Electronic Supplementary Material (ESI) for Journal of Materials Chemistry
This journal is © The Royal Society of Chemistry 2012

Supporting Information

Fine-Tuning the Balance between Crystallization and Gelation and Enhancement of CO_2 Uptake on Functionalized Calcium Based MOFs and Metallogels

Arijit Mallick,[a] Eva-Maria Schön,[b] Tamas Panda,[a] K. Sreenivas,[c] David Díaz Díaz*[b,d] and Rahul Banerjee*[a]

[a]*Physical/Materials Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-411008, India.*

[b]*Institut für Organische Chemie, Universität Regensburg, Universitätsstr.31, 93040 Regensburg, Germany.*

[c]*Complex Fluids and Polymer Engineering, Polymer Science & Engineering Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-411008, India.*

[d]*ISQCH, University of Zaragoza-CSIC, 50009 Zaragoza, Spain*

E-mail: *David.Diaz@chemie.uni-regensburg.de; Fax: + 49-941-9434121; Tel: + 49-941-9434373*

E-mail: r.banerjee@ncl.res.in; Fax: + 91-20-25902636; Tel: + 91-20-25902535

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry
This journal is © The Royal Society of Chemistry 2012

List of Contents

This journal is © The Royal Society of Chemistry 2012

Section S1: Detailed synthetic procedures for Ca-5TIA-MOF and Ca-5TIA-Xerogel

Thionyl chloride, hydrazine hydrate, diethyl ether, benzene, and *N*, *N*-dimethylformamide (DMF), benzene were purchased from Rankem chemicals. 5-Amino isopthalic acid was purchased from the Aldrich Chemicals. All starting materials were used without further purification. All experimental operations were performed in air. The Fourier transform (FT) IR spectra (KBr pellet) were taken on a *PERKIN ELMER FT-IR SPECTRUM* (Nicolet) spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded on a Phillips PANAlytical diffractometer for Cu Kα radiation (λ = 1.5406 Å), with a scan speed of 2° min^{-1} and a step size of 0.02° in 2θ. Thermo-gravimetric experiments (TGA) were carried out in the temperature range of 25-800 °C on a SDT Q600 TG-DTA analyzer under N_2 atmosphere at a heating rate of 10 °C min^{-1}.

Synthesis of *N*,*N*-dimethylformamide azine dihydrochloride (DMAz): 28.6 mL, 0.4 mol of thionyl chloride ($SOCl_2$) was added with stirring to DMF (150 mL) at 5 °C. After addition keep this mixture at 5 °C for 24 h and then added slowly aqueous hydrazine hydrate (5 mL, 0.1 mol) in 20 mL DMF. After addition the mixture was stirred at room temperature for 48 h and the white precipitate of *N*, *N*-dimethylformamide azine dihydrochloride was collected by filtration and washed with DMF and diethyl ether: 19.1 g; mp 251 °C.

***FTIR:* (KBr 4000-400 cm^{-1}):** 3473(s), 3223 (w), 2951(w), 2848(w), 2031(m), 1715(s), 1609(m), 1507(s), 1398(w), 1287(s), 1228(m), 1137(s), 1054(s), 1019(m), 877(m), 672(s), 654(m), 530(m) and 496(m).

This journal is © The Royal Society of Chemistry 2012

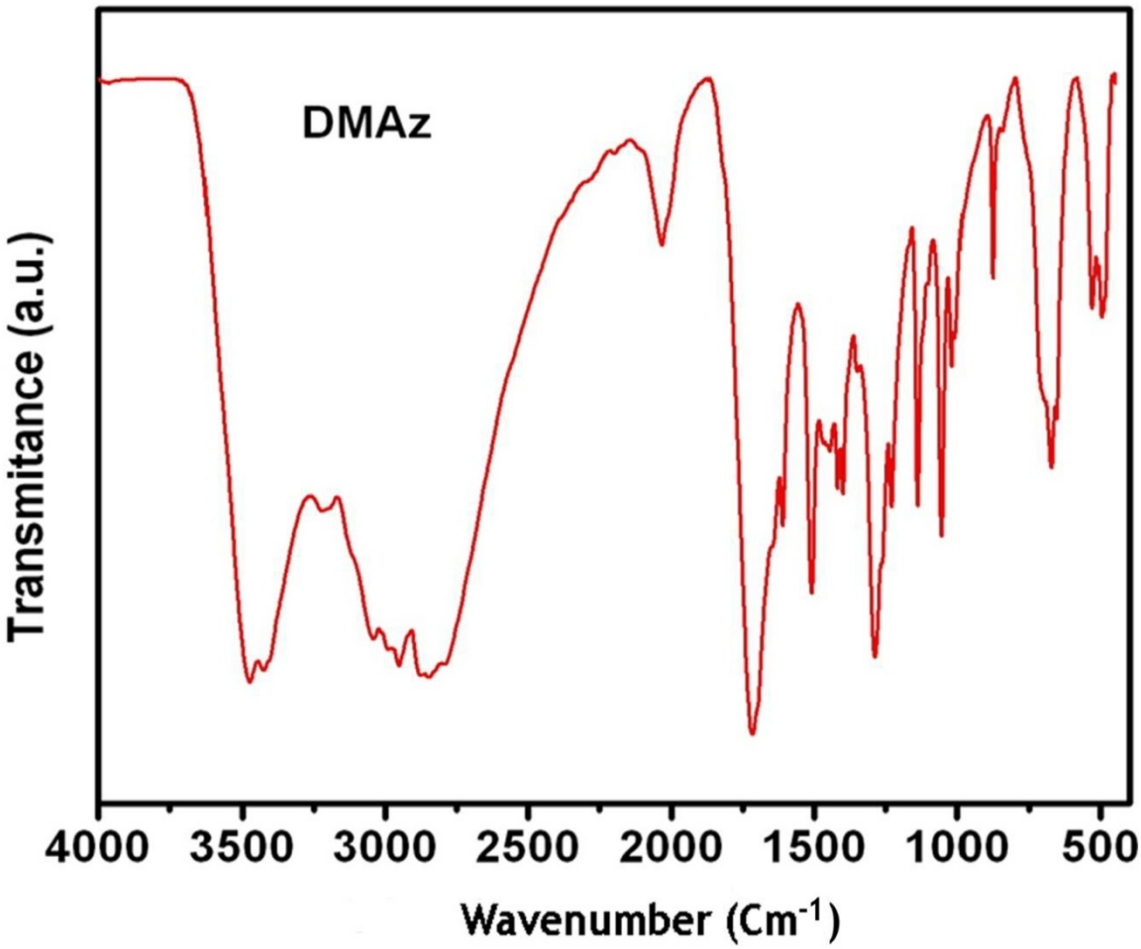


Figure S1. FT-IR spectra of *N*,*N*-dimethylformamide azine dihydrochloride (DMAz).

Synthesis of 5-triazole isopthalic acid: A mixture of *N*, *N*-dimethylformamide azine dihydrochloride (4.0 g, 1.866 mmol) and 5-amino isopthalic acid (3.38 g, 1.86 mmol) was taken in 50 mL benzene (Note: Benzene is *carcinogenic*; reaction should be conducted in a fume hood) and refluxed for 8h. A whitish solid was obtained. The solid was filtered and washed with ethanol (2 × 15 mL) and diethyl ether (1 × 17 mL); yield: 2.38 g (68%).

FT-IR: **(KBr 4000-400 cm^{-1}):** 3119(s), 2906 (w), 1699 (s), 1519 (m), 1448 (m), 1286 (s), 1224 (s), 1143 (m), 1095 (m), 889 (m), 843 (m), 755 (m) and 665 (m).

