

Larger Spontaneous Polarization Ferroelectric Inorganic–Organic Hybrids: $[\text{PbI}_3]_\infty$ Chains Directed Organic Cations Aggregation to Kagomé-Shaped Tubular Architecture

Hai-Rong Zhao,^{†,‡} Dong-Ping Li,[§] Xiao-Ming Ren,^{*,†,‡} You Song,[§] and Wan-Qin Jin[‡]

State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing University of Technology, Nanjing 210009, P. R. China, College of Science, Nanjing University of Technology, Nanjing 210009, P. R. China, and State Key Lab & Coordination Chemistry Institute, Nanjing University, Nanjing 210093, P. R. China

Received September 7, 2009; E-mail: xmren@njut.edu.cn (X.M.R.)

The inorganic–organic hybrids and polar solid-state materials are two fertile topics of research, with the former capable of merging the advantages of the organic components (straightforward synthetic approach, easily tailored molecular structure, and functional properties) to those of an inorganic network (chemical, thermal, and mechanical stabilities) and the latter possessing technologically important physical properties from optics to electronics, such as second-order nonlinear optical (NLO),¹ pyroelectricity, ferroelectricity, and triboluminescence.^{2–4} Crystal engineering has exhibited remarkable power in the self-assembly of designed functional materials over the past three decades.^{1,5} Despite a great deal of progress in the syntheses of acentric structures,⁶ challenges still remain in the synthesis of noncentrosymmetric polar packing arrangements. Therefore, it is necessary to explore new molecular self-assemblies for functional materials and to understand the structure–property relationship at the molecular level.

The inorganic octahedral PbI_6 unit has been used to construct versatile crystal structures from one-dimensional (1D) chains to a three-dimensional (3D) framework via corner-, edge-, or face-sharing mode, dependent on the counteranion feature as well as the molar ratio between lead and iodide ions.⁷ It is noticeable that, when the molar ratio of Pb^{2+} and I^- ions is 1:3 and the counterions are large in size, it is possible to form a $[\text{PbI}_3]_\infty$ chain structure. 1D lead iodide compounds are of particular interest due to the significant excitonic, NLO, ferroelectric, and ferroelastic properties.⁸ However, relevant information regarding their structure–bonding–property relationship is still rare.⁷ In this context, we introduced four achiral and flexible Schiff base cations, 3-R-Benzylidene-1-aminopyridinium ($m\text{-RBz-1-APy}^+$; R = NO_2 , Br, Cl, or F),⁹ into inorganic $[\text{PbI}_3]_\infty$ chain systems and assembled four chiral hybrids, $[m\text{-RBz-1-APy}][\text{PbI}_3]$ (R = NO_2 (**1**), Br (**2**), Cl (**3**), or F (**4**)); each hybrid compound exhibits larger spontaneous polarization as well as the resonant type ferroelectric characteristic in its dielectric frequency spectrum.

Light yellow needle-shaped single crystals of **1–4** were obtained via a slow evaporation of DMF solution of the corresponding compounds at 40 °C, which are insoluble in common organic solvents and water. Thermogravimetric analyses show that **1–4** are thermally stable up to ca. 200 °C (Figure S4). X-ray structural analyses reveal that **1–4** crystallize in polar space group $P6_3$ (the noncentrosymmetric space groups are further confirmed by the activity of the second harmonic generation with approximate responses of 2 times that of urea for **1** and comparable to that of urea for **2–4**) and are isostructural with very similar cell parameters

as well as the packing structures, so that the only description for the crystal structure of **1** is given below (for **2**, **3**, and **4**, see Supporting Information).

An asymmetric unit of **1** contains three distinct Pb^{2+} ions and three distinct I^- anions with one organic cation (Figure 1). Each Pb^{2+} ion is six-coordinated with iodides and form two different chains (chain 1 and 2) running along the *c*-axis. For chain 1, Pb(1) and Pb(2) are holodirected and coordinated into a slightly distorted octahedron with six iodides, three I(1) and three I(2). The Pb–I bond lengths are in the range 3.2087(5)–3.2496(5) Å (Table S1) and comparable to the reported $[\text{PbI}_3]_\infty$ compounds.^{1,7} For chain 2, Pb(3) is also holodirected and coordinated into a nearly ideal PbI_6 octahedron with six I(3) iodides. The Pb–I bond lengths are in the range 3.2253(5)–3.2357(5) Å and similar to those of chain 1.

