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Can enantiomer ligands produce structurally distinct homochiral MOF?

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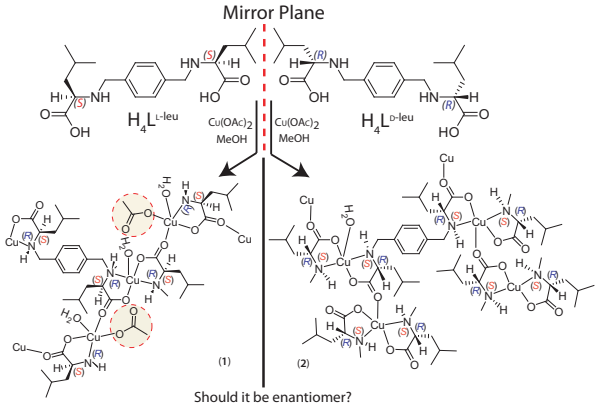
Here, we report a self assembled homochiral metal organic framework $[Cu_{1.5}(H_2L^{L\text{-}leu})(Ac)H_2O]_n.3H_2O$ (1) obtained from L-leucine derived ligand ($H_4L^{L\text{-}leu}$) and $Cu(Ac)_2{\cdot}H_2O$ in 1:1 ratio. Coordination-induced conformational change in the ligand has been monitored by circular dichroism which has been further attested by synthesizing D-leucine containing enantiomer $H_4L^{D\text{-}leu}$ and its Cu(II) complex $[Cu_{1.5}(H_2L^{D\text{-}leu})H_2O]_n.10H_2O$ (2). Structure determination revealed entirely different structures for homochiral MOF (1 and 2) obtained from L-/ D-leucine derived enantiomer ligands under analogous reaction conditions. Further, structural dissimilarity in these MOF's have been judicially supported by proton conductance studies. MOF 1 shows higher proton (10^{-5} S cm^{-1}) conductance in comparison to 2 (10^{-6} S cm^{-1}) due to dissimilar alignment of the hydrogen bonded water molecules in hydrophilic pocket as well as crystal packing.

Chirality is omnipresent in the nature and plays an essential role in many areas of science including chemistry, biology, nanoscience and medicine.[1] Metal-organic frameworks (MOFs) or coordination polymers (CPs) have attracted sustained research interest due to its possible application in diverse areas, such as gas sorption, catalysis, magnetism, electrical conductivity and many more.[2] Moreover, proton conductive solid-state porous materials have fascinated many groups because of their direct application in fuel cells and electrochemical devices.[3] The fundamental concept behind proton conductance in MOF materials may be associated with presence of the H-bonded intrinsic water molecular lattice in the MOF provides the platform for high proton conductivity.[4]

Furthermore, homochiral metal–organic frameworks (HMOFs) have recently enthralled the attention of scientific community owing to their diverse applications in enantioselective sensing, chiral recognition, chiral separation, asymmetric catalysis and nonlinear optical resolution.[5] Various strategies have been adopted for the construction of chiral MOFs.[6] To synthesize homochiral MOF, we have employed a constructive approach by using amino acid derived ligands as a cheapest enantiopure chiral source. Following similar route, Sahoo *et. al.*, reported two structurally analogous homochiral proton conductive MOF based on L-/ D-valine derived ligand which showed high proton conductivity in the order 10^{-5} S cm^{-1} [7]. Herein, we demonstrate that the enantiomer ligands derived from D-/ L-leucine not only produces two structurally distinct homochiral MOFs, but also, exhibit dissimilar proton conductance under similar conditions. To our knowledge, it is the first report of its kind.



Scheme 1 Synthetic scheme for structurally distinct homochiral MOF synthesized from enantiomer ligands.

