

CrystEngComm

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.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Single-Crystal-to-Single-Crystal Transformation of an Anion Exchangeable Dynamic Metal-Organic Framework

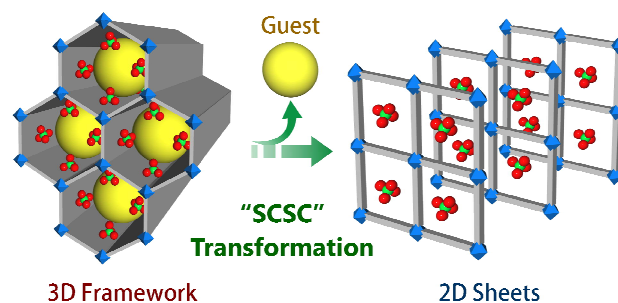
Biplab Manna, Aamod V.Desai, Naveen Kumar, Avishek Karmakar and Sujit K.Ghosh*^a

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

A three dimensional (3D) cationic Metal-Organic Framework (MOF) has been fabricated from a neutral N-donor ligand and Cd(ClO₄)₂. The cationic MOF shows guest triggered inherent dynamic behaviour at room temperature. The guest dependent structural dynamism has been well understood from the single-crystal-to-single-crystal (SCSC) transformation experiment. The framework also displays facile anion exchange behaviour and anion dependent structural dynamism.

Guest molecules in the coordination space have found a profound role in directing the structures of metal-organic frameworks (MOFs) / coordination polymers (CPs).¹ Especially in the domain of dynamic MOFs, the guest molecules residing in the porous aperture can regulate structures to impart flexibility to the framework.² Soft porous MOFs are well known to exhibit such guest dependent structural dynamism.^{2a,3} Moreover, the framework flexibility may depend upon the nature of guest molecules. MOFs entrapping high boiling solvent often show extrinsic dynamic nature, as an external stimuli like high temperature is required for conveying these molecules out of the framework.⁴ On the other hand, presence of low boiling guests in a framework may generate inherent framework flexibility which forbids the necessity of an external stimuli, except air-drying conditions.⁵ Particularly, manifestation of structural dynamism/flexibility by cationic MOFs is very easy compared to other MOFs.^{5d,6} By employing appropriate low-boiling solvent systems for synthesis, the combination of a neutral N-donor ligand with metal ions yields cationic MOFs which usually are occluded with low boiling solvents and extra framework anions.⁷ On keeping such MOFs away from mother liquor, the confined guests may easily leave the framework and create the possibility of structural changes in the system. Such structural modulations upon guest removal at room temperature renders inherent dynamism to the cationic MOFs.^{5c,5d} Recently, we have demonstrated the guest dependent dynamic behaviour of few cationic MOFs.^{5d,8} Such structural modifications can be well understood from their single-crystal-to-single-crystal (SCSC) transformation studies.^{2a,9} In addition to these guest induced effect, extra framework anions of such cationic MOFs can also be exchanged with foreign anions of varying size, shape and coordinating tendencies.^{7c,7d,10} Substitution of such anions with other anions may also lead to structural and physical changes of



Scheme 1 Schematic representation of guest driven dynamic structural transformation from a 3D framework to 2D sheets.

the host systems.^{5d,7e,11} Herein, we report a three dimensional (3D) cationic MOF built from a neutral N-donor ligand (L) and Cd (II), ClO₄⁻ anions and free guests. The framework displays inherent structural dynamism through the loss of guest solvent molecules upon air-drying. The guest dependent structural changes have been well understood from the SCSC transformation studies (Scheme 1). The extra framework anions in the compound can be easily exchanged with other anions of different sizes and coordinating tendencies. The compound also shows anion dependent structural dynamism.

