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Rational molecular and doping strategies to obtain organic polymers with ultralong RTP†

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Organic-doped polymers and room-temperature phosphorescence (RTP) mechanisms have been widely reported. However, RTP lifetimes >3 s are rare and RTP-enhancing strategies are incompletely understood. Herein, we demonstrate a rational molecular doping strategy to obtain ultralong-lived, yet bright RTP polymers. The $n-\pi^*$ transitions of boron- and nitrogen-containing heterocyclic compounds can promote a triplet-state population, and the grafting of boronic acid onto polyvinyl alcohol can inhibit molecular thermal deactivation. However, excellent RTP properties were achieved by grafting 1–0.1% (*N*-phenylcarbazol-2-yl)-boronic acid rather than (2-/3-/4-(carbazol-9-yl)phenyl)boronic acids to afford record-breaking ultralong RTP lifetimes up to 3.517–4.444 s. These results showed that regulation of the interacting position between the dopant and matrix molecules to directly confine the triplet chromophore could more effectively stabilize triplet excitons, disclosing a rational molecular-doping strategy for achieving polymers with ultralong RTP. Based on the energy-donor function of blue RTP, an ultralong red fluorescent afterglow was demonstrated by co-doping with an organic dye.

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Introduction

Ultralong and bright room-temperature phosphorescence (RTP) materials have potential applications in optoelectronic devices, bio-imaging, anti-counterfeiting, information storage, and glow-in-the-dark products. Among them, organic-doped RTP polymers are attracting much attention due to their economy, good processability, biocompatibility, and diverse mechanical properties.^{1–5} Polymers rich in hydrogen bonds such as polyvinyl alcohol (PVA) and poly-acrylamide (PAM) have been widely used as matrices in view of their high rigidity and strong interactions with the polar groups of organic dopant molecules.^{6–20} Utilizing PVA as a matrix, Huang *et al.* obtained a RTP lifetime of 3.16 s by doping carbazol-9-ylacetic acid,¹⁸ Yang *et al.* doped triphenyl-2-yl-boronic acid and realized a RTP lifetime of 3.29 s.²¹ Li *et al.* doped simple bi- and terphenylboronic acids and achieved RTP lifetimes of 2.34–2.43 s.⁶ Chen *et al.* co-polymerized 9-vinylcarbazole and acrylamide and realized a RTP lifetime of 4.2 s.¹⁹ These are the longest-lived RTP lifetimes obtained so far. Therefore, the number of organic-doped RTP polymers with ultralong lifetimes (>3 s) is limited. Moreover, the effect of comparable-structure dopants and material aggregates on organic RTP properties is incompletely understood.^{1,20,22–24}

We are interested in whether RTP lifetimes can be advanced to a higher level and the mechanism of such advancement. Considering the prominent roles played by aromatic boronic acids and carbazole units in ultralong organic-doped RTP polymers, we intended to develop boronic acid-containing *N*-phenyl-carbazoles as dopants because the coexistence of boron and nitrogen is conducive to inter-system crossing. Recently, we doped 4-(carbazol-9-yl)phenylboronic acid (P4BA) into PVA, and achieved a long component and averaged RTP lifetime of 3.21 and 2.01 s respectively.²⁰ These values are not what we hoped for because P4BA has an extended π system compared with carbazol-9-yl-acetic acid and an additional hetero atom

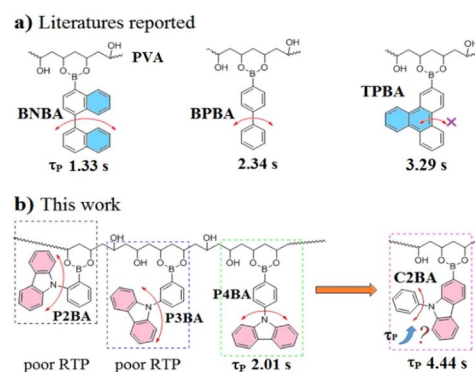


Fig. 1 (a) Structures and RTP lifetimes of arylboronic acids grafted on PVA side-chains. (b) Changing the positions of boronic acid on *N*-phenylcarbazole to suppress the internal rotation of a triplet chromophore and boost the RTP lifetime to a higher level.

