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A 3D cationic Zn(II) framework, based on Zn$_2$(CO$_3$)$_4$ paddle-wheel secondary building units (SBUs) and Zn$_{16}$(CO$_3$)$_32$ polyhedral supramolecular building blocks (SBBs) has been synthesized. At room temperature, the framework undergoes guest solvent triggered reversible structural transformation and concomitant Zn(II) to Cu(II) transmetalation in a single-crystal to single-crystal fashion.

Most of the studies on metal–organic frameworks (MOFs) are concentrated towards creation of robust frameworks, where particular emphasis has been focused on their ability to retain the architecture even after removal of guest solvent molecules for practical applications. In addition to their large well-defined pore shapes and sizes, an important feature of these frameworks is the presence of metal clusters, serving as secondary building units (SBUs). Adopting the SBU approach, a large number of novel MOFs have been constructed. MOFs that undergo single-crystal to single-crystal (SC-SC) structural transformations triggered by external stimuli have received considerable current attention. Selective molecular motions as well as metal/ligand substitution in MOF crystals without losing single crystallinity, are largely being pursued in several laboratories to design and construct functional materials. Although, substitution of a linker in a MOF by another one has often been realized in SC-SC transformation, exchange of metal, however, is experienced in only a handful of examples.

Transmetalations are primarily attractive to overcome the limitation of achieving multifunctional MOFs by direct solvothermal synthesis and to fabricate the interior as well as exterior of MOF materials with improved properties. To better elucidate the exchange mechanism, investigations of the metal replacement behaviour are indispensable. Using a rigid and angular tetracarboxylic acid ligand (H$_4$L)$_{15}$, incorporating imidazolium group in the middle and aromatic carboxylate at the terminals, a cationic Zn(II) framework (1) based on Zn$_2$(CO$_3$)$_4$ paddle-wheel SBUs and Zn$_{16}$(CO$_3$)$_32$ polyhedral supramolecular building blocks (SBBs), has been synthesized. We demonstrate that the imidazolium moiety reorients in solvents like acetonitrile, chloroform, dichloromethane, benzene, toluene to make the dihedral angle between the plane of the imidazolium moiety and the phenyl ring to be 122.56° in transformed Zn(II) framework (2) while in solvents like dimethyl sulfoxide (DMSO), dimethylformamide (DMF), methanol (MeOH), tetrahydrofuran (THF), Dimethylcarbonate (Me$_2$CO) the dihedral angle changes to 63.94° in framework 1. Interestingly, the Zn(II)-MOF (1) readily undergoes transmetalation from Zn(II) to Cu(II), whereupon 1 is converted to 2$_{Cu}$, only when the dihedral angle changes from 63.94° to 122.56°. To the best of our knowledge, this is the first report where transmetalation has been achieved as a consequence of the change in the ligand conformation. In addition, the Cu-exchanged MOF 2$_{Cu}$ transforms to 1$_{Cu}$ in a reversible SC-SC fashion when simply dipped in solvents having at least one oxygen atom as a part of their molecule such as DMSO, DMF, MeOH, THF, Dioxane. All the changes are realized in SC-SC fashion at room temperature and characterized by single crystal X-ray diffraction studies.

