

Feature article

Auxiliary ligand-assisted two novel one-dimensional indium coordination polymers: Synthesis, crystal structures and photoluminescence characterization effected by solvent and temperature



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ABSTRACT

Two new indium coordination polymers (CPs) with mixed-ligand formulated as $\{[\text{In}(1,4\text{-bda})_{1.5}(\text{phen})] \cdot 2\text{H}_2\text{O}\}_n$ (**In1**) and $\{[\text{In}(1,4\text{-bda})(2,2'\text{-bipy})\text{Cl}]\}_n$ (**In2**) (1,4-H₂bda = 1,4-benzenedicarboxylic acid; phen = 1,10-phenanthroline; 2,2'-bipy = 2,2'-bipyridine) have been synthesized and characterized by single-crystal X-ray diffraction, infrared (IR), elemental analysis and thermal gravimetric analyses (TGA). **In1** exhibits one-dimensional (1D) ladder chain, which further forms three-dimensional (3D) structure with π - π stacking interaction. Formation of 3D compact supramolecular framework in **In2** is generated through C-H...Cl hydrogen bonding contacts and π - π stacking interaction. The photoluminescence (PL) characterizations to **In1** and **In2** affected by solvent and temperature are studied in detail. Thermogravimetric curves showed that **In1** and **In2** start to undergo phase transition until ca. 450 °C and 495 °C, respectively.

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Contents

Acknowledgments	34
Appendix A. Supplementary material	34
References	34

The exploratory synthesis and characterization of coordination polymers (CPs) resulted in fruitful researches in recent years [1], motivated by their potential applications as functional materials in selective adsorption and separation of organic molecules [2–4], catalysis [5], gas separation and storage [6–8], photochemistry [9–11], etc. Since the first report of organic light-emitting diodes fabricated from tris(8-hydroxyquinolinolate) aluminum (III) (Alq₃) in 1987 [12], group 13 complexes have attracted much attention due to their variety of structures, adequate electron transport, and luminescent properties [13–17]. Inspired by the prominent work of M. C. Hong, J. Zhang, O. M. Yaghi and their co-workers [18–21], we considered that indium is a good candidate for construction of CPs due to its larger ion radii, and more fascinating coordination properties than that of B, Al, and Ga. However, the

most challenging from the synthesis process, the recognized bottleneck, is hydrolysis of group 13 metal (III) salt [22]. Although plenty of CPs about transition metals and lanthanides have been reported, CPs incorporating the IIIA group trivalent elements like In(III) ion are less well synthesized [23]. In our research group, we have been engaging in the design of indium CPs, which have been proven to be active photoluminescent (PL) materials [24–26]. The synthesis, structure and characterization of two novel indium mixed-ligand CPs $\{[\text{In}(1,4\text{-bda})_{1.5}(\text{phen})] \cdot 2\text{H}_2\text{O}\}_n$ (**In1**) and $\{[\text{In}(1,4\text{-bda})(2,2'\text{-bipy})\text{Cl}]\}_n$ (**In2**) (1,4-H₂bda = 1,4-benzenedicarboxylic acid; phen = 1,10-phenanthroline; 2,2'-bipy = 2,2'-bipyridine) were reported in this paper. In **In1**, 1D ladder chains stacked to each other with π - π interaction to form 3D supermolecular structure. Compared to **In1**, the zigzag 1D chains in **In2** produce a more stable 3D supermolecular structure with vertical cross arrangement by C-H...Cl hydrogen bonds and π - π stacking interaction. Moreover, taking into account the different architecture of **In1** and **In2**, we studied the PL characterizations.

