

# Journal of Materials Chemistry A

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.

## COMMUNICATION

## Mechanosynthesis of new azine-functionalized Zn(II) Metal-organic frameworks for improved catalytic performance

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

Mohammad Yaser Masoomi, Saeideh Beheshti and Ali Morsali \*

DOI: 10.1039/x0xx00000x

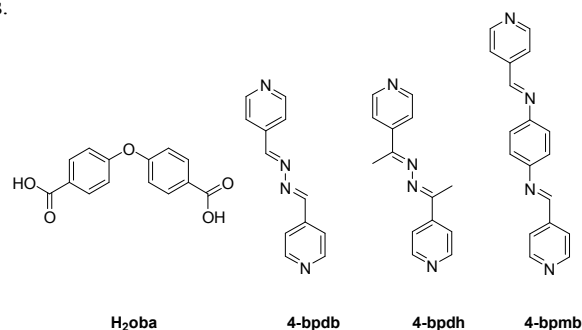
www.rsc.org/

Three 3D, porous Zn(II)-based metal-organic frameworks, TMU-4, TMU-5 and TMU-6, containing azine-functionalized pores, were readily and quickly prepared via mechanosynthesis. Catalytic performance of these MOFs and the effect of N-donor ligands with diverse basicity in Knoevenagel condensation reaction are investigated. Increasing the basicity of N-donor ligands leads to improvement in catalytic activity. Results show that among the three compounds, TMU-5 has the highest catalytic activity upon increasing its basicity of azine function in N-donor ligand. These catalysts maintain their crystalline framework after reaction and are easily recycled.

The Knoevenagel condensation of aldehydes with active methylene compounds is a useful transformation that has been widely employed for carbon-carbon bond formation in the synthesis of several fine chemicals.<sup>1</sup> The condensation is usually catalysed by solid bases like alkali or alkaline-earth metal oxides.<sup>2</sup> Over the last few years, a wide range of catalysts have been investigated for this reaction such as Lewis acids,<sup>3</sup> amine-functionalized solid supports,<sup>4</sup> cation-exchanged zeolites,<sup>6</sup> ionic liquids<sup>7</sup> and organometallic catalysts.<sup>8</sup> However, most of these methods have significant drawbacks, such as using hazardous and carcinogenic solvents, high catalyst loading or non-recoverable catalysts that sometimes contain toxic metals. Therefore, there is a great need for new catalytic methods that do not have these problems. MOFs have shown a high catalytic activity to promote condensation reactions.

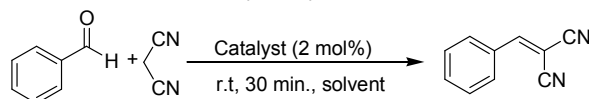
Porous metal-organic frameworks (MOFs) built up from organic linkers and inorganic connectors have recently begun to be explored as heterogeneous catalysts, owing to their well-ordered porous structures, flexible and dynamic behaviours in response to guest molecules and designable channel surface functionalities.<sup>9</sup> Although the low thermal and chemical stability of MOFs as compared to their inorganic counterparts has restricted their use only in mild conditions, there already have been several reports that showed MOFs can be excellent heterogeneous catalysts for Knoevenagel condensation.<sup>10-17</sup> In our previous study the MOFs  $[\text{Zn}_2(\text{oba})_2(4\text{-bpdh})]_n \cdot (\text{DMF})_x$ , TMU-4, and  $[\text{Zn}(\text{oba})(4\text{-bpdh})_{0.5}]_n \cdot (\text{DMF})_y$ , TMU-

