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[5]Radialene-Fused Tetrathiafulvalenes Exhibiting a Simultaneous Four- or Eight-Electron Transfer

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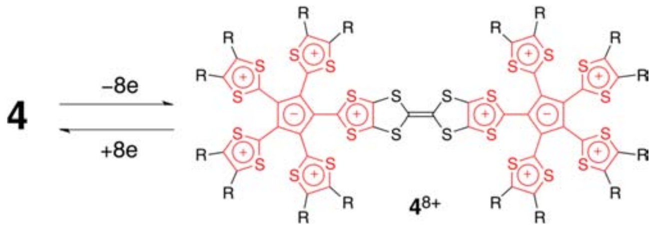
ABSTRACT



Novel bis- and tris-fused tetrathiafulvalene (TTF) analogs possessing [5]radialene with quintuple 1,3-dithiol-2-ylidene moieties (2−4) were successfully synthesized. Cyclic voltammetry and differential pulse voltammetry revealed that they exhibited a simultaneous four- or eight-electron transfer process. It is suggested that four positive charges are distributed mainly over each of one or two DT[5]radialene units in 2^{4+}, 3^{4+}, and 4^{8+}.

Tetrathiafulvalene (TTF) and its derivatives have attracted considerable attention as organic functional materials because of their multistage redox property with low oxidation potentials.[1] In the search for metallic molecular conductors, we have developed bis- and tris-fused TTFs, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP or simply TTP),[2] and 2,2′-bi[5-(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentanylidene] (BDT-TTPY or simply TTPY) (Figure 1).[3] Fused TTF donors have actually yielded a number of highly conducting or metallic radical cation salts.[4] We have also reported that TTP and TTPY can be utilized as positive electrode materials for secondary batteries[5] because of their scarce solubility in ordinary organic solvents and of the presence of multiple redox-active 1,3-dithiol-2-ylidene (DT) sites. In this connection, syntheses of TTP and TTPY analogs containing the other extended TTF moieties are of interest as multistage redox systems as well as components for functional materials.

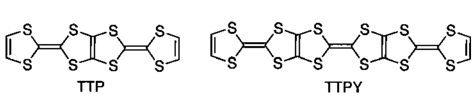


Figure 1. Structures of TTP and TTPY.

[*n*]Radialenes[6] with multiple 1,3-dithiole rings ($n = 4-6$) are known to show unique redox properties.[7] Among them, derivatives of [5]radialene with quintuple DTs (DT[5]-radialene, **1**) (Figure 2) exhibit very unique redox behavior of a simultaneous four-electron transfer process.[7d] The ^{13}C NMR spectrum of tetracationic salts of **1** revealed that observation of the redox behavior of **1** is attributed to a large

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stabilization of 1^{4+} to which an aromatic cyclopentadienide structure with twisted five 1,3-dithiolylium rings contributes significantly.[7d] In this paper, we report the synthesis, electronic structures, and electrochemical properties of new bis- and tris-fused TTF analogs possessing one or two [5]radialene moieties **2**−**4**.

