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Manifestation of helicity in one-dimensional iodobismuthate†

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We report here, the first example of an inorganic–organic hybrid material incorporating a helical iodobismuthate $[\text{BiI}_4]_\infty$ templated by 2,6-diisopropylanilinium cations. The realisation of the helical iodobismuthate opens up the possibility of a wide range of physical properties among hybrid materials.

Iodobismuthates are an important class of halometalate anions in the area of hybrid materials.¹ In the last decade, they have been shown to exhibit optical, electrical, thermochromic and photochromic properties.² Very recently, in the area of photovoltaics, iodobismuthate compounds have emerged as alternatives to the environmentally toxic methylammonium lead halide.³ The structure and dimensionality of the iodobismuthates play a key role in determining the properties of the hybrid materials. While a large number of zero-dimensional discrete iodobismuthates are known, one-dimensional structures are relatively limited in number ($[\text{BiI}_4]^{1-}$, $[\text{BiI}_5]^{2-}$, $[\text{Bi}_2\text{I}_7]^{3-}$ and $[\text{Bi}_3\text{I}_{11}]^{2-}$).^{1,4} One-dimensional structures are known to exist either in linear⁵ or zig-zag form.⁶ However, helical structures have not been reported.⁷ Hybrid materials incorporating helical chains tend to crystallize in non-centrosymmetric space groups in many cases leading to non-linear optical and piezoelectric properties. Further, pyro and ferroelectric properties can be observed if the non-centrosymmetric space group is polar.⁸

Herein, we present the first example of a one-dimensional helical iodobismuthate $[\text{BiI}_4]$ chain templated by 2,6-diisopropylanilinium cation. $[\text{2,6-Diisopropylanilinium}][\text{BiI}_4]$ (**1**) (Fig. 1A) was obtained by the reaction between $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 2,6-diisopropylaniline and hydroiodic acid in methanol under aerobic conditions and crystallised from saturated methanol solution.† The stoichiometry of the reactants is crucial in

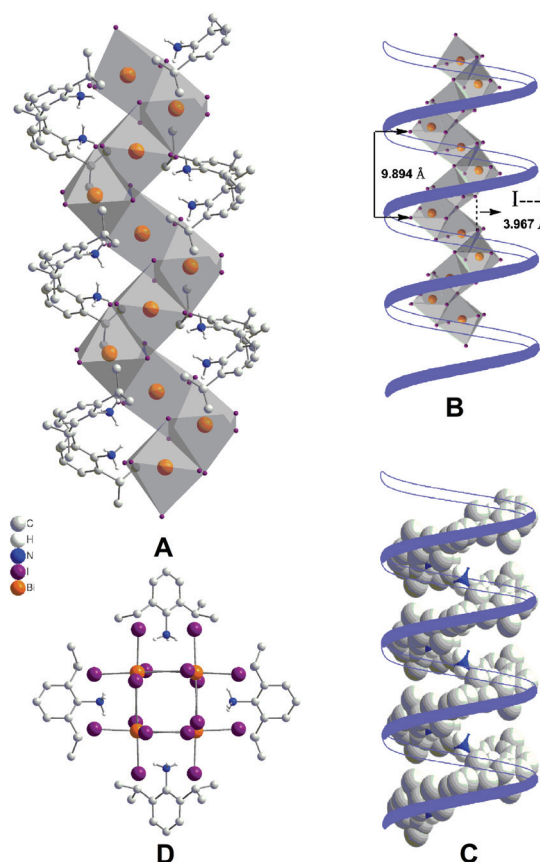


Fig. 1 (A) Solid state structure of **1**. Edge-sharing BiI_6 units have been represented as octahedra surrounded by 2,6-diisopropylanilinium cations; (B) representation of the $[\text{BiI}_4]_\infty$ helix in **1**; (C) space filling representation of the helical arrangement of cations; (D) view of **1** along the c -axis.

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† Electronic supplementary information (ESI) available: Experimental method and XRD data of **1** and **2**, TG plot of **1**, and experimental details of **2**. CCDC 1444434, 1444440, 1468858 and 1468859. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt01032f

obtaining the product. Excess of acid or the 2,6-diisopropylaniline results in $[\text{2,6-diisopropylanilinium}]_4[\text{BiI}_6][\text{I}]$ (**2**) (see the ESI, Fig. S1†).