5<sup>18</sup> ( $\text{H}_2\text{oba}$  = 4,4-oxybisbenzoic acid, 4-bpdb = 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene and 4-bpdh = 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene, Scheme 1), have shown selective  $\text{CO}_2$  adsorption due to presence of two internal Lewis basic sites per ligand in the pore walls. Considering the  $\text{CO}_2$  adsorption of these compounds, here their performance as heterogeneous catalysts for Knoevenagel condensation reaction is investigated. To the best of our knowledge, it is the first report that Knoevenagel condensation is performed using MOFs that contain azine-functionalized pores acting as base catalyst. A new 3D MOF,  $[\text{Zn}(\text{oba})(4\text{-bpmb})_{0.5}]_n \cdot (\text{DMF})_z$  TMU-6<sup>19</sup> (4-bpmb =  $N^1, N^4$ -bis((pyridin-4-yl)methylene)benzene-1,4-diamine, Scheme 1), was synthesized by introduction of phenyl ring in the pillar ligand due to the examination of the basicity of N-donor ligand and its effect on the considered reaction. Functionalization of MOF pore walls with azine groups enables greater interaction between the walls and substrate molecules, thereby increasing catalytic activity of the MOFs. TMU-4 and TMU-6 show 1D, large pores with aperture of about  $5.3 \times 9 \text{ \AA}$  and  $9.1 \times 8.9 \text{ \AA}$ , respectively, whereas MOF TMU-5 shows 3D, interconnected, narrow pores with aperture of about  $4.4 \times 6.2 \text{ \AA}$  (Fig. S1, ESI†). Interestingly, three MOFs were synthesized easily and rapidly via mechanochemical reactions.<sup>20-28</sup> Macroscale crystals of TMU-6 MOF, suitable for single-crystal X-ray diffraction, were prepared by heating a mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$ ,  $\text{H}_2\text{oba}$  and 4-bpmb, in DMF at  $80 \text{ }^\circ\text{C}$  for 72 hours.



**Scheme 1.** Chemical structure of  $\text{H}_2\text{oba}$ , 4-bpdb, 4-bpdh and 4-bpmb. Note the bridging azine group at the center of 4-bpdb and 4-bpdh.

## COMMUNICATION

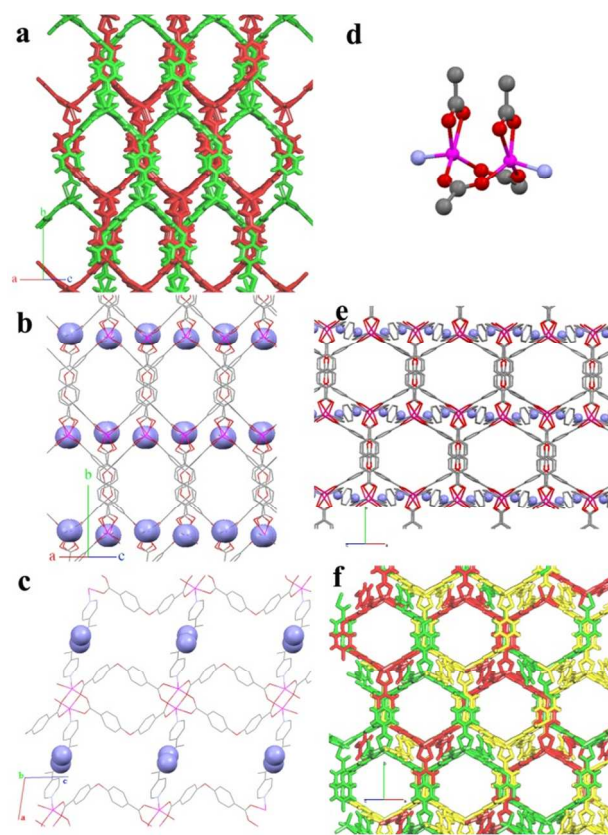
**Table 1.** Knoevenagel condensation reaction catalysed by TMU-4, TMU-5 and TMU-6 in different solvents.

Entry	Catalyst	EtOH	MeOH	H <sub>2</sub> O	n-Hexane	CH <sub>3</sub> CN	CH <sub>2</sub> Cl <sub>2</sub>	Toluene	Solvent-free
1	TMU-4	44	45	45	1	2	0	0	11
2	TMU-5	57	68	100	4	2	0	1	17
3	TMU-6	25	32	38	0	2	0	1	6
4	-	10	11	15	0	1	0	1	3

