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Simultaneously Enhancing Efficiency and Lifetime of Ultralong Organic Phosphorescence Materials by Molecular Selfassembly

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ABSTRACT: Metal-free organic phosphorescence materials are of imperious demands in optoelectronics and bioelectronics. However, it is still a formidable challenge to develop a material with simultaneous efficiency and lifetime enhancement under ambient conditions. In this study, we design and synthesize a new class of high efficient ultralong organic phosphorescence (UOP) materials through self-assembly of melamine and aromatic acids in aqueous media. A supramolecular framework can be formed via multiple intermolecular interactions, building a rigid environment to lock the molecules firmly in a three-dimensional network, which not only effectively limits the non-radiative decay of the triplet excitons, but also promotes the intersystem crossing. Thus, the supermolecules we designed synchronously achieve an ultralong emission lifetime of up to 1.91 s and a high phosphorescence quantum efficiency of 24.3% under ambient conditions. To the best of our knowledge, this is the best performance of UOP materials with simultaneous efficiency and lifetime enhancement. Furthermore, it is successfully applied in a barcode identification in darkness. This result not only paves the way toward high efficient UOP materials, but also expands their applications.

INTRODUCTION

Organic phosphorescence, which originates from the radiative transition of triplet excitons, has aroused an increasing attention in optoelectronic¹⁻² and biological³⁻⁶ areas because of their long emission lifetimes, high quantum yields, and large Stokes shifts.⁷⁻⁹ So far, most of the room temperature phosphorescence is limited to inorganic compounds or organometallic complexes, such as Ir (III), Pt (II) and Ru (III) complexes, ¹⁰⁻¹³ because the metal-induced spin orbit coupling (SOC) can promote the intersystem crossing (ISC) for phosphorescence enhancement. Considering the high cost and limited resources of noble metals, more and more efforts have been devoted on metal-free organic phosphorescence recently.¹⁴⁻²³ However, exploring metal-free organic phosphorescence compounds with ultralong lifetime is extremely difficult due to the inefficient ISC caused by weak spin orbit coupling, rapid nonradiative decay rate of the triplet excitons and some unpredictable quenching factors from the surroundings such as oxygen.²⁴⁻²⁵ Therefore, researchers usually take two ways to obtain efficient phosphorescence. One is boosting spin orbit coupling by the introduction of aromatic carbonyls, hetero atoms and heavy atoms to achieve highly efficient phosphorescence.²⁶⁻³² The other is suppressing the non-radiative transition of triplet excitons by crystal engineering,³³⁻³⁵ host-guest doping method, $^{36\text{-}39}$ the construction of metal-organic frameworks $\mathrm{(MOFs)}^{40}$ or ionic crystals, 41 and so on, $^{42\text{-}47}$ which



Figure 1. Schematic representation of design concept and supramolecular architecture.

embed phosphors into a solid matrix, making them be isolated from oxygen and structurally fixed to limit non-radiative decay, and thus the long-lived room temperature phosphorescence is realized. Recently, our group has reported UOP with an emission lifetime as long as 1.35 seconds through Haggregated molecules stabilizing the triplet excitons under ambient conditions.⁴⁸ Up to now, the researchers mainly focus on improving efficiency or lifetime of organic phosphorescence (Figure S1). Owing to weak spin orbit coupling and the rapid rate of non-radiative decay in metal-free organics, de-

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veloping organic phosphorescent materials with both high efficiency and ultralong lifetime is still a formidable challenge. 49



Figure 2. Photophysical properties of MA-IPA supermolecule framework under ambient conditions. a) The fluorescence microscope images with the excitation on and off. b) Steady-state photoluminescence (PL, blue dashed line) and phosphorescence (red solid line) spectra under 300 nm excitation. c) Excitation-phosphorescence mapping. d) Time-resolved phosphorescence decay and fitting curves (black line) of the emission bands at 466 and 488 nm, respectively.