Reaction of ligand¹² (1, 4-bis (4-pyridyl)-2, 3-diaza-1, 3-butadiene) with Cd(ClO₄)₂ in a solvent combination of CH₂Cl₂/tetrahydrofuran /methanol gave yellow colored rod shaped crystals of compound 1 [$\{Cd(L)_3.(ClO_4)_2\} \times G$]_n (where G are disordered low boiling solvent molecules). The compound 1 formed 3D kagome like structure with 1D porous channel as revealed from the single-crystal structural analysis. A very interesting aspect of compound 1 is that crystals of 1 undergo drastic structural transformation upon air drying without losing their single-crystalline nature. Single-crystal analysis of the new phase showed a remarkable one step dimensionality reduction to form a two-dimensional (2D) sheets like structure 2[$\{Cd(L)_2(OH)_2.(ClO_4)_2\} \cdot (THF)$]_n. A drastic lowering in unit cell volume also supports the formation of non porous structure (2) from the porous (1) parent framework. It is very interesting to note that low boiling guests easily come out from the framework (1) without any external stimuli like temperature, pressure and leading to the guest driven inherent dynamic nature of the cationic framework (1) (Fig S13, ESI†).

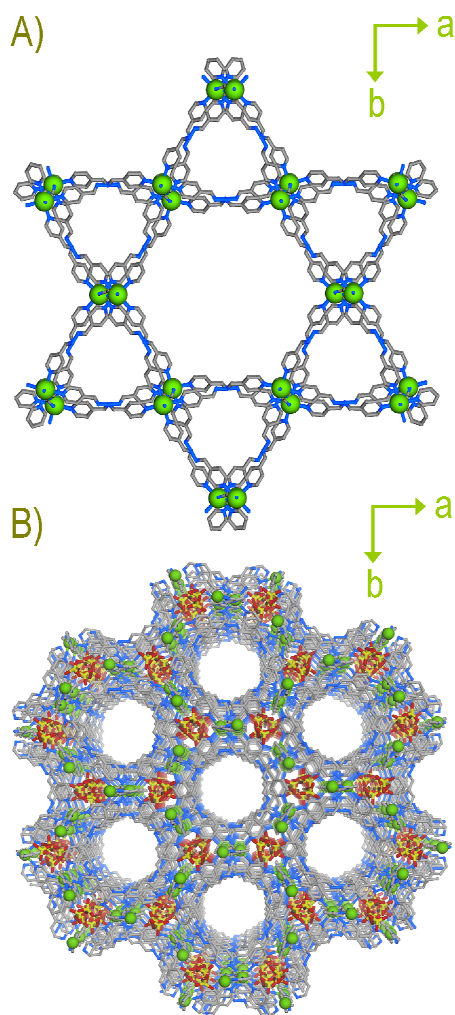


Fig.1 A) Single net packing of compound 1 along c axis. B) Perspective view of overall packing of compound (1) along c axis (free solvent molecules are hidden).

A single-crystal X-ray diffraction study (SC-XRD) revealed that compound 1 crystallize in trigonal crystal system with space group $R\bar{3}c$. An asymmetric unit of compound 1 contains half Cd(II), one and half ligands (L), one ClO_4^- anion and disordered solvent molecules (Fig S1,ESI†). SQUEEZE routine of PLATON has been used to remove highly disordered guest molecules in compound 1. Each Cd(II) shows connections with six N-pyridyl moieties of six different ligands forming a six coordinated distorted octahedral geometry. Each ligand connects two metal centres via its terminal N-pyridyl functionality to form an extended 3D cationic structure. Single net packing of the compound results in a kagome like structure with 1D pore channel along c axis (Fig 1A). Out of six ligands in a complete set of coordination of a metal centre, two shows trans geometry and four of them exhibit distorted cis geometry. Thus the overall packing of 1 shows the presence of free ClO_4^- anions in the interstitial voids of the cationic framework (Fig 1B). SCSC structural transformation revealed abrupt changes in crystal system (monoclinic) in compound 2 from 1. Complete single-crystal structural analysis of 2 shows formation of 2D cationic sheets with free ClO_4^- anions in the framework lattice (Fig

S4,S11, ESI†). It is very worth noting that two coordinated ligands in 1 are being replaced by two water molecules in 2 leading to reduction of dimensionality by one step (3D→2D) resulting the formation of 2D sheets like structure (Fig 2). Close examination of structure of 2 shows that two ligands orient in cis form and rest two are in trans form around each Cd(II) centre. Moreover, oxygen atom of ClO_4^- anion forms H-bonds with coordinated water molecules. In addition, Guest THF molecules in the structure are found to form various non-covalent interactions with C-H, ClO_4^- anions and coordinated water molecules. Powder X-ray diffraction (PXRD) patterns of 2 show that it is stable at room temperature as evident from variable time PXRD (Fig S14,ESI†). It is very important to note that 1 upon air drying changed to 2 by partial loss of guest molecules. Due to presence of such above mentioned non-covalent interactions between THF and

