Coronene Doped Ultra-Long RTP Polymers with Visible Light Excitability in Air

Guanyu Liu¹, Junwu Chen¹, Shiguo Zhang¹, Yuefa Zhang¹, Shanfeng Xue¹, Qikun Sun¹, and Wenjun Yang¹

¹Qingdao University of Science and Technology

October 28, 2023

Abstract

Abstract: It is emphasized that hetero- and heavy-atoms and specific inter-molecular interactions are essential for ultra-long organic room temperature phosphorescence (RTP), moreover, the RTP production dominantly requires high-energy UV light excitation. In the current work, we present that coronene (Cor) doped PMMA and PS can all emit bright and ultra-long RTP with lifetimes of 4.43 and 2.97 s in air under 365 nm light excitation, respectively. More significantly, it is first found that both Cor/PMMA and Cor/PS exhibit rare visible light excitability up to 500 nm, and their afterglows are naked-eye visible and the RTP lifetimes are up to 2.46 and 2.11 s under 440 nm light excitation, respectively. However, hetero- and heavy-atom-free Cor has neither common spin-orbital coupling nor visible light absorption band in polymer film, and Cor/PS is a full hydrocarbon system. Therefore, we propose that the multi-resonance effect and largely fused π systems are responsible for the abundant triplet population and the visible light excitability, signifying the significant enhancement of direct S0-T1 transition. This work demonstrates a fresh RTP material system and phenomenon and provides a new perspective of understanding organic triplet generation and radiation.
system and phenomenon and provides a new perspective of understanding organic triplet generation and radiation.

1. Introduction

In the past decade, there has been a resurgent and increasing interest in organic room temperature phosphorescent (RTP) materials due to their low cost, bio-compatibility, structure diversity, and ease of preparation in contrast to the traditional rare metal-containing inorganic salts and organic complexes. Among them, organic RTP polymers are more attracting due to additional advantages of strength, toughness, outstanding process-ability, and economy. Common polymers are almost all non-phosphorescent but can serve as doping matrices to suppress triplet thermal deactivation and oxygen quenching of conjugated organic dopants. The prerequisite for bright and ultra-long RTP is to effectively populate and stabilize triplet state. It is known that the efficient inter-system crossing (ISC) between different electron spin states is required for triplet population and radiation, which is generally facilitated in the presence of hetero and heavy halogen atoms due to the enhancement of spin-orbital coupling (SOC). The rigid yet polar polymers can provide more confined micro-environments and stronger interactions with organic dopants and are usually used as doping matrices. Following these guidelines, ultra-long organic RTP has been achieved by doping organic hetero-cyclic compounds into polymers rich in hydrogen bonds and polar groups such as polyvinyl alcohol (PVA), polyacrylamide (PAM), poly(methyl methacrylate) (PMMA), etc. Moreover, it is well known that UV light is dominantly used as excitation source. However, hygroscopic polymers can seriously deteriorate RTP and mechanical properties in air, and the bright and ultra-long RTP is rarely achieved even in PMMA matrix at present. According to the current views and results, it is impossible for pure hydrocarbon conjugated molecules and pure hydrocarbon polymers to form effective RTP systems.

On the other hand, the precondition of triplet population is the light absorption of $S_0$-$S_1$ and subsequent ISC ($S_1$-$T_n$). Since the current organic RTP molecules mainly absorb UV light or deep blue light at most, visible light excitable RTP and reverse ISC (RISC)-induced thermally-activated delayed fluorescence are rarely reported. At present, based on the relative experimental phenomena, spin-forbidden ISC, RISC, and RTP radiation ($T_1$-$S_0$) have been accepted widely and rationalized appropriately. However, the reverse process of RTP, i.e. direct $S_0$-$T_1$ population, is rarely concerned due to the very inferior probability and utilizability. Admirably, enhancing $S_0$-$T_1$ transition to the extent that the abundant triplet population occurs can bypass the conventional ISC process and provide a possibility for the visible light excited RTP. This is a very meaningful guideline in academics and practical applications but is formidably challenging.

