



# Spin manipulation in organic radicals

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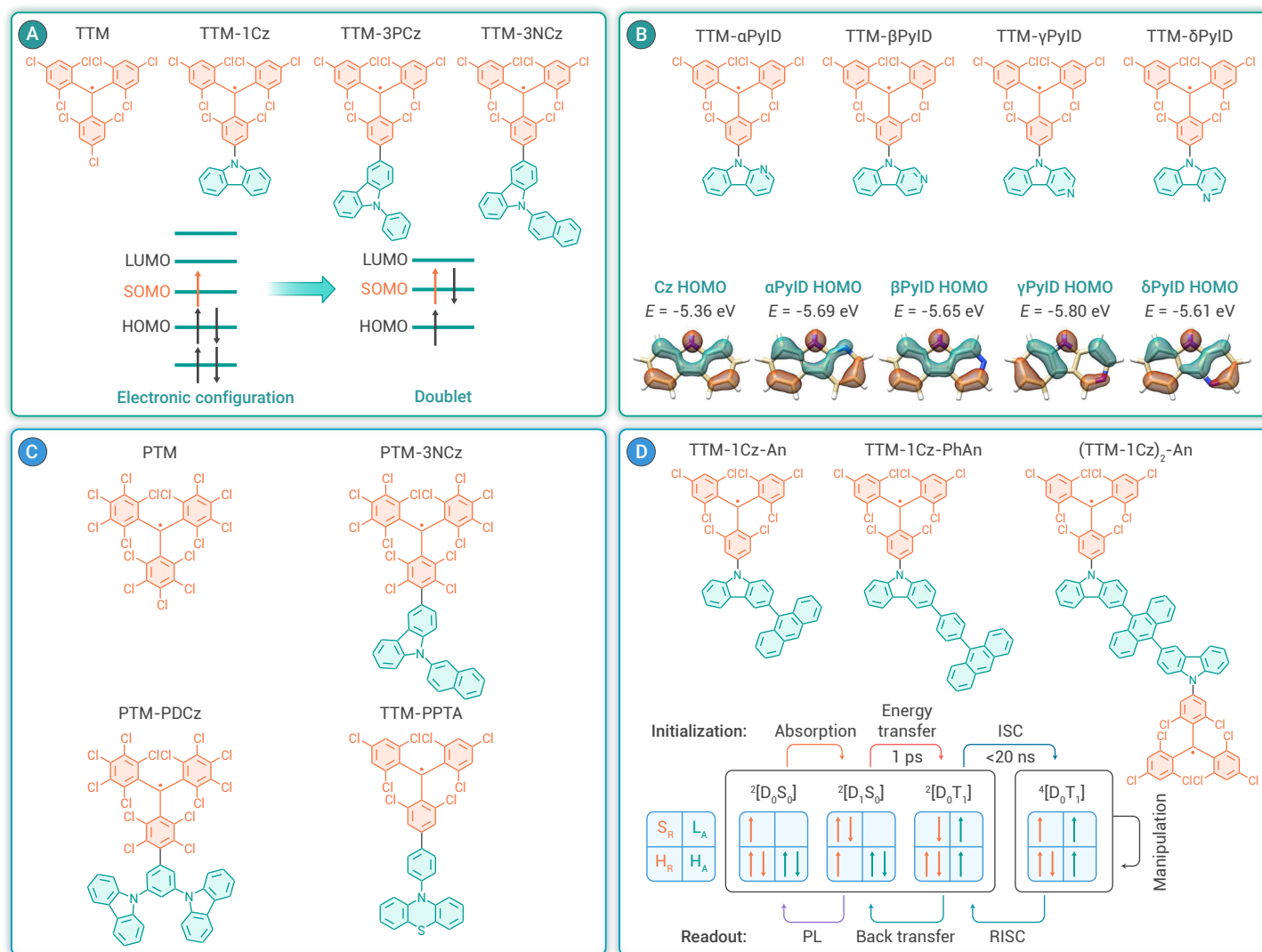
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Organic luminescent radicals have attracted significant attention as efficient doublet emitters for organic light-emitting diodes (OLEDs) due to their distinctive and unique electronic and optical properties. Unlike conventional fluorescent, phosphorescent, and thermally activated delayed fluorescence (TADF)-based luminogens, radical materials with the open-shell structures facilitate the efficient emission originating from transition between the lowest doublet excited state and doublet ground state. This ability can address the

transition problem associated with the triplet excitons, theoretically allowing an upper limit of 100% internal quantum efficiency (IQE) in purely organic radical molecules. Nonetheless, they generally exhibit lower photoluminescence quantum yields (PLQYs) and poor stability compared with the non-radical organic molecules. Therefore, quest for the development of the highly efficient radical emitters with high stability remains a highly desirable yet challenging task.