This journal is © The Royal Society of Chemistry 2012

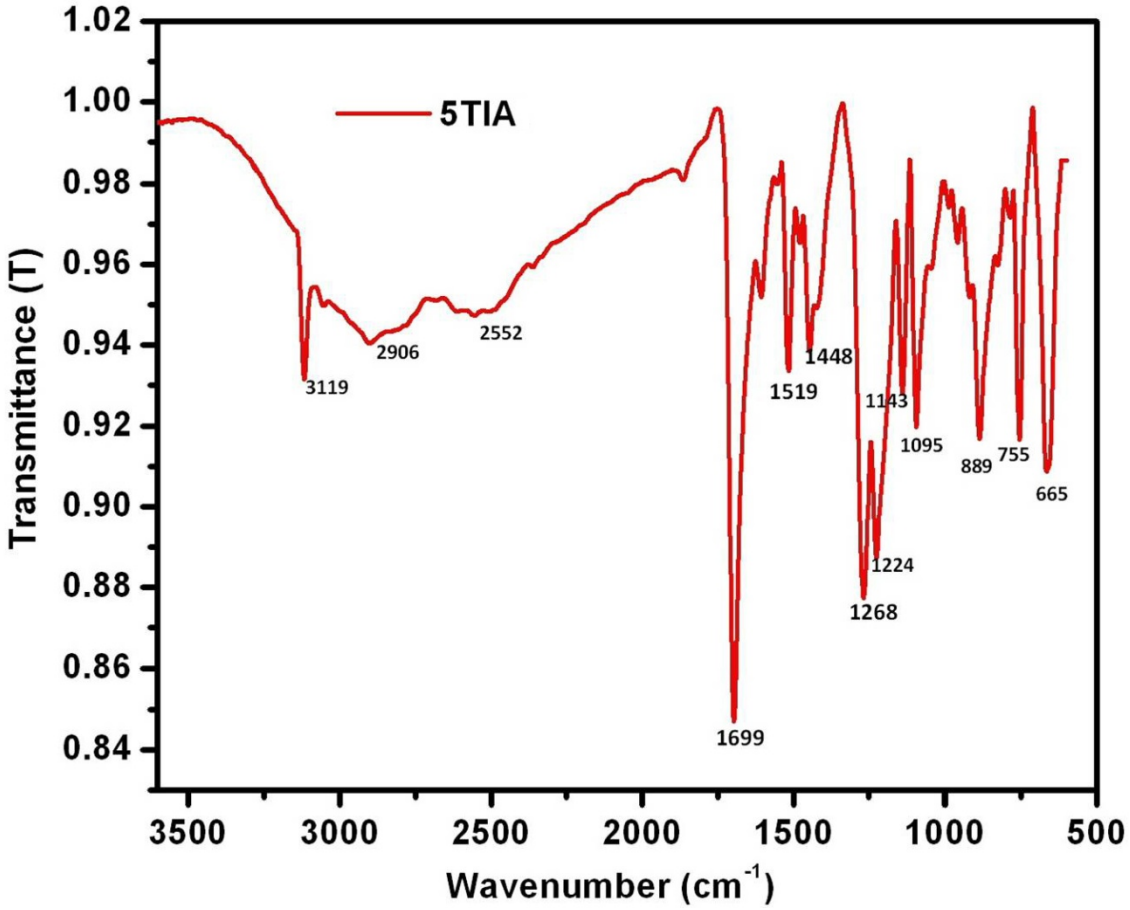


Figure S2. IR spectra of 5-triazole isopthalic acid (5TIA).

[Ca-5TIA-MOF] $Ca_2(5TIA)_2(H_2O)_2$·DMF: 0.2 mmol (0.0446 g) of 5TIA and 0.2 mmol (0.0316 g) of $Ca(OAc)_2$ was mixed in 3 mL of (1:1) DMF:H_2O solution mixture in a 5 mL vial. The mixture solution was stirred for 30 minutes and was capped and heated to 85 °C for 48 h. Colorless plate like crystals were obtained, which were filtered off and washed with EtOH. Afterwards resulting MOF was dried in air (10 min). [Yield: 72 %, 0.0227 g depending on $Ca(OAc)_2$]. ***FT-IR:*** **(4000-600 cm^{-1}):** 3216 (m, br), 1669.83 (m), 1616.42 (m), 1549.79 (s), 1450.09 (m), 1380.82 (s), 1296.55 (w), 1244.21 (m), 1169.51 (w), 1084.79 (m), 1042.68 (w), 899.52 (w), 773.42 (m), 739.67 (m) and 682.77 (m) cm^{-1}.

This journal is © The Royal Society of Chemistry 2012

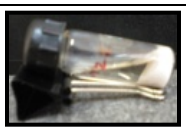
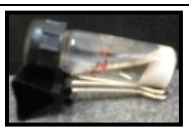
[Ca-5TIA-Gel]: 0.2 mmol (0.0316 g) of $Ca(OAc)_2$ and 0.2 mmol (0.0446 g) of 5-triazole isophthalic acid (5TIA) were added in a 5 mL vial. Then 2 mL of DMF was added to the mixture and sonicate the mixture solution (~15 min) till it become a homogeneous milk colored solution. Then the solution was kept in different temperature 30 °C, 60 °C, 90 °C and 120 °C for 2 days. In all cases white color gels are formed. ***FT-IR:*** **(4000-600 cm^{-1}):** 3348.58 (m, br), 1616.84 (m), 1550.28 (s), 1436.48 (m), 1386.03 (s), 1296.60 (w), 1248.48 (m), 1167.79 (w), 1095.51 (m), 1050.93 (w), 899.65 (w), 773.42 (m), 731.39 (m) and 669.01(w) cm^{-1}.

[Ca-5TIA-Xerogel]: Ca-5TIA-Xerogel has been synthesized by freeze-drying method (lyophilisation). At first the Ca-5TIA-Gel was frozen in liquid nitrogen and then kept under high vacuum for 24 h. After this time, a yellowish-white powder of Ca-5TIA-Xerogel was obtained.

This journal is © The Royal Society of Chemistry 2012

Section S2. Role of water in crystallization and gel formation

Table S1: Controlling of gelation and crystallisation by addition of water for the system [$Ca(OAc)_2$ (0.2 mmol) + 5TIA (0.2 mmol) + 2mL DMF]

Name	Metal salt conc.	Conc. of 5TIA ligand	Volume of DMF	Volume of H_2O	Picture	Remarks
1	0.2 mmol	0.2 mmol	2.0 mL	0.1 mL		Gel
2	0.2 mmol	0.2 mmol	2.0 mL	0.2 mL		Precipitate
3	0.2 mmol	0.2 mmol	2.0 mL	0.5 mL		Precipitate
4	0.2 mmol	0.2 mmol	2.0 mL	0.7 mL		Precipitate
5	0.2 mmol	0.2 mmol	2.0 mL	1.0 mL		Precipitate
6	0.2 m mol	0.2 mmol	2.0 mL	1.5 mL		Precipitate
7	0.2 mmol	0.2 mmol	2.0 mL	2.0 mL		Precipitate
8	0.2 mmol	0.2 mmol	2.0 mL	2.5 mL		Crystals

This journal is © The Royal Society of Chemistry 2012

Section S3. Single Crystal X-ray Diffraction Data Refinement Procedures

Experimental and Refinement Details for Ca-5-TIA MOF (Orthorhombic):

A colorless plate crystal (0.29 × 0.21 × 0.12 mm^3) of Ca-5-TIA MOF was mounted on 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a *SMART APEX* three circle diffractometer equipped with a CCD area detector (Bruker Systems Inc., 1999a)[19] and operated at 1500 W power (50 kV, 30 mA) to generate Mo K_α radiation (λ = 0.71073 Å). The incident X-ray beam was focused and monochromated using Bruker Excalibur Gobel mirror optics. A total of 31141 reflections were collected of which 3022 were unique and 2456 of these were greater than 2σ (*I*). The range of θ was from 1.69 to 24.99º. Analysis of the data showed negligible decay during collection. The structure was solved in the orthorhombic *Cmca* space group, with Z = 16, using direct methods. All carbon, oxygen and nitrogen atoms were refined isotropically with hydrogen atoms generated as spheres riding the coordinates of their parent atoms. All Ca atoms were refined anisotropically. Modeling of electron density within the voids of the frameworks did not lead to identification of coordinated solvent molecules in all structures due to the lowered resolution of the data. The attempts made to model the coordinated solvent molecules did not lead to identification it in all structures due to the limited periodicity of the solvent molecules in the crystals. Since the solvent is bonded to the framework this can be expected for the MOF structures. Many atomic coordinates that have been attributed to solvent molecules lie on a special position. However, very high displacement parameters, high esd's and partial occupancy due to the disorder make it impossible to determine accurate positions for these solvent molecules. Thus, electron density within void spaces which could not be assigned to any definite guest entity was modeled as isolated carbon and oxygen atoms, and the foremost errors in all the models lies with assignment of guest electron density.

This journal is © The Royal Society of Chemistry 2012

To prove the correctness of the atomic positions in the framework the application of the SQUEEZE routine of A. Spek has been performed. Final full matrix least-squares refinement on $F2$ converged to R_1= 0.0567 (F >2σF)) and wR_2= 0.1671 (all data) with GOF = 1.083. Another possible structure solution was possible in *Cmca* space group for Ca-5TIA-MOF. It should be noted that other supporting characterization data (Section S1) are consistent with the crystal structure.

