

Tunable Second-Level Room-Temperature Phosphorescence of Solid Supramolecules Between Acrylamide-Phenylpyridium Copolymers and Cucurbit[7]uril

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Abstract: A series of solid supramolecules based on acrylamide-phenylpyridium copolymers with various substituent groups (P-R: R=CN, -CO₂Et, -Me, -CF₃) and cucurbit[7]uril (CB[7]) are constructed to exhibit tunable second-level (from 0.9 seconds to 2.2 seconds) room-temperature phosphorescence (RTP) in amorphous state. Compared with other solid supramolecules P-R/CB[7] (R=CN, -CO₂Et, -Me), P-CF₃/CB[7] displays the longest lifetime (2.2 seconds), which is probably attributed to the fluorophilic interaction of cucurbiturils leading to stronger host-guest interaction between 4-phenylpyridium with -CF₃ and CB[7]. Furthermore, the RTP solid supramolecular assembly (donors) can further fabricate with organic dyes Eosin Y or SR101 (acceptors) to form ternary supramolecular systems featuring the ultralong phosphorescence energy transfer (PpET) and visible delayed fluorescence (yellow for EY at 568 nm and red for SR101 at 620 nm). Significantly, the ultralong multicolor PpET supramolecular assembly can be further applied in fields of anti-counterfeiting and information encryption and painting.

Introduction

Purely organic phosphors, with superiority of long-lived emission and large stoke shift and afterglow due to the uniquely radiative mechanism,^[1] have attracted widespread attention in fields of bioimaging,^[2] sensors,^[3] photoelectric materials,^[4] anti-counterfeiting field,^[5] and so forth.^[6] However, acquirement of purely organic phosphorescence with long lifetime faces great challenge because of the inherently weak spin-orbital coupling (SOC) or fast intersystem crossing (ISC) process and multiple deactivation pathways of organic molecules, all of which will shorten phosphorescence lifetime (microsecond- or millisecond-level), and even cause the lack of phosphorescence.^[7] To prepare long-lived and high-performance purely organic phosphorescence, lots of efforts have been contributed to design and synthesis, including crystallization,^[8-11] embedding chromophores into matrix,^[12-14] polymerization,^[15-17] deuterium substitution,^[18] supramolecular host-guest interaction,^[19, 20, 2e] and so on,^[21, 22] most of which are mainly based on the principle of minimizing nonradiative relaxation and enhancing ISC process of excitons from lowest singlet excited state (S₁) to triplet manifold (T_n). Although there is numerous outstanding works, second-level phosphorescence emission is still rare. It is well known that many factors can affect long-lived phosphorescence behavior of organic molecules, such as optimal molecular structure (possessing efficient ISC to generate triplet state), rigid environment (suppressing molecular motion to

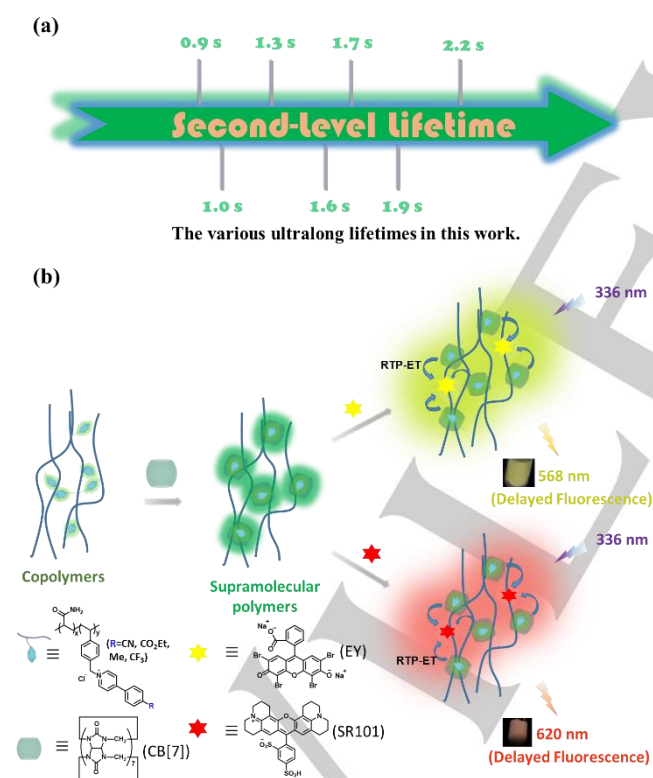
decrease nonradiative decay), useful shield (reducing the quenching from other molecules), and so on.^[6] Besides, long-lived phosphorescence is fragile and easily subjected to be extinguished by humidity, oxygen or other impurities due to the ultralong radiative relaxation time of triplet excitons.^[23, 3b] Therefore, achievement of tunable ultralong lifetime of RTP remains highly challenging. Recently, a new design of host/guest doping strategy has been developed to acquire different phosphorescence lifetimes. Huang and coworkers realized wide-range lifetime-tunable organic RTP through multi-host/guest systems with lifetimes from 3.9 milliseconds to 376.9 milliseconds (ms).^[12d] Tian and coworkers developed various phosphorescence lifetimes via a series of bicomponent RTP systems by the trace ingredient incorporation method.^[14e] However, supramolecular purely organic RTP assembly based on macrocyclic hosts (cyclodextrins, cucurbiturils) induced or enhanced phosphorescence is barely reported, especially tunable second-level RTP. It is worth mentioning that possessing long lifetimes luminescence, delayed fluorescence has been gradually developed to exhibit huge potential of application in organic light-emitting diodes (OLEDs) and time-resolved bioimaging.^[24a-c] Therefore, many efforts have been contributed to the reasearches of effective delayed fluorescence, in which phosphorescence energy transfer for achieving delayed fluorescence emission attracts extensive attention recently.^[20d, 24d, 24e]

