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Zwitterionic Open-Shell Singlet Diradical with Solvent-Dependent Singlet–Triplet Energy Gap

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Dedicated to Professor Keiji Maruoka on the occasion of his 70th birthday

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Abstract: A zwitterionic open-shell singlet diradical composed of electron-donating anion, anthroxide, and electron-accepting cation, phenazinium, was designed and synthesized. The diradical has a small HOMO–LUMO energy gap and shows near-infrared absorption. Temperature-dependent ESR measurements confirmed its small energy gap between ground singlet and thermally-excited triplet states (ΔE_{ST}). The ΔE_{ST} of the diradical was changed by solvents (toluene, 2-MeTHF, and EtOH).

Introduction

Recently, diradicals[1] with both singlet[2–9] and triplet ground states[10] have attracted attention because of their properties originating from their unique electronic structures. Diradicals with a small singlet–triplet energy gap (ΔE_{ST}) would be promising as magnetic materials because the amount of spins is changed by temperature. As such organic diradicals, not only symmetric diradicals, but also unsymmetric diradicals have been studied, and their ΔE_{ST} have been controlled by changing molecular structures.

On the other hand, diradicals whose ΔE_{ST} could be changed by external stimuli would be new magnetic materials (Figure 1a). Matsuda and Irie et al. reported a diarylethene with two nitronyl nitroxides whose ΔE_{ST} was changed by the photochromism of diarylethene.[11] Wang, Song, and Power et al. reported the diradical dication of 4,4"-bis(diphenylamino)-*p*-terphenyl whose ΔE_{ST} was changed by temperature due to the conformational change in crystal.[12] However, such stimuli-responsive diradicals are quite limited, and new molecular design is required for their development.
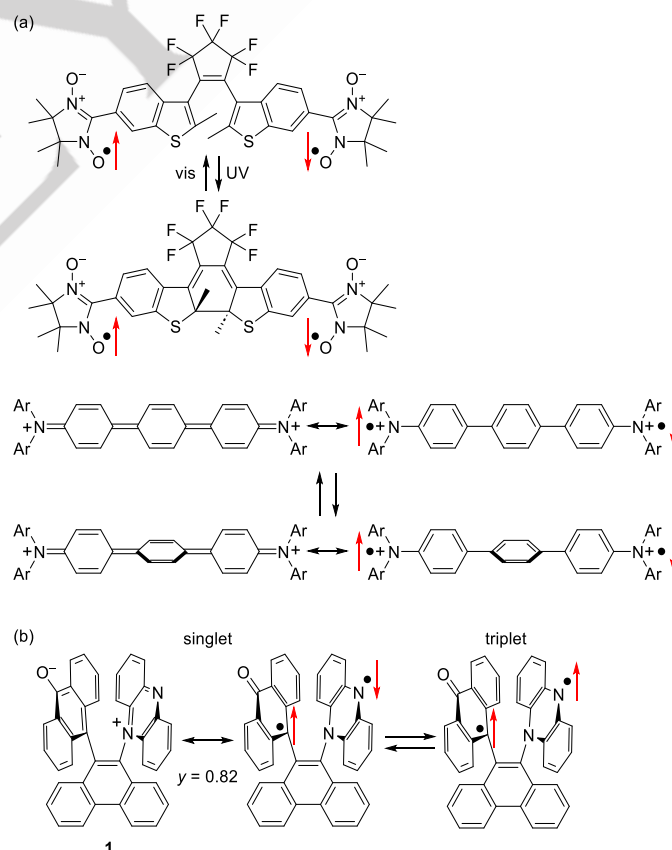

Figure 1. (a) Stimuli-responsive diradicals. (b) Resonance structures and equilibrium of **1**.

On the basis of these backgrounds, we focused on zwitterionic diradicals.[13–21] We envisaged that zwitterions composed of an electron-donating anion and an electron-accepting cation would resonate with singlet diradical canonical structures and have a small ΔE_{ST}. Their singlet states would have larger dipole moments than their triplet states and would be more stabilized in polar solvents than their triplet states. Therefore, their ΔE_{ST} would be changed by solvents. As a combination of such electron-donating anion and electron-accepting cation, we chose anthroxide and phenazinium and designed **1** having anthroxide and phenazinium moieties at 9 and 10 positions of phenanthrene expecting through-space interaction favorable for singlet state (Figure 1b).[22] We herein report the synthesis and characterization of **1**.