It is worth noting that aromatic hydrocarbon compounds are usually used as triplet-generating dopants in early studies of RTP polymers. Typically, in 1967, Kropp and Dawson doped coronene (Cor) into PMMA and afforded 5.5 s of RTP lifetime. In recent years, Adachi, Zhang, and Tao, et al. successively restudied the RTP properties of Cor/PMMA and validated the ultra-long RTP behaviors. However, these ultra-long RTP properties are all measured under oxygen isolation conditions and UV light excitation. Moreover, PS was attempted but declared not to be suitable doping matrix. Recently, pyrene (Py) has been doped into rigid yet polar PVA and PDEA and emits long-lived RTP (hundreds of ms), but Py/PS showed extremely faint RTP hard to notice by the naked eye even under a 365-nm UV lamp, which is attributed to inefficient ISC instead of ineffective suppression of non-radiative decay pathways. Our recent experiments reveal that Py/PS rather than Py crystal itself emit strong yellow low temperature phosphorescence in liquid nitrogen (Figure S1, Supporting Information), implying the existence of complex triplet population and radiation and suggesting the necessity of restudy and recognition on the RTP properties of aromatic fused hydrocarbons in polymers.

In the current work, we adopt open fabrication and measurement conditions to revisit the RTP properties of Cor/PMMA and Cor/PS in air. We now report that Cor/PMMA and Cor/PS sheets can emit bright and ultra-long RTP with lifetimes up to 4.43 s and 2.97 s after UV photo-activation for 20 s and 4 min, respectively, indicating that the insufficient photo-activation can miss important RTP phenomena and lead to the misconception on the RTP properties of some material systems. More unexpectedly, these sheets
exhibit visible light excitable RTP, and their afterglows are even naked-eye visible and camera-recordable after 500 nm light excitation although these doped films have no detectable absorption bands in visible light region. Under 440 nm light excitation, their afterglow lifetimes are still up to 2.46 and 2.11 s, respectively. These unique photo-excitation and RTP emission phenomena are hard to explain by the existing mainstream viewpoints and thus call for a fresh perspective of understanding, heralding a breakthrough in both materials and concepts.

2. Results and Discussion

Coronene (Cor) is commercially available and is further purified by vacuum thermal sublimation before use to ensure its purity. The molecular structures of Cor, PS, and PMMA as well as the sample preparation procedures in this study are depicted in Figure 1. As a class of functional polymer materials, besides the solution-casting film, an important advantage is the thermoplastic processability. Generally, it is not a good RTP material if an organic doped polymer exhibits RTP only in solution-cast film but deteriorates the RTP and mechanical properties after thermoplastic processing. Moreover, thermoplastic processing can not only fabricate diverse complex practical products but also orientate and compact polymers as well as facilitate dopant dispersion according to textbooks of polymer physics and rheology, which should provide more confined molecular environments and better oxygen-barrier effect. To our knowledge, such a valuable processing strategy has not received its deserved attention till now and the researchers are accustomed to evaluate the RTP properties using solution-cast films, which may miss some excellent RTP systems and even lead to improper RTP views.

Figure 1. The diagram of preparation procedure of Cor/PMMA and Cor/PS sheets. The mixed solution is evaporated into films for better molecular dispersion, and thermoplastic processing promotes the further dispersion and dense matrix stacking as well as produces a large patch of products of any shape and size.

