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Accessing Tunable Afterglows from Highly Twisted Organic AIEgens via Effective Through-Space Conjugation

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Abstract: Nonaromatic, cross-conjugated, and highly twisted luminogens consisting of acylated succinimides demonstrate aggregation-induced emission (AIE) characteristics and tunable multicolor photoluminescence and afterglows in their single crystals. Effective through-space conjugation among different moieties bearing n/π electrons promote the SOC and ISC transitions and lead to diverse emissive clusters with concurrently rigidified conformations, thus allowing readily tunable emissions. Derived from it, the proof of concept application for advanced anti-counterfeiting is illustrated. These results should spur the rational design of novel nonaromatic AIEgens, and moreover advance the understanding of the origin of tunable multicolor afterglows.

Since the first report in 2001, the concept of aggregation-induced emission (AIE) has attracted intense interest in the past 20 years,[1] because it provides new fundamental insights into the photophysical process and overcomes the aggregation-caused quenching (ACQ) problem of conventional luminogens, thus paving the way for both fundamental study and diverse technical applications in optoelectronic devices,[2] chemo- and biosensors,[3] biological imaging and therapy,[4] etc. Meanwhile, thus far, pure organic with persistent room temperature phosphorescence (p-RTP) have also been surging due to their promising applications in optoelectronics,[5] biological science,[6] chemical sensors,[7] and anticounterfeiting technology.[8] Despite the exciting advances in both areas, most organic AIEgens are merely fluorescent, while those with distinct p-RTP remain rare cases, on account of the inefficient intersystem crossing (ISC) in pure organics and susceptibility of triplet excitons.[9]

Emission color tunability of luminescent materials, particularly that of p-RTP, is highly desired for advanced optical and biological applications.[10] Such smart materials, fortunately, have been scatteredly found in several systems through H-aggregation of planar molecules,[11] diverse clusters,[12] and various aggregation states.[13] However, there is no general design strategy or universal mechanism for the presence of such tunability, which significantly limits its further development. Specifically, considering the difficulty in achieving efficient p-RTP from AIEgens, the realization of tunable p-RTP from them remains a highly tough task, although it is important to gain further insights into the AIE mechanism and the origin of tunable p-RTP in terms of chemical structure, conformation, and molecular packing.

Previously, it is found clustering of nonconventional chromophores with π electrons and/or lone pairs (n) is sufficient to generate diverse emissive centers with effective through-space conjugation (TSC),[14] thus offering multicolor photoluminescence (PL). Inspired by that and in order to develop novel AIEgens with tunable p-RTP, we here designed two nonaromatic luminophores, namely, N,N-carbonylbisuccinimide (CBSI) and N,N-oxalylbisuccinimide (OBSI) comprising multiple carbonyls, which can be readily obtained through acylation of succinimide (SI) by triphosphene and oxalyl chloride in mild conditions (Figure 1A, S1–S4). Such molecular design is based on the following considerations: 1) The incorporation of multiple carbonyls could boost SOC and consequent ISC processes for the generation of triplet excitons;[15] 2) Prevalent intra- and intermolecular interactions including carbonyl-carbonyl interactions could effectively stabilize the triplets;[16] 3) Both CBSI and OBSI are molecularly cross-conjugated,[17] which would further result in remarkable TSC in crystals, thereby leading to diverse extended electron delocalization. CBSI and OBSI adopt highly twisted conformations and are virtually nonluminescent in dilute solutions, while being brightly emissive in concentrated solutions or crystals,[18] with efficiencies (Φ) of up to 9.0% (Figure 1B), demonstrating typical AIE features.[1] Furthermore, as expected, tunable PL and afterglows in response to excitation wavelength (λex) are observed in their single crystals (Figure 1B). These results would advance both fields of AIE and tunable p-RTP.

![Figure 1](image-url)

Figure 1. A) Synthetic routes and typical characteristics of CBSI and OBSI. B) Photographs of CBSI/DMF solutions taken under 312 nm UV lamp and summarized photophysical data for concentrated solutions (solv., 0.01 x) and crystals (crst) of CBSI and OBSI. Notes: λex = 312 nm, λem = 365 nm; λem,pL: PL maximum, λem,RTP: RTP maximum; nd: not determined; -: no RTP emission.