Conformational change in chiral materials is one of the exciting phenomenon for scientists working in various research fields specially chemistry, material science and biochemistry.[8] Recently, for the first instance, through our work on homochiral coordination polymeric gel, we have shown that ligand undergoes conformational change upon gelation.[9] Herein, we describe synthesis of a homochiral metal-organic framework where the ligand $H_4T^{L\text{-}leu}$ undergoes conformational change upon coordination with Cu(II) in complex **1**. To attest the above phenomenon we synthesized enantiomer ligand

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†Electronic Supplementary Information (ESI) available: [Experimental details and characterization data, ESI-mass, TGA, UV-vis, EPR, proton conductance, including X-ray crystallographic data; CCDC 1425737, 1029318]. See DOI: 10.1039/x0xx00000x

$H_4T^{D\text{-}leu}$ and found that it also undergoes conformational change during complexation. Remarkably, $H_4T^{D\text{-}leu}$ produces a homochiral MOF with opposite chirality having interesting and entirely different structural motif. Hitherto, homochiral MOF involving conformational change in ligand induced by metal ions, monitored by the CD spectroscopy has not been explored.

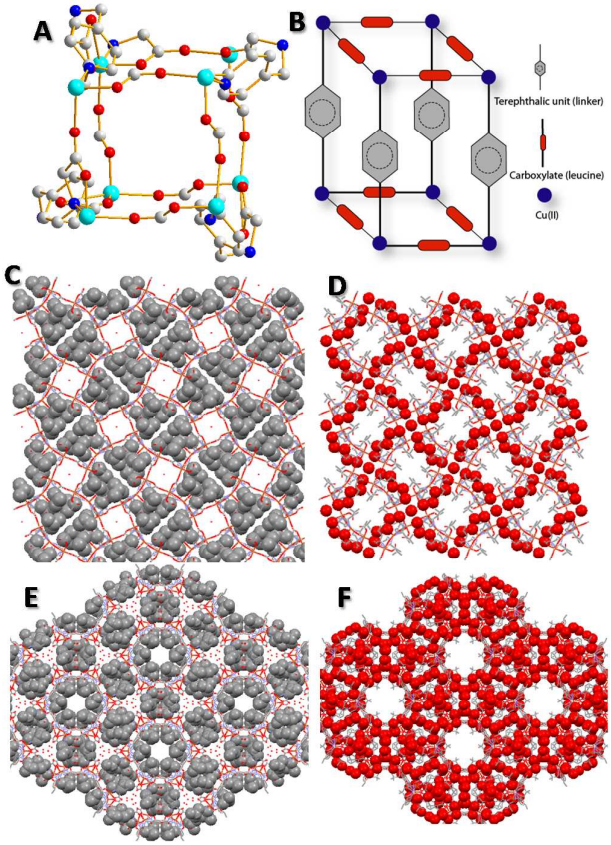

Fig. 1 (A) Crystal structure of 1 shows that eight Cu(II) centres forms the container where four Cu(II) ions connected through carboxylate and two sets of four Cu(II) centres linked by four terphthalic units; (B) a sketch model of A. Along crystallographic 'c' axis- (C) and (E) for 1 and 2, respectively; hydrophilic and hydrophobic regions separated within the crystal lattice where hydrophobic (isopropyl group of leucine) space filled; (D) and (F) for 1 and 2, respectively; extensive H-bonded water lattice.

The ligand $H_4T^{L\text{-}leu}$ was synthesized by following literature procedure.[9] Enantiomer foil $H_4T^{D\text{-}leu}$ of $H_4T^{L\text{-}leu}$ was prepared from D-leucine under similar synthetic conditions. The blue coloured crystals of **1** and **2** with different shape were readily isolated by mixing the ligand and metal salt in precisely correct proportions (1: 1) and keeping the acetonitrile saturated solution for 2-3 days (Scheme 1). The complex **1** crystallizes in chiral space group '$P42_12$', and comprises two Cu(II) centres (Cu1 and Cu2), two ligands ($H_2T^{L\text{-}leu}$ and CH_3COO^-), and three lattice water molecules in the asymmetric unit.[9] It includes two crystallographically independent Cu(II) centres each having different coordination sphere. Both Cu1 and Cu2 adopt distorted square pyramidal geometry where water and carboxylate acquire the axial positions, respectively. The Cu1 accommodates two in-plane ligand in *trans*- N2O2 fashion from L-leucine moiety, while Cu2 is fulfilled by one each of L-leucine, acetate and carboxylate in N1O3 fashion (Fig. S1). The structure **1** possesses crystallographically imposed symmetry with Cu1 on a twofold axis and that disordered water oxygen O10 is at a site with fourfold symmetry axis. The axial bond length for Cu1 is slightly shorter (Cu1-O7, 2.220(4) Å) relative to Cu2 (Cu2-O4, 2.230(3) Å). The H-bond between donor amine and acceptor acetate (N2…O6, 2.949 Å) lies at longer range. Apart from the coordinated water, it contains three water molecules in the asymmetric unit. The coordinated water, three lattice water and carboxylate are H-bonded (O7…O8 2.794, O8…O9 2.829, O9…O3 2.895 Å) in a four centre three H-bond in a complementary fashion and lead to the formation of a hydrophilic environment (Fig. S5, ESI†).