2.1 RTP properties of Cor/PMMA

Cor crystal has no RTP but emits red low temperature phosphorescence after freezing in liquid nitrogen (Figure S2, Supporting Information), indicating that crystallization itself cannot inhibit the triplet thermal deactivation but the triplet population is present at room temperature. To change the molecular environments and disperse Cor into polymers at the molecular level better, Cor and PMMA or Cor and PS are dissolved in dichloromethane (MC), and the dried film from natural evaporation is thermoplastic processed on open mill at 145°C and then is molded into 1 mm thick square sheet on flat plate press at 185°C according to common polymer processing procedures. As we know, both RTP efficiency and lifetime do not represent visual afterglow brightness and duration, so it is necessary to record and display the RTP afterglow images (Video S1, Supporting Information). The taken PL photo graphs for Cor/PMMA sheets are showed in Figure 2. Notably, the production of deserved RTP afterglow for Cor/PMMA sheets requires
15-25 s photo-activation due to the quenching effect of triplet oxygen in PMMA matrix on the organic triplet excitons,[12,31-34] where it is understandable that long-wave light excitation and low Cor doping amount need a relatively long photo-activation time. Impressively, the RTP afterglow is visible to the naked eye for more than 15 s even under fluorescent lamp, and the RTP afterglow duration in the dark is more than 40 s after ceasing 365 nm light (Figure 2a). Excitingly, when excitation light is red-shifted to visible region, RTP afterglow is still naked-eye visible, where the visible afterglow duration excited by 440 nm and 500 nm light can last for about 30 s and 2 s, respectively (Figure 2b). Thus, we not only realize the ultra-long RTP of Cor/PMMA in air but also find new and really visible light excited organic RTP materials, and these sheets all show UV-visible light excitability and reproducible RTP afterglows, regardless of the standing time in air and the change of doping amount (mass percent in polymer). Among the three doping amounts, a higher Cor doping amount (1%, PMMA1.0) is more conducive to long-wave light excitability, and PMMA0.2 affords the better comprehensive RTP in view of afterglow duration and material economy. On the other hand, it is noted that these afterglow emissions are from molecular RTP of Cor in polymers due to no observable crystalline red emission in the frozen films (Figure S3), and Cor is dispersed in polymer matrices at the molecular level.

Figure 2. (a) The RTP afterglow photographs of Cor/PMMA sheets in air (PMMAx, x represents the mass percent of Cor in polymer) before and after removing 365 nm light excitation in the dark and under fluorescent lamp. (b) The afterglow photographs of same samples excited by different wavelength visible light in the dark.

We measure steady-state PL spectra, PL efficiency, and time-resolved RTP decay curves of Cor/PMMA sheets. The prompt PL spectra reveal that fluorescence emission is within blue region with the main peak at 446 nm and accompany with RTP emission in green-yellow region (Figure 3a). Due to the not high total PL efficiency and weak RTP band measured by an integrating sphere, only 1.3%-2.5% of RTP efficiencies are calculated, implying that most of the radiated triplet excitons prefer delayed RTP afterglow emission in view of bright and ultra-long afterglow (Figure 2). The delayed PL spectra are rather broad ranging from green to red regions with the main peak at 566 nm, displaying a greenish-yellow emission color. Take PMMA0.2 as an example, unlike 365 nm light excitation, under 460 nm visible light excitation, the prompt PL spectrum has no fluorescence band and only shows RTP emission band that is same as the delayed RTP emission (the middle spectra in Figure 3a), indicating the absence of traditional $S_0$-$S_1$ transition at this time. The time-resolved RTP decay curves decrease slowly (Figure 3b), and the fitted long component lifetimes ($\tau_P$), which is also the high-ratio main component, are fairly long. The $\tau_P$ and the averaged lifetime ($<\tau>$) are 3.345 and 3.235 s, 4.431 and 4.139 s, and 3.912 and 3.697 s for PMMA0.1, PMMA0.2, and PMMA1.0 sheets, respectively. Moreover, the RTP afterglow for PMMA0.2 sheet can also exhibit up to 2.46 and 1.73 s of $t_P$. 
and $\langle t \rangle$ under 460 nm light excitation, respectively (the middle sky-blue curve in Figure 3b), which is the first example of ultra-long organic RTP excited by long-wave visible light to date.\textsuperscript{35–37}

![Figure 3](image)

Figure 3. (a) The steady-state PL spectra and transient PL efficiency of Cor/PMMA sheets in air. (b) The time-resolved RTP decay curves and the fitted RTP lifetimes in air. Where the corresponding spectra and data for PMMA0.2 sheet after 460 nm light excitation are depicted, and others are excited by 365 nm light.