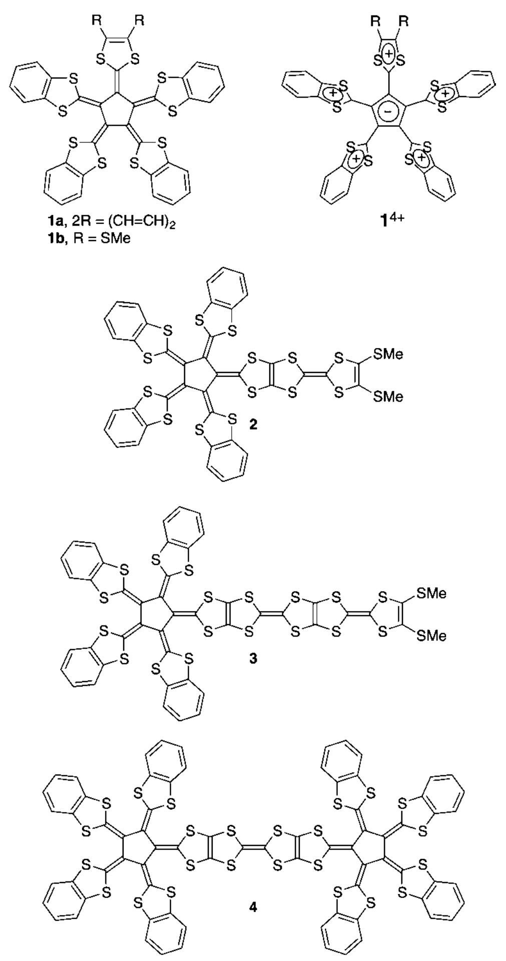
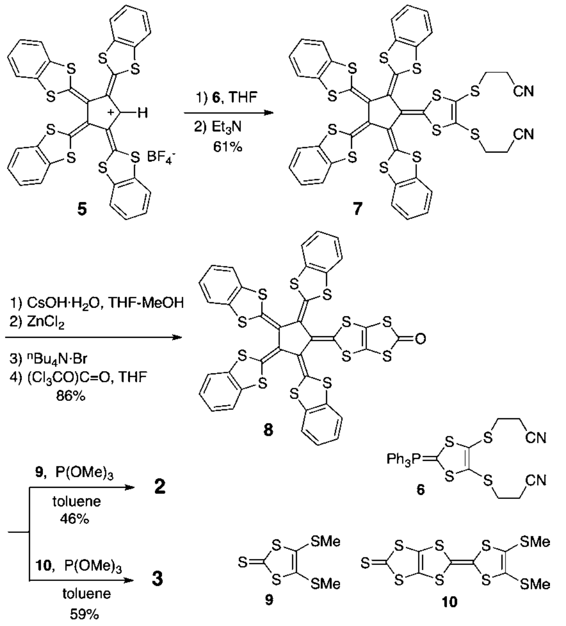


Figure 2. Structures of **1**−**4** and $\mathbf{1}^{4+}$.

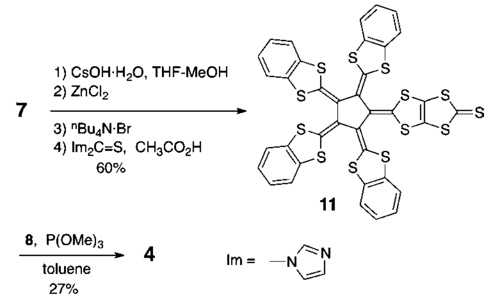
New π-electron donors **2**−**4** were successfully synthesized by the combination of the synthetic methodologies of DT[5]radialenes[7d] and TTP derivatives,[8] respectively. Scheme 1 shows the synthesis of **2** and **3**. The reaction of a salt **5**[7d] with a phosphorane **6** generated by treatment of the corresponding phosphonium salt with BuLi in THF at −78 °C followed by a reaction with triethylamine gave a DT[5]radialene derivative with 2-cyanoethylthio groups (**7**) in 61% yield.[9] Compound **7** was treated with an excess of cesium hydroxide monohydrate (4 equiv mol) in THF−methanol followed by addition with zinc(II) chloride and tetra-*n*-butylammonium bromide at room temperature. The reaction mixture was then reacted with triphosgene in THF at −78 °C to afford a DT[5]radialene fused with 1,3-dithiol-2-one (**8**).[9] The $P(OMe)_3$-mediated cross-coupling between **8** and 4,5-bis(methylthio)-1,3-dithiole-2-thione (**9**) or 1,3-dithole-2-thione fused with bis(methylthio)-TTF (**10**) gave the corresponding bis-fused donor (**2**) and tris-fused donor (**3**) in 46 and 59% yields, respectively.

Scheme 1. Synthesis of **2** and **3**



Similarly, a thione analog of **8** (**11**) was obtained in 60% yield by the reaction of **7** with thiocarbonyl-1,1-diimidazole instead of triphosgen in the presence of an excess of acetic acid (Scheme 2).[8c] A cross-coupling reaction between **11** and **8** mediated by $P(OMe)_3$ in refluxing toluene afforded the tris-fused donor containing two DT[5]radialene units (**4**) in 27% yield.

