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A novel TTF-based donor carrying four nitronyl nitroxides

Genta Harada,[a] Toshio Jin,[a] Akira Izuoka,[a,b] Michio M. Matsushita[a] and Tadashi Sugawara[a,*]

[a]*Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1, Komaba, Meguro, Tokyo 153-8902, Japan*

[b]*Department of Materials and Biological Sciences, Faculty of Science, Ibaraki University, 2-1-1 Bunkyo, Mito, Ibaraki 310-8512, Japan*

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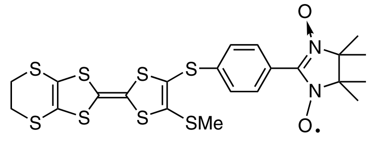
Abstract—A novel TTF-based tetraradical donor was synthesized and its electronic structure was fully characterized by spectroscopic measurements, magnetic susceptibility measurements, and electrochemical analyses. © 2003 Elsevier Science Ltd. All rights reserved.

The chemical properties and electronic structures of polyradicals, where stable radical units are connected with a π-conjugating core, have been explored for a long time and many types of polyradicals have been prepared so far.[1] Although the exchange coupling between unpaired electrons on radical units was observed, the intramolecular spin–spin interaction was not large in most of cases due to the 'disjoint character' of the spin system.[2] Accompanied by the progress of molecular magnetism, high-spin polyradicals have been synthesized on the basis of the spin-correlation in odd-alternate hydrocarbons of a non-disjoint type.[2] Moreover, dynamic molecular spin systems, in which the magnetic property can be altered by modulating a coordination-active,[3] photo-active,[4] or redox-active[5] π-conjugating core bearing radial units, have recently been reported.

Meanwhile, several tetrathiafulvalene(TTF)-based donor radicals have also been prepared.[6] When a nitronyl nitroxide group was introduced to the TTF core through a *p*-phenylenethio unit as in the case of donor radical (**1**), the donor radical turned out to afford a ground state triplet cation diradical upon one-electron oxidation due to the 'non-disjoint' character of the resulting cation diradical species. This result indicates the validity of the *p*-phenylenethio group as a ferromagnetic coupler.



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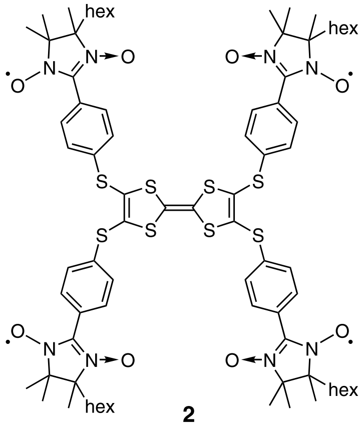

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Here we report preparation of TTF-based tetraradical donor (**2**), in which four vinylic protons of TTF are all substituted with *p*-thiophenyl nitronyl nitroxides. One of the methyl groups of the nitronyl nitroxide of **2** is substituted by a hexyl group in order to increase the solubility of the precursor of nitronyl nitroxide, that is a cyclic bishydroxylamine. A preparative method for the modified bishydroxylamine is also described. In addition, the electronic structure and magnetic property of this novel TTF-based tetraradical have been fully

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Keywords: polyradical; π-ionradical; tetrathiafulvalene; nitronyl nitroxide; high-spin molecule; spin multiplicity conversion.

* Corresponding author. Tel.: +81-3-5454-6742; fax: +81-3-5454-6997; e-mail: suga@pentacle.c.u-tokyo.ac.jp

