Bis(tetrathiafulvaleno)octadehydro[20]annulene with Multi-functionality

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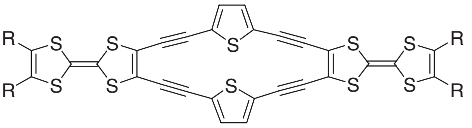
Sulfur-bridged octadehydro[20]annulene **1c** annelated with two TTF rings was synthesized and its multi-functional properties were ascertained. The annulene exhibits paratropicity, solvatochromism, electrochromism and multi-redox potentials in solution, and its cation radical in the solid state shows self-association and electric conductivity.

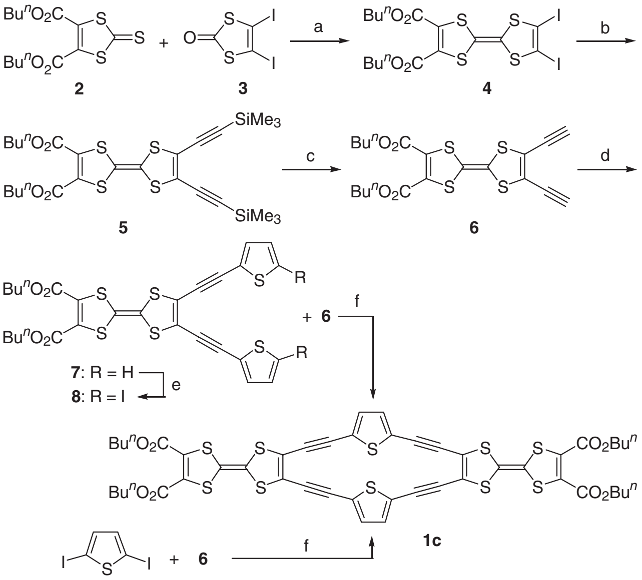
There has been considerable current interest in supramolecular tetrathiafulvalene (TTF) chemistry.[1,2] Since TTF can be reversibly oxidized to its cation radical and dication, a supramolecular system containing TTF moieties may be able to be used in redox sensors, devices, and switches. In addition, TTF oligomers linked by π-spacers are expected to show intra- and intermolecular interactions between the TTF units, and hence these molecules may exhibit multi-functionalities such as electric conductivity, solvatochromism, electrochromism, and magnetic properties.[1c] We designed sulfur-bridged bis(tetrathiafulvaleno)octadehydro[20]annulene **1** as a candidate for multi-functionality. Although MO calculations for **1a** show a nonplanar structure due to steric repulsion between the bulky sulfur bridges, intramolecular interaction between the TTF units and annulene moiety can be expected in the ground states of **1a**, **1a**$^{\bullet+}$, and **1a**$^{2+}$.



1a: R = H
1b: R = SBu^n
1c: R = CO$_2$Bu^n

We first attempted to synthesize **1b**. However, **1b** was an extremely unstable compound, and the formation of **1b** was only confirmed by its ^{1}H NMR and mass spectra. Therefore, **1c** was synthesized, because the electron-withdrawing ester substituents on the TTF units can stabilize the dimeric TTF systems.

The phosphite-mediated coupling of **2**[3] with **3**[4] yielded **4** (57%).[5] Sonogashira coupling of **4** with trimethylsilylacetylene (TMSA) afforded **5** (64%). Deprotection of **5** with KF and 18-crown-6 in aq. THF, followed by coupling with 2-iodothiophene gave **7** (81%). Reaction of **7** with lithium 2,2,6,6-tetramethylpiperidide (LiTMP) in the presence of $C_6F_{13}I$ led to **8** (69%). For the construction of the [20]annulene skeleton, we employed two pathways. Cross-coupling of **8** with **6** (2 equiv.) in the presence of Pd(PPh$_3$)$_4$ (0.5 equiv.), CuI (1 equiv.), and Et$_3$N (10 equiv.) in benzene at room temperature for 2 h produced **1c** in 28% yield, whereas reaction of 2,5-diiodothiophene with **6** (1.5 equiv.) in the presence of Pd(PPh$_3$)$_4$ (0.5 equiv.), CuI (1 equiv.), and Et$_3$N (10 equiv.) in benzene at room temperature for 2 h afforded **1c** in 10% yield. Although the yield of the second pathway is lower than that of the first, the second route has an advantage in that it produces a considerable amount of **1c** quickly.