Results and Discussion

DFT calculations at the B3LYP-D3/6-311G(d,p) level of theory show that the HOMO (−4.36 eV) and the LUMO (−3.34 eV) of the closed-shell singlet state of **1** are composed of the bonding and anti-bonding interactions of the anthroxide and phenazinium moieties, respectively (Figure 2a and Figures S2 and S3). The small HOMO–LUMO energy gap of 1.02 eV indicates the weak through-space interaction between anthroxide and phenazinium moieties. **1** is expected to have an open-shell singlet state, which is 22.0 kJ mol^{-1} lower in energy than the closed-shell singlet state, and is calculated to have a diradical index (y) of 0.82 based on the occupation number of the lowest unoccupied natural orbital (LUNO)[23–25] in the UB3LYP method. Because the spin density of the open-shell singlet state of **1** is similar to those of anthroxyl and phenazinyl radicals (Figure 2b and Figures S2 and S4), **1** would be described as the resonance of the zwitterionic and singlet diradical canonical structures (Figure 1b). The triplet state of **1** with spin densities similar to those of anthroxyl and phenazinyl radicals is only 0.49 kJ mol^{-1} higher in energy than the open-shell singlet state (Figure 2c and Figures S2 and S5). In addition, the dipole moment of the singlet state of **1** (closed-shell singlet: 7.85 D, and open-shell singlet: 6.67 D) is slightly larger than that of the triplet state of **1** (6.61 D).

Scheme 1 illustrates the synthesis of **1** starting from 5,10-dihydrophenazine (**2**).[26] Boc protection of **2** gave **3**. Amination of 9,10-dibromophenanthrene[27] with **3** gave **4**. Suzuki-Miyaura cross-coupling of **4** and 10-methoxyanthracene-9-boronic acid[28] gave **5**. **5** was deprotected using TFA to give **6**. Oxidation of **6** followed by counter anion exchange gave **7**. Demethylation of **7** using BBr$_3$ followed by counter anion exchange gave **8**, whose structure was confirmed by X-ray crystal structural analysis (Figure 3).[29] **1** was generated by deprotonation of **8** with K$_2$CO$_3$. The ^{1}H NMR analysis confirmed the consumption of **8** for the generation of **1** in a sealed tube in acetone-d_6 (Figure S6), but no signal of **1** was observed at room temperature and even at −80 °C. Although we could not obtain the crystal of **1**, the addition of trifluoroacetic acid to **1** reproduced **8**, indicating the generation of **1**. These results suggest that **1** has a singlet ground state with a small ΔE_{ST} or a triplet ground state. In addition, **1** did not decompose in acetone–toluene and acetone–EtOH (Figure S7).
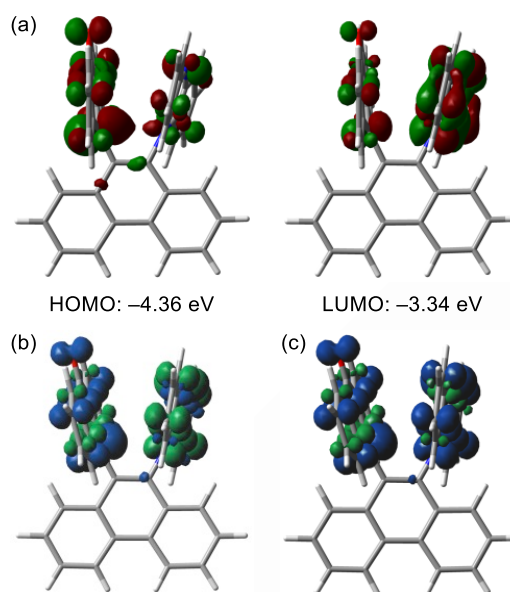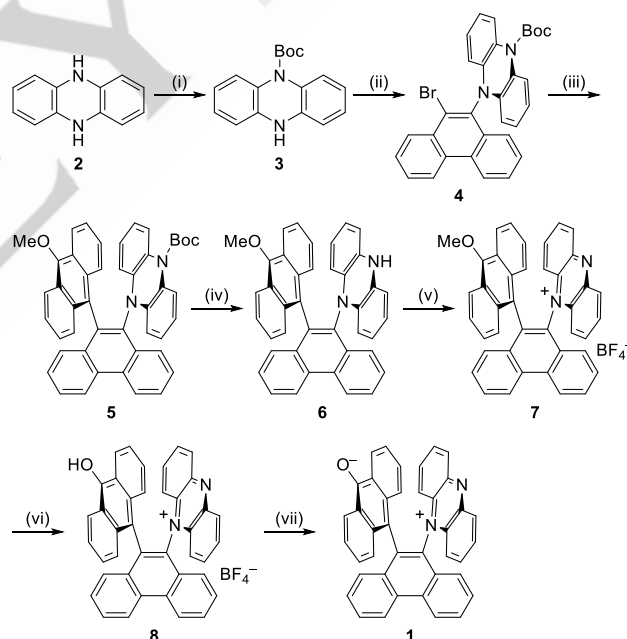

