Mechanosynthesis

DOI: 10.1002/ange.201005547

Rapid Room-Temperature Synthesis of Zeolitic Imidazolate Frameworks by Using Mechanochemistry**

*Patrick J. Beldon, László Fábián, Robin S. Stein, A. Thirumurugan, Anthony K. Cheetham, and Tomislav Friščić**

Depletion of mineral and energy sources is steering research and technology towards more economically and environmentally acceptable synthesis.[1] Mechanochemical synthesis has shown significant potential for the clean and energy-efficient construction of molecules and materials.[2] Modified mechanochemical methods such as liquid-assisted grinding (LAG) or ion- and liquid-assisted grinding (ILAG) were recently demonstrated to be highly efficient for the selective construction of pillared metal–organic frameworks (MOFs) directly from a metal oxide.[3,4] We now extend these methods to the synthesis of a very different family of metal–organic materials. We report the direct and topologically selective conversion of ZnO into porous and nonporous zeolitic imidazolate frameworks (ZIFs)[5] based on imidazole (**HIm**), 2-methylimidazole (**HMeIm**), and 2-ethylimidazole (**HEtIm**) (Figure 1 a,b). Topological diversity combined with the retention of connectivity make ZIFs particularly interesting targets and, consequently, significant attention has been given to solvothermal ZIF screening.[6] The structure-directing effects of liquids and salts suggest LAG and ILAG as milder alternatives for generating ZIFs.[4,7] Particular benefits expected from oxide-based mechanosynthesis are short reaction times and the ability to conduct reactions at room temperature without generating strong acids or requiring a base. We now demonstrate a mechanochemical approach for ZIF synthesis and screening that provided six known and two previously unknown ZIFs in a limited set of 48 experiments.

Previous work indicated that the mechanosynthesis of metal imidazolates from a metal oxide is a challenging task. Fernández-Bertrán and co-workers[8] established that manual grinding of ZnO and **HIm** leads to the partial formation of the nonporous Zn(**Im**)$_2$. Quantitative conversion of the oxide was achieved only with a large excess of **HIm**. The same product was obtained by Adams et al. in a two-step mechanochemical process starting from ZnCl$_2$ and using the external base technique.[9] In our hands, ball milling of ZnO and **HIm** for 30 min resulted in a mixture which, based on powder X-ray diffraction (PXRD), contained ZnO, **HIm**, Zn(**Im**)$_2$ with the

