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Helical Tetrathiafulvalene Oligomers. Synthesis and Properties of Bi-, Ter-, and Quatertetrathiafulvalenes

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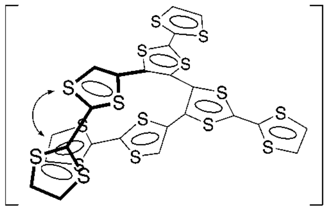
ABSTRACT



Intramolecular interactions of cation radicals

A series of fully methylthiolated bi-, ter-, and quatertetrathiafulvalenes have been synthesized using cross- and homocoupling reactions of tetrathiafulvalenylzinc derivatives; the tetracation–tetraradical derived from the helical tetrathiafulvalene tetramer exhibits an intramolecular association of the terminal cation-radicals.

Tetrathiafulvalene (TTF) has attracted much interest because of its electron-donating ability, which has been used for the synthesis of new organic metals and superconductors.[1] In particular, extended π-donors based on the TTF framework have been extensively investigated in recent years.[2,3] On the other hand, helical molecules containing a variety of structural units have also attracted considerable attention, mainly owing to their potential in materials and polymer science.[4,5] However, no helical motif could be applied to the TTF chemistry until now, presumably due to difficulties in the synthesis of oligomeric tetrathiafulvalenes. We now report here a novel synthesis of the fully methylthiolated tetrathiafulvalene oligomers **2**−**4**, together with the helical structure of the tetrathiafulvalene tetramer **4**.

The syntheses of **2**−**4** were carried out using the reaction sequence shown in Schemes 1 and 2. As shown in Scheme 1, the dimeric TTF **2**[6,7] was synthesized using a coupling reaction of the trimethylstannyl-TTF derivative **6** with Pd(OAc)$_2$, followed by methylthiolation of **7**.[8] Since the methodology for preparing oligomeric tetrathiafulvalenes is

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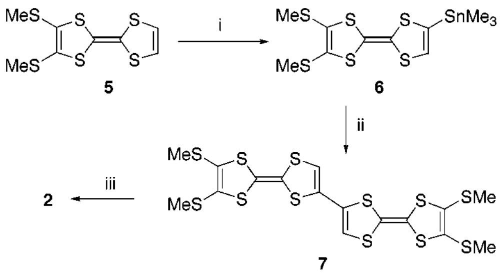
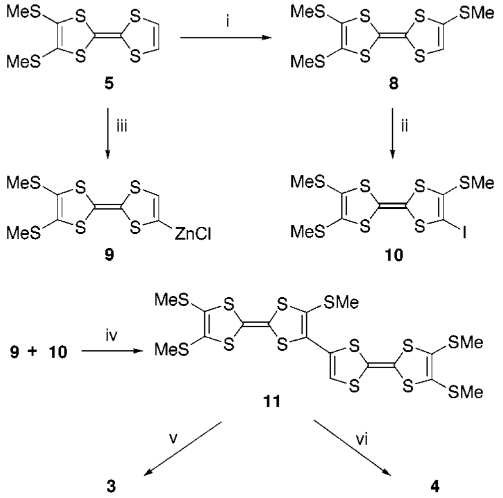
Scheme 1. Synthesis of **2**[a]



[a] Reagents and conditions: (i) 1) Bu^{n}Li (1.04 equiv), (2) Me_3SnCl (1.6 equiv) (55%); (ii) $Pd(OAc)_2$ (1.01 equiv), benzene (43%); (iii) (1) LDA (2 equiv), (2) MeSSMe (3 equiv) (40%).

still very limited, we have developed a new approach to construct the extended TTF framework using reactions of tetrathiafulvalenylzinc derivatives which can be prepared by the successive treatment of TTF derivatives with Bu^{n}Li and $ZnCl_2$. As shown in Scheme 2, the cross-coupling reaction of **9** with **10** in the presence of $Pd(PPh_3)_4$ in THF at −10 °C for 1 h and then room temperature for 1 h produced the bi-TTF derivative **11** in 77% yield based on **10**. For the synthesis of **3**, we employed a similar palladium-catalyzed cross-coupling reaction of an organozinc reagent, and the reaction of **11** with Bu^{n}Li in THF, followed by treatment with $ZnCl_2$ afforded the corresponding zinc species **12** which was reacted with **10** in the presence of $Pd(PPh_3)_4$ to form **3**[6] in 69% yield based on the recovered starting **11** (30%). As for the synthesis of **4**, a palladium-catalyzed homo-coupling reaction of an organozinc compound gave a successful result, because oligomeric tetrathiafulvalenes are unreactive and stable to palladium complexes under coupling conditions.[8,9] Thus, the organozinc compound **12** derived from **11** was treated with a stoichiometric amount of $PdCl_2(PPh_3)_2$ in THF at −10 °C for 1 h and then at room temperature for 1 h to produce **4**[6] in 52% yield based on the recovered **11** (35.5%).

