

A series of novel indium complexes derived from aromatic carboxylic acids: Hydrothermal syntheses, crystal structures, supramolecular networks and fluorescent properties



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ABSTRACT

Five new compounds with mixed-ligand formulated as $(H_4bptc)(phen)$ (**1**), $[In(phen)_2Cl_2](H_4bptc)(NO_3)(H_2O)$ (**2**), $[In(Hbptc)(phen)(H_2O)]_2$ (**3**), $In(2,6-pydc)(phen)(H_2O)Cl$ (**4**), and $\{[In(2,6-pydc)(Ox)_{0.5}(H_2O)_2](H_2O)_2\}$ (**5**) have been synthesized under hydrothermal conditions. Compounds **1–5** display white, green and blue fluorescence at 298 K in the solid state, respectively. It is shown that **1** assumes solvent-dependent photoluminescence. By contrast, the different polarities of solvents do not alter the luminescence position of **3** and **5**. The thermogravimetric curves show that binuclear compounds **3** and **5** have excellent thermal stability, whose structures are stable up to 190 and 272 °C, respectively.

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Since the first synthesis of a metal–organic complex, transition and lanthanide metal organic complexes have dominated the field of metal–organic materials. After tris(8-hydroxyquinolinolato) aluminium(III) (Alq_3) discovered as electro-luminescent material was applied in organic light-emitting diodes (OLEDs) [1], there have been growing interests to design and develop group 13 metal chelates emitting different colors [2]. We considered indium to be a good candidate for constructing complex due to the larger ion radii, more fascinating coordination properties and hypotoxicity among Group 13 elements. However, most challenges from synthesis process are the recognized bottleneck of In(III) salt hydrolysis [3]. As an important multidentate O and N-donor ligand, 2,6- H_2pydc (2,6-pyridine dicarboxylic acid), with a rigid 120° angle between the central pyridine ring and the two carboxylate groups, is a versatile ligand, and could provide various coordination modes [4]. H_4bptc (3,3,4,4-benzophenonetetracarboxylate), a flexible tetracarboxylic ligand is also worth to be introduced based on the following considerations: First, there are multiple bridging carboxylic groups, which may provide a variety of connection modes with metal centers [5]. Second, the relative flexibility around the ketone group can also generate different torsion angles between the two phenyl planes and the carboxylic groups, resulting in formation of different structures. Finally, deprotonation of H_4bptc may be affected by pH values, which will again have a significant influence on structure [6].

In this paper, we report five compounds $(H_4bptc)(phen)$ (**1**), $[In(phen)_2Cl_2](H_4bptc)(NO_3)(H_2O)$ (**2**), $[In(Hbptc)(phen)(H_2O)]_2$ (**3**), $In(2,6-pydc)(phen)(H_2O)Cl$ (**4**), and $\{[In(2,6-pydc)(Ox)_{0.5}(H_2O)_2](H_2O)_2\}$ (**5**) ($phen = phenanthroline$, $H_2Ox = oxalic acid$) prepared under hydrothermal synthesis. To the best of our knowledge, complexes **2** and **3** are the first examples of the In(III) complexes based on the H_4bptc ligand. Compounds **1–5** are characterized by single-crystal X-ray diffraction (Table S1–S6), 1H NMR and infrared (IR) analysis (Fig. S1–S6). The PXRD pattern (Fig. S7–S11) closely match the simulated patterns generated from the results of single crystal diffraction data. In compounds **1–5**, the discrete monomers are held together by hydrogen bonding and π – π interactions to form two-dimensional (2D) or three-dimensional (3D) topological structures (Table S7).

