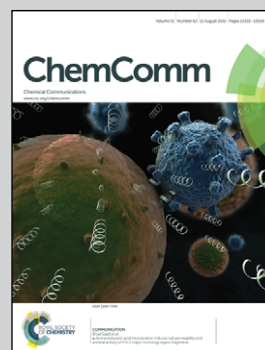


Showcasing research from the laboratory of Javier Martí-Rujas, Center for Nano Science and Technology@Polimi, Istituto Italiano di Tecnologia, Milano, Italy; and the laboratory of Massimo Cametti, Department of Chemistry, Materials and Chemical Engineering, Politecnico di Milano, Milano, Italy.

Multiple single-crystal-to-single-crystal guest exchange in a dynamic 1D coordination polymer

A 1D coordination polymer is able to trap in its 1D channels chlorinated organic volatile molecules such as trichloromethane, dichloromethane and 1,2-dichloroethane from the gas phase following multiple-single-crystal-to-single-crystal reactions. The channel structure is also stable up to 400 K.

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# Multiple single-crystal-to-single-crystal guest exchange in a dynamic 1D coordination polymer†

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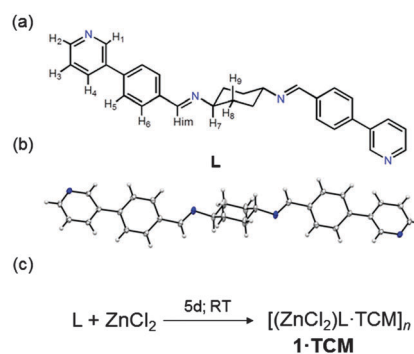
**A novel 1D coordination polymer that dynamically expands or shrinks upon the uptake of vapours of volatile small chlorinated molecules, such as 1,2-dichloroethane (DCE), dichloromethane (DCM) and trichloromethane (TCM), is reported. This system is robust enough to withstand multiple guest exchange *via* single-crystal-to-single-crystal transformation, as proved by <sup>1</sup>H-NMR and X-ray diffraction. The single crystal of guest-free, host framework, stable at 400 K, can also be obtained.**

Coordination polymers having potential internal voids, often termed as metal organic frameworks (MOFs), are versatile hybrid materials, generated by the union of organic ligands and metal ions, that have shown important applications in many areas as diverse as catalysis, gas adsorption, conductivity, *etc.*<sup>1</sup> This versatility stems from the vast library of organic ligands that modern synthesis can develop and, at the same time, the different coordination modes that metals can adopt. Such combination provides highly tunable and diversified materials, a crucial difference with respect to conventional porous materials like zeolites. MOFs are particular, as their frameworks can be robust yet maintain a degree of flexibility,<sup>2</sup> allowing for dynamic structural transformations upon external stimuli.<sup>3</sup> Such transformations have been essential to understand fundamental aspects of solid-state chemistry in general, and structure–function relationships in MOFs.<sup>4</sup>

Not surprisingly, X-ray crystallography is a central technique in such investigations, as it allows for the visualization of the

three dimensional molecular arrangement at the atomic scale, particularly when guest adsorption processes occur *via* single-crystal-to-single-crystal (SC–SC) transformations.<sup>5</sup> A less frequent type of reaction, which has been reported for 2D or 3D coordination polymers,<sup>6</sup> is represented by multiple SC–SC guest exchange processes, where different guest molecules are exchanged sequentially one after the other. These transformations require robust frameworks since structural modification could be quite demanding, especially if reiterated. This explains why multiple SC–SC processes are seldom reported in coordination networks formed by 1D polymer chains, which are generally less robust compared to the 2D or 3D counterparts.<sup>7</sup>

Here, we report on a new dynamic coordination polymer synthesized by the combination of ZnCl<sub>2</sub> with a linear non-chelating bidentate ligand (**L**) (Scheme 1). Its single crystal X-ray diffraction (SCXRD) characterization reveals 1D –Zn–**L**–Zn– chains that upon packing yield arrays of non-interpenetrated 1D channels. These channels are filled with TCM molecules (**1·TCM**). Notably, the same crystal can exchange TCM with DCM and DCE, *via* multiple SC–SC reactions whose products, **1·DCM** and **1·DCE**, respectively, were fully characterized by X-ray and NMR techniques.‡ This exchange is not performed by immersing the single



**Scheme 1** Chemical structure (a) and crystal structure (b) obtained from SCXRD of ligand **L**. Synthesis of the coordination polymer **1·TCM** upon complexation of **L** with ZnCl<sub>2</sub> *via* slow crystallization method (c).