This journal is © The Royal Society of Chemistry 2012

Table S2. **Crystal data and structure refinement for Ca-5TIA-MOF:**

Empirical formula	$C_{10}H_4CaN_3O_5$
Formula weight	286.24
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*C m c a*
Unit cell dimensions	*a* = 19.346(2)Å α = 90°
	b = 24.081(3)Å β = 90°
	c = 14.2543(15)Å γ = 90°
Volume	6640.7(12)
Z	16
Density (calculated)	1.145
Absorption coefficient	0.392
F(000)	2320
Crystal size	0.29× 0.21× 0.12 mm^3
Theta range for data collection	2.21– 27.52
Index ranges	-22<= h <= 22, -28<= k <= 28, -16<= l <= -16
Reflections collected	31147
Independent reflections	7330
Completeness to theta = 26.02°	100 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3022 / 0 / 178
Goodness-of-fit on F^2	1.083
Final R indices [I>2sigma(I)]	R_1 = 0.0567, wR_2 = 0.1671
R indices (all data)	R_1 = 0.0642, wR_2 = 0.1728
Largest diff. peak and hole	0.093 and -0.407 e.$Å^{-3}$

This journal is © The Royal Society of Chemistry 2012

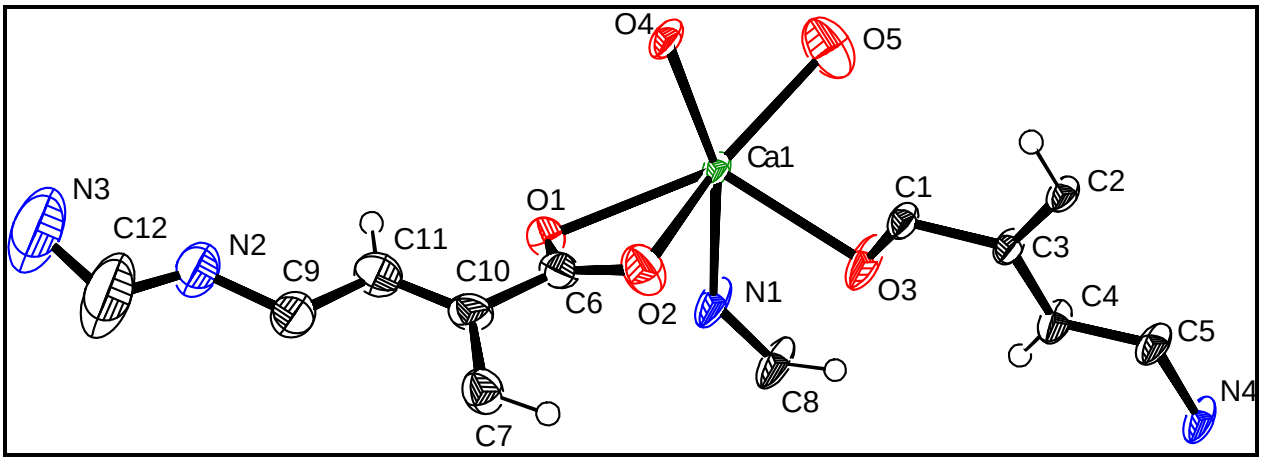


Figure S3. ORTEP drawing of the asymmetric unit of Ca-5TIA-MOF.

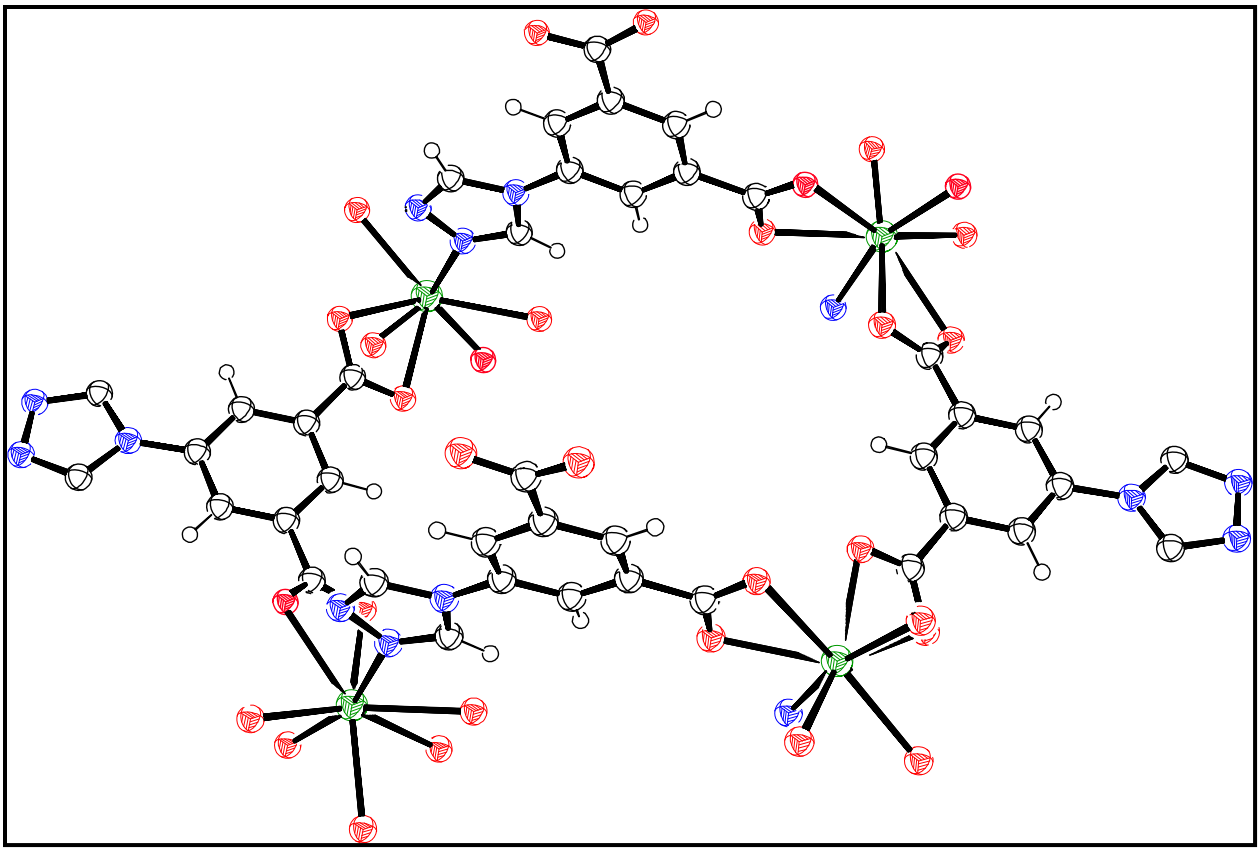


Figure S4.ORTEP drawing of the grown asymmetric unit of Ca-5TIA-MOF.

