

# Solvent-Induced Carboxylate Shift and Movement of an Anthryl Side-Group in Single-Crystal to Single-Crystal Structural Dynamics in a Gadolinium Coordination Polymer

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**Supporting Information** 

**ABSTRACT:** Single crystal to single crystal (SC–SC) transformation involving cooperative movement of atoms represents one of the most fascinating phenomena in coordination polymers. Here, we describe a novel two-dimensional coordination polymer { $[Gd_2(L)_3(DMF)_2(H_2O)_2]$ ·  $(DMF)_2 \cdot (H_2O)_{5.5}$ }, (1) synthesized from carboxylate-based flexible ligand 5-[(anthracen-9-ylmethyl)-amino]-isophthalic acid and Gd(III) ion by the solvothermal technique. The complex undergoes solvent-induced rearrangement reactions with the cleavage and formation of coordination bonds and substantial movement of the anthracene side groups without losing crystallinity to form the daughter products as { $[Gd_2(L)_3(H_2O)_4]$ ·  $(DMF)_4 \cdot (H_2O)_{1.5}$ }, (1a), { $[Gd_2(L)_3(DMF)_2(H_2O)] \cdot (DMF)_2 \cdot (DCM)_2$ ·  $(H_2O)_5$ }, (1b), and  $[Gd(L)_2(DEF)]_n$  (1c). These transformations exhibit a crystallographic snapshot of "carboxylate-shift" process which is further



supported by IR spectroscopy, elemental analysis, and powder X-ray diffraction patterns. To the best of our knowledge, it is the first example of carboxylate shift in a Gd(III) coordination polymer. The mother crystal 1 and the daughters 1a and 1c exhibit 4-connected *sql* topology, while 1b shows a 3-connected *hcb* topology. Magnetic susceptibility measurements at variable temperature indicate the existence of antiferromagnetic interactions in all the complexes. The photoluminescent properties of the complexes in the solid state are also investigated at room temperature.

# INTRODUCTION

A very important property of porous coordination polymers (PCPs) is their flexible and dynamic properties that are characteristic of the cooperative interactions involving the ligands and metals as well.<sup>1</sup> Guest responsive changes in the solid state without losing crystallinity (SC-SC transformations) are quite intriguing. Particularly, molecular motions in crystalline solids have received importance in recent years due to their potential importance in fabricating nanoscale devices.<sup>2</sup> Besides, these SC-SC transformations afford a deeper insight into the relationship between the host and the guest molecules and provide a starting point for synthesizing systems with novel applications. The structural changes in PCPs are mainly triggered by external stimuli like heat, light, pressure,<sup>3</sup> etc. that involve changes in metal coordination environment, rearrangement of bonds,<sup>5</sup> removal or insertion of guest,<sup>6</sup> and conformational changes in the flexible parts of the organic linkers.<sup>7</sup> In this context, solvent-induced structural transformations are significantly appealing. While a large number of SC-SC transformation studies are reported in the literature, those involving the first coordination sphere are comparatively much less in number.<sup>8</sup> A few examples of solvent-induced breathing effects, changes in the dimensionality of coordination network, and transposition of interpenetrating networks have been reported in recent years.<sup>9</sup> It is challenging, however, to obtain high quality crystals after solid state transformations, especially those involving changes in the coordination environment of metal ions. This could be due to breaking and formation of new coordination bonds which causes loss of the long-range structural order of the crystals.

Aromatic carboxylates with the inherent negative charge associated with them helps in the charge compensation of the metal ion in the framework. Besides, it may afford observation of the carboxylate coordination mode and its changes, termed "carboxylate shift", which is a low-energy process that allows structural flexibility and influences the overall structure.<sup>10</sup> There is an increasing body of evidence based on X-ray structural and density functional theory (DFT) that suggests this dynamic phenomenon plays crucial roles in the functioning of many enzymes including methane monooxygenase (MMO), R2 subunit of ribonucleotide reductase (RNR-R2), and hemery-thrin.<sup>11</sup> Thus, rearrangements in the carboxylate coordination modes, i.e., the "carboxylate shift" is most commonly reported in biological systems, while this phenomenon is observed<sup>12</sup> in

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only a handful of examples of coordination polymers. In order to explore such transformations, the ligand chosen should preferably be flexible or semiflexible. An aromatic dicarboxylate ligand with an anthryl group attached has been chosen in the present study (Scheme 1). This ligand  $H_2L$  is equipped with

Scheme 1. Synthetic Scheme of 5-[(Anthracen-9-ylmethyl)amino]-isophthalic Acid  $(H_2L)$ 



three distinct sets of functions: (a) two carboxylate groups as the coordination sites and (b) the flanked  $-CH_2NH-$  moiety to impart flexibility for possible dynamic behavior and (c) to explore the influence of anthracene ring skeleton on the photoluminescent properties. Herein, we report the solvothermal synthesis of a two-dimensional (2D) coordination polymer  $\{[Gd_2(L)_3(DMF)_2(H_2O)_2] \cdot (DMF)_2 \cdot (H_2O)_{5,5}\}_n$  (1) from  $H_2L$ and Gd(III) ion. A lanthanide metal ion has been chosen as its valence orbitals are buried and not exposed to ligands. Thus, lanthanide metal ions do not have preference for a particular coordination geometry.<sup>13</sup> Solvent-induced SC-SC transformations have been observed to form new coordination polymers exhibiting carboxylate shift along with substantial movement of the anthryl group. To the best of our knowledge, this fascinating feature has not been observed in gadolinium-based coordination polymers. Further characterizations of magnetic and photolumniscent properties are made on these compounds.

