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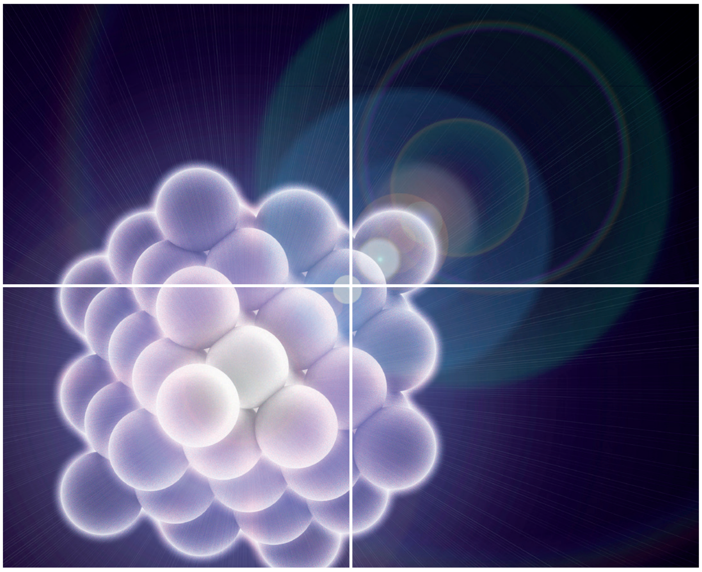

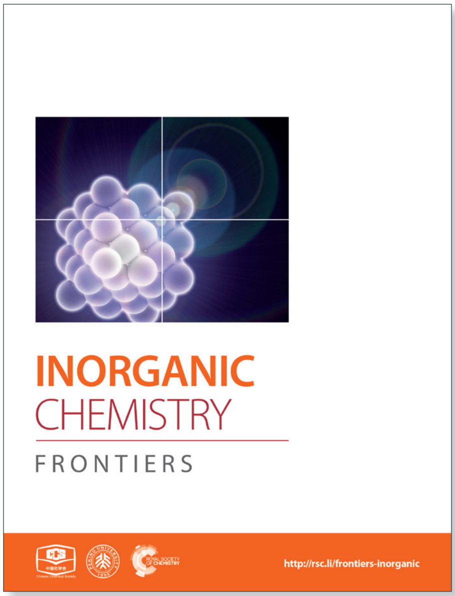

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Guest dependent reversible single-crystal to single-crystal structural transformation in a flexible Gd(III)-coordination polymer

Tapan K. Pal, Dinesh De, Subhadip Neogi and Parimal K. Bharadwaj*

Abstract

The ligand 2,6,2',6'-tetranitro-biphenyl-4,4'-dicarboxylic acid (**H_2L**) reacts solvothermally with $[Gd(NO_3)_3]\cdot6H_2O$ to produce a flexible and porous metal-organic framework, $\{[Gd_2(\mathbf{L})_3(DMF)_4]\cdot(4DMF)\cdot(3H_2O)\}_n$ (**1**) (DMF = *N,N*′-dimethylformamide). X-ray crystallographic study reveals that compound **1** contains a 3D framework structure with two different 1D channels (A and B) that are occupied by solvent DMF and water molecules. Crystal of **1** upon keeping in dicholomethane solution of 4-chlorobenzaldedhyde (4-ClPhCHO) affords the daughter product $\{[Gd_2(\mathbf{L})_3(DMF)_4]\cdot(\mathit{4\text{-}ClPhCHO})\cdot(4DMF)\}_n$ (**1a**), via single-crystal to single-crystal (SC-SC) transformation, where lattice water molecules of channel B are replaced by guest aldehyde molecules. Likewise, exposure of 4-fluorobenzaldehyde (4-FPhCHO) and 4-methylbenzaldehyde (4-MePhCHO) vapors to fresh crystals of **1** afford two isostructural daughter frameworks, $\{[Gd(\mathbf{L})_{1.5}(DMF)(H_2O)_3]\cdot(\mathit{4\text{-}FPhCHO})\cdot(DMF)\cdot(3H_2O)\}_n$ (**1b**) and $\{[Gd(\mathbf{L})_{1.5}(DMF)(H_2O)_3]\cdot(\mathit{4\text{-}MePhCHO})\cdot(2DMF)\cdot(H_2O)\}_n$ (**1c**), respectively. Here, the guest aldehyde molecules occupy both the channels of the framework. Interestingly, the later transformations exhibit drastic rearrangement of the framework channels followed by several ‘carboxylate-shift’ processes, and concomitant movement of the water molecules from the cavity to the metal center. Importantly, all the host-guest complexes revert back to the as-synthesized crystal when kept in fresh DMF, rendering the mother framework a flexible and dynamic container for the aromatic aldehydes. All these transformations transpire through SC−SC fashion

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under ambient conditions, pointing to the high flexibility of the framework and "guest-responsive fitting" of the channels. All the compounds are characterized by X-ray crystallography, thermogravimetry, elemental analysis, powder X-ray diffraction measurements and infrared spectroscopy.

Introduction

As typical porous materials, most of the studies on metal–organic frameworks (MOFs) are concentrated towards creation of robust frameworks, where particular emphasis is focused on their ability to retain open networks after solvent removal. Nevertheless, high framework stability is essential for many practical applications, including gas storage and separation; flexible MOFs can undergo structural changeovers during removal or uptake of guest molecules, resulting in highly selective guest inclusion, stepwise guest uptake, gate-opening type adsorption behavior and so on.[1] Particularly interesting are single-crystal to single-crystal (SC - SC) transformations[2], involving movements of atoms, which provide crystallographic snap-shots[3] during such dynamic structural changes. Thus, SC-SC transformations should allow a deeper insight into the relationship between the host and the guest molecules, offering ways to fabricate systems with enhanced functionalities and novel applications.[4]

Although, few SC-SC transformations (structural dynamism)[5] on metal-organic single crystals, caused by solvent exchange, temperature change or framework distortion have been reported[6], the efforts focused on the adsorption and separation of organic molecules, specially using lanthanide framework, are relatively rare.[7] For most of the frameworks, the major obstacle is associated with the catastrophic failure of single crystallinity during these transformation processes.