Herein, we report a class of tunable solid supramolecular RTP assemblies (≥ 0.9 seconds), which were constructed by acrylamide polymers with various 4-phenylpyridium derivatives and macrocyclic compound CB[7]. Considering the effects of para-substituents (-CN, -CO₂Et, -Me, -CF₃) and the complexation with macrocyclic host CB[7], the phosphorescence lifetime can be efficiently adjusted in the range of 0.9 seconds (s) to 2.2 s, successfully realizing the control of phosphorescence lifetime in second-level range (Scheme 1). In the process of preparation, 4-phenylpyridinium derivatives (CN-V, CO₂Et-V, Me-V, CF₃-V) with various substituent groups were copolymerized with acrylamide through radical binary copolymerization to produce the corresponding copolymers (P-CN, P-CO₂Et, P-Me, P-CF₃), which further complexed with CB[7] through host-guest interaction to afford supramolecular RTP assembly P-X/CB[7] (X=CN, -CO₂Et, -Me, -CF₃). 4-phenylpyridinium was selected as chromophore center because it showed excellent phosphorescence performance according to our previous researches.^[19b-d] The acrylamide skeleton was chosen to provide sufficiently rigid environment through hydrogen bond to inhibit molecular motion and to prompt possible ISC for phosphorescence emission of chromophores. Additionally, we carefully selected the functional groups capable of tuning ISC process and radiative rate and nonradiative rate of excited excitons of 4-phenylpyridinium, making efforts to achieve ultralong RTP with various lifetimes. Interestingly, the experimental results showed that although the para-position on the benzene ring of 4-phenylpyridinium were decorated with various substituent groups, these copolymers still exhibited good phosphorescence emission properties. Moreover, the

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phosphorescence lifetimes exhibited an evident change in the range of 0.9 s~ 1.7 s, including the ultralong lifetimes of 0.9 s (P-CN), 1.0 s (P-CO₂Et), 1.6 s (P-CF₃) and 1.7 s (P-Me) (Table 1). After introducing CB[7], the range of lifetime was further extended, varying from 0.9 s (P-CN/CB[7]) to 2.2 (P-CF₃/CB[7]), including the ultralong lifetimes of 1.3 s (P-CO₂Et/CB[7]) and 1.9 s (P-Me/CB[7]). These various ultralong lifetimes almost covered the most of lifetimes in the range of 0.9 s to 2.2 s. Thus, we could say that an achievement involving adjustment of phosphorescence lifetime in the range of long lifetime (0.9 s ~ 2.2 s) was successfully made through substituent group effect and host-guest complexation effect. To our surprise, the resulting supramolecular polymers could further co-assemble with organic dye Eosin Y (EY) or SR101 to form ternary supramolecular systems with PpET characteristic (Scheme 1). In the systems, the supramolecular polymers acted as donors and organic dyes were utilized as acceptors to perform highly effective PpET process. Therefore, various lifetimes (hundreds of milliseconds) and colorful delayed fluorescence emissions (yellow for EY and red for SR101) were triumphantly acquired. Benefiting from this, we realized fantastic color variation of long-persistent luminescence (from green/cyan to red/yellow) by changing the RTP donor or dye acceptor or the fraction of dye acceptor in ternary supramolecular systems.



Scheme 1. (a) The various ultralong lifetimes realized by this work. (b) The schematic illustration of tunable second-level room-temperature phosphorescence of solid supramolecules between acrylamide-phenylpyridinium copolymers and cucurbit[7]uril (Inset: the photographs of ternary supramolecular systems after withdrawing 254 nm UV radiation). RTP-ET represents room-temperature phosphorescence energy transfer.

Results and Discussion

Firstly, four monomers based on 4-phenylpyridinium derivatives containing carbon-carbon double bond (namely CN-V, CO₂Et-V, Me-V and CF₃-V, respectively), were synthesized through Suzuki coupling reaction and nucleophilic substitution (Scheme S1, Figures S1-S12), which were then utilized to perform radical copolymerization with acrylamide to give the copolymers (namely P-CN, P-CO₂Et, P-Me, P-CF₃, respectively) (Figure 1a). The NMR experiments and gel permeation chromatography (GPC) analysis proved the formation of copolymers (Figures S13-S16 and Table S1). Subsequently, the photophysical properties of these copolymers were detailedly characterized by prompt, delayed spectra and time-resolved decay plots. As revealed by the spectral information, all the resultant copolymers exhibited robust phosphorescence emissions in the solid state at room temperature. P-CN, P-CO₂Et and P-Me possessed similar phosphorescence peaks around 500 nm ($\lambda_{\text{Phos}}=503$ nm for P-CN, 500 nm for P-CO₂Et and 494 nm for P-Me) when excited at various excitation wavelength ($\lambda_{\text{Ex}}=327$ nm for P-CN, 330 nm for P-CO₂Et and 341 nm for P-Me), meaning that the variety of substituent groups had little effect on the phosphorescence emission wavelength of the chromophore (Figure 1b, Figure S17 and Table 1). Furthermore, the lifetime test and quantum yield analysis demonstrated that various ultralong phosphorescence lifetimes ($\tau=0.91$ s for P-CN, $\tau=1.04$ s for P-CO₂Et and $\tau=1.75$ s for P-Me) and unremarkable phosphorescence quantum yield (0.75% for P-CN, 1.91% for P-CO₂Et and 1.98% for P-Me) were orderly observed (Figure S18 and Table 1). The ultralong lifetimes reaching the range of seconds and the large stoke shift around 170 nm effectively certified the properties of phosphorescence emission. After ceasing 254 nm ultraviolet radiation, three copolymers (P-CN, P-CO₂Et and P-Me) displayed green afterglow lasting for several seconds, further verifying the traits of ultralong lifetime of RTP (Figure S19 and Video 1). Nevertheless, P-CF₃, distinct from the copolymers abovementioned, showed cyan phosphorescence at 486 nm with lifetime of 1.61 s and phosphorescence quantum yield of 3.84% (Figure 1b, Figure S18b and Table 1). This change might originate from the strong electron-withdrawing effect from -CF₃, which increased the energy level of triplet state and thus induced blue shift of phosphorescence emission.^[14c] The wide difference of lifetimes for these copolymers hinted that the alteration of functional groups had great effect on the rate of chromophore excitons returning from triplet excited state to ground state, which was helpful for us to gather RTP with kinds of ultralong lifetimes. Furthermore, this sensitive rate inspired us whether the range of ultralong lifetime could be further extended and more various long-lived phosphorescence emissions could be collected based on the copolymers through appropriate means and strategy, such as introduction of supramolecular host-guest interaction.