#### Article

## EXPERIMENTAL SECTION

**Materials.** Reagent-grade 9-anthracene carboxaldehyde (97%), 5aminoisophthalic acid (94%), and  $Gd(NO_3)_3$ · $GH_2O$  were procured from Sigma-Aldrich and used as received. Sodium borohydride, acetic acid, benzene, and all solvents were procured from S.D. Fine Chemicals, India. All solvents were purified following standard methods prior to use.

Physical Measurements. Infrared spectra were obtained (KBr disk, 400-4000 cm<sup>-1</sup>) on a PerkinElmer model 1320 spectrometer: ESI mass spectra were recorded on a WATERS Q-TOF Premier mass spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a JEOL-ECX 500 FT (500 and 125 MHz respectively) instrument in DMSO-d<sub>6</sub> with Me<sub>4</sub>Si as the internal standard. Thermogravimetric analyses (TGA) were recorded on a Mettler Toledo Star System (heating rate of 5 °C/min). Room temperature solid-state photoexcitation and emission spectra were recorded using a UV-vis-NIR spectrophotometer (Varian model Cary 5000) and Jobin Yvon Horiba Fluorolog-3 spectrofluorimeter, respectively. Powder X-ray diffraction patterns (CuK<sub> $\alpha$ </sub> radiation, scan rate 3°/min, 293 K) were collected on a Brüker D8 Advance Series 2 powder X-ray diffractometer. EPR spectra were recorded at room and liquid nitrogen temperatures on a Brüker ESP 300 spectrometer operating at X-band equipped with an ER 035M Brüker NMR gaussmeter and a HP 5350B Hewlett-Packard microwave frequency counter.

**Magnetic Measurements.** Variable temperature magnetic measurements of polycrystalline samples were carried out with a Quantum Design SQUID magnetometer (MPMSXL-5) at 5 T over the temperature range 1.8–300 K. Corrections are based on subtracting the sample-holder signal, contribution  $\chi_{\text{Dia}}$  estimated from Pascal constants,<sup>14</sup> and equals  $-383 \times 10^{-6}$  cm<sup>3</sup> mol<sup>-1</sup> for compounds 1 and 1a–c per Gd center. Magnetization versus magnetic field measurements were carried out at 1.8 K in the magnetic field range 0–5 T. The effective magnetic moment was calculated per Gd center from the equation:

$$\mu_{\rm eff} = 2.83 (\chi_{\rm M} T)^{1/2} (B. M.)$$

**Single-Crystal X-ray Studies.** Single crystal X-ray data on 1 and **1a**-c were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite monochromated MoK<sub> $\alpha$ </sub> radiation ( $\lambda$  = 0.71073 Å). The linear absorption coefficients, scattering factors for

#### Table 1. Crystal and Structure Refinement Data of 1 and 1a-c

parameters	1	1a	1b	1c
empirical formula	$C_{81}H_{87}N_7O_{23.5}Gd_2$	$C_{81}H_{84}N_7O_{21.5}Gd_2$	$C_{83}H_{89}N_7Cl_4O_{22}Gd_2$	$C_{51}H_{41}N_3O_9Gd$
formula wt	1849.06	1814.04	1992.91	997.12
crystal system	triclinic	monoclinic	triclinic	monoclinic
space group	$P\overline{1}$	$P2_{1}/c$	$P\overline{1}$	$P2_{1}/c$
a, Å	16.346(5)	17.779(5)	15.418(5)	25.571(5)
b, Å	17.081(5)	19.772(5)	16.274(5)	10.862(5)
<i>c,</i> Å	17.163(5)	20.507(5)	17.876(5)	16.025(5)
$\alpha$ (deg)	68.749(5)	90	109.838(5)	90
$\beta$ (deg)	86.941(5)	98.486(5)	93.621(5)	105.819(5)
γ (deg)	66.545(5)	90	111.141(5)	90
<i>U</i> , Å <sup>3</sup>	4074(2)	7130(3)	3846(2)	4282(3)
Z	2	4	2	4
$ ho_{\rm calc}~{ m g/cm^3}$	1.304	1.385	1.368	1.547
$\mu$ , mm <sup>-1</sup>	1.675	1.908	1.772	1.612
F(000)	1598	2944	1584	2016
refl collected	27 730	38 633	20 562	28 600
independent refl	15 085	13 257	14 019	7970
GOF	1.103	0.937	0.958	1.046
final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0540$	$R_1 = 0.0539$	$R_1 = 0.0700$	$R_1 = 0.0422$
	$wR_2 = 0.1550$	$wR_2 = 0.1325$	$wR_2 = 0.1787$	$wR_2 = 0.0862$
R indices	$R_1 = 0.0684$	$R_1 = 0.0856$	$R_1 = 0.1092$	$R_1 = 0.0839$
(all data)	$wR_2 = 0.1651$	$wR_2 = 0.1557$	$wR_2 = 0.2063$	$wR_2 = 0.1001$

