Spin-correlated photoabsorption and emission of a carbazole-containing Kekulé-type diradical

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Diradicals have electronic ground and excited states with both singlet and triplet spin multiplicities, which differ from those of organic closed-shell molecules and monoradicals. This unique electronic structure enables thermal equilibrium between the singlet and triplet electronic ground states, leading to spin-correlated photofunctions. An example of such photofunction is spin-state-dependent absorption reported particularly in Kekulé-type diradicals, which could realize selective excitation of the singlet or triplet state. As another example, we have reported spin-correlated emission of non-Kekulé-type diradicals.[1,2] We envisioned that a combination of spin-state-dependent absorption and emission allows a more comprehensive understanding of the relationship between the molecular structure and the spin-correlated photofunctions. In this study, Kekulé-type diradical **27R₂** was synthesized, and its magnetic and photophysical properties were compared with those of the non-Kekulé-type counterpart **36R₂**, which was previously reported to exhibit triplet-specific emission (Fig. 1a).[2]

27R₂ was shown to exhibit both spin-correlated absorption and emission. **27R₂** displayed emission at 701 nm in cyclohexane (Fig. 1b). A noteworthy observation is the difference between the absorption and the excitation spectra of **27R₂**, whereas those of **36R₂** show no such discrepancy. By measuring the absorption, emission, and excitation spectra at various temperatures (i.e. at various singlet-triplet ratios), **27R₂** was suggested to show spin-state-dependent absorption and triplet-specific emission. This was also supported by theoretical calculations and the magnetic-field effect on the luminescence. The detailed comparison of **27R₂** and **36R₂** revealed the impact of substitution position on their photofunctions.

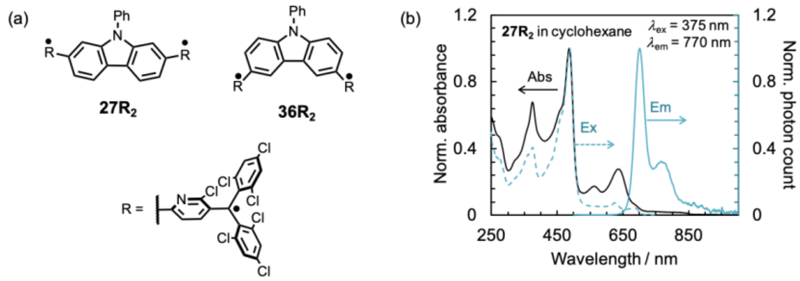

Fig. 1 (a) Chemical structures of **27R₂** and **36R₂**. (b) Absorption, emission, and excitation spectra of **27R₂** in cyclohexane (λ_{ex} = 375 nm, λ_{em} = 770 nm).

(1) R. Matsuoka *et al.*, *J. Am. Chem. Soc.*, **2023**, *145*, 13615. (2) A. Mizuno *et al.*, *J. Am. Chem. Soc.*, **2024**, *146*, 18470.