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compared with aryl boronic acids (Fig. 1). We noted that carbazol-9-yl-acetic acid did not have an aryl internal rotation unit and, among aryl boronic acids, BNBA had a more distorted internal rotation unit than BPBA, whereas fused TPBA had eliminated aryl internal rotation. These results suggested that inhibiting the internal rotation of a triplet chromophore may be an effective way of achieving ultralong RTP. For *N*-phenylcarbazole, the boronic-acid unit can be introduced at the phenyl or carbazole rings, and the latter can inhibit the triplet chromophore directly and should improve the RTP properties. However, the RTP properties of *N*-arylcarbazoles with heteroatom groups on the carbazole ring in polymer films have not been reported.

Herein, we isomerized boronic acid from phenyl to carbazole and prepared 9-phenylcarbazol-2-ylboronic acid (C2BA) as a dopant. C2BA was dispersed in a PVA matrix using solution-cast films, and then the films were thermoplastic-processed into sheets. Our organic-doped RTP polymers were prepared and characterized in the form of solution-cast films. This should not be the best aggregate state for inhibiting the thermal motion of doped molecules because most polymers usually aggregate together in loose coils according to the theory of how polymer solutions behave. Thermoplastic processing is a more extensive method of obtaining complex products for practical use. Moreover, polymers can be sheared and orientated to form denser stacking structures according to the rheology of

polymers during processing, which is conducive to limiting thermal deactivation. Moreover, few conjugated organic dopants are soluble in water or well dispersed in PVA, whereas thermoplastic processing can promote the grafting and uniform dispersion of C2BA in PVA. As a result, trace doping may also achieve excellent RTP properties. Herein, we report that thermoplastic processing boosted RTP afterglows considerably, and that C2BA/PVA was superior to the PVA sheets doped by (2/3/4-(carbazol-9-yl)-phenyl)boronic acids. Notably, C2BA doping (1.0 wt%) in PVA could achieve a RTP lifetime of 3.517 s, and the longest RTP lifetime (up to 4.444 s) was optimized by tuning the doping amount. Our experimental results indicate that ultralong and bright organic RTP depends not only on the material system but also on the molecular and doping strategies, and that direct inhibition of triplet chromophores is conducive to ultralong RTP.

Results and discussion

C2BA and (2/3/4-(carbazol-9-yl)phenyl)boronic acids (P2BA, P3BA, and P4BA) are commercially available. They were re-purified by silica-gel column chromatography and recrystallized before use. These crystals emitted very inferior RTP (Fig. S1, ESI†), which could not be explained by intermolecular interactions or chemical composition. However, they all emitted RTP in PVA due to changes in molecular-