Figure 2. (a) HOMO and LUMO of the closed-shell singlet state of **1**. Spin densities of (b) open-shell singlet and (c) triplet states of **1** (blue and green surfaces represent α and β spin densities, respectively).

Scheme 1. Synthesis route to **1**

^{a}Reaction conditions: (i) Boc$_2$O, DMAP, THF, 40 °C, 20 h, 56%. (ii) 9,10-dibromophenanthrene, Pd(OAc)$_2$, XPhos, NaO^{t}Bu, toluene, 100 °C, 19 h. (iii) 10-methoxyanthracene-9-boronic acid, Pd(PPh$_3$)$_4$, K$_3$PO$_4$, THF, 70 °C, 17% (two steps). (iv) TFA, CH$_2$Cl$_2$, RT. (v) 1) AgNO$_3$, acetone–H$_2$O, RT, 2) aq. NaBF$_4$, RT, 41% (two steps). (vi) 1) BBr$_3$, CH$_2$Cl$_2$, RT, 2) NaBF$_4$, RT, 35%. (vii) K$_2$CO$_3$, acetone, RT.
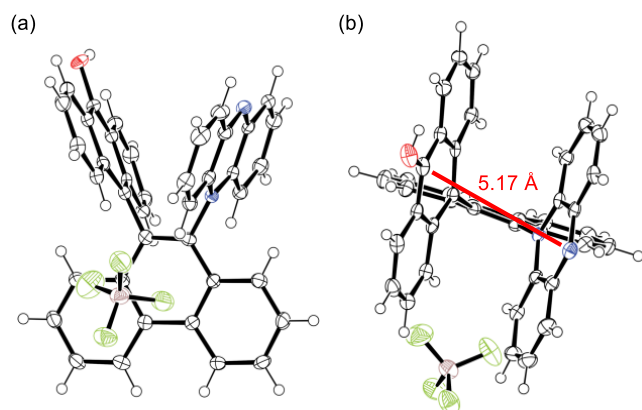
Figure 3. ORTEP drawings of (a) top view and (b) side view of **8** at 113 K. Displacement ellipsoids are drawn at the 50% probability level.

