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Crystalline nanoparticles for self-protective room-temperature phosphorescence based on synergism of multi-weak interactions in suspension solution

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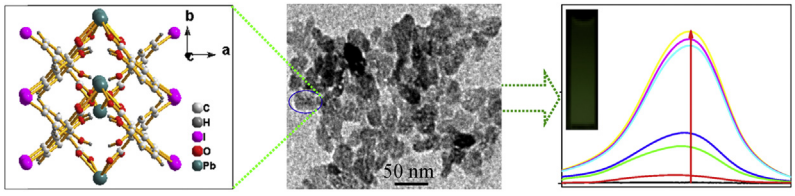
HIGHLIGHTS

- Crystalline nanoparticles emitting self-protective RTP were unexpectedly found.
- Synergism of multi-weak interactions constructed crystalline nanoparticles.
- Self-aggregation can protect the inner excited triplet state.
- Crystalline nanoparticles have a potential for bioimaging and biosensing.

GRAPHICAL ABSTRACT



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ABSTRACT

Room-temperature phosphorescence (RTP) has much longer lifetime and much broader Stokes shift than those of traditional fluorescence. However, deoxygenation procedure has always been troubling the development and application of RTP in biosystem. Herein it was unexpectedly found that the crystalline nanoparticles (CNs) generated by the ethanol solution of 5-iodosalicylic acid (5-Isal) being titrated by the aqueous solution of $PbCl_2$ (CNs 1), and titrating dichloromethane solution of 1,2-di(4-pyridyl)ethylene (BPE) or reversely titrating (CNs 2), respectively, can emit RTP without any deoxygenation operation, implying the great potential for bioimaging. The FT-IR spectroscopy predicts and XRD data reveal that 5-Isal can assemble into supramolecular cocrystals with lead ion (Cry 1) and BPE (Cry 2) through synergism of hydrogen bonding, halogen bonding, π ··· π stacking and other noncovalent interactions. The powder XRD, as well as reveals the homogeneity of CNs 1 and Cry 1, together with HPLC confirms that the CNs 2 is the physical mixture of 5-Isal and BPE but the nanometer-sized Cry 2 due to difference in solubility. Moreover, the RTP emissions and decays of the suspension powder of cocrystals in aqueous solution were investigated. The RTP at 505 nm and 545 nm for Cry 1, and 528 nm for Cry 2 under the excitation wavelength at 375 nm were observed, which were in accord with those of the CNs. Due to the compact structure of CNs and cocrystals, the dissolved oxygen was prevented from freely contacting with 5-Isal, which protected the inner excited triplet state of 5-Isal. The synergism of multi-weak interactions in aqueous solution should be instructive for developing self-protective RTP nanomaterials.

1. Introduction

Relative to the traditional fluorescence method, Room-

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temperature phosphorescence (RTP) one possesses many distinct advantages. For instance, the much longer lifetime allows an appropriate delay time, so that any autofluorescence emission and scattering light can be easily avoided [1,2]; The much broader Stokes shift can modulate the emission of fluorophores, which has the possibilities as a man-made color palette, displaying a great potential for design and synthesis of nanometer devices and machines [3,4]. Above-mentioned advantages make RTP specially favor the target detection in the complex biological, environmental and feculent systems, as well as color display. Therefore, the analytical methods based on RTP have been widely applied in the fields of life science and clinical medicine such as on-spot monitoring, sensing and imaging assays of oxygen pressure in cell and issue [5,6]. Also, RTP method has been exploited for the detection of SO_2 [7] and nitroxides [8] from atmosphere and auto exhausts, and the determination of polycyclic aromatic hydrocarbons [9], heterocyclic compounds and pesticide residuals [10], etc. Organometallic compounds are traditionally efficient phosphors, whereas they require rare and expensive elements [11]. In contrast, polycyclic aromatic hydrocarbons are cheaper, whereas the dissolved oxygen in solution or biosystem quenches the excited triplet state through energy transfer pathway, resulting in the ineffective phosphorescence. Therefore, it still remains a tremendous challenge to realize the self-protective RTP of purely organic compounds in solution.

Liang et al. [12] have reported the crystalline nanoparticles (CNs) assembled by 3-bromo- and 3-iodo-carbazole in aqueous suspended solution. The cocrystals as suspension microparticles can be very easily assembled in water by dropping water into an ethanol solution of carbazole and 1,4-diiodotetrafluorobenzene [13]. Both self-protective RTP without any deoxygenation operation were observed. The X-Ray single diffraction data reveal that the self-assemblies are driven mainly by the halogen bonding (XB) such as halogen-halogen, C-halogen $\cdots \pi$ interaction with the assistance of hydrogen bonding (HB) such as C—H $\cdots$ Halogen, and so on. Cocrystal strategy is therefore a possibly effective method for the self-protective RTP. Firstly, the dissolved oxygen is self-prevented from contacting with purely organic phosphor in cocrystal; Secondly, organic halogen in XB [14], not only as XB donor but also as triplet-promoting reagent, delocalizes the electrons donor, that is XB acceptor, partially onto the halogen, which puts the heavy atom effect to work at the carbonyl oxygen site where the triplets is produced and triplet emission is activated [15–18]. In comparison to the currently popular transition metal ions and lanthanide doped nanocrystals [1,19], uncontrollable size of self-assembly process of co-crystal usually limits further application of phosphor as well as in display, solid state lighting and optical storage.