This journal is © The Royal Society of Chemistry 2012

Section S4. Single crystal structures of Ca-5TIA-MOF

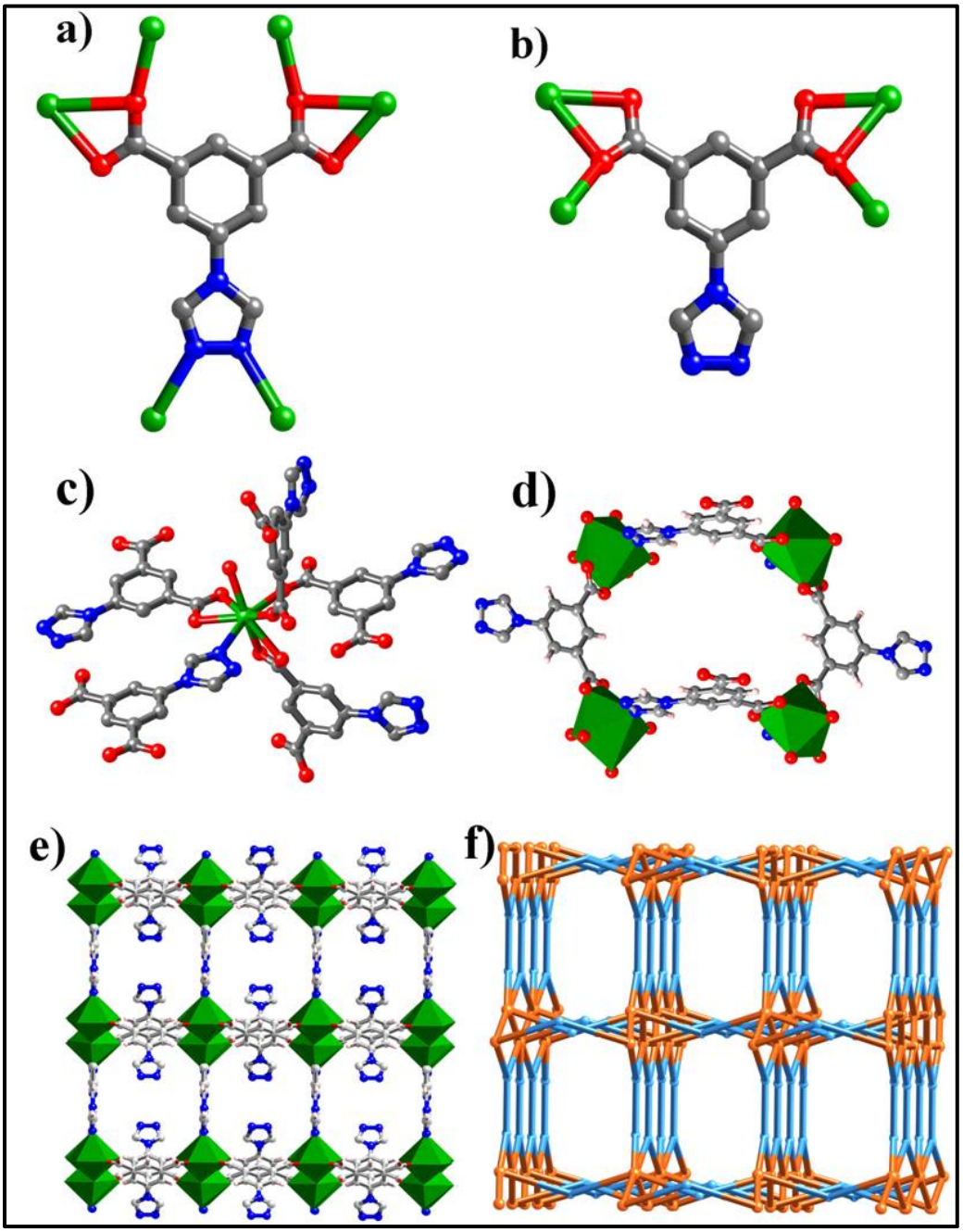


Figure S5. a) Coordination sites of 5TIA along *c* axis. b) Coordination sites of 5TIA along *a* axis. c) Coordination environment around Ca(II) centre. d) The SBU in the crystal structure of Ca-5TIA-MOF showing the arrangement of 5TIA. e) Packing diagram showing formation of one dimensional pores through *c* axis for Ca-5TIA-MOF.f) Topological simplification of Ca-5TIA-MOF through *c* axis, by joining only Ca(II) centres (orange) with 5TIA ligand (blue).

This journal is © The Royal Society of Chemistry 2012

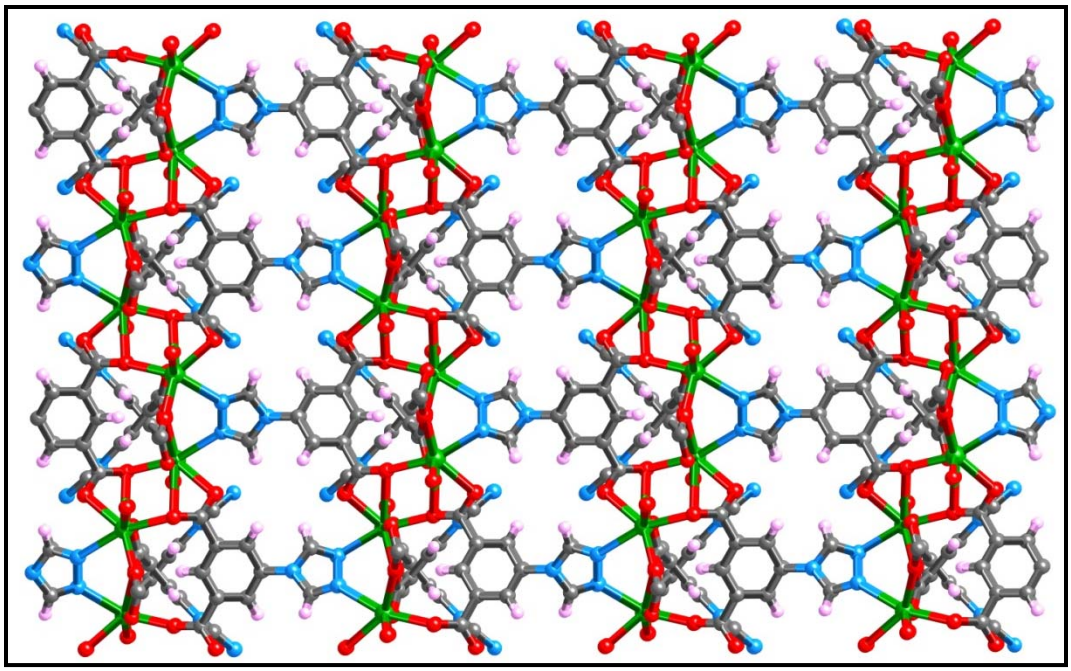


Figure S6. Packing diagram showing formation of through *a* axis for Ca-5TIA-MOF.

This journal is © The Royal Society of Chemistry 2012

Section S5. TEM data of Ca-5TIA-Gel

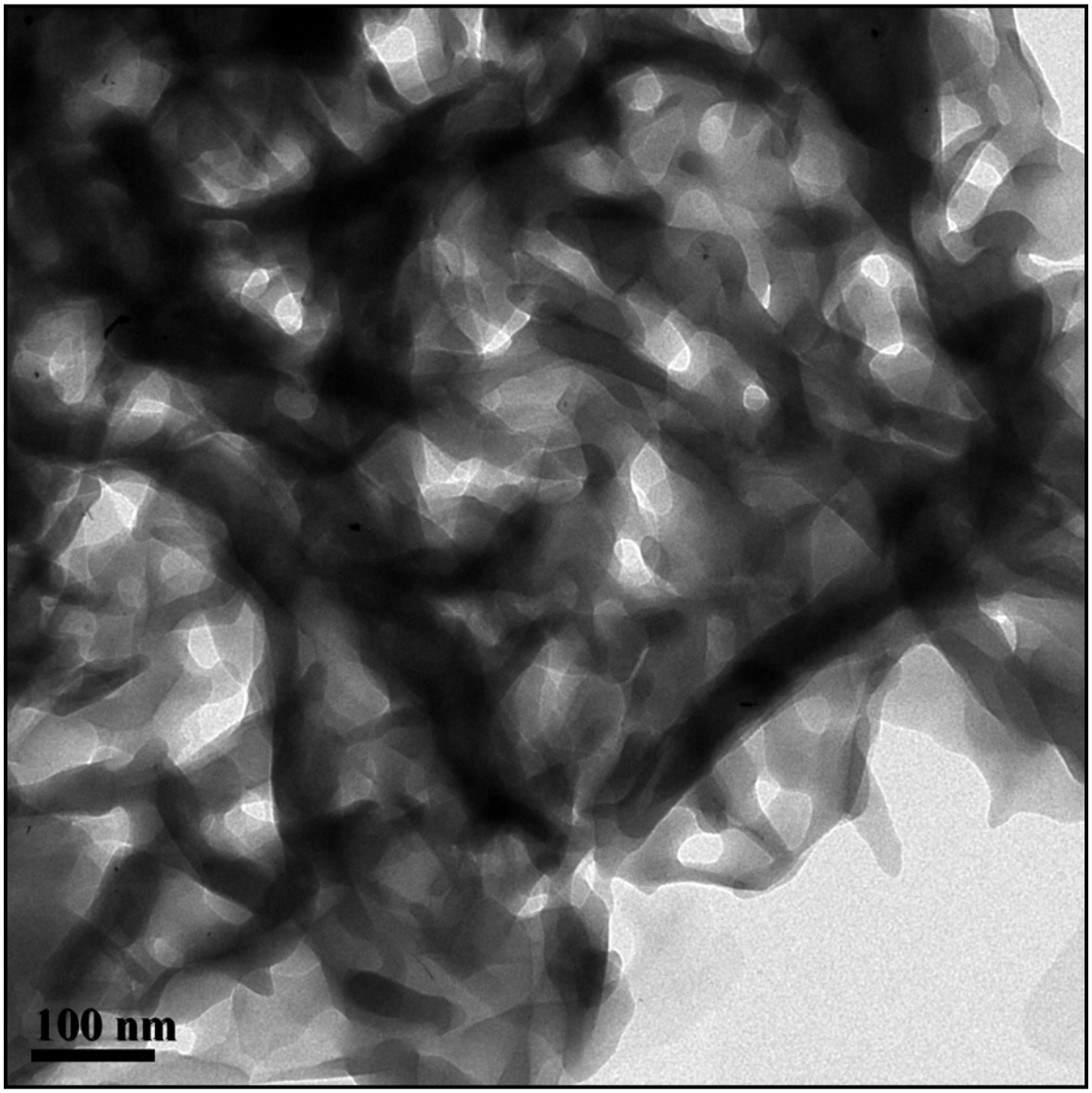


Figure S7. TEM image of Ca-5TIA-Gel prepared in 1 mL DMF + 0.05 mmol $Ca(OAc)_2$ + 0.05 mmol 5TIA, sonication at RT for 15 min, then standing at RT.