In a typical synthesis of TMU-4, TMU-5 and TMU-6 the product were prepared by mechanochemical reaction (grinding by hand) of a mixture of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O, H<sub>2</sub>oba and N-donor ligand (4-bpdb, 4-bpdh or 4-bpmb) for 15 minutes. The simulated (derived from the single crystal structure of MOFs) and experimental (resulting from the mechanothesized powder) powder X-ray diffraction (PXRD) patterns are consistent<sup>18</sup> (Fig S3), confirming that the mechanothesized TMU-4, TMU-5 and TMU-6 were structurally identical to TMU-4, TMU-5 and TMU-6 prepared via conventional heating, respectively. In MOF TMU-4, the V-shaped coordination of the oba ligand plays an important role in the linkage of the nodes resulting in a three-dimensional honeycomb framework with double interpenetration (Fig 1a). Although the double interpenetration is formed to avoid an extremely large void space, but still possesses one-dimensional (1D) open channels in which the internal surface of these pores is functionalized with the azine groups (Fig 1b, shown in blue) of the 4-bpdb ligands. The 3D framework of TMU-5 (Fig. S1b, ESI†) which is built up from a Zn<sub>2</sub>(oba)<sub>4</sub> paddle-wheel secondary building unit (SBU) is also functionalized with azine groups (Fig. 1c, shown in blue).

However it is surprising that in MOF TMU-6, introduction of phenyl ring in the pillar ligand induced the formation of a structure similar to TMU-4 but different to that of TMU-5. TMU-6 is also based on a binuclear Zn(II) unit, in which Zn(II) centers are coordinated to four carboxylate O atoms (O2, O3, O4 and O5) from three fully deprotonated oba ligands, and one N atom (N1) from the 4-bpmb ligand (Fig. 1d). The distance between two Zn#1 centers is 3.494 Å.

In TMU-6, each non-linear (C–O–C = 115.4(3)°) dicarboxylate oba ligand binds three consecutive Zn(II) centers from two different units (one carboxylate group of an oba ligand adopts a chelating bidentate mode while the other adopts a bridging bidentate mode), thereby forming 2D sheets. The 2D sheets are connected through the linear 4-bpmb, extending the structure in three dimensions. Still the threefold interpenetrated structure in TMU-6 has large 1D pore channels running along the [1 0 1] direction which has free N atoms in pores surface but not azine groups (Fig. 1e and f).



**Fig 1.** Views of TMU-4 (a) Representation showing the pore channels and that the network is doubly interpenetrated (in red and green). (b) Representation of the pores, highlighting the azine groups (blue balls). Views of TMU-5 (c) Representation of the pores, highlighting the azine groups (in blue). Views of TMU-6. (d) Binuclear Zn<sub>2</sub> cluster (O: red; N: blue; C: grey; and Zn: pink). (e) Representation of the pores, highlighting the azine groups (in blue). (f) Representation showing the pore channels and that the network is threefold interpenetrated (in red, green and yellow). Hydrogen atoms and DMF molecules are omitted for clarity.

## COMMUNICATION

Table 2. A comparison of catalytic activity of various MOFs in Knoevenagel condensation reaction of benzaldehyde and malononitrile.

Entry	Catalyst	Mol%	Time	Solvent	Temp. [°C]	Yield (%)	Ref
1	[Cd(4-btapa) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O·2DMF	5	12 h	C <sub>6</sub> H <sub>6</sub>	r.t.	98	9
2	[Cd(bipd) <sub>2</sub> (DMF) <sub>2</sub> ·(ClO <sub>4</sub> ) <sub>2</sub> ·(2DMF)	4	30 min	C <sub>6</sub> H <sub>6</sub>	r.t.	93	10
3	Pb(cpna) <sub>2</sub> ·2DMF·6H <sub>2</sub> O	3	24 h	CH <sub>3</sub> CN	r.t.	100	11
4	ZIF-8	5	3 h	Toluene	r.t.	100	12
5	ZIF-9	5	4 h	Toluene	r.t.	99	13
6	[Gd <sub>2</sub> (tnbd) <sub>3</sub> (DMF) <sub>4</sub> ·4DMF·3H <sub>2</sub> O	10	20 min	C <sub>6</sub> H <sub>6</sub>	r.t.	96	15
7	<b>TMU-5</b>	<b>2</b>	<b>30 min</b>	<b>H<sub>2</sub>O</b>	<b>r.t.</b>	<b>100</b>	<b>This work</b>

