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Engineering Molecular Orbitals for Photo- and Spin-Functional Molecules

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Abstract:

Spin-state dependent photoexcitation behavior of a stable organic di- and triradical will be presented (Figure 1a).[1,2] The diradical, composed of two benzotriazinyl radicals connected by a rigid triptycene skeleton, exhibits a small singlet–triplet energy gap of −3.0 kJ/mol ($2J/k_B$ = −360 K), indicating ca. 1:1 coexistence of the two spin states at room temperature. The diradical shows characteristic near-IR absorption bands, which are absent in the corresponding monoradical subunit. Variable temperature measurements revealed that the absorbance of the NIR band depends on the abundance of the singlet state, allowing us to identify the NIR band as the singlet-specific absorption band. Transient absorption spectroscopy disclosed that the two spin states independently follow qualitatively different excited-state dynamics. These results demonstrate a novel approach to the design and study of electronic spin isomers based on organic diradicals.

The double closed-ring isomer of a diarylethene fused dimer was synthesized by a combination of photochemical and oxidative cyclization reaction (Figure1b).[3] The double closed-ring isomer of a diarylethene fused dimer has fixed π-conjugation in a rigid planar framework so that this compound has been long-desired. However, the second-step cyclization of a diarylethene dimer with strong electronic interaction is known to be suppressed due to energy transfer. Here, oxidative isomerization was applied for the second-step cyclization, where the oxidized state spontaneously underwent thermal cyclization by radical coupling. The resulting double closed-ring isomer showed NIR absorption and underwent a ring-opening reaction forming the closed-open-ring isomer by NIR light. As a result, the fused dimer exhibits reversible stepwise switching induced by photo- and redox stimuli in the UV–vis–NIR region.

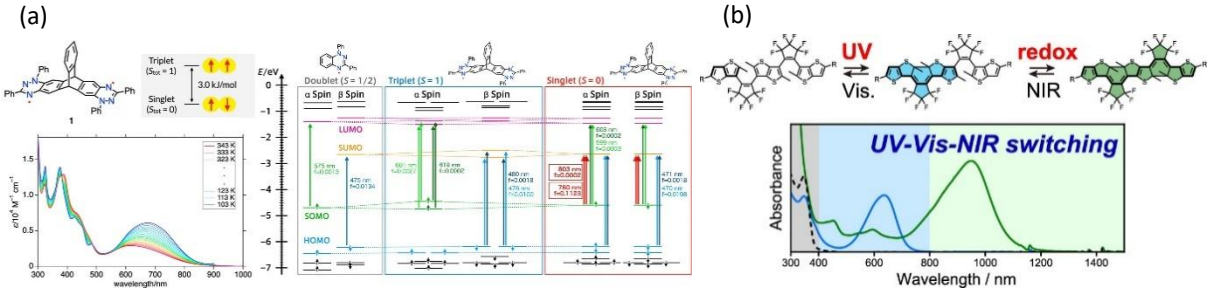

Figure 1. *(a) Spin-state dependent photoexcitation behavior of diradical. (b) The double closed-ring isomer of a diarylethene fused dimer.*

References:

[1] D. Shimizu, H. Sotome, H. Miyasaka, K. Matsuda, *ACS. Cent. Sci.* **2024**, *10*, 890.

[2] T. Aoki, H. Sotome, D. Shimizu, H. Miyasaka, K. Matsuda, *Angew. Chem. Int. Ed.* **2025**, *64*, e202418655.

[3] K. Satake, N. Ootsuki, K. Higashiguchi, K. Matsuda, *J. Am. Chem. Soc.* **2025**, *14*, 9653.