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Using preferences of different co-ordination specifics of metal ions in combination with topology of organic linkers, crystal engineering can be very fruitful[8] in the design and construction of porous flexible frameworks. To our perception, lanthanide (Ln) metal ions with their high and variable coordination numbers and different coordination geometries should be ideal for the fabrication of flexible MOFs. On the other hand, our interest in ligand $\mathbf{H_2L}$ (see Scheme 1) is mainly based on the fact that the presence of four nitro groups on the benzene ring creates steric hindrance, allowing the formation of non-interpenetrating 3D structure with sufficient pore size to host small organic molecule(s). Besides, it may afford observation of the carboxylate coordination mode and its changes, termed as a "carboxylate shift", which is a low-energy process and allows structural flexibility to influence the overall structure.[9] Earlier, we used this ligand to construct flexible framework, which showed direct crystallographic observation of catalytic reactions inside the pores.[10] Herein, we report the SC-SC encapsulation of various aromatic aldehydes inside the pores of the flexible Gd(III) framework (**1**), having two different types of channels (Channel A and B). While 4-chlorobenzaldedhyde as guest preferentially occupies channel B without substantial change of the overall structure, encapsulation of 4-fluorobenzaldehyde and/or 4-methylbenzaldehyde as guests in **1** involve drastic changes in the framework channels, along with concomitant movement of the lattice water molecules to the metal center. Given the importance to particularly desirable SC−SC transformations in dynamic frameworks, the understanding of such non-coordinating guest-driven structural transitions, followed by molecular motion can provide better insight to fabricate advanced molecular devices with the possibility of discriminating explosive or toxic organics. Furthermore, all the guest aldehydes can be recovered by soaking **1** in fresh DMF, whereupon the daughter frameworks revert back to the mother framework, again in SC-SC manner, rendering the host framework a dynamic and recoverable container[11] for the aromatic aldehydes.

Experimental section

Materials

Reagent-grade 4-chloro-3,5-dinitrobenzoic acid (97%), $Gd(NO_3)_3 \cdot 6H_2O$ (99.99%), copper powder (electrolytic grade), 4-fluorobenzaldehyde, 4-chlorobenzaldehyde and 4-methylbenzaldehyde were acquired from Sigma-Aldrich and used as received. All solvents, such as DMF, benzene, dichloromethane and ethanol were procured from S. D. Fine Chemicals, India. These solvents were purified following standard method prior to use.

Physical measurements

Infrared (IR) spectra were performed (KBr disk, 400-4000 cm^{-1}) on a Perkin-Elmer model 1320 spectrometer. Powder X-ray diffraction spectra (CuK_α radiation, scan rate 3 °/min, 293 K) were obtained on a Bruker D8 Advance Series 2 powder X-ray diffractometer. Thermogravimetric analyses (TGA) were acquired on a Mettler Toledo Star system (heating rate, 5 ° C/min). Microanalyses of all the compounds were carried out using a CE-440 elemental analyzer (Exeter Analytical Inc.). ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL-ECX 500 FT (500 and 125 MHz respectively) instrument in $CDCl_3$ or in DMSO-d_6 with Me_4Si as the internal standard. ESI mass spectra were recorded on a WATERS Q-TOF Premier mass spectrometer.

Single-crystal X-ray studies

Single-crystal X-ray data of compound **1** and the daughter compounds, **1a**-**1c** were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite monochromated MoK_α

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radiation (λ = 0.71073 Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography.[12] The data integration and reduction were carried out with SAINT[13] software. Empirical absorption correction was applied to the collected reflections with SADABS[14] and the space group was determined using XPREP.[15] The structure was solved by the direct methods using SHELXL-97[16] and refined on F^2 by full-matrix least-squares using the SHELXL-97[17] program package. In compound **1**, all the non-hydrogen atoms were refined anisotropically. In compound **1a**, atom C(74) was refined isotropically and all other non hydrogen atoms were refined anisotropically. In compound **1b**, atoms C(26), C(32) and F(1) were refined isotropically and all other non hydrogen atoms were refined anisotropically. In compound **1c**, atoms C(34), C(35), C(37), C(40), C(41), N(8), N(9) and OW4 were refined isotropically and all other non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the coordinated water molecules and cavity water molecules in compound **1b** and compound **1c** could not be located by difference Fourier synthesis. The hydrogen atoms attached to carbon atoms were positioned geometrically and treated as riding atoms using SHELXL default parameters. Several DFIX commands were used to fix the bond distances in compound **1a-1c**. The amount of guest molecules present in compound **1a, 1b** and **1c** were also confirmed by thermogravimetric analysis (TGA) calculation. In compound **1a**, two large residual electron density peaks (2.14 and 2.12 e Å^{-3}) are present that are 0.835 and 0.914 Å from the Gd(1) and Gd(2) respectively. In compound **1b**, two large residual electron density peaks (2.68 and 2.38 e Å^{-3}) are present that are 1.01 and 1.09 Å from the Gd(1) respectively. These are likely due to inefficient absorption correction for Gd(III). Selected bond distances and bond angles are given in Table S1