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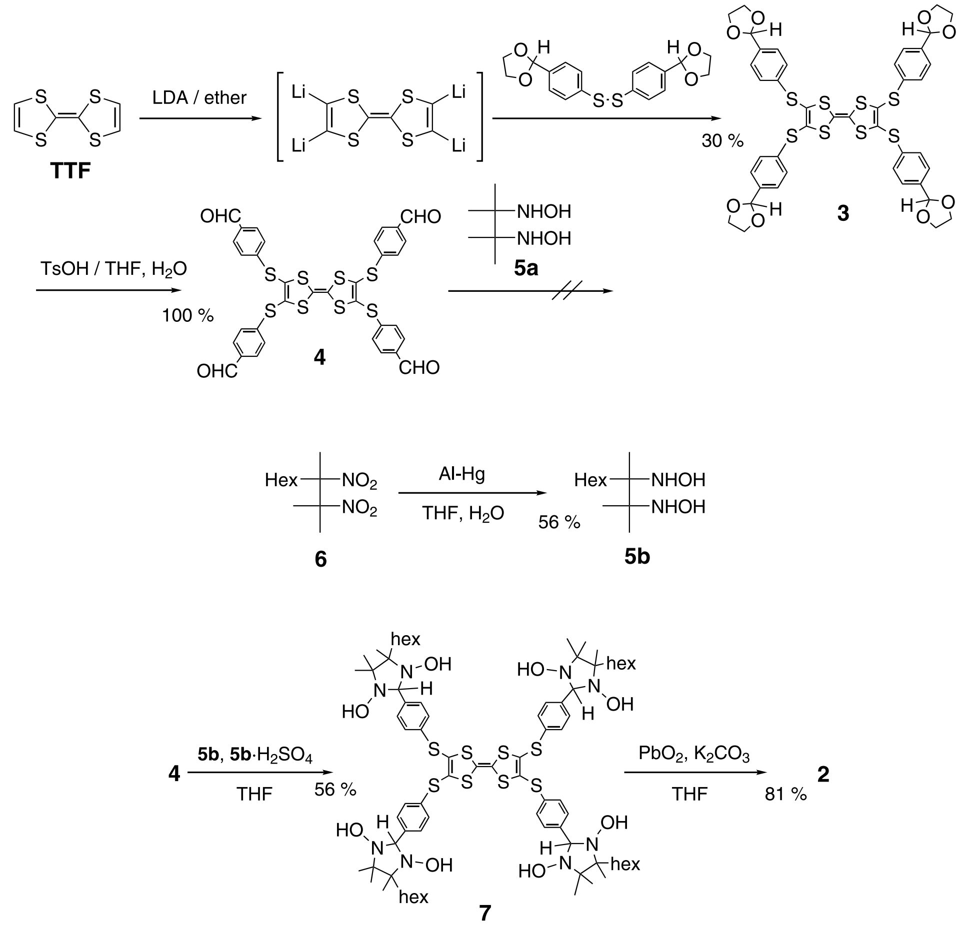
studied by UV–vis absorption spectroscopy, ESR spectroscopy, magnetic measurements, and electrochemical analyses.

Tetraradical donor **2** was prepared by the following reaction scheme (Scheme 1).[7] Vinyl protons of TTF were lithiated by adding 5 equiv. of lithium di-*iso*-propylamide in diethylether and the lithiated species was reacted with acetal-disulfide to afford tetraacetal (**3**), which was then hydrolyzed to tetraformyl derivative (**4**). The reaction between tetraformyl derivative **4** and 2,3-dimethyl-2,3-di(hydroxyamino)butane (**5a**) was found not to proceed because of the poor solubility of the condensation products. In order to increase the solubility, 2,3-dimethyl-2,3-di(hydroxyamino)nonane (**5b**), in which one of the methyl groups of **5a** is substituted by a hexyl group, was prepared according to the following reaction scheme (Scheme 1, middle). Although the preparation of an alkylated bishydroxylamine has been reported by Tamura et al.[8] the preparative condition has a room for improvement considerably. We have optimized the preparation route as follows. Dinitro compound (**6**) was obtained according to the literature based on Kornblum's method.[9] Reduction of dinitro compound **6** was successfully carried out with aluminum-amalgam[10] in aqueous tetrahydrofuran (THF) to produce 2,3-dimethyl-2,3-di(hydroxyamino)nonane **5b** in a reasonably good yield. Although bishydroxylamine **5b** was obtained as a mixture of two enantiomers, the mixture was used for later reactions without enantiomeric separation. It should be noted that this bishydroxylamine **5b** is suitable for the preparation of a cyclic bishydroxylamine, that is a precursor of a nitronyl nitroxide derivative, especially when the solubility of the corresponding tetramethyl derivative is poor. Introduction of a long alkyl chain also contributes to the fabrication of nitronyl nitroxides, in particular, for the formation of a thin film.

Tetraformyl compound **4** was reacted with bishydroxylamine **5b** to afford tetrakis(cyclic bishydroxylamine) (**7**),[11] which was oxidized by excess lead dioxide in THF to give the desired tetraradical **2**.[12] The crude tetraradical **2** was purified by column chromatography (silica-gel) with THF as an eluant and was isolated as green powders. It was found that tetraradical **2** is very stable and can be stored for a year in a refrigerator.

The UV–vis absorption spectrum of **2** in dichloromethane showed broad absorption bands at 378 and 605 nm: these bands are characteristic to a nitronyl nitroxide group directly attached to a π-conjugating system. They are red-shifted in comparison with those of phenyl nitronyl nitroxide at 362 and 597 nm, similar to those of **1**,[6a] suggesting the presence of the electronic interaction between the TTF unit and the NN-phenylthio groups even in the neutral state.



