Host–Guest Interactions

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A Synergistic Enhancement Strategy for Realizing Ultralong and Efficient Room-Temperature Phosphorescence

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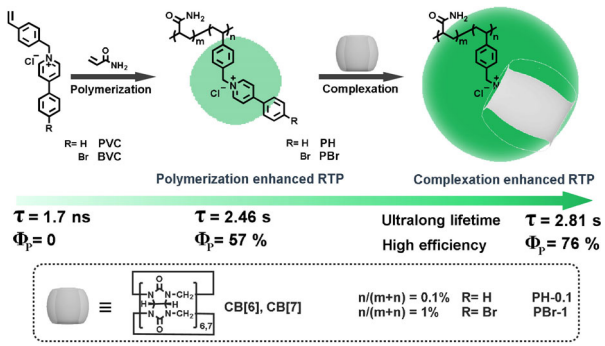
Abstract: *An enhancement strategy is realized for ultralong bright room-temperature phosphorescence (RTP), involving polymerization between phosphor monomers and acrylamide and host–guest complexation interaction between phosphors and cucurbit[6,7,8]urils (CB[6,7,8]). The non-phosphorescent monomers exhibit 2.46 s ultralong lifetime after copolymerizing with acrylamide. The improvement is due to the rich hydrogen bond and carbonyl within the polymers which promote intersystem crossing, suppress nonradiative relaxation and shield quenchers effectively. By tuning the ratio of chromophores, a series of phosphorescent copolymers with different lifetimes and quantum yields are prepared. The complexation of macrocyclic hosts CB[6,7,8] promote the RTP of polymers by blocking aggregation-caused quenching, and offsetting the losses of aforementioned interaction provided by polymer. Multiple lifetime-encoding for digit and character encryption are achieved by utilizing the difference of their lifetimes.*

Introduction

Organic room-temperature phosphorescence (RTP) materials with ultralong lifetime and bright emission have received enormous attention because of their potential for bioimaging,[1] information encryption and anticounterfeiting,[2] organic light-emitting diodes,[3] and so on.[4] Recently, much efforts have been devoted to exploring purely (metal-free) organic phosphorescent materials owing to their low cost, versatile design strategy, and abundant resources. However, realizing ultralong RTP with bright emission is difficult for these materials because the intersystem crossing (ISC) from the lowest excited singlet state (S_1) to the triplet manifold (T_n) is inherently inefficient and the long-lived triplet state (T_1) is exhausted fast by nonradiative relaxation processes and quenchers (such as oxygen, impurities).[5] Therefore, it is essential for realizing purely organic RTP with high performance to promote ISC efficiently, to suppress nonradiative relaxation processes sufficiently and to shield quenchers as much as possible. Several approaches have been reported to achieve long-lived or high-efficiency RTP, such as crystallization,[6] embedding into matrix,[7] deuterium substitution,[8] and so on.[9] Although there are outstanding results, the high-performance purely organic RTP (lifetime above 2 seconds or phosphorescence efficiency above 50%) is still rare (Supporting Information, Tables S1, S2). Therefore, developing a new strategy for realizing RTP possessing long lifetime and high efficiency is of great significance.

Recently, we developed a supramolecular method to enhance RTP by complexing phenylmethylpyridinium derivatives with macrocyclic host cucurbit[6]uril (CB[6]), which promoted ISC, suppressed nonradiative decay and shielded quenchers, resulting the improvement of RTP.[10] These inspiring results give us an impression that this kind of molecules are most probably good candidates for realizing high-performance RTP. Furthermore, some excellent work involving host-guest complexation to improve RTP are reported lately. For example, Ma and co-workers reported an aqueous phase organic RTP by the host-guest assembling strategy.[11] Tian and co-workers developed a supramolecular polymeric RTP material based on β-CD polymer and guest polymer.[12] Tang and co-workers prolonged the RTP by morphological locking of crown ether through complexation with K^+.[13]

Moreover, brilliant work of enhancing RTP by polymers also have been reported, such as doping into polymer[14] and copolymerization.[15] But the lifetimes were mostly in the range of milliseconds. Herein, we devise a synergistic enhancement strategy for realizing lifetime up to 2.81 seconds and phosphorescent efficiency more than 76% (Scheme 1). This strategy consists of two interrelated parts: polymerization enhancement and complexation enhancement. The



Scheme 1. The synergistic enhancement (polymerization and complexation enhancement) strategy for ultralong and efficient room-temperature phosphorescence. τ represents the lifetime of PH-0.1 and PH-0.1/CB[6], Φ_p is the phosphorescent efficiency of PBr-1 and PBr-1/CB[6].