Supramolecular chemistry has played an important role in chemistry and material science since the 1960s, which offers an attractive approach to prepare well-organized functional materials by self-assembly of molecular subunits or components.⁵⁰⁻⁵¹ With the intermolecular locking by multiple non-covalent forces including H-bonding, π - π stacking, van der Waals force, electrostatic interaction, *etc.* in self-assembly

system, rigid molecular environment can be constructed, thus suppressing non-radiative transition for phosphorescence enhancement. With this in mind, we designed and synthesized a new supramolecular framework (MA-IPA) with ultralong organic phosphorescence through self-assembly of melamine (MA) and aromatic acids in aqueous media (Figure 1). Impressively, MA-IPA supramolecular material showed an ultralong lifetime of 1.91 s and a high phosphorescent efficiency of up to 24.3%, which is a record result among reported organic materials so far. Given the unique ultralong phosphorescence, this type of supramolecular material was successfully applied in a barcode identification in darkness. This study will provide a simple and green method to achieve a unique supramolecular UOP system with simultaneously a high quantum efficiency and an ultralong lifetime.

RESULTS AND DISCUSSION

Synthesis. The supramolecular framework of MA-IPA was synthesized from the mixture of MA and isophthalic acid (IPA) in aqueous solution at 150 °C. During gradient cooling, a large amounts of colorless needle crystals (Figure 2a) were obtained with a high yield of 86%. The chemical structure of MA-IPA was thoroughly characterized by X-ray diffraction and elemental analysis. The phase purity of the crystals was further verified by powder X-ray diffraction shown in Figure S2.

Photophysical Properties of MA-IPA. The photophysical properties of MA-IPA in crystal state were firstly investigated under ambient conditions. Under irradiation by UV-light, the needle-like crystals took on blue emission. Interestingly, after turning off the UV-light source, the sample showed bright bluish green afterglow, which lasted for nearly 20 s by naked



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Figure 3. Single crystal structure of MA-IPA. Molecular packing along the a) a-axis and b) c-axis. Intermolecular interactions from the same plane with c) MA as the centre and d) with IPA as the centre. Intermolecular interactions of e) MA and f) IPA with adjacent planes, respectively.

eyes. As shown in Figure 2b, the steady-state photoluminescence spectrum showed a blue emission band at around 356 nm and a green emission band with peaks at 466 and 488 nm, which was different from MA with a blue emission at 460 nm and IPA with three emission peaks at approximately 390, 480 and 505 nm (Figure S3). And the strongest emission band at approximately 488 nm (Figure 2c). From the lifetime decay profiles, it was confirmed that the blue emission was assigned to the fluorescence (Figure S4a). The green emission was due to the phosphorescence with ultralong emission lifetimes of 1.91 s and 1.85 s under ambient conditions (Figure 2d), which is 5.1 and 1.4 times more than MA crystal with a lifetime of 0.37 s and IPA crystal with a lifetime of 1.36 s, respectively (Figure S5). The phosphorescence nature of ultralong emission was further confirmed by its sensitivity to oxygen (Figure S7). Surprisingly, the absolute phosphorescence quantum efficiency of MA-IPA crystals reached as high as 24.3%. To the best of our knowledge, it is the best ultralong organic phosphorescent material with both ultralong lifetime and high phosphorescence efficiency (Figure S1). Additionally, with temperature increasing from 30 to 140 °C, the phosphorescence intensity of MA-IPA gradually decreased. When the temperature was raised to 115 °C, the phosphorescence signals almost disappeared (Figure S8).

> **Mechanism Analysis for High Efficient UOP Emission.** To gain insights into the mechanism of the unique UOP for this supramolecular architecture, the molecular structure and intermolecular interactions in MA-IPA crystal were investigated by X-ray single crystal diffraction, as shown in Figure 3. In this centrosymmetric unit of MA-IPA crystal, IPA molecule loses a proton and becomes negative charged IPA⁻, while a nitrogen atom of triazine in MA molecule is protonated as cationic MAH⁺. Thus, the supermolecule of MA-IPA includes three parts, an MA cation, an IPA anion and two water mole

cules, which are linked by multiple short and intense hydrogen bonds and Van der Waals' forces, forming a lattice-like structure. Notably, the intermolecular non-covalent interactions lead the molecules to assemble in a highly ordered supramolecular network. Four molecules of water can be captured by hydrogen bonding in a network, and a pair of water dimer with hydrogen bonding links amino groups on MA to form a hexagon by hydrogen bonds (Figure 3a). Moreover, these water molecules are linked to the upper and lower molecules respectively by various hydrogen bonds (Figure 3b), which makes great contributions to hinder molecular motions for suppressing non-radiative transition of triplet excitons and promoting ultralong phosphorescence at room temperature.

