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Thermally induced single crystal to single crystal transformation leading to polymorphism



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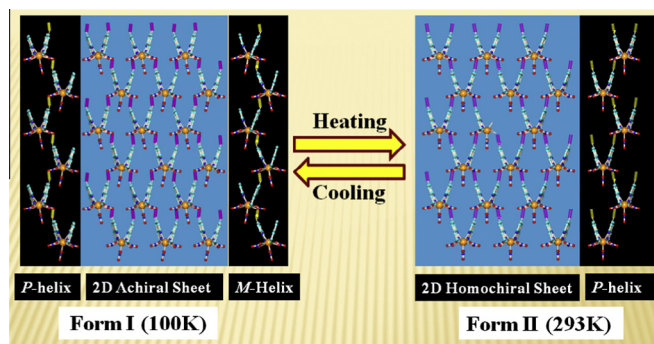
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HIGHLIGHTS

- Single crystal to single crystal transformation.
- Polymorphism.
- 2D homochiral and achiral supramolecular sheets.
- DSC analysis.
- Photoluminescence study.

GRAPHICAL ABSTRACT

[La(1,10-phen)₂(NO₃)₃] undergoes 'thermally induced reversible single crystal to single crystal transformation' between its two polymorphic phases at 100 K and 293 K. Structural analysis shows that the complex forms 2D achiral sheets at 100 K whereas at 293 K forms two different homochiral 2D sheets. DSC analysis indicates that this structural transformation occurs at 246 K. This structural transformation proceeds through coherent movement of ligands.



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ABSTRACT

The robust complex [La(1,10-phen)₂(NO₃)₃] (1,10-phen = 1,10-phenanthroline) exhibits thermally induced single crystal to single crystal transformation from one polymorphic phase to another. The complex crystallizes in monoclinic C₂/c space group with C₂ molecular symmetry at 293 K while at 100 K it shows P2₁/c space group with C₁ molecular symmetry. Supramolecular investigation shows that at 100 K the complex forms 2D achiral sheets whereas at 293 K forms two different homochiral 2D sheets. Low temperature DSC analysis indicates that this structural transformation occurs at 246 K and also this transformation is reversible in nature. We have shown that thermally induced coherent movement of ligands changes the molecular symmetry of the complex and leads to polymorphism. Photoluminescence property of complex has been studied in both solid state and in methanolic solution at room temperature. The effect of the presence low-lying LUMO orbital of π-character in the complex is elucidated by theoretical calculation using DFT method.

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Introduction

In the last decade, escalating attention has been devoted to the study of solid-state structural transformation due to its paramount importance in the field of solid state chemistry and material science [1–4]. A special case of solid-state structural transformation is ‘single crystal to single crystal’ (SC–SC) transformation in which significant changes within the crystal structure take place without appreciable loss of crystal mosaicity [2]. The challenge before us is to understand why atoms in solid move cooperatively during SC–SC transformation and how a crystal can exhibit such surprising fluidity.

Generally, solid state structural transformation occurs in response to several physical factors such as thermal perturbations, photochemical excitations etc. and also due to some chemical factors. In literature, there are several examples of such structural transformations of flexible host frameworks through removal and exchange of solvent molecules [5–12]. In contrast, such structural transformation for robust frameworks, where the complex does not contain any solvent molecule, is a rare phenomenon [13,14]. For robust complexes SC–SC transformations are mainly triggered by thermal and photochemical excitations. During structural transformations of robust frameworks, all the atoms move collectively and cooperatively in response to external stimulation. Such atomic movement leads to (i) bond breaking–bond making, (ii) movement of the ligands, or both and in turn the supramolecular interactions of the complex will also change. There are only scattered examples in literature on such structural transformations of robust frameworks [13,14]. It may be noted that Hu et al. have established that one-dimensional polymer $[\text{ZnCl}_2(\mu\text{-bipy})]_n$ is converted to two-dimensional network $[\text{Zn}(\mu\text{-Cl})_2(\mu\text{-bipy})]_n$ upon cooling below 130 K [13].

Single crystal to single crystal transformation of robust framework leads to polymorphism as both the initial and final phases have the identical composition with different geometry [15,16]. Polymorphism is of major industrial importance today [17]. While a lot of effort is being given in the study of polymorphic (organic) modifications of drugs [18], in the literature [19–22], there are only scattered examples on the systematic investigation of inorganic polymorphism available. Metal–organic complexes which contain flexible ligands can exhibit polymorphism [23–27]. Based upon various conformations of flexible ligand, such complex can achieve different type of structures and consequently polymorphism arises. But, for robust metal–organic complexes containing rigid ligands, polymorphism is rare to find [28–32].

