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Ultralong Phosphorescence from Organic Ionic Crystals under Ambient Conditions

Zhichao Cheng, Huifang Shi, Huili Ma, Lifang Bian, Qi Wu, Long Gu, Suzhi Cai, Xuan Wang, Wei-wei Xiong, Zhongfu An* and Wei Huang*

Abstract: We report on a new type of material system of organic salts in crystal state with ultralong organic phosphorescence (UOP) under ambient conditions. The change of cations (NH_4^+ , Na^+ or K^+) in these phosphors gives access to tunable UOP colors ranging from sky blue to yellow green, along with ultralong emission lifetimes of over 504 ms. Single-crystal analysis reveals that unique ionic bonding can promote an ordered arrangement of organic salts in crystal state, which then can facilitate molecular aggregation for UOP generation. Additionally, reversible ultralong phosphorescence can be realized through the alternative employment of fuming gases (ammonia and hydrogen chloride), demonstrating its potential as a candidate for visual ammonic or hydrogen chloride gas sensing. The results provide an environmental responsible and practicable synthetic approach to expanding the scope of ultralong organic phosphorescent materials as well as their applications.

Ultralong phosphorescence, i.e., persistent luminescence or afterglow emission, has drawn forth extensive attention due to its extraordinarily long emission lifetime within a wide range of potential applications, such as display, document security, and bioimaging, as well as emergency signage^[1]. Most known luminogens with ultralong phosphorescence are limited to inorganic materials with noble-metal or rare-earth elements^[2]. However, their intrinsic drawbacks, such as high bio-toxicity, harsh preparation conditions, scarcity of rare-metal resources, and insulation nature set limits on further development of inorganic phosphors, thus giving birth to a new class of analogues based on organics, i.e., ultralong organic phosphorescence (UOP)^[3]. Very recently, significant progress in organic luminogens with UOP has been achieved in which UOP materials were designed and prepared through crystallization^[4], host-guest doping^[5], the construction of metal-organic frameworks (MOFs)^[6], H-aggregation^[7], and other methods^[8]. Notably, among these phosphors, the material architectures are mainly restricted on metal-free molecular crystals with rich intermolecular interactions and MOFs with coordinate bonds, as shown in Figure 1a and 1b. Such architectures can provide rigid environments for enhanced phosphorescence by suppressing non-radiative decay of triplet



Figure 1. Schematic representation of rigid material architectures for ultralong organic phosphorescence. a) Molecular crystal, b) Metal-organic framework (MOF), and c) Organic ionic crystal as presented in this work.

excitons, from thermal, oxygen and moisture perturbation, as well as molecular motions^[9]. To date, it remains a formidable challenge to develop a new material system for ultralong organic phosphorescence under ambient conditions.

Here we report on rigid ionic crystals with UOP via unique ionic bonding based on a new class of ionic compounds: organic salts. The type of ionic crystals can be easily prepared with low cost and under moderate and environmental-friendly conditions. With cations changing from NH_4^+ to K^+ , the emission color of UOP was expressly tuned from yellow green to sky blue. Also the lifetime of ultralong phosphorescence simultaneously changed from 504 to 586 ms. Importantly, we found that reversible and repeatable ultralong phosphorescence could be obtained with ammonia and hydrogen chloride gas alternative fuming, making them ideal candidates as visible gas sensors.

The rigid crystals based on ionic compounds were incubated gradually in aqueous solution. Terephthalic acid (TPA) is a weak acid, whose solubility in water is only 1.5×10^{-5} g/mL at $20^{\circ}C^{[10]}$. But, as an organic weak acid, TPA can easily dissolve in ammonia solution due to its ionization process. First, TPA powder was added to ammonia water to form a transparent solution. Then, the water was evaporated slowly at 50°C to render ammonium hydrogen terephthalate (AHT) as block transparent crystals with a yield of over 50%. The molecular structure of AHT was verified by single crystal X-ray diffraction. The phase purity of the synthesized crystals was further validated by powder X-ray diffraction (PXRD) (Figure S1a).

