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Authors: He Tian, Xiang Ma, Chao Xu, and Jie Wang

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COMMUNICATION

Heavy-Atom-Free Amorphous Pure Organic Polymers with Efficient Room-Temperature Phosphorescence Emission

Xiang Ma,* Chao Xu, Jie Wang and He Tian*

Abstract: *Pure organic, especially heavy-atom-free room-temperature phosphorescence (RTP) materials have attracted much attention and presented potential applications in photoelectric and biochemical material fields due to rich excited state properties, with advantages of long luminescent lifetime, diversified design and facile preparation. However, recent achievements of efficient phosphorescence under ambient condition mainly focused on ordered crystal lattice or embedding into rigid matrices, which means that strict growth conditions and difficulty repeatability are inevitable. Herein, we developed a concise approach to realize RTP exhibiting considerably decent quantum yield and ultralong phosphorescence lifetime in amorphous state by radical binary copolymerization of acrylamide and different phosphors with oxygen-containing functional groups. The cross-linked hydrogen bonding networks among polymeric chains immobilize phosphors to suppress non-radiative transitions and provide microenvironment to shield quenchers in pursuit of ultralong phosphorescence. This facile and universal strategy may pave the way toward expanding amorphous heavy-atom-free organic RTP materials and their applications.*

Room-temperature phosphorescence (RTP) materials with persistent luminescence have attracted considerable attention because of unique generation process and long-lived excited state leading to visual observation of ultralong lifetimes emission from seconds to several hours.[1, 2] Thus, these RTP materials can be applied to the fields of biological imaging, [3, 4] photodynamic therapy, [5] molecular sensing, [6] information storage, [7] and so forth. Until now, phosphors with RTP are mainly coordination complexes that contain noble metals. [8-11] Since these organometallic compounds are inevitably expensive and relatively toxic, novel pure organic phosphorescent materials is necessary to be developed. For pure organic systems with RTP, two vital factors should be considered carefully when designing molecules: (1) facilitating the spin-forbidden transfer of singlet-to-triplet excited states through intersystem crossing (ISC) to populate triplet state, (2) inhibiting the non-radiative relaxation pathways as much as possible. Based on fundamental molecular design principles, crystallization-induced phosphorescent systems have been reported as an effective approach to construct RTP materials not only from the rigidity of system to suppress non-radiative transitions, but also at the isolation of oxygen molecules, which could easily quench the triplet state. [12-17] Huang et al. designed a series of pure organic molecules with ultralong RTP lifetimes ranging from 0.21 to 1.35 s through H-aggregation in single crystals. [18] Kim et al. developed a bright mixed crystal material with high RTP quantum yield through heavy-atom effect directed by halogen bonding. [19] However, it is still a challenge for crystallization-induced phosphorescent systems to prepare thin solid film light-emitting devices with facile processability and good repeatability, which further hampers the commercialized applications of RTP materials.

Thus, it is essential to develop pure organic amorphous RTP materials. The common method to obtain such materials is to embed the phosphors into rigid polymer matrixes, [20, 21] steroidal compound, [22, 23] the cavity of macrocycle hosts, [24-27] and so forth. In addition, our group designed a series of phosphors to copolymerize with acrylamide that could engender effective phosphorescence emission of different colors under ambient conditions, [27-29] in which the hydrogen bonding network restricted the molecular motions and the halogen atom (e.g. bromine) enhanced the spin-orbit coupling. In these cases, the halogen atoms are essential units in order to facilitate the intersystem crossing. [30-32] While, it is well-known that the use of heavy atoms will cause the RTP emission lifetime shortly, which is a typical blinking time for human eyes and hard to observe. [33] Although great efforts have been devoted, RTP from pure organic amorphous materials without halogen atoms remains a formidable challenge.

In this work, a concise approach was provided to realize RTP by radical binary copolymerization of acrylamide and different phosphors containing oxygen atom and benzene moiety without heavy atom substituents (Scheme 1, **P1**-**P10**). Polyacrylamide is an ideal polymer matrix to immobilize phosphors, which can also be strengthened by the hydrogen bond cross-linking between polymeric chains. Meanwhile, oxygen atom favors $n-\pi^*$ transition and hence facilitates the spin-forbidden transfer of singlet-to-triplet excited states through intersystem crossing to populate triplet excitons. As a result, the materials prepared herein can engender intense RTP signals and show an ultralong phosphorescent lifetime. To our knowledge, this would be the first report about heavy-atom-free pure organic amorphous RTP materials.