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copolymerization between phosphors and acrylamide provide plenty of hydrogen bonds and carbonyl to lock phosphors and promote ISC. Accordingly, the lifetime is prolonged from 1.66 ns to 2.46 s (PH-0.1) and bright phosphorescence is produced (efficiency from 0% to 56.7% for PBr-1). After complexing with CB[6, 7, 8], the nonradiative decay of phosphors are further suppressed, aggregation-caused quenching (ACQ) of phosphors are blocked and quenchers are shielded more sufficiently, resulting in further enhancement of RTP. Ultimately, ultralong and efficient RTP are realized (Scheme 1).

Results and Discussion

Monomers of 4-phenyl-1-(4-vinylbenzyl)pyridinium chloride (PVC) and 4-(4-bromophenyl)-1-(4-vinylbenzyl)pyridinium chloride (BVC) were copolymerized with acrylamide, respectively and corresponding polymers PH-1 and PBr-1 were produced and fully characterized (Supporting Information, Scheme S1, Figures S1–S8, and Table S3). The PVC emitted blue fluorescence ($\lambda_{max} = 395$ nm) with a lifetime (τ) of 1.66 ns (Supporting Information, Figure S14). However, the copolymer PH-1 showed cyan persistent phosphorescence ($\lambda_{max} = 490$ nm) with an ultralong lifetime of 1.46 s (Figure 1 a,b). The luminescence lasted for 8 s after ceasing the irradiation (Figure 1 c; Supporting Information, Video 1). Additionally, the large Stokes shift (158 nm) is the typical character of phosphorescence and the red-shifts (124 nm) of emission peak in phosphorescent mode comparing with fluorescence ($\lambda_{max} = 366$ nm, $\tau = 2.29$ ns) further confirms that the persistent luminescence is phosphorescence but not delayed fluorescence (Figure 1 a; Supporting Information, Figure S15 b).

The ratio of phosphors has great influence on the photoluminescence of polymers. Lower ratio of phosphors will result in a better distribution and therefore give longer lifetime, but less phosphors also mean weak emission. On the contrary, higher ratio will emit stronger phosphorescence, but cause ACQ, worse embeddedness, and less restriction for phosphors, which jointly shorten lifetime sharply. Therefore, copolymers containing different ratio of phosphors (0.1%, 0.5%, 2%, 5%, 10% and named PH-0.1, PH-0.5, PH-2, PH-5, PH-10, respectively) were synthesized and characterized (Supporting Information, Scheme S1 and Figures S9–S13). As expected, the intensity of fluorescence and phosphorescence decreased more than 10 folds and the lifetime shortened from 2.46 s (PH-0.1) to 0.262 s (PH-10) with increasing ratio of phosphors (Figure 1 b; Supporting Information, Figure S15 a, Video 1). Although the lower ratio gave a longer lifetime (2.46 s for PH-0.1 and 2.12 s for PH-0.5), we chose a compromised one (PH-1) as a mode to further study considering its stronger emission and NMR signals. The simple copolymerization can greatly promote the phosphorescence by suppressing the molecular vibrations, rotations, and inter-collisions, promoting ISC, and shielding quenchers.[7a,15d] Replacing phosphors with that possessing Br, the resulting polymer PBr-1 exhibited intense phosphorescence (phosphorescence quantum yield $\Phi_p = 56.7\%$) peak at 507 nm ($\tau = 8.58$ ms) and weak fluorescence peak at 378 nm ($\tau = 0.938$ ns), but the monomer BVC only emitted fluorescence peak at 410 nm ($\tau = 0.756$ ns; Supporting Information, Figures S16–18). Accordingly, copolymerization turned on the phosphorescence (Φ_p from 0% to 56.7%).

Ultralong and efficient phosphorescence was achieved by polymerization enhancement strategy. But the ratio-dependent phosphorescent properties spurred us to uncover the origin. As PH-1 possesses hydrophilic polyacrylamide backbone and a minor part of hydrophobic phosphors, it is hydrophobically associating polyacrylamide (HAPAM) which tends to aggregate by inter- or intra- polymeric interactions.[16] Besides, assembling-induced emission plays an important role in supramolecular systems.[17] The photoluminescence spectra of polymer with different concentration were carried out in aqueous solution to measure the aggregation. The luminescent intensity of PH-1 at 378 nm increased first, and then decreased with increasing the concentration of phosphors from 1×10^{-6} mol L^{-1} to 4×10^{-4} mol L^{-1}, appearing the peak value at 8×10^{-5} mol L^{-1} which indicated an obvious ACQ (Supporting Information, Figure S19, PC is phosphors in PH).[18] PBr-1 showed similar ACQ behavior as the concentration of phosphors exceeded 4×10^{-5} mol L^{-1} (Supporting Information, Figure S20, BC is phosphors in PBr-1). The freeze-drying polymers still suffer varying degrees of assembling and ACQ, therefore the phosphorescence lifetime of PH decreased as the increase of phosphor ratio deriving from a combination of assembling-induced emission and increasingly serious ACQ (2.46 s for PH-0.1, 2.12 s for PH-0.5, 1.46 s for PH-1, 1.16 s for PH-2, 0.666 s for PH-5, and 0.262 s for PH-10).