4-Phenylpyridinium is known as a good guest compound to bind with macrocyclic host cucurbituril through intense host-guest interaction, accompanied by the change of phosphorescence properties.^[19b-d] To confirm the assumption, the resulting copolymers P-X (X=CN, CO₂Et, Me, CF₃) were complexed with macrocyclic host CB[7] in aqueous solution to gain corresponding supramolecular polymers P-X/CB[7] (X=CN, CO₂Et, Me, CF₃), respectively. NMR experiments, UV-Vis and fluorescence spectra were utilized to characterize the formation of supramolecular polymers. With addition of CB[7], the obvious change of shifting upfield for phosphors and of splitting peaks for

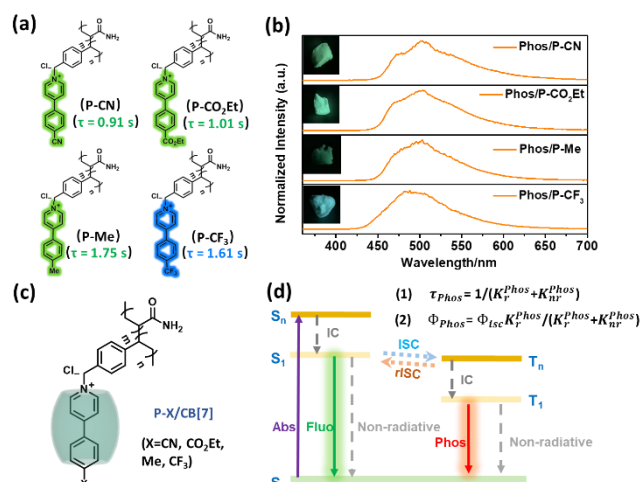


Figure 1. (a) Chemical structure and (b) Normalized phosphorescence spectra of copolymers (Inset: the photographs of copolymers in solid state after ceasing 254 nm UV radiation); (c) The structural scheme of supramolecular polymers P-X/CB[7] (X=CN, CO₂Et, Me, CF₃); (d) Jablonski diagram and the equation of τ_{Phos} and Φ_{Phos} .

host CB[7] appeared in ¹H NMR spectra, proving the effective inclusion of phosphors into cavity of CB[7] (Figures S20-S23). The UV-Vis spectra showed that the characteristic absorption peaks (λ_{Abs} =285 nm for P-CN, 294 nm for P-CO₂Et, 315 nm for P-Me and 280 nm for P-CF₃) gradually decreased and eventually remained constant with increasing the molar ratio of CB[7] (Figure S24). By contrast, the photoluminescence spectra presented that the fluorescence (λ_{Fluo} =378 nm for P-CN, 388 nm for P-CO₂Et, 390 nm for P-Me and P-CF₃) and phosphorescence (λ_{Phos} =500 nm for P-CN, 474 nm for P-CO₂Et, and 478 nm for P-CF₃) dual emissions strengthened dramatically while adding CB[7] gradually from 0 to 1.6 times that of phosphores (Figure S25). The binding mode between 4-phenylpyridinium (guest) in copolymers and CB[7] (host) was proved to be 1:1.^[19d] Associating with above characteristics, it was rational to deduce that the supramolecular polymers P-X/CB[7] (X=CN, CO₂Et, Me, CF₃) were successfully prepared (Figure 1c).

After lyophilization, the photophysical properties of solid supramolecular polymers were further investigated. According to the prompt and delayed spectra, the robust fluorescence emission (406 nm for P-CN/CB[7], 377 nm for P-CO₂Et/CB[7], 377 nm for P-Me/CB[7] and 375 nm for P-CF₃/CB[7]) and phosphorescence emission (λ_{Phos} =503 nm for P-CN/CB[7], 500 nm for P-CO₂Et/CB[7], 494 nm for P-Me/CB[7] and 486 nm for P-CF₃/CB[7]) were orderly recorded for P-X/CB[7] (X=CN, CO₂Et, Me, CF₃), respectively (Figure 2a and Figure S26). Compared with the RTP before complexing with CB[7], the phosphorescence peaks of supramolecular polymers were basically in agreement with the individual polymers, proving that CB[7] had no effect on the energy level of chromophore. Besides, the time-resolved decay spectra and quantum yield results demonstrated that P-CF₃/CB[7] possessed the greatly improved lifetime of 2.22 s and enhanced phosphorescence quantum yield of 6.33% compared to the individual polymer P-CF₃ (1.61 s and 3.84%), coupling with fluorescence lifetime of 3.27 nanoseconds (ns) and fluorescence efficiency of 2.14% (Figure 2b, Figure S27 and Table 1). Moreover, there was cyan afterglow lasting for above 13 s after withdrawing UV light,

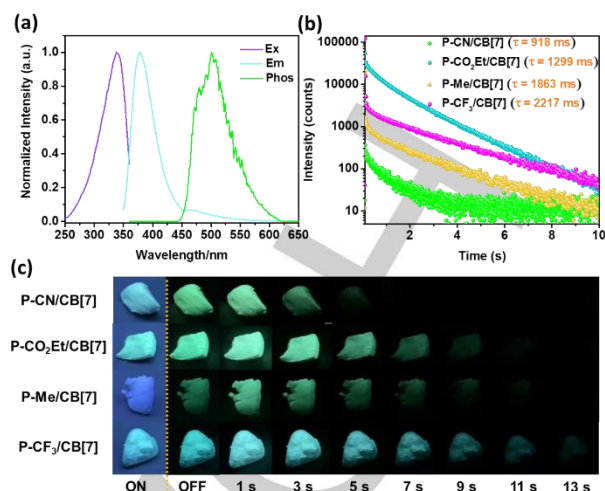


Figure 2. The photophysical properties of supramolecular polymers in solid state at room temperature. (a) Excitation (violet), photoluminescence (cyan) and phosphorescence (green) spectra of P-Me/CB[7]; (b) Time-resolved decay spectra of P-X/CB[7] (X=CN, CO₂Et, Me, CF₃); (c) The luminescence photographs of P-X/CB[7] (X=CN, CO₂Et, Me, CF₃) before and after stopping 254 nm UV light.