This journal is © The Royal Society of Chemistry 2012

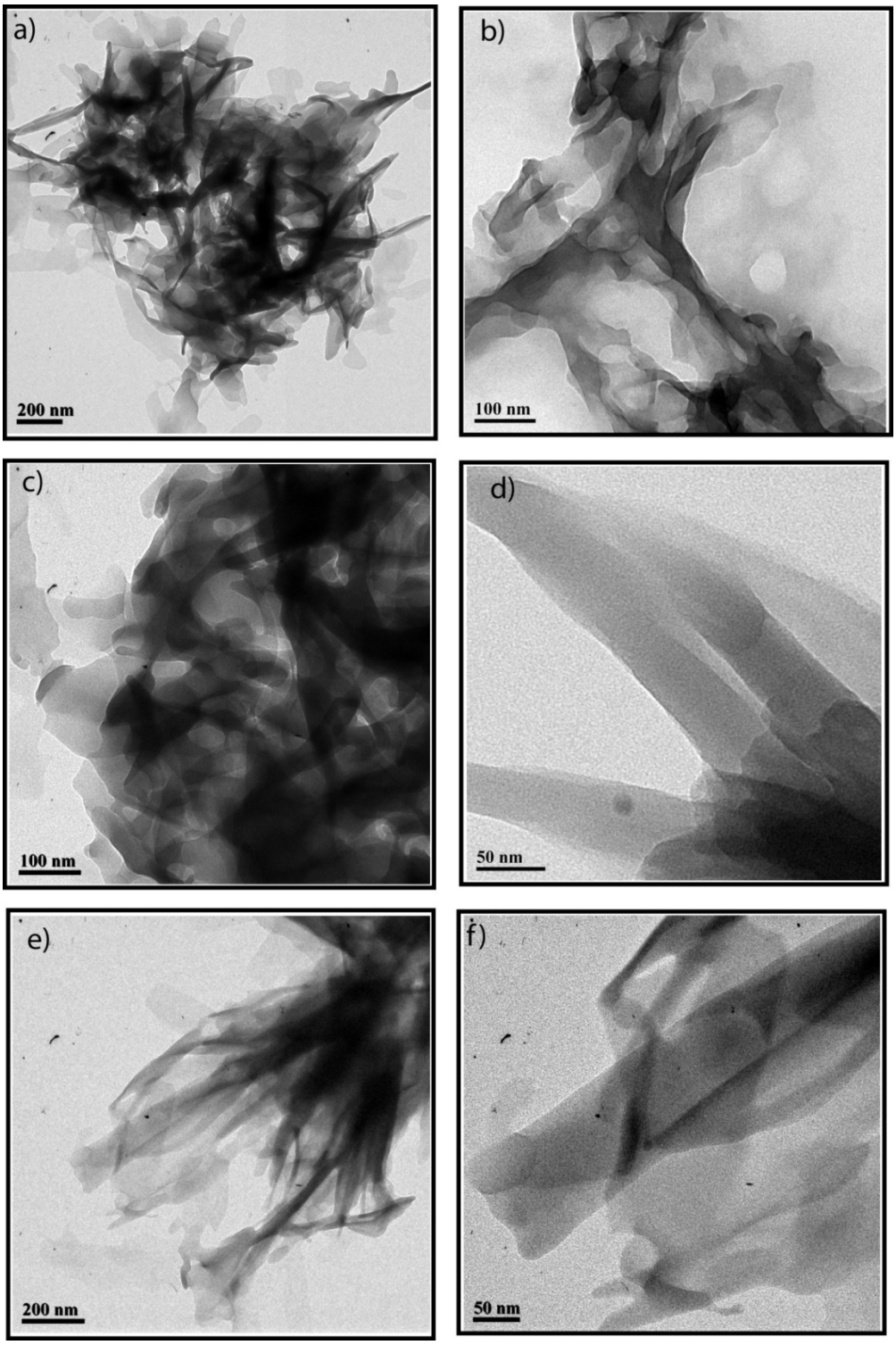


Figure S8. a-b)0.1 mmol $Ca(OAc)_2$ + 0.1 mmol 5TIA, sonication at RT for 15 min, then heating at 120 °C in an oil bath for 2 hc-d)0.1 mmol $Ca(OAc)_2$ +0.1 mmol 5TIA, sonication at RT for 15 min, then heating at 120 °C in an oil bath for 20 h.e-f) 0.1 mmol $Ca(OAc)_2$ + 0.075 mmol 5TIA, sonication at RT for 15 min, then heating at 120 °C in an oil bath for 3 h.

This journal is © The Royal Society of Chemistry 2012

Section S6. Rheology analysis of Ca-5TIA-Gel

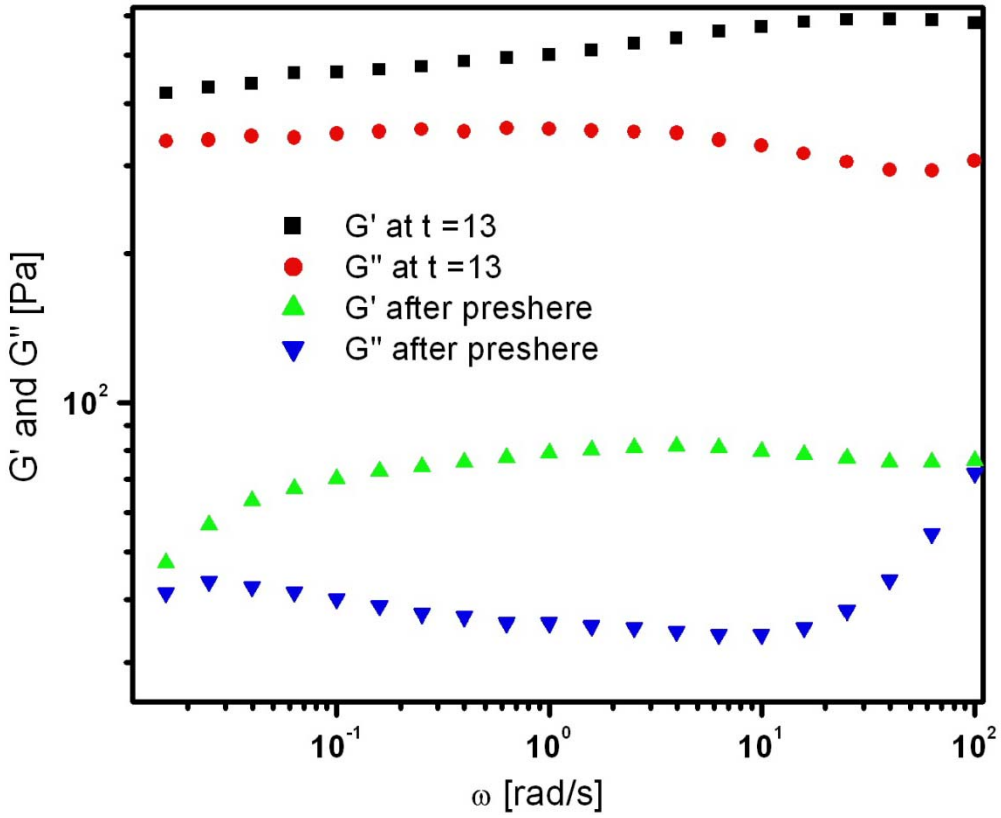


Figure S9. A plot of the solid modulus (G') and loss modulus (G'') as a function of frequency (ω) at final holding time (720 minutes) and after preshere with strain (γ) of 1% and frequency (ω) from 0.1 to100 rad·s^{-1} using Couette geometry for Ca-5TIA-Gel.

This journal is © The Royal Society of Chemistry 2012

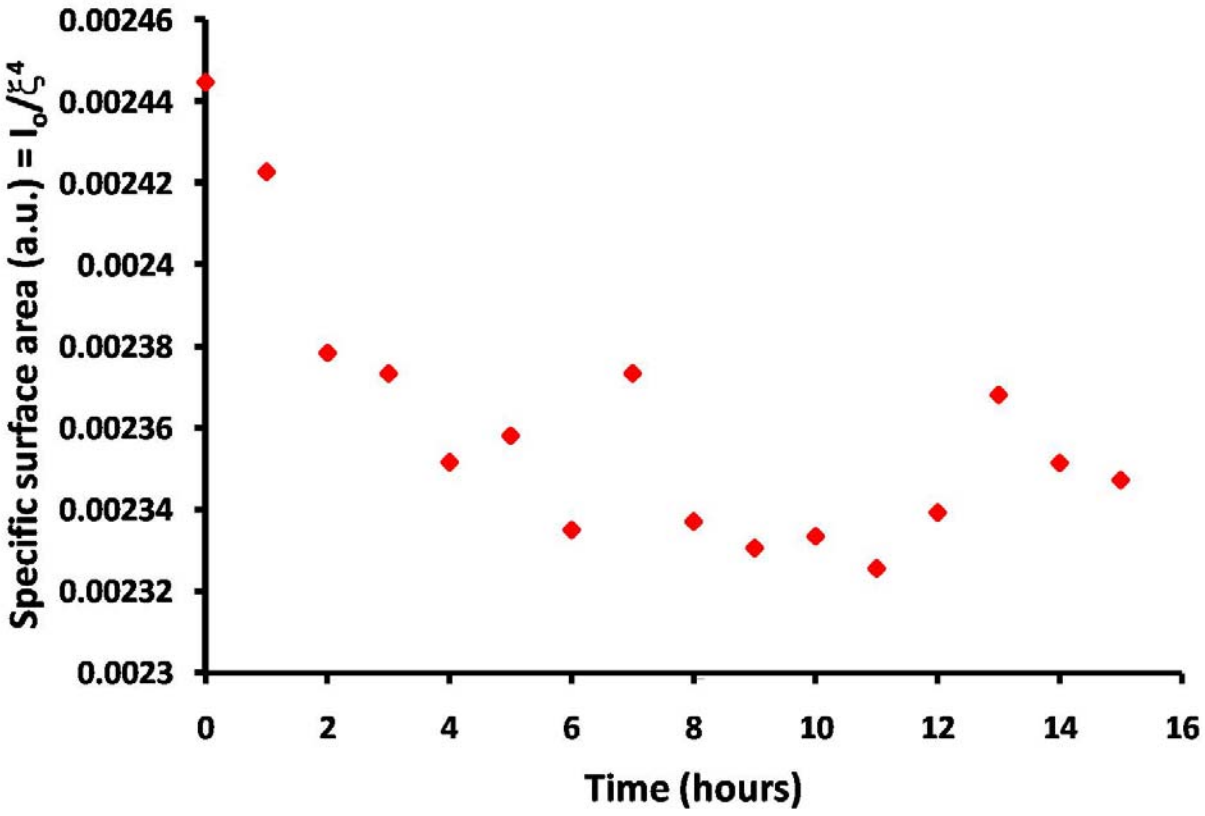


Figure S10. Plot of specific surface area with time.

