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Syntheses and Properties of Novel Dimeric Tetrathiafulvalenes Linked with an Ethenylene or Ethynylene Spacer

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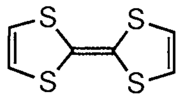
Conjugated dimeric TTFs linked with an ethenylene or ethynylene spacer were prepared as novel electron donors and preferentially formed 1:1 complexes with TCNQF$_4$ and with DDQ, which were more conductive than those of monomeric TTFs.

In the search for highly conductive organic materials, a variety of dimeric tetrathiafulvalene (TTF) donors have been prepared, in which the two TTF units are linked directly[1] or by a spacer group, such as aromatic rings,[2,3] alkyl chains,[4] thioalkyl chains,[5,6] and heteroatoms.[7] These compounds might have an intramolecular interaction between the TTF units, depending on the nature of the linking spacer, and accordingly have a possibility of forming charge-transfer complexes and ion radical salts with controlled stoichiometry, band filling, and crystal structure. However, very few highly conductive complexes have been derived from them. With regard to the intramolecular interaction, conjugated dimeric TTFs are more advantageous, but their designs have been little studied;[3] even the simplest ones carrying an ethenylene or ethynylene spacer, 1,2-di(1,4,5,8-tetrathiafulvalen-2-yl)ethene (**1**) and 1,2-di(1,4,5,8-tetrathiafulvalen-2-yl)ethyne (**2**), are still unknown. Here we report the syntheses and properties of **1** and **2** and their charge-transfer complexes, and compare their properties with those of the related monomeric compounds, such as 2-ethenyl-TTF (**3**)[8] and 2-ethynyl-TTF (**4**).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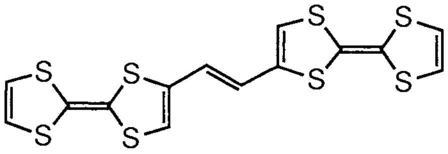
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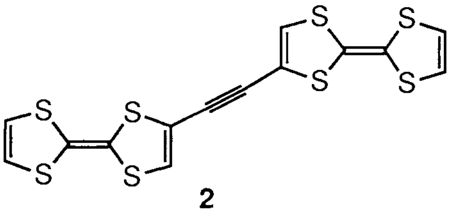
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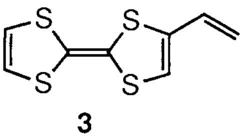
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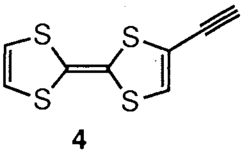
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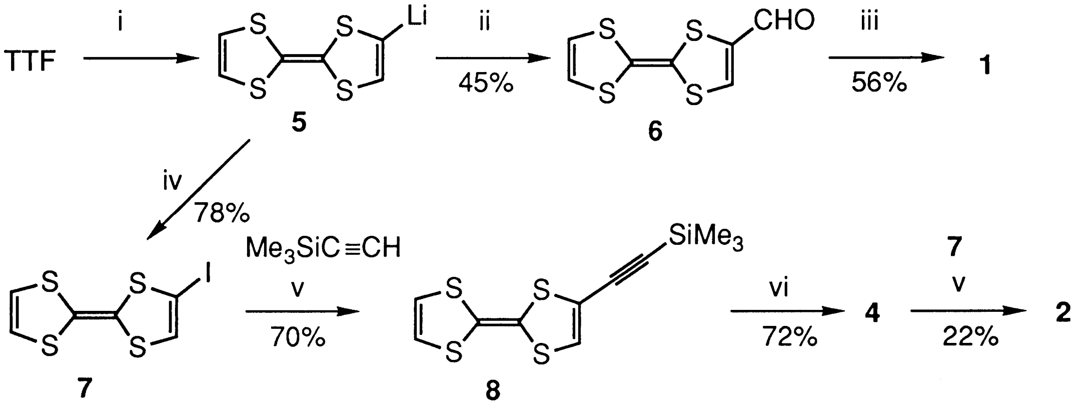
Dimeric tetrathiafulvalenes **1** and **2** were synthesized as shown in Scheme 1. 2-Formyl-TTF (**6**) was prepared in 45% yield by treatment of TTF with LDA, followed by the reaction with *N,N*-dimethylformamide according to a published method,[9] and then subjected to oxidative coupling with a low-valent titanium reagent, generated from TiCl$_4$ and Zn,[10] in refluxing THF to afford **1** in 56% yield.[11] When the coupling