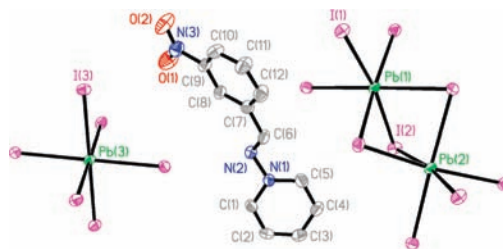


Figure 1. Asymmetric unit of **1** with non-H atomic labeling and the thermal ellipsoids at 30% probability (H atoms in the cation omitted for clarity).

Two types of highly polarizable $[\text{PbI}_3]_\infty$ chains are coupled to the hyperpolarizable organic cations by coulomb and van der Waals forces and direct the organic cations to adopt a Kagomé-like tubular architecture (Figure 2) that is collinear with the $[\text{PbI}_3]_\infty$ chains. The tubes exist in chiral forms because of the helical wind of the organic cations around the tube axis, and on the turning of the helix, the dihedral angle between the pyridyl and the phenyl rings of the cation is 51.40(24)°. Three infinite helical chains are associated in parallel to form the wall of a trigonal tube that are occupied by $[\text{PbI}_3]_\infty$ chain 1, and nine infinite helical chains are associated in parallel to form the wall of a hexagonal tube that are occupied by $[\text{PbI}_3]_\infty$ chain 2. The helical pitch, given by one full rotation around the helical axis, is 23.783 Å for the 3-fold helical chains and 71.349 Å for the 9-fold helical chains.

The hexagonal tube is stabilized by O(lone-pair)··· π interactions and further linked to six adjacent trigonal tubes via sharing organic cations to give rise to a 3D chiral framework with a Kagomé-shaped cross section (Figure S10 shows the N=O group of nitro is nearly orientated to the neighboring pyridyl ring with an O(1)··· π (centroid) distance of 2.990 Å and the interatomic separations of 2.976 and 3.016 Å for O(1)–N(1) and O(1)–C(1), respectively).

[†] State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing University of Technology.

[‡] College of Science, Nanjing University of Technology.

[§] Nanjing University.

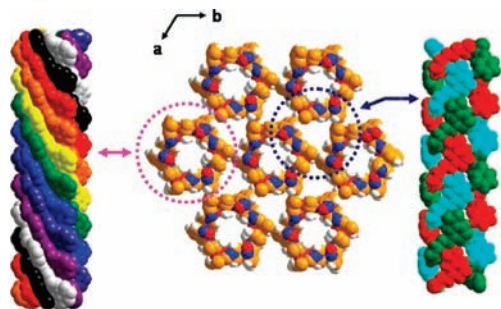


Figure 2. Space-filling representation of Kagomé-shaped supramolecular tube channel formation of organic cations as well as nonuple and triple stranded helices along $[\text{PbI}_3]_\infty$ chain 1 and 2, respectively, for **1**.

Since **1–4** crystallize in a chiral space group ($P6_3$) that belongs to a polar point group (C_6), their ferroelectric properties were examined. The single crystals of **1–4** were selected to measure the dielectric hysteresis loop on a ferroelectric tester (Radiant Technology), with electrodes made of Cu wire with an $\sim 150 \mu\text{m}$ diameter covered by Ag-conducting glue on the approximate crystallographic face (001), respectively. An electric hysteresis loop is observed (Figure 3) for **1–4** at room temperature; further the

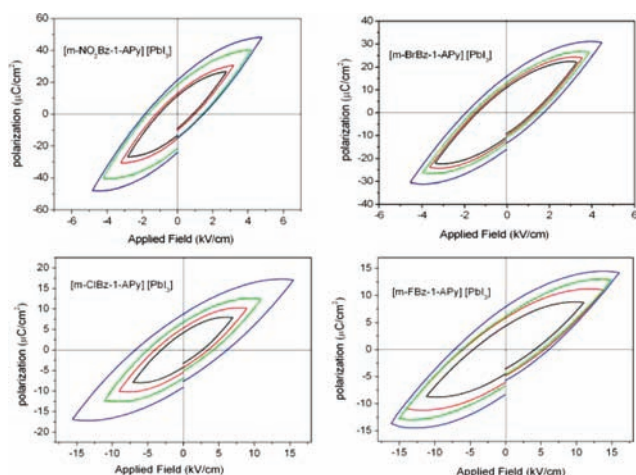


Figure 3. Dielectric hysteresis loops for **1–4** at room temperature.