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As demonstrated in Figure 2A and Video S1, in contrast to the nonluminescence in solutions, upon 312 nm UV irradiation, CBSI and OBSI single crystals show obvious yellowish-white and sky-blue emissions, respectively. Impressively, bright green and yellow afterglows lasting for ~3 s are clearly observed. Furthermore, when the excitation source is switched to 365 nm UV light, distinct bluish-white PL along with yellowish-green afterglow is observed in CBSI crystals, whereas those for OBSI crystals slightly vary (Figure 2A, Video S1). These results clearly demonstrate the tunable PL and afterglows of CBSI crystals and relatively inconspicuous tunability for OBSI crystals. To acquire more information, prompt and delayed emission spectra were measured. The prompt PL spectrum of CBSI crystals apparently changes with the variation in $\lambda_{ex}$ (Figure 2B,C, and S5), consequently resulting in the PL color changing from yellowish-white ($\lambda_{ex} = 312$ nm) to bluish-white ($\lambda_{ex} = 365$ nm). This $\lambda_{ex}$-dependent emission should be ascribed to the presence of multiple emissive species, which is confirmed by the different ns scale lifetimes ($<\tau>$) of 1.5/3.0/3.6 ns at 410/450/478 nm (Figure S6 and Table S1). To further understand the origin of such $\lambda_{ex}$-dependent PL, solution emission of CBSI was investigated. As depicted in Figure 2D and S7, 10^{-6} M CBSI/DMF solution shows comparable signals to those of the solvent, which suggests the nonluminescent nature of molecularly dissolved CBSI. With increased concentration of 10^{-5} M, emerging well-resolved peaks at 410 and 436 nm are found, whose intensities are progressively enhanced with increasing concentration up to 10^{-3} M. Even higher concentration (i.e. 10^{-2} M) exhibits apparent emission centered at 513 nm with structureless shoulders at 410/436 nm, which are believed to be associated to the aggregation. These concentration-enhanced emission and $\lambda_{ex}$-dependent PL are highly similar to those observed in nonconventional luminophores, which can be well rationalized by the clustering-triggered emission (CTE) mechanism.[14,19]

Figure 2. A) Photographs of CBSI and OBSI single crystals taken under 312 and 365 nm UV lights or after ceasing the irradiation. B) Prompt emission spectra ($t_d = 0$ ms) and C) CIE coordinate diagram of CBSI crystals with different $\lambda_{ex}$. D) PL spectra of CBSI/DMF solutions at different concentrations. E) Delayed emission spectra ($t_d = 0.1$ ms) and F) CIE coordinate diagram of CBSI crystals with different $\lambda_{ex}$. G) Afterglow decay profiles of CBSI crystals monitored at varying $\lambda_{em}$. 
Further delayed emission spectrum of CBSI crystals reveals a striking $\lambda_{\text{ex}}$-dependent afterglow, which redshifts from 505 to 575 nm (Figure 2E and S8) accompanying with the Commission Internationale de l’Éclairage (CIE) coordinate changing from (0.29, 0.36) to (0.38, 0.45), excited at intervals from 290 to 400 nm (Figure 2F). The various long lifetimes up to 543 ms with multiple components indicate the p-RTP nature of the delayed emission with the concurrence of diverse emissive clusters (Figure 2G and Table S3). The prompt emission of OBSI crystals show a noteworthy $\lambda_{\text{ex}}$-dependence with PL peaks redshifting from 389 to 470 nm (Figure S9), whereas the delayed emission ($\lambda_{\text{ex}}$: 543–648 ms, Table S3) fluctuates being less obviously varied in the range of 550 to 575 nm (Figure S9), making the afterglow colors slightly change in response to different $\lambda_{\text{ex}}$ (Figure 2A).

![Figure 3. A) Photographs of CBSI and OBSI single crystals taken under 312 and 365 nm UV lights or after ceasing the irradiation at 77 K. B,C) Phosphorescence spectra ($\lambda_{\text{ex}}$ = 0.1 ms) and D,E) CIE coordinate diagrams of B,D) CBSI and C,E) OBSI crystals with different $\lambda_{\text{ex}}$.](image)

Considering much better luminescence tunability that are generally observed at cryogenic conditions,[12,13a,14] we further checked the PL of both crystals at 77 K, aiming to gain more insights into the origin of such tunability. As illustrated in Figure 3A and Video S2, the phosphorescence of CBSI crystals displays a lager tunable range from 415 to 636 nm with comparison to that at room temperature (Figure 3B), accompanied by corresponding CIE coordinates changing from (0.18, 0.15) to (0.48, 0.45) (Figure 3D). PL decay profiles reveal the long lasting $<\tau_{\text{p}}>$ values between 685 and 1245 ms (Table S4). Similarly, for OBSI crystals, the color tunability of afterglow ($<\tau_{\text{p}}>$: 1067–1690 ms, Table S5) is significantly enhanced at 77 K (Figure 3A, Video S2). A gradual emission wavelength change from 410 to 596 nm is depicted in Figure 3C and the CIE coordinates compiled with observation and switched from (0.16, 0.08) to (0.44, 0.46) in response to the increase in $\lambda_{\text{ex}}$ (Figure 3E). Above results again testify the presence of diverse emissive species in crystals, which can be further stabilized at cryogenic temperatures, thus resulting in enhanced PL (Figure S10B) with better color tunability of phosphorescence.

