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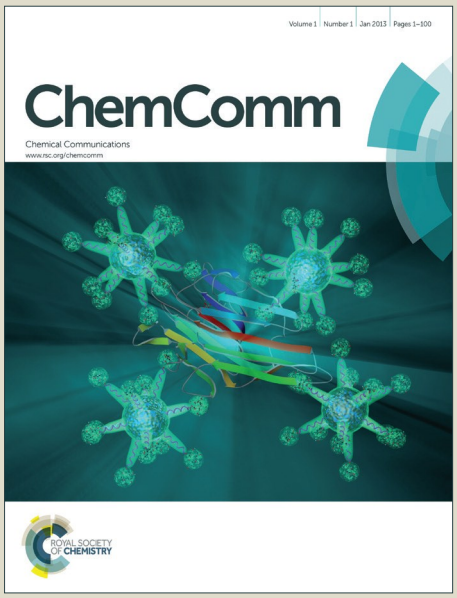

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ARTICLE TYPE

Phosphonium salt incorporated hypercrosslinked porous polymer for CO_2 capture and conversion

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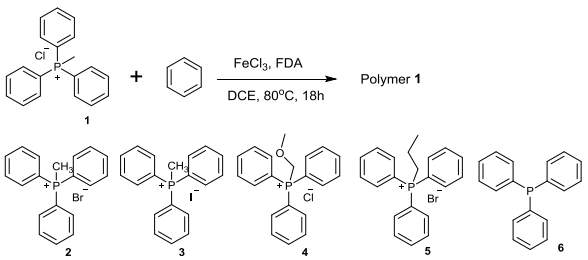
Various novel hypercrosslinked porous polymers with phosphonium salt incorporated into their networks were developed. These porous materials have high BET surface areas (up to 1168 m^2/g) and can be used to selectively capture CO_2 and efficiently convert CO_2 into cyclic carbonates.

Hypercrosslinked polymers have received considerable interests due to the ease preparation, high chemical and thermal stability, and low cost.[1] Combined with the light-weight properties and high surface area, these polymers have demonstrated potentials for gas storage and separation, catalysis and heavy metal removal in wastewater treatment.[2,3] Phosphonium salts are widely used as organocatalyst in many transformations.[4] Efforts have been devoted to synthesis porous solid phosphonium salt materials, but mainly focused on post-functionalization or immobilization methods.[5,6] In addition, a microporous quaternary phosphonium-network polymer has also been reported by a multiple-step synthesis.[7] Hence, developing a simple method for direct synthesis of porous phosphonium network from easily available starting materials is attractive.

Carbon dioxide (CO_2) is the cheapest and renewable carbon source for organic synthesis. The combination of CO_2 capture and conversion is an attractive strategy of CO_2 utilization.[8] In this respect, functionalized porous materials with both porous characteristics and active catalytic sites could be the promising materials to fulfil this mission.[9] Recently, several porous materials with metal catalytic centres have been developed for the CO_2 capture and transformation,[10] such as the salen-based porous organic polymer with metal centres [10a] and Mg-MOF materials for both CO_2 capture and conversion.[10b] More recently, Ag-MOF had demonstrated its good performance for capture and conversion of CO_2 into propiolic acids.[10d] Ru-coordinated azo-functionalized polymers for capture and conversion of CO_2 into N,N-dimethylaniline were also reported.[10e] Additionally, nitrogen containing microporous carbons were also reported for CO_2 capture and conversion under metal-free condition.[11]