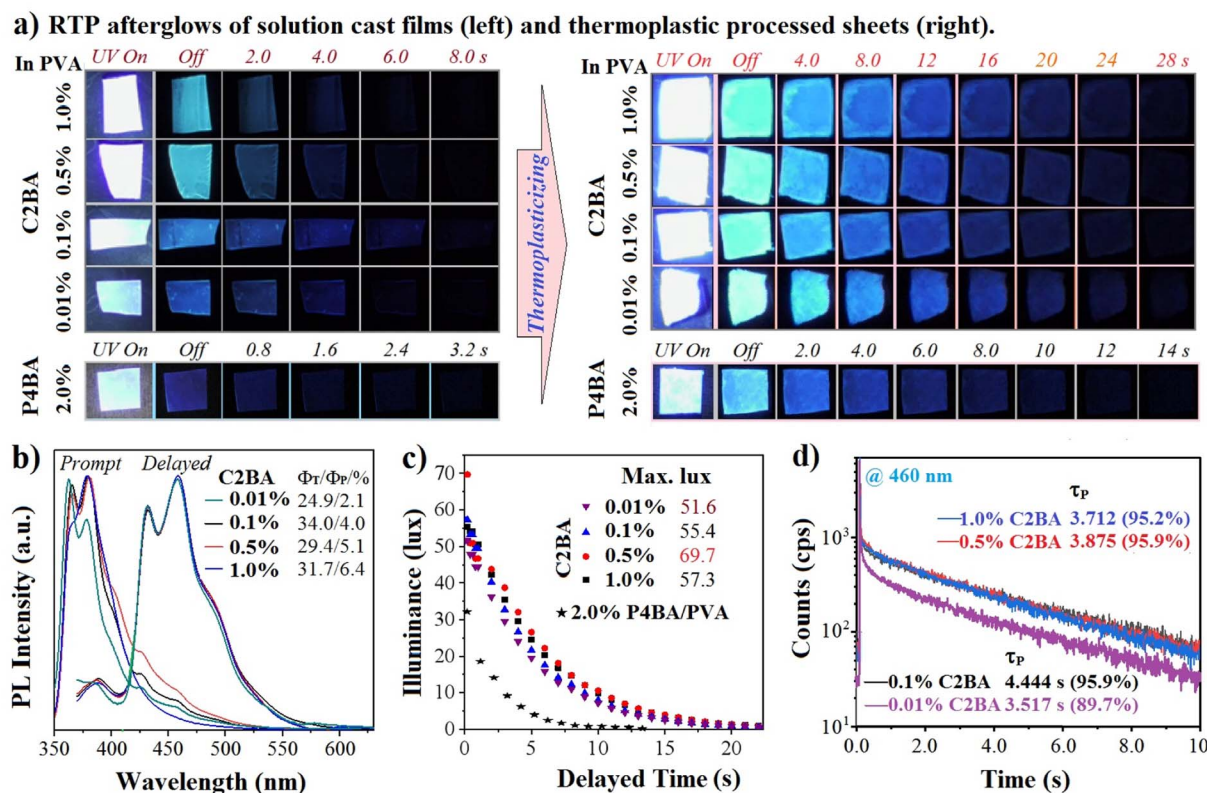


Fig. 2 (a) PL photographs of solution-cast C2BA and P4BA-doped PVA films and the corresponding thermoplastic-processed sheets with different percentages for doping weights before and after removal of 365 nm excitation light (0.3 mW cm^{-2}) for 5 s at room temperature in the dark. (b–d) Steady-state PL spectra, relative afterglow illuminance, time-resolved RTP decay curves, and the fitted RTP lifetimes of C2BA/PVA sheets under light excitation at 365 nm.



confined environments (Fig. S2†) by negating the deduction of RTP from each other in crystals and polymers. The thermoplastic-processed sheets showed an improved RTP afterglow. P4BA was the best among the three phenylboronic acids-doped PVA, and the RTP lifetime of 0.1 wt% P4BA/PVA sheet was 1.512 s (Fig. S3†). In sharp contrast, C2BA/PVA sheets exhibited significantly boosted RTP afterglows after UV excitation at 365 nm regardless of the large changes in doping weights (1.0–0.1% *versus* PVA) (Fig. 2a). The steady-state photoluminescence (PL) spectra showed that C2BA/PVA sheets emitted near-UV fluorescence and blue RTP with a maximal wavelength of 382 nm and 459 nm, respectively (Fig. 2b). Overall, the measured PL efficiency (Φ_p) by an integrating sphere and the calculated RTP efficiency (Φ_p) were reduced with a decrease in the amount of C2BA (inset in Fig. 2b and S4†). As a comparison of relative brightness, afterglow illuminance is measured under identical conditions of preparation and light excitation. C2BA/PVA sheets at 1.0, 0.5, 0.1, and 0.01 wt% showed maximal afterglow illuminance of 57.3, 69.7, 55.4, and 51.6 lux, respectively (Fig. 2c).

In contrast, the P4BA/PVA sheet exhibited low afterglow illuminance (23.5 lux). The time-resolved RTP decay curves were monitored, and the fitted long-component RTP lifetimes (τ_p) were in the range 3.512–4.444 s with high ratios (89.7–95.9%) (Fig. 2d and Table S1†). Also, doping with 0.1% C2BA led to the longest RTP lifetime (up to 4.444 s), and doping at 1.0% could achieve an RTP afterglow with a lifetime of 3.512 s and illuminance of 51.6 lux. Overall, we boosted the RTP lifetime of organic-doped PVA materials to a much higher level.^{6–10} The relatively low Φ_p but ultralong (yet bright) afterglow meant that abundant triplet excitons were mainly stabilized to emit a delayed RTP.

