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Spin Transfer and Solvato-/Thermochromism Induced by Intramolecular Electron Transfer in a Purely Organic Open-Shell System**

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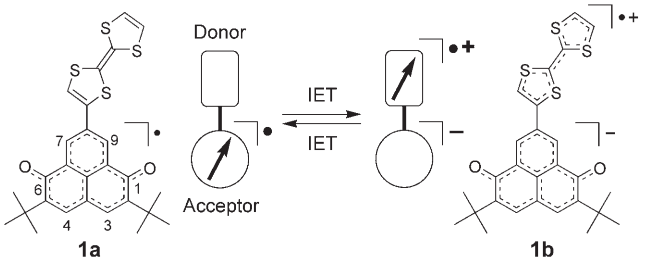
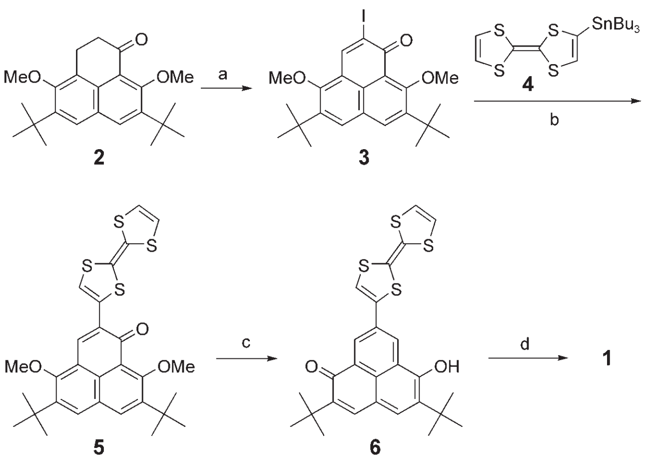


Scheme 1.

In search of organic functional materials, investigators have focused much attention on the switching of physical properties by using appropriate perturbation or stimuli. The integration of multiple controllable properties into a single-component system has been the subject of growing interest. Among such examples are the photoswitching of magnetic interaction by using a photochromic reaction[1] and thermal bistability in electric, magnetic, and optical properties of a crystalline neutral radical.[2] To realize spin-mediated new responsive materials, we are interested in reversible intramolecular electron transfer (IET), which can cause a complete transformation of magnetic and electronic properties in a purely organic system.[3] In an attempt to embody this concept, we have examined a stable neutral radical comprising electron-donor and -acceptor moieties, both of which can have spin before and after IET.

Taking advantage of the high electron-accepting ability of 2,5-di-*tert*-butyl-6-oxophenalenoxyl (6OP) stable neutral radical,[4] we have designed a diad system, **1**, in which 6OP radical is directly linked with a tetrathiafulvalene (TTF) molecule as an electron donor (Scheme 1).[5] In addition to the expected molecular spin, the diad **1** also meets the design criteria for organomagnetic materials,[6–8] single-component organic conductors,[2,9] and other potential applications.[10,11] Prior to the detailed characterization of its solid-state properties, we report herein the IET-induced transfer of spin that accompanies solvato-/thermochromism of **1** as a new molecular-scale function in solution, which is controlled by moderate change in the solvent environment and temperature.

The neutral radical **1** was synthesized from 2,7-dimethoxyphenalanone derivative **2**[4a] in five steps (Scheme 2). Iodophenalenone **3** was prepared by treating **2** with iodine and cerium(IV) ammonium nitrate (CAN). TTF was introduced into phenalenone skeleton by the Stille reaction of **3** with the tributyltin derivative **4**. Reduction and demethylation of the coupling product **5** afforded the 6-hydroxyphenalenone derivative **6**.[12] Oxidation of **6** with PbO_2 in toluene gave neutral radical **1** as a black powder,[13] which is reasonably stable in air at room temperature for weeks. The radical is very stable in degassed solutions.



Scheme 2. Synthesis of neutral radical **1**: a) I_2 (2.5 equiv), CAN (2.5 equiv), AcOH/H_2O, 50 °C, 91 %; b) **3**, $[Pd(PPh_3)_4]$ (2 mol %), CuI (10 mol %), THF, 80 °C, 76 %; c) $NaBH_4$ (40 equiv), EtOH/THF (3:1); then LiI (20 equiv), *N*,*N*-dimethylacetamide, 170 °C, 34 %; d) PbO_2 (5 equiv), toluene, RT, 87 %.

