Construction of a Noncentrosymmetric Luminescent Coordination Polymer from [BaL₃] Unit (L = Pyridine-2,6-dicarboxylate Acid) and Li(I) Ion

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Summary of main observation and conclusion  This work presents the synthesis, crystal structure and properties of a novel noncentrosymmetric (NCS) coordination polymer (CP), namely, (Me₂NH₃)₃[BaLi(2,6-PyDC)(H₂O)] (1) (2,6-PyDC = pyridine-2,6-dicarboxylate acid), which represents the first example of BaLi-CPs with 2,6-PyDC ligand. Single-crystal X-ray structural analysis reveals that the compound features a two-dimensional (2D) layered structure. The simplified structure of each layer belongs to the hcb topology. The second harmonic generation (SHG) response of 1 is about 0.5 times that of KH₂PO₄ (KDP) marker. What is more, 1 emits bright blue light upon the excitation of 365 nm UV light with the quantum yield (QY, Φ) of 1.63%. The successful construction of this compound convinces the feasibility of constructing NCS CPs via the combination of [BaL₃] unit and Li(I) ion.

Background and Originality Content

Coordination polymers (CPs) as a category of inorganic-organic hybrid materials can be embedded with diverse functionalities.¹ Compared with single-metal CPs, heterometallic CPs (HCPs) that contain more than one kind of metal ion could bring new structural types thus having more possibilities for new properties and improved performance.² While noncentrosymmetric (NCS) materials have presented increasing importance in the areas of optical switches, telecommunication, and information storage, due to their inherent properties such as nonlinear optics (NLO), pyroelectricity, piezoelectricity and ferroelectricity.³ Noticeably, the explosive research of CPs in recent years also contributed a lot to the solution for the challenging task of constructing NCS structures.²⁴

In our previous studies, we developed a feasible strategy to fabricate NCS CPs by the collaboration of heterometallic ions, e.g., Sr/Ba and Li with N-containing functional ligands.⁵ This strategy takes advantage of two aspects, that is, the NCS nature of the coordination polyhedra of Sr/Ba and Li heterometal ions with N-containing functional ligands, and the tendency of this combination to form high-dimensional (2D or 3D) structures, which may facilitate the effective transmission of the NCS nature to the whole structure.

On the basis of our previous NCS strategy, we try to go further in this contribution. Pyridine-2,6-dicarboxylate acid (2,6-PyDC) as a widely used ligand to construct CPs, exhibits special coordination ability because the pyridine N atom together with the –COO groups in both sides could strongly chelate a metal ion in a characteristicedly tridentate mode. Moreover, when meeting the metal ions with high coordination numbers, a “fan-like” unit [ML₃] (L = 2,6-PyDC) forms usually as a typical molecular building block in many CPs.⁶ In such unit, the metal ion is nine-coordinated by three 2,6-PyDC ligands, each of which is in tridentate mode. Obviously, the unique “fan-like” unit is noncentrosymmetric without an inversion centre. The Ba²⁺ ion with a large ionic radius presents usually high coordination numbers of eight to ten,⁶ which is suitable for acting as the metal centre of [ML₃] unit. However, the [BaL₃] unit has not ever been fabricated before. On the other hand, the Li ion is usually tetrahedrally or five coordinated, which rejects a centrosymmetric configuration. Thus, we anticipate that the fabrication of the two noncentrosymmetrically structural units, [BaL₃] and Li, will give rise to NCS CPs with a high chance.

With this scheme in mind, we synthesized successfully a HCP compound with chiral thus NCS structure using the solvothermal method, namely (Me₂NH₃)₃[BaLi(2,6-Py DC)(H₂O)] (1) (Scheme 1). Compound 1 represents the first example of BaLi-CPs constructed from 2,6-PyDC ligand. The structure of 1 features a 2D layered network, which is special in that the [BaL₃] units and Li ions are interlinked to form left-handed helical chains, which are further interlinked in a parallel fashion along the ab plane to form a single layer. Thus, in 1, the NCS nature of the structural units is effectively transmitted to the final structure, which convinces preliminarily the feasibility of this “[BaL₃] + Li” strategy to yield NCS CPs. The second harmonic generation (SHG) measurement shows that the SHG of 1 is about 0.5 times that of the KDP standard. In addition, the fluorescent experiments show that compound 1 emitted a ligand-centred bright blue light under UV radiation with a quantum yield (QY, Φ) of 1.63%.