A series of pure organic molecules with oxygen-containing functional groups (compound **1**-**10**) were employed to copolymerize with acrylamide and prepare amorphous polymers **P1**-**P10**. The general synthetic route of the polymer and the structures of monomers were shown in Scheme 1. All the compounds were purchased from commercial sources directly or synthesized via a few simple steps (Figure S1-S3, SI). And compound **1**-**10** were copolymerized with acrylamide at the molar ratio of 1:50 unless otherwise stated. Among all the polymers, **P3** possesses the longest phosphorescent lifetime and a decent quantum yield in the solid state. Under 254 nm irradiation, the solid powder of **P3** exhibited intense RTP emission in air. And the powder showed blue-colored persistent luminescence after removing the ultraviolet source, which could last for several seconds (Figure 1b). Thus **P3** was investigated as a model in the following discussions.

Prof. X. Ma, C. Xu, J. Wang and Prof. H. Tian
Key Laboratory for Advanced Materials and Joint International Research Laboratory of Precision Chemistry and Molecular Engineering, School of Chemistry and Molecular Engineering, East China University of Science & Technology, Meilong Road 130, Shanghai 200237, China.
E-mail: maxiang@ecust.edu.cn & tianhe@ecust.edu.cn

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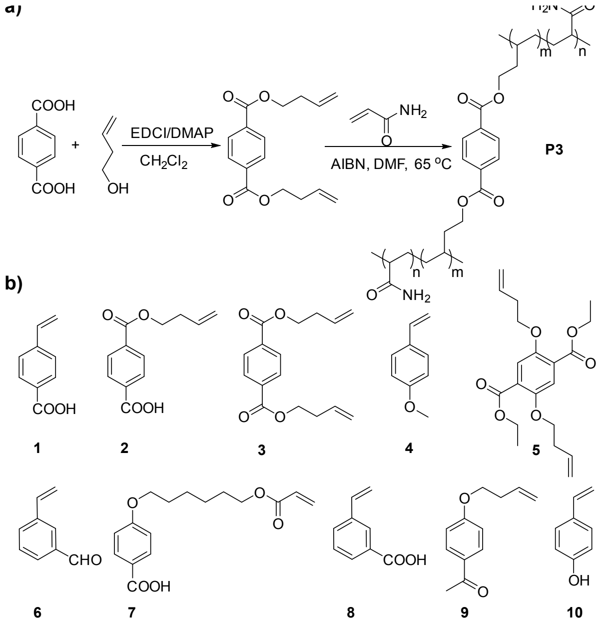

Scheme 1. a) The general synthetic route of the polymers; b) Molecular structures of compounds **1** to **10**.

As shown in Figure 1a, **P3** solid powder exhibited a delayed luminescence at a wide wavelength region (λ_{max} = 427 nm) with an ultralong lifetime (τ up to 537 ms, quantum yield Φ = 15.39%), along with fluorescence emission at λ_{max} = 322 nm (λ_{ex} = 289 nm). The lifetime of the persistent luminescence is exceptionally long for pure organic compounds. And the blue-colored afterglow could be traced in a time range of 0-4 s by the naked eye (Figure 1b). The large Stokes shift of RTP emission of **P3** is around 140 nm, corresponding to the RTP characteristics. Meanwhile, the maximum emission in phosphorescence mode (λ_{max} = 427 nm) redshifts 105 nm compared with fluorescence emission (λ_{max} = 322 nm), which further validates the afterglow belongs to phosphorescence instead of possible delayed fluorescence. Moreover, as we expected, the RTP intensity of polymers varied with the molar ratios of two monomers. Generally, an intense RTP emission could be observed at lower amount of phosphor benefiting from more efficient embeddedness and wider distribution. In contrast, a higher amount of phosphor leads to weaker rigidity and shielding effect from oxygen. Even so, an ultralow ratio will also lead to weak RTP emission. Among different ratios of copolymerization, the RTP intensity of 1/50 was determined to be the highest (Figure 2a). And the photophysical properties of **P3** with different ratios was shown in Table S1. X-ray powder diffraction (XRD) analysis was carried out to explore the microstructure of these polymers (Figure 2b). **P1**, **P3**, **P5**, **P9** and polyacrylamide (PAM) as reference polymers were analyzed. And the results verify the amorphous state of these polymers.

