Intramolecular Charge Interaction in the Radical Cations and Dications of Conjugated Tetrathiafulvalene Dimers

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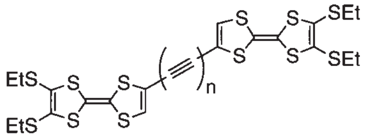
Dimeric TTFs have been synthesized by using palladium-catalyzed reactions. Although TTFs are very sensitive under oxidation conditions, the palladium-catalyzed reactions can be successfully employed for the oxidative coupling of TTF derivatives. The chemical oxidation of dimeric TTFs produced cation-radicals, dications, and tetracations selectively. Electronic spectra of the cation-radicals clearly indicate the magnitude of the intramolecular interaction between two TTF moieties.

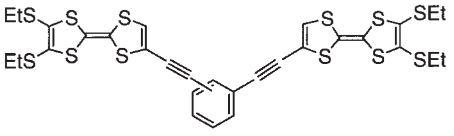
Tetrathiafulvalene (TTF) can be easily oxidized to form a stable cation-radical,[1] and the properties of the cation-radical and its derivatives have been investigated extensively for developing one-dimensional organic metals and superconductors.[2,3] Recently, dimeric TTFs **1** have received considerable attention, because they provide an opportunity to control the stoichiometry, band filling, and molecular assembly in desired conductive complexes.[4,5] In addition, the dimeric TTF can be regarded as building-blocks in supramolecular chemistry, and large 'belt-type' molecules, cage molecules, and 'tweezer-like' molecules have been investigated in order to realize redox sensors, conducting organic magnets, and novel crystal structures.[6]

$$\underset{\mathbf{1}}{\text{TTF—R—TTF}} \xrightarrow{-e^-} \underset{\mathbf{1}^{\bullet+}}{\text{TTF—R—TTF}^{\bullet+}} \underset{\text{or}}{\rightleftarrows} \underset{\mathbf{1}^{\bullet+}}{\text{TTF}^{\bullet+}\text{—R—TTF}}$$

$$\xrightarrow{-e^-} \underset{\mathbf{1}^{2+}}{\text{TTF}^{\bullet+}\text{—R—TTF}^{\bullet+}} \xrightarrow{-2e^-} \underset{\mathbf{1}^{4+}}{\text{TTF}^{2+}\text{—R—TTF}^{2+}}$$



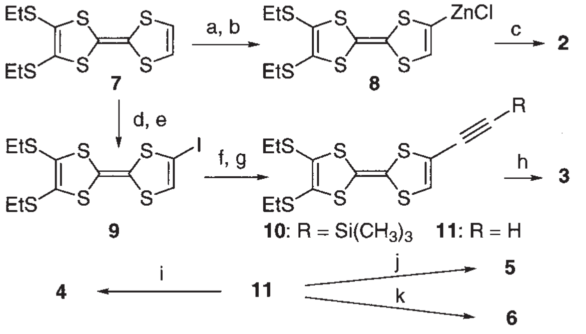
2: n = 0 **3**: n = 1 **4**: n = 2



5: *o*-isomer **6**: *p*-isomer

In the course of our studies on oligomeric TTFs,[7] we synthesized a series of dimeric TTFs (**2**–**6**), and investigated interaction of the two TTF moieties in the neutral, monocationic, dicationic, and tetracationic states **1**, $\mathbf{1}^{\bullet+}$, $\mathbf{1}^{2+}$, and $\mathbf{1}^{4+}$. We now report here an interesting intramolecular charge-transfer interaction in the cation-radicals $\mathbf{2}^{\bullet+}$–$\mathbf{4}^{\bullet+}$, although the cation-radicals $\mathbf{5}^{\bullet+}$ and $\mathbf{6}^{\bullet+}$ show no detectable intramolecular interaction.