**Figure 1.** The representative efficient luminescent organic radicals (A) Chemical structures of the TTM radical and its derivatives with the electron-rich groups including ICz, 3PCz, and 3NCz, respectively, and the schematic diagram of energy levels, (B) Chemical structures of the TTM-xPyID with aza-substitution at the site  $x = \alpha, \beta, \gamma,$  and  $\delta$ . (C) Chemical structures of the PTM radical, and the PTM- and TTM-based donor-acceptor radical derivatives. (D) Luminescent TTM-radical-acene molecular system and the schematic diagrams of the electronic transition processes.

## ELECTROLUMINESCENCE

In 2015, Li et al. reported the use of a neutral  $\pi$  radical as the emitter in a radical OLED.<sup>1</sup> The organic  $\pi$  radical, known as (4-*N*-carbazoly-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl (TTM-1Cz), exhibited an open-

shell architecture stabilized by six chlorine atoms surrounding the radical center carbon (Figure 1A). With only one unpaired electron in the highest singly occupied molecular orbital (SOMO), the excited states of TTM-1Cz allow for the spin-allowed radiative decay of the doublets, which is total

different with the triplet harvesting mechanisms in the conventional OLEDs. It is confirmed that the electroluminescence of the TTM-1Cz-based deep-red OLEDs originated from the electron transitions related to doublet states. Despite a maximum external quantum efficiency ( $\text{EQE}_{\text{max}}$ ) of 2.4%, comparable with those of the most state-of-the-art deep-red/near-infrared (NIR) OLEDs, there is still an urgent requirement to improve the efficiency and stability.

Later, Li et al. proposed an effective approach toward highly efficient luminescent radicals by incorporating 3-substituted-9-(naphthalen-2-yl)-9H-carbazole (3NCz) and 3-substituted-9-phenyl-9H-carbazole (3PCz) into the TTM radical core.<sup>2</sup> As shown in Figure 1A, the new luminescent radicals, i.e., TTM-3NCz and TTM-3PCz, were composed of 3NCz/3PCz as donor and TTM radical acceptor substitutes, resembling the structural motif of the classical TADF molecules. When doped into a common host 4,4-bis(carbazol-9-yl)biphenyl (CBP), the PLQYs of TTM-3NCz and TTM-3PCz reached nearly 90% and 60%, respectively. The resulting NIR radical OLEDs with these open-shell emitters achieved the state-of-the-art device electroluminescent performances, e.g., an ultrahigh EQE up to 27% and a peak emission at 710 nm. Additionally, it was demonstrated that the selective hole injection into the highest occupied molecular orbital (HOMO) and the electron injection into the SOMO facilitated the formation of the doublet excited states with the near unity IQE, thereby improving the device efficiency. However, these studies did not unravel why TTM and the similar radicals were remained in the dark states while the TTM-donor derivatives could be emissive.

To elucidate the luminescent mechanisms, Li et al. conducted an in-depth investigation of the luminescent nature of organic radicals.<sup>3</sup> Experimentally, four TTM-pyridindolyl derivatives were designed and synthesized through singular aza substitution at different positions of carbazole (Cz) group in TTM-1Cz (Figure 1B). The aza substitution lowered the HOMO level of the Cz unit due to the higher electronegativity of the nitrogen atom, compared with the carbon atom. This would increase the critical energy gap between the HOMO of the Cz segment and the SOMO of the TTM moiety. As a result, the four luminescent radicals exhibited the blue-shifted emission, compared with TTM-1Cz. Moreover, the aza substitution led to the significantly enhanced PLQYs in  $\text{CHCl}_3$  for TTM- $\alpha$ PyID (91%), TTM- $\beta$ PyID (89%), TTM- $\gamma$ PyID (32%), and TTM- $\delta$ PyID (99%), respectively, which were much higher than that of TTM-1Cz (5%). Such significant improvements could be related to a hybridized local and charge-transfer excited state of the lowest doublet excited state in TTM-xPyID radicals. The OLEDs based on these molecules showed the pure-red emission with the high  $\text{EQE}_{\text{max}}$  exceeding 12%, and the Commission Internationale de l'Eclairage (CIE) color coordinates of (0.67, 0.33), making them the promising candidates for the saturated red emitters. This study demonstrates that the non-alternant systems can overcome the degeneracy of the lowest energy orbital excitations, while the charge transfer can enhance the oscillator strength and improve the emissive efficiency of the radical emitters.