To obtain information about the HOMO–LUMO energy gap, cyclic voltammograms and UV-vis-NIR absorption spectra of **1** were measured. **1** showed reversible oxidation and reduction waves at −0.39 and −0.91 V vs. Fc/Fc$^+$, respectively, in THF (Figure 4a), from which the HOMO–LUMO energy gap of **1** is electrochemically estimated to be 0.52 eV. UV-vis-NIR absorption spectra of **1** were measured in toluene, THF, CH$_3$CN, and EtOH (Figure 4b). **1** showed a weak absorption band at ca. 1700 nm (0.73 eV) in toluene, ca. 1600 nm (0.77 eV) in THF, ca. 870 nm (1.43 eV) in CH$_3$CN, and ca. 800 nm (1.55 eV) in EtOH. The near-infrared (NIR) absorption is assigned to the singlet state of **1** because DFT calculations show that the singlet state of **1** has a HOMO–LUMO transition from anthroxide to phenazinium moieties (intramolecular charge transfer) at the NIR region, while the triplet state of **1** has absorption bands at shorter than 550 nm (Tables S2 and S3). The weak NIR absorption band indicates the weak interaction between anthroxide and phenazinium moieties.
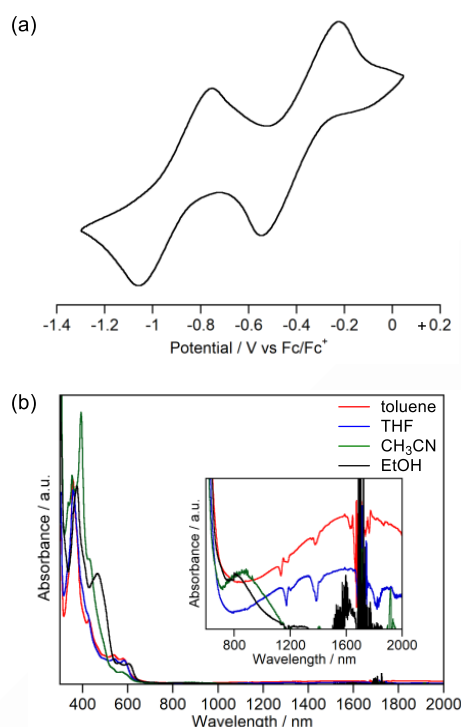

Figure 4. (a) Cyclic voltammogram of **1** in 0.1 M Bu$_4$NBF$_4$/THF. (b) UV-vis-NIR absorption spectra of **1** in toluene (red), THF (blue), CH$_3$CN (green), and EtOH (black).

The ESR spectra of **1** in a frozen toluene solution showed a triplet signal of $\Delta M_S = \pm 1$ together with the half-field transition of $\Delta M_S = \pm 2$ (Figure 5a,b and Figure S9a,b). The zero-field splitting parameters $|D|$ and $|E|$ are determined to be 0.0192 cm^{-1} and 0.0005 cm^{-1}, respectively, by the simulation of the ESR spectrum. On the basis of the point-dipole approximation, the average distance between the two unpaired electrons is calculated to be 5.47 Å, which is consistent with the distance between the carbon atom connecting to the oxygen atom and the imine nitrogen atom of **8** (5.17 Å) (Figure 3), supporting the observation of the triplet state of **1**. The intensity of the signal of $\Delta M_S = \pm 2$ decreased by lowering the temperature from 76 to 25 K, indicating that **1** has a singlet ground state (Figure S9a). The ΔE_{ST} of **1** in frozen toluene solution was determined to be −0.84 kJ mol^{-1} (−101 K) (Figure 5c).

To clarify the response toward the external stimuli, the ESR spectrum of **1** was measured in a frozen 2-MeTHF solution (Figure 5d,e and Figure S9c,d). $|D|$ and $|E|$ are determined to be 0.0191 cm^{-1} and 0.0005 cm^{-1}, respectively, which are consistent with those in toluene. The ΔE_{ST} of **1** in a frozen 2-MeTHF solution was determined to be −1.00 kJ mol^{-1} (−120 K) (Figure 5f), which is slightly larger than that in a frozen toluene solution. We also examined the effect of solvent polarity by changing the ratio of solvents. The intensity of the triplet signal of **1** decreased as the ratio of EtOH toward toluene increased (Figure 5g,h). The response toward the solvents was also expected by the DFT calculations incorporated with solvents using a PCM model. ΔE_{ST} of **1** increases as the polarity of solvents increases from toluene