The cyclic voltammogram of **1** in PhCN solution showed three fully reversible redox waves (Figure 1 a). The observed redox potentials are close to those of the two constituent molecules (Table 1), which suggests that **1** is reduced and oxidized in a stepwise manner, with each step occurring independently at each moiety. The potential difference ΔE $(=E^{ox1}_{1/2}-E^{red}_{1/2})$ can, in principle, be related to the likelihood of IET of **1**; a smaller ΔE could lead to easier IET. The use of a PhCN/CF_3CH_2OH solvent mixture significantly changed the first reduction potential $(E^{red}_{1/2})$ of **1**, depending on the mixing ratio (Figure 1 b and c), without affecting the oxidation

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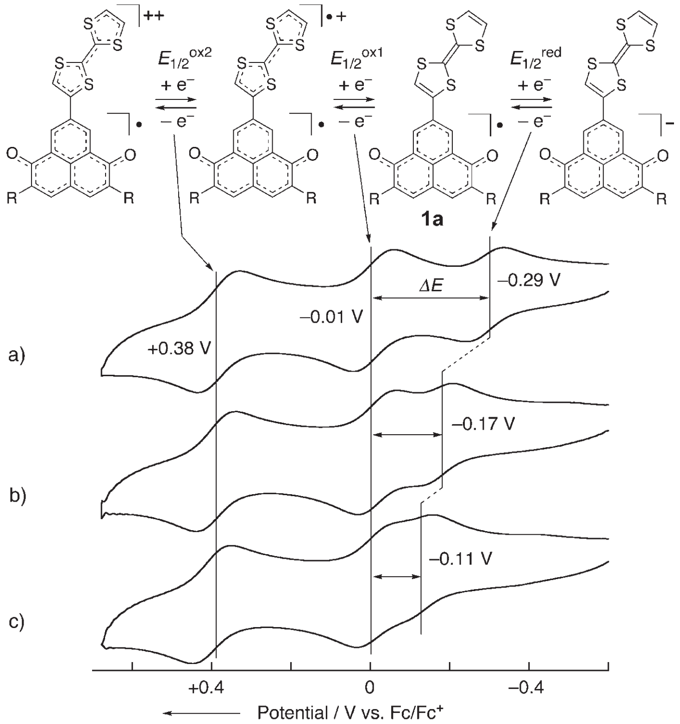

Figure 1. Cyclic voltammograms of solutions of **1** in PhCN/CF_3CH_2OH (1.0 mM) with the solvent ratio of a) 1:0, b) 9:1, and c) 4:1 measured at 293 K. Final potentials were calibrated with the ferrocene/ferrocenium (Fc/Fc$^+$) couple. R = *t*Bu.

Table 1: Redox potentials[a] of **1**, TTF, and 6OP.

	$E_{1/2}^{ox2}$	$E_{1/2}^{ox1}$	$E_{1/2}^{red}$
1	+0.38	−0.01	−0.29
TTF	+0.36[b]	−0.09	–
6OP	–	–	−0.36

[a] Potentials [V] vs. Fc/Fc$^+$ in PhCN at 293 K. Details are given in the Supporting Information. [b] Oxidation peak potential.

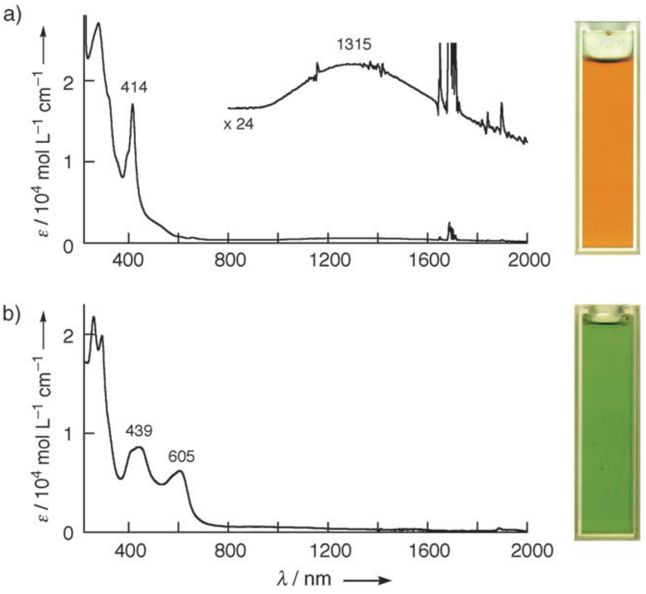

Figure 2. UV/Vis spectra and color of **1** in a) CH_2Cl_2 (1.2×10^{-4} M) and b) CF_3CH_2OH (7.6×10^{-5} M) solutions at 293 K.

