A General Design Principle for Aggregation-Induced Room-Temperature Phosphorescence via An sp^3 -Linked Donor-Acceptor Structure

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Abstract: Intramolecular motion is commonly more detrimental to room-temperature phosphorescence (RTP) than to prompt fluorescence because long-lived triplet excitons offer more possibilities of quenching. Inspired by the mechanism of aggregation-induced emission (AIE), a single molecule is endowed with AIE and RTP features at the same time. By utilizing triphenylamine (TPA) as AIE activator as well as electron donor and an sp^3 linkers as a bridge between donor and acceptor, five TPA-based AIE-active RTP luminophores were designed. RTP and low-temperature emissions reveal the co-existence of ternary emission, including fluorescence and dual phosphorescence. Single-crystal analyses and theoretical calculations suggest dual phosphorescence derives from local excitation and charge-transfer component. By utilizing hot exciton emission, color-tunable phosphorescence can act as an indicator for temperature estimation. This combinatory approach pioneers a new route for designing versatile AIE-active RTP materials.

Organic room-temperature phosphorescence (RTP) is a process that triplet excitons radiate as photons. Suppressing the nonradiative transitions and promoting the intersystem crossing (ISC) are crucial to realize high-efficiency RTP.^[1] Till now, Several RTP design principles have been proposed, such as introducing bulky hindrance groups^[2] and spiro linkers,^[3] constructing self-assemblies,^[4] host-guest composition^[5] and bonding interaction,^[6] and tuning charge-transfer (CT) states.^[7] Recently, we have put forward a new RTP design principle based on an sp^3 linked donor-acceptor structure.^[8] For example, we based on sulfur linked donor-acceptor (DSA) molecules developed a proton-activated “off-on” RTP.^[8a] However, it is hard to find a common rule to tune the RTP efficiency. Most of RTP emission is accompanied by fluorescence as the major component.^[9]

Paramount to realize efficient solid-state emission is endowing luminophores with the AIE feature, of which common emission mechanism is the restriction of intramolecular motion (RIM).^[10] Since 2001, AIE luminophores have been a research hotspot because of their enormous potential in solid-state display,^[11] bio-probes,^[12] circularly polarized luminescence,^[13]

Scheme 1. Design concept (a) and chemical structures (b) of AIE-active RTP molecules.

and “on-off” sensors.^[14] Generally, most of AIE luminophores are traditional fluorophores. Therefore, it is necessary to explore a universal design method for the development of RTP materials given their potential merits used as chemical sensors,^[15] data storage,^[16] bioimaging^[17] and OLEDs.^[18]

If combining the advantages of AIE and RTP into a single molecule, *is it possible to devise a general method for tunable AIE-active RTP for more extensive applications?* Inspired by this idea, we utilized TPA as an AIE activator as well as an electron donor. To promote the intersystem crossing process for RTP, an sp^3 linker was introduced to separate the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Based on this design concept (Scheme 1a), five TPA-functionalized AIE-active RTP molecules were developed (Scheme 1b) via simple Suzuki-Miyaura or Ullmann-type coupling reactions.

Firstly, the AIE character of **TPA1-5** are investigated. Absorption spectra conducted in THF (Figure 1a) are like those calculated by time-dependent density functional theory (TD-DFT) method (Figure S1) with optimally tuning range-separated functional (LC- ω PBE*) and TZVP basis set.^[19] According to the calculation results (Table S1), the reddest absorption band (>280 nm) of **TPA1-2** is mainly contributed by the second and

Figure 1. a) Absorption spectra (left) of **TPA1-5** in THF and corresponding hole (blue)-electron (green) distributions (right) calculated based on the TD-DFT method. b) Steady-state emission spectra of **TPA1-5** in the mixtures showing AIE process with different THF/water ratios (0-95%, v/v) and related AIE photos (water fraction: 0 and 95%, TPA concentration: 2.0×10^{-3} mol/L).