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Figure 1. Metal coordination modes in complexes (a) 1, (b) 1a, (c) 1b, and (d) 1c.

the atoms, and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography.<sup>15</sup> Data integration and reduction were carried out with SAINT<sup>16</sup> software. Empirical absorption correction was applied to the collected reflections with SADABS,<sup>17</sup> and the space group was determined using XPREP.<sup>18</sup> The structure was solved by the direct methods using SHELXTL-97<sup>19</sup> and refined on F<sup>2</sup> by full-matrix least-squares using the SHELXL-97 program<sup>20</sup> package. All non-hydrogen atoms with the exception of a few were refined anisotropically. Atoms C59, C60, and C61 in complex 1; C50, C51, C52 and C74 in complex 1a; C1, C2, C3, C32, and C68 in complex 1b; and C8 in complex 1c were refined isotropically. The H atoms attached to C atoms were positioned geometrically and treated as riding atoms using SHELXL default parameters. The hydrogen atoms of coordinated water molecules in 1, 1a, and 1b could not be located in the difference Fourier maps. For compounds 1, 1a, and 1b, squeeze refinement has been performed using PLATON<sup>21</sup> that shows two DMF and 5.5 aqua molecules in 1, four DMF and 1.5 aqua molecules in 1a, two DCM, two DMF, and five aqua molecules in 1b per formula weight, respectively. The contributions of all the solvent atoms have been included in both the empirical formulas and formula weights. Several DFIX and DANG commands were used to fix the bond distances and bond angles in 1 and 1a-c. The crystal and refinement data are collected in Table 1, while selected bond distances and angles are given in Table S1, Supporting Information.

Synthesis of 5-[(Anthracen-9-ylmethyl)-amino]-isophthalic Acid (H<sub>2</sub>L). 5-Aminoisophthalic acid (2.0 g, 0.01 mol) and 9anthracene carboxaldehyde (2.27 g, 0.01 mol) in dry methanol (50 mL) were stirred in a 100 mL round-bottom flask for an hour, whereby the mixture became viscous. To this mixture, NaBH<sub>4</sub> was added slowly at 4 °C. After 2 h at 4 °C, the solvent was removed under a vacuum. The residue was dissolved in water (50 mL) and acidified with acetic acid to pH 5–6, whereupon the product precipitated out as a pale yellow solid. It was collected by filtration, washed thoroughly with water, and then air-dried. Yield, 3.3 g (89%). <sup>1</sup>H NMR (DMSOd<sub>6</sub>, 500 MHz,  $\delta$ ): 11.46(s, 1H), 8.62 (s, 1H; H<sub>Ar</sub>), 8.27(s, 1H; H<sub>Ar</sub>), 8.11(d, 2H; H<sub>Ar</sub>), 7.75(s, 2H; H<sub>Ar</sub>), 7.59(d, 2H; H<sub>Ar</sub>), 7.55(d, 2H; H<sub>Ar</sub>), 7.50(d, 2H; H<sub>Ar</sub>), 5.11(s, 2H); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 125 MHz,  $\delta$ ): 167.9, 149.8, 132.4, 131.6, 130.7, 125.28, 129.9, 129.4, 127.9, 126.9, 125.8, 125.1, 118.2, 116.9, 55.2; ESI-MS: m/z [M – 1] 370.11(100%); IR (KBr, cm<sup>-1</sup>): 3400(s), 2880(m), 1689(s), 1603(s), 1504(s), 1438(s), 1344(m), 1276(s), 1136(w), 944(m), 890(s), 758(s), 732(s). **Synthesis of {[Gd<sub>2</sub>(L)<sub>3</sub>(DMF)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·(DMF)<sub>2</sub>·(H<sub>2</sub>O)<sub>5.5</sub>}<sub>n</sub> (1).** A mixture containing ligand H<sub>2</sub>L (40 mg, 0.11 mmol) and Gd(NO<sub>3</sub>)<sub>3</sub>· 6H<sub>2</sub>O (100 mg, 0.22 mmol) in 2 mL of DMF and 1 mL of H<sub>2</sub>O was sealed in a Teflon-lined autoclave and heated under autogenous pressure to 100 °C for 2 days and then allowed to cool to room temperature at the rate of 1 °C per minute. Block-shaped browncolored crystals of 1 were collected in ~41% yield. The crystals were washed with water followed by acetone and then air-dried. Anal. Calcd for C<sub>81</sub>H<sub>87</sub>N<sub>7</sub>O<sub>23.5</sub>Gd<sub>2</sub>: C, 52.61; H, 4.74; N, 5.30%. Found: C, 52.74; H, 4.88; N, 5.22%. IR (KBr, cm<sup>-1</sup>): 3398(s), 3059(m), 2925(w), 1668(s), 1603(w), 1547(s), 1440(s), 1378(s), 1248(w), 1092(m), 894(m), 784(s), 733(s).

