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## Co-Crystal Compounded by Coordination, Halogen and Hydrogen Bonds and its Self-Protective Phosphorescence†

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The cocrystal has been compounded by 5-iodosalicylic acid (5-Isal) and lead ion. Lead ion coordinated with two carboxyl groups of two 5-Isal molecules to form “V-like” structure. *Via* the interactions of respective two C-I...C halogen bondings (XBs) and C-H...I-C hydrogen bondings (HBs), the “V-like” structure cemented into one dimension (1D) infinite “Zigzag-like” chain structures. The oxygen molecules were prevented from freely diffuse and permeate in cocrystal due to the compact structure, resulting to the generation of non-protective room-temperature phosphorescence. The synergistic cooperation and competition among various weak interactions should be an important factor to assembly supramolecular organic solid materials and understand the generation mechanism of novel property.

**Keywords:** Supramolecular chemistry, Self-assembly, 5-Iodosalicylic acid (5-Isal), Self-protective phosphorescence.

### INTRODUCTION

The integrated utilization of intermolecular interactions in supramolecular chemistry is always a huge challenge. Hydrogen bonding (HB) is the most frequently used tool to assemble organic molecules in solid phases and it also plays an important role in stabilizing supramolecular aggregates in solution<sup>1-3</sup>. Metal-ion coordination is generally the key feature in inorganic supramolecular systems<sup>4</sup> and at all times acts as electron receptor in photoinduced electron transfer (PET) molecules to inhibit the photoinduced electron transfer process<sup>5</sup>. It has been known for a long time that the organic halogen atoms can function as Lewis acid and engage in electron donor-acceptor interaction with atoms containing lone pairs such as nitrogen, oxygen, phosphorus, sulfur and anion. This interaction is now defined as halogen bonding (XB) as suggested by Legon to emphasize the similarity with hydrogen bonding<sup>6</sup>. During recent decades, halogen bonding has been an attractive domain<sup>7,8</sup> and regarded as an efficient, reliable tool in crystal engineering<sup>9</sup> and a new palette of non-covalent interaction on disposal to self-assembly molecules into supramolecular architectures<sup>10</sup>. The emergence of halogen bonding therefore provides a new choice for rational design and control of the structure of molecular cocrystals by cooperatively combining with other traditional intermolecular interactions,

such as hydrogen bonding, coordination bonding and  $\pi$ - $\pi$  stacking<sup>11-13</sup>.

Room-temperature phosphorescence (RTP) has more advantages than traditional fluorescence method, much broader Stokes shift can easily avoid the interference from scattering light and much longer phosphorescent lifetime can easily avoid the interference from autofluorescence<sup>14,15</sup>. These merits make phosphorescence especially propitious to the detection of target species in the complex biological and environmental samples and muddy system<sup>16</sup>. The room-temperature phosphorescence-based sensing technology has been therefore widely applied in the fields of life science and clinical medicine, for example, spot monitoring and sensing and imaging of molecular oxygen in live cell and tissue<sup>17-19</sup>. However, the room-temperature phosphorescence can be easily quenched by dissolved oxygen, which greatly limited its application. At present, two methods are proposed to solve the above question. One is transition metal ions doped quantum dots (QDs). The transition metal ions capable of transferring defect-related emission are dispersed into the lattice of host materials, which prevents dissolved oxygen from contacting with transition metal ions, resulting in the room-temperature phosphorescence emission<sup>20-23</sup>. The other is halogen bonding-induced room-temperature phosphorescence. The organic halogen atom (halogen bonding donor), as well as used as heavy atom perturber of room-temperature

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phosphorescence, synergically constructed compact supramolecular co-crystal with hydrogen bonding and  $\pi$ - $\pi$  stacking to eliminate the interference of molecular oxygen<sup>24-26</sup>. The above opened a promising door for the development of application of room-temperature phosphorescence.

In this study, the 5-iodosalicylic acid (5-Isal) and lead salt were used to construct a self-assembly architecture. Different from the above-mentioned two methods, the obtained supramolecular co-crystal suspended in water can emit the same room-temperature phosphorescence as 5-iodosalicylic acid in solution under the condition of no oxygen. It was then inferred that the compact structure of co-crystal guaranteed the free oxygen not to be close to the phosphorescence center. The proposed method provided a novel approach for obtaining the room-temperature phosphorescence of self-phosphorescence compound without the removal of oxygen.

## EXPERIMENTAL

5-Iodosalicylic acid (5-Isal, purity >99 %) was the product of Alfa Aesar (Tianjin, China).  $\text{PbCl}_2 \cdot 4\text{H}_2\text{O}$  was obtained commercially and used as received. All other reagents were of analytical grade and used without further purification.