Scheme 1. Reagents and Conditions: i) LDA, ether, -78 °C, 1 h; ii) DMF, RT, overnight; iii) $TiCl_4$, Zn, THF, reflux, 1 h; iv) ICH_2CH_2I, -78 °C then RT, 12 h; v) CuI, Ph_3P, $Pd(PhCN)_2Cl_2$, Et_3N, 60-90 °C, 2-3 h; vi) KOH, aq MeOH, RT 9 h.

reaction was carried out at room temperature, the intermediate 1,2-di(1,4,5,8-tetrathiafulvalen-2-yl)ethane-1,2-diol was isolated in 51% yield. Treatment of the lithiated TTF species **5** with 1,2-diiodoethane gave 2-iodo-TTF (**7**) in 78% yield,[12] which was then reacted with trimethylsilylacetylene in the presence of palladium and copper catalysts[13] to afford 2-trimethylsilylethynyl-TTF (**8**) in 70% yield. The alkaline hydrolysis of **8** gave **4** in 72% yield, which was subsequently coupled with **7** to produce **2** in 22% yield.

The through-bond interaction between the two TTF units in **1** and **2** is demonstrated by their electronic spectral data as shown in Table 1. TTF shows three characteristic absorption peaks at 312, 365, and 450 nm. These peaks are perturbed by introduction of the ethenyl and ethynyl functional groups. The three bands still remain in **3** and **4**, but the two bands of long wavelengths coalesce into one peak and the absorbance markedly strengthens in **1** and **2**, indicating the extensive electronic conjugation of the dimeric compounds. On the other hand, the cyclic voltammetry of **1** and **2** showed the existence of two reversible redox waves of equal heights, each of which corresponded to a two-electron transfer and exhibited no appreciable splitting due to the coulombic repulsion between the two TTF units.[6] The half-wave oxidation potentials, as summarized in Table 1, are anodically shifted, compared with those of TTF. This is principally ascribable to the substituent effects of ethenyl and ethynyl groups, as similarly observed for **3** and **4**.

It is well known that TTF and TCNQ form a 1:1 charge-transfer complex which is metallic owing to the mixed valence states of the stacked components induced by an incomplete charge transfer.[14] TTF also gives 1:1 complexes with $TCNQF_4$[15] and with DDQ[16], which, however, behave like Mott insulators due to a complete charge-transfer. Dimeric TTFs **1** and **2**, unlike TTF, formed no complexes with TCNQ. The difficult

Table 1. Electronic absorption data[a] and half-wave oxidation potentials[b] of **1**-**4**

Compound	λ_{max}/nm(log ε)	$E_{1/2}(1)$/V	$E_{1/2}(2)$/V	ΔE/V
1	310(4.45), 450(3.94)	+0.41	+0.71	0.30
2	310(4.53), 445(3.86)	+0.56	+0.78	0.22
3	318(4.45), 391(3.54), 467sh(2.75)	+0.42	+0.65	0.23
4	320(4.07), 399(3.33), 484sh(2.53)	+0.51	+0.71	0.20
TTF	312(4.12), 365sh(3.31), 450(2.43)	+0.37	+0.60	0.23

a) Measured in CH_2Cl_2. b) Measured at 100 mV/sec in DMF containing 0.1 M Bu_4NClO_4 by using a Pt working electrode and an Ag/AgCl reference electrode.

