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Annulenes

A Tetrathiafulvalene-Functionalized Radiaannulene with Multiple Redox States**

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Radiaannulenes (RAs) are cyclic molecules having both exo- and endocyclic double bonds,[1] and therefore structurally lie between radialenes[2] and annulenes.[3] As they possess a quinoid-like structure (Figure 1), we decided to investigate the possibility for employing them as Wurster-type[4] two-stage redox systems. A benzannelated derivative of octadehydro[14]annulene (**1**) has previously been shown to exhibit 14π aromaticity as asserted from a diatropic ring current.[5] This same core could formally be generated from the expanded RA **2** by reduction. Herein, we have combined **2** with tetrathiafulvalene (TTF, Figure 1), a two-stage Weitz-type[4] redox system which has found wide interest in materials and supramolecular chemistry.[6] By undergoing two one-electron oxidations, TTF achieves two 6π-aromatic 1,3-dithiolium rings,[7] and fusing a TTF unit to each of the endocyclic double bonds of **2** should thus provide a TTF/RA molecule that could potentially exist in seven or more redox states. Each of these are expected to exhibit characteristic electronic excitations in the UV/Vis region and maybe even in the NIR/IR region. Molecules reversibly changing color upon charging/decharging are particularly attractive for the development of electrochromic materials.

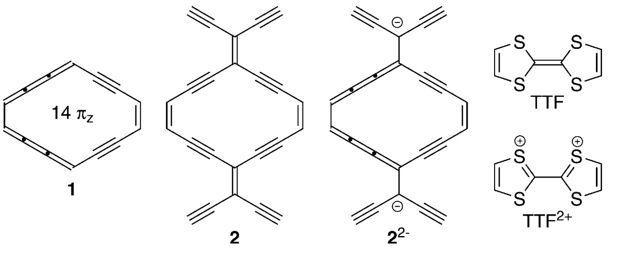
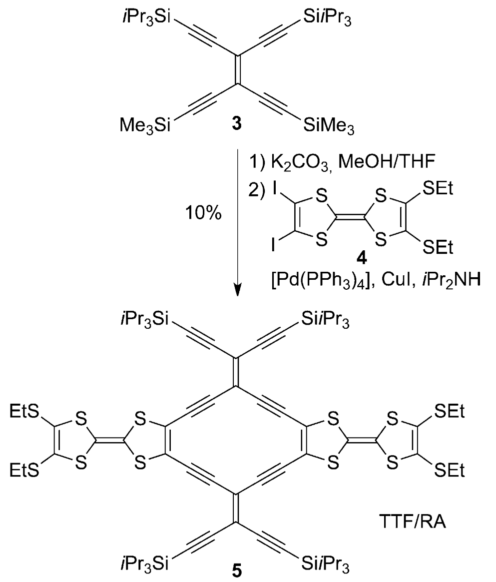


Figure 1. Structures of **1**, **2**, and TTF.

Subjecting the tetraethynylethene (TEE) **3**[8] (after desilylation) and the diiodo TTF **4**[9] to fourfold Sonogashira couplings gave the TTF/RA **5** in a yield of 10%, thus corresponding to 56% yield for each step in the cyclization (Scheme 1). The compound was dark-green in solution and as crystals, but was red when isolated as a solid film. The structure was confirmed by X-ray crystallographic analysis (Figure 2),[10] which showed some bending of the TTF units and triisopropylsilylethynyl groups away from the almost planar RA core.



Scheme 1. Synthesis of TTF/RA scaffold. THF = tetrahydrofuran.

Compound **5** comprises two TEE units, which are themselves known to be electron acceptors.[11] For a comparison of properties, we also prepared the related TTF/TEE **6**[9] (Figure 3).

Both **5** and **6** are strong chromophores with broad charge-transfer (CT) transitions in CH_2Cl_2 at approximately $\lambda = 644$ and 522 nm, respectively (Figure 4). This band extended to $\lambda = 800$ nm in the case of **5**, thus suggesting a particularly strong acceptor character of the RA core. The CT character of the absorption was supported by DFT calculations (B3LYP/6-31G(d) using Gaussian 09[12]) on the related molecule **5**(4H) with the silyl groups replaced by H atoms. The HOMO and HOMO−1 reside mainly on the two TTFs (and partially on the external diethynylethenes), while the LUMO resides mainly on the cyclic core (Figure 5).