extremely low leakage currents¹⁰ (10^{-8} – $10^{-10} \text{A} \cdot \text{cm}^{-2}$, Figure S6) demonstrate the observed hysteresis loops are clearly due to ferroelectricity. The applied electric field (E), spontaneous polarization (P_S), remnant polarization (P_r), and coercive field (E_c) for **1–4** are summarized in Table 1.

Table 1. Parameters for the Dielectric Hysteresis Loops of **1–4**

compound	$E/\text{kV} \cdot \text{cm}^{-1}$	$P_S/\mu\text{C} \cdot \text{cm}^{-2}$	$P_r/\mu\text{C} \cdot \text{cm}^{-2}$	$E_c/\text{kV} \cdot \text{cm}^{-1}$
1	4.8	48	21	1.49
2	4.5	30	16	1.75
3	15.5	17	8.75	6
4	15	12.8	6.17	5.18

The P_S and P_r values of **1–4** are much larger than those found in recently reported coordination polymers^{3,4a,b,10,11} and KDP ($P_S \approx 5.0 \mu\text{C}/\text{cm}^2$)¹² under a lower electric field. The P_S and P_r values of **1** and **2** are still larger than the spontaneous macroscopic polarization of BaTiO_3 ($P_S \approx 25 \mu\text{C}/\text{cm}^2$) and KNbO_3 ($P_S \approx 37 \mu\text{C}/\text{cm}^2$),¹³ and larger P_S and P_r values are probably due to the larger permanent dipoles of both organic cations and $[\text{PbI}_3]_\infty$ chains

as well as ionic displacement polarizations (ESI). Other arresting features for **1–4** are the resonant type ferroelectric characteristics in dielectric frequency spectra,¹⁴ which is a very rare case for the molecule-based ferroelectric materials, and multiple band emissions in the wide range of 350–620 nm (see ESI).

In summary, we have successfully assembled four isostructural and resonant type ferroelectric hybrid compounds, in which crystals of the inorganic $[\text{PbI}_3]_\infty$ chains direct the nonchiral organic cations to aggregate into chiral Kagomé-shaped channels via van der Waals forces. To the best of our knowledge, the P_S values for **1–4** are much higher than the reported coordination polymers as well as the typical ferroelectric BaTiO_3 and KNbO_3 . Additionally, such hybrid compounds show the high thermal stability, insolubility in common solvents and water, wide transparency range, and multiple band emission, which make them potential candidates for NLO, ferroelectric, and fluorescence multifunctional hybrid materials. Further investigations for the functional properties of these hybrids are in progress.

Acknowledgment. Authors thank State Key Laboratory of Materials Oriented Chemical Engineering, Nanjing University of Technology and NNSF of China (KL08-3 and 20871068) for financial support. X.M.R. thanks Prof. C. J. Fang for reading the manuscript.