Scheme 2. Synthesis of **4**



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Electrochemical properties of new radialene-type donors **2**−**4** were investigated by cyclic voltammetry and/or differential pulse voltammetry (DPV). Figure 3 shows deconvoluted cyclic voltammograms of **2**, **3** and a differential pulse voltammogram of **4** measured in benzonitrile solutions. The donors **2** and **3** exhibited three and four pairs of redox waves, respectively, while **1b** showed one pair of redox waves. The peak currents of the first redox waves of **2** and **3** are significantly larger than those of the others and are comparable to the peak current of **1**. This result strongly indicates that the first redox waves of **2** and **3** correspond to simultaneous four-electron redox processes. The peak currents of the remaining two pairs of redox waves of **2** are about one-fifth as large as that of the first redox wave. This indicates that the remaining redox involves sequential one-electron transfer processes. As for **3**, the peak current of the redox wave at the highest voltage region is about twice as large as those of the second and third redox waves, suggesting that this redox wave corresponds to the two-electron transfer process. In the DPV of **4**, three pairs of redox waves were observed.[10] The peak current of the first redox wave is about ten times as large as those of the others. This result strongly indicates that the first redox wave involves a simultaneous eight-electron transfer process. To our knowledge, this is an unusual observation of a simultaneous eight-electron process in π-conjugated systems.[11]

The redox potentials of **2**−**4** are summarized in Table 1 together with their related compounds **1b**, **12**, and **13**. The first four- or eight-electron redox potentials of **2**−**4** and **1b** are approximately equal to each other. These results suggest that four or eight positive charges formed by the first oxidation processes in **2**−**4** are distributed mainly over the DT[5]radialene moieties probably because of the significant contribution of a cyclopentadienide structure in the central five-membered ring similarly to $\mathbf{1}^{4+}$. An apparent overlap of two four-electron redox waves in **4** might be attributed to the reduction of on-site coulomb repulsion by an electron-rich spacer of a TTF moiety. The TTF or TTP moiety may contribute to the subsequent redox processes. The E_5 value of **2** is more positive by 0.36 V than the E_1 of **12** because of the influence of the DT[5]radialene moiety with four positive charges. A similar positive shift is also observed in **3**, but the E_5 value of **3** is more positive by only 0.09 V than the E_1 of **13**.[8a] This indicates that a positive charge is distributed mainly over the outer TTF moiety so that on-site coulomb repulsion is reduced. In contrast, the E_9 value of **4** is remarkably more positive by 0.82 V than the E_1 of **12**, because the cationic TTF moiety sandwiched by two tetracationic DT[5]radialenes is significantly destabilized.

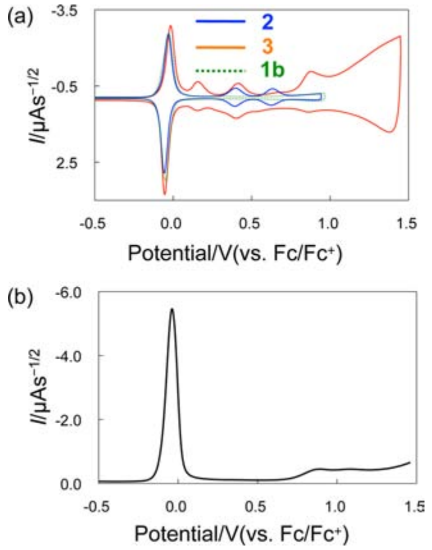


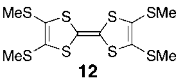
Figure 3. (a) Deconvoluted cyclic voltammograms of **2** and **3**. (b) Differential pulse voltammogram of **4**.