**Synthesis of {**[ $Gd_2(L)_3(H_2O)_4$ ]**·**(DMF)<sub>4</sub>**·**( $H_2O$ )<sub>1.5</sub>]<sub>n</sub> (1a). Crystals of 1 were dipped in benzene at room temperature for 2 days to obtain 1a. Anal. Calcd for C<sub>81</sub>H<sub>84</sub>N<sub>7</sub>O<sub>21.5</sub>Gd<sub>2</sub>: C, 53.63; H, 4.67; N, 5.40%. Found: C, 53.54; H, 4.78; N, 5.31%. IR (KBr, cm<sup>-1</sup>): 3397(s), 2927(w), 1652(s), 1534(s), 1444(s), 1380(s), 1285(m), 1145(m), 1111(m), 1094(m), 937(m), 894(m), 785(s), 733(s).

Synthesis of {[ $Gd_2(L)_3(DMF)_2(H_2O)$ ]·(DMF)<sub>2</sub>·(DCM)<sub>2</sub>·( $H_2O)_3$ }, (1b). Crystals of 1 were immersed in DCM at room temperature for 2 days to obtain 1b. Anal. Calcd for C<sub>83</sub>H<sub>89</sub>N<sub>7</sub>Cl<sub>4</sub>O<sub>22</sub>Gd<sub>2</sub>: C, 50.02; H, 4.50; N, 4.92%. Found: C, 50.18; H, 4.63; N, 4.80%. IR (KBr, cm<sup>-1</sup>): 3399(s), 2926(w), 1654(s), 1602(w), 1538(s), 1444(s), 1380(s), 1146(m), 1112(m), 999(m), 936(m), 786(s), 733(s).

**Synthesis of**  $[Gd(L)_2(DEF)]_n$  (1c). Crystals of 1 were immersed in DEF at room temperature for 2 days to obtain 1c. Anal. Calcd for  $C_{51}H_{41}N_3O_9Gd:$  C, 61.43; H, 4.14; N, 4.21%. Found: C, 61.22; H, 4.06; N, 4.35%. IR (KBr, cm<sup>-1</sup>): 3394(s), 2924(w), 1535(s), 1472(m), 1403(m), 1140(m), 1027(w), 958(m), 820(s), 781(s), 732(s).

# RESULTS AND DISCUSSION

Complex 1 is prepared by the solvothermal technique utilizing ligand  $H_2L$  with  $Gd(NO_3)_2 \cdot 6H_2O$  in a mixture of DMF and water. It is formulated as  $\{[Gd_2(L)_3(DMF)_2(H_2O)_2] \cdot (DMF)_2 \cdot (H_2O)_{5.5}\}_n$  from single-crystal X-ray studies and further corroborated by TGA and elemental analysis. The phase purity of 1 is confirmed by comparing the experimental and simulated



Figure 2. (a–e) Schematic representation of ligand coordination modes  $L^{2-}$ .

powder X-ray diffraction patterns. Once isolated, it is found to be stable in air and insoluble in common organic solvents and water. The IR spectrum of 1 shows strong absorption bands between 1400–1600 cm<sup>-1</sup> diagnostic of coordinated carboxylate groups and a broad peak in the region 3377-3442 cm<sup>-1</sup>, indicating the presence of coordinated and lattice water molecules.<sup>22</sup>

**Structural Description.** The complex  $\{[Gd_2(L)_3(DMF)_2(H_2O)_2] \cdot (DMF)_2 \cdot (H_2O)_{5.5}\}_n$  (1) crystallizes in the triclinic space group  $P\overline{I}$ . The structure consists of two Gd(III) ions, three deprotonated  $L^{2-}$  ligand moieties, two coordinated DMF, and two aqua molecules besides two DMF and 5.5 water molecules in the lattice. Both Gd1 and Gd2 show nine coordination (Figure 1a) with ligation from three chelated carboxylates, one bridging carboxylate, and one O atom each from the coordinated DMF and water molecules (Gd-O = 2.358(4)-2.718(4) Å). This gives rise to an overall distorted monocapped square antiprismatic coordination geometry (Figure S13, Supporting Information). The distances of Gd-O bonds fall within the normal statistical errors reported for other gadolinium-based coordination polymers.<sup>23</sup>

The metal core consists of  $Gd_2$  dimer  $(M \cdots M = 4.180(3) - 4.204(4) Å)$  constructed from two bridging chelating carboxylates, four chelating carboxylates, and two water and two DMF molecules. Two such binuclear  $Gd_2$  clusters are bridged by the carboxylate groups of the ligand units in the *ab* plane with distances between two such dimeric units being 9.99 and 10.17 Å along the crystallographic *a* and *b* axes, respectively. Interestingly, the ligand adopts two different binding modes as shown in Figure 2a, e and Table 2. The complex propagates in the crystallographic *a* direction through the chelating bridging and chelating modes and in the *c* direction through the chelating mode of the ligand  $L^{2-}$  to form a 2D infinite sheet-like framework (Figure 3a). In **1**, the

distance between two adjacent anthryl moieties is 9.04 Å with a dihedral angle of  $86.77^{\circ}$ .