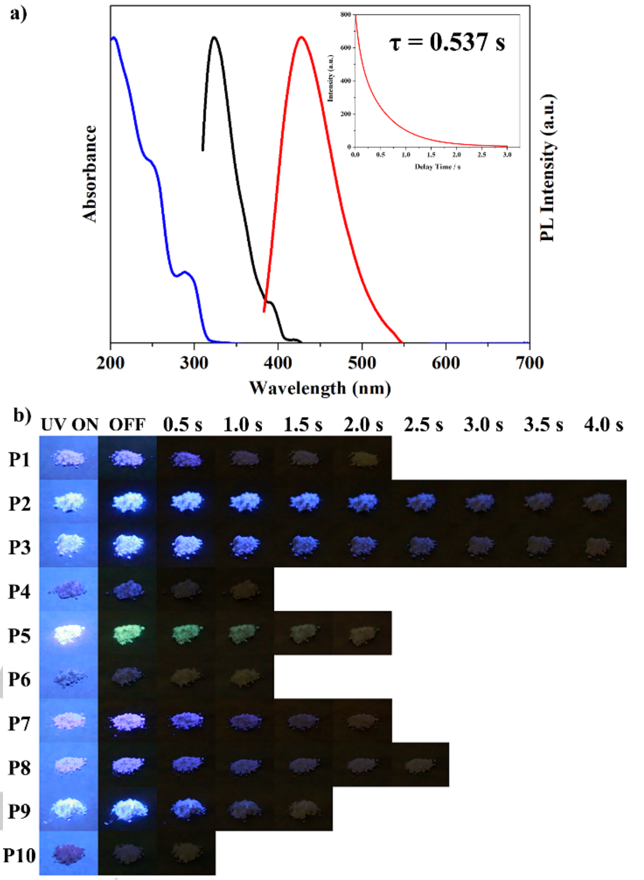

Figure 1. a) UV-Vis absorption (blue), steady-state fluorescence (black) and RTP (red) spectra of **P3**. Inset: luminescent decay lifetime of **P3** at 427 nm. b) Luminescence photographs of **P1**-**P10** powder under 254 nm UV irradiation and at different time intervals after removal of ultraviolet lamp.

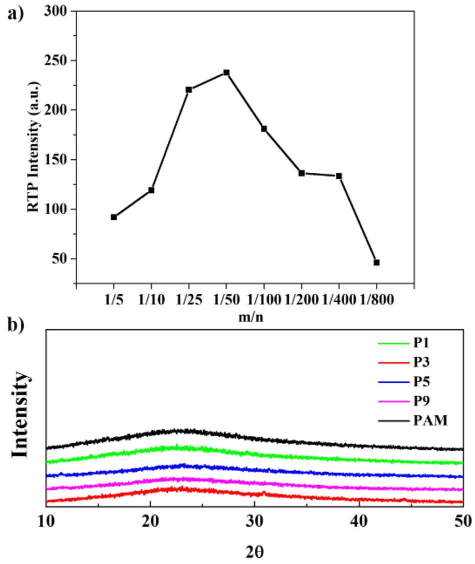

Figure 2. a) RTP intensity of **P3** with different molar ratios of m/n at 427 nm. (Phosphorescence mode; excitation slim = emission slim =10 nm; excitation voltage = 600 V in solid state. b) XRD patterns of PAM, **P1**, **P3**, **P5** and **P9**.

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To probe the mechanism of the observed ultralong luminescence from pure organic compounds, photophysical properties of compounds with different oxygen-containing functional groups were discussed. All these compounds exhibited RTP emission and triplet lifetimes ranging from 16 ms to 537 ms at the molar ratio of 1:50 with acrylamide (Table 1, Figure 1b), which validates the type and position of functional groups, length of branch chain and the cross-linked structure are not necessary key factors to RTP. The oxygen atoms with lone pair electrons are favorable for the n–π* transition, which enhances the spin–orbit coupling. This in turn populates the triplet states through singlet–triplet intersystem crossing. [18] Meanwhile, the hydrogen bonding among polymeric chains can immobilize the RTP phosphor to reduce energy dissipation from non-radiative relaxation pathways. In addition, the micro-environment with rich hydrogen bonds can shield phosphorescent moieties from oxygen quenching effect and weaken the collisional deactivation as well. As a result, pure organic ultralong phosphorescence without heavy atom under ambient conditions could be realized.

Table 1. Photophysical data of P1 to P10 in the solid at 300 K[a].