Since we have recently developed new synthetic methods of TTF derivatives,[7] the syntheses of **2**–**6** were carried out based on our synthetic methodology using palladium-catalyzed reactions. As shown in Scheme 1, **2** was prepared from bis(ethylthio)-TTF (**7**) directly. Thus, the reaction of **7** with *n*-BuLi (1.06 equiv) at −78 °C in THF, followed by treatment with $ZnCl_2$ (1.5 equiv) afforded the organozinc intermediate **8**. Homocoupling reaction of **8** with $PdCl_2(PPh_3)_2$ (0.5 equiv) at room temperature in THF produced the bi-TTF derivative **2** in 27% yield based on **7**.[8] For the synthesis of **3**, **7** was converted into the iodide **9** in 79% yield. The Sonogashira coupling of the iodide **9** with trimethylsilylacetylene (2.3 equiv) in the presence of $Pd(PPh_3)_4$ (0.12 equiv) and CuI (0.24 equiv) in Et_3N-benzene at room temperature for 4 h afforded the silylethynyl-TTF **10** (93%). Removal of the trimethylsilyl group from **10** with KOH (excess) in aq. MeOH-THF at room temperature for 2 min afforded the ethynyl-TTF **11** (99%). The Sonogashira coupling of **9** with **11** (1.05 equiv) in the presence of $Pd(PPh_3)_4$ (0.105 equiv)-CuI (0.21 equiv) in Et_3N-benzene at room temperature for 4 h produced the bis-TTF acetylene **3** in 45% yield, together with the diacetylene derivative **4** (4%), whereas a similar reaction at 65 °C for 12 h afforded **3** in 96% yield.[9] The yield of **4** was increased, when the reaction of **11** with a Pd(0) complex was carried out in the presence of α-chloroacetone.[10] Thus, treatment of **11** with $Pd(PPh_3)_4$ (0.02 equiv), CuI (0.1 equiv), and $ClCH_2COCH_3$ (1 equiv) in Et_3N-benzene at room temperature for 14 h afforded **4** in 30% yield. For the synthesis of **5** and **6**, the Sonogashira coupling of **11** with *o*- and *p*-diiodobenzene (0.5–0.57 equiv) with $Pd(PPh_3)_4$ (0.1 equiv)-CuI (0.2 equiv) in Et_3N-benzene at room temperature for 14 h led to the corresponding coupling products **5** and **6** in 50 and 77% yields, respectively, based on diiodobenzene.



Reagents and conditions: a) BuLi (1.06 equiv); b) $ZnCl_2$ (1.5 equiv.); c) $PdCl_2(PPh_3)_2$ (0.5 equiv), THF; d) LDA (1.08 equiv); e) $C_6F_{13}I$ (3 equiv); f) HC≡C-TMS (2.3 equiv), $PdCl_2(PPh_3)_2$ (0.12 equiv), CuI (0.24 equiv), Et_3N-benzene; g) KOH, CH_3OH-THF, rt, 2 min; h) **9** (0.95 equiv), $Pd(PPh_3)_4$ (0.1 equiv), CuI (0.2 equiv), Et_3N-benzene; i) $Pd(PPh_3)_4$ (0.02 equiv), CuI (0.1 equiv), $ClCH_2COCH_3$ (1 equiv), Et_3N-benzene; j) *o*-diiodobenzene (0.57 equiv), $Pd(PPh_3)_4$ (0.1 equiv), CuI (0.2 equiv), Et_3N-benzene; k) *p*-diiodobenzene (0.5 equiv), $Pd(PPh_3)_4$ (0.1 equiv), CuI (0.2 equiv), Et_3N-benzene.

Scheme 1. Syntheses of **2**–**6** starting from **7**.

As summarized in Table 1, the cyclic voltammetric analysis indicates that the planar **2**[11] has three reversible redox waves at 0.52, 0.63, and 0.90 V corresponding to two one-electron and a two-electron processes. Thus, the first oxidation of **2** forms a cation-radical $\mathbf{2}^{\bullet+}$ which is stabilized *via* conjugation like $\mathbf{1}^{\bullet+}$. In contrast, the compounds **3**–**6** reveal two two-electron redox waves, reflecting a weak interaction of two TTF moieties, although **3**–**6** can be expected to possess a planar π-conjugated structure.[11] Interestingly, hexamethylthio-biTTF (**12**) shows oxidation potentials at 0.58 and 0.85 V, presumably due to the unfavorably twisted π-conjugation of the two TTF moieties.[7,12]