Considering the ionic compound-modified porous polymers could have strong interaction with CO_2, it is interested in developing ionic porous polymers for CO_2 capture and conversion especially under metal-free condition.[9c] Previously, we reported imidazolium salts-modified porous hypercrosslinked polymers which demonstrated a synergistic effect in CO_2 capture and conversion.[12] These materials were synthesized by Friedel-Crafts reaction from benzyl halides and subsequently functionalized with N-methylimidazole. In this work, we report a novel hypercrosslinked porous polymer with phosphonium salt embedded into the network which was one-step synthesized from easily available materials. The new porous phosphonium material has high surface area and excellent CO_2/N_2 adsorption selectivity. Compared with traditional polystyrene resin-supported phosphonium salt, these materials showed higher activities for the conversion of CO_2 into cyclic carbonates,[13] and the detailed mechanism for this catalytic system has been investigated through DFT study. Compared with the reported porous materials for CO_2 capture and conversion, these porous hypercrosslinked phosphonium networks materials are easily synthesized and have a good selectivity to capture CO_2 over N_2 gas.



Scheme 1 The synthesis of hypercrosslinked phosphonium polymers.

The synthetic approach to porous hypercrosslinked phosphonium polymers was shown in Scheme 1. To overcome the limitation of Friedel-Crafts reaction for electro-deficient phenyl ring, benzene was used as co-monomer for the synthesis. The mixed monomers were then directly polymerized with formaldehyde dimethyl acetal (FDA) *via* Friedel-Crafts reactions (Polymers 1-5). Additionally, this method could be used to polymerize both phosphonium salts and triphenylphosphane (PPh_3) (polymer 2+6) in one system. Elemental analysis of synthesized products showed that the phosphonium loading in the polymers is in the range of 0.2 to 0.4 mmol/g (Table S2, ESI). The successful growth of porous network with phosphonium salts was also confirmed by Fourier transform infrared (FT-IR) and solid-state NMR. FT-IR spectroscopy displayed a series of bands around 1600 cm^{-1} (Fig. S1, ESI†), which could be attributed to benzene skeleton stretching.[14] The peak at 1437 cm^{-1} corresponds to the vibrations of the P-CH_2 bond.[15] For solid-state ^{13}C NMR (Fig. S2, ESI†), the resolved resonance around 129 ppm and 136

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ppm correspond to the aromatic carbons of benzene ring, and the signal around 36 ppm was assumed to be the methylene carbon formed *via* Friedel-Crafts reaction. The signal around 17 ppm correspond to the methyl carbon of phosphonium salt. For solid-state ^{31}P NMR (Fig. S3a, ESI†), the signal around 21 ppm was assumed to be the phosphorous atom of phosphonium salts,[3a] and the new signal around 28 ppm in polymer 2+6 indicated the successful installation of both phosphonium salt and PPh_3 (Fig. S3b, ESI†). Thermal gravimetric analysis showed that the phosphonium polymers were stable up to 300 ^{o}C (Fig. S4, ESI†). The morphology of the hypercrosslinked porous phosphonium polymers was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It reveals a relative uniform sphere aggregation (Fig. S5, ESI†).

Table 1 Physical properties for hypercrosslinked polymers [a]

Polymers	S_{BET}[a]/ m^2/g	S_{micro}[b]/ m^2/g	V_{total}[b] cm^3/g	V_{micro}/ cm^3/g	[c] Pore size/ nm
1	1168	430	1.00	0.19	1.18
2	1015	364	0.97	0.16	1.27
3	904	343	0.92	0.15	1.36
4	852	283	0.84	0.12	1.27
5	823	389	0.63	0.18	1.27
2+6	770	390	0.58	0.18	1.29

[a]The BET surface area was calculated in a relative pressure range P/P_0 = 0.01-0.1. [b]The micropore surface area S_{micro} and micropore volume V_{micro} were estimated from the *t*-plot method. [c] Based on NLDFT.