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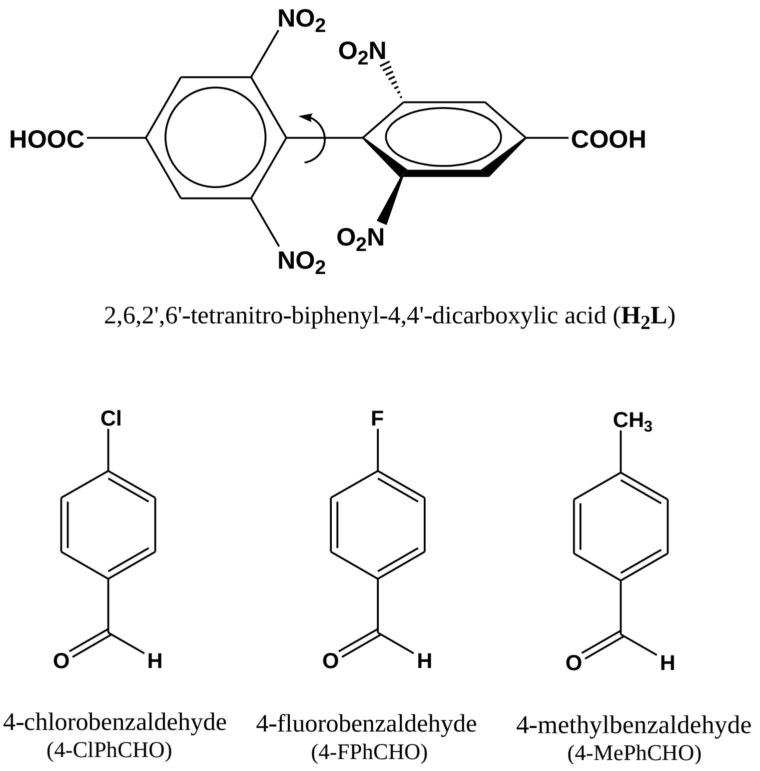
(ESI†).While details crystal parameters of all the compounds, data collection and refinement for the compounds are summarized in Table S2 (ESI†).



Scheme 1 Schematic diagram of H_2L[18] and guest aldehyde molecules, used in the study.

Results and discussion

The framework, $\{[Gd_2(\mathbf{L})_3(DMF)_4]\cdot(4DMF)\cdot(3H_2O)\}_n$ (**1**), is solvothermally synthesized in high yield by treating $Gd(NO_3)_3\cdot 6H_2O$ and the ligand $\mathbf{H_2L}$ (Scheme 1), as reported earlier.[10] Once isolated, the compound is insoluble in common organic solvents as well as in water. The IR stretching frequency of compound **1** divulges (Fig. S1, ESI†) a broad band at 3379 cm^{-1} besides strong peaks at 1652 and 1351-1537 cm^{-1}, indicating the presence of water, DMF and

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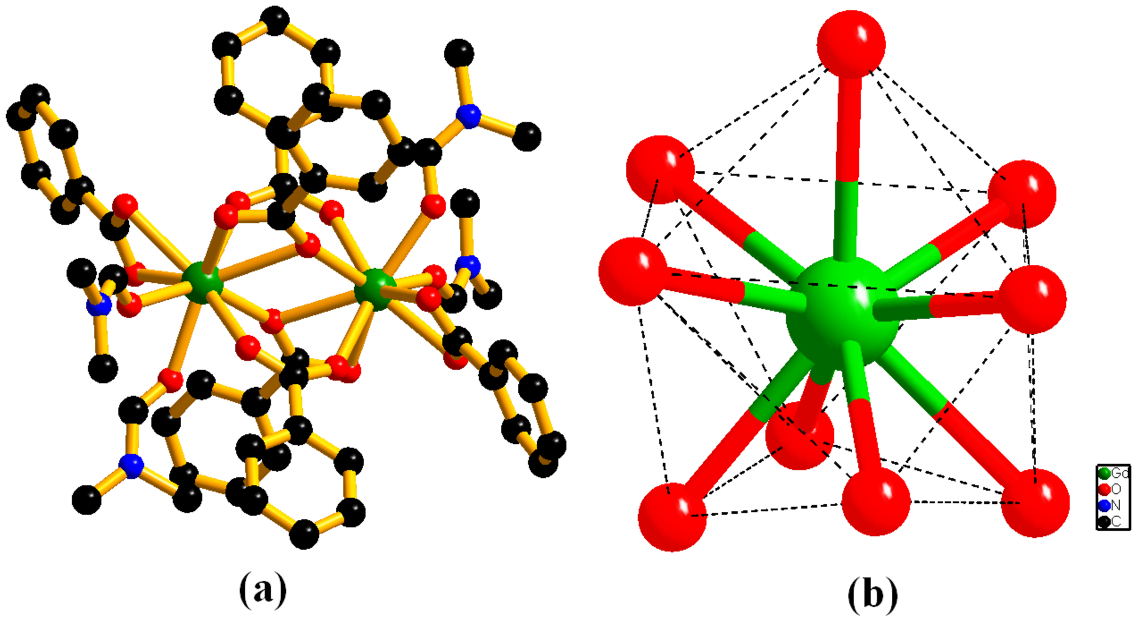
coordinated carboxlates, respectively. Single crystal X-ray study reveals that **1** crystallizes in monoclinic space group $P2_1/n$. The structure of **1** consists of a dimeric Gd_2 (M···M =4.0481(11) Å) secondary building unit (SBU), constructed from two *syn*-*syn* bridging carboxylates, two terminal chelating carboxylates and two chelating as well as bridging carboxylates from six different $\mathbf{L}^{2-}$ units (Fig. 1a). Each Gd(III) ion is further coordinated to two DMF molecules, providing a total of 9-coordination at the metal centre with distorted tri-capped trigonal prismatic geometry (Fig. 1b). Two such binuclear Gd_2 clusters are connected by ligand $\mathbf{L}^{2-}$ to form a 3D framework, where distances between each dimeric units are 15.84 and 9.94 Å along the crystallographic *a* axis (Fig. 2).



(a) (b)

Fig. 1 The perspective view of (a) coordination environment around the Gd_2 dimer in compound **1**, (b) geometry around metal center (hydrogen atoms are omitted for clarity).

