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Novel Spin-Polarized TTF Donors Affording Ground State Triplet Cation Diradicals

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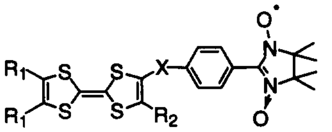
Abstract: The concept of "spin-polarized" donor was successfully extended to TTF-based donor radicals. A series of TTF derivatives carrying a phenyl nitronyl nitroxide group were prepared, and they turned out to afford ground state triplet cation diradicals through one-electron oxidation. Such "spin-polarized" TTF donors are expected to become building blocks for organic conducting ferromagnets.

Keywords: Electron donors; Electron spin resonance; Radicals and radical reactions; Sulfur heterocycles.

In the course of the remarkable progress made in the field of molecular magnetism, a number of organic ferromagnets have been reported recently.[1] The transition temperatures of genuine organic ferromagnets, however, are still extremely low. One promising approach to raise transition temperatures is to utilize conduction electrons which itinerate along a stacking of organic donor radicals.[2] A crucial point in this methodology is the introduction of ferromagnetic coupling between the conduction electrons and localized spins. Although several organic donor radicals which carry a stable radical unit have been reported,[3] the radical group is connected with a donor unit in a non-π-conjugating manner. In these cases, the magnetic interaction between the radical unit and the donor unit in the singly oxidized state is negligibly small, if any.

From the viewpoint of introducing a ferromagnetic exchange interaction between a localized spin on the radical unit and a π-spin generated on the donor unit, we proposed an open-shell donor, where the π-donor and π-radical units are connected through cross-conjugation.[4] In order to obtain an organic metallic ferromagnet, the donor unit is required to construct a sufficient conduction path when the donors are assembled and partially doped. As a prototypal building block for this purpose, here we present novel TTF-based donor radicals (**1-4**) and discuss the ground state spin multiplicity of the cation-diradicals derived from these donor radicals.



1 : X = none, $R_1 = R_2 = H$
2 : X = none, R_1-R_1 = SCH_2CH_2S, $R_2 = H$
3 : X = none, R_1-R_1 = SCH_2CH_2S, $R_2 = SCH_3$
4 : X = S, R_1-R_1 = SCH_2CH_2S, $R_2 = SCH_3$

The donor radicals **1-3** were prepared by the following reaction scheme (Scheme 1).[5] Lithiated TTF derivatives **5a-c** were treated with trimethyltin chloride to afford stannyl derivatives **6a-c**. They were converted to *p*-formylphenyl derivatives **7a-c** by cross-coupling with *p*-bromo- or *p*-iodobenzaldehyde using a palladium catalyst. These *p*-formylphenyl derivatives were converted to nitronyl nitroxides **1-3** by the ordinary method.[6]

The aldehyde precursor **11** was synthesized from a lithiated TTF derivative **5c** (Scheme 2)[7] and disulfide **9** which was prepared from *p*-methylthiobenzaldehyde, making use of Pummerer rearrangement.[8] The coupling product **10** was hydrolyzed to give the aldehyde **11**, which was converted to the nitronyl nitroxide derivative **4**.[9]

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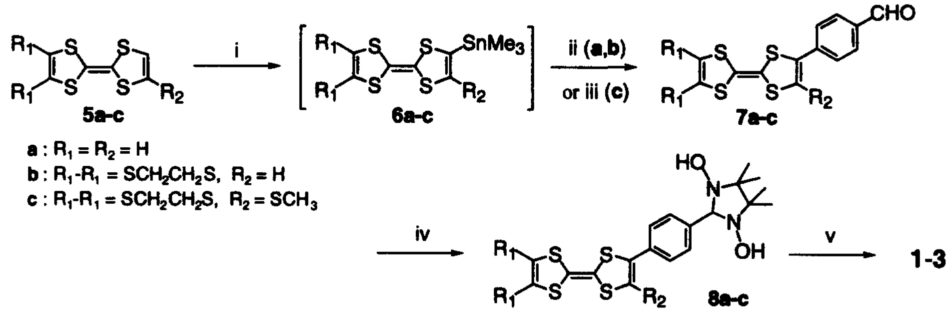
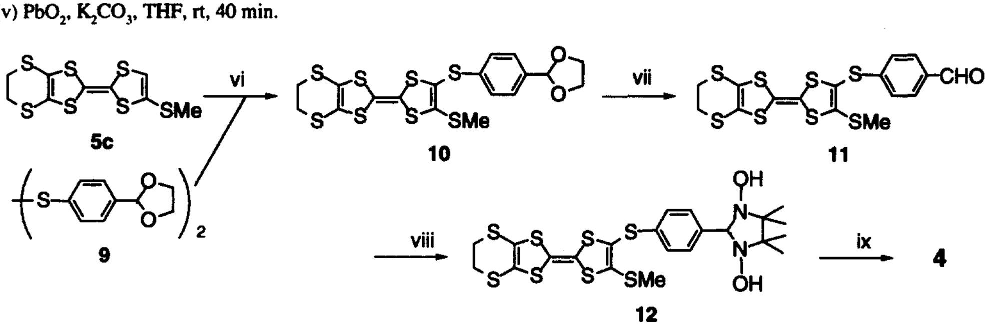