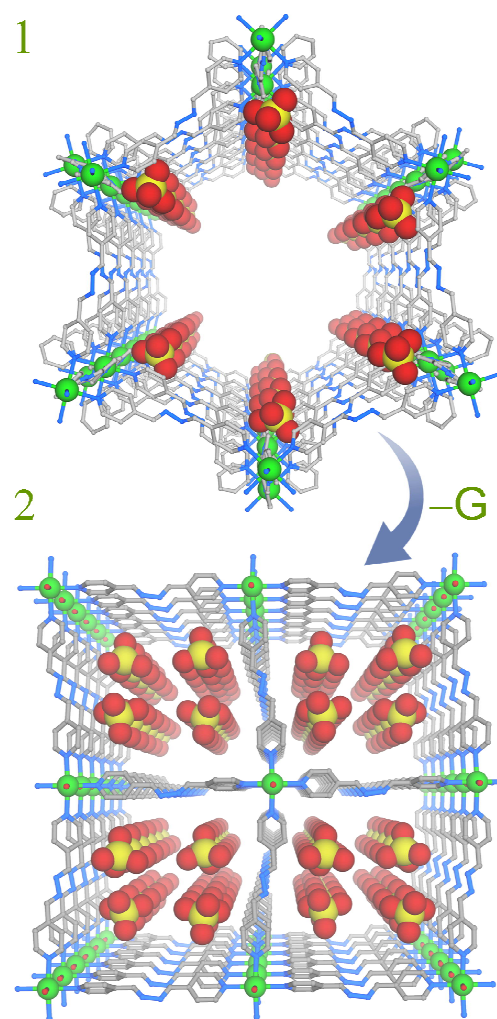


Fig. 2 Guest driven structural transformation upon air drying from 1 (3D) to 2(2D) (Free solvent molecules are hidden).

framework, compound 2 is stable and does not lose any further guests on standing at room temperature (Fig S12, ESI†). Thermogravimetric analysis (TGA) of 2 shows ~ 8% wt loss around 100°C and does not show any further wt loss up to

290°C (Fig S18, ESI†). Framework dynamic behaviour was also observed during the replacement of host anions by some incursive anions of different sizes, shapes and coordinating tendencies. From the above structural description it is evident that compound 2 contain free ClO_4^- anions in its lattice. To inspect the anion-driven framework's dynamic behaviour anion exchange experiments were performed. Strongly coordinating anions (viz. N_3^- and SCN^-) of different sizes and shapes have been chosen for

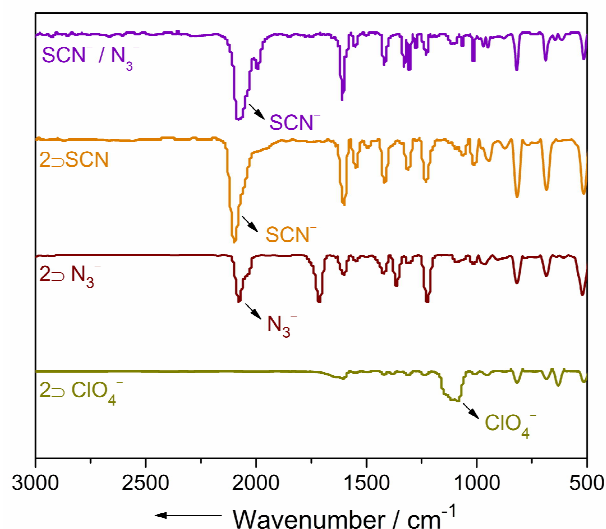
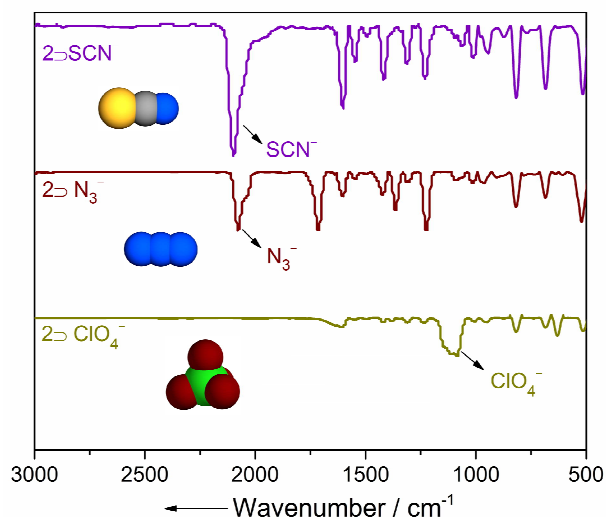