To prepare the crystal compounded by 5-Isal and  $\text{PbCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{PbCl}_2$  and 5-Isal (0.0528 mg) in 1:2 molar ratio were dissolved in 5 mL mixed solution of 1:1 (v/v) water and ethanol, respectively. The aqueous solution of  $\text{PbCl}_2$  was added dropwise into aqueous solution of 5-Isal at room temperature, the mixture was successively kept stirring for 0.5 h and subsequently filtered. The precipitation was re-dissolved in water and the white block crystal was obtained on the bottom of the beaker one month later.

The room-temperature phosphorescence spectrum was recorded on an F-4600 (Hitachi, Tokyo, Japan). The crystal was grinded into powder and then suspended in water. The measurements were performed with excitation wavelength at 375 nm equipped with a plotter unit and a quartz cell (1 cm  $\times$  1 cm). Single-crystal data were collected at room temperature with a SMART APEX diffractometer (Bruker, Germany) using  $\text{CuK}\alpha$  X-ray radiation ( $\lambda = 1.54056 \text{ \AA}$ ), graphite monochromator and scans, 2700 reflections collected, 2100 independent reflections ( $R_{\text{int}} = 0.0675$ ). Data collection and reduction were performed by SMART and SAINT and absorption correction. The structures were solved by direct method with SHELXS-97 and refined full-matrix least-squares on  $F^2$  with SHELXL-97.

## RESULTS AND DISCUSSION

**Cocrystal data and intermolecular interactions:** The most relevant crystallographic data of the structure reported in this study is as follows: Blue blocks,  $M = 733.20$ ,  $C2/c$ ,  $a = 25.404(3)$ ,  $b = 4.8376(6)$ ,  $c = 13.3374(15) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 96.402(1)$ ,  $\gamma = 90^\circ$ ,  $V = 1628.9(3) \text{ \AA}^3$ ,  $D_c = 2.990 \text{ Mg m}^{-3}$ ,  $F_{(000)} = 1312.0$ ,  $K$ ;  $R_{\text{int}} = 0.0414$  for 1542,  $GF2 = 1.068$ ,  $F_{R1} [I > 2(I)] = 0.036$ ,  $F_w R^2 = 0.1326$  for all 1581 independent reflections. 5-Isal is a multi-site molecule. Theoretically, the C-I can act as halogen bonding donor, while carbonyl on the carboxyl, halogen bonding acceptor and 2-hydroxyl and carboxyl are both as hydrogen bonding donor and three oxygen atoms can act as the electron donor of coordination bond,

halogen bonding and hydrogen bonding at the same time. So it is very hard to accurately predict the concrete interactions of supramolecular system self-assembled by 5-Isal molecule and lead salt without the acquirement of the exact crystal data.

Actually, X-ray single crystal diffraction revealed that 5-Isal molecule acted as donor and acceptor halogen bonding and hydrogen bonding. Meanwhile, the two oxygen atoms on carboxyl group served as electron donor and coordinated with lead ion, resulting in the formation of a unique "V-like" structure (Fig. 1a). Within the "V-like" structure, the distances between Pb1O1 and Pb1O2 are 2.360(6) and 2.526(6)  $\text{Å}$ , respectively, which are within the sum of van der Waals radii, demonstrating the existence of coordination bond. The two "V-like" structures were linked by two C-H...I hydrogen bondings and two C-I...C halogen bondings (Fig. 1b). The H...I and I...C separations of 3.6788(6) and 3.930(1)  $\text{Å}$  is shorter than the sum of van der Waals radii, indicating the hydrogen bondings and halogen bondings played a key role in stabilizing the supramolecular architecture. Of course, there is an intramolecular hydrogen bonding between H2 and O2, however, which did not contribute to the stabilization of cocrystal. One dimension (1D) infinite "Zigzag-like" chain structures were formed by coordination bond, halogen bonding and hydrogen bonding in turn among "V-like" structures. Fig. 1c is the project of a selected "zigzag-like" structure along a line perpendicular to paper. The di-planar angles are 81.6, 81.8 and 82.1 $^\circ$ , respectively.