the third singlet excited states (S_2 and S_3) while that of **TPA3-5** is dominated by S_3 and the fourth singlet excited state (S_4). The hole-electron distribution analysis performed by Multiwfn 3.7(dev) program^[20] indicates excitation transitions of all TPA molecules are controlled by local excitation, and the lowest singlet excited state (S_1) is the dark state. Therefore, it is rational that TPA molecules are almost non-emissive due to excited-state energy dissipation via intramolecular rotation role and CT pathways, leading to S_1 as the dark state. As increasing the fraction of water, a typical AIE process (Figure 1b) can be observed due to confinement of the nonradiative pathway of S_1 . Moreover, all TPA molecules in THF/water (5/95, v/v) show RTP-scale emission, and the afterglow can be seen in **TPA1** aggregates (Figure S2).

Due to the character that the whole is more brilliant than the part, the luminescent properties of aggregates **TPA1-5** will be the main focus. For **TPA1** and **TPA2**, the steady-state emission showcases a main fluorescence emission (Figure 2a) with a long tail, indicative of the existence of RTP. It is confirmed by the emission lifetime of >300 ms (Figure 2b, right) and spectral overlap with the delayed emission. It has to be noted the structured RTP emission of **TPA1** contains a broad shoulder (425-500 nm), which does not look like the vibrational energy level from the lowest triplet excited state emission (T_1). To shed light on the origin of this shoulder peak, time-resolved emission spectra were collected. At the same delay interval, all the RTP emission contours are similar (Figure 2c), but the intensity ratio between 525 nm and 485 nm ($I_{525/485}$) rises as prolonging the delay time (Figure S3). The increase in intensity ratio indicates that the lifetime of T_1 emission is longer than that of emission at 485 nm, which is consistent with the lifetime measurement (Figure S4). The low-temperature (77 K) emission exhibits a huge emission intensity enhancement around 425-485 nm

(Figure 2d), which further demonstrates the wide shoulder emission band does not originate from the vibrational energy level of T_1 . When **TPA1** was doped in poly (methyl methacrylate) (PMMA), we found that phosphorescence spectra exhibit a blue shift of ~ 70 nm as temperature decreases from 298 K to 77 K (Figure 2e), suggesting a radiative transition from a higher triplet state. Here, we preliminarily conclude this higher triplet emission derives from the second triplet excited state (T_2). A schematic illustration for this ternary emission (fluorescence and dual phosphorescence) is presented in Figure 1f. Although the T_2 emission band disappears in **TPA2** at room temperature (Figure 2a and S5), it shows up in low-temperature phosphorescence (77 K, LTP) emission (Figure S6), indicating that T_2 of **TPA2** more susceptible to triplet oxygen and thermal quenching than that of **TPA1**. Notably, two phosphorescence peaks of **TPA2** in PMMA can be distinguished below 190 K (Figure S7). In aggregates, the disappearance of T_2 emission and the red-shifted T_1 emission may also be caused by exciton splitting, which could shrink the energy gap between two triplet states and promote the efficiency of internal conversion.^[21] To best of our knowledge, due to the relatively large energy gap between T_1 and T_2 and different transition patterns, the internal conversion may slow down to some extent.^[22] Hence, it is rational that T_2 emission can compete with the internal conversion.

In order to tune the ISC process for enhancing the RTP ratio, the acceptor subunit is replaced by benzophenone. **TPA3** and **TPA4** show an obvious red-shift emission (Figure 2a). Different from **TPA1** and **TPA2**, the lifetimes of **TPA3** and **TPA4** collected at steady-state emission maximum are also in the RTP scale (Figure S8). Delayed emissions show a further redshift and a longer RTP (T_1) lifetime (Figure 2b, right) compared with those of the steady-state emissions. Besides, fluorescence emission at 450 nm (for **TPA3**) and at 420 nm (for **TPA4**) can be collected

