P. Chen, J. Yu, A. A. Yakovenko, Z. U. Wang, L.-B. Sun, P. B. Balbuena and H.-C. Zhou, *Chem. Commun.*, 2012, **48**, 9995; (*c*) M. Pintado-Sierra, A. M. Rasero-Almansa, A. Corma, M. Iglesias and F. Sánchez, *J. Catal.*, 2013, **299**, 137; (*d*) F. Vermoortele, R. Ameloot, A. Vimont, C. Serre and D. D. Vos, *Chem. Commun.*, 2011, **47**, 1521; (*e*) T. Toyao, M. Saito, Y. Horiuchi and M. Matsuoka, *Catal. Sci. Technol.*, 2014, **4**, 625; (*f*) B. Li, Y. Zhang, D. Ma, L. Li, G. Li, G. Li, Z. Shi and S. Feng, *Chem. Commun.*, 2012, **48**, 6151.

10 (*a*) A. U. Czaja, N. Trukhan and U. Müller, *Chem. Soc. Rev.*, 2009, **38**, 1284; (*b*) 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.

11 E. Merino, E. Verde-Sesto, E. M. Maya, M. Iglesias, F. Sánchez and A. Corma, *Chem. Mater.*, 2013, **25**, 981. (Note: During the initial submission of our manuscript to a different journal, we noticed the publication of this work).

12 C. Perego and P. Ingallina, *Green Chem.*, 2004, **6**, 274.

13 (*a*) T. Ben and S. Qiu, *CrystEngComm*, 2013, **15**, 17; (*b*) T. Ben, C. Pei, D. Zhang, J. Xu, F. Deng, X. Jing and S. Qiu, *Energy Environ. Sci.*, 2011, **4**, 3991; (*c*) H. Ma, H. Ren, X. Zou, F. Sun, Z. Yan, K. Cai, D. Wang and G. Zhu, *J. Mater. Chem. A*, 2013, **1**, 752; (*d*) X. Zou, H. Ren and G. Zhu, *Chem. Commun.*, 2013, **49**, 3925.

14 (*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. Yuan, W. Lu, D. Zhao and H.-C. Zhou, *Adv. Mater.*, 2011, **23**, 3723; (*d*) M. G. Rabbani and H. M. El-Kaderi, *Chem. Mater.*, 2012, **24**, 1511; (*e*) M. H. Weston, O. K. Farha, B. G. Hauser, J. T. Hupp and S. T. Nguyen, *Chem. Mater.*, 2012, **24**, 1292; (*f*) Y. Zhu, H. Long and W. Zhang, *Chem. Mater.*, 2013, **25**, 1630; (*g*) M. Dogru, M. Handloser, F. Auras, T. Kunz, D. Medina, A. Hartschuh, P. Knochel and T. Bein, *Angew. Chem., Int. Ed.*, 2013, **52**, 2920; (*h*) S. Fischer, J. Schmidt, P. Strauch and A. Thomas, *Angew. Chem., Int. Ed.*, 2013, **52**, 12174; (*i*) S. Li, D. Wu, C. Cheng, J. Wang, F. Zhang, Y. Su and X. Feng, *Angew. Chem., Int. Ed.*, 2013, **52**, 12105; (*j*) A. Nagai, X. Chen, X. Feng, X. Ding, Z. Guo and D. Jiang, *Angew. Chem., Int. Ed.*, 2013, **52**, 3770; (*k*) X. Zhu, C. C. Tian, S. M. Mahurin, S. H. Chai, C. M. Wang, S. Brown, G. M. Veith, H. M. Luo, H. L. Liu and S. Dai, *J. Am. Chem. Soc.*, 2012, **134**, 10478; (*l*) S. Kandambeth, D. B. Shinde, M. K. Panda, B. Lukose, T. Heine and R. Banerjee, *Angew. Chem., Int. Ed.*, 2013, **52**, 13052.

15 T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu and G. Zhu, *Angew. Chem., Int. Ed.*, 2009, **48**, 9457.

16 (*a*) S. M. Cohen, *Chem. Rev.*, 2012, **112**, 970; (*b*) Z. Wang and S. M. Cohen, *Chem. Soc. Rev.*, 2009, **38**, 1315; (*c*) A. D. Burrows, C. G. Frost, M. F. Mahon and C. Richardson, *Angew. Chem., Int. Ed.*, 2008, **47**, 8482; (*d*) D. J. Lun, G. I. N. Waterhouse and S. G. Telfer, *J. Am. Chem. Soc.*, 2011, **133**, 5806; (*e*) W. Lu, D. Yuan, J. Sculley, D. Zhao, R. Krishna and H.-C. Zhou, *J. Am. Chem. Soc.*, 2011, **133**, 18126; (*f*) W. Lu, J. P. Sculley, D. Yuan, R. Krishna, Z. Wei and H.-C. Zhou, *Angew. Chem., Int. Ed.*, 2012, **51**, 7480; (*g*) R. K. Deshpande, J. L. Minnaar and S. G. Telfer, *Angew. Chem., Int. Ed.*, 2010, **47**, 4598.

17 N. Wadhwani, S. G. Wadhwani and V. D. Gupta, *Def. Sci. J.*, 1994, **44**, 61.

18 T. Kavc and W. Kern, *Chem. Mater.*, 2000, **12**, 1053.

19 G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040.

20 (*a*) J. S. Beck, J. C. VartUli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834; (*b*) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.