This journal is © The Royal Society of Chemistry 2012

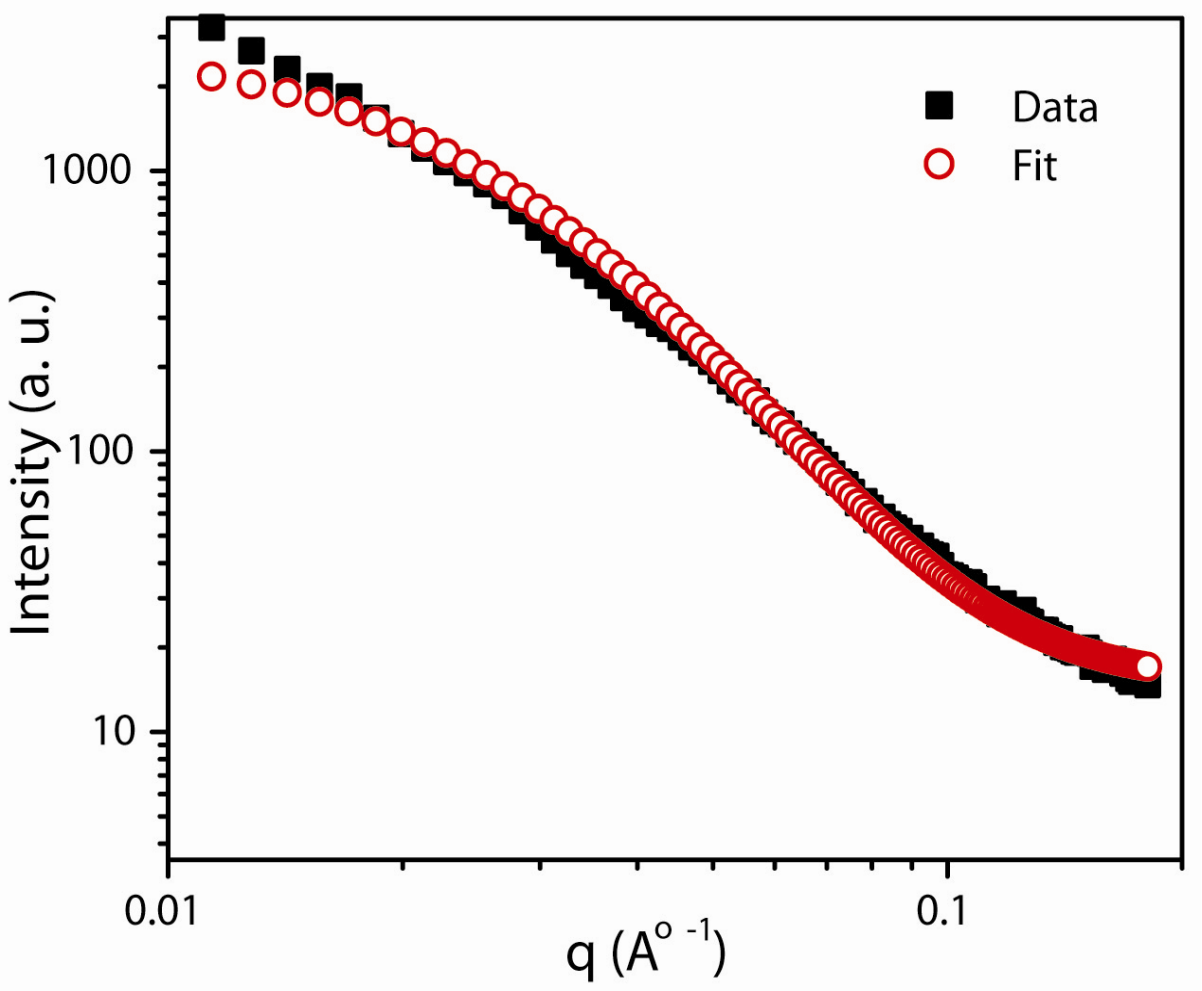


Figure S11.SAXS plot of q ($Å^{-1}$) as a function of scattering intensity (a. u.) for experimental data of Ca-5TIA-Gel (black) and Debye-Bueche model (red).

This journal is © The Royal Society of Chemistry 2012

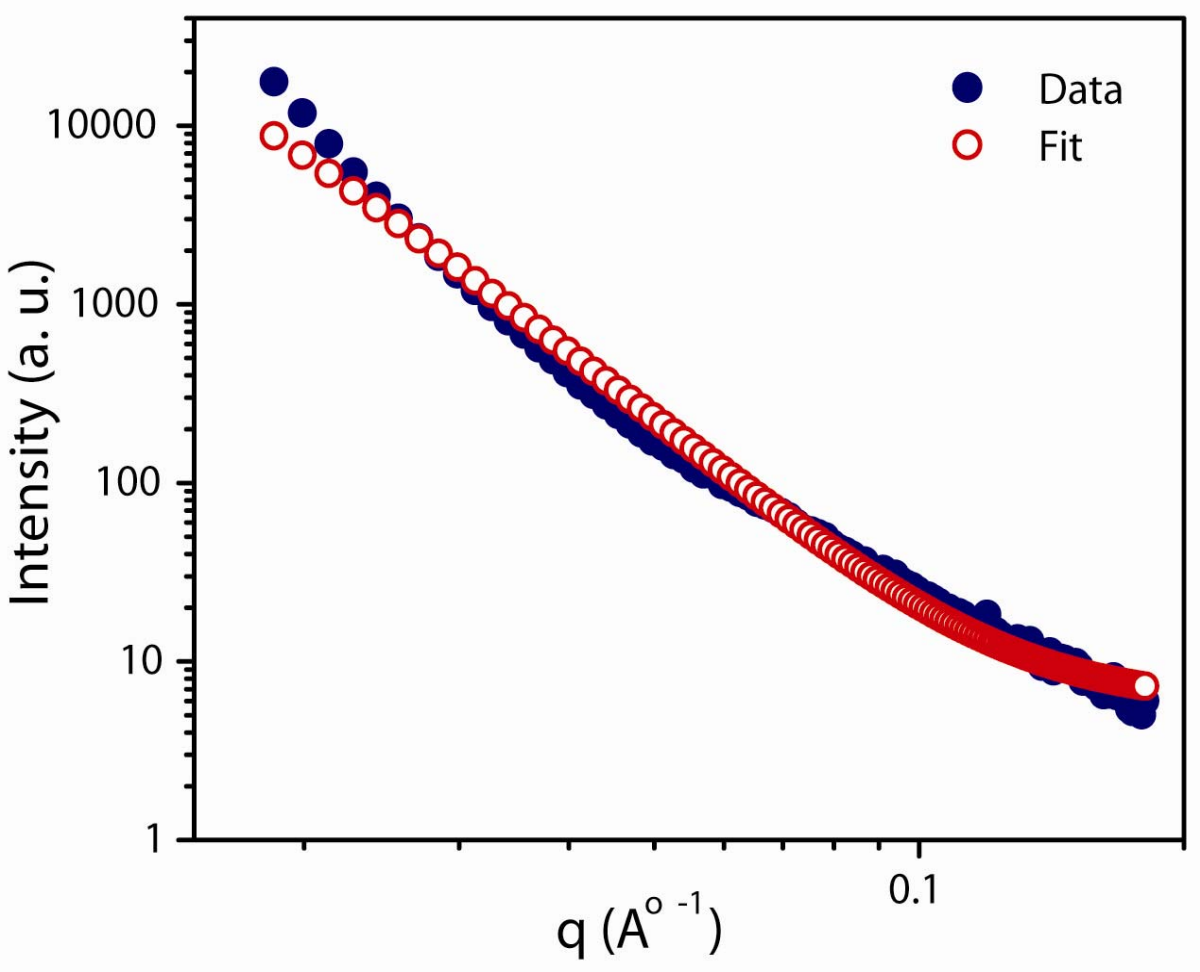
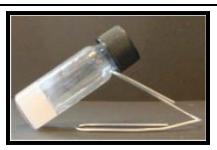
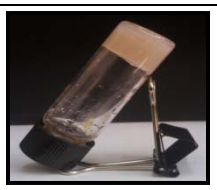
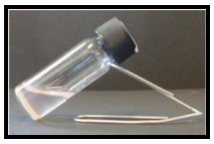


Figure S12.SAXS plot of q ($Å^{-1}$) as a function of scattering intensity (a. u.) for experimental data of Ca-5TIA-Xerogel (blue) and Debye-Bueche model (red).