Table 1. Redox potentials of **2**–**6** and **12**[a]

Compound	$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$
2	0.52	0.63	0.90
3	0.57	0.88	
4	0.58	0.88	
5	0.55	0.83	
6	0.54	0.84	
12[b]	0.58	0.85	

[a]Condition: n-Bu_4NClO_4, benzonitrile, room temperature, Pt working and counter electrodes. Potentials were measured aginst an Ag/Ag^+ electrode and converted to the value *vs* SCE ($Fc/Fc^+ = 0.46$ V). [b]Ref. 7.

Although the solid-state properties of the radical-cations of TTF and its derivatives have been widely studied, the intramolecular interaction of TTF moieties in the cation radicals of dimeric TTFs in solution was investigated in only limited cases[13] due to the intermolecular stacking and insolubility of the cation radicals in solution. Since $\mathbf{2}^{\bullet+}$–$\mathbf{6}^{\bullet+}$, $\mathbf{2}^{2+}$–$\mathbf{6}^{2+}$, and $\mathbf{2}^{4+}$–$\mathbf{6}^{4+}$ are soluble in organic solvents, we examined a comparison of the electronic spectra of $\mathbf{2}^{\bullet+}$–$\mathbf{6}^{\bullet+}$, $\mathbf{2}^{2+}$–$\mathbf{6}^{2+}$, and $\mathbf{2}^{4+}$–$\mathbf{6}^{4+}$ in diluted solutions ($<10^{-4}$ M), which exclude the intermolecular interaction. We expected that electronic spectra of radical cations reflect a static interaction, whereas the CV analysis shown in Table 1 reveals a dynamic process corresponding to a strong interaction. As shown in Table 2, $\mathbf{2}^{\bullet+}$–$\mathbf{4}^{\bullet+}$ exhibit absorption maxima at *ca.* 450 and 780 nm, together with very broad long wavelength CT-absorptions at 1400, 1300, and 1200 nm, respectively. In contrast, $\mathbf{5}^{\bullet+}$ and $\mathbf{6}^{\bullet+}$ have absorptions at *ca.* 450 and 800 nm without CT-bands. These results clearly indicate that $\mathbf{2}^{\bullet+}$–$\mathbf{4}^{\bullet+}$ exhibit intramolecular CT-interaction between the TTF-unit and its cation-radical, whereas $\mathbf{5}^{\bullet+}$ and $\mathbf{6}^{\bullet+}$ show no CT-interaction. Interestingly, the magnitude of the CT-interaction is $\mathbf{2}^{\bullet+} > \mathbf{3}^{\bullet+} > \mathbf{4}^{\bullet+}$, reflecting the distance between the two TTF units. It is worth noting that the longest absorption maxima of the dications $\mathbf{2}^{2+}$, $\mathbf{3}^{2+}$, and $\mathbf{4}^{2+}$ exhibit a bathochromic shift of 44, 30, and 14 nm, respectively, from the corresponding absorption maxima of $\mathbf{2}^{\bullet+}$, $\mathbf{3}^{\bullet+}$, and $\mathbf{4}^{\bullet+}$ owing to the head-to-tail orientation of the two cation-radicals (Davydov red shift).[13] To our knowledge, this is the first example of the Davydov red shift observed in TTF cation-radicals.

Table 2. Electronic spectral data of the cationic species derived from **2**–**6**[a]