View along the *a* axis reveals (Fig. 2) that the 3D structure contains two different channels with dimensions of 3.33 × 8.65 Å^2 (channel A) and 2.40 × 8.24 Å^2 (channel B, channel sizes are measured by taking atom-to-atom distances considering the van der Waals radii of constituting

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atoms). Owing to the different disposition of nitro groups, attached to the **L**$^{2-}$ ligand unit, these two channels possess different electronic environments, which also allows guest molecules to rest inside the channels in diverse ways. Thus, channel A is occupied by six DMF molecules, while channel B includes two DMF and six water molecules (Fig. 2). The –NO_2 groups are directed toward the centre of each channel and involved in H-bonding interactions (3.037-3.63 Å) with the solvent molecules. It should be noted that the guest DMF and aldehyde molecules residing inside metal-organic framework cavity are disordered in nature, while inherent disorder of the nitro groups in **L**$^{2-}$ ligand unit has been realized earlier.[10]

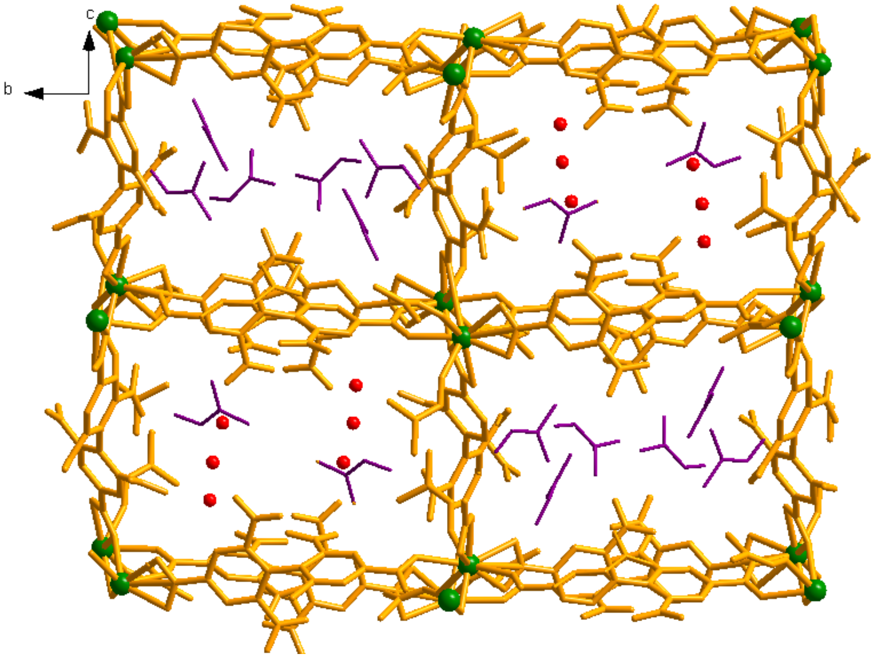

Fig. 2 Perspective view of two dissimilar channels, A and B in compound **1**, hosting different solvent guests.

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Hydrogen bonding interactions (2.66-2.82 Å) also exist between the methyl hydrogen atom of the lattice DMF and carboxylate oxygen atom of the nearby ligand unit. In addition, C-H···N interactions are present between the solvent molecules. Details of all these interactions (Fig. 3) are summarized in Table S3 (ESI†). The phase purity of the bulk material is confirmed from the similarity in powder X-ray diffraction pattern of **1** with that of the simulated pattern, obtained from the single-crystal data (Fig. S2, ESI†).

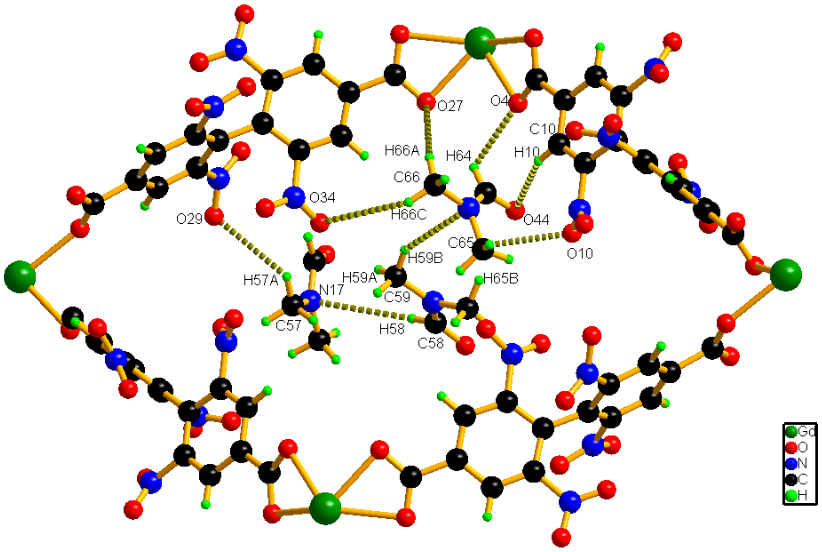

Fig. 3 Schematic representations of the interaction of solvent molecules inside a pore of the compound **1**.

Reversible single-crystal to single-crystal transformation of 1 to 1a

Keeping our previous findings in mind, we decided to examine utilization of the framework **1** in hosting different aromatic aldehydes. As a starting point to elaborate the SC-SC transformation, we evaluated the encapsulation scenario of 4-chloro benzaldehyde molecule. A crystal of **1** was kept in DCM solution of 4-chlorobenzaldehyde (Scheme 1) at room temperature for 5 days. Single crystal X-ray analysis reveals that the encapsulated water molecules in channel B are

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completely replaced by 4-chlorobenzaldehyde molecules to afford the daughter framework, $\{[Gd_2(\mathbf{L})_3(DMF)_4]\cdot(\mathit{4\text{-}ClPhCHO})\cdot(4DMF)\}_{\mathbf{n}}$ (**1a**) (Fig. 4). Structural investigation also shows that the overall framework, including carboxylate connectivities to the Gd_2 SBU, remain the same (*vide supra*) to that of **1**.