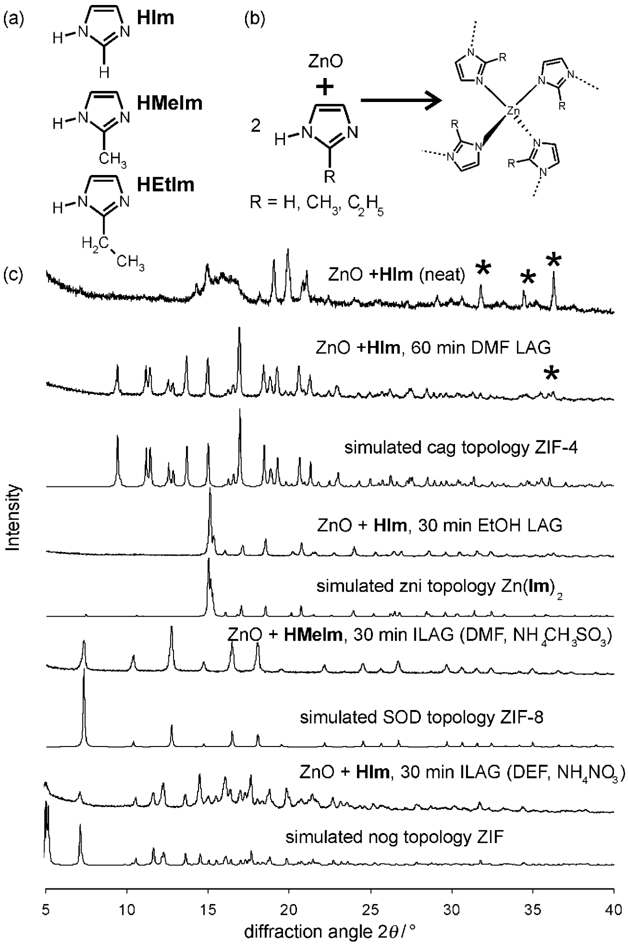

Figure 1. a) Imidazole ligands. b) The expected mechanochemical reaction. c) PXRD patterns (from top to bottom; vertically offset): neat grinding of ZnO and **HIm**; product of 60 min LAG of ZnO and **HIm** using DMF; simulated for cag topology ZIF-4; product of 30 min LAG of ZnO and **HIm** using EtOH; simulated for zni topology Zn(**Im**)$_2$; product of 30 min ILAG involving ZnO, **HMeIm**, DMF and NH$_4$CH$_3$SO$_3$; simulated for SOD topology ZIF-8. Reflections of ZnO are labeled with *.

---

[*] P. J. Beldon, Dr. T. Friščić
Department of Chemistry, University of Cambridge
Lensfield Road, Cambridge, CB2 1EW (UK)
E-mail: tf253@cam.ac.uk
Dr. L. Fábián
University College Cork, Department of Chemistry
Kane Building, College Road, Cork (Ireland)
Dr. R. S. Stein
Bruker UK Ltd, Banner Lane, Coventry CV4 9GH (UK)
Dr. A. Thirumurugan, Prof. A. K. Cheetham
Department of Materials Science and Metallurgy
University of Cambridge, Cambridge CB2 3QZ (UK)

[**] This work was supported by the Herchel Smith Fund (research fellowship to T.F.) and the ERC (Advanced Investigator Award to A.K.C.). We acknowledge the EPSPC for financial support administered though the University of Cambridge Nano Doctoral Centre (P.J.B, T.F.).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201005547.

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

zni topology[10] (CCDC code IMIDZB01) and an as yet unidentified material characterized by a broad set of reflections in the 2θ range 10–20° (Figure 1c). ZnO did not react with either **HMeIm** or **HEtIm** by grinding and we conclude that neat grinding is of limited scope for oxide-based ZIF synthesis.

Mechanochemical reactivity is expected to improve upon addition of a small amount of a liquid phase which enhances mobility, while avoiding limitations related to solubility.[11] Indeed, LAG of ZnO and **HIm** in the presence of *N*,*N*-dimethylformamide (DMF) led to the quantitative formation of ZIF-4 with the porous cag topology[10] after 60 min (Figure 1c).[12] The product was identified by comparing its PXRD pattern with the one simulated for the known structure (CCDC code VEJYUF). LAG with **HMeIm** led to partial formation of ZIF-8 with the sodalite (SOD) topology (CCDC code VELVOY). No reaction was observed with **HEtIm**.

Improved ZIF synthesis by LAG led us to explore sub-stoichiometric amounts (ca. 5–10 mol %) of salts as a means to further improve reactivity. Such ILAG was recently shown to accelerate the formation and direct the geometry of large-pore pillared MOFs.[4] We performed a limited screen of mechanochemical reactions using DMF, *N*,*N*-diethylformamide (DEF) and ethanol (EtOH) as grinding liquids and NH_4NO_3, $(NH_4)_2SO_4$ and $NH_4CH_3SO_3$ as salt additives. Results were analyzed by PXRD and reflectance FTIR spectroscopy.

The results in Table 1 make evident the potential of ILAG in ZIF synthesis. In almost all cases the addition of the salt enhanced the reactivity of ZnO towards the ligand, such that the product was obtained quantitatively within 30–60 min, in contrast to conventional solvothermal syntheses.[12b] The relative importance of added liquid or salt on the product topology varied with the ligand. For **HIm**, the ZIF topology was determined by the liquid phase: LAG with DMF yielded cag, whereas EtOH yielded zni topology ZIFs (Figure 1c). Grinding with DEF did not lead to a reaction unless a salt was added: ILAG with NH_4NO_3 resulted in an open structure with the nog topology (CCDC code HIFWAV),[13] while $(NH_4)_2SO_4$ and $NH_4CH_3SO_3$ provided a yet unidentified product that spontaneously transformed into the nog framework upon aging. We ascribe such dynamic behavior to the compatibility of the DEF guest with several frameworks of similar energy in the Zn(**Im**)$_2$ phase space.[14] In contrast, all reactions with **HMeIm** yielded the SOD topology ZIF-8; the major effect of salt addition was to accelerate the reaction so that quantitative yields were obtained within 30 min (Figure 1c). Persistent formation of ZIF-8 is consistent with the notable stability of this framework.[12a] To compare the efficiency of our mechanosynthesis with other methods, we attempted microwave-assisted melt reactions of ZnO with **HIm** and **HMeIm**. The reactions, even after several hours, did not show any selectivity among topologically diverse ZIFs and gave mixtures of products at low conversion (see the Supporting Information).