The porosities of the hypercrosslinked porous polymers were evaluated by N_2 adsorption-desorption isotherms (Fig. S6, ESI†). The micropore size distributions of these materials are predominantly around 1.18~1.36 nm (Fig. S7, ESI†). However, there are also meso- and macro-porous structures (> 2.0 nm) observed based on related isotherms curves. The textural properties of these materials are shown in the Table 1. The BET surface areas are in the range from 770 to 1168 m^2/g. The total pore volume and the micropore volume are in the range of 0.63~1.00 cm^3/g and 0.12~0.19 cm^3/g, respectively. Furthermore, both anions and cations influence the surface area and pore size, the surface area decreases and pore size increases with increasing anion diameter from Cl^-, Br^- and I^- (polymer 1 vs 2 vs 3, Table 1), and the surface area decreases with increasing alkyl chain length of cations (Polymer 1 vs 4 and 2 vs 5).

Additionally, these materials contained both microporosity and phosphonium salts functionality, which have been identified as important characteristics for CO_2 adsorption.[1, 16] As expected, the phosphonium salts embedded hypercrosslinked porous polymers exhibited good CO_2 capture capacity (9.6~12.5 wt%) at 273 K (Fig. S8, ESI†) and 4.8~7.5 wt% at 298 K and 1 bar (Fig. S9, ESI†). Furthermore, the CO_2 capacity increased in the order of Br^->I^->Cl^- (polymer 1 vs 2 vs 3, Table 2), which was not directly correlated with micropore volumes and contents of phosphonium salts. To provide a better understanding of this phenomenon, the interaction energies between phosphonium salts and CO_2 were calculated by DFT study at a molecular-level. The calculation was conducted by use of the B3PW91 functional with the 6-311++G (d, p) basis set as implemented in Gaussian 09 program package and all of the optimized structures between phosphonium salt and CO_2 were shown in Fig. S10 (see ESI†). The interaction energies are around 2.46~3.85 kJ/mol, which are much stronger than reported phenol and naphthol monomers (phenol: 2.05 kJ/mol, 1-naphthol: 1.97 kJ/mol, 2-naphthol: 2.09 kJ/mol).[1c, 2] Interestingly, it was found that CO_2 capture capacities were in the same order with the value of interaction energies (Table 2). The phosphonium units in the polymer framework have high interaction energies with CO_2 and also represent high CO_2 capture capacity.

Table 2 CO_2 capture capacities of hypercrosslinked polymers

Polymers	CO_2 uptake/wt%[a]		Selectivity over N_2	Interaction energy (kcal/mol)[b]	Q_{st} (kJ/mol)[c]
	273 K	298 K			
1	9.6	4.8	56	2.46	35.5
2	12.3	7.1	45	3.20	27.2
3	10.2	6.4	36	2.85	24.2
4	12.5	6.8	28	3.85	25.9
5	11.3	6.5	46	3.82	29.2
2+6	12.9	7.5	-	-	30.1

[a]Measured at a pressure of 1 bar. [b]Interaction energy between monomer and CO_2 calculated by DFT. [c]Q_{st} is heat of adsorption.

The isosteric heat of adsoption was calculated from the CO_2 isotherms measured at 273 K and 298 K (Fig. S11, SI†). At the onset of adsorption, the heat of adsorption was in the range from 24 to 35 kJ/mol, and the values were comparable to the heterocyclic (Th-1, 27 kJ mol^{-1}; Py-1, 36 kJ mol^{-1}; Fu-1, 28 kJ mol^{-1})[1b] and acid-functionalized porous polymers (CMP-1-COOH, 32.6 kJ mol^{-1}; PPN-6-SO_3H, 30.4 kJ mol^{-1}).[17] It is worth to mention that the values of the heat of adsorption indicate the strong physisorption model. Additionally, for a post-combustion CO_2 adsorption, CO_2 should be adsorbed preferentially over N_2. To test the separation capacity of these polymers, single-component gas sorption experiments were carried out at 298 K and up to 1.05 bar. The selectivity was calculated using Henry' Law constants from isotherms in the linear low pressure (<0.1 bar) range (Fig. S9 and S12, SI†). Encouragingly, these materials show very good selectivity at 298 K in the range from 28 to 56. The selectivity observed for these materials is as high as covalent electron-rich organonitridic framework,[19] and lower than N-contained porous polymers (Table S1, SI†).[20] For different anions, the selectivity increased in the order of Cl^->Br^->I^- (polymer 1 vs 2 vs 3, Table 2). There was no obvious change of selectivity with increasing alkyl chain length. Additionally, the CO_2 adsorption is fully reversible (Fig. S13, ESI†).