As the ultralong lifetime (as long as 2.46 s for PH-0.1) and high phosphorescence quantum yield (up to 56.7% for PBr-1) are results after suffering ACQ, undoubtedly, there will be further promotion of phosphorescent performance if the ACQ is prevented. Considering the positive charge and hydrophobically aromatic structure of phosphor group, macrocycles CB[7,8] are probably most suitable hosts.[19] Besides, our previous work demonstrated that CB[6] could complex 4-phenylmethylpyridium molecules and promote their RTP.

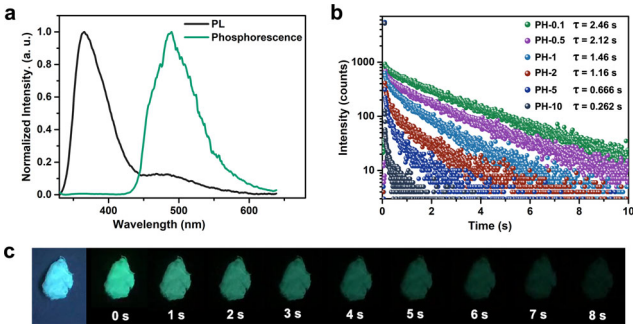

Figure 1. Photophysical properties of copolymers PH. a) Photoluminescence (black) and phosphorescence spectra (olive) of PH-1 in the solid state (excitation wavelength: 332 nm); b) Time-resolved PL decay of PH-0.1, PH-0.5, PH-1, PH-2, PH-5, and PH-10 at 490 nm in the solid state at room temperature; c) Luminescence photographs of PH-1 under 254 nm light and at different time intervals after ceasing irradiation.