effectively verifying the great efficiency of CB[7] for improving the ultralong lifetime of RTP. The excellent enhancement might originate from the unique fluorophilic interaction of CB[7], which strengthened the host-guest interaction between 4-phenylpyridinium derivative with -CF₃ and CB[7].^[25] For the other polymers, the ultralong lifetimes presented diverse change after complexing with CB[7]. The relevant lifetimes were prolonged from 0.91 s to 0.92 s (P-CN), from 1.04 s to 1.30 s (P-CO₂Et), from 1.75 s to 1.86 s (P-Me), respectively (Figure 2b and Table 1). The afterglow properties and quantum yield also showed similar improvements where the corresponding phosphorescence quantum yields varied from 0.75% to 2.11% (P-CN), from 1.91% to 3.99% (P-CO₂Et), from 1.98% to 3.39% (P-Me), along with fluorescence quantum yields from 0.65% to 1.36% (P-CN), from 0.92% to 2.16% (P-CO₂Et), from 13.63% to 24.35% (P-Me), respectively (Figure 2c and Table 1). With the above experimental results in mind, we successfully prolonged the lifetimes of copolymers through introduction of CB[7], accomplishing the second adjustment of RTP lifetimes. To sum up, the diversely various ultralong RTP lifetimes via various functional groups and supramolecular host-guest interaction had been realized, including 0.9 s, 1.0 s, 1.3 s, 1.6 s, 1.7 s, 1.9 s and 2.2 s (Table 1). These various lifetimes almost covered the range of 0.9 s to 2.2 s. To our best knowledge, this was the first case of achieving such a full coverage of different phosphorescence lifetimes in the ultralong lifetime range. In addition, the analysis of XRD patterns proved the amorphous structures of P-X and P-X/CB[7] (X=CN, CO₂Et, Me, CF₃), demonstrating that the excellent RTP behaviour was attributed to the compact and subtle microenvironment and strong host-guest interaction, but not from crystal environment (Figure S28). This advantage laid a essential foundation for preparing ultralong RTP materials through scalable industrial process.

To investigate the possible mechanism of various ultralong lifetimes, we collected the kinds of rate constants of copolymers and supramolecular polymers (Table 1). On the one hand, the installation of various substituent groups or input of CB[7]

Table 1. The photophysical properties of copolymers and supramolecular polymers in solid state at ambient.

Compounds	Ex (nm)	Fluorescence (nm)	Phosphorescence (nm)	τ_{Fluo} (ns)	Φ_{Fluo} (%)	τ_{Phos} (ms)	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]
P-CN	327	383	503	4.88	0.65	908	0.75	1.33×10^6	2.02×10^8	1.54×10^6	8.26×10^{-3}	1.09
P-CO ₂ Et	330	370	500	3.65	0.92	1038	1.91	2.52×10^6	2.66×10^8	5.23×10^6	1.84×10^{-2}	0.945
P-Me	341	381	494	2.22	13.63	1746	1.98	6.14×10^7	3.80×10^8	8.92×10^6	1.13×10^{-2}	0.561
P-CF ₃	327	425	486	5.73	0.81	1608	3.84	1.41×10^6	1.66×10^8	6.70×10^6	2.39×10^{-2}	0.598
PH-1 ^[f]	332	366	490	2.29	17.5	1463	10.1	7.46×10^7	3.16×10^8	4.41×10^7	6.90×10^{-2}	0.614
PBr-1 ^[f]	316	378	507	0.94	6.60	8.58	56.7	7.04×10^7	3.91×10^8	6.04×10^8	66.1	50.5
P-CN/CB[7]	328	406	504	5.05	1.36	918	2.11	2.69×10^6	1.91×10^8	4.18×10^6	2.30×10^{-2}	1.07
P-CO ₂ Et/CB[7]	336	377	502	4.72	2.16	1299	3.99	4.58×10^6	1.99×10^8	8.45×10^6	3.07×10^{-2}	0.739
P-Me/CB[7]	340	377	501	2.04	24.35	1863	3.39	1.19×10^8	3.54×10^8	1.66×10^7	1.82×10^{-2}	0.518
P-CF ₃ /CB[7]	328	375	486	3.27	2.14	2217	6.33	6.54×10^6	2.80×10^8	1.94×10^7	2.86×10^{-2}	0.422
PH-1/CB[7] ^[f]	323	358	490	1.54	32.4	2333	12.4	2.10×10^8	3.58×10^8	8.05×10^7	5.32×10^{-2}	0.375
PBr-1/CB[7] ^[f]	326	372	507	0.78	13.1	9.02	52.7	1.68×10^8	4.39×10^8	6.76×10^8	58.4	52.4

[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 $K_{nr}^{Phos} = (1 - \Phi_{Phos}) / \tau_{Phos}$. [f] reference [19d].