Table 1: ZIF topologies obtained in mechanochemical screening.[a]

Ligand	Liquid	Salt			
		none	NH_4NO_3	NH_4MeSO_3	$(NH_4)_2SO_4$
HIm	none	mixture[b]	zni	zni	mixture[b]
HIm	DMF	cag	cag	cag	cag
HIm	DEF	–[c]	nog	unknown[d]	unknown[d]
HIm	EtOH	zni	zni	zni	zni
HMeIm	none	–	SOD	SOD	–
HMeIm	DMF	SOD	SOD	SOD	SOD
HMeIm	DEF	SOD	SOD	SOD	SOD
HMeIm	EtOH	SOD	SOD	SOD	SOD
HEtIm	none	–	qtz	RHO[e]	–
HEtIm	DMF	–	qtz	ANA	RHO
HEtIm	DEF	–	qtz	ANA	RHO
HEtIm	EtOH	–	qtz	qtz	RHO

[a] Each product was obtained by grinding for 30 min, "–" indicates no reaction. [b] Mixture of starting materials, zni-type ZIF and an as yet unidentified material characterized by reflections in the 2θ range 10–20°. [c] No reaction is evident initially, but 24 h aging leads to cag- or nog-type ZIFs. [d] Initial product is an as yet unidentified material, characterized by a reflection at 5.6°, which transforms into the nog-type ZIF on 24 h aging. [e] Forms the qtz-type ZIF on 7 days aging.

For **HEtIm**, the salt had a more pronounced effect on the product topology. Addition of $(NH_4)_2SO_4$ consistently led to the formation of a zeolite RHO topology (CCDC code MECWOH).[13] The reproducible formation of the RHO topology by ILAG is notable as this structure was previously obtained only as a minor byproduct in complex reactions involving mixtures of **HMeIm** and **HEtIm**.[13] With NH_4NO_3, a previously unknown crystalline material was obtained. Crystal structure determination from PXRD data, supported by CP-MAS ^{13}C and ^{15}N NMR spectroscopy, revealed the product is a close-packed hexagonal framework with the β-quartz (qtz) topology (Figure 2a).[15] In contrast, the use of $NH_4CH_3SO_3$ led to different products, depending on the grinding liquid. With EtOH the qtz structure was obtained, while with DMF or DEF ILAG yielded ZIF-14 with the analcime (ANA) topology (CCDC code MECWIB, Figure 2b).[6,13]

The role of salt in enhancing and directing mechanosynthesis of open MOFs was previously related to ion inclusion in the porous structure.[4] The herein described synthesis of ZIFs with qtz and zni topologies demonstrates that ILAG also facilitates the construction of nonporous materials. To investigate the factors behind such reactivity, we followed the course of the reaction between ZnO and **HEtIm** in the presence of NH_4NO_3 at different reaction times. After grinding for 5 or 10 min, the reaction product was not the close-packed qtz structure, but a mixture of RHO and ANA topologies. After 20 min only ANA was obtained, and grinding for 60 min yielded pure qtz framework. Although the final product is close-packed, initial stages of reaction involve porous materials, suggesting a pathway for ion inclusion and control of reactivity.[16,17]

The observed development of topologies (Figure 2c) is reminescent of the Ostwald's rule of stages: the sequence RHO→ANA→qtz reflects the increase in density of tetrahedral sites (Figure 2c) which linearly follows framework energies.[14,18] The metastable nature of the RHO framework is consistent with difficulties related to its reproducible synthesis from solution. The sequence also reflects the decrease in solvent-accessible volume: RHO(60.1 %) >