Arylboronic acid-doped PVA is a special system in which PVA can esterify arylboronic acid to form a graft polymer. To verify esterification, a conventional dissolution-extraction experiment was conducted because it should be simpler and more reliable than spectroscopy for trace doping and grafting. Thus, the C2BA/PVA sheet was redissolved in water and extracted with acetone (solvent for C2BA). Fig. 3a shows that C2BA/PVA showed excessive swelling rather than dissolution, possibly due to the

heat-induced partial crosslinking of PVA. Importantly, RTP afterglows of dried residues continued to be ultralong, indicating that triplet dopant molecules had not been removed. To examine the effect of grafting on RTP properties further, C2BA was esterified by 1,3-propanediol in advance to form C2BE and then to dope PVA. C2BE/PVA sheets also emitted a commendable RTP afterglow but it was inferior to that of C2BA/PVA (Fig. 3b and S5†). However, the C2BE/PVA residue no longer showed ultralong RTP after dissolution-extraction under an identical procedure. Experimental results verified boron esterification between PVA and C2BA molecules as well as the positive effect of chemical bonding of triplet chromophores onto PVA chains by inhibiting triplet thermal deactivation.

Based on the results stated above, we propose a stabilizing RTP mechanism (Fig. 4). Organic aromatic backbones are weakly compatible with a polymer matrix even if they are dispersed in the matrix at the molecular level by a co-solvent method. A nano cavity is formed and the free volume is increased, which is not conducive to inhibition of molecular thermal motion. Strong intermolecular interactions (especially

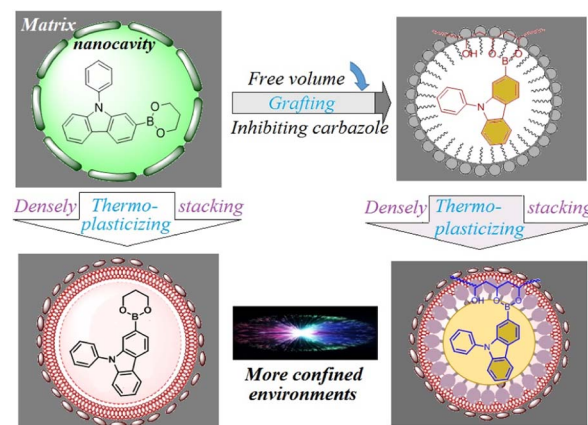


Fig. 4 Effect of chemical grafting and thermoplasticization on the confined environment and degree of organic dopant molecule (schematic). The poorly compatible dopant forms a nanocavity in the matrix. Thermoplasticization and grafting compress the free volume to inhibit molecular motions and decrease triplet thermal deactivation.