(–0.49 kJ mol^{-1}, –105 K) to EtOH (–1.35 kJ mol^{-1}, –162 K) (Table S4). These results show that ΔE_{ST} of **1** is changed by solvents.
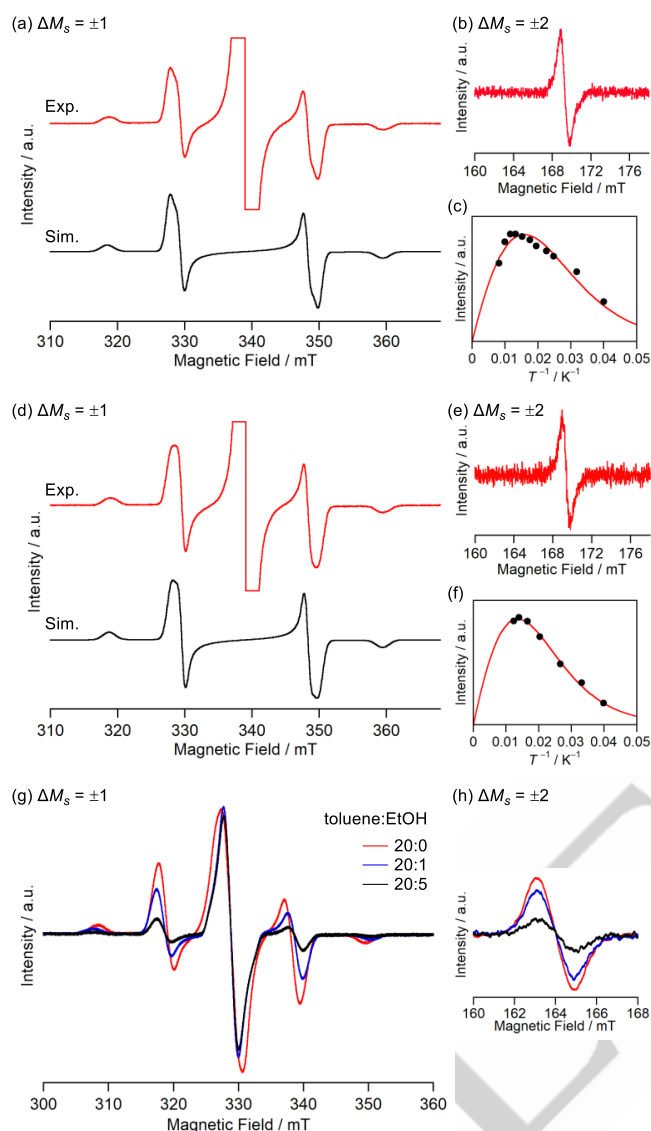

Figure 5. ESR spectra of **1**. (a) $\Delta M_S = \pm 1$ (red, experiment; black, simulation using g = 2.0039, $|D|$ = 0.0192 cm^{-1} and $|E|$ = 0.0005 cm^{-1}) and (b) $\Delta M_S = \pm 2$ in toluene at 75 K, (d) $\Delta M_S = \pm 1$ (red, experiment; black, simulation using g = 2.0037, $|D|$ = 0.0191 cm^{-1} and $|E|$ = 0.0005 cm^{-1}) and (e) $\Delta M_S = \pm 2$ in 2-MeTHF at 79 K, and (g) $\Delta M_S = \pm 1$ and (h) $\Delta M_S = \pm 2$ in toluene–EtOH (20:0, 20:1 and 20:5) at 140 K. Plots of the temperature dependence of the triplet signal intensity of $\Delta M_S = \pm 2$ of **1** versus T^{-1} in (c) toluene and (f) 2-MeTHF.

Conclusion

We have successfully designed and synthesized a zwitterionic open-shell singlet diradical composed of electron-donating anion and electron-accepting cation. The small HOMO–LUMO energy gap of the diradical was confirmed by cyclic voltammetry measurements and UV-Vis-NIR absorption spectra. The singlet state would be stabilized by through-space interaction and zwitterionic character. The ΔE_{ST} of the diradical was changed by solvents, probably due to their polarity.

Supporting Information

The authors have cited additional references within the Supporting Information.[26–28,30,31]

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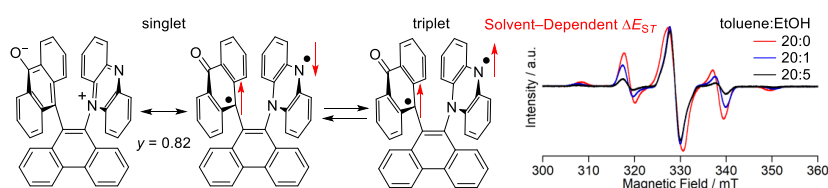
A zwitterionic open-shell singlet diradical composed of electron-donating anion, anthroxide, and electron-accepting cation, phenazinium, was designed and synthesized. The diradical has a small HOMO–LUMO energy gap and shows near-infrared absorption. Its small energy gap between ground singlet and thermally-excited triplet states, which was changed by solvents, was experimentally confirmed.