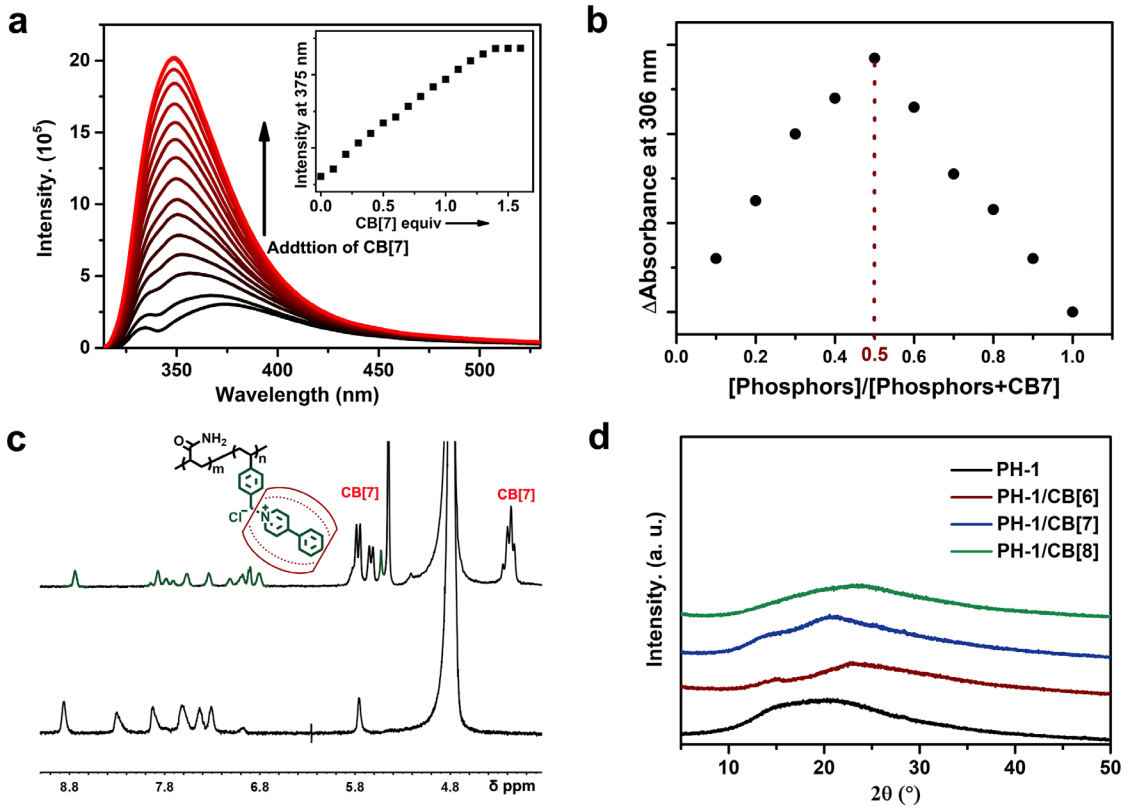

Figure 2. a) Photoluminescence spectra of PH-1 as the titration of CB[7]; b) The Job plots of PH-1/CB[7]; c) Partial ^{1}H NMR of PH-1/CB[7] and PH-1 (400 MHz, D_2O, 298 K, [phosphors] = [CB7] = 1.9 mM); d) XRD patterns of PH-1, PH-1/CB[6], PH-1/CB[7] and PH-1/CB[8].

Therefore, we deduced that the binding of CB[6,7,8] could further enhance the phosphorescence by blocking ACQ and encapsulating phosphors. To verify our hypothesis, the complexes of PH-1/CB[6,7,8] and PBr-1/CB[6,7,8] were prepared and characterized by UV/Vis, photoluminescence spectra and NMR experiments. Obviously, the absorbance spectra of PH-1 and PBr-1 decreased gradually and bathochromic shifted as the addition of CB[7] or CB[8], and ultimately no more change could be observed after adding excess CB[7] or CB[8], indicating the binding of CB[7, 8] to the phosphors in PH-1 and PBr-1 (Supporting Information, Figure S21). Moreover, the photoluminescent intensity of PH-1 exhibited 6-fold and 16-fold increase with the titration of CB[7] and CB[8], respectively (Figure 2a; Supporting Information, Figure S22). For PBr-1, the addition of CB[7] resulted 6-fold enhancement of fluorescent intensity and the addition of CB[8] resulted the decrease of fluorescence and the increase of phosphorescence at 505 nm simultaneously (Supporting Information, Figures S23, 24). All the increase of intensity proved that the complexation of CB[7] and CB[8] was an effective method to prevent ACQ and enhance the photoluminescence for these polymers. To uncover the binding mode between the phosphors (guests) in copolymers (PH-1/PBr-1) and CB[7, 8] (hosts), the Job plots were measured by UV/Vis spectra, which showed that the binding stoichiometry of guest : host was 1:1 for CB[7] and 2:1 for CB[8] (Figure 2b; Supporting Information, Figures S25–S28). Besides, the new peaks appearing in the higher-field region of ^{1}H NMR suggested that the phosphors in PH-1 were encapsulated into the cavity of CB[7] (Figure 2c). Similar phenomenon also appeared in the complexes of PH-1/CB[6], PH-1/CB[8] and PBr-1/CB[6,7,8], which proved the complexation of CB[6,7,8] to the phosphors (Supporting Information, Figures S29–S33). For PH-1/CB[6] and PBr-1/CB[6], no change in UV/Vis spectra and photoluminescence spectra could be observed and therefore the complexation was proved by ^{1}H NMR (Supporting Information, Figures S29, S31, and S34).

Normally, the enormous enhancement of photoluminescence in solution forebode the similar improvement in solid state. Indeed, for PH-1, the complexation of CB[6] and CB[7] prolonged the lifetime from 1.46 s to 2.37 s and 2.33 s, respectively, accompanying with short lifetimes of fluorescence (Figure 3c; Supporting Information, Figure S35). The phosphorescence quantum yields (Φ_p) also increased from 10.1% (PH-1) to 16.0% (PH-1/CB[6]) and 12.4% (PH-1/CB[7]), with a concomitant improvement of fluorescence quantum yields (Φ_F) from 17.5% (PH-1) to 47.4% (PH-1/CB[6]) and 32.4% (PH-1/CB[7]), respectively (Supporting Information, Figures S36–S41). The luminescence of PH-1/CB[6,7] lasted 12 s after removing the UV irradiation (Figure 3e; Supporting Information, Video 2). It was noticed that the lifetime of PH-1 ($\tau = 1.46$ s), PH-0.5 ($\tau = 2.12$ s) and PH-0.1 ($\tau = 2.46$ s) reached a similar value after complexing with CB[7] (2.81 s for PH-0.1/CB[7], 2.53 s for PH-0.5/CB[7], and 2.33 s for PH-1/CB[7]), indicating that phosphors in these complexes possessed similar circumstances provided by CB-