The solid state structure of **1** (Fig. 1A) was elucidated by single crystal X-ray diffraction (XRD) studies. **1** crystallises in

an orthorhombic crystal system with the apolar non-centrosymmetric space group $C222_1$ and a Flack parameter of 0.059(7). The structure consists of a helical one-dimensional $[\text{BiI}_4]_\infty$ iodobismuthate chain whose charge is balanced by 2,6-diisopropylanilinium cations. It is noteworthy that **1** crystallises without the inclusion of solvent molecules in the crystal lattice. The Bi–I distances in each octahedron are in the range of 2.8823(11) to 3.3879(10) Å. The *cis* I–Bi–I angles are found in the range of 82.84(2) to 96.65(3)° while the *trans* I–Bi–I angles are in the range of 168.57(3) to 179.34(3)°.

The helical 1-D $[\text{BiI}_4]_\infty$ chain is formed by the sharing of two edges of each BiI_6 octahedron with the neighbouring ones. The pitch of the helix in the 1-D $[\text{BiI}_4]_\infty$ chain is 9.894 Å (Fig. 1B). Each turn in the helix consists of four BiI_6 octahedra. The arrangement of the edge sharing BiI_6 octahedra in the $[\text{BiI}_4]_\infty$ helix can be viewed as a repetitive ABCDA... type (A, B, C and D are BiI_6 octahedra). This structure differs from the conventional ABABAB... type of the BiI_6 octahedral arrangement in the literature known zig-zag 1-D $[\text{BiI}_4]_\infty$ chain.⁶ The helicity in the $[\text{BiI}_4]_\infty$ chain is stabilised by a weak I...I interaction of 3.968 Å as shown in Fig. 1B. Such weak inter-halogen interactions have been observed previously in the case of other iodobismuthate structures.⁹

2,6-Diisopropylanilinium ions are also arranged in a helical manner around the $[\text{BiI}_4]_\infty$ helix (Fig. 1C) and thus **1** is a double helix. The interaction between the anion and cations occurs *via* hydrogen bonding. Each nitrogen atom of the 2,6-diisopropylanilinium cation is located near five iodine atoms of four neighbouring BiI_6 octahedra of the iodobismuthate chain with a distance varying from 3.736 to 4.175 Å indicating the presence of hydrogen bonds. The role of the templating cation is an important factor in stabilizing the helical structure of **1**. The space filling representation of the 2,6-diisopropylanilinium ions shows that they effectively pack around the $[\text{BiI}_4]_\infty$ helix *via* hydrogen bonding. A related templating cation, 1-naphthylammonium cation, is known to stabilise only the zig-zag $[\text{BiI}_4]_\infty$ chain.^{6c} The role of the isopropyl groups in the 2,6-diisopropylanilinium cation may be one of the crucial factors to preserve the helical $[\text{BiI}_4]_\infty$ chain in **1**.

1 was further analysed by thermogravimetric analysis (TGA), elemental analysis, powder XRD studies and UV-Vis spectroscopy. In the crystalline form, **1** is stable under ambient aerobic conditions for several months and does not show any sign of decomposition. TGA analysis points out that **1** is stable up to 453 K (see the ESI, Fig. S2†). The purity of **1** was confirmed by elemental analysis and the crystallinity of the bulk sample was established by powder XRD studies (Fig. 2).

After elucidating the non-centrosymmetric helical structure of **1**, we were prompted to undertake a preliminary study of the physical properties. **1** exhibits an effective piezoelectric coefficient of 28.4 pC N^{−1}. The piezoelectric properties exhibited by **1** can be attributed to the internal strain in both the iodobismuthate and the templating cation. More investigations have to be performed in order to understand the piezoelectric tensors of **1**.

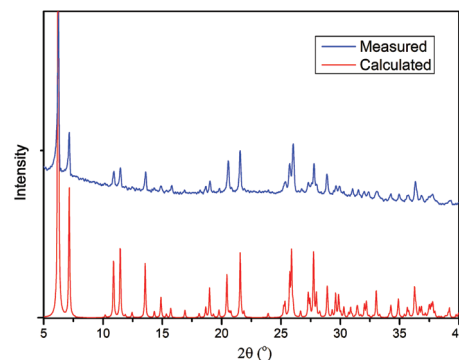


Fig. 2 PXRD pattern of **1** measured after several weeks stored under ambient conditions.