To gain deeper insights into AIE behaviors and the origin of color tunable afterglow, single crystal structures of both compounds were determined at 298 or 173 K (Table S6).[20] As illustrated in Figure 4A and B, both compounds adopt highly distorted conformations in crystals, with such effective intermolecular interactions as C−H⋯O=C, O=C⋯O=C, C−N⋯O=C, and O=C⋯C=C=O. These short contacts, on one hand, stiffen the molecular conformations, on the other hand, facilitate 3D network among different moieties with n and/or π electrons. Therefore, the AIE behaviors can be rationalized by the restriction of intramolecular motions in the aggregates,[14] which significantly diminishes the nonradiative dissipations, thereby offering bright emission in crystals. And the occurrence of noticeable p-RTP should be ascribed to the combined effect of the presence of C=O and nitrogen atoms as well as the effective short contacts. Notably, TSC of the subgroups with n/π electrons produce diverse clusters with simultaneously rigidified conformations, thus offering bright tunable PL and moreover p-RTP in response to varying excitations. Namely, such color tunability can be well explained in terms of the CTE mechanism.[14] Meanwhile, these interactions would be enhanced at cryogenic temperatures on account of much denser molecular packing and shortened interaction distances (Figure S11), thus leading to better color tunability at 77 K. Theoretical calculations for monomer, dimer, trimer, and tetramers sustain this assumption by indicating effective TSC in crystals. As depicted in Figure 4C, the HOMO-LUMO energy gaps between ground states and excited states (Figure 4C, S12 and Table S7), thus offering $\lambda_{\text{exc}}$-dependent p-RTP. Similar clustering-enriched triplets and enhanced TSC are also confirmed by the calculation for OBSI (Figure S13, S14 and Table S8), which again testify the rationality of CTE mechanism.
Figure 4. Crystal structure (298 K) with denoted intermolecular interactions around one molecule and fragmental molecular packing with highlighted through-space conjugation for A) CBSI and B) OBSI. C) Electron densities of HOMO and LUMO levels for monomer, dimer, trimer, and tetramer of CBSI.

Figure 5. Anti-counterfeiting applications with pattern “ON” using A) TPA and B) CBSI solid powders.

Bestowed with the unique multicolor emission, these compounds provide a multilevel anti-counterfeiting based on the color variation under ambient conditions. As shown in Figure 5, the letter “ON” was composed of conventional luminescent terephthalic acid (TPA) and CBSI solid powders, respectively. Under 312 and 365 nm UV lights, the letter “ON” of TPA powders shows consistent deep blue emission while its CBSI counterpart glows yellowish-white and bluish-white, respectively, which renders CBSI more advanced anti-counterfeiting agent with much higher security than TPA. Furthermore, the multicolor RTP feature of CBSI makes the corresponding pattern exhibit distinct afterglows of green and yellow colors after ceasing the 312 and 365 nm UV lights, while the former pattern of TPA shows unchanged yellow color, thus providing additional and dynamic insurances for security applications. In a word, dynamic λex-dependent PL and p-RTP empower more advanced anti-counterfeiting effect when compared with traditional afterglow materials. Such color tunable emission characteristic makes CBSI a promising multilevel security material.

In summary, two nonaromatic phosphors, namely CBSI and OBSI, with both AIE and tunable afterglows were rationally designed and synthesized. While individual molecules are practically nonluminescent in solutions, their highly concentrated
solutions and crystals exhibit bright emission. Effective TSC among the moieties with n and/or r electrons leads to diverse clusters with extended electron delocalization, thereby generating tunable PL and afterglows. Such CTE assumption was further confirmed by solution and cryogenic experiments together with theoretical calculation. These results are believed to advance the rational design of nonaromatic AIEgens with tunable p-RTP. Furthermore, it sheds new lights on the understanding of universal underlying mechanism of such color tunability for both PL and p-RTP.

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Keywords: Aggregation-induced emission • Clustering-triggered emission • Persistent room temperature phosphorescence • Through-space conjugation • Tunable afterglow


18. Unless specified, all measurements were conducted at ambient conditions.


20. CCDC 1976366 (CISI, 298 K), 1976367 (CISI, 298 K), and 1976368 (CISI, 173 K) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

AIE meets tunable afterglows:
Highly distorted and nonaromatic CBSI and OBSI are nonluminescent when molecularly dissolved in solutions, but exhibit distinct AIE and tunable p-RTP features at aggregation states, on account of the effective through-space conjugation among the moieties with π and/or n electrons, which results in the formation of diverse emissive clusters with highly rigidified conformations.

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Page No. – Page No.

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