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Aggregation of star-shaped tris(tetrathiafulvalenylethynyl) benzene in solution and in the solid state

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Abstract—Neutral hexabutylthio-1,3,5-tris(tetrathiafulvalenylethynyl)benzene aggregates in CD_3CN–$CDCl_3$ and $CDCl_3$, whereas stronger stacking of the cationic counterparts in solution has been observed. In the solid state, X-ray analysis of hexamethylthio-1,3,5-tris(tetrathiafulvalenylethynyl)-benzene shows a columnar structure, reflecting the threefold face-to-face stacking interaction of the TTF units.

Tetrathiafulvalenes (TTFs) have attracted much interest due to their electron-donating ability, which have been used for the synthesis of new organic metals and superconductors,[1,2] and recently for supramolecular architectures.[3,4] The most remarkable property of TTF and its derivatives is their great facility for molecular association in the radical cation state as well as the one-dimensional column formation of the radical cations to give a conduction path in organic metals. In general, two or more neutral TTF molecules stack with S···S interactions in the solid state to afford a dimeric or columnar structure (Fig. 1).[5] However, neutral TTF dissociates into monomers in solution through van der Waals interactions. The radical cation of TTF and neutral TTF form a mixed valence state $(TTF)_2^{\cdot+}$, both in solution and in the solid state, and the mixed valence dimer is stabilized by a large exchange interaction.[6] The metallic conductivities of organic radical salts require a stacking structure of $(TTF)_n^{\cdot+}$.[2a] Two radical cations can also form the stable dimer $(TTF^{\cdot+})_2$, which is stabilized by exchange and spin–spin interactions in solution and in the solid state.[6]

Although recent investigations have been carried out into the aggregation of large cyclic and helical molecules in solution and in the solid state for the construction of supramolecular wires and channels,[7,8] only a few of these studies reported on the self-assembly of star-shaped molecules such as tri-, tetra- and hexa(ethynyl)benzenes.[9] Our approach to anchoring the star molecules in solution and in the solid state is to introduce TTF units as terminal substituents of poly(ethynyl)benzenes. Thus, the title compound **1** dimerizes in solution and in the solid state because three neutral TTF units or their cationic counterparts interact cooperatively to form stacking structures (**2** and **3**).

To investigate aggregation properties of **1**, three alkylthio derivatives **1a–c** have been synthesized (Scheme 1). The reaction of 1,3,5-triethynylbenzene (**4**) with 4,5-bis(methylthio)-4′-iodo-TTF (**5a**)[10] under the Sonogashira conditions afforded **1a** in 75% yield.[11] For the synthesis of **1b**,**c**, we employed a different combination of the acetylene and iodide components. Thus, the Sonogashira coupling of ethynyl-TTF (**6b** or **6c**)[12] with 1,3,5-triiodobenzene proceeded smoothly to produce **1b** or **1c** in 89% or 92% yield. In a similar manner, the reaction of **6b** with 1,3-diiodobenzene under the Sonogashira conditions afforded **7b** in 63% yield. The tris–TTF derivative **1a** is hardly soluble in C_6D_6 and $CDCl_3$, whereas **1b** and **1c** are moderately and highly soluble in C_6D_6 and $CDCl_3$, respectively.

Interestingly, the ^1H NMR spectra of **1c** in $CDCl_3$–CD_3CN (v/v = 7:3) indicate either a concentration or a temperature dependence. At 20 °C, the chemical shift of the aromatic proton H_a in **1c** varied from δ 7.513 to 7.470 as the concentration changed from 0.462 to

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Keywords: Aggregation; Tetrathiafulvalene; Face-to-face interaction; X-ray analysis.