Fig.3 FTIR spectra of compound 2 and its various anion exchanged products with highlighted bands of corresponding anions (top). FTIR spectra of different binary mixtures of anions of compound 2(bottom).

the same. In a typical experiment, crystals of compound 2 were separately dipped in aqueous solution of NaN_3 and KSCN for about ~ 7 days. FTIR spectroscopic tool was utilized to monitor the anion-exchange studies. It showed complete replacement of anions by incursive anions took place in ~ 7 days. Strong bands related to ClO_4^- ($\sim 1100 \text{ cm}^{-1}$) in compound 2 almost completely vanished and in place new bands appeared at $\sim 2050 \text{ cm}^{-1}$ for $2>\text{N}_3^-$ and at $\sim 2080 \text{ cm}^{-1}$ for $2>\text{SCN}^-$ respectively (Fig 3). The exchanged compounds ($2>\text{N}_3^-$ and $2>\text{SCN}^-$) showed differences

in PXRD patterns compared to compound 2(Fig S15, ESI†) Such differential PXRD patterns emerge owing to the different coordinating tendencies size and shapes of foreign anions suggesting dynamic nature of the framework. During the course of anion exchange we made several attempts to get X-ray quality single crystals of exchanged compounds, but unfortunately we were unable to obtain the same. During the course of anion exchange, we observed that the supernatant solution of individual anion precursor remain colorless and transparent indicating MOF particles did not dissolve and recrystallize from the solvent. Owing to the differential PXRD patterns of anion exchanged products, the compound shows anion-responsive structural dynamism. Reversibility of the anion exchange experiment was also performed by taking a NaClO_4 solution (1mM/10mL H_2O). No strong bands at $\sim 1100 \text{ cm}^{-1}$ for ClO_4^- appeared in re exchanged products as revealed in FTIR spectra indicating reversibility could not be achieved in these cases.

Encapsulation of a particular anion by a cationic moiety in presence of other competing anions is very important. Hence to perform the guest anion affinity by cationic framework 2, we investigate anion exchange experiment by taking binary mixture of anions: $\text{N}_3^- / \text{SCN}^-$. In a representative experiment, crystals of compound 2 were immersed in aqueous solution of equimolar mixtures of NaN_3 and KSCN . An investigation of FTIR spectra showed a strong band related to SCN^- at $\sim 2080 \text{ cm}^{-1}$ suggesting preferential uptake of SCN^- over N_3^- (Fig 3).

Conclusions

To conclude we have synthesized a 3D cationic MOF using a N-donor ligand. The cationic MOF showed inherent dynamic behaviour owing to the loss of low boiling solvent at room temperature. Guest driven dynamic behaviour of the cationic framework has been well validated by SCSC transformation experiment. Apart from the guest driven dynamic behaviour, the cationic MOF also exhibited anion-responsive structural dynamism. The compound showed easy anion-exchange behaviour with strongly coordinating anions of different sizes and shapes in aqueous medium. Moreover, different guest anion-affinity was also achieved with the cationic framework.

Notes and references

B.M is thankful to CSIR for research fellowship. We are thankful to IISER Pune, DST (Project No.GAP/DST/CHE-12-0083) for the financial support. We are also thankful to DST-FIST (SR/FST/CSII-023/2012) for micro focus SC-XRD facility.

^a Department of Chemistry, Indian Institute of Science Education and Research, Dr.Homi Bhabha Road, Pashan, Pune 411008, India.