	λ_{ex}[nm]	λ_{Fluo} [nm]	λ_{Phos} [nm]	τ_p[ms]	Φ_p [%]
P1	243	368	434	123	6.40
P2	289	n.d.[b]	425	522	17.87
P3	289	322	427	537	15.39
P4	277	n.d.[b]	426[c]	81	4.06
P5	321	413	497[c]	218	5.45
P6	259	n.d.[b]	430	28	0.01
P7	260	313	418	198	5.15
P8	280	314,383	424	106	4.04
P9	280	n.d.[b]	433	195	30.55
P10	278	n.d.[b]	423[c]	16	6.38

[a] The spectral data are shown in Figures S13-S21. [b] Not detected. [c] The intensity of the phosphorescence emission is weak.

In order to confirm the necessity of copolymerization between the phosphorescent monomer and acrylamide for the achievement of RTP emission, compound **2** was doping into polyacrylamide (PAM) as control experiments because PAM was only water-soluble and compound **2** exhibited better water-solubility than other monomers. Comparing the emission intensities of phosphorescence (Fig. S10), **P2** manifested better RTP-emissive property superior to the mixture (**dP2**), which indicated that the covalent bonding from copolymerization effectively restricted the translational motion of the phosphor. As mentioned above, the hydrogen bond cross-linked networks could restrict the molecule motion of phosphor monomer, which greatly enhanced the intensity of RTP emission. To evaluate this influence, copolymerization of compound **3** and *N*,*N*-dimethyl acrylamide was conducted (**P3'**). The experiment detail and structure of **P3'** were shown in Figure S11. With the low degree of hydrogen bond cross-linked network formed by *N*,*N*-dimethyl acrylamide, no signal of RTP at 427 nm was detected (Fig. S12).

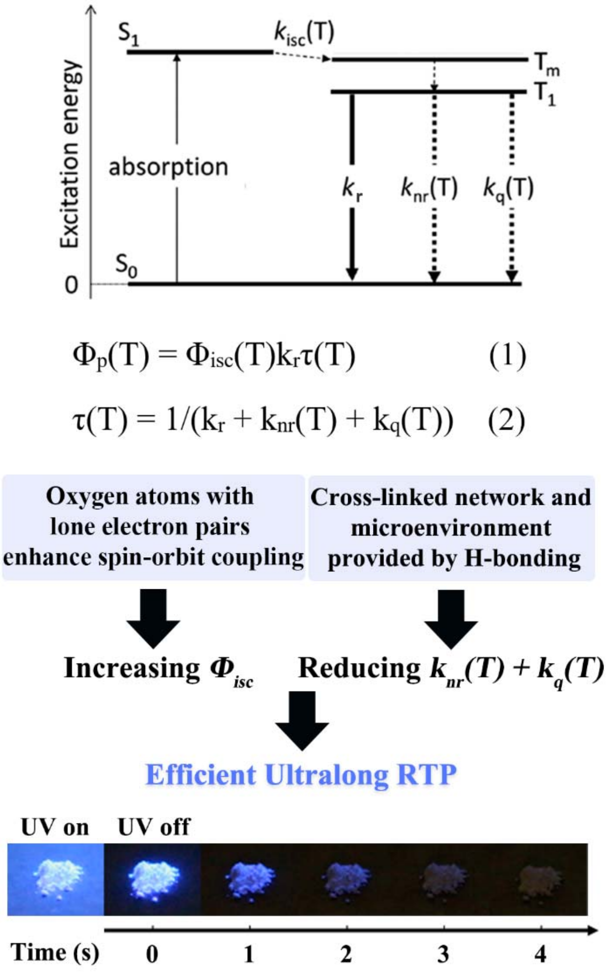

Figure 3. Jablonski diagram showing radiative and non-radiative processes from the lowest excited triplet state in aromatic compounds (k_r is the radiative rate constant of phosphorescence, k_{nr}(T) is the non-radiative rate constant from the T_1 state at T [K], k_q(T) is the tripet exciton quenching rate constant derived from interactions with oxygen at T [K]). Material design of significant decrease of the non-radiative decay rate provides **P3** with efficient ultralong RTP in air.

From Fig. 3 Equations (1) and (2), k_{nr}(RT) + k_q(RT)<k_r and a high Φ_{isc}(RT) value are required to realize bright ultralong RTP emission under ambient conditions. For terephthalic acid (TPA) with similar structure to compound **3**, intrinsic k_r is 1.75×10^0 s^{-1} in crystal.[33] Therefore, the key is to minimize the non-radiative decay rate (k_{nr}) and the quenching rate constant (k_q) of the lowest triplet excited state (T_1 state) at R.T. The cross-linked hydrogen bonding networks among polymeric chains hinder molecular motions (rotations, vibrations and collisions) significantly, thus suppressing non-radiative deactivations. Meanwhile, such microenvironment with rich hydrogen bonds can efficiently shield quenchers like oxygen. As a result, the value of k_{nr}(RT) + k_q(RT)<<<k_r<1.75×10^0 s^{-1}. Although the use of heavy atoms is useful in attaining a high Φ_{isc}(RT) and thus contributes to a high