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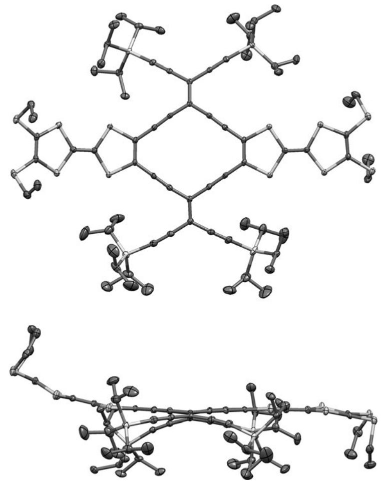

Figure 2. Molecular structure of **5** (H atoms omitted). Displacements ellipsoids shown at 50% probability for non-H atoms. Crystals grown from CH_2Cl_2/MeOH.

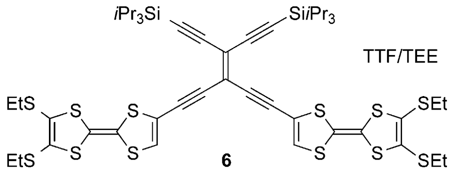

Figure 3. Structure of **6**.

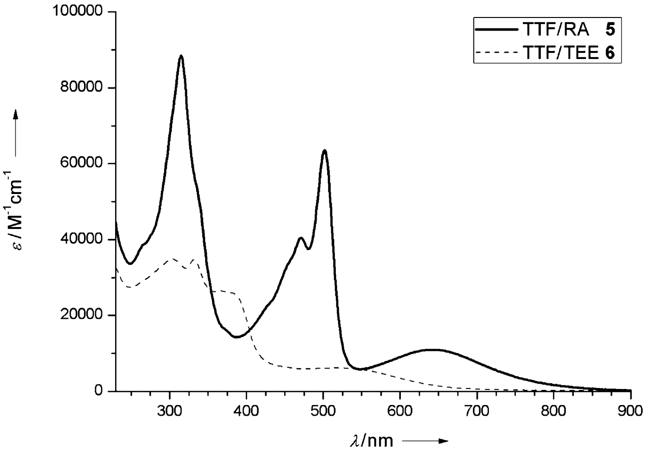

Figure 4. UV/Vis absorption spectra of **5** and **6** in CH_2Cl_2.

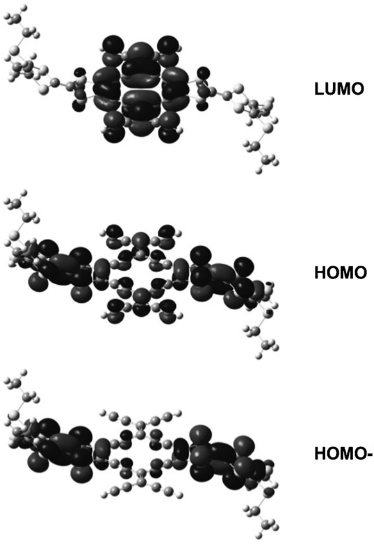

Figure 5. Frontier orbitals of **5**(4 H).

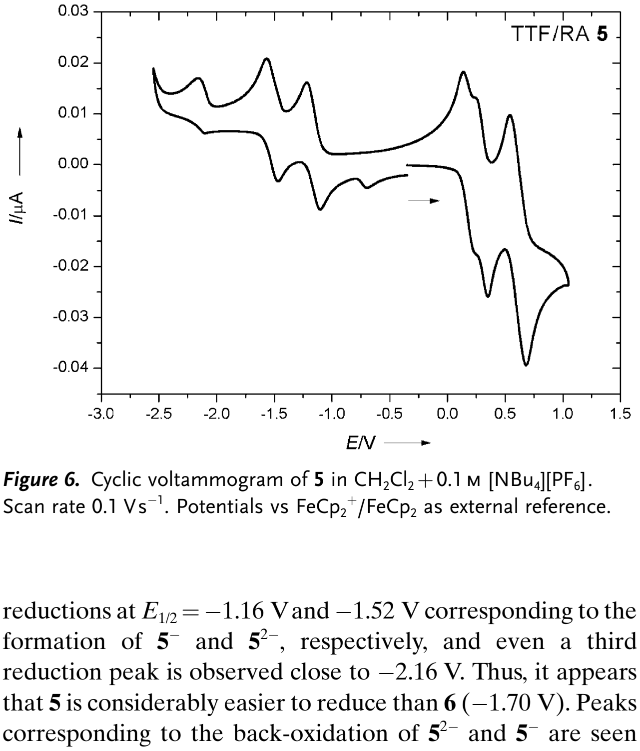

Figure 6. Cyclic voltammogram of **5** in CH_2Cl_2 + 0.1 M $[NBu_4][PF_6]$. Scan rate 0.1 Vs^{-1}. Potentials vs $FeCp_2^+/FeCp_2$ as external reference.