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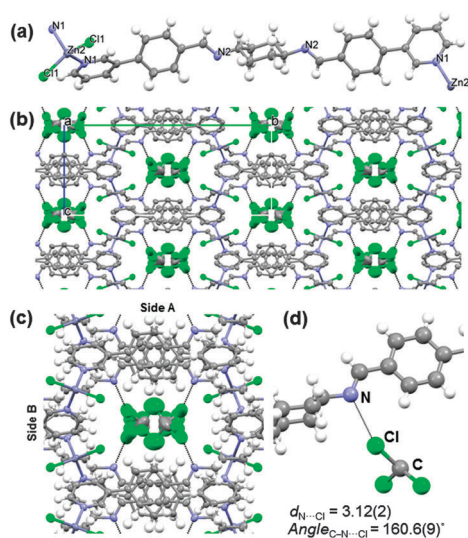
† Electronic supplementary information (ESI) available: Experimental details, crystal structure description, additional figures. CCDC 1055113 (**L**), 1055102 (**1·TCM**), 1055103 (**1·DCM**), 1055104 (**1·DCE**) and 1055101 (**1**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc02372f



crystals into a solution of the chosen solvent, but by directly exposing them to solvent vapours. Interestingly, solvent guest exchange is not always reversible, in that once **1-DCE** is formed, exposure of its crystals to TCM or DCM vapours has no effect. This points to a marked selectivity in the solvent exchange process. Notably, the crystals are stable at room temperature, in contact with air for more than one month and are thermally stable up to 400 K.

The synthesis of **L** was performed by reacting 1,4-diamino-cyclohexane and 4-(3-pyridinyl)benzaldehyde under refluxing conditions.<sup>8</sup> Single crystals of **1-TCM** were grown using a three layer TCM–nitrobenzene–methanol solution (ESI<sup>†</sup>).<sup>8</sup> The **1-TCM** crystal structure was fully characterized at 100 K by SCXRD.<sup>8</sup> As shown in Fig. 1a, the Zn–N coordination results in 1D linear polymer chains which in turn pack as a consequence of the bulkiness of the central cyclohexyl moieties and the 3-pyridinyl substitution. The tendency of  $\pi$ – $\pi$  stacking aggregation of the flat aromatic region is hampered by this structural mismatch. Weak intermolecular C–H  $\cdots$   $\pi$  interactions between the cyclohexane ring in one polymer chain and the pyridine rings of the adjacent polymer chains can be also detected. As a result of the relative orientations among the stacked 1D chains, a channel structure including TCM guest molecules (disordered) is formed. The channels expand infinitely along the crystallographic *a*-axis (Fig. 1b) and account for *ca.* 23.8% of the unit cell volume which corresponds to 791 Å<sup>3</sup>.<sup>9</sup>

The internal surface of the channels exposes **L**'s cyclohexyl rings and iminic N atoms on one side (side A), while stacked aromatic rings and the Zn-centres point their C–Hs and Zn-coordinated chloride units inwards at the other side (side B) (Fig. 1c). As a consequence of such a channel environment,