Interestingly, difference in shape of the crystals of complex **2** from that of **1** motivated us to determine its crystal structure. It crystallizes in a different chiral space group '$P6_422$', where Cu1 and Cu2 adopt square pyramidal geometry similar to **1**. The structure **2** also possesses a crystallographically-imposed twofold symmetry, with Cu1 on a twofold axis. The ligand with N3 and O5 directly bonded to Cu2 has its aromatic ring also lying about a symmetry-related twofold axis. The Cu2 accommodates ligand and a water molecule as the fifth axial ligand (Cu1-O7, 2.190(6) Å) like **1**. Remarkably, Cu2 accommodated the in-plane D-leucine which coordinates in *trans*- N2O2 fashion and carboxylate occupies the fifth axial position in **2**, instead of L-leucine, acetate and carboxylate in N1O3 fashion in **1** (Scheme 1). For **1** the *tau* values are found to be τCu1, 0.218; τCu2, 0.327 and for **2** it came out to be τCu1, 0.375; τCu2, 0.317 which indicates greater distortion about Cu1 in complex **2** than **1**. The comparable *tau* values for Cu2 in **1** and **2** suggest analogous distorted geometry around the Cu2 centre both in the complexes **1** and **2**. The four Cu(II) centres are inter connected through carboxylate of leucine and further the terphthalic unit acts as a linker to connect next four Cu(II) centres forming the robust MOF **1** having a four large symmetry-related voids (195 $Å^3$) (Fig. 1 and S2, ESI†). While, in MOF **2** eight Cu(II) units create the large solvent accessible symmetry-related hydrophobic void (2162 $Å^3$). Under similar reaction conditions, structurally distinct homochiral MOF **1** and **2** obtained from the enantiomer ligands are highly reproducible. To have better understanding, we also tried to synthesize the MOF by using a mixture of two enantiomer ligands $H_4T^{L\text{-}leu}$ and $H_4T^{D\text{-}leu}$ in 1:1 ratio with Cu(II) under similar conditions, but regrettably, could not acquire crystals. The preference of acetate binding to Cu(II) over the L-leucine core selectively in **1**, unlike **2** may be due to conformational change, in turn, orientation of the bulky hydrophobic isopropyl arm during crystal packing which can be ascribed to the self-assembly process (Scheme 1).[10]

The flack parameters found close to zero [-0.03 (2), **1**; 0.01(4), **2**] indicate that the absolute configuration is correct (Table S1). The amine functionality in ligands $H_4T^{L\text{-}leu}$ and $H_4T^{D\text{-}leu}$ presents a prochiral centre which after binding with Cu(II) in **1** and **2** transforms into a chiral centre with *R* and *S* configuration, respectively. Indeed, this prochiral to chiral centre (*R*) conversion is induced by the neighbouring chiral

carbon (*S*) centre into a homochiral complex **1** with *S* and *R* configuration (Scheme 1). The aforesaid con-figuration is *R* and *S* for the homochiral complex **2**.

The hydrophilic and hydrophobic regions within the crystal lattice are well separated, where isopropyl group of the hydrophobic leucine arm creates hydrophobic environment and H-bonded water channel forms the hydrophilic part (Fig. S2-5, ESI†). Interestingly, the lattice water molecules are aligned in a highly ordered fashion forming crossed wave like chain structure in **1**, while in **2** these are arranged in a haphazard fashion (Fig. 1). The presence of three and six lattice water molecules in **1** and **2**, respectively have been well characterized by thermogravimetric analysis (Fig. S10 and Experimental Section, ESI†). Solid state room temperature magnetic moments for **1** and **2** are 2.09 and 1.98 μ_B, respectively, which recline within the expected range for square pyramidal Cu(II) complexes (Experimental Section, ESI†). The conductance measurement of methanolic solution for **1** and **2** behaves as a charge neutral species (Experimental Section, ESI†). Elemental analysis supported proposed formulation of the complexes. The ESI-Mass spectra of the ligands and their corresponding complexes well support their proposed formulations (Experimental section, Fig. S6, ESI†). The EPR spectra of **1** and **2** in methanol at 77 K are all commensurate with Cu(II) assemblies (Fig. S7, ESI†).