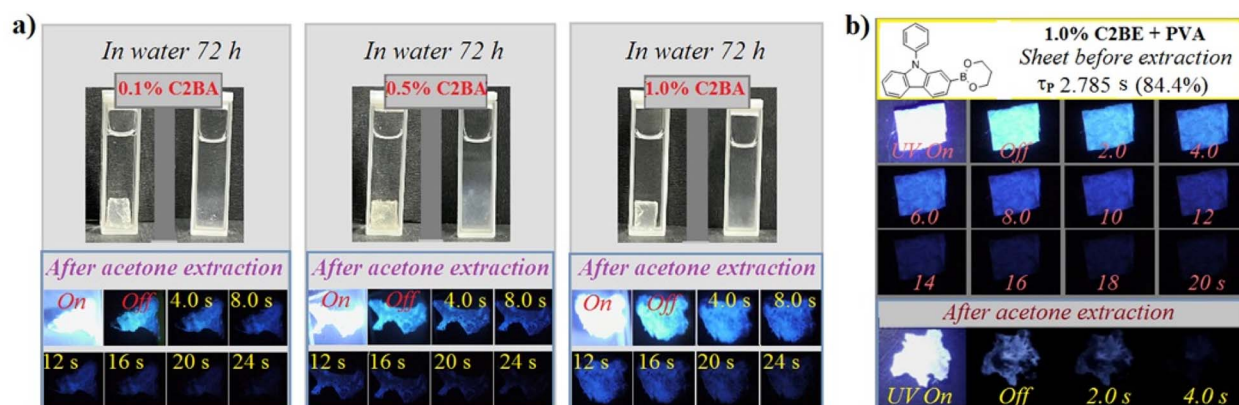


Fig. 3 (a) Dissolution photographs of C2BA/PVA sheets in water and the corresponding residue PL photographs after acetone extraction. (b) PL photographs of a C2BE/PVA sheet and its residue after dissolution-extraction. Samples were excited by light at 365 nm at room temperature.



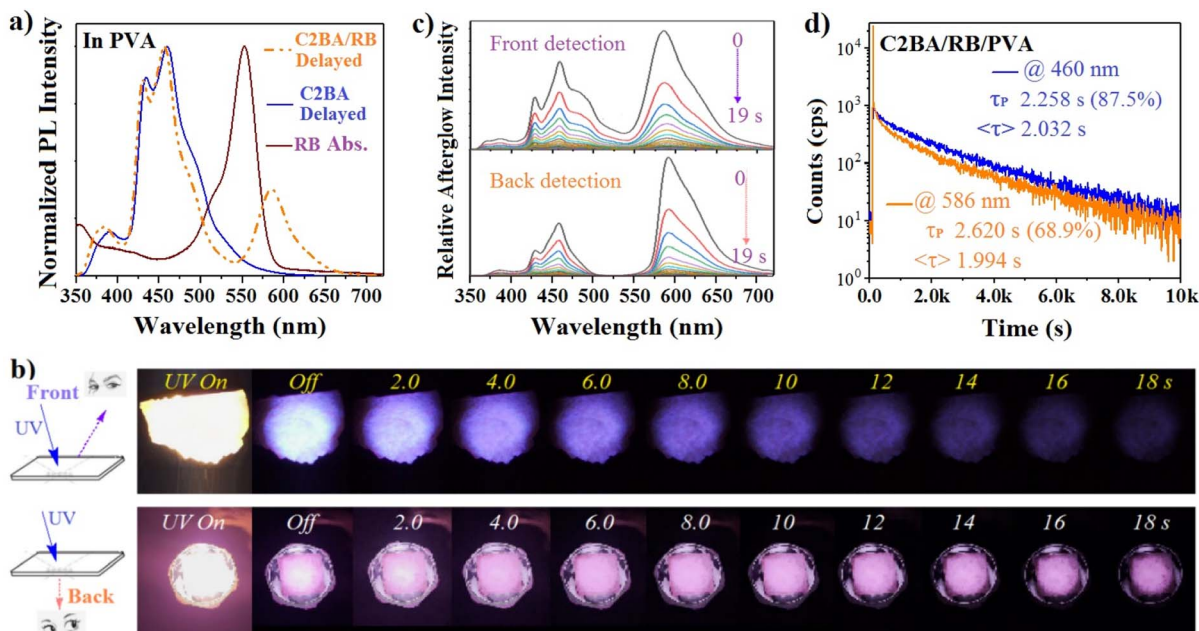


Fig. 5 (a) Absorption spectrum of a RB/PVA film and delayed PL spectra of C2BA/PVA (1 : 100) and C2BA/RB/PVA (1 : 0.2 : 100) sheets excited by light at 365 nm. (b) PL photographs of C2BA/RB/PVA sheets taken from UV light-excited front and back sides. (c) Time-dependent afterglow spectra of C2BA/RB/PVA sheets recorded by a CCD spectrometer from light-excited front and back sides. (d) Time-resolved afterglow decay curves and fitted afterglow lifetimes under light excitation of 365 nm.

covalent bonding) can reduce the free volume, and densely stacking the matrix by thermoplastic processing can also have a similar role. If polymers have strong intermolecular interactions with triplet chromophores, the free volume and thermal motions of aromatic backbones should be reduced conspicuously. As a consequence, triplet excitons are stabilized effectively and increasingly radiate decay, thereby enabling ultralong and bright RTP afterglows. In this context, for a conjugated organic molecule, the bonding positions of peripheral polar groups require an appropriate design, and their RTP properties in polymers cannot be evaluated by solution-cast films alone.