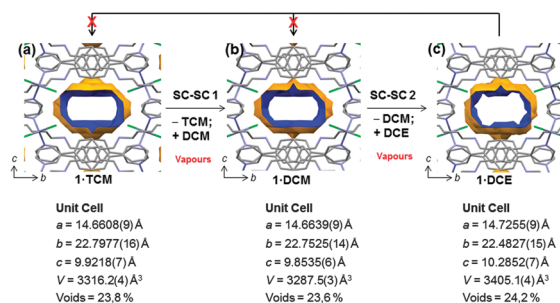
**Fig. 1** Single crystal structure of **1-TCM**. (a) View of the 1D polymer chain in **1-TCM**; (b) crystal packing viewed along the crystallographic *a*-axis showing the host guest interactions (dashed line). Hydrogen atoms have been omitted for clarity; (c) detailed view of the interior of a channel; (d) zoomed view of one of the disordered trichloromethane molecules showing the specific host–guest interactions in the channel. Colour code: carbon (gray); nitrogen (blue); chlorine (green); hydrogen (white).

$N \cdots Cl$  ( $d = 3.12(2)$  Å and  $C-Cl \cdots N$  angle =  $160.6(9)^\circ$ ) contacts between TCM and the nitrogen at the iminic bond are observed (see Fig. 1d).<sup>10</sup> In contact with air, at room temperature, the single crystallinity of **1-TCM** is maintained.

The presence of 1D channels in **1-TCM** allows for guest exchange studies. Although not very common, materials of this kind were indeed used to trap different guest molecules from the gas phase *via* gas/solid reaction.<sup>11</sup> We started investigating the replacement of TCM with the structurally very similar DCM. Thus, a single crystal of **1-TCM** glued in a glass capillary was placed in an enclosed chamber including a vial with 1 mL of DCM. The sealed chamber containing **1-TCM** and DCM was then left overnight (*ca.* 12 h). Once the crystal was removed from the chamber, it was observed under optical microscopy and showed no change in size, morphology and had no cracks. Then, the single crystal was mounted in the diffractometer and analysed by SCXRD at 100 K.<sup>8</sup>

Crystallographic analysis revealed that DCM replaced the original TCM guest to give the new porous coordination polymer **1-DCM**. As a result of the guest exchange, a small variation in the lattice parameters (Fig. 2b) occurs, resulting in a decrease of unit cell volume whilst maintaining the space group (*Pnma*). After the guest exchange, the variation in the channel shape is not very significant and a similar volume space occupied by DCM (23.6% of the unit cell (775 Å<sup>3</sup>)) is observed. While in **1-TCM** the solvent is disordered over two positions, DCM is found over four positions in **1-DCM**.<sup>8</sup> Importantly, the guest exchange occurs without loss of crystallinity and, therefore, *via* a SC–SC transformation. Due to the similarity of the two guest solvents and their considerable disorder, additional confirmation by <sup>1</sup>H NMR is also provided (*vide infra*).

Since the crystallinity is maintained after the first SC–SC guest exchange, we attempted a second SC–SC transformation by exposing **1-DCM** overnight to a third different chlorinated guest molecule: DCE. The single crystal maintained its integrity allowing complete single crystal structure elucidation after the second guest exchange process, again in a SC–SC fashion.<sup>8</sup> SCXRD clearly shows that the incoming DCE guest molecules are actually in the channel, therefore forming the coordination



**Fig. 2** Voids corresponding to the contact surface area depicting the framework adaptability to various guest molecules *via* multiple SC–SC gas–solid reactions and unit cell parameters: channel view along the *a*-axis of as synthesized **1-TCM** (a); TCM replaced by DCM (SC–SC-1) (b); DCM replaced by DCE (SC–SC-2) (c). The data were recorded at 100 K. Hydrogen atoms are omitted for clarity. Colour code as in Fig. 1.



polymer **1-DCE**. We note that in this case, no specific host guest interactions can be detected.<sup>12</sup> The channel shape shows a considerable change (24.2% of unit cell that corresponds to 823 Å<sup>3</sup>) when compared to **1-DCM** due to an anisotropic lattice variation (Fig. 2c). DCE molecules did not escape the channels even after keeping the crystals in contact with air at room temperature for one month.