The result of single-crystal X-ray diffraction analysis reveals that the asymmetric unit of **1** contains one H_4bptc and one phen molecule (Fig. 1a). Two adjacent H_4bptc units link with each other through O6–H6–O4 forming the centrosymmetric dimeric [graph set: $R_2^2(26)$]. With 28-membered hydrogen bonded loop [graph set: $R_4^4(28)$], the wave chains are stitched together resulting in the wavelike 2D layer network. Meanwhile, there is also the face to face π – π stacking interaction (3.79 Å). If considering the H_4bptc and phen as 8-connected and 4-connected nodes respectively, and the O–H–O and C–H–O hydrogen bonds as linkers, the resulted supramolecular structure could be simplified into a 2D topology structure (Fig. S12). In the asymmetric unit of **2** (Fig. 1b), In(III) cation is six-coordinated by four nitrogen atoms (N1, N2, N3 and N4) from two phen molecules and two terminal chloridions, showing a distorted $[InN_4Cl_2]$ octahedral geometry (Fig. S13). The

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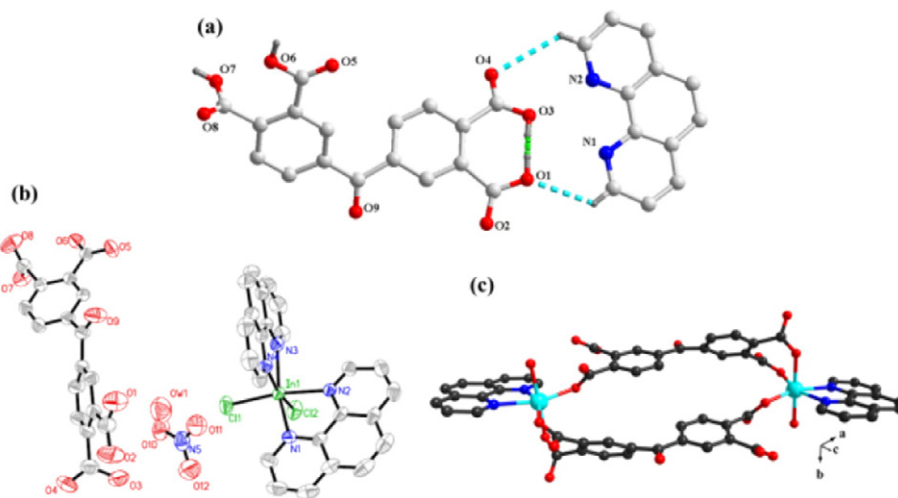


Fig. 1. (a) The crystal structure of **1**; (b) the coordination environment of the In(III) cation in **2**; (c) perspective view of the crystal unit in **3**.

H₄bptc ligand is fully protonated and does not participate in the coordination with In(III) cation. The 2D and 3D supermolecular structures are linked together via C–H–O resulting in the 2D + 3D → 3D supermolecular structure of **2** (Fig. S14). Compound **3** is a Hbptc³⁻-bridged In^{III}₂ system derived from the partially deprotonated ligand H₄bptc (Fig. 1c). In(III) cation center adopts slightly distorted [InN₂O₄] octahedral geometry. The dinuclear moieties are connected by O–H–O together with π – π interaction (3.44 Å) leading to a 3D structure (Fig. S15).

In compound **4** (Fig. 2), the central In(III) cation is seven-coordinated by three nitrogen atoms (N1, N2 and N3) from one 2,6-pydc²⁻ and two phen ligands, three oxygen atoms (O1, O3 and O5) from 2,6-pydc²⁻ and water molecule, and one Cl⁻ anion (Fig. S16). The self-assembly molecules in **4** are connected via O5–H5B–O2 synthon to form the 1D wave chain (Fig. S17). The adjacent wave chains are extended by C4–H4A–O4, C10–H10A–Cl1 and π –stacking interaction (3.59 Å) to complete the 2D layer structure.

As shown in Fig. 3, In(III) cation is coordinated by six carboxylate O atoms from two water molecules, one Ox²⁻, one 2,6-pydc²⁻, and one N atom from 2,6-pydc²⁻ anion in a centrosymmetric binuclear structure of **5**, showing [InO₆N] pentagonal bipyramid sphere as **4**. It is clear that the binuclear formation is further extended to 1D chain and 2D layer structure by O–H–O. Moreover, the π – π stacking interaction (3.55 Å) combining with the above-mentioned O–H–O hydrogen bonds expand the discrete In₂(2,6-pydc)₂(Ox)(H₂O)₄ into a 3D hydrogen-bonded supramolecular net.