Thermogravimetric analysis (TGA) of mechanochemically synthesized **TMU-4**, **TMU-5** and **TMU-6** before washing with DMF revealed a unique weight loss occurring in the range of 315-500 °C, 290-500 °C and 380-500 °C, respectively, corresponding to the decomposition of each framework (Fig. S2, ESI†). In **TMU-6**, 3-fold interpenetrated framework minimizes empty spaces, preventing network from collapsing while significantly enhancing stability of the framework.<sup>29</sup>

To characterize the possible base-type catalytic behavior of **TMU-4**, **TMU-5** and **TMU-6**, Knoevenagel condensation reaction in the presence of these three MOFs was performed. Our experiments employed a 1:1.1 molar ratio of benzaldehyde and malononitrile in different solvents such as ethanol, methanol, H<sub>2</sub>O, *n*-hexane, acetonitrile, dichloromethane and toluene at room temperature. It can be deduced from these results that higher yields were achieved in polar protic solvents, whereas the reaction occurred with difficulty in solvents with lower polarity. However, the reactions under solvent-free condition were slow. The reaction between aldehydes and active methylene compounds hardly progressed in the absence of MOFs, suggesting the potential base-catalytic activity of MOFs in this reaction (Entry 4). As shown in Table 1, best results were obtained when **TMU-5** was used as catalyst. 2 mol% catalyst **TMU-5** lead to a 100% yield in H<sub>2</sub>O as solvent. Interestingly, catalytic performance of **TMU-4** and **TMU-5** is higher than **TMU-6**. This may be attributed to lone pair-lone pair electron repulsion and alpha effect. Electron lone-pairs on adjacent nitrogen atoms of azine groups destabilize each other by electronic repulsion and hence increase the ground state.<sup>30-32</sup> Basicity of **TMU-4** and **TMU-5** increases based on this criterion, and they become more reactive. **TMU-5** has narrower pores because of methyl groups. Thus, interactions of walls with azine groups (as Lewis base) and substrate molecules enhance leading to an increase in its catalytic activity. Catalytic activity of **TMU-6** is the lowest, because it does not have alpha effect that leads to a decrease in the nitrogen density of electrons and therefore reducing the base strength.

The efficiency of **TMU-5** in comparison with various MOFs that have been used as catalyst in condensation reaction between benzaldehyde and malononitrile is shown in Table 2.

The PXRD patterns of catalysts **TMU-4**, **TMU-5** and **TMU-6** measured after the reactions, show the same profiles as the as-prepared samples, indicating the unchanged coordination framework although the crystallinity seems to be weakened due to broadening of the diffraction peaks (Fig. S4, ESI†).<sup>33, 34</sup>

To further verify the heterogeneity of systems, a procedure similar to Sheldon *et al.* is performed.<sup>35</sup> After the reaction mixture was stirred for 10 minutes, removal of the catalyst via filtration resulted in the complete shutdown of the reaction and hence, the systems are totally heterogeneous in nature with no leaching under reaction conditions (Fig. S9-S11, ESI†).

## Conclusions

Three MOFs- [Zn<sub>2</sub>(oba)<sub>2</sub>(4-bpdb)]<sub>n</sub>(DMF)<sub>x</sub> (**TMU-4**), [Zn(oba)(4-bpdh)<sub>0.5</sub>]<sub>n</sub>(DMF)<sub>y</sub> (**TMU-5**) and [Zn(oba)(4-bpmb)<sub>0.5</sub>]<sub>n</sub>(DMF)<sub>z</sub> (**TMU-6**) with different structures and pore sizes were mechanochemically synthesized quickly on large scale. The N-donor linkers with various basicity appeared in the walls of all three MOFs which is favorable for catalytic reaction. These MOFs were used as new solid base catalysts in Knoevenagel condensation reaction. This study demonstrated that the basicity of azine functionalized pores is probably an important factor in the catalytic performance. **TMU-5** with narrow and interconnected pores in three dimensions has higher catalytic activity upon increasing basicity of its N-donor ligand.

## Notes and references

Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, Tehran, Islamic Republic of Iran. Tel: (+98) 21-82883449; E-mail: morsali\_a@modares.ac.ir.