Scheme 1. Reagents and conditions: (i) (1) LDA, THF, -70°C, 1h, (2) Me_3SnCl, THF, -70°C, 2h; (ii) BrPhCHO, $Pd(PPh_3)_2Cl_2$, toluene, reflux, 8h, a:50%, b:60%; (iii) IPhCHO, $Pd(PPh_3)_4$, toluene-1M Na_2CO_3aq, reflux, 20h, 55%; (iv) $(C(CH_3)_2(NHOH))_2$, cat.$(C(CH_3)_2(NHOH))_2 \cdot H_2SO_4$, CH_2Cl_2-hexane(2:1), reflux, overnight, a:85%, b:35%, c:90%; (v) PbO_2, K_2CO_3, THF, rt, 40 min.



Scheme 2. Reagents and conditions: (vi) (1) LDA, THF, -70°C, 1h, (2) **9**, THF, -70°C to rt, overnight, 55%; (vii) $TsOH \cdot H_2O$, $CHCl_3$-acetone, overnight, 90%; (viii) $(C(CH_3)_2(NHOH))_2$, cat.$(C(CH_3)_2(NHOH))_2 \cdot H_2SO_4$, benzene-MeOH, reflux, 12h, 50%; (ix) PbO_2, K_2CO_3, THF, rt, 40 min.

The oxidation potentials of donor radicals **1**-**4** determined by cyclic voltammetry are summarized in Table 1. The data indicate that the donor abilities of these donor radicals are practically the same as those of the parent compounds, judged from the first and the second oxidation potentials. Since the oxidation of nitronyl nitroxide (NN) radical should be observed at 0.8-1.0 V referring to that of phenyl NN, the second or third oxidation potentials of donor radicals **1**-**4** may be assigned to that process. This assignment does not conflict with the results obtained by ESR spectroscopy on the singly oxidized donor radicals (*vide infra*).

Table 1. Oxidation potentials of donor radicals measured in 0.1 M $^nBu_4N \cdot ClO_4$-CH_2Cl_2 solution (V *vs* Ag/AgCl, scanned 200 mV/s).

Donors	$E_{1/2}^{Ox1}$	$E_{1/2}^{Ox2}$	$E_{1/2}^{Ox3}$
1	0.44	0.79	
2	0.54	0.88	
3	0.62	0.92	0.94
4	0.68	0.97	0.99
TTF	0.34	0.71 (irr.)	
BEDT-TTF	0.61	0.99 (irr.)	
PhNN	0.85		

The donor radicals **1**-**4** were oxidized with excess iodine in tetrahydrofuran solution. The ESR spectra of iodine-doped **1**-**4** showed a set of fine structured signals due to a triplet species (Figure 1(a)). Zero-field splitting parameters of the triplet species were determined by computational simulation as summarized in Table 2. The triplet species were characterized as cation diradicals $\mathbf{1}^{+\bullet}$-$\mathbf{4}^{+\bullet}$ generated from the donor radicals. The temperature dependence of the signal intensity was measured in the temperature range of 4-120 K, and the plot gave a straight line (Figure 1(b)). The result suggests that the triplet is the ground state of these cation diradicals (or the S-T energy gap is smaller than *ca.* 10 cal/mol).

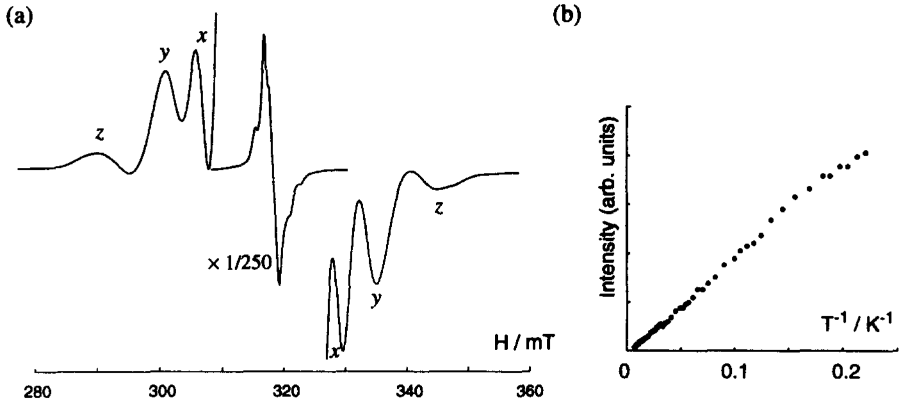


Figure 1. (a) ESR spectrum of iodine-doped **3**. (b) Temperature dependence of triplet signal intensity of $3^{+\bullet}$.

Table 2. Zero field splitting parameters and anisotropic g values for triplet species.