endows the chromophore (4-phenylpyridinium) with various ISC rates (Table 1) in polymeric environment, suggesting that the suitable groups or introducing supramolecular host-guest interaction is beneficial for ISC process of excited electrons, which is the key for generation of triplet excitons and important foundation for phosphorescence emission. Intriguingly, these K_{isc} values are different but not that far apart. The maximum value (1.94×10^7 S⁻¹ for P-CF₃/CB[7]) is about twelve times as the minimum value (1.54×10^6 S⁻¹ for P-CN). This means that there may be occurrence of similar but various phosphorescence properties for the copolymers and supramolecular polymers, which are consistent with the results of various ultralong lifetimes in this work. On the other hand, the low radiative decay rate (K_r^{Phos}) and the nonradiative decay rate (K_{nr}^{Phos}) of phosphorescence, which are the vital parts of achieving ultralong phosphorescence emission, hint the long-lived characteristic of the RTP (Table 1). According to the equation (1) in Figure 1d, the lifetime is closely associated with K_r^{Phos} and K_{nr}^{Phos} . Decreasing value of ($K_r^{Phos} + K_{nr}^{Phos}$) is beneficial to the long-lived emission and will elongate the lifetime. Additionally, it is worth noting that there is only subtle difference for K_r^{Phos} within the small scope of 8.26×10^{-3} S⁻¹ (P-CN) to 3.07×10^{-2} S⁻¹ (P-CO₂Et/CB[7]) and for K_{nr}^{Phos} within the small scope of 0.422 S⁻¹ (P-CF₃/CB[7]) to 1.09 S⁻¹ (P-CN), respectively. Such small change, which is the other indispensable part of obtaining phosphorescence with various ultralong lifetimes, is more conducive to us retaining the excellent phosphorescence behavior and making precise adjustments to it within a certain range. In the range, the functional groups and CB[7] exhibit different effect on the K_r^{Phos} and K_{nr}^{Phos} of triplet excitons. P-CF₃/CB[7] and P-CN possess the minimum value (0.4506 S⁻¹) and the maximum value (1.098 S⁻¹) of ($K_r^{Phos} + K_{nr}^{Phos}$), respectively, thus exhibiting the longest lifetime (2.2 s) and the shortest lifetime (0.9 s), respectively. Similarly, P-CO₂Et/CB[7], P-CF₃ and P-Me/CB[7] successively show the various ultralong lifetimes of 1.3 s, 1.6 s and 1.9 s via this integrated effect from functional groups and macrocyclic host CB[7], successfully filling in the blanks with various ultralong lifetimes in the range of

0.9 s to 2.2 s. While the various substituents are removed, the phosphorescence still displays second-level lifetimes (PH-1 and PH-1/CB[7]) according to the previous work (Figure 4a, Table 1). Nevertheless, replacing these substituent groups with bromine atom which can greatly enhance the ISC rate and relaxation rate through heavy-atom effect, the phosphorescence only exhibit millisecond-level lifetime (PBr-1 and PBr-1/CB[7]), suggesting that the high ISC rate and relaxation rate go against requirement of long-lived phosphorescence.

Time-dependent density functional theory (TD-DFT) investigation indicated that there was only one main transition ($S_1 \rightarrow T_1$) with small difference of energy level (0.0004 eV-0.0022 eV) for various substituent group, demonstrating that the change of substituent group had no obvious effect on the number of main transition and energy level of ISC process (Scheme S2). The small difference of energy level ($S_1 \rightarrow T_1$) was beneficial for ISC process and therefore facilitated phosphorescence emission, which was in agreement with our extraordinary RTP. Additionally, the study of spin-orbit coupling (SOC) matrix elements (ξ) displayed that, other than R=CF₃, R=Me possessed larger $\xi(S_1, T_1)$ compared to R=CN and R=CO₂Et to facilitate the ISC process. The longer lifetime of R=CF₃ was probably due to the intense hydrogen bonds in polymeric environment. Thus, we introduced one hydrogen bond between fluorine and acrylamide into the calculation. The $\xi(S_1, T_1)$ of R=CF₃ varied from 0.010 cm⁻¹ to 0.028 cm⁻¹, further confirming the effect of hydrogen bonds (Scheme S3). From the above results, it was rational to deduce that different substituent groups could influence the ISC process of excited electrons by controlling the $\xi(S_1, T_1)$ value, thereby further regulating phosphorescence.

Such excellent RTP behavior is a great promotion for us to perform deeper exploration. It is well known that light-harvesting organisms, widely present in green plants and photo-synthetic bacteria, can capture light and then transfer absorbed energy to the reaction center by orderly packed chlorophyll molecules through fluorescence resonance energy transfer (FRET), which plays an indispensable role in normal life activities of green plants or photo-synthetic bacteria.^[26] However, most FRET

processes are mainly based on fluorescent donors. The energy transfer involving long-lived phosphorescence is rarely reported. Therefore, we attempted to construct a series of solid ternary supramolecular system through utilization of our supramolecular polymers as donors and organic dyes as acceptors, aiming at realizing highly efficient PpET from phosphors to dye center. Benefiting from the diversity of supramolecular polymers and organic dyes, the ternary supramolecular system was diverse and tunable.

SR101 with red fluorescence and EY with yellow fluorescence,^[20, 27] whose UV-Vis absorption has great overlap with the phosphorescence emissions from supramolecular polymers (Figure 3a and Figure S29a), are chosen as acceptors to assess the rationality and feasibility of the ternary supramolecular system. As an original exploration, various molar ratios of SR101 were introduced to the supramolecular polymer P-CN/CB[7] by co-assembling in aqueous solution, which were further treated with lyophilization and dried under vacuum to afford solid ternary supramolecular system P-CN/CB[7]-SR101. The results suggested that the unique photophysical behavior from P-CN/CB[7]-SR101 was obviously distinct from that of the supramolecular polymer P-CN/CB[7]. There was only one delayed emission at 500 nm for P-CN/CB[7], while P-CN/CB[7]-SR101 exhibited two delayed peaks located at 504 nm and 620 nm in spectra, respectively (Figure 3b and Figure S29b). Considering the phosphorescence of P-CN/CB[7] and fluorescence of SR101, it was rational to deduce that the two emission peaks were probably assigned to the phosphorescence from P-CN/CB[7] and fluorescence from SR101, respectively. The ultralong RTP-ET process between P-CN/CB[7] and SR101 endowed the fluorescence with long-lived property, thus resulting in its appearance in delayed spectra. To