Homogeneous phosphonium salts as organocatalyst for the conversion of CO_2 into cyclic carbonate have attracted significant interest[21] and have recently commercialized as part of the OMEGA process by Mitsubishi Chemicals.[22] In this respect, solid phosphonium salts as stable and recyclable heterogeneous catalysts are especially interesting from the viewpoint of green chemistry and industrial application. Thus, the catalytic activities of the porous phosphonium salts embedded polymers were

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investigated for the conversion of CO_2 and propylene oxide (PO) into propylene carbonate (PC). Interestingly, these materials demonstrated much higher activities than the conventional PS-supported phosphonium catalyst under the same reaction conditions (entries 1-8 vs 9, Table 3). Clearly, bromide containing materials have much higher catalytic activity in this reaction, and high yield of 94 % was obtained for catalyst 2 in 9 h (entry 6). In addition, the activity slightly increased when adding PPh_3 in the network (entry 7 vs 2). Moreover, when $ZnBr_2$ (0.9 wt% of Zn) was added to the polymer with both phosphonium salts and PPh_3 units, the catalytic activity was remarkable increased due to the fact that $ZnBr_2$ could further activate epoxide (entry 8).[23] The multifunctional $ZnBr_2$-based porous phosphonium catalyst could be recycled for at least 6 times without obvious loss of its activity after second run (Fig. S14, ESI†). As measured by ICP-MS, there was 4.4 % of Zn leached during the first run reaction. However, there was no Zn species detected in the filtrate of reaction mixture after the second run.

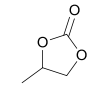
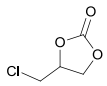
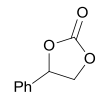
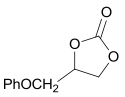
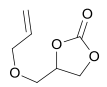
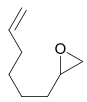
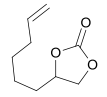
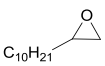
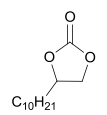
Table 3 The activities of the phosphonium salts embedded polymers for the conversion of CO_2 with propylene oxide into propylene carbonate [a]

Entry	Polymers	PO conv.[b] (%)	PC yield[b] (%)
1	1	16	16
2	2	43	43
3	3	10	9
4	4	26	25
5	5	38	38
6[c]	2	94	94
7	2+6	48	48
8[d]	2+6	90	90
9[e]	PS-supported PPh_3Cl	4	4

[a]Reaction conditions: PO (1.43 mmol), catalyst (0.5 mmol% based on the phosphonium salts), DMF (2 ml), CO_2 pressure (1 MPa), 130 °C, 4 h. [b]Yield and conversion were determined by GC using biphenyl as the internal standard. [c]9 h. [d]$ZnBr_2$ supported on polymer A2+A6 (BET surface areas = 603 m^2/g). [e] PS = polystyrene resin

Quantum calculations were carried out to investigate the reaction mechanism with methyl triphenyl phosphonium bromide as the model catalyst (Fig. S15, ESI†). The calculation was conducted using the B3PW91 functional with the 6-311++G (d, p) basis set as implemented in Gaussian 09 program package. All of the intermediates and transition states are shown in Fig. S16 (see ESI†). The catalytic cycle was presumed to occur in three steps (Fig. S17, ESI†). The first step is ring-opening through the attack of the nucleophile (Br^- from phosphonium salt) on epoxide, which was considered to be the most difficult step with high activation energy (ΔE = 23.15 kcal/mol). The second step was the insertion of CO_2, which occurred spontaneously. The last step was the formation of cyclic carbonate with activation energy of 11.38 kcal/mol. This catalytic cycle is exothermic with relatively low activation barrier, which allows the reaction to be performed under mild condition.

