

Excited State Dynamics of Molecular System with Coexisting Singlet and Triplet States at Room Temperature

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[Introduction] Recently, spin-related photochemical processes such as thermally activated delayed fluorescence (TADF) and triplet-triplet annihilation (TTA) have attracted much interest. These phenomena can be induced by controlling the relative energy of excited triplet (T_1) state to the excited singlet (S_1) state. In this work, we focused on relative energy of T_1 state not to S_1 but to S_0 state. When S_0 - T_1 energy gap ($|\Delta E_{ST}|$) is lower than thermal energy (*ca.* 5 kJ/mol), S_0 and T_1 states coexist in equilibrium around room temperature. As a model compound of such system, we designed diradical **1** with BDPA and verdazyl radicals (Figure 1a) and studied its photochemical properties.

[Results and Discussion] The ESR spectrum of **1** was reproduced by a sum of two simulated spectra with parameters (g, A_{N1}, A_{N2}) = (2.0022, 6.3 G, 4.5 G) and (g, A_{H1}, A_{H2}) = (2.0016, 1.9 G, 1.8 G), which were assigned to verdazyl and BDPA, respectively. These parameters were comparable to reported verdazyl and BDPA radicals, suggesting small interaction between the two radicals and thus small $|\Delta E_{ST}|$.^[1,2] The absorption spectrum of **1** showed a band around 500 nm due to BDPA unit along with a shoulder band around 600 nm due to verdazyl unit (Figure 1c).^[1,3] Besides, characteristic absorption band around 700–1000 nm was observed, which was assigned to a S_1 -specific band from the calculation results.

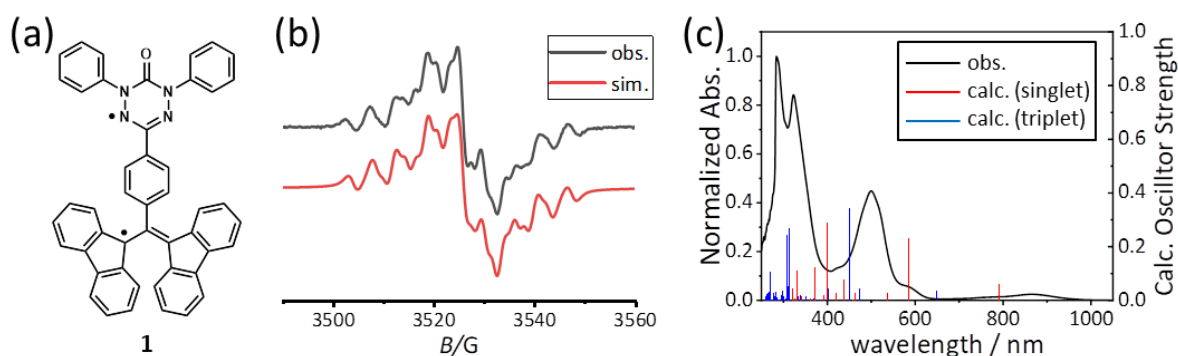


Figure 1. (a) Diradical **1**. (b) Observed (black) and simulated (red) ESR spectra of **1** (CH_2Cl_2 , 298 K). (c) Absorption spectrum of **1** in toluene (black) and calculated oscillator strengths of S_0 (red) and T_1 (blue) states of **1**.

[References] [1] D. Matuschek, A. Studer *et al.*, *Chem. Sci.*, **2015**, *6*, 4712. [2] O. Haze, T. M. Swager *et al.*, *J. Am. Chem. Soc.*, **2012**, *134*, 14287. [3] J. L. Muñoz-Gómez, J. Vidal-Gancedo *et al.*, *Org. Biomol. Chem.*, **2015**, *13*, 2689.