The DCE molecules are tightly packed inside the MOF as their inclusion leads to the most anisotropic structural deformation (max *a* and *c* axis, min *b* axis) in the framework, which also presents the largest volume. Interestingly, we also notice that the above SC-SC transformations are not always reversible, *viz.*, by exposing **1-DCE** single crystals to vapours of DCM or TCM no reversed guest exchange was observed,<sup>13</sup> while **1-DCM** can be converted back to **1-TCM** by exposing it to TCM vapours. At the moment, we have no elements to exclude kinetic factors as being responsible for the observed lack of reversibility for the **1-DCE** case. Also, the different vapour pressure of the three solvents, despite being remarkably different ( $P_{25^\circ\text{C}} = 87, 194, 432 \text{ mmHg}$ , for DCE, DCM and TCM, respectively), does not have any impact on the data interpretation since each solvent is in large excess with respect to the MOF material, in all cases, under the experimental conditions.

Despite the fact that the X-ray characterization of **1-TCM**, **1-DCM** and **1-DCE** is convincing about the identity of the solvent guest present,<sup>14</sup> we sought to gather additional confirmation by performing <sup>1</sup>H-NMR analysis on the three species. We collected *ca.* 5 mg of **1-TCM**, as crystallized, and about the same quantity of **1-DCM** and **1-DCE** after a first and second solvent guest exchange, respectively. The samples were dissolved in DMSO-*d*<sub>6</sub> by heating and Fig. 3 shows the outcome of such analysis. In each case, the spectrum shows signals only of the solvent that was previously indicated by the X-ray analysis. TCM is observed in **1-TCM** (Fig. 3a), but not in **1-DCM** (Fig. 3b) where DCM appears, due to solvent exchange. Similarly, no DCM is present in **1-DCE**, while the presence of DCE is confirmed (Fig. 3c). First of all, this rules out the possibility of an erroneous identification of the

included solvent identities from the X-ray data. Secondly, this clearly confirms the occurrence of a complete solvent exchange, in accordance with the X-ray data. In all the spectra, contamination by nitrobenzene (NB) is observed, and that is due to the crystallization conditions employed. NB is a high boiling point solvent and it cannot be easily removed from the samples. Concerns about the possibility of actual inclusion of the NB evidenced by NMR into the channels can be dismissed by the fact that there is no evidence of NB from X-ray diffraction data. Moreover, attempts to include chlorobenzene, a molecule of similar size, also failed. We believe that substituted benzenes are too big to enter the MOF channels. As a reference, a spectrum of **L** is also shown (Fig. 3e). These above NMR analyses can also provide a quantitative evaluation of the guest solvent content of the three MOF samples, since an internal reference of known concentration, nitromethane, was added (signal at 4.41 ppm, final concentration  $4.5 \times 10^{-3} \text{ M}$ ). Data from two independent measurements indicate a solvent:ligand ratio, *R*, equal to 0.40, 0.15 and 0.55 for the TCM, DCM and DCE, respectively. The above figures are lower than those derived from X-ray diffraction analysis which indicated *R* = 1 in all cases. The need to heat the sample for a complete dissolution of the material could be the reason for such discrepancy in the solvent guest content in the MOF, especially for the DCM.

A very important aspect in functional materials is represented by their stability. Thermal stability, of course, but also the ability to refrain from structural collapse upon removal of eventually trapped guest molecules. Thermo-gravimetric analysis carried out on a microcrystalline sample of **1-TCM** (*vide ante*) shows that complete solvent guest release is obtained at *ca.* 137 °C.<sup>8</sup> Thus, the thermal stability of **1-TCM** was tested by *in situ* heating a single crystal to 400 K overnight.<sup>15</sup>

The single crystal diffracted well at 400 K and therefore SCXRD was measured at that temperature (*i.e.*, high temperature phase). Crystallographic analysis revealed that TCM was removed from the channels and the framework did not collapse allowing structure solution of the host framework **1** (Fig. 4a and b). We note that the changes in the lattice parameters are anisotropic and despite increasing the temperature to 400 K, the *b*-axis shows a length decrease of 0.28 Å. However, the channel volume after guest release is 858 Å<sup>3</sup> which corresponds to 25% of the unit cell volume.<sup>9</sup> The anisotropic variation in the unit cell parameters is readily observed in the shift of the diffraction peaks in the simulated XRPD pattern (Fig. 4c and d). Finally, we also analyzed by <sup>1</sup>H-NMR a sample of **1** and, consistently, its spectrum shows no sign of TCM (Fig. 3d).