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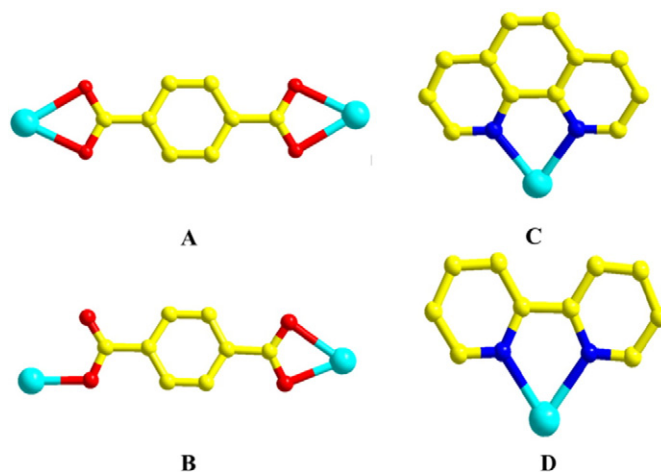
All of the syntheses were performed in 15 mL Teflon-lined stainless steel autoclaves under autogenous pressure. All reactants are of reagent grade and used as purchased commercially without further purification. Infrared spectra were obtained from KBr pellets using a Nicolet Avatar-360 Infrared spectrometer in a 4000–400 cm^{-1} region. Powder X-ray diffraction (PXRD) patterns were recorded in the 2θ range of 5–50° using Cu $K\alpha$ radiation by Shimadzu XRD-6000 X-ray Diffractometer. Elemental analysis was performed on a Perkin-Elmer 240c element analyzer. The thermal analysis was performed on a ZRY-2P thermogravimetric analyzer from 30 °C to 700 °C with a heating rate of 10 °C min^{-1} under a flow of air.

A mixture of $\text{In}(\text{NO}_3)_3$ (60.1 mg, 0.2 mmol), 1,4- H_2bda (16.6 mg, 0.1 mmol) and phen (18.0 mg, 0.1 mmol) was dissolved in distilled water (5 mL) and stirred at room temperature for 30 min. After that, it was transferred into a 15 mL Teflon-lined stainless steel autoclave and heated at 120 °C for 4 days. After slow cooling to room temperature, colorless rectangular block crystals of **In1** were obtained by filtration and washed with filter liquid (yield, 60%, based on 1,4- H_2bda). High quality rectangular blocks were chosen for the X-ray crystallography from the as-made samples. IR (KBr pellet, cm^{-1}): 3435 (br, s), 3063 (w), 2936 (w), 1698 (s), 1567 (s), 1401 (vs), 1277 (w), 1111 (w), 1019 (w), 851 (w), 723 (w), 524 (w). Anal. calcd for $\text{C}_{24}\text{H}_{18}\text{InN}_2\text{O}_8$: C, 49.89; N, 4.85; H, 3.12%. Found: C, 50.10; N, 4.91; H, 3.23%.

A mixture of InCl_3 (44.2 mg, 0.2 mmol), 1,4- H_2bda (16.6 mg, 0.1 mmol) and 2,2'-bipy (15.6 mg, 0.1 mmol) was dissolved in distilled water (5 mL). After stirring for 30 min in air at room temperature, it was transferred into a 15 mL Teflon-lined stainless steel autoclave and heated at 160 °C for 6 days. After cooling to room temperature slowly, the colorless crystalline solids were retrieved by filtration and washed with filter liquid (yield, 45%, based on 2,2'-bipy). High quality colorless crystal blocks were chosen for the X-ray crystallography from the as made samples. IR (KBr pellet, cm^{-1}) for **In2**: 3066 (br, s), 1677(w), 1554 (s), 1396 (vs), 1029 (s), 1157 (w), 1029 (w), 860 (s), 746 (s), 547 (w), 523 (s). Anal. calcd for $\text{C}_{18}\text{H}_{12}\text{ClInN}_2\text{O}_4$: C, 45.90; N, 5.95; H, 2.55%. Found: C, 46.10; N, 5.79; H, 2.46%.

The X-ray diffraction data taken at room temperature for **In1** and **In2** were collected on a Rigaku R-AXIS RAPID IP or a Siemens SMART 1000 CCD diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal structures were resolved by direct method and refined by Semi-empirical formula from equivalents and full-matrix least squares based on F^2 using the SHELXTL 5.1 software package [27]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions and refined by using a riding mode except water molecules. The CCDC 1012875 and 1012876 correspond to the crystallographic data of **In1** and **In2**, respectively, in this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/ deposit.

