

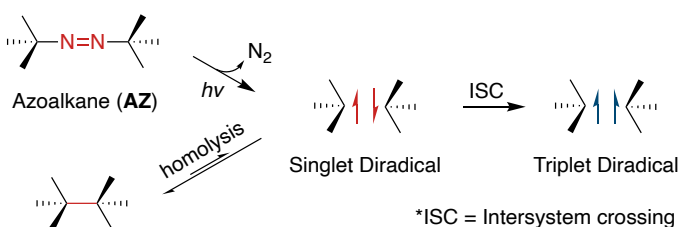
Reactivity of Singlet Diradicaloids Embedded in Macrocyclic Skeleton and Non-Aufbau Electronic Configuration of Triplet Diradicals

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Chapter 1. General Introduction

Localized diradicals having two unpaired electrons are well-known chemical species in the denitrogenation of azoalkanes or bond homolysis reactions. Diradicals have two spin states, a singlet and a triplet (Scheme 1). Due to the ferromagnetically coupled two electrons, triplet diradicals show great potential for application to molecular magnetic materials. On the other hand, singlet diradicals are key intermediates in the bond homolysis processes, thus, elucidating their chemistry will provide a deeper understanding of the fundamental processes of bond-formation and bond-breaking processes. Recently, the non-linear optical property and singlet-fission phenomenon were found in open-shell singlet species. So, singlet diradicals have attracted attentions not only in fundamental chemical research but also in the field of materials science.



Scheme 1. Generation of diradicals.

Chapter 2. Reactivity of Singlet Diradicaloid Embedded in Macrocyclic Skeleton

Singlet cyclopentane-1,3-diyl diradicaloids with bonding orbital in the highest occupied molecular orbital (HOMO) are promising candidates for carbon-carbon π -single bonding species (Figure 1). Such species possess extremely small HOMO–LUMO gap, which show unique



Figure 1. π -Single bonding character of singlet 2,2-dialkoxy cyclopentane-1,3-diyl diradicaloids.

chemical properties such as high redox activity and non-linear optical property. Generally, the localized singlet diradicaloids having π -single bonding character are highly reactive species to give the corresponding σ -bonding compounds. The short-lived character hampers experimental investigations of their nature. We implemented the approach of “stretch effect” for cyclopentane-1,3-diyl diradicaloids to access kinetically stabilized singlet diradicaloids (Figure 2). The stretch effect induced by macrocyclic skeleton can suppress the bond-formation process by pulling the two radical carbons into the opposite direction against the bond-formation. Thus, the transition states TS and σ -bonded products CP are supposed to be destabilized, and, singlet diradicaloid S-DR could be kinetically stabilized. To this end, a macrocyclic structure was designed to generate the long-lived singlet diradicaloid, enabling the experimental investigation on the singlet diradicaloid with π -single bonding character.

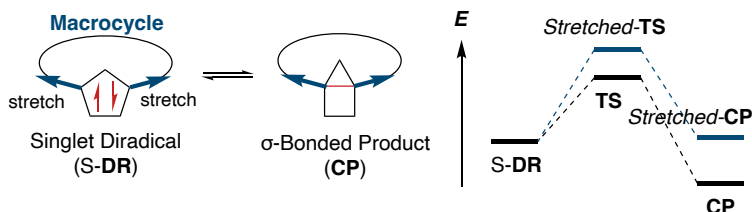
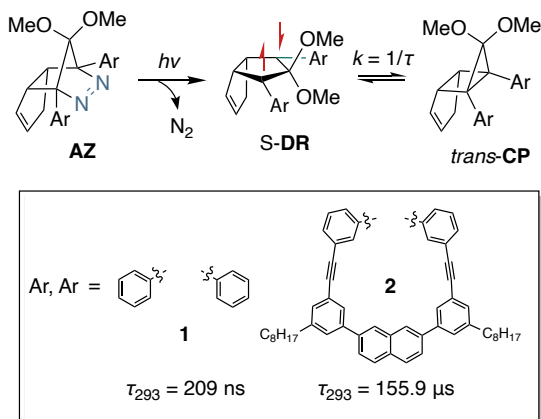


Figure 2. Concept of the stretch effect to kinetically stabilize the singlet diradicaloid.