From the diffuse reflectance UV-VIS spectrum of **1**, a Tauc plot of Kubelka–Munk function¹⁰ vs. energy considering indirectly allowed transition was obtained (Fig. 3). The optical band gap in **1** was found to be 2.07 eV, which is one of the lowest values among the compounds bearing 1-D iodobismuthate chains.¹

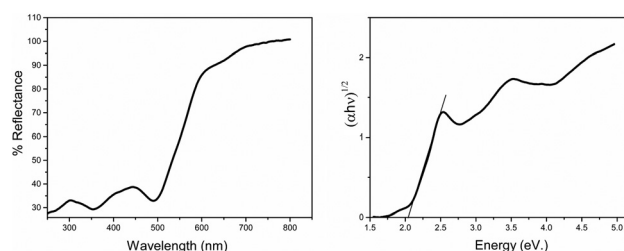


Fig. 3 Diffuse reflectance UV-visible spectrum of **1** (left) and the Tauc plots (right) determined from the diffuse reflectance spectrum showing the optical band gap of compound **1**.

1 exhibits thermochromic properties. In the solid state, at ambient temperature, **1** is dark red in colour. At 77 K, (liquid nitrogen) the colour changes to bright orange (Fig. 4). The origin of thermochromism in iodobismuthate compounds is attributed to either phase transitions or changes in interatomic distances.^{9d,6b,11} Single crystal diffraction studies of **1** at 296 and 85 K showed no changes in the cell parameters confirming the absence of phase transition. However, small changes in the interatomic distances were observed from the

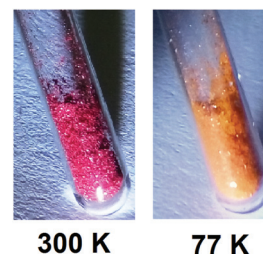


Fig. 4 Thermochromism exhibited by **1**; digital photographs of crystalline **1** at 300 K and 77 K.



single crystal XRD experiments at 296 and 85 K (Bi–I: 0.003–0.009 Å, Bi···Bi: 0.005–0.007 Å, N···I: 0.002–0.025 Å, I···I: 0.004–0.026 Å, ESI, Table T5, Fig. S3†).

In summary, an unprecedented inorganic–organic hybrid material possessing a $[\text{BiI}_4]_\infty$ helix has been obtained. The 2,6-Diisopropylanilinium cation plays a significant role in stabilising the helical structure of $[\text{BiI}_4]_\infty$. Preliminary investigations on **1** point out that it exhibits piezoelectric properties, a low optical band gap and thermochromism. Further studies on the physical properties of **1** are currently underway.

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Notes and references

† Synthesis of the $[\text{BiI}_4][\text{C}_{12}\text{H}_{20}\text{N}]$ (**1**): to a 10 mL MeOH solution of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.15 g, 0.3 mmol), 2,6-diisopropylaniline (0.05 g, 0.3 mmol) in 10 mL methanol was added under ambient laboratory conditions. This was followed by the addition of hydroiodic (1.2 mmol) acid. The turbid reaction mixture became red and clear upon completion of the addition of the acid. The reaction mixture was stirred for 12 hours at 50 °C, the solvent was removed under vacuum, the residue was washed with pentane and dried under vacuum (10^{-2} mbar) for a few hours. The compound was crystallised from a saturated methanol solution. Yield 72%. Elemental analysis calculated for $\text{C}_{12}\text{H}_{20}\text{NBiI}_4$ C 16.11, H 2.25, N 1.57 and found C 16.19, H 2.31, N 1.61. IR analysis: 3066(s), 2962(s), 2800(m), 1616(w), 1556(w), 1452(s), 1340(m), 1016(m), 794(s), 725(m), 499(m); crystal data for **1**: $\text{C}_{12}\text{H}_{20}\text{NBiI}_4$, $M = 894.87$, orthorhombic, $a = 17.363(2)$ Å, $b = 24.703(3)$ Å, $c = 9.894(1)$ Å. $\alpha = \beta = \gamma = 90^\circ$, $V = 4244.0(9)$ Å³, $T = 296(2)$ K, space group $C222_1$, $Z = 8$, 9052 reflections collected, 3734 independent reflections, ($R_{\text{int}} = 0.0244$). R_1 , wR_2 [$I > 2\sigma(I)$] 0.0280, 0.0557. R_1 , wR_2 [all data] 0.0436, 0.0607. The goodness of fit on F^2 was 0.872 and the Flack parameter was 0.059(7). CCDC number 1444434.

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