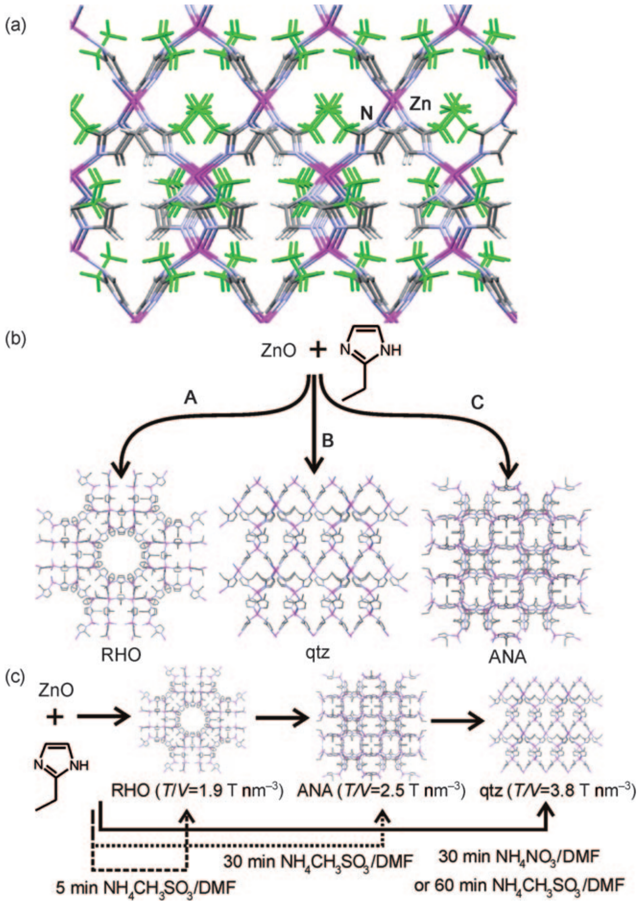

Figure 2. a) Crystal structure of qtz-Zn(**EtIm**)$_2$ with ethyl groups in green. b) Overview of mechanochemical reactivity of ZnO towards **HEtIm**: A) ILAG with $(NH_4)_2SO_4$; B) ILAG with NH_4NO_3 or $NH_4CH_3SO_3$ in the presence of EtOH and C) ILAG with $NH_4CH_3SO_3$ and DMF or DEF as the liquid phase. c) Time-dependent ZIF transformations under ILAG conditions, *T/V* is the number of tetrahedral sites (T) per nm^3.

ANA(44.1 %) > qtz(nonporous).[19] This is consistent with a mass action effect at early stages of the reaction: the high initial ratio of liquid to solid would favor a structure that binds a large amount of solvent.[20] Stepwise behavior was also observed for ILAG reactions with $NH_4CH_3SO_3$ but with lower rates of interconversion: the RHO topology persisted up to 20 min grinding in mixture with ANA, and the qtz topology was observed after 60 min grinding with DMF (Figure 2c). With DEF as the grinding liquid, the ANA topology was the only product even after 60 min grinding. With $(NH_4)_2SO_4$ as the salt additive the RHO topology remained the only product even after 60 min.

It is remarkable that ammonium salts facilitated the synthesis of ZIFs even in the absence of a liquid. We have also explored additional reactions using KNO_3 and K_2SO_4 (see the Supporting Information). However, potassium salts were significantly less effective in facilitating reactivity: the reactions largely resembled those in the absence of salt and, in particular, potassium salts did not support synthesis by neat grinding.[21] We speculate that enhanced ZIF synthesis could be associated with the acid–base properties of NH_4^+ ions; reactions are accompanied by the formation of NH_3, recognized by a faint odor and alkaline reaction of moist indicator paper. To verify the deprotonation of NH_4^+, we conducted solid-state NMR studies on qtz-type Zn(**EtIm**)$_2$ and ZIF-8 made with ^{15}N-labeled NH_4NO_3. ^{15}N NMR spectra revealed the NH_4^+ signal near $\delta = 0$ ppm is replaced by signals between $\delta = -10$ and -22 ppm in both cases, consistent with partial deprotonation (see the Supporting Information).[22] However, although deprotonation of NH_4^+ could participate in the reaction mechanism, it could also be caused by basic defects on the ZIF external surface.[23]

In summary, we have demonstrated a mechanochemical approach for the room-temperature and topologically selective ZIF synthesis and discovery using ZnO as the starting material. The otherwise inefficient reaction of imidazoles with ZnO is facilitated by sub-stoichiometric amounts of ammonium salts, such that topologically selective ZIF synthesis occurred within 30–60 min. In almost all cases, quantitative yields were obtained. Salts enabled synthesis with imidazoles that are otherwise inert to ZnO, and even enabled the reaction to take place in a solvent-free manner. The NH_4^+ ions appear particularly beneficial for mechanosynthesis and we are now investigating the mechanistic details of this process.