Table 3 Substrate scope [a]

Entry	Epoxide	Product	Time/h	Conv./%[b]	Yield/%[b]
1			4	90	90
2			7	92	91
3			12	96	96
4			10	94	94
5			14	93	92
6			16	92	91
7			10	trace	trace

[a] Reaction condition: Epoxide (1.43 mmol), $ZnBr_2$/polymer (A2+A6) (0.5 mmol% based on the phosphonium salts), DMF (2 ml), CO_2 pressure (1 MPa), Temperature (130 °C). [b]Yield and conversion were determined by NMR.

The epoxide substrate scope was then screened using multifunctional $ZnBr_2$-based porous phosphonium polymer as the catalyst. As shown in Table 3, the catalytic system was found to be effective for a variety of terminal epoxides (entries 1-6, Table 3). Furthermore, alkene functionalized epoxides were also suitable substrates for this catalytic system (entries 5-6). However, the epoxide with long hydrophobic chain was not active under the same condition (entry 7).

Conclusions

Hypercrosslinked phosphonium embedded porous polymers were developed and applied in CO_2 capture and conversion. The materials were synthesized in one-step method using easily available starting materials. These porous materials displayed high BET surface areas, good capacity and excellent selectivity towards CO_2 capture. Furthermore, the porous phosphonium polymers displayed higher catalytic activities than the PS-supported phosphonium catalyst in the conversion of CO_2 and epoxides to cyclic carbonates. It represents a novel and easily synthesized solid phosphonium material which could have potential in CO_2 capture and transformation.

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Notes and References

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† Electronic Supplementary Information (ESI) available: general experimental and DFT computational methods, experimental details, characterization of cyclic carbonates, supporting figures, supporting tables and also cartesian coordinates for the optimized geometries of all intermediates and transition states. See DOI: 10.1039/b000000x/

1 (*a*) S. J, Xu, Y. L.Luo, B. E. Tan, *Macromol. Rapid Commun.*, 2013, **34**, 471; (*b*) Y. L. Luo, B. Li, W. Wang, K. Wu and B. E. Tan, *Adv. Mater.*, 2012, **24**, 5703; (*c*) R. Dawson, L. A. Stevens, T. C. Drage, C. E. Snape, M. W. Smith, D. J. Adams and A. I. Cooper, *J. Am. Chem. Soc*., 2012, **134**, 10741; (*d*) R. T. Woodward, L. A. Stevens, M. Vijayaragha, T. Hasell, I. P. Silverwood, A. V. Ewing, T. Ratvijitvech, J. D. Exley, S. Y. Chong, F. Balnc, D. J. Adams, S. G. Kazarian, C. E. Snape, T. C. Drage and A. I. Cooper, *J. Am. Chem. Soc.*, 2014, **136**, 9028; (*e*) X. Zhu, S. M. Mahurin, S. H. An, C. L. Do-Thanh, C. C. Tian, Y. K. Li, L. W. Gill, E. W. Hagaman, Z. J. Bian, J. H. Zhou, H. L. Liu and S. Dai, *Chem. Commun.*, 2014, **50**, 7933; (*f*) S. W. Yao, X. Yang, M. Yu, Y. H. Zhang and J. X. Jiang, *J. Mater. Chem. A*, 2014, **2**, 8054; (*g*) C. F. Martin, E. Stockel, R. Clowes, D. J. Adams, A. I. Cooper, J. J. Pis and C. Rubiera, F. Pevida. *J. Mater. Chem*., 2011, **21**, 5475.

2 B. Li, R. Gong, W. Wang, X. Huang, W. Zhang, H. Li, C. Hu and B. Tan, *Macromolecules* 2011, **44**, 2410;

3 (*a*) B. Y. Li, Z. H. Guan, W. Wang, X. J. Yang, J. L. Hu, B. E. Tan and T. Li, *Adv. Mater*., 2012, **24**, 3390; (*b*) S. Bhunia, B. Banerjee and A. Bhaumik, *Chem. Commun.*, 2015, **51**, 5020.