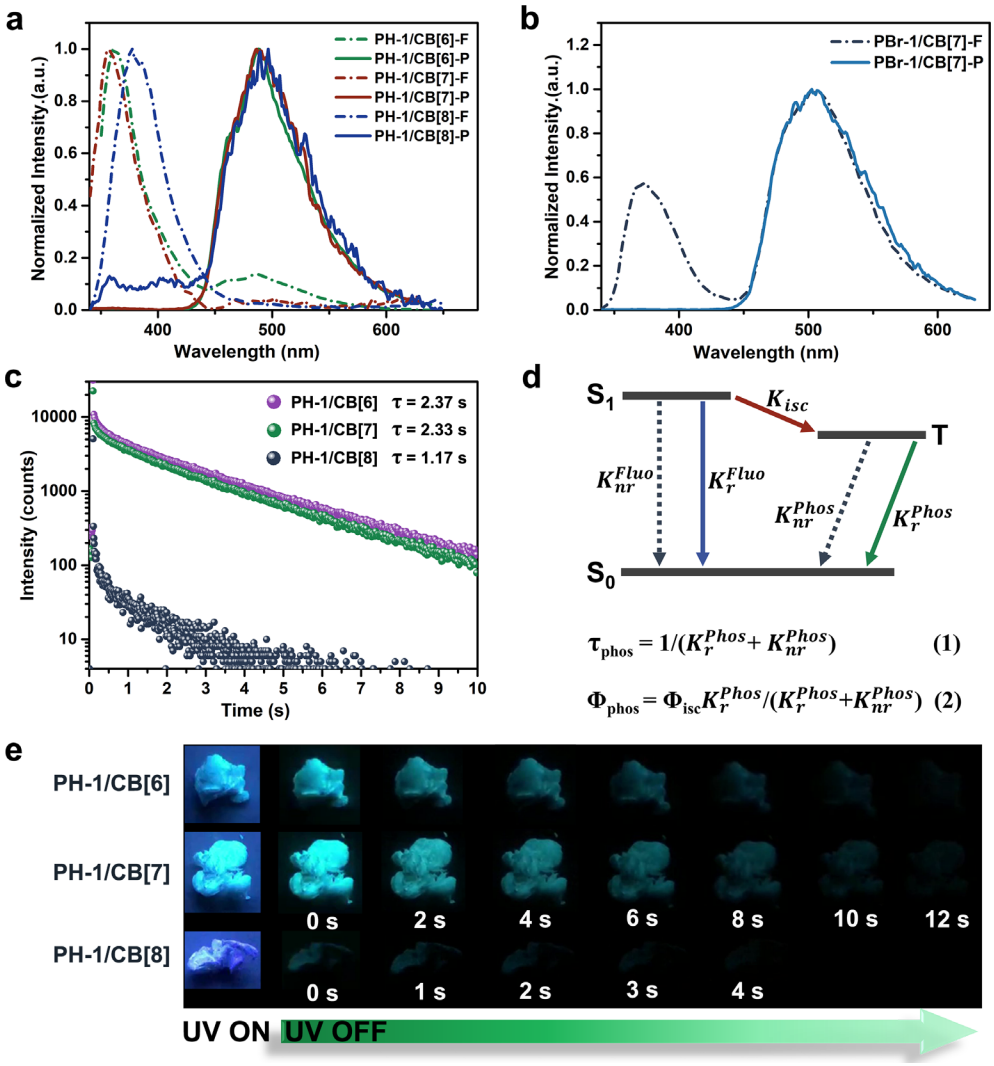

Figure 3. Photophysical properties of PH-1/CB[6,7,8] and PBr-1/CB[7]. a) Photoluminescence (dash dot line) and phosphorescence spectra (solid line) of PH-1/CB[6,7,8] in the solid state (excitation wavelength: 323 nm for PH-1/CB[6,7] and 332 nm for PH-1/CB[8]). b) Photoluminescence (dash dot line) and phosphorescence spectra (solid line) of PBr-1/CB[7] in the solid state (excitation wavelength: 325 nm). c) Time-resolved PL decay of PH-1/CB[6,7,8] at 490 nm in the solid state at room temperature. d) The Jablonski diagram and the equation of τ_p and Φ_p. e) Luminescence photographs of PH-1/CB[6,7,8] under UV light and at different time intervals after ceasing irradiation.

[7], and the longer lifetime of lower ratio complexes, which is probably due to better dispersion and complexation (Figure 3c; Supporting Information, Figure S42).The shorter lifetime of PH-1/CB[8] ($\tau = 1.17$ s) hinted that two phosphors in one host was not favorable to the promotion of lifetime (Figure 3c). Furthermore, photoluminescence and phosphorescence spectra showed that all phosphorescent peaks of PH-1 and PH-1/CB[6,7,8] were about 490 nm, revealing that the encapsulation of CB[6,7,8] to phosphors only affected lifetime and luminescent intensity but not the phosphorescent wavelength (Figure 3a and Table 1). This result made it clear that the complexation of CB[6,7,8] prevented the ACQ of PH-1 and provided a good shelter without perturbing the excited-state level of the phosphors, which reappeared in PBr-1/CB[6,7,8] (Figure 3b; Supporting Information, Figure S43).