The solid-state photoluminescence (PL) studies were carried out for H₄bptc, 2,6-H₂pydc, phen, H₂Ox ligands and compounds **1–5** at 298 K and 77 K (Fig. S18–S22 and Table S8). On the basis of the emission

peaks, the O-donor H₄bptc ligand shows contribution to the fluorescent emissions of **1–3**. The emission peaks of **4** and **5** can be ascribed to $\pi^* \rightarrow \pi$ transitions of phen and 2,6-H₂pydc respectively, because the similar peak appears for these ligands [7]. For compound **1**, it can be observed that a broad emission occurs from higher-energy (HE) emission 420 nm to lower-energy (LE) emission at 566 nm, generating light with Commission Internationale d'Éclairage (CIE) coordinates of 0.30, 0.33, which is generally considered white (Fig. 4). Compared with **1**, **2** exhibits better monochromatic, which generates blue light ($\lambda_{\text{max}} = 420, 492^{\text{sh}}$ nm) with CIE coordinates of 0.16, 0.12. Binuclear compound **3** shows emission band at 517 nm, generating green light with CIE coordinates of 0.28, 0.54. Compared with the mononuclear complex **2**, its emission peak is largely red-shifted by 97 nm. It is due to the chelating of the Hbptc³⁻ ligand to In(III) cation, which could increase rigidity of the ligands and decrease the HOMO–LUMO energy gap [8]. Compounds **4** and **5** exhibit luminescence in the blue region at 394 nm and 441 nm, respectively. These bands can be assigned to ligand-centered fluorescent emissions of phen and 2,6-H₂pydc, respectively [9]. Compared with **4**, **5** displays lower emission energy with the maximum emission spectrum red shifted 47 nm. This phenomenon could be attributed to the much larger conjugated system of **5** [10]. At 77 K (Fig. S23), the crystalline solids of **2** undergoes an obvious red shift (*ca.* 158 nm) chromic process (420, 492^{sh} nm → 578 nm), and gives light with CIE coordinates of 0.44, 0.47, extending down into the yellow region of the visible spectrum ($\lambda_{\text{max}} = 578$ nm). The emission spectra of **3–5** are much broader and more structured than those at 298 K. On the contrary, the PL spectrum of **1** ($\lambda_{\text{em}} = 494^{\text{sh}}, 531$ nm) becomes more narrow than it at 298 K, with CIE coordinates of 0.27, 0.51 in the green region. It is showed that the lifetimes of **1–5** at 77 K increase

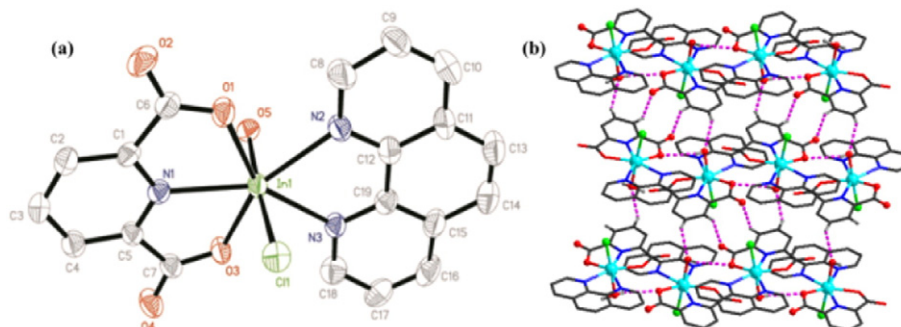


Fig. 2. (a) Coordination environment of In(III) cation center in **4**; (b) the 2D supramolecular framework generated through O–H–O, C–H–Cl and π -stacking interactions.

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