potentials for the TTF moiety ($E_{1/2}^{ox1}$, $E_{1/2}^{ox2}$). These results are interpreted as a marked effect of protonation or hydrogen-bonding interactions of a protic solvent to carbonyl groups, which stabilizes the anionic R-O$^-$ structure.[14,15] This electrochemical study suggests that the IET of **1** can be controlled by the solvent environment.

The UV/Vis spectrum of a solution of **1** in CH_2Cl_2 (Figure 2a) showed a sharp absorption band at 414 nm, typical of the 6OP radical,[4a] which indicates the presence of the neutral radical **1a**. In addition, a weak broad absorption centered at 1315 nm was observed, which can safely be assigned to an IET band, not an intermolecular band, as proven by dilution studies (between 1.2×10^{-5} and 1.2×10^{-3} M). In contrast, a solution of **1** in CF_3CH_2OH did not show the sharp peak at 414 nm or the broad IET band while a new absorption at 605 nm appeared (Figure 2b). These changes are explained by assuming the zwitterionic structure **1b** with a TTF radical cation and 6OP anion moiety; all the spectral features can be reproduced by superimposition of the component spectra (see Supporting Information). Interestingly, the diad **1** shows solvatochromism depending on the IET states, as is evident from the different absorption wavelengths of **1a** and **1b** (Figure 2).

To confirm the electronic structures of the two IET states, we have recorded the ESR spectra of **1** in aprotic and protic media. In a degassed toluene solution (1.0×10^{-4} M), radical **1** showed well-resolved hyperfine structures at 290 K with a *g* value of 2.0047 (Figure 3a). Electron-nuclear multiple resonance spectroscopy (^{1}H ENDOR/TRIPLE) unequivocally determined the hyperfine coupling constants (hfccs) of protons and their relative signs (Table 2). The obtained hfccs and *g* value are typical of 6OP radicals,[4a] which is clear evidence of the neutral radical structure **1a**. Although a small amount of spin density is delocalized into the TTF moiety, the spin structure virtually holds the 6OP-type distribution (Figure 4a).

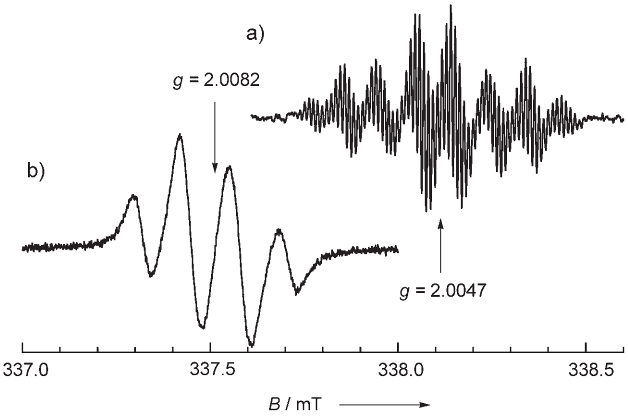

Figure 3. Liquid-phase ESR spectra of **1** in a) toluene (1.0×10^{-4} M) and b) CF_3CH_2OH (3.0×10^{-5} M) at 290 K. The microwave frequency used was 9.487717 GHz.

Table 2: Proton hyperfine coupling constants [mT] and *g* values of **1a**, 6OP neutral radical, **1b**, and TTF radical cation.

	3, 4	7, 9	2,5-*t*Bu	TTF	*g* value
1a[a]	+0.199	+0.082	+0.011	−0.096	2.0047
6OP[a,b]	+0.206	+0.078	+0.012	–	2.0046
1b[c]	–	–	–	−0.126	2.0082
$TTF^{\bullet+}$[d]	–	–	–	−0.126	2.0084

[a] In toluene. [b] See ref. [4a]. [c] In CF_3CH_2OH. [d] In CH_2Cl_2. See reference [18].