This journal is © The Royal Society of Chemistry 2012

Section S7. Role of metal counteranion in gel formation.

Table S3: Gelation ability of the system [Ca-salt (0.1 mmol) + 5TIA (0.1 mmol)] in DMF (1.0 mL) using different metal counteranions.

Metal salts	Conc. of metal salts	Conc. of 5TIA ligand	Volume of DMF added	Pictures	Description of the obtained material
$Ca(OH)_2$	0.1 mmol (7.4 mg)	0.1 mmol (22.3 mg)	1.0 mL		Gel (white opaque)
CaO	0.1 mmol (6.5 mg)	0.1 mmol (22.3 mg)	1.0 mL		Gel (brownish)
$Ca(OAc)_2$	0.1 mmol (15.8 mg)	0.1 mmol (22.3 mg)	1.0 mL		Gel (white opaque)
$CaSO_4$	0.1 mmol (13.6 mg)	0.1 mmol (22.3 mg)	1.0 mL		Pinkish solution and solid material at the bottom of the vial
$CaCl_2$	0.1 mmol (11.1 mg)	0.1 mmol (22.3 mg)	1.0 mL		Clear solution
$CaCO_3$	0.1 mmol (10.0 mg)	0.1 mmol (22.3 mg)	1.0 mL		Pinkish solution and solid material at the bottom of the vial
$Ca(NO_3)_2$	0.1 mmol (7.4 mg)	0.1 mmol (22.3 mg)	1.0 mL		Clear yellowish solution

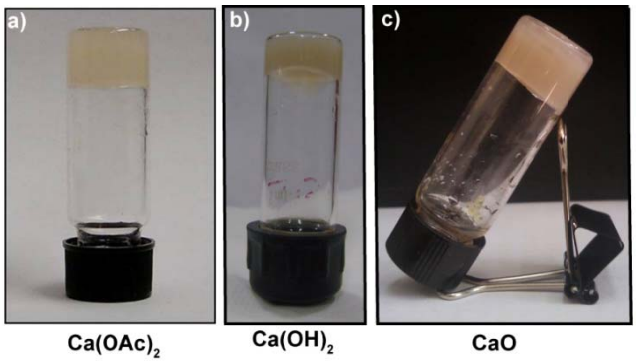


Figure S13. Digital pictures of the gel materials made from a) $Ca(OAc)_2$, b) $Ca(OH)_2$, c) CaO. Conditions: Ca-salt (0.1 mmol), 5TIA (0.1 mmol), DMF (1.0 mL).

Section S8. PXRD analysis.

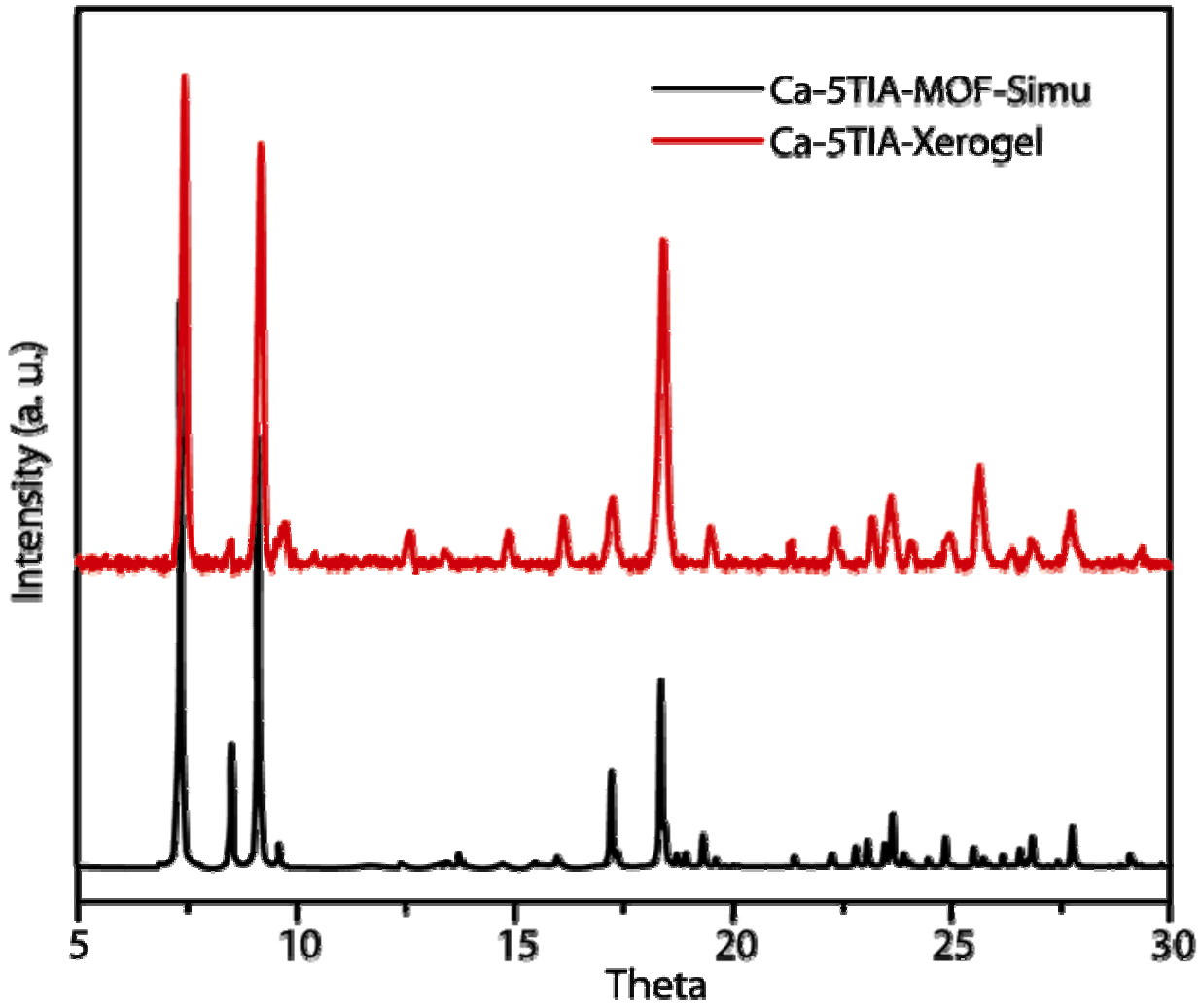


Figure S14.Comparison of PXRD patterns of the Ca-5TIA-Xerogel[$Ca(OAc)_2$](red) with the simulated pattern from the single-crystal structure of Ca-5TIA-MOF (black).