Scheme 2. Synthesis of **3** and **4**[a]



[a] Reagents and conditions: (i) 1) Bu^{n}Li (1.6 equiv), (2) MeSSMe (1.7 equiv) (67%); (ii) (1) LDA (1.5 equiv), (2) $CF_3(CF_2)_5I$ (1.5 equiv) (64%); (iii) (1) Bu^{n}Li (1.1 equiv), (2) $ZnCl_2$ (1.2 equiv); (iv) $Pd(PPh_3)_4$ (20 mol %), THF, −10 °C, 1 h then rt 1 h (77%); (v) (1) Bu^{n}Li (1.1 equiv), (2) $ZnCl_2$ (1.2 equiv), 3) **10**, $Pd(PPh_3)_4$ (20 mol %), THF (69%); (vi) 1) Bu^{n}Li (1.1 equiv), (2) $ZnCl_2$ (1.2 equiv), (3) $PdCl_2(PPh_3)_2$ (50 mol %) (52%).

The oxidation potentials of **1**−**4** and **11** measured by cyclic voltammetry are shown in Table 1. The bi-TTF derivatives (**2** and **11**) show two two-electron redox waves and slightly lower donating ability than that of **1**.[8] The cyclic voltammograms of the ter- and quater-TTF derivatives (**3** and **4**) indicated four redox waves, corresponding to one-, two-, one-, and two-electron redox steps in **3** and four two-electron redox steps in **4**, respectively. It is worth noting that the first oxidation potential of **3** is a little larger than that of **1**, whereas that of **4** is slightly smaller than those of **1**- **3**. In addition, the fourth oxidation potential of **4** is larger than the corresponding oxidation peaks of **1-3** and **11**. The HOMO levels (**1**: −6.58, **2**: −6.70, **3**: −6.72, and **4**: −6.53 eV) calculated at the HF/3-21G*//PM3 level[10] show a relatively good correlation between the calculated HOMOs and the first oxidation potentials of **1**-**4**.

Table 1. Redox Potentials[a] of **1**−**4** and **11**

compd	$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$	$E^4_{1/2}$
1	0.52	0.77		
2	0.58	0.85		
3	0.58	0.61	0.82	0.86
4	0.51	0.53	0.88	0.92
11	0.56	0.86		

[a] Conditions: $Bu^n{}_4NClO_4$, benzonitrile, room temperature, Pt working and counter electrodes. Potentials were measured against an Ag/Ag^+ electrode and converted to the value vs SCE ($Fc/Fc^+ = 0.46$ V).

As shown in Figure 2a, the neutral tetramer **4** can adopt a tight helical conformation, having closely situated terminal TTF rings. The calculations of **4** also show fairly independent four TTF moieties, and the calculated HOMO levels of the TTF moieties in **4** locate their own rings. Although the cationic charges in the dication $\mathbf{4}^{2+}$ are mainly localized in