further verify the assumption, polyacrylamide (PAM) doped with SR101 was prepared. Photoluminescence spectrum showed that the fluorescence emission occurred at 620 nm while SR101 was doped in PAM, which forcefully confirmed that the peak at 620 nm in Figure 3b indeed belonged to fluorescence of SR101 (Figure 3e). Furthermore, doping SR101 into polymeric environment would not induce the delayed emission at 620 nm of SR101 (Figure 3f). Additionally, the intensity of phosphorescence and delayed fluorescence were closely related to the molar ratio of SR101 (Figure 3b and Figure S29b). When the fraction of SR101 increased from 0.1% to 1%, the intensity at 504 nm decreased, and the emission at 620 nm enhanced greatly. With increasing the ratio continuously, however, both intensities at 504 nm and 620 nm diminished sharply, and even no emission signals could be detected when the fraction of SR101 was up to 30%, indicating that the excess of SR101 was harmful to the PpET behaviour. More intriguingly, the color of persistent luminescence of P-CN/CB[7]-SR101 also showed corresponding variation with addition of SR101 (Figure 3d and Video 3). When excited by 254 nm UV light, the luminescence exhibited colors from natterblue to red because of the simultaneous existence of fluorescence and phosphorescence from donor (P-CN/CB[7]) and acceptor (SR101). After withdrawing the excitation, the short-lived fluorescence was eliminated instantly and the long-lived luminescence (including phosphorescence from P-CN/CB[7] and delayed fluorescence from SR101) was still retained. Therefore, colorfully persistent luminescence, with color ranging from cyan (0.1% SR101) to pale yellow (1% SR101) and to red (above 1% SR101), was orderly observed. Interestingly, the color of ternary supramolecular system also present corresponding change with time. To understand the PpET behavior deeply, time-resolved

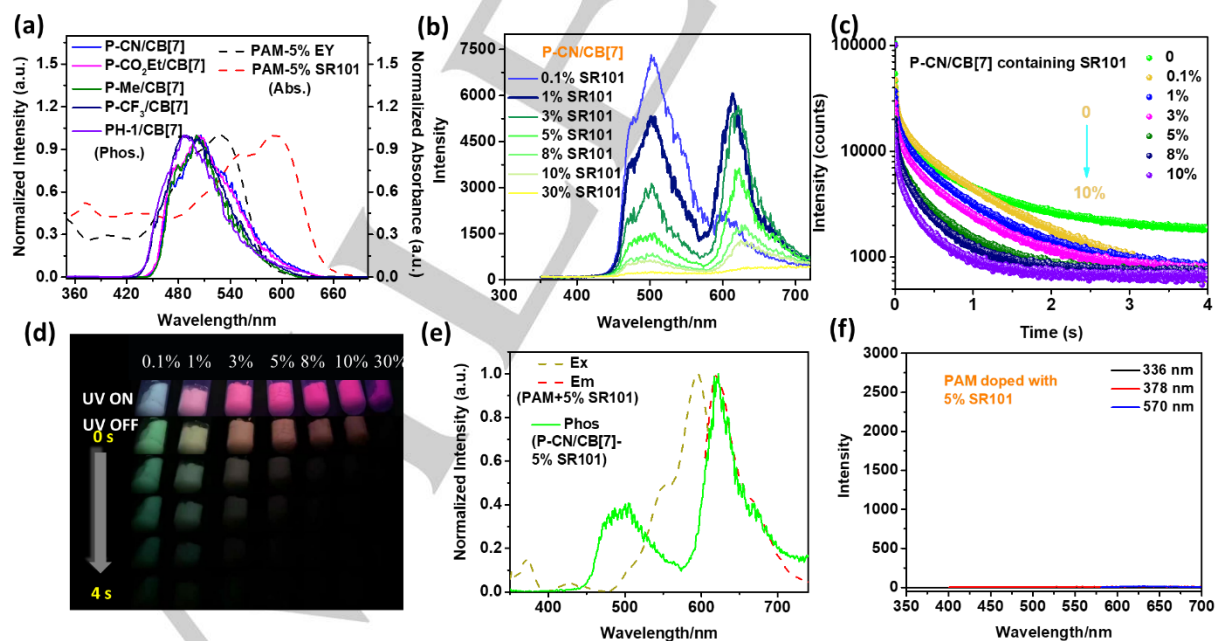


Figure 3. (a) The solid UV-Vis spectra of PAM-5%SR101 and PAM-5%EY and phosphorescence spectra of supramolecular polymers in solid state; (b) Delayed spectra (excitation wavelength: 328 nm, excitation slit/emission slit: 10 nm/5 nm), (c) Time-resolved decay spectra of P-CN/CB[7] at 504 nm with increasing molar ratio of SR101 in solid state at ambient (The same counts: 10^5); (d) Luminescence photographs (before and after ceasing 254 nm UV light) of P-CN/CB[7] with adding different molar ratios of SR101 in solid state at ambient; (e) Excitation and photoluminescence (dash) spectra of PAM containing 5% SR101 and delayed (solid) spectrum of ternary supramolecular system P-CN/CB[7]-5%SR101 in solid state at ambient; (f) Delayed spectra of PAM containing 5% SR101 under various excitation wavelengths.

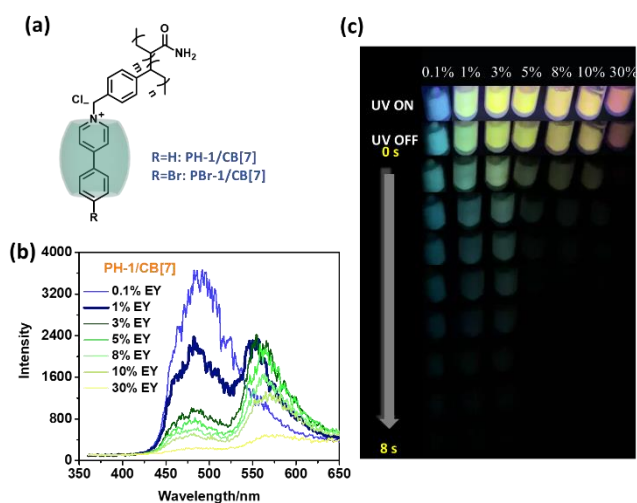


Figure 4. (a) The structural illustration of supramolecular polymers PH-1/CB[7] and PBr-1/CB[7] in previous work;^[19d] (b) Delayed spectra (excitation wavelength: 328 nm, excitation slit/emission slit: 10 nm/5 nm) and (c) Luminescence photographs of PH-1/CB[7] with adding different molar ratios of EY in the solid state at room temperature (before and after ceasing 254 nm UV light).

decay spectra was performed to record the lifetimes of emission peaks at 504 nm and 620 nm. As rising the ratio of SR101, the lifetime at 504 nm shortened from 791 ms (0.1% SR101) to 203 ms (10% SR101) (Figure 3c, Figure S30 and Table S2). In the contrast, the lifetime at 620 nm was prolonged first and then shortened, appearing maximal value of 395 ms while containing 1% SR101 (Figure S31 and Table S3), which was consistent with the information depicted in delayed spectra. Hence, 1% SR101 was a suitable ratio to perform RTP-ET and to fabricate the efficient ternary supramolecular system with P-CN/CB[7]. Additionally, the difference of lifetimes and delayed spectra under various delay time further explained the reason why the ternary supramolecular system displayed color change over time (Table S2, Table S3 and Figure S31h).