The kinetically stabilized diradicaloid S-

DR2 was generated by the photochemical denitrogenation of azoalkane **AZ2** to exhibit a small carbon–carbon coupling reaction rate of $6.4 \times 10^3 \text{ s}^{-1}$ (155.9 μs), approximately 1000 times slower than that of the parent system without the macrocycle **S-DR1** ($5 \times 10^6 \text{ s}^{-1}$, 209 ns) at 293 K in benzene (Scheme 2). In addition, a significant dynamic solvent effect was observed in the intramolecular radical–radical coupling reactions. The lifetime of singlet diradicaloid **S-DR2** showed a longest lifetime up to 400.2 μs in viscous glycerin triacetate ($\eta = 23.00$) at 293 K. Furthermore, the σ -bonded product **CP2** was highly destabilized by the stretch effect, it decomposed

immediately after exposing to air atmosphere, although the σ -bonded product with no-macrocyclic structure **CP1** was stable under air. The theoretical and experimental studies demonstrate that the stretch effect and solvent viscosity play important roles in retarding the σ -bond formation process, thus enabling a thorough examination of the nature of the singlet diradical and paving the way toward a deeper understanding of reactive intermediates.



Scheme 2. Singlet diradicaloids investigated in this study.

Chapter 3. SOMO–HOMO Conversion in Triplet Cyclopentane-1,3-diyl Diradicals

According to the Aufbau principle, singly occupied molecular orbitals (SOMOs) are energetically higher lying than the highest doubly occupied molecular orbital (HOMO) in the electronically ground state of radicals. However, in the last decade, SOMO–HOMO energy converted species have been reported in a limited group of radicals, such as distonic anion radicals and nitroxides. In this study, SOMO–HOMO conversion was found in triplet 2,2-difluorocyclopentane-1,3-diyl diradical **DR3F** by theoretical computations, which contain the anthracyl unit at the remote position. The SOMO–HOMO conversion vanished in dihydro-substituted ($X = \text{H}$) or naphthyl-substituted ($n = 0$) triplet diradicals, indicating that the high HOMO energy in the anthracyl moiety and the low-lying SOMO–1 due to the fluoro-substituent effect are the keys to the SOMO–HOMO conversion phenomenon (Figure 3). Furthermore, the cation radical generated through the one-electron oxidation of neutral diradical was found to be a SOMO–HOMO-converted monoradical, and the dication was a diradical with triplet ground state (Figure 4). This computational study provides an approach for molecular design of SOMO–HOMO-converted species.

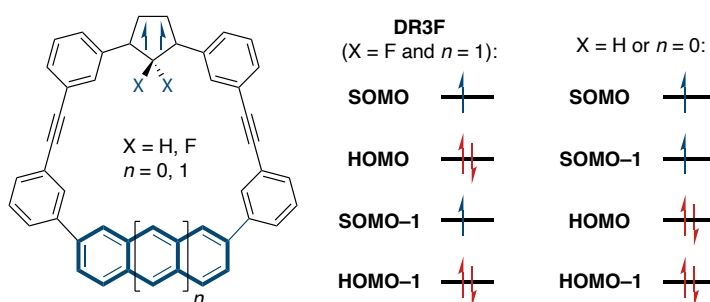


Figure 3. SOMO–HOMO-converted triplet diradical **DR3F** and its electronic configuration. Dihydro- or naphthyl-substituted triplet diradicals adapted the Aufbau configuration.

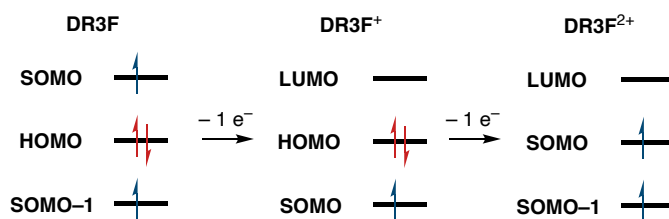


Figure 4. Electronic configuration of oxidized species generated by one-/two-electronic oxidation of **DR3F**.