Colorless octagonal crystals of [[Zn$_2$(L)(H$_2$O)$_2$]]$_n$$\cdot$$x$DMF$\cdot$yH$_2$O, (1) were synthesized solvothermally by reacting 1,3-bis-(3,5-dicarboxyphenyl) imidazoliumchloride ([LC$^+$] = H$_2$L$^{2+}$) with Zn(NO$_3$)$_2$$\cdot$6H$_2$O in DMF at 90°C for 3 days. The single-crystal X-ray diffraction study demonstrates (Table S1, ESI†) that 1 crystallizes in...
tetragonal P4_222 space group. Structural investigation revealed that the asymmetric unit contains one half of ligand L, two crystallographically independent Zn(II) ions (Zn1 and Zn2) each with half occupancy and one water molecule. Both Zn1 and Zn2 lie on the C4 axis and adopt the square pyramidal geometry to coordinate with four \( \mu_2 \eta^1 \), \( \eta^1 \) carboxylates of L to form the paddlewheel \([\text{ML}_4\text{CO}_4]\) with average Zn–Zn distance of 3.009 Å (Zn1–Zn1, 2.999(1) Å; Zn2–Zn2, 3.0186(6) Å) (Fig. S4, ESI†). The fifth coordination site is occupied by a solvent water molecule. Notably, the paddle-wheel Zn\(_2\)(CO\(_4\))\(_4\) carry no charge that enables the entire framework to be cationic, owing to the positive charge on the central imidazolium ring.\(^{14}\) The nitrate anion rests in the cavity. Although we could not locate this nitrate anion, due to the inherent disorder nature, its presence is confirmed by IR spectra (Fig. S8a, ESI†). As illustrated in Figure 1, eight L ligands are linked with eight Zn(II)-paddle-wheels, to produce a Zn\(_{16}\)(CO\(_4\))\(_{32}\) gyrobifastigium polyhedra (combination of two triangular prism), having eight vertices, eight faces and fourteen edges, in which the core cavity is accessible through four triangular and four square faces. A close look into the packing diagram of 1 reveals that the water molecules coordinated to the Zn(II) ions of SBUs are projected towards the hexagonal channels and are also directed along the a- and b- axes (Fig. S23, ESI†). This observation led us to probe for possible substitution of the axial sites by other solvent molecules. Interestingly, when a single crystal of 1 is dipped into a solution of CH\(_3\)CN for 24 h at room temperature, the colour and morphology of the crystal remains the same (Fig. S28, ESI†), the structure reveals the formation of \([(\text{ZnL})_2(\text{H}_2\text{O})_2] \cdot \text{NO}_3 ∙ \gamma\text{H}_2\text{O} ∙ z\text{MeCN}\) \((2-\text{MeCN})\) where space group changes to \(14/amd\), with considerable changes in the lattice parameters (Table S1, ESI†). Single-crystal X-ray analyses indicate the presence of three crystallographically independent Zn(II) ions and one entire ligand in the asymmetric unit. A comparison between the structure of 1 and 2-\text{MeCN} shows that the coordination modes of L ligands as well as the metal bound water molecules remain intact with the difference that the paddle-wheel SBUs are twisted with respect to the isophthalate moiety, as a consequence of the free rotation of imidazolium ring around the C-N bond (Fig. 2a). This twist also affects many of the key dihedral...
paddlewheel SBUs does not drastically affect the overall 3D packing of the framework, the rotational rearrangement leads to positional changes of the individual atoms in 2-MeCN (Fig. 2b). The total solvent-accessible volume, as estimated using PLATON,

\[ V_{\text{solvent}} \text{ (PLATON)} \]

shows the calculated guest accessible area per unit cell volume for 2-MeCN (64.2%) is similar to that of 1. In relation to the mother framework 1 here also, highly disordered guest solvent molecules cannot be mapped by single crystal XRD. Bulk purity of 2-MeCN is corroborated by PXRD measurement, which reveals perfect agreement between the simulated pattern and also with the pattern obtained for 1 (Fig S25, ESI†). After careful screening of different solvents (Table S4, ESI†), we conclude that the above SC-SC structural deformation phenomena transpire in the presence of solvents (DCM, chloroform, carbon tetrachloride, acetonitrile, toluene, benzene) that do not have any oxygen atom as a part of their molecule.

Besides, 2-MeCN undergoes reversible SC-SC transformation to 1 (Table S2, ESI†) at room temperature, on exposing the former to solvents that have at least one oxygen atom as a part of their molecule, like DMSO, DMF, DEF, DMA, THF, Me2CO, and alcohol (methanol, ethanol, propanol). It should be pointed here that independent solvothermal synthesis of 2 by mixing H4L+ and Zn(II) in the solvents that do not have oxygen atom as a part of their molecule proved unsuccessful, signifying that SC-SC transformation is the only route towards its formation. The aforementioned results strongly indicate that the rotational movement of the molecular components in the crystal actually depends on the nature of solvent molecules. We assume that H-bonding interaction between the ligand moiety and guest solvent molecule is crucial for such solvent induced reversible single-crystal to single-crystal transformation. Unfortunately, we could not model the guest solvent molecule to assess those particular interactions. In order to further check the influence of the oxygen atom containing solvent on the transformation of 1 to 2, additional experiments with different solvent ratio were carried out. As summarized in Table S4 (ESI†), we confirm that even a small amount of oxygen atom containing solvent is sufficient to inhibit the aforesaid transformation.

Direct synthesis of the copper analogue of 1 by replacing Zn(NO3)2·6H2O with Cu(NO3)2·3H2O, as described above, was not successful. Presence of paddlewheel SBUs and accessibility of polyhedral SBBs from the large channels prompted us to explore the possibility of metal ion exchange within the framework via the post-synthesis approach. In principle, metal centers, having similar preferred coordination geometries will undergo metal-exchange reactions more readily, since low energy is needed to overcome changes in coordination geometry. To test our above hypothesis, crystals of 1 were immersed in a DMF solution of Cu(NO3)2·3H2O (0.04 M) at room temperature, whereupon no apparent colour change occurred even throughout a period of long one month. Quite in contrast, crystals of 1 when dipped in acetonitrile solution of Cu(NO3)2·3H2O (0.04 M), the original colourless crystals gradually turned into green-blue in 12h while maintaining their original shapes and sizes (Fig S28 ESI†). The metal replacement was confirmed by the EPR spectrum (Fig. S29, ESI†) of green-blue crystals. We attempted to confirm the Cu-exchanged framework by single-crystal XRD analysis, which indicates (Table S1, ESI†) that the completely exchanged product has similar framework as 2 with the formula \[ [(Cu_2(L)(H_2O)_2)]NO_3\cdot yH_2O\cdot zMeCN \](2Cu-MeCN).