Subsequently, the photophysical properties of AHT in crystal under ambient conditions were investigated. Under irradiation by a hand-held 365 nm lamp blue-violet emission can be observed. Unexpectedly, upon removal of the excitation light source, the emission changed to green and faded gradually with a remarkably persistent luminescence of several seconds (Figure 2a). As shown in Figure 2b, the steady-state photoluminescence (PL) of AHT in crystal showed a red-edge effect^[11]. With excitation wavelength increased from 300 to 400 nm, the emission peak

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Figure 2. Photophysical properties of AHT in crystal under ambient conditions. a) Chemical structure and photographs of AHT crystal before and after irradiation with a hand-held 365 nm UV lamp. b) Normalized photoluminescence (PL) spectra of AHT under different excitation wavelengths. c) Excitationphosphorescence mapping of AHT crystal. d) Time-resolved phosphorescence decay curve of the emission band at 502 nm excited at 328 nm.

showed a continuous red-shift from 370 to 460 nm, which were confirmed to be fluorescence accroding to the lifetime measurement (Figure S2a). In light of these photophysical properties, combined with the excitation spectra shown in Figure S3, it is speculated that multiple excited states may exist for this variable feature in PL spectra^[12]. According to the literatures^[13], there may exist proton transfer between terephthalate anions and ammonium cations, resulting in more than two molecular configurations in crystal state due to protonation. Combining with theoretical calculation shown in Figure S4, we speculated that multiple excited states might result from the different degrees of luminophore protonation in crystal upon photo-excitation. Whereas, the profiles of phosphorescence spectra were fixed with a dominant peak at 502 nm as excitation wavelengths changed from 250 to 450 nm (Figure 2c). The time-resolved phosphorescence decay curve of AHT crystal revealed a luminescent lifetime of 586 ms under amibient conditions, demonstrating the UOP feature (Figure. 2d). The time-resolved emission spectra (TRES) were also conducted for AHT. As shown in Figure S5a, the emission of AHT crystal at short wavelengths first disappeared with time delays. The profiles of the emission spectra at long wavelengths are similar at different delay times. Addtionally, it is worthy to note that this unique UOP was stable even under oxygen atmosphere (Figure S6a).

In order to gain insights into the molecular mechanism of ultralong phosphorescence in AHT crystal, the intermolecular interactions and stackings were investigated through single-crystal annalysis, as shown in Figure 3. In AHT crystal there exists a torsion angle of 9.56° between carbonyl group and benzene ring, which is larger than that in terephthalic acid crystal (5.37°) and



Figure 3. Intermolecular interaction analysis of AHT in crystal. a) Illustration of torsion angle between carboxyl group and benzene ring. b) Molecular packing in dimer. The distance between intermolecular planes or centers is highlighted in blue. c) Intermolecular interactions viewed along b axis. d) Intermolecular stacking viewed along c axis. With the ammonium cation inducement, terephthalate anions show well-aligned intermolecular stacking through face – to-face interaction.

which may facilitate intersystem crossing (ISC) for triplet exciton generation^[14]. With amnonia ion inducement the benzene chromorphores show a face-to-face stacking with a distance of 3.510 Å. Figure 3b demonstrates that the angle (θ =80.02°) between the interconnected axis and the long axis in the terephthalic acid group is larger than the critical value of 54.7° for distinction of H- and J-aggregation^[15], proving the presence of Haggregation in crystal^[16]. Apart from intermolecular interactions, including C=O···H-O, C=O···H-N, C-H···π, etc. in crystal (Figure 3c), ionic bonding between ammonium cations and terephthalate anions also play an important role in locking the terephthalate anion conformation and restricting the molecular motions and vibrations, thus reducing the non-radiative transition of triplet excitons to boost ultralong phosphorescence at room temperature. In view of the above-mentioned results and H-aggregation's increasing luminescence lifetimes^[17], we speculate that Haggregation with strong coupling may stabilize the triplet excitons for ultralong phosphorescence^[7].

Notably, as shown in Figure 3d, an ordered face-to-face arrangement between terephthalic acid chromorphores was induced by ammonium cations, which may promote UOP generation. Inspired by this concept, we further synthesized two organic salts, namely, dipotassium terephthalate (DPT) and disodium terephthalate (DST), by replacing ammonium cations with potassium and sodium cations, respectively. Both DPT and DST crystals showed UOP at 456 and 508 nm, respectively,as shown in Figure 4a and 4c, with the UOP color changed from sky blue to yellow green (Figure 4b and 4d). With excitation wavelength variation, no UOP change was observed. The UOP lifetimes of DPT and DST crystals reach 504 and 585 ms under ambient conditions, respectively. Like AHT crystal, UOP of both DPT and DST crystals were also little affected by oxygen (Figure S6b and S6c). In order to investigate the sourse of their UOP