For better understanding of the structure, topological analysis<sup>24</sup> is employed which shows that on considering Gd<sub>2</sub> dimeric unit as a node and L<sup>2–</sup> ligand as a line, 1 can be simplified as a 4-connected *sql* net with the point symbol {4<sup>4</sup>.6<sup>2</sup>}. Further, these corrugated 2D rectangular nets with dimensions 13.98 × 9.17 Å<sup>2</sup> are stacked in an ---AAA--- fashion (Figure 4a) through extensive CH- $\pi$  (2.66–2.86 Å) and  $\pi$ – $\pi$  (3.24–3.38 Å) interactions between the anthracene moieties of adjacent layers resulting in an overall 3D supramolecular framework.

Solvent-Dependent Reversible Structural Transformations in SC-SC Fashion. A crystal of 1 of suitable size is taken as the mother crystal and studied in all SC-SC transformation reactions. When this crystal is kept immersed in benzene at room temperature (RT) for 2 days, it forms  $\{[Gd_2(L)_3(H_2O)_4] \cdot (DMF)_4 \cdot (H_2O)_{1.5}\}_n$  (1a) without losing crystallinity. Compound 1a crystallizes in the monoclinic space group  $P2_1/c$ . The structure of 1a consists of two Gd(III) ions, three deprotonated L<sup>2-</sup> ligand units, four coordinated aqua molecules with four DMF, and 1.5 H<sub>2</sub>O molecules in the lattice. When compared with the structure of 1, several structural alterations are observed in 1a: (i) replacement of coordinated DMF with aquo ligand, (ii) appreciable change in Gd–O bond distances of chelating bridging carboxylate groups in 1a from 2.666(4) to 2.897(5)-2.941(6) Å, (iii) differences in the binding modes of the ligand  $L^{2-}$  (Figure 2a, b, d), (iv) bond rearrangements in the Gd<sub>2</sub> dimeric unit (Figure 1b) where two chelating carboxylate groups in the mother crystal undergoes carboxylate shift and is converted to bridging carboxylate group in 1a (Figure 5), (v) the distance between adjacent anthryl moieties is reduced from 9.04 to 5.21 Å and (vi) the anthracene rings move away from orthogonality with

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lc	5.432	2.26-2.39	7	monocapped trigonal prismatic	bridging, monodentate µ <sub>3-</sub> η¹:η¹:η¹:η0	sqlAAA	61.03
1b	3.729	2.35-2.53	6	monocapped square antiprismatic	chelating bridging, chelating $\mu_3 \cdot \eta^1 \cdot \eta^2 \cdot \eta^1 \cdot \eta^2$	hcbAAA	81.66
la	4.057	2.31-2.94	6	monocapped square antiprismatic	chelating bridging, chelating $\mu_{3}$ , $\eta'$ , $\eta'$ , $\eta'$ , $\eta'$ bridging, bridging $\mu_{4}$ , $\eta'$	sqlAAA	19.34
1	4.18-4.204	2.36–2.72	6	monocapped square antiprismatic	chelating bridging, chelating $\mu_3 \eta^1 \eta^2$ : $\eta^1 \eta^1$ chelating, chelating $\mu_2 \eta^1 \eta^1 \eta^1 \eta^1$	sqlAAA	86.77
parameters	metal core Gd…Gd distance (Å)	Gd–O distance (Å)	coordination no.	geometry of Gd(III)	igand binding modes	topology (a) type (b) stacking	tihedral angle b/w two adjacent anthracene moieties (deg)

change in the dihedral angle from 86.77 to 19.34°. The ligand  $H_2L$  is flexible due to the presence of a flanked anthracene moiety linked via a -CH<sub>2</sub>NH- spacer, which facilitates its easy movement and hence allows such structural changes to occur. In the core structure of complex 1a, the distance between Gd… Gd in the dimeric unit reduces slightly to 4.057(4) Å, and distances between two such dimeric units are increased to 10.32 and 11.71 Å (Figure 6).

Simplification of the structure using the Topos software<sup>24</sup> reveals that complex 1a has the same sql topology as the mother crystal with the point symbol  $\{4^4.6^2\}$ . However, the sql net in this case is wavy with dimensions  $10.28 \times 9.89$  Å<sup>2</sup>. Adjacent grids stack on each other in ---AAA--- fashion (Figure 4b) similar to that in 1. The stacking of the layers is attributed to extensive CH- $\pi$  (2.80-2.86 Å) and  $\pi - \pi$  (3.29-3.34 Å) interactions extending the structure into a 3D framework (Figure 3b). When the crystal (1a) is dipped in DMF for 2 days at RT, the mother crystal is regenerated, showing reversibility of the transformation between 1 and 1a. The reversibility of the transformation has been supported further by PXRD and TGA analyses on bulk samples.