To gain deeper insight into the influence of water molecules on UOP emission, we conducted a set of control experiments after dehydration by heating. After MA-IPA crystal underwent thermal treatment at 150 °C for 2 h, both the lifetime and quantum efficiency of phosphorescence decreased dramatically into 1.21 s and 4.37% (Figure S10 and Table S1 and S2), indicating the water played a vital role for UOP enhancement. From powder XRD (PXRD) analysis in Figure S2a, it is worth noting that the PXRD pattern has significant changes after MA-IPA crystal was dehydrated by heating. Therefore, we speculated that after thermal treatment, multiple hydrogen bonds in MA-IPA crystal might be destroyed to get a loose structure to accelerate non-radiative transitions and thus quenched phosphorescence.

Specifically, taking an MA cation as a core, there exist multiple intermolecular interactions within the same plane and between the upper and lower layers, including N-H \cdots O, N \cdots H-O, N-H \cdots N, C \cdots H-O, etc. (Figure 3c and 3e). Taking an IPA anion as a core, apart from some common bonds above,



Figure 4. Photophysical properties and single crystal structure of MA-TPA in solid state under ambient conditions. a) The fluorescence microscope images (left) and photographs (right) of MA-TPA crystals before and after irradiation with a hand-held 310 nm UV lamp. b) Normalized photoluminescence (PL, blue line) and ultralong phosphorescence (red line) spectra of MA-TPA under 310 nm excitation. c) Transient photoluminescence decay mapping of MA-TPA crystals. The color changed from red to blue indicates the decrease in emission intensity. d) Intermolecular interactions viewed along the c axis. e) Intermolecular stacking viewed along the b axis.

there also exist many multiple intermolecular interactions within the same plane and between the upper and lower layers, such as O-H···O, O-H···H-O, C-H···H- π , etc. (Figure 3d and 3f). The detailed hydrogen bond types and bond lengths are showed in Table S3. These intermolecular interactions in this supramolecular network play important roles in restricting the molecular motions to reduce the non-radiative transition for ultralong phosphorescence.

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Furthermore, the theoretical calculations via first-principle time-dependent density functional theory (TD-DFT) were conducted on single molecule and self-assembly structures in both singlet and triplet excited states. From the calculated results shown in Figure S11, the energy gaps between the singlet and triplet states for both IPA monomer and MA-IPA dimer containing one water molecule were small, which will facilitate ISC process. After self-assembly of MA, IPA and water, the SOC ξ (S₁, T_n) increased largely from 19.4 (IPA monomer) to 33.9 cm⁻¹. That is to say, in the process of self-assembly, hydrogen bonds locked the monomers firmly to promote the ISC from singlet to triplet states, and then leading to high efficient phosphorescence, which was further confirmed by a faster ISC rate $(9.3 \times 10^7 \text{ s}^{-1})$ for MA-IPA supramolecular framework than those for MA $(1.7 \times 10^6 \text{ s}^{-1})$ and IPA $(8.7 \times 10^6 \text{ s}^{-1})$ (Table S4). Furthermore, it was found that MA-IPA supramolecular framework showed faster radiative transition (0.13 s^{-1}) and slower nonradiative decay rates (0.40 s^{-1}) compared with monomers (Table S4), which were contributed to prolonging emission lifetime of MA-IPA supramolecular framework. Taken these results together, we reasoned that high efficient UOP was ascribed to suppressing non-radiative transition and populating triplet excitons through supramolecular selfassembly.

To view the universality of this new material system with remarkable UOP feature under ambient conditions, we designed expanded experiments that MA assembled with terephthalic acid (TPA) and phthalic acid (PA) into supramolecular frameworks of MA-TPA and MA-PA, respectively. The UOP lifetime of MA-TPA was prolonged to 1.09 s and the phosphorescence quantum efficiency reached 19.4%. Like MA-IPA, both lifetime and efficiency of UOP in MA-TPA crystal also improved substantially compared with building monomers (Figure S5). For MA-TPA crystals, the bulk morphology in micro-nanoscale was observed by fluorescence microscope, as shown in Figure 4a. Under irradiation by a 310 nm illuminant, the sample took on sky-blue emission. After turning off the UV lamp, the sample presented a bluish green UOP, lasting for several seconds. And the PL emission located at