The complexes **1** and **2** display broad *d-d* transitions at 581 nm, expected for distorted square pyramidal Cu(II) complexes (Fig. S8 and Table S2, ESI†).[11] Through our earlier work, we have demonstrated that addition of the metal ion to ligand changes conformation of the ligand along with creation of a new chiral centre at amine which leads to gelation.[9] Herein, we set out to acquire circular dichroism (CD) spectra and found that the ligand $H_4T^{L\text{-}leu}$ in methanol shows positive and negative Cotton effect at 213 and 228 nm, respectively. Interestingly, corresponding complex **1** shows the negative, 202; positive, 232, 246; and negative at 285 nm Cotton effects. Observed inversion in the CD signals associated with ligand at 213 and 228 nm in complex **1** confirms the conformational change within the ligand (Fig. S9, ESI†). Appearance of a new signal at 285 nm in complex **1** may be attributed to the creation of additional asymmetric centres at prochiral amine upon binding with Cu(II) (Fig. 2A and Table S2, ESI†). Notably, anti terephthaldehyde derived ligands are well known for creation of the helical structures. However, in the present study we observed that incorporation of an amino acid as chiral precursor in the ligand $H_4T^{L\text{-}leu}$ and its coordination with Cu(II) induces conformational change. To attest the above observation we synthesized $H_4L^{D\text{-}leu}$ which is an enantiomer of $H_4T^{L\text{-}leu}$ and observed that it also shows coordination induced CD signal inversion in complex 2. The CD signals for ligand $H_4L^{D\text{-}leu}$ exhibited negative (213) and positive (228 nm) while related complex **2** displayed positive (202) negative (231, 246) and positive (285 nm) Cotton effects (Fig. 2A). The CD spectrum of enantiomer L-/ D-ligands and respective complexes **1** and **2** show close to mirror image of each other (Fig. 2A and Table S2, ESI†). Further, diffuse reflectance CD spectra could not be acquired for any comparative studies. Moreover, conformational change in the ligand upon coordination with Cu(II) is mainly responsible for CD signal inversion (Fig. S9, ESI†). To avoid any artefact we would like to unequivocally state here that measured CD signal inversion for the ligands along with respective complexes is not simply an intrinsic property of the molecule, but rather depends on the molecular conformation.

The loss of weight corresponding to one water molecule in high temperature range 102-171 °C supports the presence of coordinated water in **1** and **2** (Experimental Section and Fig. S10, ESI†). The robustness of frameworks was further examined by variable temperature PXRD experiment on evacuated crystals of **1** and **2.** As shown in figure S11 (ESI†), evacuated compound **1** is stable up to 100 °C while **2** losses the crystalline nature upon evacuation. Further, we attempted gas adsorption (CO_2, N_2 and H_2) studies on these frameworks, but unfortunately, could not obtain any significant results. At this juncture, we assume that MOF **1** and **2** might be good candidates for comparative proton conductance study due to different types of alignment of H-bonded water molecules within the crystal.