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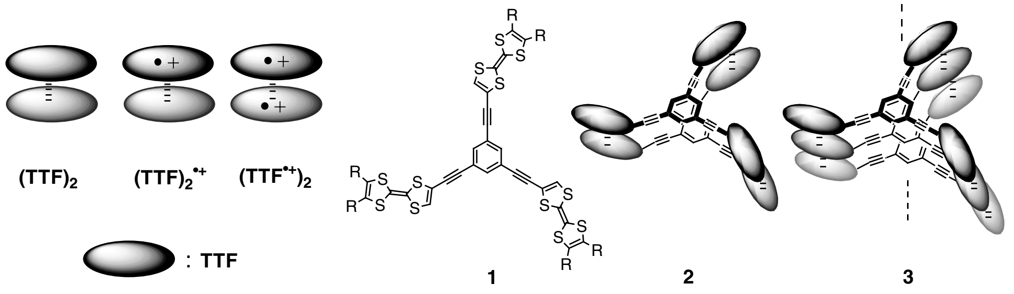
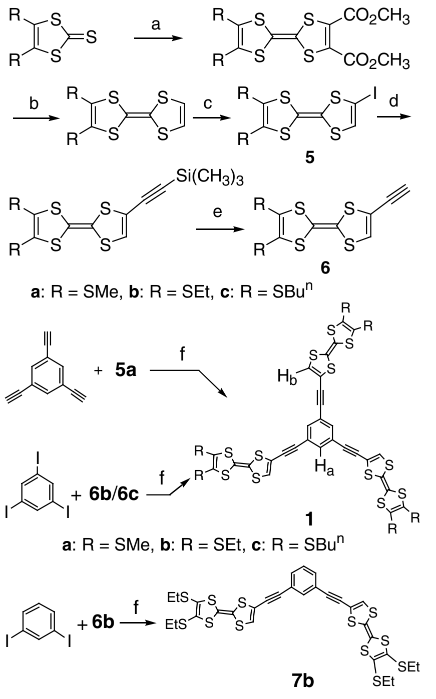


Figure 1. Face-to-face interaction between TTFs.



Scheme 1. Reagents and conditions: (a) dimethyl 1,3-dithiole-2-one-4,5-dicarboxylate, $P(OEt)_3$, 60 °C, 4 h; (b) LiBr·H_2O, HMPA, 60–150 °C, 1 h; (c) Bu^nLi, THF, −90 °C; then $C_6F_{13}I$, −90 °C to rt; (d) trimethylsilylacetylene, $Pd(PPh_3)_4$, CuI, Et_3N; (e) KOH, H_2O, MeOH, THF; (f) $Pd(PPh_3)_4$, CuI, Et_3N, benzene.

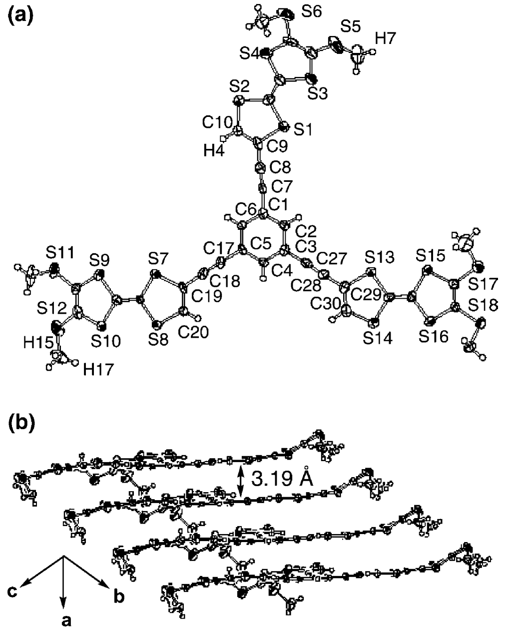
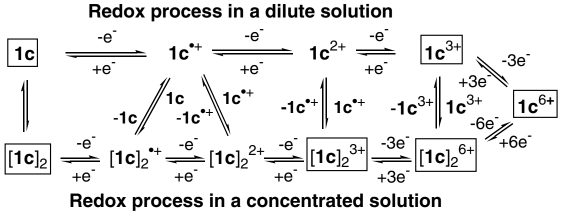


Figure 2. ORTEP drawing of **1a**. (a) Top view; (b) packing structure.

10.0 mM in $CDCl_3$–CD_3CN. In the case of the 8.44 mM solution, the chemical shift of H_a varied from δ 7.477 to 7.404 as the temperature changed from 20 to −30 °C. In a similar manner to that of the H_a-proton, the H_b-proton showed a concentration and temperature dependence. This interesting phenomenon indicates that the star molecule **1c** self-associates in solution. The ^1H NMR spectra of **1c** in $CDCl_3$ show a similar behavior in spite of weaker association. Since a monomer–dimer equilibrium can be anticipated as the predominant process in this self-association, the ^1H NMR measurements were used to determine the dimerization constant, K_2 and to calculate the other thermodynamic parameters ΔG, ΔH, and ΔS [**1c** in $CDCl_3$–CD_3CN (v/v = 7:3): $K_2 = 5.01$ (298 K), $\Delta G = -0.87$ kcal/mol (298 K), $\Delta H = -3.98$ kcal/mol, $\Delta S = -10.3$ cal/mol K]. The fact that tetraethylthio-1,2- and -1,4-bis(tetrathiafulvalenylethynyl)benzenes[12] show no association behavior under similar conditions suggests that the association depends mainly on the S···S interaction of the terminal TTF groups.