To investigate the universality of this synergistic enhancement strategy, we further investigated the phosphorescent properties of PBr-1 and PBr-1/CB[6,7,8]. The complexation of CB[6,7,8] prolonged its lifetime to 10.9 ms (PBr-1/CB[6]), 9.02 ms (PBr-1/CB[7]) and 9.30 ms (PBr-1/CB[8]) with the change of phosphorescence quantum yields from 56.7% (PBr-1) to 76.0% (PBr-1/CB[6]), 52.7% (PBr-1/CB[7]), and 65.3% (PBr-1/CB[8]) (Supporting Information, Figures S44a–c and S45–S51). Therefore, the synergistic enhancement strategy of utilizing polymerization and host–guest complexation was proved to be effective and versatile to realize ultralong and efficient RTP. As the microstructure (crystalline or amorphous state) of materials exert enormous influence on their photophysical properties, X-Ray powder diffraction (XRD) analysis was carried out to uncover the structures of PH-1, PH-1/CB[6,7,8], PBr-1 and PBr-1/CB-[6,7,8], revealing that all of them were amorphous. (Figure 2d; Supporting Information, Figure S52).

Table 1: Photophysical data of PH-1, PH-1/CB[6,7,8], PBr-1, and PBr-1/CB[6,7,8].

Entry	Compound	Ex [nm]	Fluor-escence [nm]	Phosphor-escence [nm]	τ_{Fluo} [ns]	τ_{Phos} [ms]	Φ_{Fluo} [%]	Φ_{Phos} [%]	K_r^{Fluo} [s^{-1}][a]	K_{nr}^{Fluo} [s^{-1}][b]	K_{isc} [s^{-1}][c]	K_r^{Phos} [s^{-1}][d]	K_{nr}^{Phos} [s^{-1}][e]
1	PH-1	332	366	490	2.29	1463	17.5	10.1	7.64×10^{7}	3.16×10^{8}	4.41×10^{7}	6.90×10^{-2}	0.614
2	PH-1/CB-[6]	324	362	488	2.60	2372	47.4	16.0	1.82×10^{8}	1.41×10^{8}	6.15×10^{7}	6.74×10^{-2}	0.354
3	PH-1/CB-[7]	323	358	490	1.54	2333	32.4	12.4	2.10×10^{8}	3.58×10^{8}	8.05×10^{7}	5.32×10^{-2}	0.375
4	PH-1/CB-[8]	333	378	490	7.76	1166	54.5	13.8	7.02×10^{7}	4.08×10^{7}	1.78×10^{7}	0.118	0.739
5	PBr-1	316	378	507	0.938	8.58	6.60	56.7	7.04×10^{7}	3.91×10^{8}	6.04×10^{8}	66.1	50.5
6	PBr-1/CB-[6]	326	391	508	0.864	10.9	22.1	76.0	2.56×10^{8}	2.20×10^{7}	8.80×10^{8}	69.7	22.0
7	PBr-1/CB-[7]	326	372	507	0.779	9.02	13.1	52.7	1.68×10^{8}	4.39×10^{8}	6.76×10^{8}	58.4	52.4
8	PBr-1/CB-[8]	323	380	506	0.623	9.30	3.10	65.3	4.98×10^{7}	5.07×10^{8}	1.05×10^{9}	70.2	37.3

[a] The radiative decay rate constant of fluorescence $K_r^{Fluo}=\Phi_{Fluo}/\tau_{Fluo}$. [b] The nonradiative decay rate constant of fluorescence $K_{nr}^{Fluo}=(1-\Phi_{Fluo}-\Phi_{Phos})/\tau_{Fluo}$. [c] The intersystem crossing rate constant $K_{isc}=\Phi_{phos}/\tau_{Fluo}$. [d] The radiative decay rate constant of phosphorescence $K_r^{phos}=\Phi_{Phos}/\tau_{phos}$. [e] The nonradiative decay rate constant of phosphorescence $K_{nr}^{phos}=(1-\Phi_{Phos})/\tau_{phos}$.