Scheme 1 Known knowledge and conceptual advance of this contribution

(a) Reported results:

[M(2,6-PyDC)₃] unit → functional coordination polymers

(M = Ln, TM, Ca, Sr)

(b) This work:

[Ba(2,6-PyDC)₃] unit + Li⁺ → (Me₂NH₃)₃[BaLi(2,6-PyDC)(H₂O)]

noncentrosymmetric luminescent coordination polymer

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Results and Discussion

Crystal structure

The structure of 1 belongs to the chiral $P2_1$ space group featuring a 2D layered anionic network with $[\text{Me}_2\text{NH}_3]^+$ acting as counter ions. The asymmetric unit of 1 contains one formula unit including one $\text{Ba}^{2+}$ ion, one $\text{Li}^+$ ion, three 2,6-$\text{PyDC}^-\text{H}_2$ ligands, one terminal water molecule and three $[\text{Me}_2\text{NH}_3]^+$ cations. As shown in Figure 1a, the nine-coordinated $\text{Ba}^{2+}$ ion is occupied by three chelated 2,6-$\text{PyDC}^-\text{H}_2$ ligands to give rise to a chiral fan-like $[\text{Ba}_{12}(2,6-$PyDC$\text{H}_2)_3]^+$ unit. This type of $[\text{M}(2,6-$PyDC$\text{H}_2)_3]^+$ unit has been proved to be a successful building block to construct functional coordination polymers.\(^{[10]}\) like in magnetism,\(^{[11]}\) luminescence,\(^{[11]}\) photocatalysis.\(^{[12]}\) The tetrahedrally coordinated $\text{Li}^+$ ion is coordinated by three carboxylate O atoms from three 2,6-$\text{PyDC}^-\text{H}_2$ ligands and one O atom from a $\text{H}_2\text{O}$ molecule. Three unique 2,6-$\text{PyDC}^-\text{H}_2$ ligands adopt three different coordination modes (Figure S1c).

As shown in Figure 1, the construction of the chiral framework of 1 could be described as follows. Firstly, the two NCS units of $[\text{Ba}_{12}]$ and $\text{Li}$ (Figure 1a) are interlinked with each other to form left-handed 2 helical chains with a pitch of 11.55 Å along the $b$ axis (Figure 1b). Then, these chains are interconnected with each other in a parallel fashion within the $ab$ plane to form a 2D layer, in which both units could be viewed as three-connected nodes (Figure 1c). Finally, upon molecular interactions, the adjacent layers are accumulated in a way that rejects the inversion centre resulting in the final NCS structure of 1 (Figure 1d). To gain a more clear view of the structural type of 1, the simplified structures (also known as the topology) are shown in Figure 2. What’s more, an alternative way of structural description of 1 is presented in the electronic supplementary information (ESI). From the step-by-step analysis of the structure, we can conclude that the combination of the two unique NCS units of $[\text{Ba}_{12}]$ and $[\text{LiO}_3]^-$ could be a potential way to obtain NCS CPs with a high chance.

PXRD and thermal stability analysis

The phase purity of compound 1 was confirmed by PXRD (Figure S3) and elemental analyses. As shown in Figure S4, compound 1 began to lose weight at about 260 °C, with a slight weight loss of 2.8% till about 305 °C, which could be ascribed to $\text{H}_2\text{O}$ molecules coordinated to Li ions (2.3%). Then a sharp weight loss of 31.7% in the region of 305—335 °C appeared, which is much larger than the calculated ones of guest $\text{Me}_2\text{NH}$ groups (17.0%), indicating the releasing of guest molecules was accompanied by the process of pyrolysis of the 2,6-$\text{PyDC}^-$ ligand. Without any platform, the decomposition of ligand and thus degradation of the framework continued in the temperature range from 335 to 800 °C.

Luminescent properties

The photoluminescence (PL) properties of compound 1 and 2,6-$\text{PyDC}^-\text{H}_2$ ligand in the solid state were investigated at room temperature. As shown in Figure 3a, the emission bands of 1 and 2,6-$\text{PyDC}^-\text{H}_2$ ligand are centred at 415 and 423 nm excited by 317 and 370 nm wavelengths, respectively, both locating in the blue region as illustrated in the CIE chromaticity diagram (Figure 3b). The quantum yield (QY) value of 1 is 1.63%. Considering the elec-

Figure 2  Simplified view of the structure of 1 by linking $\text{Ba}^{2+}$ and $\text{Li}$ metal nodes. (a) A single layer showing the screw axes in yellow, (b) packing of the layers. Gray lines represent the linking between adjacent helical chains within each layer.