Scheme 1. Synthetic route to tetraradical donor **2**.

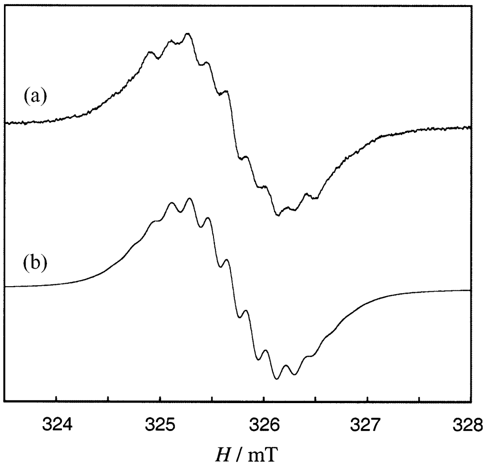


Figure 1. (a) ESR spectrum of TTF-based tetraradical **2** in benzene at room temperature. (b) Simulated spectrum with $g = 2.0062$, $a_N = 0.181$ mT, and half line-width of 0.18 mT for $\nu = 9.14548$ GHz.

The ESR spectrum of a benzene solution of tetraradical **2** showed multiple lines with $g = 2.0062$ and $a_N = 0.181$ mT as shown in Figure 1a. The g value of **2** is close to that of monoradical **1**, and the a_N value is 1/4 of that of the monoradical,[13] strongly suggesting that the unpaired electron of **2** is exchange coupled with four equivalent nitronyl nitroxides. Although the spectrum of **2** was poorly resolved, the spectral shape was reproduced reasonably well using the g value, the a_N of eight equivalent nitrogen atoms, and the half line-width of 0.18 mT as shown in Figure 1b.[14] These data provide a good proof for the tetraradical structure of **2**. Although the line width of **2** is broader than that of monoradical **1**, the broadened line shape of **2** was not sharpened even when the temperature was raised up to 346 K. This result suggests that the line broadening is derived from neither the restricted rotation of the congested substituents nor the slow tumbling motions of the whole molecule in solution. The line-broadening was presumably due to the presence of five diastereomers derived from the chirality in four radical moieties.

The temperature dependence of the magnetic susceptibility of a powdered sample of **2** was measured by a SQUID magnetometer and the $\chi_p T$ plot of **2** was shown in Figure 2, together with the calculated line according to Curie–Weiss law, $\chi_p = C/(T-\theta)$. The constant $\chi_p T$ values at higher temperatures suggest the paramagnetic behavior of tetraradical **2**. The Curie constant (C) of 1.51 was four times larger than the value (0.375) for paramagnetic spins of $S = 1/2$, indicating the presence of four radical centers in one molecule. The negative Weiss constant of $\theta = -0.88$ K was reproduced reasonably well by the mean-field approximation. Therefore, the negative Weiss constant may be ascribed to the intermolecular antiferromagnetic interaction. The intramolecular spin–spin coupling is, if any, to be smaller than that of the intermolecular one in the neutral state.

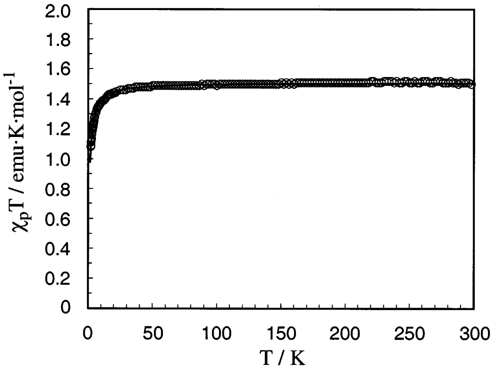


Figure 2. Temperature dependence of the magnetic susceptibility of **2**. The open circle shows the product of the magnetic susceptibility and temperature ($\chi_p T$) of **2**, whereas the solid line shows the calculated value with $\theta = -0.88$ K.