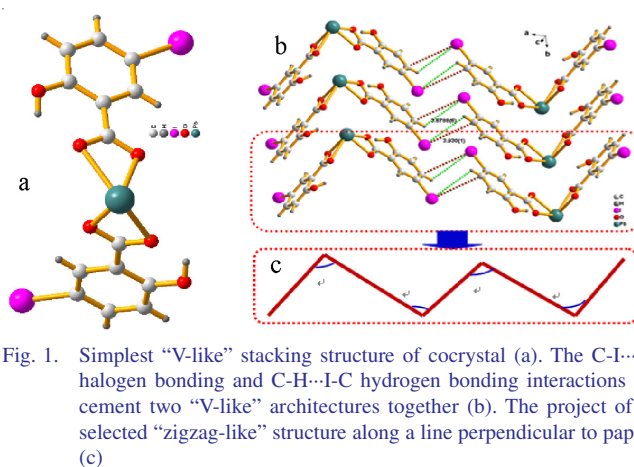


Fig. 1. Simplest "V-like" stacking structure of cocrystal (a). The C-I...C halogen bonding and C-H...I-C hydrogen bonding interactions to cement two "V-like" architectures together (b). The project of a selected "zigzag-like" structure along a line perpendicular to paper (c)

**Self-protective room-temperature phosphorescence of cocrystal:** Room-temperature phosphorescence can be easily quenched by dissolved oxygen. The routine processes achieving room-temperature phosphorescence include solid matrix room-temperature phosphorescence, ordered surfactant media room-temperature phosphorescence and cyclodextrin-induced room-temperature phosphorescence, *etc.* However, the above operations are very complicated and unstable, which greatly limited the application of room-temperature phosphorescence. The novel room-temperature phosphorescence method protected by compact supramolecular co-crystal opens a promising door<sup>24-26</sup>. The room-temperature phosphorescence of cocrystal was therefore investigated in this study. As shown in Fig. 2a, when the powder of cocrystal was suspended in water, the excitation and emission wavelength of room-temperature

phosphorescence located at 375, 505 and 545 nm, respectively, which is the same with those of solid 5-Isal. This indicated the room-temperature phosphorescence is from 5-Isal molecule. However, 5-Isal emits no room-temperature phosphorescence in solution. So the cocrystal prevented the oxygen from approaching the benzene ring of 5-Isal, resulting in the emission of room-temperature phosphorescence. The protective mechanism was also simply discussed. As shown in Fig. 2b, the separation of two neighbour benzene rings is only 4.8376(6) Å. In that way, the perpendicular distance would be much shorter, which makes the oxygen molecules not freely diffuse and permeate in cocrystal. This observation indicated that the complex may be an excellent candidate for the potential room-temperature phosphorescence protective materials.

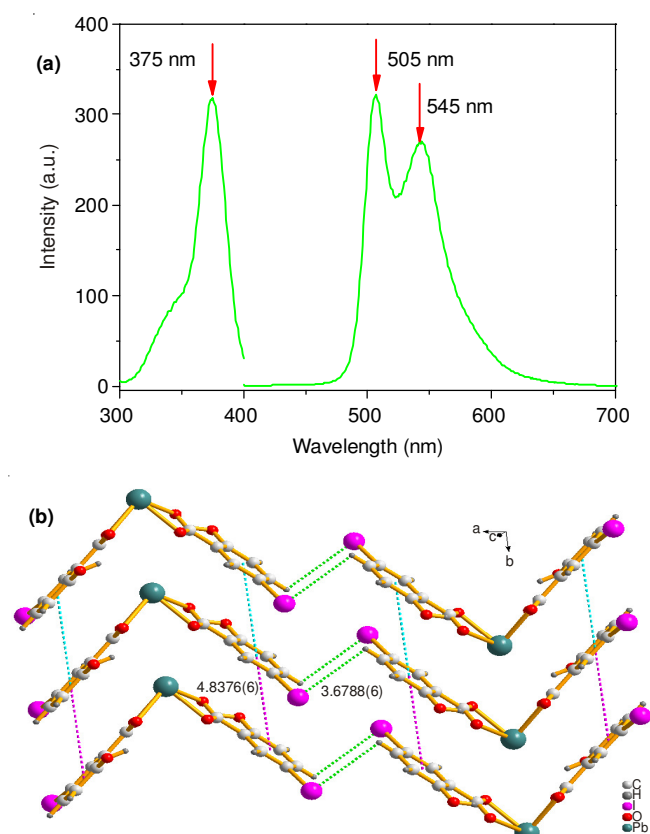


Fig. 2. Room-temperature phosphorescence excitation and emission spectra of cocrystal suspended in water (a) and compact structure of cocrystal (b)

## Conclusion

Cocrystals compounded by 5-Isal and lead ion was obtained. Single crystal diffraction data indicated that cocrystal contains 5-Isal and lead ion in a molecular ratio of 2:1. A novel 1D infinite “Zigzag-like” chain structures was cemented

through the interactions of respective two C-I...C halogen bondings and C-H...I-C after the formation of coordination compound with 2:1 molar ratio of 5-Isal and lead ion. The results observed testified synergistic interactions by halogen bonding, hydrogen bonding and coordination bond had heuristic meaning for the understanding for interaction of drug-receptor and new luminescent materials design.

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