4 T. Werner, *Adv. Synth. Catal*., 2009, **103**, 856.

5 P. Tundo and P. Venturello, *J. Am. Chem. Soc.*, 2014, **136**, 9028.

6 M. Benaglia, A. Puglisi and F. Cozzi, *Chem. Rev*., 2003, **103**, 3401.

7 Q. Zhang, S. B. Zhang and S. H. Li, *Macromolecules*, 2012, **45**, 2981.

8 (*a*) M. Aresta, *Carbon dioxide as chemical feedstock*, Willey-VCH, Weinheim, 2010; (*b*) D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2365; *(c*) R. W. Dorner, D. R. Hardy, F. W. Williams and H. D. Willauer, *Energy Environ. Sci.*, 2010, **3**, 884; (*d*) C. Villiers, J. P. Dognon, R. Pollet, P. Thuéry and M. Ephritikhine, *Angew. Chem. Int. Ed.*, 2012, **51**, 187; (*e*) C. Das Neves Gomes, O. Jacquet, C. Villiers, P. Thuéry, M. Ephritikhine and T. Cantat, *Angew. Chem. Int. Ed.*, 2012, **51**, 187; (*f*) S. Bontemps, L. Vendier and S. Sabo-Etienne, *Angew. Chem. Int. Ed.*, 2012, **51**, 1674; (*g*) A. Schäfer, W. Saak, D. Haase and T. Müller, *Angew. Chem. Int. Ed.*, 2012, **51**, 2981; (*h*) N. MacDowell, N. Florin, A. Buchard, J. Hallett, A. Galindo, G. Jackson, C. S. Adjiman, C. K. Williams, N. Shah and P.Fennell *Energy Environ. Sci.*, 2010, **3**, 1645; (*i*) Z. Z. Yang, L. N. He, J. Gao, A. H. Liu and B. Yu, *Energy Environ. Sci*., 2012, **5**, 6602; (*j*) Q. Liu, L. P. Wu, R. Jackstell and M. Beller, *Nature Commun.*, 2015, **6**, 5933; (*k*) C. Martin, G. Florani and A. W. Kleji., *ACS Catal.*, 2015, **5**, 1353; (*k*) D. Y. Yu, S. P. Teong and Y. G. Zhang, *Coord. Chem. Rev*., 2015, **293-294**, 279; (*l*) S. N. Riduan and Y. G. Zhang, *Dalton Trans*. 2010, **39**, 3347.

9 (*a*) R. Dawson, D. J. Adams and A. I. Cooper, *Chem. Sci.*, 2011, **2**, 1173; (*b*) Y. G. Zhang and S. N. Riduan, *Chem. Soc. Rev.*, 2011, **41**, 2083; (*c*) Y. G. Zhang, J. Y. Ying, *ACS Catal*. 2015, **5**, 2681; (*d*) P. Kaur, J. T. Hupp and S. T. Nguyen, *ACS Catal*. 2011, **1**, 819.

10 (*a*) Y. Xie, T. T. Wang, X. H. Liu, K. Zou and W. Q. Deng, *Nature Commun.*, 2013, **4**, 1960; (*b*) D. A. Yang, H. Y. Cho, J. Kim, S. T. Yang and W. S. Ahn, *Energy Environ. Sci.*, 2012, **5**, 6465; (*c*) Z. Z. Yang, Y. F. Zhao, H. Y. Zhang, B. Yu, Z. S. Ma, G. P. Ji and Z. M. Liu, *Chem. Commun.*, 2014, **50**, 13910; (*d*) X. H. Liu, J. G. Ma, Z. Niu, G. M. Yang and P. Cheng, *Angew. Chem. Int. Ed*, 2015, **54**, 988; (*e*) Z. Z.Yang, H. Y. Zhang, B. Yu, Y. F. Zhao, Z. S. Ma, G. P. Ji, B. X. Han and Z. M. Liu, *Chem. Commun.*, 2015, DOI: 10.1039/c5cc03151f; (*f*) X. F. Sheng, H. C. Guo, Y. S. Qin, X. H. Wang and F. S. Wang, RSC *Adv.*, 2015, **5**, 31664.