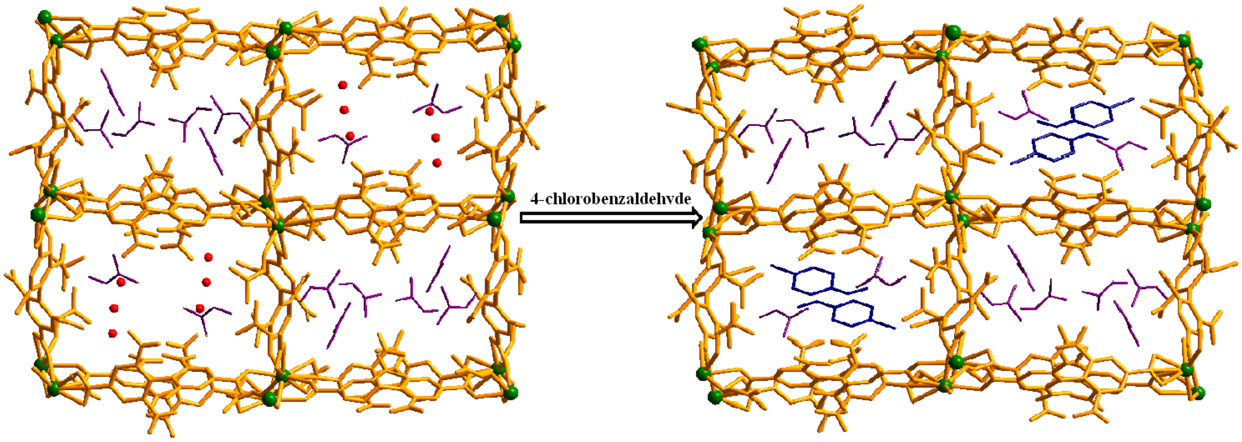

Fig. 4 Single-crystal to single-crystal guest-exchange process in compound **1** (hydrogen atoms have been removed for clarity).

A close inspection of the structure of **1a** depicts that the phenyl rings in $\mathbf{L}^{2-}$ are rotated, which causes an expansion of channel B (to 3.145 x 8.735 $Å^2$) and facilitates accommodation of the guest 4-chlorobenzaldehyde molecules approximately in the middle of the channel (Fig. 4). Several weak host-guest interactions are observed in **1a** (Table S4, ESI†), which include: (a) C−H···O interactions (2.6176-3.182 Å) between methyl H atom of the coordinated DMF molecule and the O (–CHO) atom; (b) interaction between O ($–NO_2$) atom and H (–CHO) atom, (c) C−H···Cl interaction (3.233 Å) between Cl atom of the guest aldehyde and H atom of the carboxylate ligand. All these interactions (Fig. 5) assist to stabilize the 4-chlorobenzaldehyde guests inside the framework. Similar to the mother framework, here also, the DMF solvent and

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aldehyde guest molecules are disordered. The IR spectrum of **1a** exhibits (Fig. S3, ESI†) sharp peak at 1700 cm^{-1}, corresponding to the aldehyde stretching vibration. The bulk phase purity of **1a** is confirmed from similarity of the PXRD pattern with that of the simulated pattern (Fig. S4, ESI†).

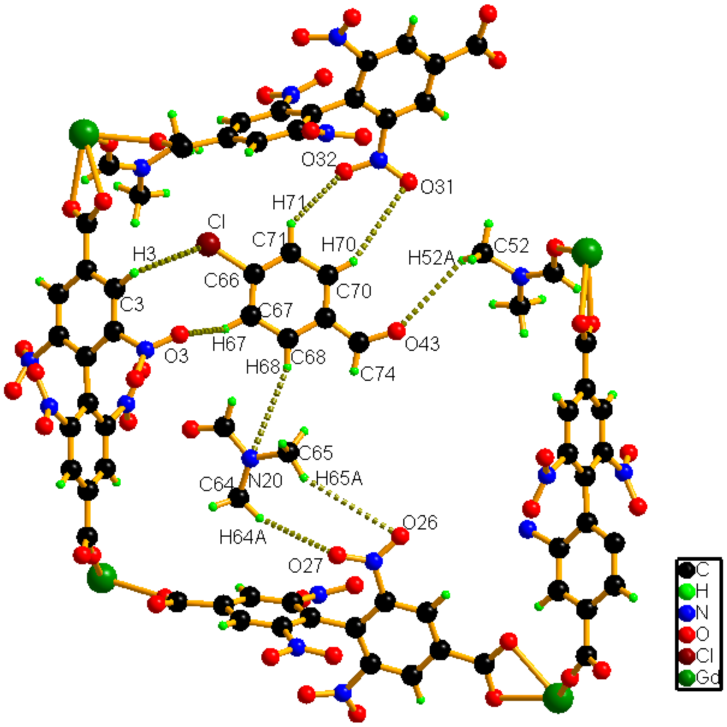

Fig. 5 Schematic representation of the interactions between guest 4-chlorobenzaldehyde molecule with the host framework as well as with solvent molecules in **1a**.

Independent synthesis to achieve **1a**, by mixing 4-chlorobenzaldehyde with Gd(III) and **H$_2$L** in appropriate stoichiometric ratio proved unsuccessful, indicating that SC-SC transformation is the only route towards its formation. Thermogravimetric analysis of **1a** shows a gradual weight loss of 12.8% (calculated, 12.7%) up to 235 ℃, accounting for the removal of four lattice DMF guest molecules. Complete decomposition of the framework occurs beyond that temperature (Fig. S5, ESI†), due to expulsion of the coordinated DMF molecule.