In this endeavor, we are going to report that the robust complex $[\text{La}(1,10\text{-phen})_2(\text{NO}_3)_3]$ containing rigid 1,10-phenanthroline and nitrate ligands undergoes thermally induced structural transformation between its two polymorphic phases. Single crystal structure analyses indicate the complex changes its space group from $P2_1/c$ to $C2/c$ upon heating from 100 K to 293 K. Low temperature DSC analysis indicates that this reversible structural conversion occurs at ~ 248 K.

Experimental

Materials and method

All the chemicals used were of A.R. grade. The solvents and chemicals were purified and dried before use by standard procedures. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Merck) and 1,10-phenanthroline (1,10-phen) (Merck) were used as received. Elemental analysis (C, H, N) were carried out using a Perkin–Elmer 240C elemental analyzer. The thermal analyses were carried out using a Mettler Toledo TGA–DTA 85 thermal analyzer under a flow of N_2 (30 ml/

min). The sample was heated at a rate of $10^\circ\text{C min}^{-1}$ with inert alumina as a reference. The electronic spectra were recorded by Shimadzu UV-2401PC spectrophotometers and IR spectra were measured on Nicolet Impact 410 spectrometer between 400 and 4000 cm^{-1} , using the KBr pellet method. Low temperature and high temperature DSC analyses were carried out using DSC 204 F1, NETZSCH at nitrogen atmosphere. The sample was first cooled from room temperature to -80°C and followed by heating to room temperature at a rate of $10^\circ\text{C min}^{-1}$.

Synthesis of complex $[\text{La}(1,10\text{-phen})_2(\text{NO}_3)_3]$

5 ml aqueous solution of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1.08 g, 0.0025 mol) was added drop-wise to 5 ml methanolic solution of 1,10-phen (0.90 g, 0.005 mol). The resulting solution was filtered off. Colorless single crystals started to appear and were collected by filtration and dried. Fig. S1 depicts image of the crystal recorded by polarizing microscope. Anal. calc. (%) for $\text{C}_{24}\text{H}_{16}\text{LaN}_7\text{O}_9$: C: 42.06; H: 2.35; N: 14.31. Found (%): C: 42.02; H: 2.39; N: 14.36. IR (KBr, cm^{-1}): 33507br, 3062vw, 2836vw, 1625s, 1592s, 1575s, 1470m, 1385s, 1292m, 1102m, 1027w, 843m, 730w, 637w.

Crystallographic data collection and refinement

Suitable single crystal of the complex was mounted on a Bruker SMART diffractometer equipped with a graphite monochromator and Mo $\text{K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. The single crystal data of the complex have been recorded at 100 K and 293 K. The structures were solved by Patterson method using the SHELXS97 software. Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the non-hydrogen atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and their displacement parameters were fixed to be 1.2 times larger than those of the attached non-hydrogen atom. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least squares refinement. All calculations were carried out using SHELXS 97 [33], SHELXL 97 [34], PLATON 99 [35], ORTEP-32 [36] and WinGX software Ver-1.64 [37]. Data collection, structure refinement parameters and crystallographic data are given in Table 1. Selected coordination bond lengths, bond angles and non-covalent interaction parameters are presented in Tables S1–S6.

Computational details

Full geometry optimization of the structures obtained at 100 K and 293 K were carried out in singlet state using Gaussian 09 software package [38]. For this particular purpose the analytical gradient methods of DFT with Becke’s three parameters (B3) exchange functional together with the Lee–Yang–Parr (LYP) non-local correlation functional (symbolized as B3LYP) was employed. We have chosen LANL2DZ basis set with effective core potential and the HOMO–LUMO energy gap has been determined at the same level.

Result and discussion

Crystal structure description of the complex at 100 K

According to the results of X-ray single crystal structural study, the complex has monoclinic structure with $P2_1/c$ space group at 100 K. Each asymmetric unit consists of one La^{3+} ion, three nitrate anions and two 1,10-phenanthroline moieties, as shown in Fig. 1. Each lanthanide ion is 10 coordinated. For $\text{La}(\text{III})$ ion, four N donor atoms (N1, N2, N3 and N4) of two different phen ligands, six

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