Another important feature of this coordination polymer is that it can be produced in larger scale using fast crystallization methods.<sup>16</sup> The white microcrystalline powder obtained shows a good agreement with the simulated powder X-ray diffraction pattern of **1-TCM** (Fig. 4e).<sup>17</sup> Therefore, **1-TCM** can be easily obtained in high phase purity, quickly and in high yields as a microcrystalline powder. This is an important aspect for the realization of any industrial applications.

In conclusion, we have synthesized a new 1D coordination polymer that contains 1D channels and displays significant

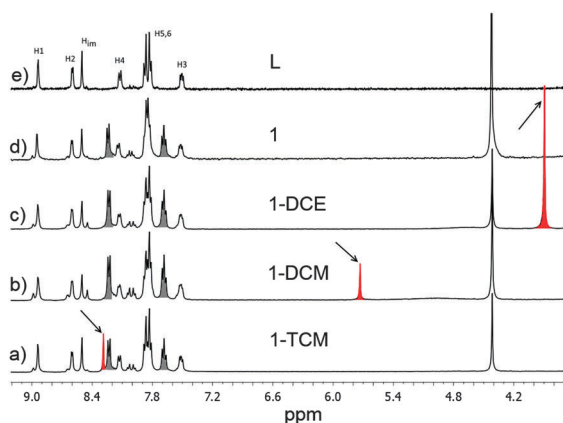


Fig. 3 Portions of <sup>1</sup>H-NMR (400 MHz) spectra of **1-TCM** (a), **1-DCM** (b), **1-DCE** (c), **1** (d) and **L** (e) in DMSO-*d*<sub>6</sub>. Signal at 4.41 ppm is nitromethane used as an internal reference ( $4.5 \times 10^{-3} \text{ M}$ ). The included solvents are highlighted in red, while residual nitrobenzene is in grey.





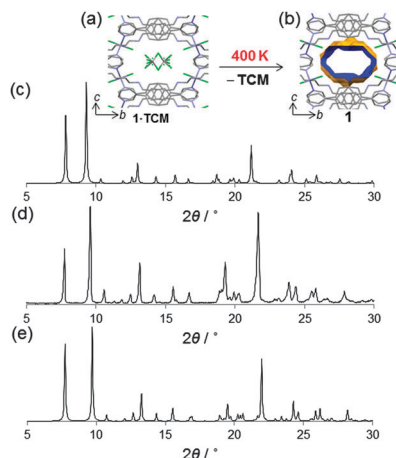


Fig. 4 Crystal structure of the host framework **1** obtained by *in situ* heating **1-TCM** to 400 K (a, b). Simulated XRPD pattern of **1** at 400 K (c). Experimental XRPD pattern obtained by rapidly mixing a TCM solution of **L** and  $\text{ZnCl}_2$  (MeOH) at 300 K (d); and simulated pattern from single crystal X-ray diffraction (100 K) **1-TCM** (e). Colour code as in Fig. 1.

thermal stability. According to its guest behaviour, **1-TCM** fits in Kitagawa's third type classification<sup>18</sup> displaying breathing-like dynamic behaviour. Indeed the channel structure can dynamically adapt to various guest molecules (*i.e.*, TCM, DCM and DCE) that can be exchanged *via* a multi-SC-SC reaction. While this process is more favourable in 2D and 3D linked MOFs (*i.e.*, due to the higher number of coordination bonds), the process reported herein is noteworthy as it occurs in a 1D coordination polymer. The resulting **1-solvent** species are stable and can be stored for various weeks. Importantly, our data also show preferential absorption behaviour as **1-DCE** is stable in the presence of vapours of DCM and TCM at room temperature. Finally, the host framework **1** is also remarkably stable up to 400 K and, in light of the properties described above, we believe that this material could be promising for the development of a selective chemical trap for volatile organic molecules and could thus constitute a novel non-destructive remediation method to remove pollutants from the atmospheric environment.