Finally, we demonstrated persistent ultralong blue RTP and red fluorescence dual emission with afterglow lifetimes of >2 s by co-doping C2BA and rhodamine B (RB) into PVA. A very broad absorption spectrum with a main absorption band at ~550 nm was observed for RB in PVA (Fig. 5a), which overlapped with the RTP emission of C2BA/PVA only in the blue-green region. Therefore, persistent partial-energy transfer contributed to the ultralong mixed-color emission composed of blue RTP and orange fluorescence. When C2BA (1.0 wt%) and RB (0.2 wt%) were doped, the C2BA/RB/PVA sheet (thickness = 1.0 mm) was semi-transparent. The afterglow color viewed by the naked eye from the excitation back was redder than that viewed from the excitation front (Fig. 5b). Hence, more blue afterglow energy was transferred to RB during its propagation in the PVA matrix. The different colors and degree of energy transfer was confirmed by time-dependent charge-coupled device (CCD) spectroscopy (Fig. 5c). It is interesting and rarely reported that different color ultralong afterglows were observed from a sample by viewing from different sides. The measured PL efficiency for C2BA, C2BA/RB and RB in PVA was 31.7%, 32.1%

and 23.5%, respectively (Fig. S6†). C2BA/RB/PVA showed much lower PL efficiency than the sum (55.2%) of C2BA/PVA and RB/PVA, which suggested inter-molecular interactions and energy transfer between C2BA and RB.

We measured the time-resolved PL decay curves of C2BA/RB/PVA sheets at 460 nm and 586 nm under light excitation of 365 nm (Fig. 5d). The fitted long-component afterglow lifetime was 2.258 s (87.5%) and 2.620 s (68.9%), respectively, but the average lifetime was almost identical (2.032 s and 1.994 s, respectively), which implied a persistent and proportional energy transfer from the triplet state of C2BA to the singlet state of RB. This triplet-to-singlet energy transfer is thought to follow the Förster theory.^{25–28} Thus, the efficiency of energy transfer could be calculated according to the equation $\Phi_{ET} = 1 - \tau_D/\tau_{D0}$, where τ_D and τ_{D0} are the RTP lifetimes of an energy donor (C2BA) in PVA in the presence and absence of an energy acceptor (RB), and introduction of an energy acceptor reduces the RTP lifetime of an energy donor. Based on C2BA (1.0 wt%), the average RTP lifetime of C2BA/PVA and C2BA/RB/PVA was 3.168 s and 2.032 s, respectively, and Φ_{ET} was calculated to be 35.8%. A high amount of RB doping could improve Φ_{ET} , but afterglow brightness and the lifetime could be reduced markedly due to the strong hiding power and self-absorption of RB.

Conclusions

In summary, we have demonstrated that the RTP properties of organic-doped polymers are determined by the organic dopant, polymer matrix and preparation method of the materials. PVA rich in hydrogen bonds has strong rigidity and cohesion, and can form covalent linkages with arylboronic acid to stabilize the triplet



state and achieve ultralong RTP. However, for a given aromatic compound, the introduction positions of polar groups can significantly affect the RTP properties. Our experimental results show that the direct interactions between the triplet chromophore and polymer *via* strong hydrogen bonding and covalent bonding were conducive to the inhibition of triplet thermal deactivation. We also present that thermoplastic processing solution-cast films could densely stack the matrix to help stabilize ultralong RTP. RTP lifetimes of 3.517–4.444 s were achieved by tuning the position of boronic acid on *N*-phenylcarbazole. In this way, new ultralong organic RTP polymers not limited to a PVA matrix or carbazole derivative-dopants are being developed by our research team.

Author contributions

S. X., W. Y. and Q. S. supervised the project. Y. Z. and W. Y. designed the experiments. Y. Z., S. Z. and G. L. carried out all experiments. Y. Z. and S. Z. undertook data analyses. Y. Z. and W. Y. contributed to experimental design. Y. Z. wrote the manuscript with the help of W. Y., Q. S. and S. X.

Conflicts of interest

There are no conflicts of interest to declare.

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