The host–guest complexation was proved to be effective for promoting the RTP of polymers, what if binding the monomers with hosts immediately? To verify if the polymerization was indispensable, the complexes of monomers and CB[6,7,8] (PVC/CB[6,7,8] and BVC/CB[6,7,8]) were prepared (Supporting Information, Figures S53–S58). Photoluminescence and phosphorescence spectra showed that the complexation of CB[6,7,8] induced the phosphorescence (peaks at 510 nm) with short lifetime (0.306 ms for BVC/CB[6], 0.271 ms for BVC/CB[7], and 0.286 ms for BVC/CB[8]) accompanying with fluorescence peaks about 410 nm (Supporting Information, Figures S59, S60). For PVC/CB-[6,7,8], the absence of heavy atom made their phosphorescence too feeble to be detected by detector. Hence, we measured their lifetime in long wavelength. Small value (0.222 ms for PVC/CB[6], 0.223 ms for PVC/CB[8], and 0.0847 ms for PVC/CB[7]) indicated that the ineffective complexation-induced RTP was an universal phenomenon for these guests (Supporting Information, Figure S61 a–c). Taking into account that both 4-vivnylphenyl and 4-phenylpyridium moiety could be bonded by CB[6,7,8] which was reported by literatures[20] and verified by ^{1}H NMR, this phenomenon was rational because the additional binding sites perturbed the binding between 4-phenylpyridium moiety and hosts (Supporting Information, Figures S53–S58). After copolymerizing with acrylamide, only phosphor moiety (4-phenylpyridium and 4-bromophenylpyridium) are accessible for CB[6,7,8], which ensure effective and proper complexation. Furthermore, 1% PVC monomers were doped into pure PAM to explore the necessity of copolymerization. The doped polymer DP-1 only emitted weak phosphorescence peak at 506 nm with short lifetime (0.272 ms), which was far less than copolymerized one (PH-1, $\tau=1.46$ s; Supporting Information, Figure S62). Therefore, polymerization between acrylamide and monomers is indispensable for this synergistic enhancement strategy.

With all the above experimental results in mind, a possible mechanism of synergistic enhancement strategy for RTP can be deduced. As one of indispensable parts for this strategy, polymerization offers abundant hydrogen bond to suppress non-irradiation decay of phosphors and shield quenchers (oxygen, impurity, and so on) and provides rich carbonyl to promote ISC from the lowest excited singlet state (S_1) to the triplet manifold (T_n), which endow copolymers with outstanding RTP ($\tau=1.46$ s for PH-1 and $\Phi_p=56.7\%$ for PBr-1).[15d] Equation (1) and (2) in Figure 3 d reveal that ultralong lifetime require small ($K_r^{Phos}+K_{nr}^{Phos}$), while high efficiency (Φ_p) should possess efficient ISC (high Φ_{isc}) and competitive radiative decay from excited triplet state (high $K_r^{Phos}/(K_r^{Phos}+K_{nr}^{Phos})$) simultaneously. The fairly slow radiative decay rate of phosphorescence ($K_r^{Phos}=6.90\times10^{-2}\,s^{-1}$ for PH-1 and 66.1 s^{-1} for PBr-1) and fast intersystem crossing rate ($K_{isc}=4.41\times10^{7}\,s^{-1}$ for PH-1 and $6.04\times10^{8}\,s^{-1}$ for PBr-1 which are comparable to corresponding radiative decay rate of fluorescence K_r^{Fluo}) demonstrate the effectiveness of polymerization for enhancing RTP (Table 1, entries 1 and 5). But the ACQ arising from the self-assembly of copolymers diminish this enhancement. Therefore, the host-guest complexation as another critical part of synergistic enhancement strategy starts to work. If hosts only play the role of blocking ACQ, the missing elements (hydrogen bond, shield effect, and rich carbonyl) provided by polymer will sharply weaken the RTP of PH-1 and PBr-1 after complexing with CB[6,7,8]. However, the promoted RTP indicates that the complexation of hosts also restrict the non-irradiation variation, shield quenchers and facilitate ISC apart from preventing ACQ. The slower K_r^{Phos}($5.32\times10^{-2}\,s^{-1}$ for PH-1/CB[7] and $58.4\,s^{-1}$ for PBr-1/CB[7]) and faster intersystem crossing rate ($K_{isc}=8.05\times10^{7}\,s^{-1}$ for PH-1/CB[7] and $6.76\times10^{8}\,s^{-1}$ for PBr-1/CB[7]) demonstrate that the complexation is more effective than polymerization in promoting RTP (Table 1, entries 3 and 7). Besides, faster K_r^{Phos} (0.118 s^{-1} for PH-1/CB[8] and 70.2 s^{-1} for PBr-1/CB[8]) reveals that the binding of CB[8] is unable to offset the losing interactions provided by polymers (Table 1, entries 4 and 8).