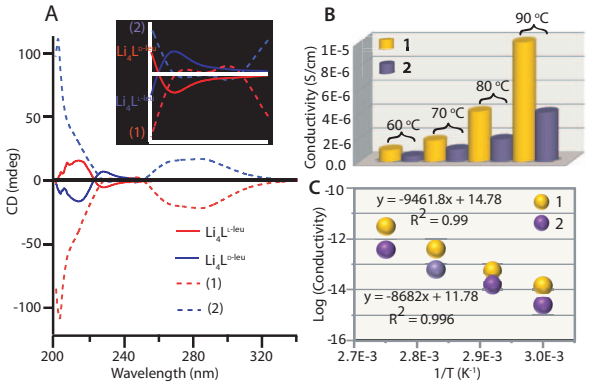

Fig. 2 (A) Circular dichroism spectra of ligand $H_4T^{L\text{-}leu}$ (red continuous line) and its complex **1** (red dotted line); $H_4L^{D\text{-}leu}$ (blue continuous line) and complex **2** (blue dotted line), in methanol. Inset shows inversion of the peak due to ligands in respective complexes in the wavelength region 220-260 nm; (B) Comparative proton conductivity of **1** and **2** calculated at different temperatures, 90% RH; (C) comparative Arrhenius plots for **1** and **2**.

Water containing MOFs are well known candidates for proton conduction. Notably, herein, we decided to perform proton conduction experiment with an objective to verify the two structurally distinct homochiral MOF **1** and **2** by taking the advantage of entirely different array of water lattice. Ionic mobility in solid phase materials occurs intrinsically through the material and/or *via* some carrier mediated pathway, like, H_2O, H_3O^+, OH^- *etc*. Proton conduction in homochiral MOF samples were measured by two probe method and Nyquist plots for **1** and **2** are shown in figure S12 (ESI†). Both the samples displayed distorted semicircle in higher frequency region followed by a tail in the low frequency region, which has been attributed solely to the ion movement. The conductivity has been calculated from the resistance obtained at low frequency intercept at the x-axis by semicircle fitting. As shown in figure 2B (ESI†), the conductivity of samples improved linearly with temperature at constant 90 % relative humidity (RH). **1** ($1x10^{-5}$ S/cm) displayed one order magnitude

improvement in the conductivity compared to **2** ($4.12x10^{-6}$ S/cm), at 90 °C, 90 % RH. Moreover, activation energy (Ea) obtained from the Arrhenius plot (Fig. 2C) was found to be 0.7944 and 0.7481 eV for **1** and **2**, respectively. The obtained Ea values directly indicate Grotthuss mechanism for proton conduction. The better conductivity of **1** relative to **2** has unequivocally been assigned to better aligned water channels along with well separated hydrophobic and hydrophilic pockets within the crystal lattice. Moreover, better conductivity of **1** at high temperature (90 °C) may be due to arrangement of the water molecules in hydrophilic pockets *via* strong H-bonding with the carboxylate groups. Slightly increased Ea for **1** compared to **2** indicates the Grotthuss mechanism along with some other processes such as direct diffusion of the additional protons with water molecules. Despite higher Ea for **1**, it possesses higher conductivity compared to **2**, which is indicative of high carrier concentration originating from the combination of metal complex coordinated and non-coordinated solvent molecules under humid conditions. Variable temperature PXRD experiment also well supports the higher conductance value of **1** at elevated temperature than **2**. Hence, the proton conductivity not only proves the two structurally distinct MOFs but also concludes that profusion of water in MOF is not liable for better conductivity, but better alignment is vital.

Conclusions

In conclusion, we have synthesized two structurally dissimilar type of homochiral Cu(II)-MOFs, **1**-**2**, using L-/ D-leucine derived enantiomer ligands. Exceptionally, these MOFs adopt entirely different type of 3D architecture under similar reaction conditions. The ligands undergo conformational change upon binding with the Cu(II) which has been characterized by CD signal inversion in the respective complexes. The crystal lattice of **1** contains H-bonded water molecules in well ordered linear fashion in hydrophilic part, while **2** accommodates in haphazard fashion. Further, MOF **1** showed better proton conductivity than **2** which also attest their distinct structures. It also proves that alignment of the water is responsible for better conduction. These results offer a platform toward enantiomer can have dissimilar coordination mode, consequently, can be helpful in structure prediction of many unexplored counterpart of enantiomer.

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Notes and references

1 (1) (a) I. Agranat, H. Caner and J. Caldwell, *Nat. Rev.,* 2002, **1**, 753; (b) Y. Wang, J. Xu, Y. Wang and H. Chen, *Chem. Soc. Rev.*, 2013, **42**, 2930; (c) U. Knof and A. V. Zelewsky, *Angew. Chem. Int. Ed.*, 1999, **38**, 302; (d) L. D. Barron, *Nature*, 2000, **405**, 895.