2.2 RTP properties of Cor/PS

We next examine the RTP properties of Cor/PS sheet with 0.1% doping amount. Unlike Cor/PMMA, no RTP afterglow is observed for Cor/PS sheet after tens of seconds of photo-activation, however, when the photo-activation time is prolonged to 200–250 s, depending on excitation wavelengths, the unexpected bright and ultra-long afterglow appears (Figure 4a). In the dark, the afterglow duration is more than 30 s, whereas the discernible afterglow is long over 15 s under fluorescent lamp after 365 nm light excitation. Moreover, the RTP afterglow can also be seen under visible light excitation although the duration is relatively short and the photo-activation time becomes long. The long photo-activation time is possibly due to a high active oxygen concentration in PS matrix rather than the ineffective suppression of PS matrix on triplet thermal deactivation (\textit{vide infra}). Furthermore, it is noted that, unlike Cor/PMMA, the photo-activated Cor/PS is stood in air for over 15 min, and the production of deserved RTP afterglow needs again photo-activation for 3–4 min, implying a faster and higher oxygen permeability in PS matrix. Also, it is found that the degassed Cor/PS sheet in vacuo can produce the deserved afterglow only after 20 s photo-activation (Figure S4), where degassing shortens the photo-activation time but does not obviously affect the afterglow brightness and duration,
Figure 4. (a) The RTP afterglow photographs of Cor/PS sheet in air before and after removing different wavelength excitation light in the dark and under fluorescent lamp. (b) The time-resolved RTP decay curves of Cor/PS sheet in air and the fitted RTP lifetimes after 365 and 440 nm light excitation. Further verifying the serious oxygen quenching effect in PS matrix. Interestingly, the thermoplastic processed sheet is cooled and instantly excited by UV light for 10 s can produce bright and ultra-long RTP (Figure S5), which is ascribed to less active oxygen residue in the matrix. The PL spectra and RTP efficiency of photo-activated Cor/PS are very similar to that of Cor/PMMA (Figures 4b,c). Impressively, the fitted RTP lifetimes are very ultra-long and up to 2.968 s and 2.110 s under 365 and 440 nm light excitation, respectively (Figure 4d). These experiments indicate that rigid and non-polar PS can also stabilize some triplet organic dopants to emit ultra-long RTP, but a long photo-activation time is usually required in air to eliminate the serious oxygen quenching effect. Therefore, the insufficient photo-activation can indeed miss some RTP phenomena (systems) and even lead to the improper explanations and conclusions.

2.3 Discussions on the RTP phenomena

The experimental results have fully validated that aromatic fused hydrocarbons such as Cor and pyrene can produce abundant triplet excitons and radiate bright and ultra-long molecular RTP in polymers. However, Cor’s SOC values have been calculated to be almost zero for both $S_1$-$T_n$ and $T_1$-$S_0$ due to the absence of hetero- and heavy-atoms (Table S1). Thus, SOC-facilitated ISC is no longer convincing here. Moreover, since bright and ultra-long RTP is also observed for Cor/PS, the reason for ISC promotion cannot be ascribed to the external hetero- or heavy-atom effect as well as the charge transfer mediation, and it needs to be reconsidered. On the other hand, unlike twisted fused polycyclic structures, non-substituted planar aromatic fused structures have been reported to decrease triplet population according to the El-Sayed rule. Moreover, if the abundant triplet population of Cor is ascribed to the small rate constant of fluorescence emission that results from symmetric forbidden radiation transition, the singlet excitons may prefer non-radiative $S_1$-$S_0$ transition rather than spin-forbidden ISC, and the abundant triplet population problem is still pending.