Experimental Section

Reactions were performed at 1 mmol scale, by placing a 1:2 mixture of ZnO and the ligand into a 10 mL stainless steel jar, along with the grinding liquid and two 7 mm diameter stainless steel balls. The amount of salt in each experiment was 10 mg. The mixture was ground for 5–60 min in a Retsch MM200 mill at 30 Hz. Reactions were repeated to ensure reproducibility. Starting temperature was between 21 and 22 °C, and 30 min grinding typically led to a temperature increase of 4 °C. Temperature was monitored by thermocouples embedded in the walls of the jar. Experimental details and PXRD, FTIR, and NMR data are given in the Supporting Information. Crystal data for qtz-Zn(**EtIm**)$_2$: $C_{10}H_{14}N_4Zn$, $M_r = 255.6$, hexagonal, $P6_4$, $a = 8.4788(3)$ Å, $c = 12.8634(6)$ Å, $V = 800.86(6)$ Å^3, $Z = 3$, $\lambda(Cu_{K\alpha}) = 1.5406$ Å, $R = 0.065$, $wR = 0.096$, $2\theta = 3.0$–$80.0°$. Structure solution and refinement were done using DASH.[24] CCDC 790342 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: September 4, 2010
Revised: October 1, 2010
Published online: November 12, 2010

Keywords: grinding · imidazoles · mechanosynthesis · metal–organic frameworks · zeolite analogues

---

[1] N. Armaroli, V. Balzani, *Angew. Chem.* **2007**, *119*, 52; *Angew. Chem. Int. Ed.* **2007**, *46*, 52.

[2] a) A. Lazuen-Garay, A. Pichon, S. L. James, *Chem. Soc. Rev.* **2007**, *36*, 846; b) W. J. Belcher, C. A. Longstaff, M. R. Neckenig, J. W. Steed, *Chem. Commun.* **2002**, 1602; c) D. Braga, S. L. Giaffreda, F. Grepioni, A. Pettersen, L. Maini, M. Curzi, M. Polito, *Dalton Trans.* **2006**, 1249; d) T. Friščić, *J. Mater. Chem.* **2010**, *20*, 7599; e) G. Kaupp, *CrystEngComm* **2006**, *8*, 794; f) M.

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Schlesinger, S. Shulze, M. Hietschold, M. Mehring, *Microporous Mesoporous Mater.* **2010**, *132*, 121.

[3] a) W. Yuan, T. Friščić, D. Apperley, S. L. James, *Angew. Chem.* **2010**, *122*, 4008; *Angew. Chem. Int. Ed.* **2010**, *49*, 3916; b) T. Friščić, L. Fábián, *CrystEngComm* **2009**, *11*, 743; c) T. Friščić, A. V. Trask, W. Jones, W. D. S. Motherwell, *Angew. Chem.* **2006**, *118*, 7708; *Angew. Chem. Int. Ed.* **2006**, *45*, 7546.

[4] T. Friščić, D. G. Reid, I. Halasz, R. S. Stein, R. E. Dinnebier, M. J. Duer, *Angew. Chem.* **2010**, *122*, 724; *Angew. Chem. Int. Ed.* **2010**, *49*, 712.

[5] a) Y.-Q. Tian, C.-X. Cai, X.-M. Ren, C.-Y. Duan, Y. Xu, S. Gao, X.-Z. You, *Chem. Eur. J.* **2003**, *9*, 5673; b) Y.-Q. Tian, Y.-M. Zhao, Z.-X. Chen, G.-N. Zhang, L.-H. Weng, D.-Y. Zhao, *Chem. Eur. J.* **2007**, *13*, 4146.

[6] R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Science* **2008**, *319*, 939.