Figure 2. a) Emission spectra of **TPA1-5** in air at room temperature (excitation: 365 nm for **TPA1**, **TPA2** and **TPA 4**; 430 nm for **TPA3**; 450 nm for **TPA5**) and corresponding photos showing **TPA1-5** excited by 365-nm UV light. b) Time-resolved decay profiles of **TPA1-5** in air at room temperature (right: fluorescence; left: RTP). c) Time-resolved emission spectra of **TPA1**. d) Phosphorescence emission spectra of **TPA1** doped in PMMA film (excitation: 375 nm; doping concentration: 3%, weight ratio) at different temperatures. e) Emission spectra of **TPA1** at 77 K. f) Schematic illustration of ternary emission process; process 1: fluorescence; process 2: intersystem crossing; process 3&4: phosphorescence; process 4: internal conversion.

(Figure 2, left). Similar to **TPA1**, the emission band can be easily differentiated below 500 nm appears in time-resolved RTP spectra and LTP emission (Figure S9 and S10), which can also be ascribed to T_2 emission. The lifetime of T_2 is shorter than that of T_1 (Figure S9c and S10c). Similarly, the phosphorescence emissions of **TPA3** and **TPA4** in PMMA both consist of two-component phosphorescence (Figure S11). As a result, room-temperature emissions of **TPA3** and **TPA4** includes a weak fluorescence and a majority of two-state phosphorescence. Therefore, a higher RTP ratio (Figure 2a and Table S2) in **TPA3** and **TPA4** than that in **TPA1** and **TPA2** is realized due to the small energy gap between S_1 and the higher triplet state (T_2), which could boost the ISC between the S_1 and triplet states. By further changing the acceptor into acetophenone (**TPA5**), the steady-state and RTP emission spectra show almost same profile (Figure 2a), the lifetime of which is up to 31.1 ms (Figure 1b). Delayed emission spectra exhibit a progressive redshift (Figure S12a, from 560 nm to 590 nm), which finally indicates the T_1 state is centered at 590 nm ($\tau=36.3$ ms, Figure S12b), which is confirmed by the LTP emission (Figure S13a). Given that there is no overlap at 475 nm between the steady-state and T_1 emission at 77 K, the 200-ms-scale lifetime at 475 nm implies the other phosphorescence emission (T_2) (Figure 13b). Besides, a very short fluorescence lifetime can be collected at 480 nm at room temperature and 77 K (Figure 1b and S13c). As expected, an evident blue phosphorescence emission (T_2) also appears below 190 K in PMMA doped with **TPA5** (Figure S14). Consequently, it is easy to explain why **TPA5** shows almost pure

phosphorescence at room temperature due to S_1 and T_2 are degenerated.

Next, single-crystal measurements of **TPA1** and **TPA3-5** was conducted to investigate the origin of ternary emission (fluorescence and dual phosphorescence) except for **TPA2**, which always generate polycrystals. As shown in Figure 3, donor and acceptor moieties of TPA derivatives adopt a highly twisted conformation due to the separation of an sp^3 linker, resulting in a twisted about $110-120^\circ$. Furthermore, aromatic rings in donor also take the twisted configuration because of the role of the nitrogen atom. The whole twisted conformation of donor- sp^3 linker-acceptor structure renders there is no strong $\pi-\pi$ stacking intermolecular interaction for the origin of phosphorescence. As a matter of fact, other intermolecular interaction mainly acts as the lockers to suppress the intramolecular motion of TPA, which is responsible for the AIE phenomenon. Therefore, dual phosphorescence may primarily originate from the locally excited (LE) state of TPA and the intramolecular CT state between donor and acceptor subunits.