Figure 5. Application of ultralong phosphors. The UOP material was printed on a piece of filter paper to form a two-dimensional code painting. a) Two-dimensional code painting of our institute. The gray part is covered with MA-IPA material. Photographs taken b) under 365 nm lamp and c) after removal of 365 nm UV lamp.

approximately 345, 415, 482 and 509 nm, respectively (Figure 4b). Time-resolved emission spectrum (TRES) revealed a remarkable luminescence lifetime of MA-TPA crystals (Figure 4c). Critically, the crystalline sample gave rise to the longest lifetime (1.09 s) when irradiated at around 310 nm. In order to investigate the origin of the enhanced UOP lifetime, its single crystal structure was analyzed. Similarly, MA-TPA is also arranged in a highly ordered structure through hydrogen bonding self-assembly. In this process, MA gets a proton to become a cation MAH⁺, which is connected with adjacent molecules through a large amounts of intermolecular forces (hydrogen bonding and Van der Waals' forces), such as N-H...N, N- $H \cdots \pi$, N-H \cdots O, etc. (Figure 4d and 4e). Meanwhile, two protons in TPA are lost, forming TPA22, which forms a very symmetrical topological structure with adjacent four MA and two water molecules by intermolecular forces, including C-H···O, C-H···H-O, C-H···N and so on (Figure S7). The detailed hydrogen bond types and bond lengths are summarized in Table S5. As a result, molecular motions in the supramolecular architecture were effectively limited so that the ultralong phosphorescence was achieved. Similarly, the theoretical simulations were carried out to verify our concept (Figure S13). After self-assembly, the SOC ξ (S₁, T_n) of MA-TPA increased largely from 1.89 (TPA monomer) to 16.1 cm⁻¹, facilitating ISC process for phosphorescence generation. As we expected, MA-PA also showed blue ultralong phosphorescence with a lifetime of 0.68 s and a quantum yield of 0.82% (Figure S16 and Table S1 and S2) after stoppage of excitation, surpassing the corresponding monomers but below MA-IPA and MA-TPA. From its single crystal analysis, it was found that there was no water molecule in crystal (Figure S15), which was different from MA-IPA and MA-TPA crystals. Additionally, no hydrogen bonding was observed between PA molecules, to some extent, possibly accelerating non-radiative transitions to weaken UOP compared with MA-IPA and MA-TPA crystals (Table S4).

Application in barcode identification. Given the high efficient UOP feature of the supramolecular framework, a 2-dimensional barcode of our institute's (Institute of Advanced Materials @ Nanjing Tech University) WeChat identification pattern was fabricated using the phosphors of MA-IPA. As illustrated in Figure 5, the pattern was painted with MA-IPA on a piece of filter paper by screen-printing. The gray part of the pattern was the ground MA-IPA material (Figure 5a). Under UV-lamp excitation, it showed bluish violet luminescence in a dark room, which cannot be recognized by the WeChat scanning (Figure 5b). When the UV lamp was switched off, however, MA-IPA emitted luminous blue-green ultralong phosphorescence (Figure 5c), which can be identified immediately by scanning the barcode and the identified information

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was showed in Figure S17. Thus, we realized a barcode identification by this UOP supramolecular material in the darkness.

CONCLUSIONS

In summary, a new class of supramolecular frameworks with high efficiency ultralong organic phosphorescence were synthesized by self-assembly of melamine and aromatic acids in aqueous media. With multiple intermolecular interactions, the supramolecular frameworks showed three-dimensional networks, which not only effectively limited the non-radiative decay of the triplet excitons, but also promoted the intersystem crossing. Impressively, a record performance of UOP with both an ultralong emission lifetime of up to 1.91 s and a high phosphorescence quantum efficiency of 24.3% was demonstrated under ambient conditions. Taking advantage of its high efficient UOP, MA-IPA was successfully utilized in a barcode identification in a dark environment. This study not only provides an innovative and universal approach to achieving highly efficient UOP materials, but also expands the potential application of ultralong organic phosphorescence.

ASSOCIATED CONTENT

Supporting Information.

Scheme S1, chemical structures in this work, Figure S1-17 and Table S1-6, displaying phosphorescence lifetime and efficiency chart of organic materials, PXRD patterns, emission spectra, lifetime decay profiles, detail crystal date, the TD-DFT calculations and energy levels, the additional measurement supporting applications. SV1-2, complementary videos. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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SYNOPSIS TOC



Supramolecular framework