With a quest to probe reversibility of the SC-SC transformation, i.e., whether the as-synthesized framework can be regenerated from its guest-loaded framework, the crystal of **1a** was dipped into a DMF solution for 4 days. To our delight, the cell parameters from single crystal X-ray diffraction data exactly matches to that of **1** affording the structure identical to that of the mother crystal, corroborating complete reverse transformation. Unaltered crystal morphology during the entire process (Fig. S6, ESI†) confirms that no dissolution of **1a** occurs in DMF. In the regenerated framework, the absence of any aldehyde guest is also corroborated from the lack of a peak at 1700 cm^{-1} in the IR spectrum (Fig. S7, ESI†). Moreover, the similarity of PXRD patterns (Fig. S8, ESI†) of **1** and DMF soaked **1a** support the bulk phase transformation.

Reversible single-crystal to single-crystal transformation of 1 to 1b or 1c

Encouraged by the successful entrapment of 4-chlorobenzaldehyde guest by **1**, we further checked its potential usage towards hosting 4-fluorobenzaldehyde and 4-methyl benzaldehyde guests (Scheme 1). Crystals of **1** do not show any loss of single crystallinity when kept separately in vapors of the above mentioned aldehydes at room temperature for 5 days. The possibility of dissolution of **1** in aldehyde vapor, followed by recyrstalization at the surface and growth of a new phase is excluded by photographs of the mother crystals (Fig. S6, ESI†) at different time intervals, which show no change in size, color, morphology and transparency during the entire process. Individual single crystal-X-ray diffraction measurement reveals that although the crystal systems remain unaltered, the space group changes to *C*2/*c* (Table S2, ESI†), producing two new daughter frameworks $\{[Gd(\mathbf{L})_{1.5}(DMF)(H_2O)_3]\cdot(\mathit{4\text{-}FPhCHO})\cdot(DMF)\cdot3(H_2O)\}_n$ (**1b**) (Fig. 6) and $\{[Gd(\mathbf{L})_{1.5}(DMF)(H_2O)_3]\cdot(\mathit{4\text{-}MePhCHO})\cdot2(DMF)\cdot(H_2O)\}_n$ (**1c**).

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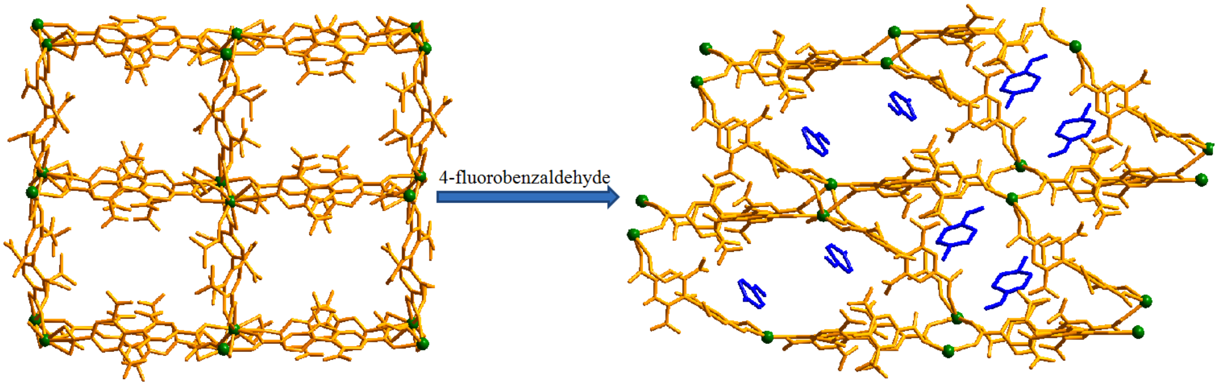

Fig. 6 single-crystal to single-crystal loading of 4-chlorobenzaldehyde guest in compound **1**, forming the daughter compound **1b**. The noticeable rearrangement of the framework channels is depicted. DMF and water molecules have been removed for clarity.

Since **1b** and **1c** have similar structure, only structure of the former is described here. The structure of **1b** is quite different from its mother framework or **1a**, with several bond transformations. To our surprise, the lattice water molecule moves to the metal center. In this *modus operandi*, the η^2-bridging carboxylate in the mother crystal undergoes a pronounced ‘carboxylate shift’ and transforms into mono-dentate η^1-carboxylate (Fig. 7). This carboxylate shift also causes significant increase in the Gd…Gd separation from 4.048 (11) Å to 5.031(11) Å (Fig. 7). Moreover, the terminal chelating carboxylate group, attached to each Gd(III) centre in **1** opens up to mono-dentate η^1-ligation mode in **1b**. Consequently, the coordination number around each metal center of Gd_2 SBU diminishes to eight with coordination from two *syn* carbxylates, two η^1-carboxylates, three water molecules and one DMF molecule (Fig. 7).

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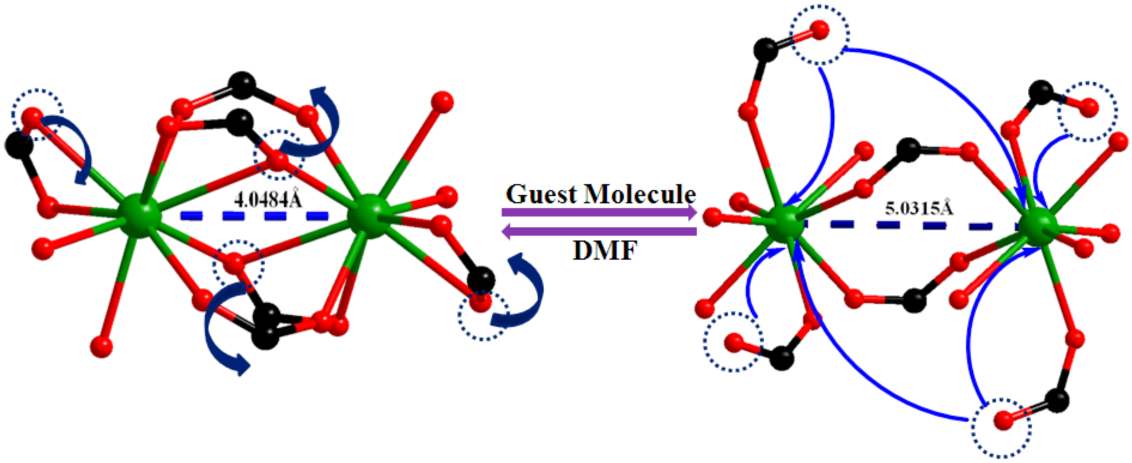