Information encryption and anti-counterfeiting are increasingly demanded in this information age.[21] Owning to the diversified RTP properties of these polymers, multiple encoding for information encryption was fabricated. The digits were written by different polymers in flexible paper, among which the number "54" was written by bright polymer PBr-1, "66" was labeled by long-lived PH-1 and the green black part in "88" was coated with PH-5 (Figure 4a). Nothing could be found in the daylight. However, when irradiating with 254 nm UV lamp, luminous cyan number "54" appeared because of the high quantum yield of PBr-1 (Figure 4a; Supporting Information, Video 3). After ceasing the irradiation, the "54" disappeared immediately because of the short lifetime of PBr-1 (8.58 ms), leaving long-lived PH-1 (1.46 s) and PH-5 (666 ms) emitting the luminescence of "88". Thereafter, the phosphorescence of PH-5 attenuated to be invisible and the surviving phosphorescence of PH-1 contributed to the moderated cyan "66". Apart from digits, the polymer can also be applied to encrypting Chinese characters (Figure 4b; Supporting Information, Video 4). Characters of "sen" (means forest), "lin" (means woods), and "mu" (means tree) appeared in sequence upon turning on and off the UV light. Therefore, we realized triple lifetime-encoding for digit and character encryption by taking advantage of different lifetimes of these polymers.

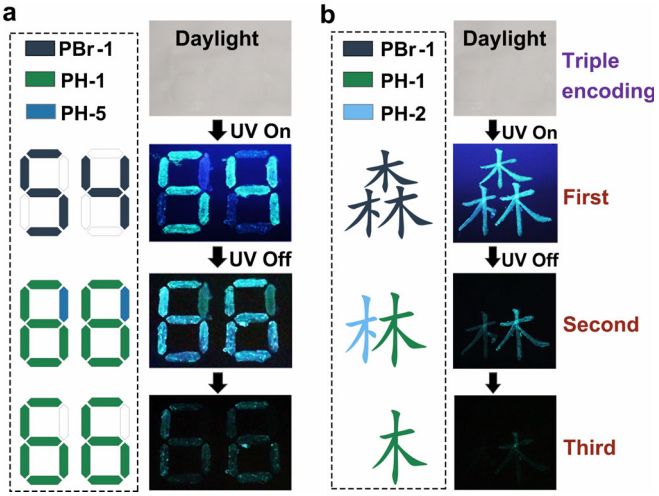

Figure 4. Illustration of triple lifetime-encoding for digit and character encryption. a) Digit encryption. b) Chinese character encryption.

Conclusion

This work establishes a synergistic enhancement strategy involving polymerization and host-guest complexation to achieve ultralong and efficient RTP. By copolymerizing with acrylamide, the phosphorescence of monomers is turned on with the lifetime and phosphorescence efficiency as high as 2.46 s (PH-0.1) and 56.7% (PBr-1), higher than most of the reported organic RTP systems. Decreasing the ratio of phosphors result the increase of lifetime because of enhanced assembling-induced emission for RTP and weakened ACQ. Notably, the complexation of CB[6, 7, 8] can promote RTP of polymers by preventing ACQ, fascinating ISC, restricting nonradiative decay and shielding quenchers. As a result, we achieve enhanced lifetime (2.81 s for PH-0.1/CB[7]) and phosphorescence efficiency (76.0% for PBr-1/CB[6]). Moreover, the complexation itself cannot produce high-performance RTP without polymerizing with acrylamide, which indicates that polymerization and host–guest complexation are two indispensable parts for our synergistic enhancement strategy. Significantly, several polymers are successfully applied in triple lifetime-encoding for digit and character encryption by utilizing the difference of their lifetimes. This synergistic enhancement strategy provides a new approach for realizing purely organic RTP with ultralong lifetime and high phosphorescence efficiency.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: anti-counterfeiting · cucurbiturils · host–guest interactions · polymers · RTP

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Research Articles

Host–Guest Interactions

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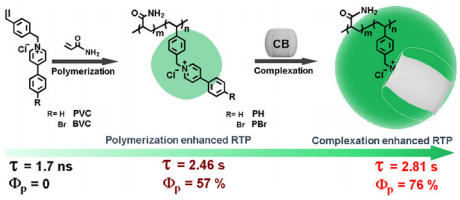
A Synergistic Enhancement Strategy for Realizing Ultralong and Efficient Room-Temperature Phosphorescence



A synergistic enhancement strategy is realized for ultralong bright RTP, involving polymerization between phosphor monomers and acrylamide and host–guest complexation interaction between phosphors and cucurbit[6, 7, 8]urils (CB-[6, 7, 8]). The phosphorescence lifetime and efficiency is up to 2.81 s and 76%. Multiple lifetime-encoding for digit and character encryption are achieved.