The stacking properties of **1** have been also observed by X-ray analysis of **1a**.[13] Recrystallization of **1a** from CS_2/hexane yielded single crystals. Although the crystals contained 40 molar % of disordered CS_2 in the crystal lattice, the X-ray analysis at −90 °C gave fairly good results for the structural determination. As shown in Figure 2, **1a** adopts an almost planar 1,3,5-triethynylbenzene core. The three boat-shaped TTF-moieties have a slightly twisted conformation with upside carbons of C10, C20, and C30, and the dihedral angles between the central benzene ring and TTF moieties are 3.3° (C6–C1–C9–C10), 0.9° (C4–C5–C19–C20), and 18° (C4–C3–C29–C30), respectively. This molecule stacks along the *b*-axis, and the face-to-face distance between the C4 and the neighboring molecular plane is 3.192 Å. There are seven intermolecular S···S and S···H contacts, which are less than the sum of van der Waals radii (S 1.85 and H 1.20 Å), in spite of no short intramolecular contacts. Of the three S···S contacts, two are intrastack interac-



Scheme 2. Possible redox pathways of **1c** in dilute and concentrated solutions. The species in the squares were observed by CV analysis of **1c**.

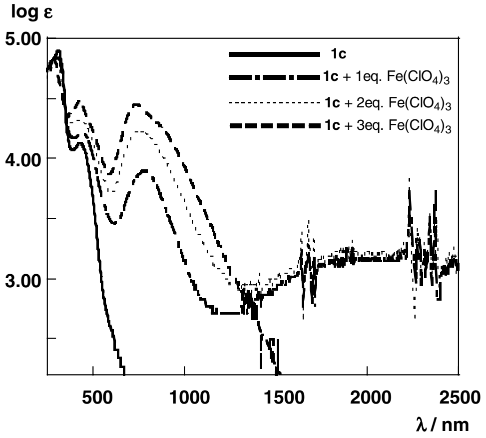


Figure 3. Electronic spectra of **1c**, **1c** + 1 equiv of $Fe(ClO_4)_3$, **1c** + 2 equiv of $Fe(ClO_4)_3$, and **1c** + 3 equiv of $Fe(ClO_4)_3$ in CH_2Cl_2/CH_3CN (4/1).

tions [S8···S10 3.483 Å and S11···S11 3.390 Å], and the other one is an interstack interaction [S7···S18 3.594 Å]. In the case of S···H contacts, three are intrastack interactions and the other one is an interstack hydrogen bond. Although MO calculations at the RHF/3-21G level show that a C_{3h} arrangement is the most stable conformation for **1** (R = H), the X-ray structure for **1a** is oriented unsymmetrically, presumably due to the intra- and interstack S···S and S···H interactions.

Cyclic voltammetric (CV) analysis[14] indicates that **1c** in dilute CH_2Cl_2 solution (0.011 mM, 100 mV/s) has two reversible redox waves at $E_1^{1/2} = 0.50$ and $E_2^{1/2} = 0.85$ V, corresponding to two three-electron redox waves. The first oxidation of **1c** forms **1c**$^{3+}$, and the second oxidation affords **1c**$^{6+}$. Since **7b** shows the redox waves at 0.53 and 0.83 V under similar conditions, the CV data in dilute solutions revealed no intra- or intermolecular interactions between the TTF units in **1c**. In contrast, CV analysis of **1c** in a concentrated CH_2Cl_2 solution (5.4 mM, 25 mV/s) displays three reversible redox waves at $E_1^{1/2} = 0.42$, $E_2^{1/2} = 0.60$, and $E_3^{1/2} = 0.93$ V. The possible oxidation steps are summarized in Scheme 2. The three redox waves in the concentrated solution reflect the formation of (**1c**)$_2$, (**1c**)$_2^{3+}$, and (**1c**)$_2^{6+}$ via the association of **1c** and/or its cationic counterparts.