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(6) Physical and spectroscopic data. **2**: red crystals; mp 185.5−186 °C; FAB-MS *m/z* 682 (M^+); ^1H NMR (500 MHz, $CDCl_3$) δ 2.425 (s, 6H), 2.426 (s, 6H), 2.428 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.26* (an asterisk shows a ^{13}C NMR signal overlapped), 19.64, 110.67, 110.82, 122.92, 127.35, 127.83, 131.31; UV λ_{max} (log ϵ) 340 (4.57), 425 (sh, 3.90) nm. **3**, dark violet microcrystals, mp 78−79 °C.; FAB-MS *m/z* 976 ($M^+ + 1$); ^1H NMR (500 MHz, $CDCl_3$) δ 2.427 (s, 12H), 2.435 (s, 6H), 2.436 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.24, 19.26, 19.29, 19.87, 110.13, 110.18, 111.22, 111.65, 122.83, 126.18, 127.11, 127.58, 127.82, 132.27; UV λ_{max} (log ϵ) 338 (4.78), 500 (sh, 3.78) nm. **4**: dark brown microcrystals; mp 132.5−133.5 °C; FAB-MS *m/z* 1270 ($M^+ + 1$); ^1H NMR (500 MHz, $CDCl_3$) δ 2.410 (s, 6H), 2.419 (s, 12H), 2.441 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.13, 19.20, 19.26*, 19.57, 109.83, 110.32, 110.47, 111.37, 121.73, 125.03, 126.10, 126.99, 127.54, 127.57, 127.66, 131.35; UV λ_{max} (log ϵ) 343 (4.86), 520 (sh, 3.81) nm.

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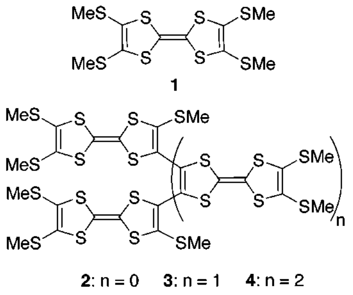

Figure 1. TTF oligomers.

the inside TTF rings, the dication $\mathbf{4}^{2+}$, which is generated by electrochemical oxidation, can be stabilized by the intramolecular stacking of the two TTF rings (Figure 2b). In a similar manner, the tetracation $\mathbf{4}^{4+}$ is stabilized by the face-to-face interaction of the TTF rings. On the contrary, the third and fourth oxidations ($E^{\mathrm{ox}}{}_{1/2}$ = 0.88 and 0.92, respectively) are restrained by the repulsion of positive charges on the terminal TTF units, which makes it more difficult to generate the hexa- and octacations $\mathbf{4}^{6+}$ and $\mathbf{4}^{8+}$.[12]

To clarify the structure of the cationic species derived from TTF oligomers, chemical and electrochemical oxidations of **1**−**4** were carried out. The cationic species $\mathbf{1}^{\bullet+}\cdot\mathrm{ClO_4}^-$, $\mathbf{2}^{2+}\cdot(\mathrm{ClO_4}^-)_2$, $\mathbf{3}^{\bullet3+}\cdot(\mathrm{ClO_4}^-)_3$, and $\mathbf{4}^{4+}\cdot(\mathrm{ClO_4}^-)_4$ were prepared in $\mathrm{CH_2Cl_2}$ in the presence of $\mathrm{Bu^n{}_4NClO_4}^-$ by controlled electrolysis at constant potentials and were characterized by elemental analyses. All cation-radical salts have a moderate solubility in $\mathrm{CH_2Cl_2}$ despite hardly soluble $\mathbf{7}^{2+}\cdot(\mathrm{ClO_4}^-)_2$ under similar conditions.[13] As shown in Figure 3, $\mathbf{1}^{\bullet+}\cdot\mathrm{ClO_4}^-$ (828 nm), $\mathbf{2}^{2+}\cdot(\mathrm{ClO_4}^-)_2$ (820 nm), and $\mathbf{3}^{\bullet3+}\cdot(\mathrm{ClO_4}^-)_3$ (822 nm) indicate similar electronic absorptions, whereas the spectrum of $\mathbf{4}^{4+}\cdot(\mathrm{ClO_4}^-)_4$ has an intense band at 764 nm with a broad band at 1050 nm corresponding to the dimeric structure of $\mathrm{TTF}^{\bullet+}$.[12] Since all spectra were measured over the concentration range of 7.9 × 10^{-6} to 3.8 × 10^{-5} M in $\mathrm{CH_2Cl_2}$, these absorptions are not due to any intermolecular aggregated forms of these cation-radicals. Interestingly, the absorption maximum (820 nm) of the dication $\mathbf{2}^{2+}\cdot(\mathrm{ClO_4}^-)_2$, which contains a head-to-tail arrangement of the transition dipoles, is almost unchanged as compared to that (828 nm) of $\mathbf{1}^{\bullet+}\cdot\mathrm{ClO_4}^-$, although Davydov red shift can be expected theoretically.[14] In contrast, the two transition dipoles of $\mathbf{4}^{4+}\cdot(\mathrm{ClO_4}^-)_4$ interact side-by-side to show Davydov blue shift (764 nm) with the charge-transfer absorption (1050 nm). Consequently, the spectrum of $\mathbf{4}^{4+}\cdot(\mathrm{ClO_4}^-)_4$ indicates a helical interaction as shown in Figure 1b ($n = 4$). Chemical oxidation of **1**−**4** with $\mathrm{AgClO_4}$ or $\mathrm{Fe(ClO_4)_3}$ in $\mathrm{CH_2Cl_2}$ produced the corresponding cation-radicals which indicated similar electronic spectra to those obtained by electrochemical oxidation. The dichloromethane solutions of $\mathbf{1}^{\bullet+}\cdot\mathrm{ClO_4}^-$, $\mathbf{2}^{2+}\cdot(\mathrm{ClO_4}^-)_2$, $\mathbf{3}^{\bullet3+}\cdot(\mathrm{ClO_4}^-)_3$, and $\mathbf{4}^{4+}\cdot(\mathrm{ClO_4}^-)_4$ at room temperature exhibited single ESR signals at g = 2.0075, 2.0075,