In the past few years, some fused aromatic hetero-cycles with electron donor (N or O) and acceptor (B) atoms are found to emit thermally-activated delayed fluorescence (TADF, Figure 5a), but inferior SOC is calculated in such multiple hetero atom-containing molecules. Consequently, their multiple resonance (MR) structures are thought to be responsible for enhancing RISC that induces effective TADF in electroluminescence and photoluminescence processes. Very recently, only electron donor nitrogen-containing fused aromatic hetero-cycle is also reported to show MR-promoted RISC and TADF emission. Obviously, the precondition of photo-induced RISC is the ISC, thus, MR should promote ISC first. In this context, the bright and ultra-long RTP indicates the presence of abundant triplet population in Cor, hexabenzocoronene, truxene, and pyrene doped polymers. This means that ISC and RTP radiation here may be promoted by MR effect of
aromatic fused hydrocarbons. Moreover, the fused planar aromatic rings can eliminate molecular internal rotation and decrease molecular thermal vibration, which even enables the non-polar rigid PS to stabilize Cor to emit bright and ultra-long RTP. In contrast, no RTP is observed for HPB (Figure 5b) in both PMMA and PS matrices (Figure S6).

Figure 5. (a) The typical multi-resonance-induced TADF fused aromatic hetero-cycles with donor (N or O) and acceptor (B) atoms (upper), and hole and particle pairs in natural transition orbitals (NTOs) analysis for S0-S1 and S0-Tn transitions of coronene. (The energy level of a triplet state (Tn) lies within the range of ± 0.3 eV to E S1) (bottom). (b) The molecular structures of hexaphenylbenzene, PS and PMMA. (c) The absorption spectra of Cor in polymer films (upper) and the corresponding RTP excitation spectra monitored at RTP emission peaks (bottom). (d) The Joblonski diagram of Cor in polymers under UV and visible light excitation.

Another issue is why visible light can excite Cor doped polymers to emit RTP. Notably, no absorption band and fluorescence emission are detected under visible light excitation (the upper in Figure 5c and the middle in Figure 3a), thus, the traditional ISC pathway for triplet population (S0-S1-Tn) no longer works at this time. However, the measured excitation spectra for 567 nm RTP indicate the presence of excitation contribution of long-wave visible light to RTP emission (the bottom in Figure 5c). Consequently, the triplet excitons for RTP afterglow under visible light excitation are speculated to be from the direct triplet population (S0-T1), Figure 5d). Unfortunately, the enhanced S0-T1 absorption is hard to detect at present even if the absorption coefficient is increased by several orders of magnitude,[42] but it has indeed been enhanced to the extent that abundant triplet population enables RTP after-glow to be observed clearly by the naked eye, regardless of excitation wavelengths. On the other hand, we fail to figure out whether the S0-T1 absorption is also present under UV light excitation at present. Nevertheless, the discovery of long-wave visible light excited RTP in Cor doped polymers will evoke the researches to find more examples not limited aromatic fused hydrocarbons, leading to new breakthroughs in organic RTP materials and mechanisms.

2.4 Applications of Cor/polymers

Cor emits bright and ultra-long greenish-yellow RTP in PMMA, which enables its triplet state to act as energy donor and excite red fluorescent dye with green-yellow absorption band to emit persistent red afterglow via Forster resonance energy transfer (FRET).[43–45] Thus, 0.2% perylene red (PR) and 0.2% Cor are co-doped into PMMA, where the absorption band of the former overlaps well with the RTP spectrum of the latter (the upper, Figure 6a). The prompt PL spectrum of PR/Cor/PMMA is dominated by red emission of PR excepting the residual weak fluorescence band of Cor. The delayed PL spectrum is almost all PR red emission, indicating an almost complete triplet-to-singlet state FRET (the bottom, Figure 6a). The inset shows the time-resolved PL decay curve monitored at 620 nm, and a slow decay is observed and the fitted afterglow lifetime is up to 2.93 s, which is consistent with ultra-long red afterglow recorded by a digital camera (Figure S7). Moreover, PR/Cor/PMMA inherits the visible light excitability of Cor/PMMA, enabling the first visible light excited ultra-long red afterglow to date.