When the mother crystal (1) is immersed in DCM for 2 days at RT, it transforms into  $\{[Gd_2(L)_3(DMF)_2(H_2O)] \cdot (DMF)_2 \cdot$  $(DCM)_2 \cdot (H_2O)_5$ , (1b). This complex (1b) crystallizes in the triclinic space group  $P\overline{1}$  like in the case of 1 but with different cell parameters. Interestingly, structure of 1b is quite different from the mother with several bond transformations. Here, both Gd1 and Gd2 are coordinated to nine oxygen atoms (Figure 1c). The Gd1 is coordinated to seven O atoms from ligand units, one O atom from a DMF, and one O atom from a water molecule, while Gd2 is coordinated to eight O atoms from ligand units and one O atom from a DMF molecule (Gd-O = 2.350(7)-2.530(7) Å). Although the coordination numbers remain the same as in the mother crystal, the coordination environment around Gd ions has undergone substantial changes. In 1b, one of the chelating carboxylates in the mother crystal undergoes "carboxylate shift" and is transformed into the chelating bridging carboxylate mode. This results in significant decrease in the Gd…Gd separation from 4.204(4) Å to 3.729(4) Å and release of one water molecule from Gd2. In addition, the Gd-O bond distances coresponding to chelating bridging carboxylate groups show significant shortening to 2.522(7) Å from 2.666(4) Å (Figure 7). Further, slight movement of anthryl moieties is observed with a small alteration in the dihedral angle between two. Interestingly, remarkable changes are also noted in the core unit of 1b. In the case of the mother crystal, the core unit is composed of four Gd<sub>2</sub> dimeric units connected by six ligand units to form a pseudo-double boat-like structure, while in 1b it is composed of six Gd<sub>2</sub> dimeric units connected by 12 ligand units to form a double chairlike structure as shown in Figure 8. Moreover, this represents the first solid-state structural dynamics which is frozen in a boat and chairlike structure that can be triggered reversibly by varying the solvent. Interestingly, this transformation can be reversed by soaking the crystal 1b in DMF for 2 days, regenerating the mother crystal 1.

Simplication of the structure using Topos software<sup>24</sup> shows that the mother crystal and 1b are topologically different. On considering Gd<sub>2</sub> dimeric unit as a 3-connecting node, 1b can be simplified as a uninodal *hcb* net (Figure 4c) with point symbol  $\{6^3\}$ , while the mother crystal is a *sql* net. Furthermore, these corrugated honeycomb layers are stacked in a ---AAA--- manner through an intricate array of CH- $\pi$  (2.77–2.81 Å) and  $\pi$ - $\pi$ 

Table 2. Comparison of Mother Crystal 1 with SC-SC Transformed Daughter Products 1a-c



Figure 3. 3D polyhedral representation of (a) 1, (b) 1a, (c) 1b, and (d) 1c.



Figure 4. Topology and stacking for (a) 1, (b) 1a, (c) 1b, and (d) 1c.

(3.38 Å) intermolecular interactions resulting in a 3D supramolecular architecture (Figure 3c).

When the mother crystal is dipped in DEF for 2 days at RT, it forms the crystal  $[Gd(L)_2(DEF)]_n$  (1c). The conversion of mother crystal to 1c without losing crystallinity is remarkable considering the cleavage/formation and rearrangement of coordinate bonds that are required for the process. Importantly, immersion of complex 1c into a mixture of DMF and H<sub>2</sub>O (1:1, v/v) affords the mother crystal 1. Single crystal X-ray analysis shows that 1c crystallized in the monoclinic space group  $P2_1/c$ . The structure of 1c consists of one Gd(III) ion, two deprotonated L<sup>2-</sup> ligand units, and one coordinated DEF molecule. The coordination sphere of each Gd(III) ion is different from that of the mother crystal and is completed by six O of three L<sup>2-</sup> ligand units and one O of the DEF molecule (Gd-O = 2.261(4) - 2.387(4) Å) (Figure 1d). Thus, 1c has a distorted MO7 monocapped triagonal prismatic geometry (Figure S14, Supporting Information) compared to distorted square antiprismatic MO<sub>9</sub> coordination geometry in the mother



Figure 5. Diagrammatic depiction of cooperative bonding rearrangements that occur during the reversible SC-SC transformation from 1 to 1a.



Figure 6. Representation of changes in core unit on SC-SC transformation from (a) 1 to (b) 1a.



Figure 7. Diagrammatic depiction of cooperative bonding rearrangements that occur during the reversible SC-SC transformation from 1 to 1b.