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## Notes and references

‡ Single crystal data collection of **L**, **1-TCM**, **1-DCM**, **1-DCE** and **1** was recorded with a Bruker X8 Prospector APEX-II/CCD diffractometer equipped with a microfocusing mirror ( $\text{Cu-K}\alpha$  radiation,  $\lambda = 1.54178 \text{ \AA}$ ). XRPD experiments were carried out using a Bruker D2 diffractometer.

- (a) B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1989, **111**, 5962; (b) M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151; (c) S. Subramanian and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 1995, **34**, 2127; (d) O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1995, **117**, 10401; (e) M. Kondo, T. Okubo, A. Asami, S. I. Noro, T. Yoshitomi, S. Kitagawa, T. Ishii, H. Matsuzaka and K. Seki, *Angew. Chem., Int. Ed.*, 1999, **38**, 140; (f) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (g) S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (h) G. Férey, *Chem. Soc. Rev.*, 2008, **37**, 191.
- S. Horike, S. Shimomura and S. Kitagawa, *Nat. Chem.*, 2009, **1**, 695.
- (a) G. K. Kole and J. J. Vittal, *Chem. Soc. Rev.*, 2013, **42**, 1755; (b) C. P. Li, J. Chen, C. S. Liu and M. Du, *Chem. Commun.*, 2015, **51**, 2768; (c) C.-T. He, P.-Q. Liao, D.-D. Zhou, B.-Y. Wang, W.-X. Zhang, J.-P. Zhang and X.-M. Chen, *Chem. Sci.*, 2014, **5**, 4755.
- (a) O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1995, **117**, 10401; (b) C. J. Keppert and M. J. Rosseinski, *Chem. Commun.*, 1999, 375; (c) K. Biradha, Y. Hongo and M. Fujita, *Angew. Chem., Int. Ed.*, 2000, **39**, 3843; (d) M. P. Duh, J. E. Ko and H. J. Choi, *J. Am. Chem. Soc.*, 2002, **124**, 10976; (e) S.-i. Noro, R. Kitaura, M. Kondo, S. Kitagawa, T. Ishii, H. Matsuzaka and M. Yamashita, *J. Am. Chem. Soc.*, 2001, **124**, 2568; (f) C. Serre, F. Millange, C. Thouvenot, M. Nogués, G. Marsolier, D. Louër and G. Férey, *J. Am. Chem. Soc.*, 2002, **124**, 13519; (g) S. Das, H. Kim and K. Kim, *J. Am. Chem. Soc.*, 2009, **131**, 3814; (h) K. Ohara, J. Martí-Rujas, T. Haneda, M. Kawano, D. Hashizume, F. Izumi and M. Fujita, *J. Am. Chem. Soc.*, 2009, **131**, 3860; (i) J. Martí-Rujas, Y. Matsushita, F. Izumi, M. Fujita and M. Kawano, *Chem. Commun.*, 2010, **46**, 6515; (j) J. Martí-Rujas, N. Islam, D. Hashizume, F. Izumi, M. Fujita and M. Kawano, *J. Am. Chem. Soc.*, 2011, **133**, 5853; (k) J. Martí-Rujas, N. Islam, D. Hashizume, F. Izumi, M. Fujita, H. J. Song, H. C. Choi and M. Kawano, *Angew. Chem., Int. Ed.*, 2011, **50**, 6105; (l) J. Martí-Rujas and M. Kawano, *Acc. Chem. Res.*, 2013, **46**, 493; (m) T. D. Bennett and A. K. Cheetham, *Acc. Chem. Res.*, 2014, **47**, 1555; (n) J.-K. Sun, B. Tan, L.-X. Cai, R.-P. Chen, J. Zhang and J. Zhang, *Chem. – Eur. J.*, 2014, **20**, 2488; (o) C. Lavenn, L. Okhrimenko, N. Guillou, M. Monge, G. Ledoux, C. Dujardin, R. Chiriac, A. Fateeva and A. Demessence, *J. Mater. Chem. C*, 2015, **3**, 4115.