Scheme 1. Conditions: (a) P(OMe)$_3$, toluene, reflux, 4 h; (b) TMSA, Pd(PPh$_3$)$_4$, CuI, diisopropylamine, benzene, rt, 15 h; (c) KF, 18-crown-6, THF–H$_2$O (98:2), 0 °C, 1 h; (d) 2-iodothiophene, Pd(PPh$_3$)$_4$, CuI, Et$_3$N, benzene, rt, 15 h; (e) LiTMP, $C_6F_{13}I$, THF, −78 °C to rt; (f) Pd(PPh$_3$)$_4$, CuI, Et$_3$N, benzene, rt, 2 h.

The ^{1}H NMR spectrum of **1c** shows an up-field shift of the thiophene protons at δ 6.90 compared with those of **7** (δ 7.02, 7.31, and 7.37), reflecting a paramagnetic ring current of the central 4nπ ring. The cyclic conjugation in **1c** also reduces the acetylenic character of the C≡C bonds, as shown by the IR data (**1c**: $\nu_{C\equiv C} = 2158\ \mathrm{cm}^{-1}$; **7**: $\nu_{C\equiv C} = 2171\ \mathrm{cm}^{-1}$; **8**: $\nu_{C\equiv C} = 2173\ \mathrm{cm}^{-1}$). As predicted by MO calculations, **1c** is a nonplanar molecule that exhibits no aggregation behavior. Accordingly, vapor pressure osmometric (VPO) analysis of **1c** showed no self-association, although **1c** has a partial dipole based on the ester groups which may work cooperatively for aggregation.[6] Since **1a** is presumed to be mobile based on calculations,[7,8] self-association of **1c** in solution may be inhibited by the movement of the sulfur bridges. Interestingly, **1c** shows solvatochromism, and the colors of **1c** in CS$_2$ and THF are violet ($\lambda_{\max} = 533$ nm) and red ($\lambda_{\max} = 500$ nm), respectively.

As shown in Figure 1, LDI-TOF MS of **1c** showed a peak at $m/z = 1064.8$ (**1c**: M$^+$ = 1063.99), together with small peaks at 2129.9 and 3192.6 corresponding to MM$^+$ ($m/z = 2127.98$) and MMM$^+$ ($m/z = 3191.97$), respectively. Thus, laser irradiation on a thin film of **1c** led to the formation of aggregates of its cation radical.

The TTF units in **1c** are redox-active and show two reversible two-electron redox waves by cyclic voltammetric (CV) analysis (Table 1). The TTF derivatives **7** and **8**, with electron-withdrawing ester and acetylene groups, show higher oxidation potentials due to the reduced donor ability. In the case of **1c**,

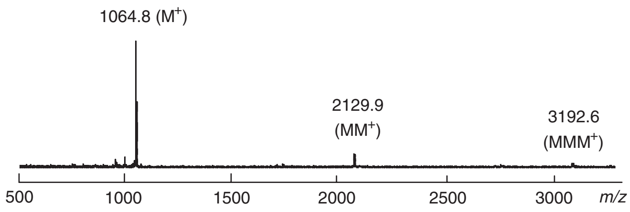


Figure 1. LDI-TOF MS of the tetrathiafulvaleno[20]annulene **1c**.

Table 1. Redox potentials of **1c**, **7**, **8**, and TTF referred to Ag/Ag$^+$.[a]

Compound	$E^{ox1}{}_{1/2}$ /V	$E^{ox2}{}_{1/2}$ /V	$\Delta E(E^2 - E^1)$ /V
1c	0.57 (2e)[b]	0.78 (2e)[b]	0.21
7	0.53 (1e)[b]	0.83 (1e)[b]	0.30
8	0.56 (1e)[b]	0.83 (1e)[b]	0.27
TTF	0.11 (1e)[b]	0.39 (1e)[b]	0.28

[a]Conditions: 0.1 M Bu_4NClO_4 in *o*-dichlorobenzene, Ag/Ag$^+$ reference electrode, Pt working and counter electrodes, 100 mV s^{-1}; the oxidation potential of ferrocene, Fc/Fc$^+$ = 0.29 V referred to Ag/Ag$^+$. [b]The number of electrons transferred.