Finally, unlike organic RTP crystals that mostly present all-or-nothing luminescence upon light excitation...
and are hard to store complex information, the initial generation of RTP emission for some organic doped polymers requires a certain time of photo-activation to eliminate oxygen quenching effect inside polymer matrix, and after that, the photo-activated region can instantly produce RTP after brief light re-excitation. Both Cor/PMMA and PR/Cor/PMMA are such materials. This unique excitation and emission property provides plenty of time window to label and read information. Considering that dense planar lattice can better manifest pattern fineness, we cover a 200-mesh screen on the surface of the spliced Cor/PMMA and PR/Cor/PMMA sheet and then 20 s of UV photo-activation is applied. After removing UV light and screen, a clear afterglow image is observed (Video S2). Impressively, the fine structures in the image can be distinguished after excited by UV-visible light (Figure 6b), moreover, a small rabbit hidden in the central area can be identified by enlarging the image (Figure S8). After storage for hours in ambient air, the photo-patterned spots still remember the ever photo-activated history, and the image reproduction only requires a brief photo-excitation (2–5 s), exhibiting the ultra-long memory and readout function of photo-patterning information. After 16 h, the excited pattern becomes blurry possibly due to the combined effect of oxygen infiltration and cumulative photo-activation. The memory effect can be eliminated by standing the sheets for three days at room temperature or for 1 h at 80 °C in oven, and a new photo-pattern can be printed.

Figure 6. (a) The absorption spectrum for PR and the RTP spectrum for Cor in PMMA matrix (upper), and the prompt and delayed PL spectra as well as the time-resolved afterglow decay curve for PR/Cor/PMMA in air (bottom). (b) The afterglow photographs of photo-activated patterns on the spliced Cor/PMMA and PR/Cor/PMMA sheet surface under the different excitation wavelength and standing time.

3. Conclusion

In summary, we restudy the molecular RTP properties of coronene (Cor) in PMMA and PS matrices. It is found that Cor/PMMA can emit bright and ultra-long RTP afterglow with the lifetime of over 4.4 s without air isolation after 365 nm light activation for 20 s. More significantly, it is first revealed that Cor/PMMA can emit RTP under up to 500 nm visible light excitation, and the RTP lifetime is still ultra-long and reaches to 2.46 s under 460 nm light excitation. Further, we indicate that Cor/PS can also exhibit ultra-long RTP properties and visible light excitability, but the photo-activation time for eliminating oxygen quenching effect takes more than 200 s, implying that the insufficient photo-activation will miss some RTP phenomena and lead to improper cognition and conclusion. Hetero- and heavy-atom-free Cor hardly has spin-orbital coupling but can produce abundant triplet population, implying the presence of a new paradigm that enhances ISC, and we propose that it is the multi-resonance effect of fused aromatic hydrocarbons. On the other hand, Cor/polymers have no visible light absorption bands but plenty of triplet excitons are still produced under visible light excitation, which is attributed to the enhancement of direct \( S_0 - T_1 \) population. This work will intrigue the interest in visible light excitable RTP polymers and new fused aromatic cyclic compounds as
dopants. We are broadening and deepening our work to find more unique RTP phenomena and further evidence the fresh RTP mechanisms.

**Acknowledgements**

Financial support for this research was provided by National Natural Science Foundation of China (No. 52273183), Natural Science Foundation of Shandong Province (No. ZR2020QE-083), Taishan Scholar Constructive Engineering Foundation of Shandong Province of China (No. tsp202211164). We thank the open project of The State Key Laboratory of Supra-molecular Structure and Materials of Jilin University (No. sklssm2023029).

**Conflict of Interests**

The authors declare no conflict of interests.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Received: ((will be filled in by the editorial staff)) Revised: ((will be filled in by the editorial staff)) Published online: ((will be filled in by the editorial staff))

**References**


Coronene (C) doped polymers can emit bright and ultra-long RTP with lifetimes of 3.0–4.4 s and up to 500 nm visible light excitability in air, breaking common RTP viewpoints and guidelines. Unlike C/PS sheets, C/PMMA sheets show photo-activation memory effect of hours and high-level optical encryption and anti-counterfeiting.

**Keyword:** coronene, room temperature phosphorescence, visible light excitability, PMMA and PS, photo-activation memory effect

Guanyu Liu, Junwu Chen, Shiguo Zhang, Yuefa Zhang, Shanfeng Xue, Qikun Sun,* Wenjun Yang*

Coronene Doped Ultra–Long RTP Polymers with Visible Light Excitability in Air