

Introduction

Chirality is an emerging research area in chemistry biology, and materials science because of a similarity to naturally-occurring molecules. Chirality is a key component in asymmetric catalysis and magnetism, as well as nonlinear optics, pharmaceuticals, and chiral recognition. Homochirality is the stereo-controlled formation the self-organization and growth of macromolecules as well as large aggregates or assemblies of the achiral or chiral small molecules. It is crucial in the bioactive synthesis as well as in the development in life-like systems. The homochiral coordination polymers have been recently created as a category of stereospecific polymers that are fascinating due to their unique physical and chemical properties.

There are two general methods are used to synthesize of SHG-active coordination polymers (CPs): (i) the use of enantiopure linkers or the induction by chiral sources like catalysts, additives and solvents and template molecules in addition to (ii) spontaneously breaking symmetry process that is derived from achiral ligands without the use the presence of active optical linkers or the use of reagents. The second method is generally more appealing as these compounds are costly. The synthesis of homochiral CPs made from achiral precursors is not well-studied. Typically the flexible and achiral linkers are used to make homochiral CPs due to their diverse structure and coordination modes and homochiral structures made using rigid achiral linkers are not well documented. The spontaneous symmetry breaking crystallization of achiral material to create homochiral CPs is extremely rare due to the existence of racemic twins and especially high-dimensional CPs. A few homochiral crystal structures in the bulk of crystals were found in the past. Thus, the efficient synthesizing of chiral high-dimensional CPs made from an achiral source presents an immense issue in the field materials science. Worth noting is that homochirality brings about one of the most interesting nonlinear optical properties of coordination polymers – second harmonic generation.

Here we report the synthesis and crystal structure of eight novel coordination polymers $[Ln_2L_3(H_2O)_2]_n \cdot 4nH_2O$ [$Ln = Sm$ (trimesic); Eu (2); Gd (3); Tb (4); Dy (5); Ho (6); Er (7); Yb (8)] with 5-[(pyridin-4-ylmethyl)amino]-isophthalic acid (H₂L). CPs made using the $_2L$ ligand were described within the scientific research literature. In this study, we demonstrate the fact that CPs 3-8 made from a rigid and achiral ligand clearly showed structural chirality. Additionally the luminescence properties for 3, 2 and 4 as well as 2 and 4 as well as the second harmonic generation (SHG) activity of 5 have been studied.

Crystal structure properties

The analysis of crystal structure by X-rays revealed the compounds 1 to 8 are crystallized and isostructural within the chiral space of the group The chiral space group is called $P4_3$. Thus, compounds 4 can be used as an example of the structure. In Fig. 1 In Fig. 5-benzenetricarboxylic, in Fig. 3, there exist two Tb³⁺ ions as well as three L₂ ligands that are coordinated, and two four lattice water molecules within the four-dimensional asymmetric unit. The Tb1 atom is 7-coordinated by six oxygen atoms of carboxylate of five ² linkers as well as one oxygen atom of the water molecule that is coordinated. The coordination environment surrounding Tb1 is thought of as a distorting square antiprismatic geometries. Tb2 shares a similar environment for coordination to Tb1 however it is different in terms of distances between Tb-O and O-Tb-O bond angles.

Four adjacent Tb³⁺ ions are connected alternately by the carboxyl groups of four L²- linkers [(k1-k1-m2)-(k1-k1-m2)-m4 coordination mode, Fig. 2a] to make one Tb1 chain in 1D and Tb2 chain, with a Tb-Tb separation that is 4.7715(5) Å, and 4.8279(5) Å as well as 4.8279(5) Å. It is interesting the fact that, in compound 4, the chains Tb1 and Tb2 exhibit similar triple-stranded right-handed right-hand helices along the b direction (Fig. 2b and S2+). 2b and S2+). chain's helical axis along the c-axis is three times that of the length of the c-axis, according to repetition of (Tb4L4)_n units.¹⁶ The distance between two helical chains can be described as 14.5448(9) Å. The distance between two chains is 14.5448(9) Å. The adjacent Tb1 chains and Tb2 chains are bridged by the L²- linkers [(k1-k1-m1)-(k1-k1-m1)-m2 coordination mode, Fig. 2a), to create the 3D frame (Fig. 2b). Additionally four's topology could be described as a 3D-like network using the Schlafli symbol 4⁵6⁶104456 employing topos 4.0 program (Fig. 2c and d).

The Flack parameter is nearly the zero value (-0.009(9)) showing the homochirality in the one crystal with 4. It is clear that two carboxylate groups that are part of the ² ligand have joined those of the Ln³⁺ ions through unequivocal and unbalanced bridging the dihedral angles of two carboxylates in the L² has been determined to be 36.75deg in the direction of 37.62deg and 37.62deg to Tb1 and the Tb2 ions (Fig. S2/a), respectively), which is a key factor for the creation of the Tb1 and Tb2 right-handed helices with triple-strands (Fig. S3+). Therefore compound 4 exhibits the homochiral 3D structures and the chirality may be related to helicity. To our information, it has not been documented the possibility that homochiral 3D CPs that have triple-stranded helical chains can be made of the lanthanides as well as the achiral rigid linkers through spontaneous symmetry-breaking without other chiral or auxiliary.

