

Supplemental information

S1. Conventional ESR spectra of 2

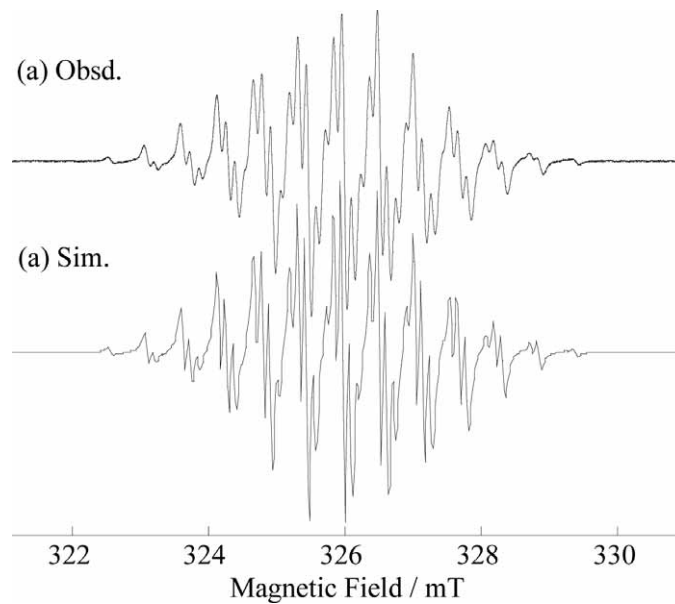


Fig. S1 Conventional ESR spectrum of **2** in toluene solution at room temperature. (a) Observed spectrum; (b) simulation.

S2. Electronic structures in the ground states calculated by the *ab-initio* molecular orbital calculations

In order to clarify the electronic structures, the molecular orbital calculations in the electronic ground states of **3** and the parent verdazyl radical, **2**, were carried out based on the density functional theory (DFT) using Gaussian 98.²⁵ In the case of the parent molecule **2**, the molecular structure was optimized by the DFT calculation (Ubecke 3LYP/STO-3G). For the molecule **3**, the structure optimization was carried out using a semi-empirical method (MNDO/AM1), because the large molecular size. For the optimized molecular structures, the more accurate calculations ((Ubecke 3LYP/6-31G(p,d)) were carried out, in order to clarify the role of the spin polarization effect. Figure S2 shows the calculated total spin density distribution in the doublet ground states of **2** and **3**. Unfortunately, the *ab-initio* MO calculation using the same level was not succeeded in the case of **1**, because the structure optimization was not converged. Figure S2 shows that in both cases the unpaired electrons of the molecules are localized in the radical moiety of the doublet ground state. A slight delocalization occurs but is restricted to the pendant phenyl group. This result is consistent with the results of the conventional solution ESR spectra in the electronic ground states.

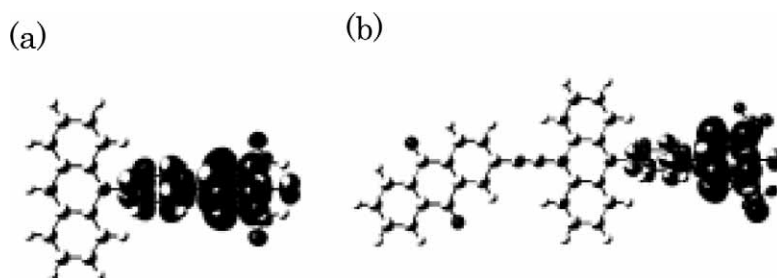


Fig. S2 Spin density distributions in the ground states of **2** and **3** calculated by the *ab-initio* MO calculations.

S3. TRESR spectra of the parent molecule 2

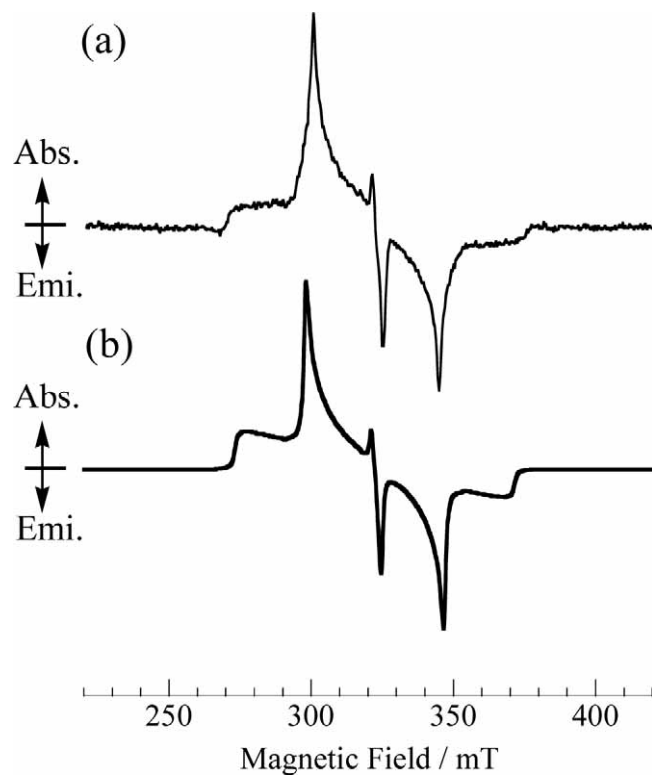


Fig. S3 TRESR of **2** at 30 K in 2-MTHF glass matrix.⁹ (a) Observed spectrum; (b) simulation obtained by assuming the selective population only to the zero-field wavefunctions (SO-ISC mechanism).