Hydrothermal methods are widely used in the syntheses of inorganic-organic compounds, especially when organic carboxylate ligands are applied. The powerful hydrothermal synthetic methods could enhance the solubility of ligand and obtain single crystals suitable for X-ray diffraction [28]. The 1D constructions of **In1** and **In2** were accomplished by introducing the N containing bidentate ligands phen and 2,2'-bipy into the reaction system, which may act as deprotonation reagents. Meanwhile, reaction temperature, time and counter anion show a remarkable influence on the final structure. **In1** was synthesized at a relatively low temperature (120 °C) with $\text{In}(\text{NO}_3)_3$. The 1D ladder infinite chain is formed by 1,4- bda^{2-} with $\mu_2-\eta^1:\eta^1:\eta^0$ and $\mu_2-\eta^1:\eta^1:\eta^1$ bridging mode (Scheme 1). After replacing $\text{In}(\text{NO}_3)_3$, phen with InCl_3 , and 2,2'-bipy, respectively, **In2** was synthesized at a higher temperature (160 °C), and formed 1D zigzag infinite chains with vertically staggered structure. Compared with **In1**, three synthetic strategies contribute to novel 1D staggered structure of **In2**: One is the use of InCl_3 as metal-salt, which could provide the chlorine atom coordinating to In(III) ion as terminal ligand. It is noted that the molar ratio of metal to ligand is important for the synthesis of **In2**. More In(III) salts (InCl_3) may be



Scheme 1. The coordination modes of 1,4- H_2bda , phen and 2,2'-bipy ligands in **In1** (A, B, C) and **In2** (A, D).

helpful for chloride atoms participating into the coordination to central In(III) ions. However, the molar ratio is not especially important for the synthesis of **In1**. When the molar ratio is 1:1:1, **In1** still can be obtained, only in a smaller amount. The second is the elevated temperature from 120 °C to 160 °C. At high temperature 160 °C, 1,4- bda^{2-} acts as a bridging ligand to link two adjacent In(III) ions only with chelating coordination mode and gives rise to 1D zigzag chain. The third one is the use of the neutral N containing ancillary ligand 2,2'-bipy in substitution for phen. Since the size of 2,2'-bipy is smaller than phen ligand, it could offer enough space for forming the vertically staggered arrangement of 1D chains and presents more stable and compact structure. The vertically staggered structure of **In2** is obtained also because the system evolves toward the thermodynamically preferred product. The two CPs are insoluble in common solvents such as toluene, n-hexane and dichloromethane, but soluble in dimethyl sulfoxide (DMSO), acetonitrile (CH_3CN), methanol (CH_3OH), and chloroform (CHCl_3).

The IR spectra of the CPs give supportive evidence toward a better understanding of the coordinating behavior of the ligands. The IR spectra of **In1** and **In2** are shown as Fig. S1. In the IR spectrum, the broad band at 3435 cm^{-1} indicates the presence of water molecules to **In1**. The bands at 3063 cm^{-1} for **In1** and **In2** are associated with the benzene ring stretching vibrations. The absence of strong absorption bands at 1720–1670 cm^{-1} in **In1** and **In2** indicates that the 1,4- H_2bda ligand adopts the completely deprotonated 1,4- bda^{2-} form, which is consistent with the X-ray structural analysis. The asymmetric stretching vibrations (ν_{as}) and symmetric stretching vibrations (ν_{s}) of carboxylate groups are observed in the ranges from 1567 to 1532 cm^{-1} and 1428 to 1369 cm^{-1} , respectively [29]. Weak bands in the region of 546–508 cm^{-1} are observed in the spectra of CPs, which are assigned to $\nu(\text{In}-\text{N})$ and $\nu(\text{In}-\text{O})$ stretching vibrations [30]. These results are coincident with the crystal structure analysis.

Single-crystal X-ray crystallography reveals that **In1** crystallizes in a monoclinic $C2/c$ space group and forms a 1D ladder chain structure (Table S1). The asymmetric unit consists of one independent In(III) ion, one and a half 1,4- bda^{2-} anions, one coordinated phen molecular, and two free water molecules, which are omitted for clarity (Fig. 1a). Selected bond distances and angles are provided in Table S2. The In(III) ion is seven-coordinated with five carboxyl oxygen atoms (O(1), O(3), O(4), O(5), O(6)) from three 1,4- bda^{2-} anions, two nitrogen atoms (N(1), N(2)) from one phen molecule, forming a slightly distorted pentagonal bipyramid geometry $\{\text{InO}_5\text{N}_2\}$ (Fig. 1b). The In–O bond lengths are in the range of 2.094(4)–2.643(6) Å, meanwhile, In–N bond lengths are 2.266(5) and 2.297(5) Å, respectively. The O–In–O bond angles are ranging from 56.61(7) to 162.96(7)°, and the N–In–N bond angle is 72.36(8)°. These distances and angles are generally intermediate

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