[7] T. Friščić, A. V. Trask, W. D. S. Motherwell, W. Jones, *Cryst. Growth Des.* **2008**, *8*, 1605.

[8] J. F. Fernández-Bertrán, M. P. Hernández, E. Reguera, H. Yee-Madeira, J. Rodriguez, A. Paneque, J. C. Llopiz, *J. Phys. Chem. Solids* **2006**, *67*, 1612.

[9] a) C. J. Adams, M. A. Kurawa, A. G. Orpen, *Dalton Trans.* **2010**, *39*, 6974; b) C. J. Adams, M. F. Haddow, R. J. I. Hughes, M. A. Kurawa, A. G. Orpen, *Dalton Trans.* **2010**, *39*, 3714; c) C. J. Adams, H. M. Colquhoun, P. C. Crawford, M. Lusi, A. G. Orpen, *Angew. Chem.* **2007**, *119*, 1142; *Angew. Chem. Int. Ed.* **2007**, *46*, 1124.

[10] A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2010**, *43*, 58.

[11] a) T. Friščić, S. L. Childs, S. A. A. Rizvi, W. Jones, *CrystEngComm* **2009**, *11*, 418; b) D. Braga, M. Curzi, A. Johansson, M. Polito, K. Rubini, F. Grepioni, *Angew. Chem.* **2006**, *118*, 148; *Angew. Chem. Int. Ed.* **2006**, *45*, 142.

[12] a) K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, O. M. Yaghi, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 10186; b) O. M. Yaghi, H. Furukawa, B. Wang, U.S. Pat. Appl. No. US 2010/0186588A1, **2010**.

[13] Y.-Q. Tian, C.-X. Cai, Y. Ji, X-Z. You, S.-M. Peng, G.-H. Lee, *Angew. Chem.* **2002**, *114*, 1442; *Angew. Chem. Int. Ed.* **2002**, *41*, 1384.

[14] D. W. Lewis, A. Rabdel Ruiz-Salvador, A. Gómez, L. Marleny Rodriguez-Albelo, F.-X. Coudert, B. Slater, A. K. Cheetham, C. Mellot-Draznieks, *CrystEngComm* **2009**, *11*, 2272.

[15] A. L. Spek, A. J. M. Duisenberg, M. C. Feiters, *Acta Crystallogr. Sect. C* **1983**, *39*, 1212.

[16] a) D. Cinčić, T. Friščić, W. Jones, *J. Am. Chem. Soc.* **2008**, *130*, 7524; b) S. Karki, T. Friščić, W. Jones, *CrystEngComm* **2009**, *11*, 470.

[17] The rearrangement also occurred spontaneously with samples kept in a closed vial at room temperature.

[18] a) C. S. Cundy, P. A. Cox, *Microporous Mesoporous Mater.* **2005**, *82*, 1; b) M. Wiebcke, B. Marler, *Solid State Sci.* **2004**, *6*, 213.

[19] A. L. Speck, PLATON, a multipurpose crystallographic tool. Utrecht University, Utrecht, The Netherlands, 2001, http://www.cryst.chem.uu.nl/platon/.

[20] F. C. Strobridge, N. Judaš, T. Friščić, *CrystEngComm* **2010**, *12*, 2409.

[21] While this contrasts ILAG synthesis of pillared MOFs,[4] such reactions involved carboxylic acids as reactants.

[22] J. B. Lambert, G. Binsch, J. D. Roberts, *Proc. Natl. Acad. Sci. USA* **1964**, *51*, 735.

[23] a) C. Chizallet, S. Lazare, D. Bazer-Bachi, F. Bonnier, V. Lecocq, E. Soyer, A.-A. Quoineaud, N. Bats, *J. Am. Chem. Soc.* **2010**, *132*, 12365; b) C. Chizallet, N. Bats, *J. Phys. Chem. Lett.* **2010**, *1*, 349.

[24] A. J. Florence, N. Shankland, K. Shankland, W. I. F. David, E. Pidcock, X. Xu, A. Johnston, A. R. Kennedy, P. J. Cox, J. S. O. Evans, G. Steele, S. D. Cosgrove, C. S. Frampton, *J. Appl. Crystallogr.* **2005**, *38*, 249.

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim