Host–guest materials with room temperature phosphorescence: Tunable emission color and thermal printing patterns

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Abstract
The research of purely organic materials with long afterglow has drawn more and more attention, especially for those with stimulus-response characteristic. So far, this kind of material is really very scarce and their performance is not good enough. In this study, we successfully developed an efficient heating-responsive room-temperature phosphorescence material with phosphorescence efficiency and lifetime up to 13.4% and 2.08 s through the simple host–guest doping strategy. Further on, by introducing the additional energy acceptor of fluorescein with concentration-dependent emission to construct ternary doping systems, the afterglow color was extended from blue to yellow. Accordingly, the multicolor thermal printings have been easily realized, showing the great practical application prospects.

KEYWORDS
color-tunable afterglow, organic luminescent materials, thermal printing, thermal response effect

Featured by the ultralong emission lifetime and high exciton utilization, the research of organic room-temperature phosphorescence (RTP) has drawn considerable attention for its potential applications in data storage, encryption, display, bioimaging, and so forth.¹–⁴ Particularly, the applications of encryption and bioimaging with RTP materials show a great advantage in comparison with the traditional materials, as the time-resolved technology could be utilized for their long afterglow after turning-off the UV irradiation, thus largely promoting the corresponding performance.⁵–¹⁰ To develop efficient RTP materials, a series of strategies have been explored, such as host–guest interactions, H-aggregation, heavy-atom effect, intermolecular electronic coupling, intermolecular π–π or hydrogen bond interaction, and so forth.¹¹–¹⁸ Among them, host–guest interactions performed very well.¹⁹–²¹ For example, Bolton et al.
developed an efficient RTP system with efficiency and lifetime of 55% and 8.3 ms through diluting the aldehyde chromophore into a host crystal with the similar halogen-bonding motif. Zhang et al.\textsuperscript{20} utilized the nanosupramolecular assembly between pyridinium chloride complexation and cucurbit[6]uril to give a greatly enhanced phosphorescence with quantum yield and lifetime of 81.2% and 5.40 ms in ambient. Kabe and Adachi\textsuperscript{21} innovatively exploited the strategy of photo-induced charge transfer to fully utilize the excited state energy in a host–guest doping system, realizing a long persistent luminescence with emission quantum yield and afterglow up to 21% and 2 h in N\textsubscript{2}. Lei et al.\textsuperscript{22} induced efficient phosphorescence of triphenylamine derivatives by confinement in a rigid matrix, achieving a phosphorescence efficiency and lifetime of 18.2% and 610 ms. Zhang et al.\textsuperscript{23} dissolved 1,8-naphthalic anhydride in certain organicsolid hosts to realize an RTP lifetime of over 600 ms and overall quantum yield of over 20%. Regardless of these beautiful works, the organic RTP materials with both high efficiency ($\Phi_p > 10\%$) and long lifetime ($\tau_p > 2$ s) in air are still really scarce, especially the ones with stimulus-response characteristic, badly limiting their corresponding applications to some extent.\textsuperscript{24–29}

In 2020, our group innovatively utilized the distance-sensitive Förster resonance energy transfer process in the development of stimulus-responsive RTP system, in which, N,N-dimethylpyridin-4-amine (DMAP) with rigid crystal environment was selected as host/energy donor, and di-(naphthalen-2-yl)-amine (Cdp) with potential RTP emission acted as guest/energy acceptor.\textsuperscript{30} Based on its unique heating/force-responsive RTP effect, the application of encrypted thermal printing was realized for the first time. For this RTP system, there was still room for further improvement in some aspects: such as moderate RTP efficiency (4.04%) and lifetime (768 ms), single luminescent color. To further promote RTP performance and maintain the stimulus response characteristics, a new guest material of N,N,N',N'-tetramethylbenzidine (Tmb) was introduced in this study, as it has been reported to show ultralong blue luminescence in rigid environment.\textsuperscript{21,31–33} As shown in Figure 1, although no obvious room temperature phosphorescence could be observed

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure1.png}
\caption{(A) The design strategy to develop color-tunable organic afterglows with ternary doping systems of rigid host (DMAP), blue RTP guest (Tmb), and energy acceptor (Fluc) with concentration-dependent emission. (B) The photographs of DMAP, Tmb, DMAP-Tmb cocrystal, and DMAP-Tmb-Fluc cocrystals under white LED, 312 nm UV on and off. DMAP, N,N-dimethylpyridin-4-amine; Fluc, fluorescein; RTP, room temperature phosphorescence; Tmb, N,N,N',N'-tetramethylbenzidine}
\end{figure}
As shown in Figures 2 and S1–S3, dominated fluorescence existed for the individual DMAP and Tmb crystals, while no obvious RTP emission could be observed. When they were mixed together with mass ratio of 400:1 to form cocrystal, two emission peaks could be found, in which the one at 385 nm was fluorescence with a lifetime of 4.04 ns, the other at 480 nm was phosphorescence with an ultralong lifetime of 2.08 s (Figure S4). Besides, its RTP efficiency was measured to be as high as 13.4%, which was among the highest values for organic RTP materials with a lifetime longer than 2.0 s.\textsuperscript{1–23} Thus, a bright blue afterglow lasting for more than 10 s could be achieved after switching off the 312 nm UV irradiation. Carefully analyzing the photoluminescence (PL) spectra of DMAP, Tmb, and their cocrystal, it was not difficult to find that the fluorescence of DMAP-Tmb cocrystal was in good consistent with that from Tmb, indicating the

\textbf{FIGURE 2}  (A) The steady-state PL spectra of DMAP, Tmb, and DMAP-Tmb cocrystal with mass ratio of 400:1. (B) The RTP decay curve (@480 nm) of DMAP-Tmb cocrystal. (C) The PL spectrum of host (DMAP crystal) and UV-visible absorption spectrum of guest (Tmb in dichloromethane solution). (D) The RTP behavior of DMAP-Tmb cocrystal. DMAP, N,N-dimethylpyridin-4-amine; PL, photoluminescence; RTP, room temperature phosphorescence; Tmb, N,N,N′,N′-tetramethylbenzidine
guest material of Tmb acted as the main emitter in their cocrystal.

Then why could Tmb show so efficient RTP emission in cocrystal? To make it clear, the low-temperature PL behavior of Tmb solution was studied to verify its phosphorescent property, as the nonradiative motion could be largely restricted at this time (Figure S5). It was strange to find that just weak phosphorescence could be detected at 77 K for Tmb, although its corresponding lifetime could be up to 1.55 s. Also, when Tmb was doped in polymethyl methacrylate film with mass ratio of 1:100, nearly no RTP emission could be detected (Figure S6). These suggested the much-enhanced phosphorescence performance has happened for Tmb once doped in DMAP host. To explore the internal mechanism, their UV–vis absorption spectra were measured. As shown in Figure 2C, a large spectral overlap between the DMAP (host) emission and the Tmb (guest) absorption could be observed, which would lead to the efficient energy transfer from DMAP to Tmb. Furthermore, a new shoulder peak at about 360 nm appeared in the UV–vis absorption spectrum of cocrystal in comparison with the individual DMAP and Tmb samples (Figure S7), indicating the intermolecular charger transfer between DMAP and Tmb. Accordingly, the intersystem crossing (ISC) could be largely promoted, thus leading to

FIGURE 3 (A) The UV-vis absorption spectra of mixed samples (DMAP and Tmb) after heating at different temperatures. (B) The PL spectra of mixed samples (DMAP and Tmb) after heating at different temperatures. (C) The RTP decay curves (@480 nm) of mixed samples (DMAP and Tmb) after heating at different temperatures. (D) Photographs of mixed samples (DMAP and Tmb with mass ratio of 400:1) after heating at different temperatures. The corresponding heating time was 10 min, then the RTP behaviors were studied when the samples were cooled to room temperature. DMAP, N,N-dimethylpyridin-4-amine; PL, photoluminescence; RTP, room temperature phosphorescence; Tmb, N,N,N',N'-tetramethylbenzidine.
the efficient RTP emission of Tmb in the cocrystal state.\textsuperscript{37,38}

To make a deep insight into the RTP mechanism of DMAP-Tmb cocrystal, the time-dependent density functional theory calculations were carried out (Figures S8–S10). Particularly, the ground state geometries of DMAP-Tmb mixtures with different ratios from 1:1 to 3:1 were optimized, and the corresponding frontier molecular orbitals and spin-orbit coupling (SOC) constants were calculated. As shown in Figure S9, in molecular dimer or trimer with DMAP:Tmb = 1:1 or 2:1, Tmb acted as the main emitter and showed the typical $\pi-\pi^*$ transition from the HOMO of Tmb to the corresponding LUMO, which were well identical to the experimental results. As for the tetramer with DMAP:Tmb = 3:1, obvious intermolecular charge transfer could be observed, from the occupied orbital of Tmb to the vacant orbital of the neighboring DMAP, which has been frequently considered to be much beneficial for the ISC transition as well as the resultant RTP emission in previous reports.\textsuperscript{35–38} Further on, the energy levels and the corresponding SOC constants between $S_1$ and $T_n$ were calculated. In general, the energy level difference between $S_1$ and $T_n$ less than 0.3 eV is considered to be able to process ISC and the larger SOC values indicate more efficient ISC transition.\textsuperscript{39,40} As shown in Figure S10, because of the existence of intermolecular charge transfer, two important ISC channels could be observed in the tetramer with DMAP:Tmb = 1:3, in which, one is $S_1$ to $T_7$ with SOC value of 0.98213 cm$^{-1}$, another is $S_1$ to $T_{11}$ with 0.36984 cm$^{-1}$. As for Tmb and DMAP:Tmb = 1:1 or 2:1, the SOC constants between $S_1$ and $T_n$ were all less than 0.56, indicating the much weaker ISC transition (Figure S10). Thus, the intermolecular charge transfer could be well certified as the main origin to promote RTP effect of Tmb. Based on these calculated results, the RTP mechanism of DMAP-Tmb cocrystal could be well understood.