	$\lvert D \rvert$	$\lvert E \rvert$	g_x	g_y	g_z	$g_{av.}$
1	0.0255 cm^{-1}	0.0023 cm^{-1}	2.0111	2.0084	2.0046	2.0080
2	0.0245	0.0022	2.0090	2.0070	2.0060	2.0073
3	0.0252	0.0021	2.0077	2.0053	2.0070	2.0067
4	0.0265	0.0023	2.0090	2.0080	2.0070	2.0080

The reason for generating ground state triplet cation diradicals can be rationalized by the characteristic electronic structure of the donor radicals. In a UHF-MO description, the unpaired electron, which resides in SOMO, causes spin-polarization of the π-electrons in HOMO. Accordingly, the orbital energy of a β spin in HOMO is destabilized, while that of an α spin is relatively unaffected (Figure 2).[10] Under this circumstance, the electron to be removed is the β spin upon one-electron oxidation, giving rise to a triplet species. Since the resulted SOMO' and SOMO are of a space-sharing type, an effective ferromagnetic exchange interaction operates between these two orbitals. Such a donor radical can be classified as "spin-polarized" donors as in the case of amine-based nitronyl nitroxide derivatives.[4,11]

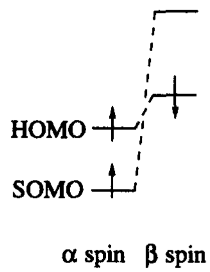
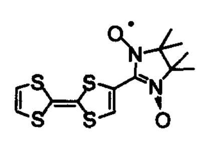


Figure 2. UHF description of the spin polarization of HOMO caused by SOMO in a spin-polarized donor.

The experimental result is in sharp contrast with the result of TTF-NN (**13**), which we reported previously.[4a] The ground-state spin multiplicity of the cation diradical of TTF-NN ($13^{+\bullet}$) is singlet and the observed triplet signal is ascribed to a thermally populated one with an S-T energy gap of 200 cal/mol. Although the TTF and NN groups in TTF-NN are connected through cross-conjugation, they are considered to be severely twisted due to steric repulsion. As a result, delocalization of HOMO or SOMO' to the radical site is surppressed, leading to a breakdown of the electronic feature of a spin-polarized donor.



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It is to be noted that this unfavorable steric hindrance was released by inserting a *p*-phenylene (**1-3**) or *p*-thiophenylene (**4**) group as seen from the ESR experimental results. It is interesting to compare the efficiency of *p*-phenylene and *p*-thiophenylene groups as a transmitter of the spin-polarization caused at the radical site. Provided that the entire molecule is coplanar, the coefficients on the NN group in SOMO' of **4** is appreciably larger than those of **3** when these relevant MOs are calculated by a PM3/UHF method. This tendency may lead to a larger ferromagnetic exchange interaction in **4** which contains a *p*-thiophenylene group as a transmitter.

In conclusion, the novel TTF-based donor radicals described here were found to afford ground-state triplet cation diradicals upon one-electron oxidation. The present result clearly demonstrates that the concept of a spin-polarized donor is successfully extended to the TTF-based donor radicals. If a columnar stacking of these donors is realized and partially doped, such a self-assembled material is expected to afford an organic conducting ferromagnet.

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5. ^{1}H-NMR : **7a** ($CDCl_3$) δ 10.00 (s, 1H), 7.87 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 6.75 (s, 1H), 6.36 (s, 2H); **7b** ($CDCl_3$) δ 10.00 (s, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.54 (d J = 8.4 Hz, 2H), 6.74 (s, 1H), 3.31 (s, 4H); **7c** ($CDCl_3$) δ 10.03 (s, 1H), 7.95 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 3.31 (s, 4H), 2.38 (s, 3H); **8a** (DMSO-d_6) δ 7.51 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.21 (s, 1H), 6.76 (s, 2H), 4.51 (s, 1H), 1.07 (s, 6H), 1.04 (s, 6H); **8b** (Acetone-d_6) δ 7.51 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 6.96 (s, 1H), 4.66 (s, 1H), 3.39 (s, 4H), 1.13 (s, 6H), 1.04 (s, 6H); **8c** (DMSO-d_6) δ 7.56 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 4.80 (s, 1H), 3.30 (s, 4H), 2.33 (s, 3H), 1.19 (s, 6H), 1.15 (s, 6H).
6. Compound **1**: ESR (benzene) g = 2.0062, a_N = 0.74 mT (2N). Compound **2**: ESR (benzene) g = 2.0062, a_N = 0.75 mT (2N). Compound **3**: ESR (benzene) g = 2.0056, a_N = 0.73 mT (2N). Anal. calcd. for $C_{22}H_{23}N_2O_2S_7$: C 46.20 H 4.05 N 4.90 S 39.25 %, found: C 46.65 H 4.15 N 4.76 S 38.06 %.
7. ^{1}H-NMR : **11** ($CDCl_3$) δ 9.96 (s, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 3.30 (s, 4H), 2.48 (s, 3H); **12** (DMSO-d_6) δ 7.79 (s, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 4.50 (s, 1H), 3.32 (s, 4H), 2.50 (s, 3H), 1.07 (s, 6H), 1.04 (s, 6H).
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9. Compound **4**: ESR (benzene) g = 2.0072, a_N = 0.75 mT (2N). FAB-MS calcd. for $C_{22}H_{23}N_2O_2S_8$ (M^+) 602.95, found 602.8.
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