Phone: +91 20 2590 8076 Fax: +91 20 2590 8186;

E-mail: sghosh@iiserpune.ac.in

† Electronic Supplementary Information (ESI) available: Characterization, Figures, FT-IR spectra, TGA, SC-XRD details, PXRD, Anion exchange experiments. CCDC 1044688 is for Compound1; Compound 2 CCDC 1044689.

See DOI: 10.1039/b000000x/

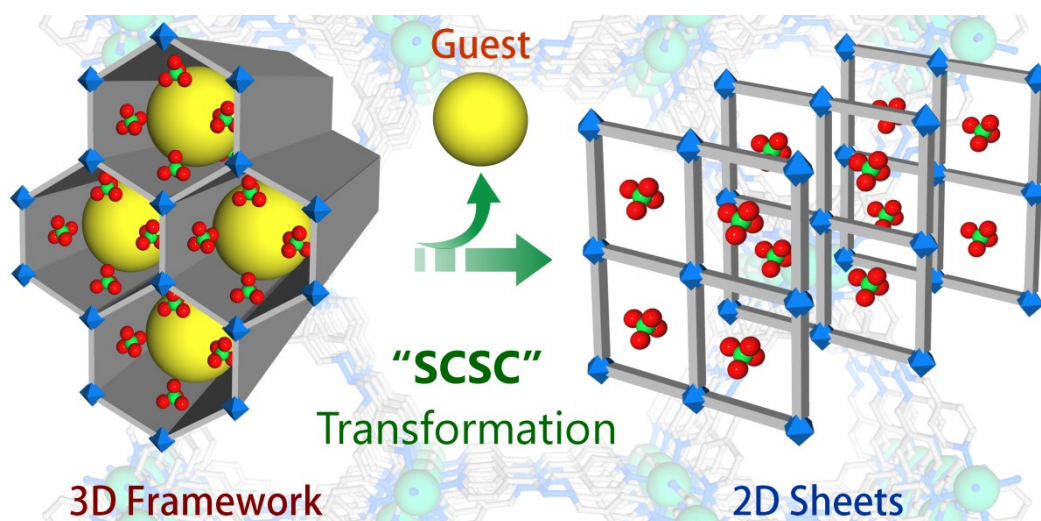
- (a) H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 673–674; (b) c) A. C. McKinlay, R. E. Morris, P. Horcajada, G. Ferey, R. Gref, P. Couvreur and C. Serre, *Angew. Chem. Int. Ed.*, 2010, **49**, 6260 – 6266; (c) J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450-1459; (d) S. Kitagawa, R. Kitaura and S. I. Noro, *Angew. Chem. Int. Ed.*, 2004, **43**, 2334 – 2375; (e) I. H. Park, A.