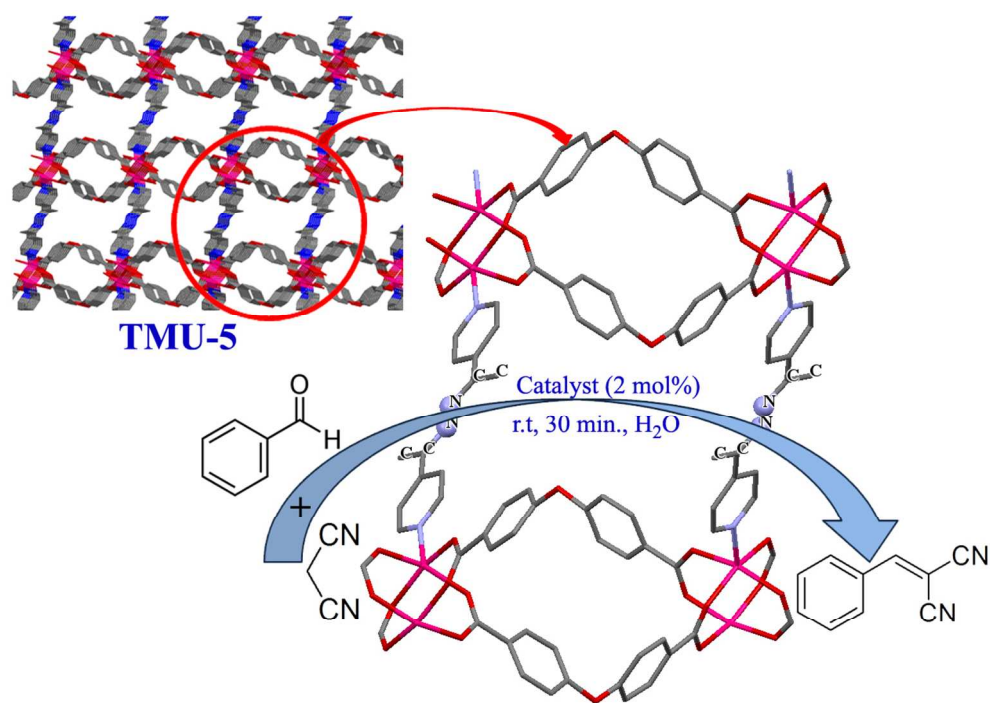
† Electronic Supplementary Information (ESI) available: [CCDC 991867. Other figures, full synthetic and analytical details]. See DOI:

10.1039/c000000x/

1. L. F. Tietze, *Chem. Rev.*, 1996, **96**, 115-136.
2. S.-I. Fujita, B. M. Bhanage, D. Aoki, Y. Ochiai, N. Iwasa and M. Arai, *Appl. Catal., A*, 2006, **313**, 151-159.
3. D. Prajapati, K. C. Lekhok, J. S. Sandhu and A. C. Ghosh, *J. Chem. Soc., Perkin Trans. 1*, 1996, 959-960.
4. J. Mondal, A. Modak and A. Bhaumik, *J. Mol. Catal. A: Chem.*, 2011, **335**, 236-241.