Fig. 7 The carboxylate shift process at the metal centre, occurring through the reversible SC-SC transformation from **1** to **1b** and *vice versa***.**

It should be pointed that although a number of SC-SC transformations are reported in the literature, those involving changes in the first coordination sphere are comparatively fewer in number.[19] Moreover, while rearrangements in the carboxylate coordination modes, i.e. the "carboxylate shift" is more commonly reported[20] in biological systems, this phenomenon is observed[21] in only a handful of examples for coordination polymers. The O atoms of dissociated terminal chelating carboxylate, which was earlier bound to the Gd(III) centre in **1**, is rotated towards a neighboring guest aldehyde molecule to form intermolecular hydrogen bonds (Fig. S9, ESI†) in **1b**. The overall structure of **1b** is also unique in a sense that unlike **1** or **1a**, the two channels (A and B) undergo substantial distortion during the guest encapsulation process (Fig. 8). Thus, the revised channel dimensions in **1b** approximate to 3.40 × 12.19 $Å^2$ (channel A) and 2.95 × 6.60 $Å^2$ (channel B).

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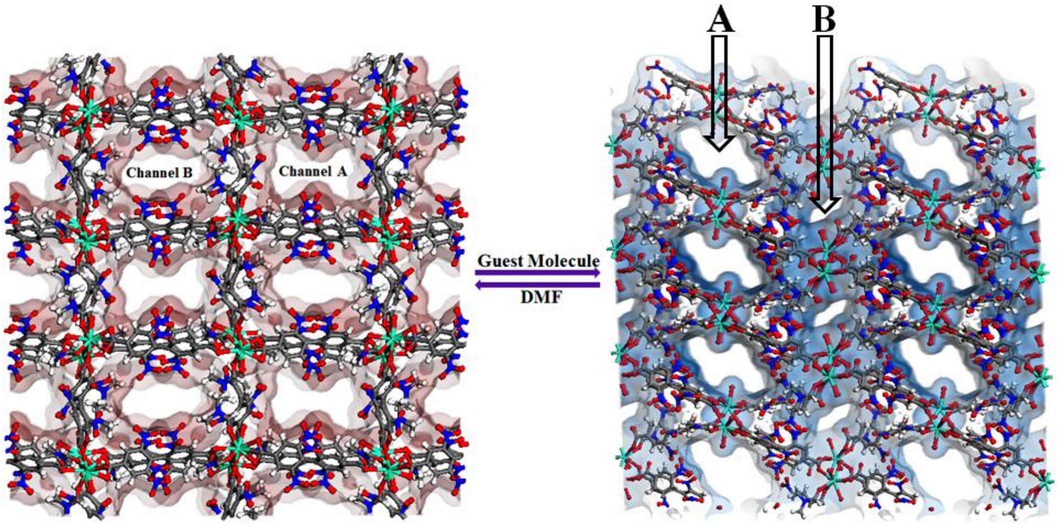

Fig. 8 Perspective view of the channel rearrangement during reversible SC-SC transformation from **1** to **1b** and *vice versa*.

As depicted in Fig. 6, unlike in **1a**, both the channels here contain aldehyde molecules, where the guest 4-fluorobenzaldehyde molecules are not positioned in the middle of the channels; rather they are slightly sifted towards the edge (Fig. 9), exhibiting C-H···π and π···π stacking interactions (For detail interaction, see Fig. S9, and Table S5, ESI†) with the nearby benzene ring of $\mathbf{L}^{2-}$. We speculate that this different positioning of the guest aldehyde molecules in **1b**, leads to such pronounced distortion in framework channels.

The other daughter compound **1c** has a comparable structure to that of **1b**, involving: (a) the coordination environment and coordination number around each metal center (Fig. S10, ESI†), (b) ligation modes of the carboxylate groups, carboxylate shifts and lattice water movement to the metal center (Fig. S10 and S11, ESI†) (c) rearrangement of the framework channels (Fig. S12, ESI†) and (d) positioning of guest 4-methylbenzaldehyde (Fig. S12, ESI†) molecules inside the channels (for detail interaction, see Fig. S13 and Table S6, ESI†).

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We failed to synthesize **1b** or **1c** independently, by mixing 4-fluorobenzaldehyde or 4-methylbenzaldehyde with Gd(III) and **H$_2$L** separately in appropriate stoichiometry ratio, indicating that SC-SC transformation is the only route towards their formation.