TTF/TEE **6** exhibits two reversible two-electron oxidations at $E_{1/2} = +0.12$ and $+0.52$ V vs $FeCp_2^+/FeCp_2$, and the two TTF units are independent redox centers. In contrast, the CV of the TTF/RA **5** (Figure 6) revealed a small splitting of the first oxidation wave into two one-electron oxidations at $E_{1/2} = +0.20$ and $+0.29$ V ($\Delta E_{1/2} = 0.09$ V), thus implying that the two TTFs are oxidized to radical cations sequentially. The first oxidation generates a mixed-valence state as ascertained spectroscopically (see below; Class II compound under the Robin-Day classification system).[13] In a third two-electron oxidation (+0.61 V), the tetracation $\mathbf{5}^{4+}$ is generated. Moreover, **5** shows two electrochemically reversible one-electron reductions at $E_{1/2} = -1.16$ V and -1.52 V corresponding to the formation of $\mathbf{5}^{-}$ and $\mathbf{5}^{2-}$, respectively, and even a third reduction peak is observed close to -2.16 V. Thus, it appears that **5** is considerably easier to reduce than **6** (-1.70 V). Peaks corresponding to the back-oxidation of $\mathbf{5}^{2-}$ and $\mathbf{5}^{-}$ are seen during the reverse scan together with a minor oxidation peak at -0.70 V. The latter is most likely caused by the oxidation of a monoanion resulting from partial protonation of $\mathbf{5}^{2-}$, probably by residual water. Similar electrochemical behavior has been observed in other cases.[14]

The different charge states of **5** are characterized further by UV/Vis/NIR or NIR/IR spectroelectrochemistry. The tight potential window of the three oxidation events (0 to +1 to +2 to +4) made it impossible to obtain separated spectra of the species owing to disproportionation and comproportionation reactions. However, careful oxidation from the neutral species to the radical cation $\mathbf{5}^{+}$ shows an intense broad band in the NIR centered at 4431 cm^{-1} ($\lambda = 2257$ nm; Figure 7).

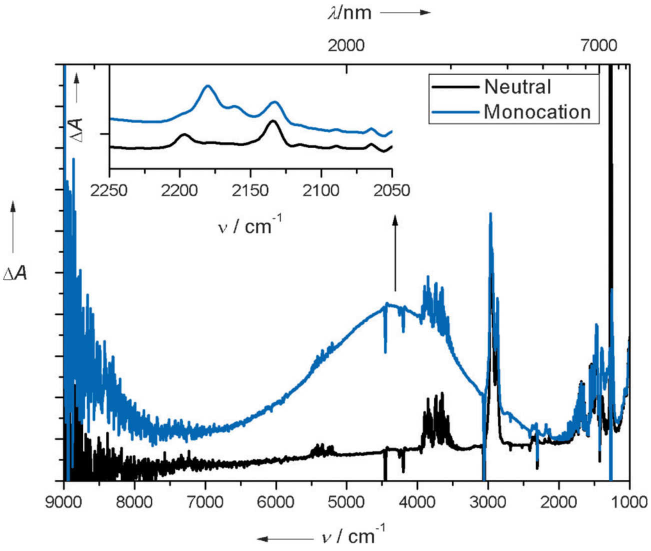

Figure 7. IR Spectra showing the oxidation of **5** to **5**$^+$ (2.1×10^{-3} M in $CH_2Cl_2 + 0.1$ M $[NBu_4][PF_6]$).

This band implies electronic interaction between the TTFs through the RA spacer and is ascribed to an intervalence CT band.[15] Formation of the dication **5**$^{2+}$ causes a lowering of this band, although it does not fully disappear because of dis/comproportionation. The dication **5**$^{2+}$ exhibits a broad absorption at $\lambda = 930$ nm (Figure 8), which is characteristic of alkylthio-substituted TTF radical cations.[15b,16] Additional oxidation to the tetracation **5**$^{4+}$ results in an absorption blue shift to $\lambda = 813$ nm. Reduction of **5** to the radical anion **5**$^-$ causes the peak at $\lambda = 473$ nm to collapse while a strong absorption appears at $\lambda = 845$ nm (Figure 8) together with some lower-energy absorptions (see the Supporting Information). Neutral **5** shows very weak C≡C stretching bands at 2197 and 2134 cm^{-1} (see the Supporting Information). However, upon reduction to **5**$^-$ they become far more intense and shift to lower energy (2167–1989 cm^{-1}). This weakening of triple bonds indicates increased π-electron delocalization in the reduced species. The neutral species can be regenerated upon oxidation, that is, formation of the radical anion is chemically reversible.