Figure 8. Perspective view of the changes in the core unit on SC-SC transformation from 1 to 1b and their corresponding conformations.

crystal. The Gd–O bond distances fall within the normal range reported for other Gd(III) complexes.<sup>23</sup> In this solid state structural transformation, the coordinated DMF molecule in the mother crystal is replaced by a DEF molecule. In addition, the Gd<sub>2</sub> dimeric unit shows drastic changes in coordination where two chelating bridging carboxylate groups undergo "carboxylate shift" to bridging carboxylate groups undergo "carboxylate shift" to bridging carboxylates with a concomitant decrease in Gd–O bond distances as shown in Figure 9. This is accompanied by an increase in Gd…Gd separation from 4.204(4) Å to 5.432(3) Å. Crucially, the movement of anthryl ring leads to a change in the distance and dihedral angle from 9.04 to 5.19 Å and 86.77 to 61.03°, respectively. Here, the ligand  $L^{2-}$  adopts only one coordination mode, i.e., bridging and monodentate mode (Figure 2c), in contrast to two coordination modes exhibited by the mother crystal.

The Gd<sub>2</sub> dimeric units are further connected to other similar units in the *bc* plane with a separation of 6.21 and 10.82 Å in the *b* and *c* direction respectively to form an infinite 2D framework (Figure 10b). This 2D framework is stabilized by hydrogen bonding interactions (2.47–2.53 Å), which is further reinforced by extensive NH– $\pi$  (2.84 Å) interactions to give rise to a 3D supramolecular framework (Figure 3d). Topological analysis<sup>24</sup> shows that on considering Gd<sub>2</sub> dimeric units as nodes, **1c** can be simplified as a uninodal 4-connected *sql* net



Figure 9. Representation of reversible SC–SC transformations from 1 to 1c.

with the point symbol  $\{4^4.6^2\}$ , which is similar to the topology obtained for the mother crystal **1**. The 2D net in **1c** is stacked in a ---AAA--- fashion (Figure 4d), generating rhombic channels of dimensions 9.68  $\times$  9.68 Å<sup>2</sup> in contrast to rectangular channels generated in the case of the mother crystal **1**.

During the SC-SC transformations, the transparency and morphology of the crystal are retained as depicted in the photographs taken of the mother crystal 1 and after its transformations to 1a, 1b, and 1c (Figure 11).

**TGA Analyses.** Thermal stabilities of all the complexes are examined.<sup>25</sup> Complex 1 shows a gradual weight loss of ~22.87% (calculated = 23.12%) up to 325 °C that corresponds to loss of 5.5 water and two DMF molecules in the lattice and two DMF and two water molecules that are coordinated. Complex 1a exhibits a gradual weight loss of ~21.36% (calculated = 21.58%) up to 350 °C, which is attributed to the release of 1.5 water and four DMF molecules from the lattice and four coordinated aqua molecules from the framework. Complex 1b undergoes a gradual weight loss of ~28.55% (calculated = 28.62%) up to 360 °C corresponding to five water, two DCM, and two DMF molecules from the lattice

la lb



Figure 11. Photographs of single crystals of 1, 1a, 1b, and 1c.

and one water and two DMF molecules that are coordinated. Complex 1c shows a weight loss of ~10.08% (calculated = 10.14%) corresponding to the release of one coordinated DEF molecule around 240 °C. The desolvated framework is stable up to 330 °C (Figures S9–S12, Supporting Information).

**PXRD Analysis.** The powder XRD pattern for all the compounds are in close agreement with the simulated ones (Figures S15–S18, Supporting Information). The slight differences observed in intensity could be due to preferred orientation of the powder samples.

**Magnetic Studies.** Variable temperature magnetic susceptibility of complex 1 and those obtained through SC–SC transformations, namely, 1a, 1b, and 1c, were carried out over the temperature range, 1.8–300 K. The effective magnetic moment of 1, 1a, 1b, and 1c at 300 K per Gd(III) center arising from the ground state of  ${}^{8}S_{7/2}$  are presented in Table 3, while the theoretical value for an isolated Gd(III) ion with an isotropic g value of 2.00 is 7.94  $\mu$ B.<sup>26</sup>

Temperature dependence of  $\chi_{Gd}T$  for complexes 1, 1a, 1b, and 1c shows a decreasing  $\chi T$  value with lowering the temperature from 300 to 1.8 K (Figures 12 and 13). Their values change from 6.96 cm<sup>3</sup> mol<sup>-1</sup> K at 300 K up to 5.55 cm<sup>3</sup> mol<sup>-1</sup> K at 1.8 K for complex 1, from 7.97 cm<sup>3</sup> mol<sup>-1</sup> K at 300 K up to 6.77 cm<sup>3</sup> mol<sup>-1</sup> K at 1.8 K for complex 1a, from 7.64 cm<sup>3</sup> mol<sup>-1</sup> K at 300 K up to 6.56 cm<sup>3</sup> mol<sup>-1</sup> K at 1.8 K for



Figure 10. Diagrammatic representation of changes in the core unit in reversible transformation from (a) 1 to (b) 1c.