Subsequently, the universality and compatibility of ternary supramolecular system were estimated by experiments of replacing supramolecular polymers donors or dye acceptors. A series of supramolecular system, consisting of various supramolecular polymers (P-CO₂Et/CB[7], P-CF₃/CB[7], PH-1/CB[7]) and organic dyes (SR101 or EY), were prepared similar to the method of P-CN/CB[7]-SR101. As exhibited in the photographs, P-CO₂Et/CB[7]-SR101, P-CF₃/CB[7]-SR101 and PH-1/CB[7]-SR101 all displayed varicolored persistent luminescence phenomena (Figure S32a, Figure S33a, Figure S34a, Video 4-6). The colors successively varied from green to red for P-CO₂Et/CB[7]-SR101 and PH-1/CB[7]-SR101, and from cyan to red for P-CF₃/CB[7] as increasing the fraction of SR101 progressively, which symbolized that the RTP-ET process was still effectively performed while using various supramolecular polymers as phosphorescence donors. Likewise, the spectral experiments also revealed that there were new peaks appearing at 620 nm in the delayed spectra for the three supramolecular systems, suggesting the emergence of long-lived delayed fluorescence of SR101 (Figure S32b, Figure S33b and Figure S34b). The intensity at 620 nm reached maximal value while

doping 3% SR101 in P-CO₂Et/CB[7], 3% SR101 in PH-1/CB[7], 7% SR101 in P-CF₃/CB[7], respectively. On the other hand, we further probed the effect of altering acceptor on the ternary supramolecular system. Intriguingly, the acceptor EY was induced to engender the yellow delayed emission after absorbing the phosphorescence energy from supramolecular polymers (Figure 4c, Figure S35, and Video 7-8). Increasing the molar ratio of EY gradually, the yellow delayed fluorescence was more and more prominent, and the period of persistent luminescence was shortened evidently, which was in line with the results abovementioned. Spectral studies showed that the new peaks located at 568 nm in delayed spectra emerged and reached the optimal emission when the fraction of EY was 1% for PH-1/CB[7] and 5% for P-CO₂Et/CB[7], respectively (Figure 4b and Figure S35b). Correspondingly, the PpET processes between other phosphorescence donors and EY were also proved via delayed spectra (Figure S36). Doping EY in PAM did not induce the similar effect (Figure S37). Thereby, it could be concluded that the ternary supramolecular system presented superior compatibility for supramolecular polymer donors and dye acceptors. Additionally, the time-resolved photoluminescence decay plots showed corresponding change with increasing dye acceptors (Figs S38 and S39). The energy transfer efficiency was calculated as 15.0% for P-CN/CB[7]-1%SR101, 49.9% for P-CO₂Et/CB[7]-3%SR101, 26.2% for PH-1/CB[7]-3%SR101 and 68.9% for P-CF₃/CB[7]-7%SR101, 27.3% for PH-1/CB[7]-1%EY and 29.6% for P-CO₂Et/CB[7]-5%EY, respectively. Furthermore, the photoluminescence spectra through direct excitation of donors and acceptors of ternary supramolecular systems were carried out to show that there was no amplified effect of acceptor emission (Figures S40 and S41). To sum up, a new type of energy transfer system has been successfully constructed via the high-performance RTP-ET between the supramolecular polymers and organic dyes. Due to the variety of donor and acceptor, the ternary supramolecular system displays kinds of photophysical traits, including different lifetimes, colorfully delayed fluorescence, prominent PpET efficiency, and so forth.

The assembly property and excellent RTP of supramolecular polymers are of great significance for effective PpET. On the one hand, the supramolecular donors co-assemble with dye acceptors through hydrophilic and hydrophobic effect and electrostatic interaction to provide the beneficial distance and matched orientation of transition dipoles during the preparation process, both of which are crucial factors for the energy transfer process apart from spectral overlap.^[28, 29] On the other hand, the strong oscillator strength for excellent donor phosphorescence ($T_1 \rightarrow S_0$) effectively facilitates dipole-dipole coupling between the excited donor and ground-state acceptor and thus further promoted the phosphorescence energy transfer.^[24d] Nevertheless, an excess of dye molecules goes against the PpET process, which is probably due to inevitable aggregation-caused quenching (ACQ) effect and damage to highly ordered supramolecular coassembly as increasing the amount of acceptors.

Depending on the excellent photophysical features, we successfully applied these supramolecular polymers and the ternary supramolecular systems in writing, coloring and information encryption (Figure 5). Kinds of supramolecular polymers and ternary supramolecular systems were dispersed into methanol under ultrasound condition to provide