- Chanthapally, Z. Zhang, S. S. Lee, M. J. Zaworotko and J. J. Vittal, *Angew. Chem. Int. Ed.*, 2014, **53**, 414–419; (f) A. Shigematsu, T. Yamada and H. Kitagawa, *J. Am. Chem. Soc.*, 2012, **134**, 13145–13147; (g) M. C. Das and P. K. Bharadwaj, *J. Am. Chem. Soc.*, 2009, **131**, 10942–10949; (h) S. Sen, S. Neogi, K. Rissanen and P. K. Bharadwaj, DOI: 10.1039/C4CC09955A; (i) J.-P. Zhang, P.-Q. Liao, H.-L. Zhou, R.-B. Lin and X.-M. Chen, *Chem. Soc. Rev.*, 2014, **43**, 5789–5814; (j) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, T. C. Kobayashi, S. Horike and M. Takata, *J. Am. Chem. Soc.*, 2004, **126**, 14063–14070; (k) S. K. Ghosh and S. Kitagawa, *CrystEngComm*, 2008, **10**, 1739–1742; (l) B. Chen, Y. Yang, F. Zapata, G. Lin, G. Qian and E. B. Lobkovsky, *Adv. Mater.*, 2007, **19**, 1693–1696; (m) M. C. Das, S. K. Ghosh, E. C. Sañudo and P. K. Bharadwaj, *Dalton Trans.*, 2009, 1644–1658; (n) W. Zhang, Yingli Hu, J. Ge, H.-L. Jiang and S.-H. Yu, *J. Am. Chem. Soc.*, 2014, **136**, 16978–16981; (o) J.-W. Zhang, H.-T. Zhang, Z.-Y. Du, X. Wang, S.-H. Yu, H.-L. Jiang, *Chem. Commun.*, 2014, **50**, 1092–1094; (p) K. F. Konidaris, C. N. Morrison, J. G. Servetas, M. Haukka, Y. Lan, A. K. Powell, J. C. Plakatouras and G. E. Kostakis, *CrystEngComm*, 2012, **14**, 1842–1849; (q) K. S. Asha, K. Bhattacharyya and S. Mandal, *J. Mater. Chem. C*, 2014, **2**, 10073–10081.
- 2 (a) S. Horike, S. Shimomura and S. Kitagawa, *Nat. Chem.*, 2009, **1**, 695–704; (b) G. Férey and C. Serre, *Chem. Soc. Rev.*, 2009, **38**, 1380–1399; (c) N. Yanai, K. Kitayama, Y. Hijikata, H. Sato, R. Matsuda, Y. Kubota, M. Takata, M. Mizuno, T. Uemura and S. Kitagawa, *Nat. Mater.*, 2011, **10**, 787–793; (d) P. K. Thallapally, P. McGrail, S. J. Dalgrano, H. T. Schaefer, J. Tian and J. L. Atwood, *Nat. Mater.*, 2008, **7**, 146–150; (e) P. K. Thallapally, J. Tian, M. Radha Kishan, C. A. Fernandez, S. J. Dalgrano, P. B. McGrail, J. E. Warren, and J. L. Atwood, *J. Am. Chem. Soc.*, 2008, **130**, 16842–16843.
- 3 (a) C. Serre, C. M. Draznieks, S. Surblé, N. Audebrand, Y. Filinchuk, G. Férey, *Science*, 2007, **315**, 1828–1831; (b) S. K. Ghosh, S. Bureekaew and S. Kitagawa, *Angew. Chem. Int. Ed.* 2008, **47**, 3403–3406; (c) S. K. Ghosh, J.-P. Zhang and S. Kitagawa, *Angew. Chem. Int. Ed.*, 2007, **46**, 7965–7968; (d) B. Joarder, A. K. Chaudhari, S. S. Nagarkar, B. Manna and S. K. Ghosh, *Chem. Eur. J.*, 2013, **19**, 11178–11183; (e) J.-H. Wang, M. Li and D. Li, *Chem. Sci.*, 2013, **4**, 1793–1801.
- 4 (a) Y. Takashima, V. M. Martinez, S. Furukawa, M. Kondo, S. Shimomura, H. Uehara, M. Nakahama, K. Sugimoto, S. Kitagawa, *Nat. Commun.*, 2011, **2**, 168; (b) D. N. Dybtsev, H. Chun and K. Kim, *Angew. Chem. Int. Ed.*, 2004, **43**, 5033–5036.
- 5 (a) A. Kondo, H. Noguchi, L. Carlucci, D. M. Proserpio, G. Ciani, H. Kajiro, T. Ohba, H. Kanoh, and K. Kaneko, *J. Am. Chem. Soc.*, 2007, **129**, 12362–12363; (b) A. Kondo, H. Kajiro, H. Noguchi, L. Carlucci, D. M. Proserpio, G. Ciani, K. Kato, M. Takata, H. Seki, M. Sakamoto, Y. Hattori, F. Okino, K. Maeda, T. Ohba, K. Kaneko and H. Kanoh, *J. Am. Chem. Soc.* 2011, **133**, 10512–10522; (c) K. Biradha and M. Fujita, *Angew. Chem. Int. Ed.* 2002, **41**, 3392–3395; (d) B. Manna, A. K. Chaudhari, B. Joarder, A. Karmakar and S. K. Ghosh, *Angew. Chem. Int. Ed.*, 2013, **52**, 998–1002; (e) R. Kotani, A. Kondo and K. Maeda, *Chem. Commun.*, 2012, **48**, 11316–11318.