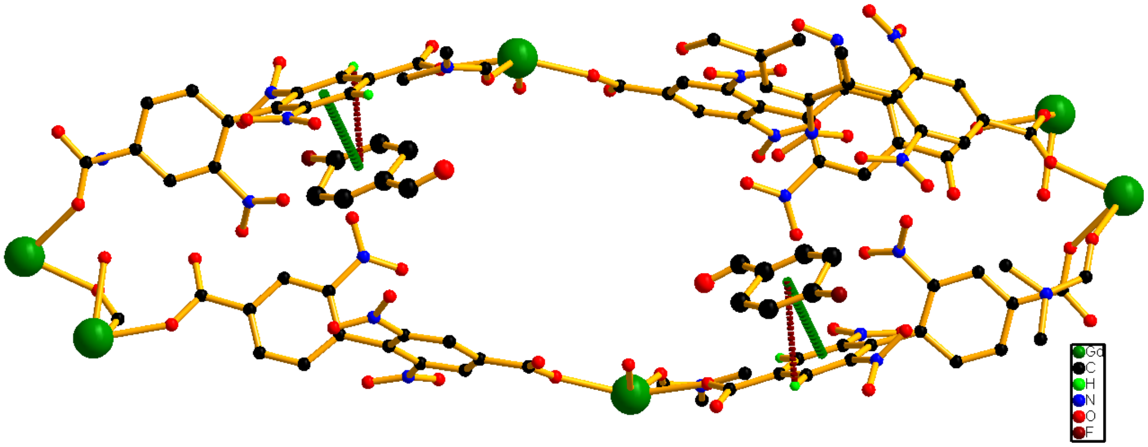

Fig. 9 Schematic representations of the interaction of guest 4-fluorobenzaldehyde molecule with the host framework inside the pore of a compound **1b**.

The bulk phase purity of both **1b** and **1c** are corroborated from the concurrence of their individual PXRD patterns (Fig. S14 and Fig. S15, ESI†) with that of the simulated patterns, obtained from respective single crystal data. The IR spectrum of compound **1b** and **1c** exhibits sharp peaks at 1706 cm^{-1} and 1695 cm^{-1}, respectively (Fig. S16 and Fig. S17, ESI†) that corresponds to the aldehyde stretching vibration. Thermogravimetric analysis of **1b** shows 4.5% (calculated, 4.6%) weight loss at 80 ℃ due to loss of three water molecules from the cavity. A further 17.1% (calculated, 16.9%) weight loss in the temperature range 90-205 ℃ attenuates the loss of one 4-fluorobenzaldehyde molecule and one DMF molecule from the cavity. Beyond that temperature the coordinated DMF molecule is lost and decomposition of the framework occurs

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(Fig. S18, ESI†). Thermogravimetric analysis of **1c** shows a gradual weight loss 24% (calculated, 23.7%) in the temperature range 60-240 ℃, corresponding to the loss of one water, two DMF and one 4-methylbenzaldehyde molecules from the cavity (Fig. S19, ESI†).

Interestingly, when the daughter crystals **1b** and **1c** are soaked in DMF for 4 days, the unit cell parameters changes to that of the mother crystal **1**, giving the identical structure of the mother crystal, corroborating reverse SC-SC transformation. This observation is further shown in IR measurements (Fig. S20 and S21, ESI†), which show no peak for the aldehyde molecules. Similarity between PXRD patterns of respective DMF soaked daughter crystals and **1** supports the bulk transformation (Fig. S8, ESI†). Thus, the mother framework represents a dynamic porous coordination polymer in true sense, where *guest shape-responsive fitting* and *guest release* inside the channels are realized in complete single-crystal-to-single-crystal manner. This unique property renders framework **1,** a deliverable container for aromatic guest aldehydes under ambient condition. We further searched for the SC-SC transformation cycles for the individual guest loaded frameworks **1a**, **1b** and **1c**. In each case, the PXRD patterns clearly demonstrate that the structural integrity is maintained up to two cycles, after which the framework collapses (Fig. S22, S23 and S24, ESI†). However, the cross exchange of guest aldehyde molecules in the cavity is not possible between the daughter crystals, even after long term exposure. We were also unsuccessful to load other aromatic aldehydes, like 4-nitrobenzaldehyde, 4-hydroxybenzaldehyde, 4-methoxybenzaldehyde and 4-bromobenzaldehyde inside **1**, which reflects substantial affinity of the host framework to those above discussed aldehydes (Scheme 1) only.

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Conclusion

In conclusion, by rationally choosing the flexible ligand **H_2L**, we have synthesized a flexible Gd(III) framework (**1**), containing two different channels. The lattice water molecules of channel B can be completely replaced by 4-chlorobenzaldedhyde guest to afford the guest encapsulated framework **1a**, via SC-SC transformation. The overall framework of **1a**, including carboxylate connectivities to the Gd(III) centre, and dimentionalities of channels remain the same to that of the mother framework. On the other hand, two new daughter frameworks are formed when crystals of **1** are separately exposed to the vapors of 4-fluorobenzaldehyde (**1b**) and 4-methylbenzaldehyde (**1c**). In sharp contrast to **1a**, both the later transformations involve several “carboxylate shift” processes, accompanied by substantial changes in the ligand conformation and metal coordination environment. Additionally, the later SC-SC transformations accompany substantial opening of channel A and closing of channel B. We assume that such pronounced channel distortion is a consequence of different positioning of the guest aldehyde molecules inside framework voids. The understanding of such a non-coordinating guest-driven, anomalous structural transition, followed by molecular motion offers ways to explain various dynamic aspects of coordination polymers, besides being potentially used in fabricating molecular devices. More significantly, all the host-guest complexes revert back to the mother crystal (**1**) in single-crystal-to-single-crystal manner when kept in DMF, rendering framework **1** as a flexible and deliverable container for the aromatic aldehydes. Given the immense importance to realize the “guest shape-responsive fitting” or dynamic guest accommodation of the voids, the present research focus allows the prospect to trap even very reactive species that are unstable outside the restricted environment. We are currently working along these lines.

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Notes and references

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†Electronic supplementary information (ESI) available: Several spectroscopic, thermogravimetric analysis, powder X-Ray diffraction of all the compounds and photographs of all the single crystals. X-ray crystallographic data for **1**, **1a**, **1b** and **1c** in CIF format are provided. Respective CCDC Nos. are: 843413, 1032264, 1032265 and 1032266.

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