Figure 3a shows the cyclic voltammogram of tetraradical **2**. Three reversible redox waves indicates that each oxidation state is reasonably stable. Since the separation of the redox waves was not sufficient, the differential pulse voltammogram of **2** was measured for the determination of the accurate redox potentials. As shown in Figure 3b, three redox peaks were observed at 720, 850, and 1070 mV versus Ag/AgCl with the ratio of 1:4:1. Judging from the first redox potential, tetraradical **2** has a reasonable donor ability. The first,

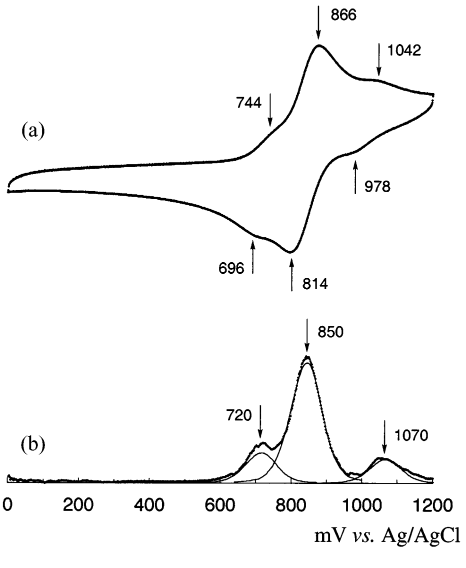


Figure 3. Redox potentials of TTF-based tetraradical donor **2** measured in dichloromethane in the presence of 0.1 mol l^{-1} tetra-*n*-butylammonium perchlorate as an electrolyte, using a BAS CV-50 W electrochemical analyzer. A platinum electrode (BAS PTE, 1.6 mm diameter) was employed as the working electrode, an Ag/AgCl electrode (BAS RE-1B) as the reference electrode, and the counter electrode was a platinum wire (0.5 mm diameter). (a) Cyclic voltammogram of **2** with a scanning rate of 200 mV s^{-1}. (b) Differential pulse voltammogram of **2**.

second, and third redox peaks are assigned to the oxidation process of the TTF moiety, four nitronyl nitroxides, and the cation radical of TTF moiety, respectively, on the basis of the relative intensity of redox peaks and the redox potentials of reference compounds. It is important that the first oxidation does not occur at the radical moiety, because if the first oxidation process removed the unpaired electrons from the radical sites of tetraradical **2**, it would afford an undesired closed-shell tetracation species.

Based on above experimental data, the singly oxidized species of the tetraradical **2** is considered to exist as a pentaradical of a ground state sextet spin-multiplicity,[15] because the *p*-phenylenethio unit act as a ferromagnetic coupler between $TTF^{+\bullet}$ and nitronyl nitroxide groups.[6a] Moreover, if the tetraradical **2** forms charge transfer complexes with acceptors, it may provide a ferrimagnetic spin system.[16] In summary, the newly synthesized TTF-based tetraradical **2** would be an important paramagnetic building block to construct novel organic spin systems.

Acknowledgements

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11. The radical precursor **7** is also a mixture of optical and diastereomeric isomers. Spectrum data for **7**: ^1H NMR (DMSO-d_6): $\delta = 0.87$ (t, 12H), 0.98, 1.02, 1.05, 1.08, 1.09 (s, 36H), 1.18–1.77 (m, 40H), 4.51, 4.54 (s, 4H), 7.40 (d, 8H, $J = 7.69$ Hz), 7.51 (d, 8H, $J = 7.69$ Hz), 7.48 (s, 2H), 7.69 (s, 2H), 7.74 (s, 2H), 7.96 ppm (s, 2H). FAB-MS; calcd for $C_{78}H_{116}N_8O_8S_8$ (M^+): 1550.33. Found: 1549.9.
12. Elemental analysis data of **2**; calcd for $C_{78}H_{104}N_8O_8S_8$: C, 60.90; H, 6.81; N, 7.28; O, 8.32; S, 16.68%. Found: C, 61.01; H, 6.85; N, 7.31; S, 16.50%. IR (KBr, cm^{-1}); 2927 (s), 2855 (m), 1466 (w), 1424 (s), 1363 (s), 1300 (s), 826 (w).
13. The ESR spectrum of a benzene solution of monoradical **1** shows five lines of the 1:2:3:2:1 relative intensity with $g = 2.0072$, $a_N = 0.75$ mT for two equivalent nitrogen atoms. See Ref. 6a.
14. The calculated relative intensity of a heptadecet is 1: 8: 36: 112: 266: 504: 784: 1016: 1107: 1016: 784: 504: 266: 112: 36: 8: 1.
15. Although the fine structures were observed in the ESR spectrum of the singly oxidized species of **2** in frozen matrix of 2-methyltetrahydrofuran and they were presumably derived from the high spin species, the spectrum was too complicated to be interpreted by the second order high-field approximation because of the presence of conformational isomers. The detail of the assignment will be discussed elsewhere.
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