As demonstrated above, the mixtures of DMAP and Tmb could produce bright RTP emission if they were uniformly mixed in cocrystal, since efficient energy transfer and intermolecular charge transfer could be realized between them. Then could other approaches be utilized to enhance the intermolecular interactions between DMAP and Tmb, thus leading to the bright RTP emission, just like in cocrystal?

Therefore, heating and grinding the mixtures of DMAP and Tmb were explored. As shown in Figure 3, when the samples of DMAP and Tmb were mixed at room temperature or heated at lower than 60°C, no apparent RTP emission could be observed. If the heating temperature was further increased, much enhanced and prolonged RTP emission could be realized for the accelerated molecular motion, then resulting in the enhanced intermolecular interactions between DMAP and Tmb. At about 110°C, the bright blue RTP emission lasting for more than 10 s could be achieved, showing the obvious heating-responsive RTP effect. During the thermal stimulation, the changes of UV-vis absorption, PL spectra, and the corresponding RTP lifetimes of their mixtures were monitored. As shown in Figure 3A, with the increased heating temperature, the newly formed shoulder peak at about 360 nm in UV-vis absorption spectra became more and more stronger, indicating an enhanced intermolecular charge transfer between DMAP and Tmb. As for their PL spectra, an obvious decrease in 335 nm from DMAP and increase in about 395/480 nm from Tmb could be found. Correspondingly, a slight prolonged RTP lifetime from 1.39 to 1.97 s could be observed (Figure S11 and Table S1). These could well suggest an enhanced energy transfer from DMAP to Tmb under the thermal stimulus. Thus, the synergistic effect of the promoted energy transfer and intermolecular charge transfer between DMAP and Tmb could also give rise to the turn-on RTP effect for the enhanced intermolecular interactions between DMAP and Tmb. However, possibly for the excessively damaged crystal packing, the resultant RTP emission could just last for about 6 s (Figure S12).

To further extend the color range of afterglow in this host–guest doping system, additional energy acceptor of fluorescein (Fluc) was added to construct the ternary cocrystal systems. On one hand, the maximum absorption peak of Fluc located at about 495 nm, showing a larger overlap with the RTP emission of DMAP-Tmb cocrystal (Figure S13). This would be much beneficial for the energy transfer from DMAP-Tmb to Fluc molecules. On the other hand, Fluc showed interesting concentration-dependent emission property, whose emission color could change from green (514 nm) to yellow (550 nm) through simply changing its concentrations (Figure S14). Thus, when trace Fluc was doped in the DMAP-Tmb system to form ternary cocrystal, obvious energy transfer happened, resulting in the changed afterglow color from blue to green. Additionally, through increasing the doped concentrations of Fluc, the afterglow color could be further extended to yellow region, showing the inherited concentration-dependent afterglow emission. In the meantime, the long afterglow up to 10 s could be maintained for the ternary cocrystal systems, regardless of the adjusted emission color.

Besides, the PL spectra and the corresponding lifetimes were measured to characterize the changed PL behaviors in detail (Figure S15 and Table S2). As shown
in Figure 4B, when the trace Fluc was doped in DMAP-Tmb system with the mass ratio of 12 000:1 between DMAP and Fluc, a new shoulder peak of 535 nm appeared in addition to the main peak of 480 nm. With the increase of Fluc concentration, obvious red-shifted emission to about 575 nm could be observed for the newly formed shoulder peak, while that at 480 nm was nearly unchanged. To better characterize the colors of afterglows, the CIE color coordinates were calculated based on the corresponding RTP spectra, and they were found to change from (0.18, 0.36) in blue region to (0.29, 0.40) in green-yellow one. On the other hand, emission lifetime just showed slightly decrease to 1.71–2.07 s for the ternary cocrystal systems in comparison with the binary one. Based on these results, it could be well certified that the introduction of additional energy acceptor to construct ternary cocrystal systems was indeed an efficient way to adjust the afterglow color without sacrificing luminance performance severely.