Nevertheless, the development of luminescent radicals still faces significant challenges, including limited molecular structures and inferior stability. In the case of radicals with a non-Aufbau electronic structure, the SOMO lay below the doubly occupied HOMO, leading to a SOMO-HOMO conversion and inversion processes. This phenomenon contributed to the greatly enhanced photostability. Additionally, incorporating the bulky substituents to shield the radical site can further improve the stability of radical molecules. Therefore, Li's group further designed a series of donor-acceptor radical derivatives based on the electron-poor perchlorotriphenylmethyl (PTM) and TTM radicals combined with various electron-rich donors, such as 9-(naphthalene-2-yl)-9H-carbazole (NCz), 1,3-di(9H-carbazol-9-yl)benzene (PDCz), and phenylphenothiazine (PPTA), respectively (Figure 1C).<sup>4</sup> Due to the strong electron-withdrawing ability of the PTM and TTM radicals, the energy level of the SOMO in either PTM or TTM unit was lower than that of the HOMO in the donors. This violation of the Aufbau principle led to the dramatically improved photostability. As demonstrated, the fluorescence intensity of PTM-3NCz remained almost unchanged under pulsed ultraviolet laser irradiation. Furthermore, the radical OLED exhibited the NIR emission peaking at 700 nm, accompanied with an  $\text{EQE}_{\text{max}}$  of 5.3%. The simple design strategy of utilizing organic luminescent radicals with non-Aufbau electronic structures demonstrates the potential for achieving high PLQYs and superior photostability simultaneously for radical emitters.

## OPTICAL READOUT OF HIGH-SPIN STATES

In addition to their applications in optoelectronic devices, organic luminescent radicals offer a versatile platform for quantum information science and show potential for sensing and computation applications. Recently, Evans *et al.* reported a series of the TTM-anthracene-based radicals with an energy resonance between the emissive doublet and triplet levels, enabling both efficient luminescence and near-unity generation yield of excited states with spin multiplicity  $S > 1$  (Figure 1D).<sup>5</sup> These findings illustrate the capability to generate, manipulate, and optically read pure high-spin states in organic radicals. By leveraging the luminescent properties of radicals and engineering the excited-state manifold with the small energy offsets, high-spin states, such as quartet or quintet, can be generated. These radicals can manipulate the triplet excitons in the hybridized states, allowing reversible access to the high-spin manifold. As a result, a luminescent state can be restored from high-spin states at room temperature. This work establishes a solid foundation for incorporating organic radicals into emerging quantum technologies.

## CONCLUDING REMARKS

Undoubtedly, the significance and practical implications of organic radical research are situated within realms of not only electroluminescence but also spin electronics and quantum computing. By manipulating the spin states of luminescent organic radicals, novel LEDs, spin storage devices, and spin logic gates can be developed. Moreover, the reversible spin-optical interface provides a new avenue for creating the optically controlled spin systems. These findings will significantly contribute to the advancement of spin electronics and the ongoing development of emerging quantum computing technologies.

In addition, the current radical-based emitters predominantly exhibit deep-red and near-infrared emissions, which hinders a broader range of applications. Consequently, there is an urgent need to create new radicals capable of emitting blue and green colors. Nevertheless, it remains a formidable challenge due to the extremely low energy level of the radical doublet excited state. Introducing the multiple strong electron-withdrawing substituents (such as the cyan group) to decorate the carbazole donor may be a feasible approach. That is because the HOMO-SOMO gap can be enlarged, which leads to the emission with the hypsochromic shift. In the future, some in-depth investigations into radical structures and luminescent mechanisms are pivotal for better understanding of the design of the luminescent radicals toward the short-wavelength region, which holds a significant potential for advancing radical-based materials for diverse applications.

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## DECLARATION OF INTERESTS

The authors declare no competing interests.