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Figure 4. Phosphorescence properties and crystal structures of DPT and DST crystals under ambient conditions. a) and c) Excitation-phosphorescence mapping of DPT and DST, respectively. b) and d) Lifetime decay profiles of the emission bands at 456 and 508 nm for DPT and DST crystals, respectively. e), f), g), h), i) and j) Illustration of torsion angle between carboxyl group and benzene ring; molecular stacking diagrams, and crystal structures viewed along the b axis in DPT and DST crystals, respectively.

coupled with emission color change, their single-crystal structures were analyzed, along with theoretical simulation. As anticipated, both DPT and DST exhibited well-organized arrangements in their crystal state, as shown in Figure 4e-4j, owing to the ionic inducement (K⁺ and Na⁺). In addition to the face-to-face molecular packing in these organic ionic crystals, the intermolecular π - π stacking distance decreases from 3.571 Å (DPT) to 3.268 Å (DST), which is consistent with the increasing tendency of their UOP lifetimes. The shorter π - π stacking distance may lead to

more stable H-aggregation for longer UOP emission. To gain insight into the change of UOP color, the lowest triplet states of these chromophores were evaluated through time-dependent density functional theory (TD-DFT) method at M062X/cc-pVDZ level. Because of the ion inducement, the geometric structures of terephthalic chromophore units in crystal show significant distortion, with torsion angles changing from 13.20° (DST) to 6.62° (DPT) (Figure 4e and 4h). As shown in Table S4 and S5, the variation of triplet excitation energies from DST to DPT model



Figure 5. Structural characterization and phosphorescence spectra of TPA powders before and after exposure to fumigants under ambient conditions. a) PXRD patterns of a series of TPA phosphors fumed with ammonia or hydrogen chloride gas and with different exposure times. Inset: Corresponding photographs of the samples taken after the irradiation source is removed. The X-ray diffraction peaks with stars are the characteristic peaks of ammonium chloride. b) The corresponding phosphorescence spectra of the same products used in PXRD measurement.

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agree well with the blue-shift tendency of UOP spectra in crystal. Therefore, it is speculated that the inducement of cations play a critical role for colorful UOP in organic ionic crystals.

In light of the visual UOP color change within AHT crystal, as well as the intrinsic volatility of ammonia gas, a chemo-sensor based on TPA powder was conducted for ammonia gas sensing under ambient conditions. As shown in Figure 5a, untreated TPA powder showed visible yellow UOP after irradiation by a 365 nm lamp. When the TPA powder was fumed by ammonia gas, with exposure time ranging from 10 to 60 min, UOP color of the sample shifted blue-green, correspondingly, phosphorescence spectra was blue-shifted from 520 to 506 nm (Figure 5b). Additionally,an emission band at around 390 nm disappeared gradually with the prolonged fuming time. From PXRD analysis, it is worthy to note that the sample transformed into AHT salt and further evolved into diammonium terephthalate salt, providing another simple method to obtain the AHT phosphor (Figure 5a). Interestingly, the yellow UOP from TPA powders could be recovered when the fumed sample was treated with hydrogen chloride gas for 7 h, which was confirmed by PXRD and phosphorescent spectra (Figure 5). With prolonged fuming time, the sample returned to TPA and NH₄Cl, and the original raw TPA powder phosphorescence spectrum profile was recovered. Furthermore, this type of gas probe was reversible and recyclable, whose sensing performance can be repeated for more than four times (Figure S7).

summarv. a new material sourse of In ultralong phosphorescence, organic ionic crystals, was formulated and prepared through ionic bonding in water or through gas fuming. With cationic variations from Na⁺, NH₄⁺ to K⁺, the UOP color could be intentionally tuned from sky blue to yellow green. The emission lifetimes of these phosphors exceed 504 ms. In light of both experimental and simulated results, it is proposed that this unique ionic bonding can promote an ordered molecular arrangement to influence molecular aggregation, which in turn can enhance ultralong phosphorescence. More importantly, reversible and repeatable ultralong phosphorescence was observed through the alternating application of fuming gases (ammonia and hydrogen chloride), demonstrating the potential for visual ammonic or hydrogen chloride gases sensing. This work not only provides a concise, as well as green synthetic approach to expanding the scope of organic luminescent materials with UOP features, but also helps to pave the way toward potential applications ranging from anti-counterfeiting to visual gas sensing.

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A new type of material system—organic ionic crystals with ultralong organic phosphorescence (UOP) was reported. The change of cations (NH4*, Na* or K*) in these phosphors gives access to tunable UOP colors ranging from sky blue to yellow green. Additionally, reversible ultralong phosphorescence can be realized through the alternative employment of fuming gases (ammonia and hydrogen chloride), demonstrating its potential as a candidate for visual gas sensing.



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