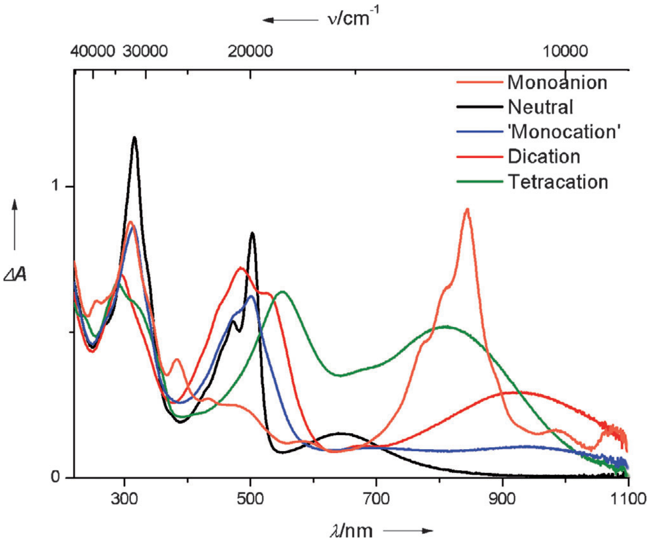

Figure 8. UV/Vis Absorption spectra of **5** in different charge states (0.6×10^{-3} M in $CH_2Cl_2 + 0.1$ M $[NBu_4][PF_6]$).

The remarkably easy two-step reduction of the TTF/RA core agrees with a Wurster-type redox system and may indicate a gain in aromaticity in passing from **5** to **5**$^{2-}$. To shed further light on this aspect, we performed a series of nucleus independent chemical shift (NICS) calculations, an index introduced by Schleyer and co-workers as a probe for aromaticity.[17] The values for compounds **1**, **2**, and **5**(4H) are shown in Table 1. In fact, both NICS(0) and more refined NICS indices clearly reveal a gain in aromaticity (more negative NICS), when proceeding from neutral RAs **2** and **5**(4H) to their corresponding dianions. While the values for **2**$^{2-}$ and **5**(4H)$^{2-}$ are rather similar, they are, nevertheless, less negative than those of the parent octadehydro[14]annulene (**1**).

Table 1: NICS values (B3LYP/6-31G(d)) for the octadehydro[14]annulene part of the planar, closed-shell RAs in comparison to **1**.

Compound	NICS(0)	NICS(0)$_{zz}$	NICS[π]	NICS[π]$_{zz}$
1	−16.8	−43.4	−21.0	−49.6
2	−0.7	+5.3	−6.2	−6.4
2^{2-}	−10.9	−24.8	−16.1	−35.9
5(4H)	−0.7	+7.1	−7.1	−8.4
5(4H)$^{2-}$	−8.7	−16.4	−15.4	−33.2

In conclusion, a cyclization involving four Sonogashira couplings has provided a fused Weitz/Wurster-type redox system, which formally gains Hückel aromaticity by either oxidation (6π-dithiolium units) or reduction (14π-octadehydroannulene unit). Moreover, the RA core allows a mixed valence TTF/RA/TTF$^+$ structure. Substitution of the silyl groups with electron-withdrawing groups may enhance the electron affinity even further and is subject of future work. The six redox states (−2/−1/0/+1/+2/+4) characterized by electronic excitations covering altogether the UV/Vis/IR region could be attained electrochemically, thus making TTF/RAs interesting for future development of advanced electrochromic and electrically conducting materials.

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[10] Crystal data for **5**. $C_{76}H_{104}S_{12}Si_4$, $M_r = 1514.67$, triclinic, P-1, $a = 13.143(3)$, $b = 15.909(3)$, $c = 20.719(3)$ Å, $\alpha = 82.89(2)$, $\beta = 79.25(1)$, $\gamma = 82.90(2)°$, $V = 4200.9(14)$ Å^3, $T = 123$ K, $\mu(\text{Mo}_{K\alpha}) = 0.408\ \text{mm}^{-1}$, $2\theta_{\max} = 50.8°$, 83611 reflections measured, 14403 unique reflections ($R_{\text{int}} = 0.079$), 11539 observed reflections, $R1(I>2\sigma(I)) = 0.047$, $wR2(\text{all data}) = 0.105$, $S = 1.10$. CCDC 871959 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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