Here it was found that when the ethanol solution of 5-Isal was titrated by aqueous solution of Pb^{2+}, the suspension CNs 1 was generated, the strong RTP without any deoxygenation operation was observed in aqueous solution. The FT-IR spectroscopy predicts and XRD datum confirms the synergistic interactions of HB, XB and $\pi \cdots \pi$ stacking. Similarly, though the suspension CNs 2 generated by either ethanol solution of 5-Isal titrating the dichloromethane solution of BPE or reverse operation can also emit self-protective RTP, the component finally evidenced by Powder XRD and HPLC was the physical mixture of 5-Isal and BPE, but the nanometer-sized Cry 2. The RTP emissions of two cocrystals were investigated after the cocrystals were ground into micrometer-level powder followed by suspending in aqueous solution. The results display the RTP at 505 nm and 545 nm for Cry 1, and 528 nm for Cry 2 under the excitation wavelength at 375 nm were observed, implying due to the compact structure of cocrystals and CNs, the dissolved oxygen was prevented from freely diffusing and permeating, which protected the inner excited triplet state of 5-Isal.

2. Experimental

2.1. Chemicals

5-iodosalicylic acid (5-Isal, purity over 99%) and 1,2-di(4-pyridyl)ethylene (BPE, purity 99%) were the products of Alfa Aesar (Tianjin, China). $PbCl_2.4H_2O$ was commercially purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All other reagents were of analytical grade and used without further purification.

2.2. Apparatus

The RTP, fluorescence spectra and lifetime evaluation were recorded on an F-4600 (Hitachi, Tokyo, Japan), and the measurements were performed with different excitation wavelength equipped with a plotter unit and a quartz cell (1 cm × 1 cm) in a variety of modes. Single crystal data were collected at room temperature with a SMART APEX diffractometer (Bruker, Germany) using Cu Ka X-ray radiation (l = 1.54056 Å), a graphite monochromator and φ and ω scans, and 5276 for Cry 1 and 9497 for Cry 2 reflections were collected, with 1581 for Cry 1 and 2539 for Cry 2 independent reflections (Rint Z 0.0402 for Cry 1 and 0.0198 for Cry 2). Data collection and reduction were performed using SMART and SAINT and absorption correction. The structures were solved by a direct method with SHELXS-97 and refined full-matrix least-squares on F2 with SHELXL-97. Scanning electron microscopy (SEM) images of the product were taken on a field emission scanning electron microscope (FESEM, JEOL, JSM 7500F). Fourier transform infrared (FT-IR) spectra (4000–400 cm^1) in KBr were recorded on a Nicolet-6700 spectrometer (Nicolet, Madison, WI, USA). The morphology of the colloidal particles were characterized by transmission electron microscopy (TEM) on a JEM-200CX (JEOL, Tokyo, Japan) microscope operating at a 200 kV accelerating voltage. The component of colloidal crystal was analyzed on a Welch Materials XB-C18 column (5 mm, 4.6 × 150 mm ID) with methanol-water (70:30, v/v) as the mobile phase at a flow rate of 1.0 mL/min by high performance liquid chromatography (HPLC) on an Agilent 1200 equipped with a vacuum degasser, a quaternary pump, an auto-sampler, a diode array detector (DAD) and an Agilent ChemStation (Agilent, Santa Clara, CA, USA). The powder X-ray diffraction (XRD) spectra were collected on a Shimadzu XRD-6000 diffractometer with Cu Kα radiation.

2.3. Preparations of CNs 1 and Cry 1

According to previous report with slight modification, the CNs 1 and Cry 1 were obtained [20]. Briefly, $PbCl_2$ and 5-Isal (52.80 mg) in 1:2 M ratio were dissolved in 5 mL mixed solution of 1:1 (v/v) water and ethanol, respectively. The $PbCl_2$ aqueous solution was added dropwise into 5-Isal aqueous solution at room temperature, the mixture was successively kept stirring for 30 min. The resultant suspension CNs was CNs 1. The solid samples of CNs 1 were obtained after the suspension solution was filtered prior to drying in oven at 60°. The solid sample was redissolved in water, and the white block crystal was obtained on the bottom of the beaker one month later. The block crystal was ground into powder followed by dispersing in water to form suspended solution for RTP measurement.

2.4. Preparation of CNs 2

The suspension CNs 2 was prepared by either 10 mM of 5-Isal ethanolic solution (2.0 mL) being successively dropped into dichloromethane solution of BPE with the same concentration and