Further on, the possible heating-responsive emission properties were explored for the ternary doping system with DMAP as host, Tmb as guest, and Fluc as additional energy acceptor. As shown in Figure S16, no obvious afterglow could be observed for the mixtures of DMAP-Fluc at room temperature, regardless of the changed concentrations of Fluc. Once being heated at 60°C for about 10 min, slightly enhanced afterglows could appear and last for about 3 s (Figure S17). When the heating temperature was further increased to 100°C, obvious afterglows from green to yellow lasting for about 10 s could be observed for the ternary doping systems with different Fluc concentrations (Figure S18), indicating the typical heating-responsive emission properties. At this moment, the emission lifetimes were measured to be as long as 1.60–1.74 s. Thus, through introducing additional energy acceptor with concentration-dependent emission property, heating-responsive property of multicolor afterglows could be easily realized, which would largely expand the corresponding applications. On the other hand, the afterglows could also be activated after grinding the mixtures of DMAP-Tmb-Fluc. Also, adjustable afterglow color could be realized through changing the concentrations of Fluc, although the corresponding
lasting times were not so long, just about 5 s, possibly for the damaged crystallinity of DMAP host (Figure S12).

Inspired by the efficient heating-responsive emission property for the mixed DMAP-Tmb-Fluc samples, the application of thermal printing was further explored. A thermal printer works mainly through heating the selected area of thermochromic paper (thermal paper) to print the preset image or letter.41,42 In comparison with other printing techniques (inkjet and laser printings), thermal printing equipment shows the advantages of cheap in cost, small in size, light in weight, low in energy consumption, and so forth. Hence, this technology has been widely used in receipt printers, mobile label printers, and fax machines. The corresponding thermal paper was designed and divided into three layers: Layer A with DMAP or DMAP-Fluc mixture, Layer B with Tmb, and transparent encapsulation film (Layer C). When the thermal paper passed over the print head, the intermolecular interactions between DMAP-Fluc and Tmb would be largely enhanced under the combined actions of heating and pressure; thus, the preset images with multicolor afterglow could appear. As shown in Figure 5, the thermal paper based on DMAP (Layer A) and Tmb (Layer B) could show a preset image of “horse” with blue afterglow more than 7 s, after it was heated by thermal printer. When additional Fluc was added on Layer A to form another kind of thermal paper, the afterglow color for the printed images could be turned from green to yellow through simply changing the Fluc concentrations. For these afterglow images, their emission lifetimes were all longer than 1 s, further certifying their outstanding RTP performance (Figure S19). Thus, with these materials with thermal-response characteristic, the multicolor thermal printings were easily realized. Additionally, as these afterglow images were only clearly recognized after turning off the UV irradiation, the information encryption could be achieved.

In this study, according to the concept of molecular uniting set identified characteristic,15,43–48 we have successfully developed a new organic system with color tunable afterglows from blue to yellow by expanding the host–guest afterglow system from binary to ternary. For the initial binary cocystal system with rigid DMAP as host and potential phosphorescence emitter of Tmb as guest, an outstanding RTP performance with phosphorescence quantum yield and lifetime up to 13.4% and 2.08 s was achieved for the efficient energy transfer and intermolecular charge transfer between DMAP and Tmb. Then, to expand the emission color range of afterglow, additional energy acceptor of Fluc with concentration-dependent emission property was added to construct ternary cocystal. Accordingly, tunable afterglow from blue to yellow could be realized by simply changing the concentrations of Fluc. More excitedly, besides cocystal, heating the mixtures of DMAP-Tmb or DMAP-Tmb-Fluc could also lead to the obviously turn-on afterglow with different emission colors. Based on it, the application of multicolor thermal printings could be easily achieved. This study has not only opened up a simple way to develop the multicolor long afterglow materials with stimulus-response characteristics, but also realized the effective application of this kind of materials.

FIGURE 5  (A) Manufacturing method of thermal paper (Layer A was coated by DMAP or DMAP-Fluc mixture and the Layer B was coated by Tmb). (B) Photographs of the thermally printed image of “horse” based on DMAP-Tmb, and multicolor letters of “MUSIC” based on DMAP-Tmb or DMAP-Tmb-Fluc, taken before and after the irradiation of a 312-nm UV lamp
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CONFLICT OF INTERESTS
The authors declare that there are no conflict of interests.

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