Φ_p(RT), it also accelerates k_r and k_{nr}(RT), which typically results in a shorter τ_p(RT) lifetime based on Equation (2). Therefore, oxygen-containing functional groups with lone pair electrons in favour of n–π* transition were introduced to enhance the spin–orbit coupling,[34] realizing heavy-atom-free amorphous RTP materials with larger Φ_P(RT). Compared with other molecules, **P3** is ideal in this regard with a quantum yield =15.39 % and a lifetime =0.537 s because of the promotion of the n-π* transition from constituting oxygen atoms and the intrinsic cross-linked structure with more rigidity as well. The existence of heavy atom in similar polymers just resulted in a shorter lifetime (τ=1.15 ms). [28]

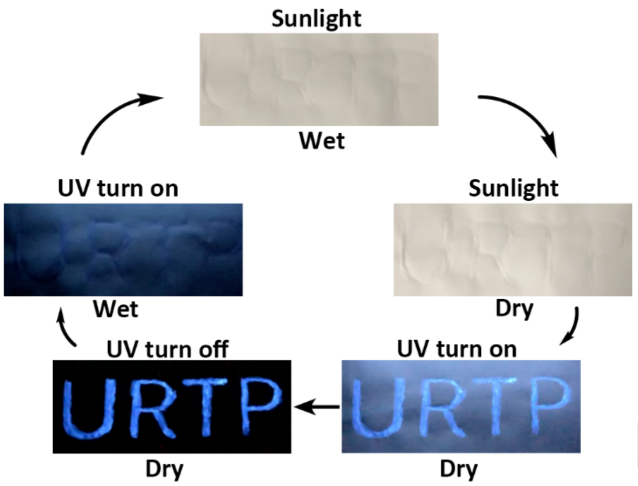

Figure 4. Photographs of letters (URTP) before and after drying under sunlight, 254 nm UV light and after the removal of excitation source.

Benefiting from the excellent solubility in water and distinguishable RTP lifetime, these amorphous materials could be used to develop niche applications in document security. E.g. aqueous **P3** solution (m/n = 1/50, 20 mg/ml) as the ink and letters ‘URTP’ were prepared manually on a piece of non-fluorescent paper. Upon drying under far-infrared light for 1 min, all letters are virtually invisible under sunlight (Figure 4). And the patterned security features of ‘URTP’ encrypted with ultralong phosphorescence could be observed by naked eye after the removal of UV light (Movie S1). After spraying with a small amount of water, the letters became invisible immediately under both sunlight and UV light, because of the destruction of hydrogen bond cross-linked networks in solid and RTP quenching by collision and oxygen. This process is totally reversible.

In summary, we successfully presented a concise and very simple chemical approach to construct amorphous pure organic RTP materials based on heavy-atom-free polymers. The principle, which involves the inhibition of non-radiative relaxation pathways through hydrogen bonding cross-linked networks, provides convenient access to ultralong-lived luminescence observed by naked eye in a diverse array of pure organic molecules under ambient conditions. Notably, **P3** powder exhibited a phosphorescence lifetime of 537 ms and an appreciable quantum yield of 15.39 %. This method possesses the merits of facile preparation, simplicity, universality and R. T. phosphorescence emission without the rigorous condition including deoxygenization and low temperature. The understanding gained from the experimental results will allow for the construction of next-generation amorphous RTP materials that may inspire the development of organic devices, molecular imaging, water sensing and data security.

Acknowledgements

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Keywords: room-temperature phosphorescence • heavy-atom-free • amorphous polymer

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

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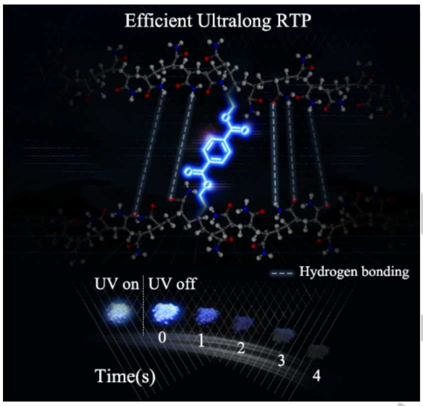

Xiang Ma, Chao Xu, Jie Wang and He Tian**

Page No. – Page No.

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