11 X. Y. Ma, B. Zou, M. H. Cao, S. L. Chen and C. W. Hu, *J. Mater. Chem. A*, 2014, **2**, 18360.

12 (*a*) J. Q. Wang, W. H. Sng, G. S. Yi and Y. G. Zhang, *Chem. Commun.*, 2015, 51, 12076; (*b*) Y. G. Zhang, D. S. W. Lim, *ChemSusChem*, 2015, DOI: 10.1002/cssc.201500745.

13 (*a*) M. North, R. Pasquale and C. Young, *Green Chem.*, 2010, **12**, 1514; (*b*) M. O. Sonnati, S. Amigoni, E. P. Taffin de Givenchy, T. Darmanin, O. Choulet and F. Guittard, G*reen Chem.*, 2013, **15**, 283; (*c*) J. Q. Wang, *Curr. Green Chem.*, 2015, **2**, 3.

14 H. X. Li, F. Zhang, Y. Wan and Y. F. Lu, *J. Phys. Chem. B.* 2006, **110**, 22942.

15 W. H. He, F. Zhang, H. X. Li, *Chem. Sci*., 2011, **2**, 961.

16 Y. Q. Zhang, S. J. Zhang, X. M. Lu, Q. Zhou, W. Fan and X. P. Zhang, *Chem. Eur. J.*, 2009, **15**, 3003.

17 (*a*) R. Dawson, D. J. Adams and A. I. Cooper, *Chem. Sci*., 2011, **2**, 1173; (*b*) W. Lu, D. Yuan, J. Sculley, D. Zhao, R. Krishna and H. C. Zhou, *J. Am. Chem. Soc*., 2011, **133**, 18126.

18 (*a*) M. North, R. Pasquale and C. Young, *Green Chem.*, 2010, **12**, 1514; (*b*) T. Sakakura, J. C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365.

19 P. Mohanty, L. D. Kull and K. Landskron, *Nat. Commun*., 2011, **2**, 401.

20 (*a*) M. Saleh, H. M. Lee, K. C. Kemp and K. S. Kim, *ACS Appl. Mater., Interfaces* 2014, **6**, 7325; (*b*) J. H. Lee, H. J. Lee, S. Y. Lim, B. G. Kim and J. W. Choi, *J. Am. Chem. Soc.*, 2015, **137**, 7210; (*c*) H. A. Patel, S. H. Je, J. Park, D. P. Chen, Y. S. Jung, C. T. Yavuz and A. Coskun, *Nat. Commun.*, 2013, **4**, 1357.

21 M. Cokoja, M. E. Wilhelm, M. H. Anthofer, W. A. Herrmann and F. E. Kühn, *ChemSusChem*, 2015, DOI: 10.1002/cssc.201500161.

22 (*a*) T. Sakakura, J. C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365; (*b*) T. Sakakura and K. Kohno, *Chem. Commun.*, 2009, **11**, 1312; (*c*) G. Florani W. Guo and A. W. Kleij, *Green Chem.*, 2015, **17**, 1375.

23 (*a*) S. S. Wu, X. W. Zhang, W. L. Dai, S. F. Yin, W. S. Li and Y. Q. Ren, *Appl. Catal. A. Gen.* 2008, **341**, 106; (*b*) B. Liu, M. S. Liu, L. Liang and J. M. Sun, *Catalysts*, 2015, **5**, 119; (c) Y. Zhang, J. Y. G. Chan, *Energy Environ. Sci*., 2010, **3**, 408.

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