- 6 (a) T. K. Maji, R. Matsuda, S. Kitagawa, *Nat. Mater.*, 2007, **6**, 142–148.
- 57 (a) K. S. Min and M. P. Suh, *J. Am. Chem. Soc.*, 2000, **122**, 6834–6840; (b) Y.-Q. Chen, G.-R. Li, Z. Chang, Y.-K. Qu, Y.-H. Zhang and X.-H. Bu, *Chem. Sci.*, 2013, **4**, 3678–3682; (c) X. Li, H. Xu, F. Kong, R. Wang, *Angew. Chem. Int. Ed.*, 2013, **52**, 13769–13773; (d) J.-P. Ma, Y. Yu, Y.-B. Dong, *Chem. Commun.*, 2012, **48**, 2946–2948; (e) B. Manna, B. Joarder, A. V. Desai, A. Karmakar and S. K. Ghosh, *Chem. Eur. J.*, 2014, **20**, 12399–12404; (e) S. Muthu, J. H. K. Yip and J. J. Vittal, *J. Chem. Soc., Dalton Trans.*, 2001, 3577–3584.
- 8 (a) A. Karmakar, B. Manna, A. V. Desai, B. Joarder and S. K. Ghosh, *Inorg. Chem.*, 2014, **53**, 12225–12227; (b) B. Manna, S. Singh and S. K. Ghosh, *J. Chem. Sci.*, 2014, **126**, 1417–1422.
- 9 (a) T. K. Maji, K. Uemura, H.-C. Chang, R. Matsuda and S. Kitagawa, *Angew. Chem. Int. Ed.*, 2004, **43**, 3269–3272; (b) M. P. Suh, J. W. Ko, and H. J. Choi, *J. Am. Chem. Soc.*, 2002, **124**, 10976–10977; (c) H.-X. Li, Z.-G. Ren, D. Liu, Y. Chen, J.-P. Lang, Z.-P. Cheng, X.-L. Zhu and B. F. Abrahams, *Chem. Commun.*, 2010, **46**, 8430–8432; (d) W. M. Bloch and C. J. Sumby, *Chem. Commun.*, 2012, **48**, 2534–2536; (e) W. M. Bloch, A. Burgun, C. J. Coghlan, R. Lee, M. L. Coote, C. J. Doonan and C. J. Sumby, *Nat. Chem.*, 2014, **6**, 906–912; (f) Y.-P. Cai, X.-X. Zhou, Z.-Y. Zhou, S.-Z. Zhu, P. K. Thallapally and J. Liu, *Inorg. Chem.*, 2009, **48**, 6341–6343.
- 10 A. Aijaz, P. Lama and P. K. Bharadwaj, *Inorg. Chem.*, 2010, **49**, 5883–5889.
- 11 (a) B. Manna, S. Singh, A. Karmakar, A. V. Desai and S. K. Ghosh, *Inorg. Chem.*, 2015, **54**, 110–116; (b) T. K. Maji, R. Matsuda, S. Kitagawa, *Nat. Mater.*, 2007, **6**, 142–148; (c) B. Chen, L. Wang, F. Zapata, G. Qian, and E. B. Lobkovsky, *J. Am. Chem. Soc.*, 2008, **130**, 6718–6719.
- 12 D. M. Ciurtin, Y.-B. Dong, M. D. Smith, T. Barclay and H.-C. z. Loye, *Inorg. Chem.*, 2001, **40**, 2825–2834.

Single-Crystal-to-Single-Crystal Transformation of an Anion Exchangeable Dynamic Metal-Organic Framework

Biplab Manna, Aamod V.Desai, Naveen Kumar, Avishek Karmakar and Sujit K.Ghosh^{*a}

Table of Content



Scheme 1 Schematic overview of guest driven dynamic structural transformation from a 3D framework to 2D sheets

A three dimensional (3D) cationic Metal-Organic Framework (MOF) has been fabricated with a neutral N-donor ligand and $\text{Cd}(\text{ClO}_4)_2$. The cationic MOF shows guest triggered inherent dynamic behaviour at room temperature. The guest dependent structural dynamism has been well understood from the single-crystal-to-single-crystal (SCSC) transformation experiment. The framework also displays easy anion exchange behaviour with various kinds of anions and anion dependent structural dynamism.