Figure 3  (a) Solid-state fluorescence spectra of compound 1 and the free ligand at room temperature. The solid and dashed lines represent the emission and excitation spectra of each compound, respectively. (b) CIE chromaticity diagram of the emission colors of compound 1 and 2,6-$\text{PyDC}^-\text{H}_2$ ligand. Inset is the photograph of 1 under 365 nm UV light.
tronic configuration of Ba\(^{3+}\)/Li\(^+\) ions, the PL of 1 shall probably be assigned to the ligand–centered (intraligand, π→π*) emission.\(^{[13]}\) The blue shifted emission of 1 compared with free ligand should be attributed to the effectively increased rigidity of 2,6-PyDCH after the incorporation of the metal ions, which reduces the loss of energy via intramolecular vibrational and rotational motions.\(^{[14]}\)

Second-harmonic generation properties

The colourless nature of compound 1 endows it a large band gap of 4.0 eV, which is ideal for optical media materials (Figure 4a). Considering its NCS structural nature, the SHG response of 1 was investigated on the powder sample of 1 by using the Kurtz-Perry method.\(^{[17]}\) An approximate estimation was carried out on a pulsed Q-switched Nd:YAG laser at a wavelength of 1.064 μm. The intensity of the green light (λ = 532 nm) produced by the crystal powder is about 0.5 times that of a KDP marker in the same particle size (Figure 4b). The second-order susceptibility \(\chi_2^\text{eff}\) of a KDP powdered sample is about 0.36 pm/V, so the derived second-order susceptibility \(\chi_2^\text{on}\) for 1 is 0.18 pm/V.

Figure 4  (a) UV-vis absorption spectrum of 1. Inset is the crystal photograph of 1 under a microscopy. (b) Oscilloscope trace of the SHG signals of compound 1 and KDP in the particle size of 150—212 μm.

Conclusions

As an expansion of our previously developed heterometallic strategy to design NCS CP, we combined two NCS building blocks of [BaL\(_3\)] unit and [LiO\(_2\)] unit together to successfully obtain a NCS CP. The NCS nature of the two building blocks was effectively transmitted to the final structure in this fashion. This compound shows multi-functionalities of moderate SHG response and bright blue photoluminescence. Further work will continue to develop this feasible NCS strategy using other ions as building blocks.

Experimental

All analytical grade chemicals employed in this study were commercially available and used without further purification. Powder X-ray diffraction (PXRD) pattern was recorded in the angular range of 2θ = 5°—65° on a Miniflex II diffractometer using Cu Kα radiation. Thermogravimetric analysis was carried out with a NETZSCH STA 449F3 unit at a heating rate of 10 °C/min under a nitrogen atmosphere. Elemental analyses (EA) for C, H, N were performed on a German Elementary Vario EL III instrument. Fourier transform infrared (FT-IR) spectroscopy was taken on a Nicolet Magna 750 FT-IR spectrometer in the 4000—400 cm\(^{-1}\) region by using KBr pellets. Fluorescent emission and excitation spectra of the compounds were recorded on a PerkinElmer L555 luminescence spectrometer. The quantum yield of the compound 1 was determined using an integrating sphere with a Varian Cary 500 Scan UV-visible system. A BaSO\(_4\) plate was used as a standard (100% reflectance). The Powder SHG response was measured on a powdered sample by using the experimental method adapted from that reported by Kurtz and Perry.\(^{[17]}\) 1064 nm radiation generated by a Q-switched Nd:YAG solid-state laser was used as the fundamental frequency light (BaSO\(_4\)) coating from Edinburgh Instruments FLS920. Optical diffuse reflectance spectrum was measured at room temperature.

Compound 1 was synthesized by solvothermal method in a stainless steel reactor with a 28 mL Teflon liner and heated in the oven. The reaction of a mixture of Ba\(_2\)C\(_2\)O\(_4\), H\(_2\)O (77 mg, 0.32 mmol), LiNO\(_3\) (28 mg, 0.41 mmol), 2,6-PyDCH (107 mg, 0.64 mmol), 4 mL DMF and 0.5 mL water at 120 °C for 67 h resulted in colorless block-like crystals as a pure phase. The crystals were washed with anhydrous ethanol followed by drying in the air. The production was calculated based on 2,6-PyDCH ligand, yielding about 110 mg, 62%. C\(_2\)H\(_{18}\)N\(_3\)O\(_3\)BaLi: C, 40.75%; H, 4.43%; N, 10.56%; Found: C, 40.31%; H, 4.38%; N, 10.40%.

Suitable single crystal of compound 1 was carefully selected under an optical microscope and glued to a thin glass fiber. Data collection was performed on an Oxford Xcalibur Eos diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. The structure was solved by direct methods and refined by full-matrix least-squares on \(F^2\) by using the programs SHELX-2016.\(^{[18]}\) Non-hydrogen atoms were refined with anisotropic displacement parameters, and the hydrogen atoms attached to the C atoms were located at geometrically calculated positions, while those attached to the O atom of the terminal water molecule were added according to the difference-Fourier synthesis. The empirical formula was confirmed by the EA results. Crystallographic data and structural refinement parameters are summarized in Table S1.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.201800518.

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References