5. R. Xing, H. Wu, X. Li, Z. Zhao, Y. Liu, L. Chen and P. Wu, *J. Mater. Chem.*, 2009, **19**, 4004-4011.
6. S. Saravanamurugan, M. Palanichamy, M. Hartmann and V. Murugesan, *Appl. Catal., A*, 2006, **298**, 8-15.
7. D.-Z. Xu, Y. Liu, S. Shi and Y. Wang, *Green Chemistry*, 2010, **12**, 514-517.
8. S. Neogi, M. K. Sharma and P. K. Bharadwaj, *J. Mol. Catal. A: Chem.*, 2009, **299**, 1-4.
9. S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita and S. Kitagawa, *J. Am. Chem. Soc.*, 2007, **129**, 2607-2614.
10. M. K. Sharma, P. P. Singh and P. K. Bharadwaj, *J. Mol. Catal. A: Chem.*, 2011, **342-343**, 6-10.
11. X.-M. Lin, T.-T. Li, L.-F. Chen, L. Zhang and C.-Y. Su, *Dalton Trans.*, 2012, **41**, 10422-10429.
12. U. P. N. Tran, K. K. A. Le and N. T. S. Phan, *ACS Catalysis*, 2011, **1**, 120-127.
13. L. T. L. Nguyen, K. K. A. Le, H. X. Truong and N. T. S. Phan, *Catal. Sci. Tech.*, 2012, **2**, 521-528.
14. M. Opanasenko, A. Dhakshinamoorthy, M. Shamzhy, P. Nachtigall, M. Horacek, H. Garcia and J. Cejka, *Catal. Sci. Tech.*, 2013, **3**, 500-507.
15. R. K. Das, A. Aijaz, M. K. Sharma, P. Lama and P. K. Bharadwaj, *Chem. Eur. J.*, 2012, **18**, 6866-6872.
16. S.-N. Kim, S.-T. Yang, J. Kim, J.-E. Park and W.-S. Ahn, *CrystEngComm*, 2012, **14**, 4142-4147.
17. M. Hartmann and M. Fischer, *Micropor. Mesopor. Mat.*, 2012, **164**, 38-43.
18. M. Y. Masoomi, K. C. Stylianou, A. Morsali, P. Retailleau and D. Maspoch, *Cryst. Growth Des.*, 2014, **14**, 2092-2096.
19. , For mechanothesized TMU-4, TMU-5 and TMU-6:  $x = y = z = 0$ . Using conventional heating reaction:  $x = 2$  and  $y = z = 1.5$ .
20. W. Yuan, T. Friščić, D. Apperley and S. L. James, *Angew. Chem. Int. Ed.*, 2010, **49**, 3916-3919.
21. T. Friscic and L. Fabian, *CrystEngComm*, 2009, **11**, 743-745.
22. K. Fujii, A. L. Garay, J. Hill, E. Sbircea, Z. Pan, M. Xu, D. C. Apperley, S. L. James and K. D. M. Harris, *Chem. Commun.*, 2010, **46**, 7572-7574.
23. P. J. Beldon, L. Fábán, R. S. Stein, A. Thirumurugan, A. K. Cheetham and T. Friščić, *Angew. Chem. Int. Ed.*, 2010, **49**, 9640-9643.
24. T. Friščić, D. G. Reid, I. Halasz, R. S. Stein, R. E. Dinnebier and M. J. Duer, *Angew. Chem. Int. Ed.*, 2010, **49**, 712-715.
25. M. J. Cliffe, C. Mottillo, R. S. Stein, D.-K. Bucar and T. Friscic, *Chem. Sci.*, 2012, **3**, 2495-2500.
26. T. Friscic, *Chem. Soc. Rev.*, 2012, **41**, 3493-3510.
27. W. Yuan, J. O'Connor and S. L. James\*, *CrystEngComm*, 2010, **12**, 3515-3517.
28. T. D. Bennett, S. Cao, J. C. Tan, D. A. Keen, E. G. Bithell, P. J. Beldon, T. Friscic and A. K. Cheetham, *J. Am. Chem. Soc.*, 2011, **133**, 14546-14549.
29. H.-L. Jiang, T. A. Makal and H.-C. Zhou, *Coord. Chem. Rev.*, 2013, **257**, 2232-2249.
30. F. A. Carey, Sundberg, Richard J., *Advanced Organic Chemistry*, Springer US, New York, 2007.
31. J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, 1962, **84**, 16-24.
32. W. P. Jencks and J. Carriuolo, *J. Am. Chem. Soc.*, 1960, **82**, 675-681.
33. J. Zhang, A. V. Biradar, S. Pramanik, T. J. Emge, T. Asefa and J. Li, *Chem. Commun.*, 2012, **48**, 6541-6543.
34. 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**, 9995-9997.
35. H. E. B. Lempers and R. A. Sheldon, *J. Catal.*, 1998, **175**, 62-69.





Functionalization of MOF pore walls with azine groups enables greater interaction between the walls and substrate molecules, thereby increasing catalytic activity of the MOFs.  
337x239mm (96 x 96 DPI)