This journal is © The Royal Society of Chemistry 2012

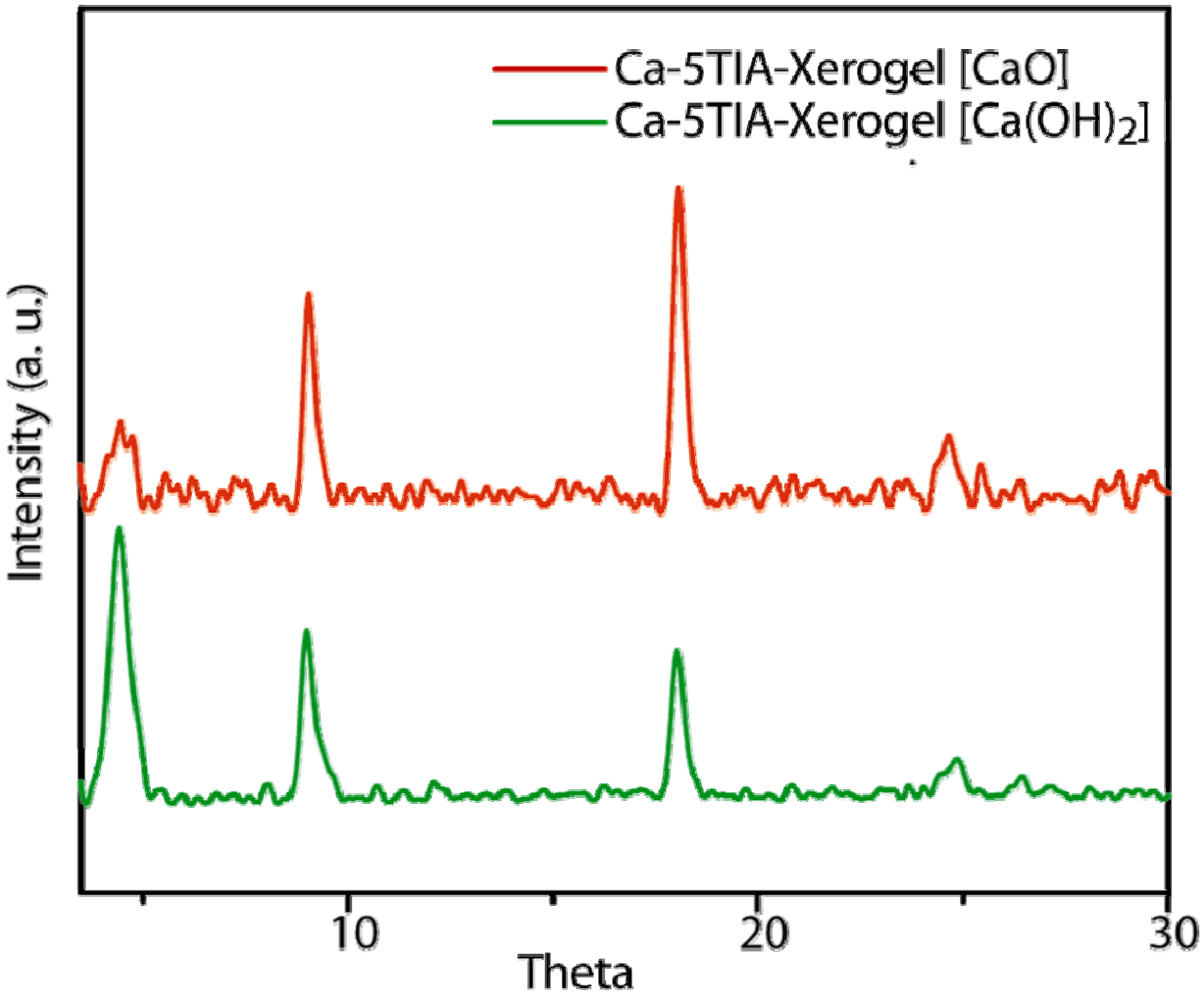


Figure S15.Comparison of PXRD patterns of the Ca-5TIA-Xerogel [CaO](red) and Ca-5TIA-Xerogel [$Ca(OH)_2$](green).

This journal is © The Royal Society of Chemistry 2012

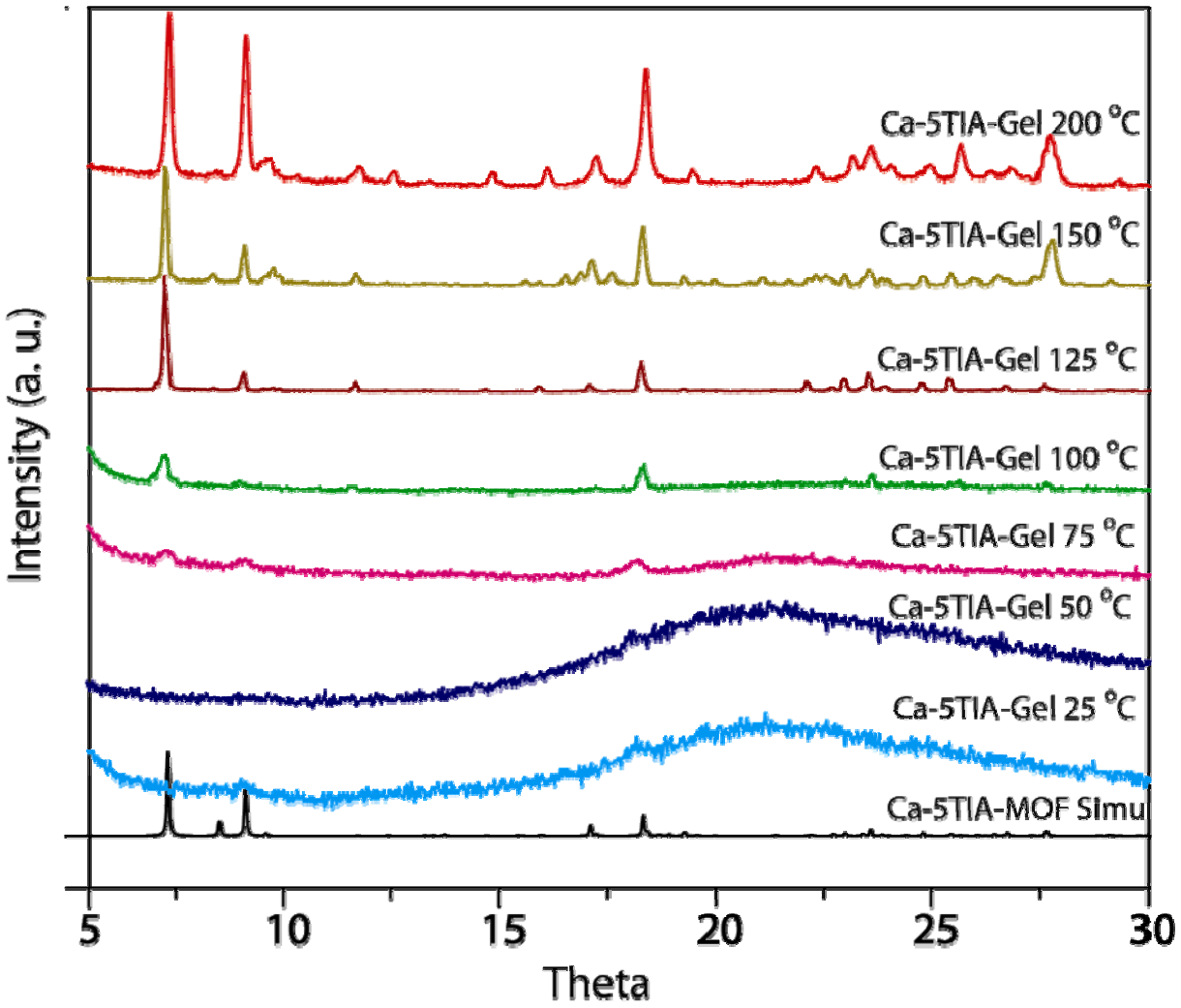


Figure S16. VT-PXRD patterns of the Ca-5TIA-Gel in the tempetature range of 25-200 °C.

This journal is © The Royal Society of Chemistry 2012

References

1. Bruker, *APEX2*. Version 5.053. Bruker AXS Inc., Madison,Wisconsin, USA, 2005.
2. G. M. Sheldrick, *CELL_NOW*. University of Göttingen, Germany, 2004. Steiner, Th. 1998. *Acta Cryst*. B54, 456.
3. Bruker, *SAINT-Plus* (Version 7.03). Bruker AXS Inc., Madison, Wisconsin, USA, 2004.
4. G. M. Sheldrick, *SADABS* (Version 2.03) and *TWINABS* (Version 1.02).University of Göttingen, Germany, 2002.
5. G. M. Sheldrick, *SHELXS '97* and *SHELXL '97*. University of Göttingen, Germany, 1997.
6. L. J. Farrugia, *J. Appl. Cryst.,* 1999, **32**, 837.
7. A.L.Spek, PLATON, *A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2005.
8. L. A. Dakin, P. C.Ong, J. S.Panek, R. J.Staples, P. Stavropoulos, *Organometallics,*2000,**19**,2896.
9. S. Noro, R. Kitaura, M. Kondo, S. Kitagawa, T. Ishii, H. Matsuzaka, M. Yamashita, *J. Am. Chem. Soc.,*2002,**124,**2568.
10. M. Eddaoudi, J. Kim, D. Vodak, A. Sudik, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Proc. Natl. Acad. Sci. U.S.A.,*2002, **99**,4900.
11. R. A. Heintz, H. Zhao, X. Ouyang, G. Grandinetti, J. Cowen, K. R. Dunbar, *Inorg. Chem.,* 1999, **38**,144.
12. K. Biradha, Y. Hongo, M. Fujita, *Angew. Chem. Int. Ed.,* 2000, **39**, 3843.
13. P. Grosshans, A. Jouaiti, M. W. Hosseini, N. Kyritsakas, *New J. Chem, (Nouv.J. Chim,),* 2003, **27**,793.
14. N. Takeda, K. Umemoto, K. Yamaguchi, M. Fujita, *Nature (London),* 1999, **398**,794.

This journal is © The Royal Society of Chemistry 2012

15. M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science,*2002, **295**,469.

16. B. Kesanli, , Y. Cui, M. R. Smith, E. W. Bittner, B. C. Bockrath, W. Lin, *Angew. Chem. Int. Ed.* 2005, **44,** 72.

17. F. A. Cotton, C. Lin, C. A. Murillo, *Inorg. Chem.* 2001, **40***,*478.