Supporting Information Available: Crystallographic data in CIF format as well as the profiles of PXRD, TG, UV–visible, and emission spectra in solids for **1–4** in PDF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Guloy, A. M.; Tang, Z. J.; Miranda, P. B.; Srdanov, V. I. *Adv. Mater.* **2001**, *13*, 833–835.
- (2) (a) Chang, H. Y.; Kim, S. H.; Halasyamani, P. S.; Ok, K. M. *J. Am. Chem. Soc.* **2009**, *131*, 2426–2427. (b) Chang, H. Y.; Kim, S. H.; Ok, K. M.; Halasyamani, P. S. *Chem. Mater.* **2009**, *21*, 1654–1662.
- (3) Xu, G.; Li, Y.; Zhou, W. W.; Wang, G. J.; Long, X. F.; Cai, L. Z.; Wang, M. S.; Guo, G. C.; Huang, J. S.; Batorb, G.; Jakubas, R. *J. Mater. Chem.* **2009**, *19*, 2179–2183.
- (4) (a) Guo, Z.; Cao, R.; Wang, X.; Li, H.; Yuan, W.; Wang, G.; Wu, H.; Li, J. *J. Am. Chem. Soc.* **2009**, *131*, 6894–6895. (b) Zhao, H. X.; Zhuang, G. L.; Wu, S. T.; Long, L. S.; Guo, H. Y.; Ye, Z. G.; Huang, R. B.; Zheng, L. S. *Chem. Commun.* **2009**, 1644–1646. (c) Lang, S. B. *Phys. Today* **2005**, *58*, 31–36. (d) Horiuchi, S.; Tokura, Y. *Nat. Mater.* **2008**, *7*, 357–366. (e) Horiuchi, S.; Kumaia, R.; Tokura, Y. *Chem. Commun.* **2007**, 2321–2323. (f) Sage, I.; Bourhill, G. *J. Mater. Chem.* **2001**, *11*, 231–245. (g) Hardy, G. E.; Kaska, W. C.; Chandra, B. P.; Zink, J. I. *J. Am. Chem. Soc.* **1981**, *103*, 1074–1079.
- (5) (a) Radhakrishnan, T. P. *Acc. Chem. Res.* **2008**, *41*, 367–376. (b) Desiraju, G. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 8342–8356.
- (6) (a) Lacroix, P. G.; Clement, R.; Nakatani, K.; Zysy, J.; Ledoux, I. *Science* **1994**, *263*, 658–660. (b) Day, P. *Philos. Trans. R. Soc. London, Ser. A* **1985**, *314*, 145–158.
- (7) (a) Tang, Z.; Guloy, A. M. *J. Am. Chem. Soc.* **1999**, *121*, 452–453. (b) Wang, S.; Mitzi, D.; Field, C. A.; Guloy, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 5297–5302. (c) Billing, D. G.; Lemmerer, A. *CrystEngComm* **2007**, *9*, 236–244. (d) Bi, W.; Louvain, N.; Mercier, N.; Luc, J.; Rau, I.; Kajzar, F.; Sahrroui, B. *Adv. Mater.* **2008**, *20*, 1013–1017. (e) Louvain, N.; Mercier, N. *Solid State Sci.* **2008**, *10*, 1269–1275.
- (8) (a) Calabrese, J.; Jones, N. L.; Harlow, R. L.; Herron, N.; Thorn, D. L.; Wang, Y. *J. Am. Chem. Soc.* **1991**, *113*, 2328–2330. (b) Ishihara, T.; Takahashi, J.; Goto, T. *Phys. Rev. B* **1990**, *42*, 11099–11107. (c) Koutselas, B.; Mitzi, D. B.; Papavassiliou, G. C.; Papaioannou, G. J.; Krautscheid, H. *Synth. Met.* **1997**, *86*, 2171–2172. (d) Vanek, P.; Havrankova, M.; Hybler, J. *Solid State Commun.* **1992**, *82*, 509–512.
- (9) Yao, B. Q.; Sun, J. S.; Tian, Z. F.; Ren, X. M.; Gu, D. W.; Shen, L. J.; Xie, J. L. *Polyhedron* **2008**, *27*, 2833–2844.
- (10) Nakagawa, K.; Tokoro, H.; Ohkoshi, S. *Inorg. Chem.* **2008**, *47*, 10810–10812.
- (11) Zhang, W.; Xiong, R. G.; Huang, S. D. *J. Am. Chem. Soc.* **2008**, *130*, 10468–10469.
- (12) Zhao, H.; Qu, Z. R.; Ye, Q.; Abrahams, B. F.; Wang, Y. P.; Liu, Z. G.; Xue, Z. L.; Xiong, R. G.; You, X. Z. *Chem. Mater.* **2003**, *15*, 4166–4168.
- (13) Resta, R.; Posternak, M.; Baldereschi, A. *Phys. Rev. Lett.* **1993**, *70*, 1010–1013.
- (14) Pattnaik, R. K.; Toulouse, J. *Phys. Rev. B* **1999**, *60*, 7091–7098.

JA907562M