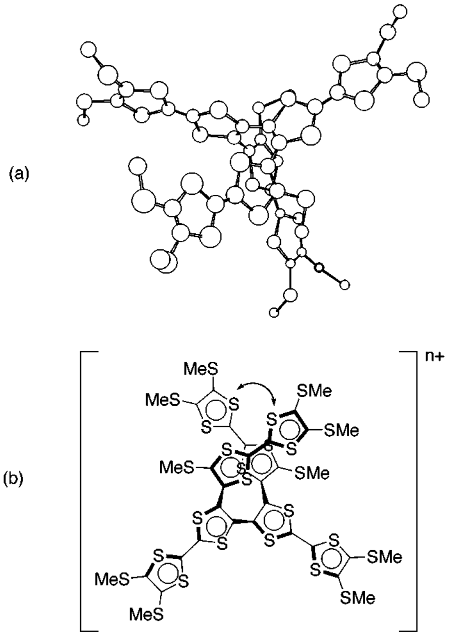

Figure 2. (a) PM3-optimized structure of **4**. Hydrogen atoms are omitted for clarity. (b) An intramolecular interaction (curved arrow) of the TTF units in $\mathbf{4}^{n+}$ (n = 2 and 4).

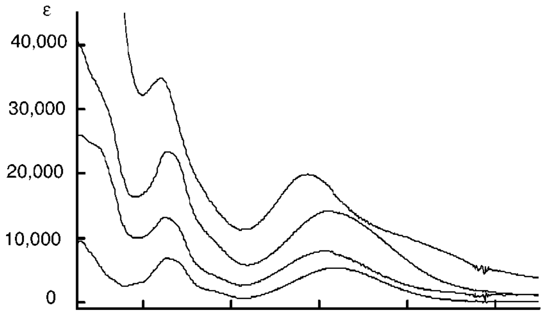

Figure 3. Electronic spectra of $\mathbf{1}^{\bullet+}\cdot\mathrm{ClO_4}^-$, $\mathbf{2}^{2+}\cdot(\mathrm{ClO_4})_2{}^-$, $\mathbf{3}^{\bullet3+}\cdot(\mathrm{ClO_4})_3{}^-$, and $\mathbf{4}^{4+}\cdot(\mathrm{ClO_4}^-)_4$ in $\mathrm{CH_3CN}$.

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(10) The calculations were carried out at the HF/3-21G* level on the PM3[11] optimized geometries using the Gaussian 98 program. HF/3-21G*: Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039. Gaussian 98: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. GAUSSIAN98; Gaussian, Inc.: Pittsburgh, PA, 1998.

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2.0070, and 2.0073, respectively. Therefore, the helical structure of **4**$^{4+}\cdot(\mathrm{ClO_4}^-)_4$ had no effect on the ESR spectra at room temperature. The X-ray structures of the di- and tetracations **4**$^{2+}$ and **4**$^{4+}$ are now under investigation.

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Supporting Information Available: The cyclic voltammograms of compound **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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