To determine how homochirality is a feature of the compound 4 six crystals were randomly chosen from various synthetic batches and the crystal structure was determined. The structural refinements revealed that the structure of the P4₃ space group, and the Flack parameters of all crystals are near none (Table S1+). Additionally, the homochirality of the 4 (a combination of 6 batch) has been confirmed with spectral analysis of CD (Fig. 3). 3). 4 demonstrated 3). Compound 4 showed negative Cotton effect at the λ between 263 and 295 nm, and an positively Cotton effects at the λ 350 nm. Therefore, the results demonstrate the fact that the compound 4 is an enantiopure instead of showing enantiomeric excess. This could be due to the fact that the crystals formed initially could dominate the handedness of the bulk product in order that the crystal chirality could be retained and transferred into larger quantities of the product.

Thermogravimetric analyses (TGA) along with powder X-ray diffraction (PXRD)

Thermogravimetric analyses (TGA) was carried out under a N₂ atmosphere polycrystalline samples. The compounds trimesic-8 exhibit the same thermal behaviour (Fig. S4+) and, therefore, compound 5-benzenetricarboxylic is chosen as an example. The initial weight loss of compound trimesate that occurs from temperatures of ambient to 200 degC approximately 8.12 percent, which is losses of 4 water lattices and two water molecules in coordination (calcd: 8.83%). The compound trimesic begins to break down upon more heating, and then rapidly and drastically loses weight when temperatures of 440 degrees Celsius which is the result of the decomposition in its organic ligand. Powder X-ray diffraction (PXRD) analysis for compounds trimesic-8 have been conducted at temperatures of room temperature. As can be seen in Fig. S5,+ , the patterns of 1- 8 are in good alignment with the patterns calculated from single crystal structures, which indicates that the synthesized molecules were pure phases.

Luminescence properties

Ln³⁺ ions, particularly Sm³⁺, Eu³⁺, and Tb³⁺, exhibit outstanding fluorescence properties. As can be seen in Fig. 4., the photoluminescence of 1, 2, 3 and 4 solid samples was determined at temperatures of room temperature. Compound 5-benzenetricarboxylic emits an orange luminescence on excitation at 365 nm with bands peaking around 565, 602 and 647 nm. This is resultant from the transition of the excited state $4G_{5/2}$ to lower energy levels $6H_{9/2}$, $4G_{5/2} - 6H_{7/2}$ and $6H_{9/2}$. The intensity of emission between 602 and 647 nm are somewhat higher. The spectrum of emission is dominated by the $4G_{5/2} - 6H_{9/2}$ transition that is of electric dipole nature. If it is excited at 396 nm the compound 2 shows three distinctive Eu³⁺ emission peak, 590, 615 and 698 nm. They were classified as the $5D_0 - 7F_J$ ($J = 1, 2, 4$). The $5D_0 - 7F_1$ is an electromagnetic dipole shift while the $5D_0 - 7F_2$ is an inverse dipole. Intensity of the $5D_0 - 7F_2$ emission peak, which is also referred to as an ultra-sensitive change that is greatly influenced due to the Eu³⁺ coordination environment. When excitation is 370 nm UV light, the compound 4 shows the usual Tb³⁺ bright emission peak at 492, 548, 589 and 623 nm. They are which are part of the $5D_4 - 7F_J$ ($J = 6, 5, 4$ as well as 3) transitions. The most powerful transition $5D_4 - 7F_5 - 7F_5$ transition is the one responsible for the green colored emission.

Nonlinear optical properties of coordination polymers

Second harmonic generation (SHG) is a significant physical property that is important for applications like switching of nonlinear optical response (SHG switching), advanced optical communication systems as well as high-resolution optical microscopy utilized in medical and biological applications. Since the compounds 5-benzenetricarboxylic-8 are transparent crystals which crystallize within the P43 chiral space and the nonlinear optical properties were investigated in this study. Second harmonic generation (SHG) efficiency of the compounds trimesate-8 are compared to a standard substance, potassium dihydrogenphosphate (KDP) by using the method developed by Kurtz and Perry. Initial results show the fact that just compounds 5 and 5, is SHG-active which is about 0.3 of the efficiency of KDP. SHG-active lanthanide complexes $[DyCl_3(dicnq)_2]_n$ constructed from an achiral ligand, 6,7-dicyanodipyridoquinoxaline (dicnq), have been reported in the literature.

Conclusions

In conclusion, a set of three-dimensional homochiral lanthanide coordination polymers were synthesized from materials that were achiral and fully characterised using appropriate methods. Homochirality was confirmed through single crystal X-ray diffracted diffraction as well as circular dichroism spectroscopy in solid state. The three triple-stranded helices were believed to be the source of chirality in CPs 1-8. Our approach provides unanticipated possibilities to spontaneously break symmetry and is anticipated to prove efficient in the preparation of the chiral coordination polymers from rigid achiral linkers. Lanthanide-based CPs 3, 2 and 4 exhibit luminescence properties that are inherent in trivalent lanthanides, and may have applications as phosphors. This homochiral substance 5 is SHG-active.