As suggested by CV analysis, the cationic species derived from **1c** exhibit stronger self-association in solution than the neutral **1c**. As reported previously,[15] oxidation of **1c** with 1–3 equiv of $Fe(ClO_4)_3 \cdot 6H_2O$ in CH_2Cl_2–CH_3CN (4:1) affords the corresponding cationic species, because the oxidation state depends on the amount of $Fe(ClO_4)_3 \cdot 6H_2O$ employed. Interestingly, the electronic spectra of **1c**$^{\cdot+}$ and **1c**$^{2+}$ showed very broad absorption at 2000 nm (Fig. 3), although **7b**$^{\cdot+}$ and **7b**$^{2+}$ prepared by oxidation of **7b** with $Fe(ClO_4)_3 \cdot 6H_2O$ exhibited no long wavelength absorption around 1500–2000 nm. On the basis of the electronic spectra of 1,8-bis(tetrathiafulvalenyl)naphthalene and its cationic species, the very broad band at 2000 nm was assigned to the intermolecular charge-resonance (CR) absorption of (**1c**)$_2^{2+}$ or (**1c**)$_2^{4+}$ formed by the face-to-face stacking of **1c**$^{\cdot+}$ or **1c**$^{2+}$.[15] In addition, the tri-cation **1c**$^{3+}$ exhibited an absorption maximum at 726 nm with a shoulder at 846 nm, reflecting the formation of the π-dimer triad; the former can be assigned to the face-to-face stacked absorption of the TTF$^{\cdot+}$ units (Davidov blue shift), and the latter to the intermolecular CT absorption of the stacked TTF$^{\cdot+}$ units.[6] Since **1c**$^{\cdot+}$, **1c**$^{2+}$, and **1c**$^{3+}$ exhibit self-association in very dilute solutions over the concentration range of 0.0676–0.135 mM,[16] a strong π–π stacking of these cationic species can be expected in solution.

Interestingly, oxidative doping of a pellet of **1a** with vaporous iodine led to semiconducting black salt formation ($\sigma_{rt} = 3.6 \times 10^{-4}$ S/cm), whereas a similar doping of **1c** resulted in the conducting liquid as the salt. Further studies on the stacking ability of oligomeric TTFs for constructing unique supramolecular structures are in progress.

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11. Physical and spectroscopic data. Compound **1a**: red needles, mp 182.5 °C (DSC), MALDI-TOF MS m/z 1032 (M^+); ^{1}H NMR ($CS_2/CDCl_3 = 2/1$) δ 7.44 (s, 3H), 6.57 (s, 3H), 2.43 (s, 9H), 2.42 (s, 9H); ^{13}C NMR ($CS_2/CDCl_3 = 2/1$) δ 134.1, 127.8, 127.4, 125.6, 123.0, 115.3, 112.9, 109.5, 91.4, 82.4, 19.23, 19.19. Compound **1b**: red solid, mp 69 °C (DSC), MALDI-TOF MS m/z 1116 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.43 (s, 3H), 6.59 (s, 3H), 2.88–2.83 (m, 12H), 1.33–1.30 (m, 18H). Compound **1c**: red solid, mp 61.5 °C (DSC), MALDI-TOF MS m/z 1286 (M^+); ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.44 (s, 3H), 6.60 (s, 3H), 2.83 (t, 6H, $J = 7.3$ Hz), 2.82 (t, 6H, $J = 7.3$ Hz), 1.65–1.59 (m, 12H), 1.48–1.40 (m, 12H), 0.93 (t, 9H, $J = 7.3$ Hz), 0.92 (t, 9H, $J = 7.3$ Hz). Compound **7b**: red solid, mp 120–121.5 °C, FABMS m/z 771 (M^++1); ^{1}H NMR ($CDCl_3$) δ 7.54 (s, 1H), 7.41 (d, 2H, $J = 7.8$ Hz), 7.31 (t, 1H, $J = 7.8$ Hz), 6.57 (s, 2H), 2.86 (q, 4H, $J = 7.4$ Hz), 2.85 (q, 4H, $J = 7.3$ Hz), 1.33 (t, 6H, $J = 7.4$ Hz), 1.32 (t, 6H, $J = 7.3$ Hz).
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