Table 2. UV–vis data of **1c**, **1c**$^{\bullet+}$, **1c**$^{2+}$, and **1c**$^{4+}$ in benzene/CH_3CN (4:1).[a]

Compound	Color	λ_{max} nm ($\log \varepsilon$)
1c[b]	red	310 (4.85), 371 (4.84), 504 (3.82)
1c$^{\bullet+}$[c]	orange yellow	311 (4.84), 371 (4.76), 819 (3.86), ca. 1850 (2.90)
1c^{2+}[d]	brownish yellow	315 (4.71), 373 (4.62), 419 (4.62), 862 (4.25)
1c^{4+}[e]	bluish green	315 (4.72), 391 (4.61), 707 (4.23)

[a]Cations **1c**$^{\bullet+}$, **1c**$^{2+}$, and **1c**$^{4+}$ were prepared by mixing **1c** with 1, 2, and 4 equiv. $Fe(ClO_4)_3 \cdot 3H_2O$ in benzene/CH_3CN (4:1), and the ε-values were determined by quantitative formation of cations. [b]7.30×10^{-5} M. [c]1.90×10^{-4} M. [d]1.59×10^{-4} M. [e]1.11×10^{-4} M.

the first oxidation potential ($E^{ox1}{}_{1/2}$) is higher than that of **7**, whereas the second oxidation potential is lower than that of **7**. The higher $E^{ox1}{}_{1/2}$ of **1c** reflects a lower HOMO, and the lower $E^{ox2}{}_{1/2}$ of **1c** exhibits reduced on-site Coulomb repulsion.

As expected from the CV data, **1c** can be chemically oxidized to the corresponding cationic species. Unfortunately, **1c**$^{\bullet+}$, **1c**$^{2+}$, and **1c**$^{4+}$ are fairly unstable compounds, presumably due to ring strain of the 20-membered ring. However, the UV–vis spectra of **1c**$^{\bullet+}$, **1c**$^{2+}$, and **1c**$^{4+}$ in solution could be satisfactorily measured. Oxidation of **1c** with 1, 2, and 4 equiv. of $Fe(ClO_4)_3$ in benzene–CH_3CN (4:1) formed colored solutions of the corresponding cations (Table 2). The intramolecular interaction between TTF and TTF$^{\bullet+}$ is weak but observed in **1c**$^{\bullet+}$.[9] Thus, the major cation radical charge is localized on one ring, and the other participates in delocalization to accept a partial charge density [class II].[10] The long absorption wavelength in **1c**$^{\bullet+}$ is assigned to the intramolecular CT band. In the case of **1c**$^{2+}$, intermolecular π-dimer formation (blue shift of the absorption maximum)[11] did not take place in solution, because the longer cation radical absorption was observed at 862 nm,[11,12] presumably due to the nonplanar structure of **1c**$^{2+}$. Interestingly, **1c** shows an electric conductivity of $\sigma_{rt} = 2.64 \times 10^{-3}$ S·cm^{-1} after doping with iodine.[13]

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5 Physical and spectroscopic data of new compounds. **1c**: black fine cryst., mp (DSC) 137.6 °C (dec.), LDI-TOF MS *m/z* 1064.5 (M$^+$); ^{1}H NMR (C_6D_6) δ 0.72 (t, 6H), 1.12 (sextet, 4H), 1.33 (quint, 4H), 3.97 (t, 4H), 6.30 (s, 4H); ^{13}C NMR (CS_2/C_6D_6=9/1) δ 13.90, 19.38, 30.46, 65.83, 90.33, 93.16, 108.94, 111.26, 122.68, 125.33, 131.42, 132.01, 157.81; UV–vis (CH_2Cl_2) λ_{max} ($\log \varepsilon$) 309 (4.82), 369 (4.80), 502 (3.79) nm. **7**: brown powder, mp 113–115 °C, LDI-TOF MS *m/z* 615.6 (M$^+$); ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 6H), 1.41 (sextet, 4H), 1.68 (quint, 4H), 4.24 (t, 4H), 7.02 (dd, J = 5.2, 3.7 Hz, 2H), 7.31 (dd, J = 5.2, 0.9 Hz, 2H), 7.37 (dd, J = 3.7, 0.9 Hz, 2H), ^{13}C NMR ($CDCl_3$) δ 13.78, 19.16, 30.46, 66.79, 84.41, 92.98, 109.82, 111.01, 120.21, 121.82, 127.56, 129.20, 132.10, 133.45, 159.61; UV–vis (CH_2Cl_2) λ_{max} ($\log \varepsilon$) 314 (4.68), 472 (3.76) nm. **8**: dark purple needles, mp 116–119 °C (dec.), LDI-TOF MS *m/z* 867.2 (M$^+$), ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 6H), 1.41 (sextet, 4H), 1.68 (quint, 4H), 4.24 (t, 4H), 6.95 (d, J = 3.7 Hz, 2H), 7.17 (d, J = 3.7 Hz, 2H); UV–vis (CH_2Cl_2) λ_{max} ($\log \varepsilon$) 332 (4.76), 484 (3.89) nm.

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13 During the doping experiment of **1c** with iodine, the electric conductivity first increased to 2.64×10^{-3} S·cm^{-1}, and then decreased to ca. 1.5×10^{-3} S·cm^{-1}.

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