corresponding pigments. The lotus and the words (“Merry Christmas”) were designed to evaluate the efficiency of dynamically colorful variety realized by the multicolor long-lived luminescence (Figures 5a and 5c). In order to lively simulate the shape of lotus and to present beautiful blessings, we divided the lotus and blessings into several parts and decorated these parts with various pigments. For example, the lotus was colored orderly by P-CF₃/CB[7] (the stem), PH-1/CB[7]-3%EY (the pistil), P-CO₂Et/CB[7]-5%SR101 (the center of petal), P-CO₂Et/CB[7] (the rim of petal), respectively. Correspondingly, the words, “Merry Christmas”, were accomplished by P-CF₃/CB[7] (“Me”), P-CO₂Et/CB[7]-7%SR101 (“rry”), P-CO₂Et/CB[7]-3%SR101 (the star), PH-1/CB[7]-3%EY (“Christmas”) and P-CO₂Et/CB[7] (the tree). Under excitation of 254 nm UV lamp, the words and the lotus were activated, and the vivid patterns were exhibited in the pictures (Figures 5a and 5c, Video 9-10). Impressively, the patterns further evolved into other polychromatic works while removing light source because of disappearance of the prompt fluorescence. Furthermore, as time went by, the hidden information (“Me” and the tree) in the picture of “Merry Christmas” became more and more prominent and came into our view gradually. Additionally, triplet digit encryption based on the lifetime difference of supramolecular polymers was also realized. Various digit information of “2021”, “8888” and “1920” were successively displayed under different time periods through the rational design (Figure 5b and Video 11). This unique long-lived luminescence pigments developed a novel pathway to show beautiful works, words or to encrypt the key information that we wanted to present.

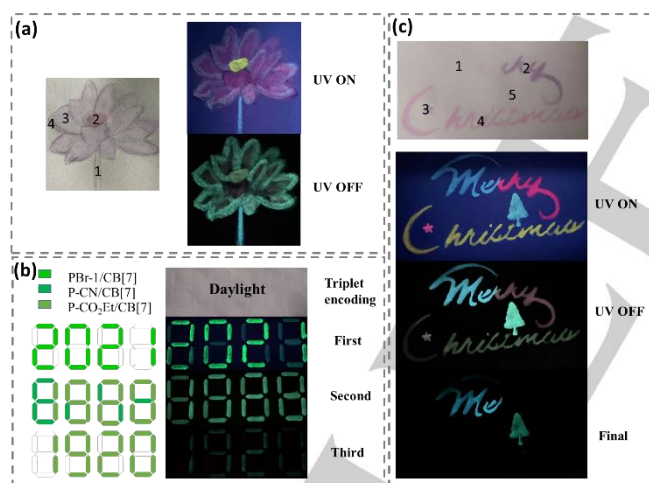


Figure 5. (a) The lotus colored by various supramolecular polymers and ternary supramolecular systems before and after excited by 254 nm ultraviolet lamp (1, 2, 3 and 4 represented P-CF₃/CB[7], PH-1/CB[7]-3%EY, P-CO₂Et/CB[7]-5%SR101 and P-CO₂Et/CB[7], respectively); (b) The schematic illustration of triplet digit encryption fabricated by supramolecular polymers PBr-1/CB[7], P-CN/CB[7] and P-CO₂Et/CB[7] (Light source: 254 nm ultraviolet lamp); (c) The words “Merry Christmas” written by supramolecular polymers and ternary supramolecular system before and after ignited by 254 nm ultraviolet lamp (1, 2, 3, 4 and 5 represented P-CF₃/CB[7], P-CO₂Et/CB[7]-7%SR101, P-CO₂Et/CB[7]-3%SR101, PH-1/CB[7]-3%EY and P-CO₂Et/CB[7], respectively).

Conclusion

In summary, a class of tunable solid supramolecular RTP assemblies are designed and synthesized based on acrylamide polymers with different 4-phenylpyridium derivatives and macrocyclic compound CB[7]. Benefiting from the effects of substituent groups (-CN, -CO₂Et, -Me, -CF₃) and complexation with macrocyclic host CB[7], the solid supramolecular RTP assemblies orderly exhibit various ultralong RTP emissions with lifetime varying from 0.9 s to 2.2 s (including 0.9 s, 1.0 s, 1.3 s, 1.6 s, 1.7 s, 1.9 s and 2.2 s) through adjustment of ISC rate and radiative relaxation rate and nonradiative relaxation rate of excitons in chromophores. The simple preparation and amorphous structures of copolymers and supramolecular polymers provide a significant foundation for industrial production and practical application. Additionally, the studies show that the resulting supramolecular polymers are not only the excellent RTP emitters, but also a type of prominent donors to construct ternary supramolecular system with PpET properties. Combining with organic dyes (SR101 or EY) as acceptors, the supramolecular polymers effectively transfer the absorbed energy to the dye center in term of ultralong RTP-ET, thus realizing the ultralong delayed fluorescence emissions of dye molecules (yellow delayed fluorescence for EY and red delayed fluorescence for SR101). By tuning the ratio of acceptors added to the ternary supramolecular system, multicolor long-persistent luminescence is observed visibly. Significantly, the multicolor ultralong persistent luminescence materials are triumphantly applied in encrypting digits, words and coloring pictures, implying extensive applications in the fields of writing, information encryption and painting. This work not only provides an effective approach to develop RTP materials with various ultralong lifetimes, and but also give a guideline to construct high-performance phosphorescence energy transfer systems and multicolor persistent luminescence materials.

Acknowledgements

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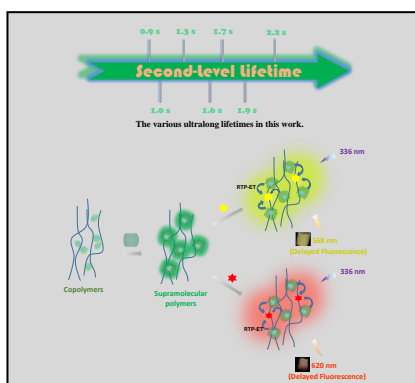
Keywords: cucurbituril • energy transfer • phosphorescence • supramolecules • ultralong lifetime

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Solid supramolecules based on acrylamide-phenylpyridium copolymers with various substituent groups and cucurbit[7]uril not only exhibit tunable ultralong phosphorescence with lifetimes varying from 0.9 s to 2.2 s, but also co-assemble with organic dyes Eosin Y or SR101 to display high-performance phosphorescence energy transfer with multicolor delayed fluorescence properties.



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Page No1. – Page No8.

Tunable Second-Level Room-Temperature Phosphorescence of Solid Supramolecules Between Acrylamide-Phenylpyridium Copolymers and Cucurbit[7]uril