In contrast, an ESR spectrum of **1** in a degassed CF_3CH_2OH solution (3.0×10^{-5} M) at 290 K gave a more downfield absorption ($g = 2.0082$) with three nearly equivalent ^1H couplings (Figure 3b). The observed hfccs and *g* value (Table 2) identified this species as the zwitterionic radical **1b** in which the TTF radical cation moiety is the spin-bearing center (Figure 4b). The localization of the spin densities at the TTF moiety may be associated with a possible twisted structure of **1b** induced by charge separation due to IET.[16]

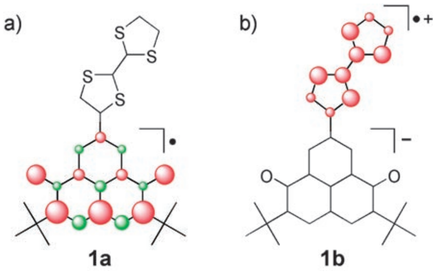

Figure 4. Postulated spin structures of a) **1a** and b) **1b**, assuming dominant contributions from 6OP neutral radical and TTF radical cation, respectively. Spin densities are calculated for the constituent molecules at the UBLYP/6-31G(d) level. Red and green denote positive and negative signs, respectively. Only the σ skeletons of **1a** and **1b** are depicted.

It is of interest to explore the possibility of the interconversion between the two states of **1** in a more controllable manner. By changing the solvent mixing ratio, we found an intermediate experimental condition that gave a mixture of **1a** and **1b**, which may be sensitive to additional perturbation or stimuli. A solution in CH_2Cl_2/CF_3CH_2OH (199:1) gave such an intermediate state at 263 K, the ESR spectrum of which is the superimposition of the spectra of **1a** and **1b** (Figure 5c). Furthermore, we observed a smooth transition from the **1b**-only pattern at 243 K to the **1a**-only pattern at 293 K in the ESR spectra (Figure 5). This process that accompanies themochromism is reversible, which suggests a temperature-dependent equilibrium between **1a** and **1b**. The mechanism of this interconversion needs to be studied further by considering quantitative analysis and solvent effects.[17]

In summary, we have described a purely organic open-shell donor–acceptor diad system, **1**, which exhibits an IET-induced spin transfer by solvatochromism, depending on the nature of solvent. Both the neutral radical, **1a**, and zwitterionic radical, **1b**, have been unequivocally characterized by UV/Vis and ESR spectroscopies in aprotic and protic media, respectively. The thermochromic interconversion between the two IET states of **1** has also been realized in a mixed solvent system. A possible switching of these combined properties by applying external stimuli such as an electrostatic field is of particular interest for molecular functionality, as well as for the characterization of its solid-state properties.

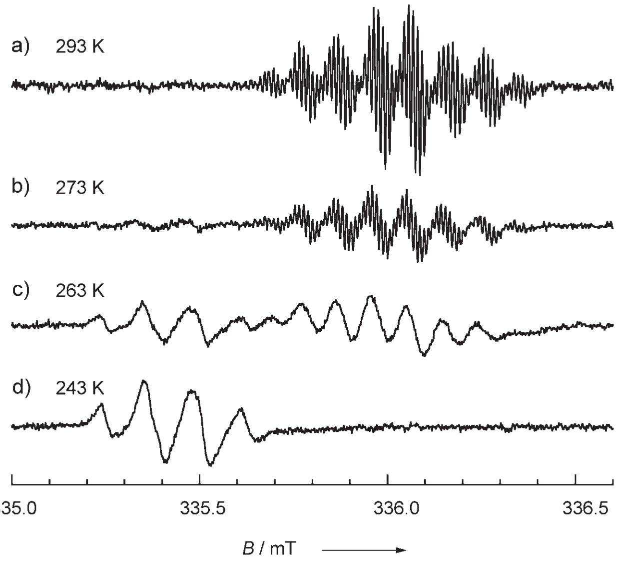

Figure 5. Temperature dependence of the liquid-phase ESR spectra of **1** in a CH_2Cl_2/CF_3CH_2OH (199:1) solution (7.7×10^{-5} M) at a) 293 K, b) 273 K, c) 263 K, and d) 243 K. The microwave frequency used was 9.4283 GHz.

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[13] Selected physical data for **1**: m.p. 166–168 °C (decomp); elemental analysis (%) calcd for $C_{27}H_{25}O_2S_4 \cdot H_2O \cdot 0.5\,C_6H_5CH_3$: C 63.84, H 5.45, N 0.00, S 22.35; found: C 63.67, H 5.22, N 0.00, S 22.25.

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