Furthermore, X-ray fluorescence spectroscopy (XFS) studies demonstrates that no significant amount of Zn(II) ions is left in the framework 2Cu-MeCN. Since a transmetalation reaction principally demands cleavage and formation of coordinate bonds, the aforesaid observations led us to hypothesize that solvent induced ligand flipping and consequent SBU twisting in 1 perturb the coordination geometry at the Zn(II) center, which ultimately facilitates replacement by Cu(II) through SC-SC fashion. The kinetics of the Zn2+ to Cu2+ ion exchange process was monitored by energy-dispersive X-ray spectroscopy, which showed that nearly 50% of the framework Zn2+ ions were replaced by Cu2+ within 1 h, and 95% of the Zn2+ ions were exchanged by Cu2+ within 12h (Fig. 3). Complete exchange (99%) is achieved in two days.

Having successfully converted framework 1 to 2Cu, we finally examined whether we can generate the structure 1Cu through the solvent induced reversible SC-SC structural transformation. As monitored from single crystal X-ray diffraction studies (Table S1, ESI†), the blue crystals of 2Cu-MeCN indeed change to 1Cu-DMF, when kept in DMF for 2days, as a consequence of the reorientation of the imidazolium moiety. During the transmetalation reaction, the average M–M distance in the M2(CO3)4 paddle wheel units (Table S3, ESI†) changes from 3.008 Å (Zn–Zn) in 1 to 2.658 Å (Cu–Cu) in 2Cu-MeCN (Fig. S6, ESI†) that further changes to 2.679 Å in 1Cu-DMF (Fig S7, ESI†). The experimental PXRD patterns of 1Cu-DMF and 2Cu-MeCN (Fig. S26 and S27, ESI†) respectively, are identical to their simulated patterns, signifying the bulk purity. Moreover, the PXRD patterns of the transmetalated frameworks are similar to that of their corresponding mother Zn(II)-frameworks, demonstrating that the frameworks were preserved throughout the metal-ion exchange. In a similar way, 2 also undergoes structural transformation with concomitant transmetalation to 1Cu (Table S1, ESI†) in Cu(NO3)2 solution of a solvent that does not have any oxygen atom as a part of their molecule. It should be noted that the straightforward metal replacement, i.e. 2 to 2Cu, does not occur,
demonstrating once more (*vide supra*) that flipping of the imidazolium moiety with parallel twist in Zn$_2$(CO$_3$)$_4$ SBUs is an essential prerequisite for the metal exchange to take place in these frameworks. However, the reverse transmetalation processes do not occur, i.e., for both 1$_{Cu}$-DMF and 2$_{Cu}$-MeCN, Cu(II) ions cannot be replaced by Zn(II) ions even in a concentrated DMF/MeCN solution of Zn(NO)$_3$·6H$_2$O (1 M) under long exchange time (1 month), suggesting that the Cu(II)-frameworks are more stable than the corresponding Zn(II)-frameworks.\(^{13c}\)

In conclusion, using an aromatic tetracarboxylic acid ligand H$_4$L*, incorporating imidazolium group, we have synthesized a 3D cationic Zn(II) framework, based on Zn$_2$(CO$_3$)$_4$ paddle-wheel SBUs and Zn$_{12}$(CO$_3$)$_{12}$ polyhedral SBUs. At room temperature, the framework undergoes reversible SC-SC structural transformation as a consequence of the reorientation in the imidazolium moiety, in presence of solvents that do not have any oxygen atom as a part of their molecule. Although, the straightforward metal replacement, i.e. 1 to 1$_{Cu}$ does not occur, framework 1 undergoes transformation with concomitant transmetalation to 2$_{Cu}$ in the presence of solvents that have no oxygen atom as a part of their molecule. Similarly, 2-MeCN undergoes metal exchange to 1$_{Cu}$ only when dipped in solvents that have least one oxygen atom as a part of their molecule. The results demonstrate that flipping of the imidazolium moiety with parallel twist in Zn$_2$(CO$_3$)$_4$ SBUs is an essential prerequisite for the metal exchange to take place in these frameworks. To the best of our knowledge, this is the first report exemplifying SC-SC transmetalation as a consequence of change in ligand conformation and should provide insight in fabricating switch emergent molecular devices. Possibility of transmetalation reactions and their kinetics with different transition metal ions, are currently underway.

Notes and references

We gratefully acknowledge the financial support from the Department of Science and Technology, New Delhi, India (J.C. Bose National Fellowship to P.K.B.). S.N. thanks IIT Kanpur for a postdoctoral fellowship. Dr. Fangfang Pan (Chem Dept, Jyväskylä) is thanked for some preliminary structural work on 1 and 2-MeCN. The Academy of Finland (KR. grant no. 265328 and 263256) is kindly acknowledged for financial support.