Article

Table 3. Magnetic Data for Complexes 1 and 1a-c

	effective moment	magnetic u <sub>eff</sub> (B.M.)		
complex	T = 1.8  K	T = 300 K	Curie constant C (cm <sup>3</sup> mol <sup>-1</sup> K)	Weiss constant $\Theta$ (K)
1	6.67	7.46	6.83	-0.36
1a	7.37	7.99	8.03	-0.27
1b	7.25	7.82	7.65	-0.22
1c	9.19	10.10	12.45	-0.27

complex **1b** and from 12.74 cm<sup>3</sup> mol<sup>-1</sup> K at 300 K up to 10.54 cm<sup>3</sup> mol<sup>-1</sup> K at 1.8 K for complex **1c**. Since there is no spinorbit coupling in Gd(III) ions, the decrease of  $\chi_{Gd}T$  at low temperature indicates the presence of weak antiferromagnetic interaction between Gd(III) ions. The values of magnetization per gadolinium center of **1**, **1a**, **1b**, and **1c** complexes are presented in Table 4 and Figures 12 and 13.

The susceptibility data obey the Curie–Weiss law over the whole temperature range. The Curie–Weiss fit for the experimental data gives a Curie constant and Weiss constant of all the complexes which are presented in Table 3. The negative value of the Weiss constant only indicates weak antiferromagnetic coupling of gadolinium magnetic centers in the crystal lattice of the complexes.

**Luminescence Studies.** Lanthanide coordination polymers are being explored due to their unique luminescence properties and their potential applications in chemical sensors, light emitting devices, and biomedicine.<sup>27</sup> In this regard, the luminescence properties of complexes 1 and 1a-c and metal-free  $H_2L$  ligand have been investigated in the solid state at

room temperature. As depicted in the emission spectrum in Figure 14, all the complexes exhibit a blue emission with the band centering at 458, 450, 475, 473 nm for complexes 1, 1a, 1b, and 1c respectively with  $\lambda_{ex} = 396$  nm.

Metal-free H<sub>2</sub>L ligand also fluoresces in the solid state in the blue region with an emission peak at 452 nm. The profile of the emission bands suggest the possibility of intraligand  $(\pi - \pi^*)$ transitions.<sup>28</sup> However, no 4f-4f transition of the Gd(III) ion is observed in the emission spectra. This is probably because metal-centered electronic levels of Gd(III) ion are known to be located at  $\sim$ 31000 cm<sup>-1</sup>, typically well above the ligand centered electronic levels.<sup>29</sup> Thus, the possibility of ligand-tometal charge transfer (LMCT) and metal-to-ligand charge transfer (MLCT) are ruled out. Further, since the Gd…Gd separation is more than  $\sim$ 3.6 Å, the transitions are also not cluster centered. Though the emission profile of the complexes is similar to the free-organic ligand  $H_2L$ , the emission maxima of all the complexes show a slight shift in wavelength. This inequality in emission behavior could be due to the structural changes accompanied by the SC-SC transformations. In addition to the slight shift in wavelength, significant luminescence enhancement in the complexes compared to the ligand H<sub>2</sub>L is observed, which results from increased rigidity of the ligand upon metal coordination which reduces the loss of energy by radiationless decay.<sup>30</sup> We also tried to observe changes in the emission with changing solvents, but no changes in the emission were observed.

#### CONCLUSIONS

In conclusion, we have synthesized a novel Gd(III) coordination polymer 1 by rationally choosing a flexible ligand



Figure 12. Experimental magnetic data plotted as (a)  $\chi_{Gd}T$  and  $1/\chi_{Gd}$  versus T for complex 1, (b) variation of the magnetization M versus the magnetic field H for Gd center of complex 1, (c)  $\chi_{Gd}T$  and  $1/\chi_{Gd}$  versus T for complex 1a, and (d) variation of the magnetization M versus the magnetic field H for Gd center of complex 1a.



**Figure 13.** Experimental magnetic data plotted as (a)  $\chi_{Gd}T$  and  $1/\chi_{Gd}$  versus *T* for complex **1b**, (b) variation of the magnetization *M* versus the magnetic field *H* for Gd center of complex **1b**, (c)  $\chi_{Gd}T$  and  $1/\chi_{Gd}$  versus *T* for complex **1c**, and (d) variation of the magnetization *M* versus the magnetic field *H* for Gd center of complex **1c**.



Table 4. Magnetization Values for Complexes 1 and 1a-c



 $H_2L$  that exhibits dynamic behavior. It undergoes reversible SC–SC structural transformations dependent on the polarity of solvents. These transformations involve breaking and formation of coordination bonds accompanied by changes in the ligand conformation, metal coordination environment, and overall structure of the complexes. Interestingly, a carboxylate shift phenomenon is also observed in these SC–SC transformations, which to our knowledge is the first example of a Gd(III) coordination polymer. Temperature-dependent magnetic measurements reveal antiferromagnetic interactions between Gd-(III) centeres in the complexes. Solid-state emission characteristics of the complexes are also discussed. Presently we are studying the role of solvent polarity on structural dynamics in SC–SC mode as it is still remains comparatively less explored.

# ASSOCIATED CONTENT

#### **S** Supporting Information

X-ray crystallographic data in CIF format, table for selected bonds and distances for 1, 1a, 1b, and 1c and complete data for <sup>1</sup>H NMR, <sup>13</sup>C NMR, ESI-MS, IR, TGA analysis, PXRD, EPR, and figures. This material is available free of charge via the Internet at http://pubs.acs.org/.

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# Notes

The authors declare no competing financial interest.

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