2 (a) H. K. Chae, P. D. Y. Siberio, J. Kim, Y. Go, M. Eddaoudi, A. J. Matzger, M. O'Keeffe and O. M. Yaghi, *Nature*, 2004, **427**, 523; (b) J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450; (c) M. Kurmoo, *Chem. Soc. Rev.*, 2009, **38**, 1353; (d) H. C. Zhou, J. Long and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 673; (e) J.-R. Li, J. Yu, W. Lu, J. Sculley, P. B. Balbuena and H. C. Zhou, *Nat. Commun.*, 2013, **4**, 1538.

3 (a) O. Diat and G. Gebel, *Nat. Mat.*, 2008, **7**, 13; (b) K. D. Kreuer, S. J. Paddison, E. Spohr and M. Schuster, *Chem. Rev.*, 2004, **104**, 4637; (c) Z. Zhou, S. Li, Y. Zhang, M. Liu and W. Li, *J. Am. Chem. Soc.*, 2005, **127**, 10824; (d) M. Yoon, K. Suh, S. Natarajan and K. Kim, *Angew. Chem. Int. Ed.*, 2013, **52**, 2688.

4 (a) M. Sadakiyo, T. Yamada, K. Honda, H. Matsui and H. Kitagawa, *J. Am. Chem. Soc.*, 2014, **136**, 7701; (b) M. Sadakiyo, T. Yamada and H. Kitagawa, *J. Am. Chem. Soc.*, 2009, **131**, 9906.

5 (a) L. Ma, J. M. Falkowski, C. Abney and W. Lin, *Nat. Chem.*, 2010, **2**, 838; (b) L. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C. Y. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011; (c) M. M. Wanderley, C. Wang, C. D. Wu and W. Lin, *J. Am. Chem. Soc.*, 2012, **134**, 9050; (d) C. Valente, E. Choi, M. E. Belowich, C. J. Doonan, Q. Li, T. B. Gasa, Y. Y. Botros, O. M. Yaghi and J. F. Stoddart, *Chem. Commun.*, 2010, **46**, 4911; (e) X. Liang, F. Zhang, H.; Zhao, W. Ye, L. Long and G. Zhu, *Chem. Commun.*, 2014, **50**, 6513.

6 (a) J. Yu and R. Xu, *J. Mater. Chem.*, 2008, **18**, 4021; (b) J. Zhang, S. Chen, H. Valle, M. Wong, C. Austria, M. Cruz and X. Bu, *J. Am. Chem. Soc.*, 2007, **129**, 14168; (c) Z. Qu, H. Zhao, Y. Wang, X. Wang, Q. Ye, Y. Li, R. Xiong, B. F. Abrahams, Z. Liu, Z. Xue and X. You, *Chem. Eur. J.*, 2004, **10**, 53.

7 S. C. Sahoo, T. Kundu and R. Banerjee, *J. Am. Chem. Soc.*, 2011, **133**, 17950.

8 (a) A. Khan, C. Kaiser and S. Hecht, *Angew. Chem. Int. Ed.*, 2006, **45**, 1878; (b) S. Weigelt, C. Busse, L. Petersen, E. Rauls, B. Hammer, K. V. Gothelf, F. Besenbacher and T. R. Linderoth, *Nat. Mat.*, 2006, **5**, 112; (c) F. Wang, J. H. Moon, R. Nandhakumar, B. Kang, D. Kim, Kim, M. K. J. Y. Lee and J. Yoon, *Chem. Commun.*, 2013, **49**, 7228; (d) M. Dubey, A. Kumar, R. K. Gupta and D. S. Pandey, *Chem. Commun.,* 2014, **50**, 8144.

9 M. Dubey, A. Kumar and D. S. Pandey, *Chem. Commun.,* 2014, **50**, 1675.

10 (a) I. Burneo, K. C. Stylianou, I. Imaza and D. Maspoch, *Chem. Commun.*, 2014, **50**, 13829; (b) M. Dubey and M. Ray, *Cryst. Eng. Comm.*, 2013, **15**, 9648.

11 M. Dubey, R. R. Koner and M. Ray, *Inorg. Chem.*, 2009, **48**, 9294.