- (a) M. Kawano and M. Fujita, *Coord. Chem. Rev.*, 2007, **251**, 2592; (b) T. Kawamichi, T. Haneda, M. Kawano and M. Fujita, *Nature*, 2009, **461**, 633; (c) Y. Inokuma, M. Kawano and M. Fujita, *Nat. Chem.*, 2010, **2**, 349; (d) J.-P. Zhang, P.-Q. Liao, H.-L. Zhou, R.-B. Lin and X.-M. Chen, *Chem. Soc. Rev.*, 2014, **43**, 5789; (e) G. K. Kole, T. Kojima, M. Kawano and J. J. Vittal, *Angew. Chem., Int. Ed.*, 2014, **43**, 2143; (f) G. Mukherjee and K. Biradha, *Cryst. Growth Des.*, 2014, **14**, 3696.
- (a) B. D. Chandler, G. D. Enright, K. A. Udachin, S. Pawsey, J. A. Ripmeester, D. T. Cramb and G. K. H. Shimizu, *Nat. Mater.*, 2008, **7**, 229; (b) M.-S. Chen, M. Chen, S. Takamizawa, T.-A. Okamura, J. Fana and W.-Y. Sun, *Chem. Commun.*, 2011, **47**, 3787; (c) A. Demessence and J. R. Long, *Chem. – Eur. J.*, 2010, **16**, 5902; (d) J. Xiao, Y. Wu, M. Li, B.-Y. Liu, X.-C. Huang and D. Li, *Chem. – Eur. J.*, 2013, **19**, 1891.
- (a) S. M. Mobin, A. K. Srivastava, P. Mathur and G. K. Lahiri, *Dalton Trans.*, 2010, **39**, 8698; (b) Y.-P. Cai, X.-X. Zhou, Z.-Y. Zhou, S.-Z. Zhu, P. K. Thallapally and J. Liu, *Inorg. Chem.*, 2009, **48**, 6341.
- For further information see the ESI†.
- The void space was calculated using a  $1.2 \text{ \AA}$  probe radius: L. J. Barbour, *Chem. Commun.*, 2006, 1163.
- Some might indicate this interaction as a rare halogen bond between a  $\text{sp}^2 \text{ N}$  and a Cl atom of TCM. However, we are well aware of the risk of resting such an assumption only over a simple metric analysis.
- S. Takamizawa, E. I. Nakata, H. Yokoyama, K. Mochizuki and W. Mori, *Angew. Chem., Int. Ed.*, 2003, **42**, 4331.
- A. Gavezzotti, *CrystEngComm*, 2013, **15**, 4027.
- Single crystal X-ray diffraction unequivocally shows that DCE guest molecules are in the channels.
- Unit cell indexing made over several different single crystals of **1-TCM**, **1-DCM** and **1-DCE** gave good reproducible data and each time was consistent with the inclusion of a specific guest.
- The SCXRD data set at 400 K was measured using the Oxford Cryostream device on the diffractometer. See ESI† for further details.
- At room temperature, the rapid mixing of  $0.045 \text{ mmol}$  of  $\text{ZnCl}_2$  in  $1 \text{ mL}$  of MeOH into a vigorously stirring solution of  $0.045 \text{ mmol}$  of **L** in  $5 \text{ mL}$  of TCM resulted in the immediate formation of a white precipitate.
- On some occasions, we have also detected another phase which has a different XRPD pattern than that of **1-TCM**. So far, this phase remains unknown and we are currently investigating the conditions which can select the formation of this phase or the other, and its structural characteristics.
- S. Kitagawa and M. Kondo, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1739.