complexation is explained by their weaker electron donating abilities than that of TTF, as supported by no charge-transfer absorpton band in the solution of the component mixture. Therefore, **1** and **2** need stronger electron acceptors, such as TCNQF$_4$ and DDQ, for complexation. As summarized in Table 2, all complexes showed 1:1 stoichiometry. Even when the acceptor was used in large excess, the 1:1 complexes were formed. This indicates that both TTF moieties electronically interact with each other through the conjugated spacer, and the first formed TTF radical cation prevents the second complexation of another TTF moiety. A complete charge transfer is revealed by the IR spectra of the TCNQF$_4$ complexes; the nitrile vibrational frequencies at around 2200 cm^{-1} are nearly equal to 2201 cm^{-1} for sodium salt of TCNQF$_4$ radical anion.17) If the two TTF moieties are reasonably interactive, they could be in a mixed valence state. In agreement with this consideration, the TCNQF$_4$ and DDQ complexes of **1** exhibited very high electrical conductivities of 3.6 and 1.1×10^{-1} Scm^{-1}, respectively, measured on a pellet sample. The similar complexes of **2** showed somewhat lower values, 1.9×10^{-2} and 8.8×10^{-4} Scm^{-1}. The difference in conductivity between the CT complexes of **1** and **2** may reflect their different crystal structures. In addition, electrocrystallizations of **1** and **2** provided 1:1 radical cation salts with ClO$_4$ counter anion; the conductivities were of the order of 10^{-3} Scm^{-1}. For comparison, 1:1 complexes of monomeric TTFs **3** and **4** with TCNQF$_4$ and with DDQ were produced, but their conductivities were markedly low: **3**•TCNQF$_4$, 2.8×10^{-5} Scm^{-1}; **3**•DDQ, 4.2×10^{-4} Scm^{-1}; **4**•TCNQF$_4$, 2.6×10^{-7} Scm^{-1}, **4**•DDQ, 8.4×10^{-6} Scm^{-1}.

In conclusion, the present dimeric TTFs carrying an ethenylene or ethynylene spacer formed charge-transfer complexes with high electrical conductivities induced by controlled stoichiometry.

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Table 2. Properties of some complexes of **1** and **2**

Complex	D:A a)	Appearance b)	Dp/°C	σ/Scm^{-1} c)	ν_{CN}/cm^{-1} d)
1•TCNQF$_4$	1:1	Black powder	237	3.6	2200
1•DDQ	1:1	Black powder	237	1.1×10^{-1}	2223
1•ClO$_4$	1:1	Black powder e)	255	3.1×10^{-3}	------
2•TCNQF$_4$	1:1	Deep blue powder	178	1.9×10^{-2}	2198
2•DDQ	1:1	Black powder	206	8.8×10^{-4}	2210
2•ClO$_4$	1:1	Black fine crystals f)	242	3.6×10^{-3}	------

a) Determined on the basis of elemental analyses; b) Prepared by a direct method in chlorobenzene; c) Measured on a compressed pellet with a four-probe method; d) Measured on a KBr disk; e) Prepared by electrocrystallization in THF; f) Prepared by electrocrystallization in PhCl.

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11) All new compounds gave satisfactory elemental analyses and were characterized by spectroscopic analyses. The stereochemistry of the double bond of **1** is trans, because its NMR spectrum indicates a single isomer and IR spectrum a strong absorption at 905 cm^{-1} which is assigned as a CH out-of-plane twisting mode of trans disubstituted ethylene. Selective properties of **1**: orange powder; mp 135 °C (dec); MS *m/z* 432 (M^+); IR (KBr) 905 cm^{-1}; ^1H NMR ($DMSO-d_6$) δ 6.42 (s, 2H), 6.75 (s, 4H), 7.01 (s, 2H). **2**: reddish brown fine crystals; mp 92 °C(dec); MS *m/z* 430(M^+); ^1H NMR ($CDCl_3$) δ 6.34 (s, 4H), 6.57 (s, 2H). **4**: orange needles; mp 44-45 °C; MS *m/z* 228 (M^+); IR (KBr) 2156, 3265 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.23 (s, 1H), 6.33 (s, 2H), 6.58 (s, 1H). **7**: orange fine crystals; mp 65-66 °C; MS *m/z* 330 (M^+); ^1H NMR ($CDCl_3$) δ 6.33 (s, 2H), 6.43 (s, 1H). **8**: yellowish orange needles; mp 65-66 °C; MS m/z 300 (M^+); IR (KBr) 2150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.21 (s, 9H), 6.32 (s, 2H), 6.51 (s, 1H).

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