Compound	λ_{max} nm ($\log \varepsilon$)[b]
$\mathbf{2}^{\bullet+}$	266 (4.39), 446 (4.13), 772 (3.87), 1400br (3.1)
$\mathbf{2}^{2+}$	276 (4.28), 438 (4.27), 816 (4.22), 1098sh (3.62)
$\mathbf{2}^{4+}$	308sh (4.28), 442 (4.02), 680 (4.40)
$\mathbf{3}^{\bullet+}$	306 (4.45), 450 (4.16), 778 (3.89), 1300br (3.05)
$\mathbf{3}^{2+}$	278 (4.41), 446 (4.33), 808 (4.29)
$\mathbf{3}^{4+}$	274 (4.48), 440 (4.07), 688 (4.48)
$\mathbf{4}^{\bullet+}$	326 (4.58), 472 (4.24), 790 (3.93), 1200br (2.92)
$\mathbf{4}^{2+}$	452 (4.39), 470 (4.39), 804 (4.26)
$\mathbf{4}^{4+}$	292sh (4.47), 444 (4.11), 688 (4.56)
$\mathbf{5}^{\bullet+}$	274 (4.63), 446 (4.12), 802 (3.88)
$\mathbf{5}^{2+}$	274 (4.61), 448 (4.32), 790 (420)
$\mathbf{5}^{4+}$	276sh (4.60), 452 (4.07), 658 (4.36)
$\mathbf{6}^{\bullet+}$	334 (4.78), 450 (4.25), 790 (3.91)
$\mathbf{6}^{2+}$	334 (4.68), 452 (4.37), 796 (4.24)
$\mathbf{6}^{4+}$	320 (4.63), 462 (4.23), 688 (4.43)

[a]Measured in CH_3CN-CH_2Cl_2 (1 : 4) using $Fe(ClO_4)_3 \cdot 6H_2O$ as the oxidation reagent, sh: shoulder, br: broad. [b]Calculated assuming quantiative oxidation of the neutral species.

In conclusion, we have disclosed a novel intramolecular interaction of the two TTF moieties in the cation radical state. We hope to use this information to design new, valuable extended TTF oligomers.

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8 All new compounds gave satisfactory spectral data. **2**: orange crystals, mp 161.0–161.9 °C; FAB-MS m/z 646 (M^+); ^1H NMR ($CDCl_3$) δ 1.32 (t, $J = 7.3$ Hz, 6H), 1.33 (t, $J = 7.3$ Hz, 6H), 2.86 (q, $J = 7.3$ Hz, 4H), 2.87 (q, $J = 7.3$ Hz, 4H), 6.22 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 15.06, 15.07, 30.6, 110.6, 111.2, 118.0, 126.9, 127.9, 128.4. **3**: red crystals, mp 122.8–123.5 °C (decomp.); FAB-MS m/z 672 (M^+); ^1H NMR ($CDCl_3$) δ 1.31 (t, $J = 7.4$ Hz, 6H), 1.32 (t, $J = 7.4$ Hz, 6H), 2.85 (q, $J = 7.4$ Hz, 4H), 2.86 (q, $J = 7.4$ Hz, 4H), 6.57 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 15.0, 30.5, 84.4, 110.2, 111.8, 114.7, 126.3, 127.7, 128.1. **4**: red crystals, mp 123–123.5 °C (decomp.); TOF-MS m/z 694 (M^+); ^1H NMR ($CDCl_3$) δ 1.31 (t, $J = 7.4$ Hz, 6H), 1.32 (t, $J = 7.4$ Hz, 6H), 2.85 (q, $J = 7.4$ Hz, 4H), 2.86 (q, $J = 7.4$ Hz, 4H), 6.71 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 15.0, 30.6, 75.2, 77.8, 110.9, 111.3, 114.7, 127.6, 128.2, 129.5. **5**: orange solid, mp 124–125 °C (decomp); FAB-MS m/z 771 ($M^+ + 1$); ^1H NMR ($CDCl_3$) δ 1.30–1.34 (m, 12H), 2.83–2.90 (m, 8H), 6.70 (s, 2H), 7.29–7.30 (m, 2H), 7.42–7.44 (m, 2H). **6**: red solid, mp 174.5–176 °C (decomp.); FAB-MS m/z 770 (M^+); ^1H NMR ($CDCl_3$) δ 1.31 (t, $J = 7.3$ Hz, 6H), 1.32 (t, $J = 7.3$ Hz, 6H), 2.85 (q, $J = 7.3$ Hz, 4H), 2.86 (q, $J = 7.3$ Hz, 4H), 6.56 (s, 2H), 7.38 (s, 4H).

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