To verify this hypothesis, **TPA1** and **TPA2** were selected as examples to carry out a series of theoretical calculations via TD-DFT at LC- ω PBE*/TZVP level in the gas state. The calculated energy diagram of vertical excitation and spin-orbit coupling constants reveal the multiple ISC channels from S_1 to T_n for RTP generation (Figure S15). Molecular orbital transitions of T_1 and T_2 of **TPA1** are from LE and hybridized excited states (LE and CT), respectively (Figure 4a). A similar scenario appears in **TPA2** with the inverse character of two triplet states (Figure 4b).

Figure 3. Capped stick models (Top) of **TPA1** and **TPA3-5** obtained from single-crystal structure and their detailed wireframe packing diagrams (bottom) proving no strong π - π intermolecular interactions in the solid state.

Figure 4. Theoretical calculated molecular orbitals of **TPA1** (a) and **TPA2** (b) and corresponding main transition configuration (>5%) based on the optimized ground state (H= HOMO, L= LUMO). Vertical emission energy levels of **TPA1** (c) and **TPA2** based on optimized S_1 , T_1 and T_2 , respectively.

Moreover, the vertical emission calculations demonstrate two almost degenerate states (S_1 and T_2) and a relatively big energy gap between T_1 and T_2 (Figure 4c and 4d), which could promote ISC and decrease the rate of the internal conversion according to the energy gap law.^[23] Therefore, it is reasonable that dual phosphorescence showcases in **TPA1** at room temperature and **TPA2** at 77 K.

Finally, to demonstrate the potential application value of this design principle for versatile AIE-active RTP molecules, we further synthesized **TPA6** (Figure 5a). As Figure 5b shows, **TPA6** exhibits a fluorescence emission at 425 nm (with a lifetime of 0.7 ns). With a setup of 3-ms delay, an obvious afterglow can be observed by the naked eye and an RTP emission band can be collected with a lifetime of 83 ms in air at room temperature. Interestingly, as temperature decreases, a new emission band appears after 440 nm with an emission maximum at 455 nm (Figure 5c), which remarkably differs from the RTP profile. From

Figure 5. a) Chemical structure of **TPA6**. b) Steady-state and RTP emission (initial delay: 3 ms) spectra of **TPA6** in air at room temperature; inset: photo showing **TPA6** solid excited by 365-nm UV light. c) Steady-state emission spectra of **TPA6** at different temperatures. d) Temperature-dependent phosphorescence emission spectra of **TPA6**. e) Relationship between the intensity ratio ($I_{455/425}$) and temperature. f) Image showing phosphorescence emission colors at different temperatures.

Figure 5d, temperature-dependent phosphorescence emissions exhibit progressively blue shift as temperature decreases. According to the investigation of **TPA1-5**, the emission centered at 455 nm of **TPA6** is mainly contributed by T_2 , which acts as the receiver state for efficient ISC. Different from **TPA1-5**, the T_2 emission of **TPA6** in aggregates is more sensitive to temperature variation. The intensity of ratio between 455 nm and 425 nm ($I_{455/425}$) versus temperature satisfies a highly correlated

inverse S-shaped curves (Figure 5e). Taking advantage of this character, T₂ emission could be utilized as an indicator for rough temperature estimation like PH test stripes for the approximate estimation of the PH value. As Figure 5f shows, **TPA6** exhibits a specific emission color at different temperature points.

In summary, by introducing an AIE activator into the donor-*sp*³ linker-acceptor structure, several ternary emissive AIE-active RTP molecules with prompt fluorescence and dual phosphorescence were designed. A tunable emission with different RTP ratio can be realized via changing the acceptor subunit. By rationally utilizing T₂ excitons, color-tunable phosphorescence could be utilized as a temperature indicator. This design principle opens a new opportunity for developing AIE-active RTP materials.

Acknowledgements

We would like to thank the National Key R&D program of China (2017YFA0303500 to G. Z.), the National Natural Science Foundation (GG2340000364 to G. Z.), and the National Natural Science Foundation of China (21903054 to X.S.).

Keywords: aggregation-induced emission • ternary emission • room-temperature phosphorescence • dual phosphorescence • Temperature indicator

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