The spectroelectrochemistry of **4** was investigated to elucidate the electronic structures of their oxidative species. Figure 4 shows the UV−vis−NIR spectra of **4** and its oxidative species generated by applying constant voltages in benzonitrile solutions. When the voltage at +0.19 V (vs Fc/Fc$^+$) was applied, new absorption bands probably ascribed to $\mathbf{4}^{8+}$ appeared at 402, 514, and 682 nm, respectively. This spectrum has a resemblance with that of $\mathbf{1b}^{4+}$

Table 1. Redox Potentials[a] of **2**−**4** and Their Related Compounds

	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8	E_9	E_{10}
2	−0.04 (4e)				+0.40	+0.63				
3	−0.03 (4e)				+0.16	+0.41	+0.87 (2e)			
4	−0.05 (8e)								+0.86	+1.07
1b	−0.04 (4e)									
12	+0.04	+0.36								
13	+0.07	+0.28	+0.56	+0.70						

[a] Conditions: $^n\mathrm{Bu_4N\cdot PF_6}$ (0.1 M), benzonitrile, 25 °C, Pt working and counter electrodes. Potentials were measured against the Ag/Ag$^+$ electrode and converted to the value vs Fc/Fc$^+$.



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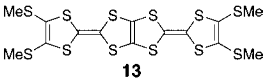

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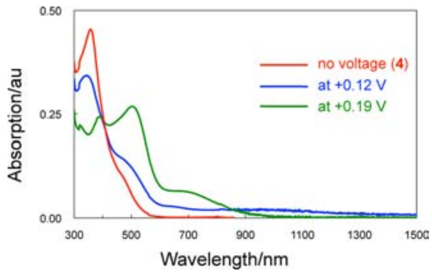

Figure 4. UV−vis−NIR spectra of **4** and its oxidative species.

(397 and 519 nm)[12] except for the absorption band at 682 nm. This result suggests that four positive charges are distributed mainly over each of the two DT[5]radialene units as is mentioned above. The observation of a band at 682 nm might be attributed to intramolecular charge transfer (ICT) from the TTF core to the tetracationic DT[5]radialene units.

When a constant voltage at +0.12 V was applied, other absorption bands were observed at 500, 652, and 800−1500 nm in addition to the absorption maxima of **4** and **4**$^{8+}$. This spectrum has a resemblance to that of **1b**$^{2+}$ (408, 648, and 989 nm).[12] Therefore, we tentatively think that these absorption bands might be attributed to **4**$^{4+}$ and that two positive charges mainly locate on each of the two DT[5]radialene moieties.

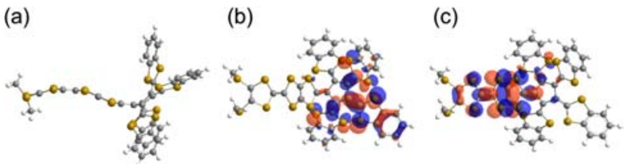

Figure 5. (a) An optimized structure of **2** (side view), and its (b) HOMO and (c) HOMO−1.

Theoretical calculations for **2**−**4** were carried out based on the density functional theory (DFT) using B3LYP/6-31G(d). An optimized structure of **2** is shown in Figure 5a. The molecule adopts a nonplanar structure. The central five-membered ring of the DT radialene moiety adopts an envelope conformation with a dihedral angle of 44°. All the DT units are largely distorted so as to avoid steric hindrance with each other. The dihedral angles between the adjacent DT units are 36°−71°. Such nonpalanar structures of the central ring and largely distorted DT units were observed in all the DT[*n*]radialenes whose molecular structures were determined by X-ray structure analyses.[7a−c] The HOMOs of **2** mainly locate on the outer DT[5]radialene moieties, hardly locating on the TTF unit (Figure 5b). In contrast, the HOMO−1 is distributed mainly on the TTF moiety (Figure 5c). This result is inconsistent with the results of CV that the DT[5]radialene moiety contributes to first four-electron redox. This is probably because of the occurrence of a large structural change with oxidation from **2** to **2**$^{4+}$; that is, the central five-membered ring of the radialene moiety changes from a nonplanar envelope conformation in the neutral state to a planar and aromatic cyclopentadienide structure in the tetracationic state.[7d,12]

In summary, we have demonstrated that new multifused *π*-electron donors with DT[5]radialene moieties (**2**−**4**) exhibit a simultaneous four- or eight-electron transfer process because of the presence of one or two DT[5]radialene moieties. Further investigations, in particular, the preparation of conducting materials of **2**−**4** with various organic acceptors and inorganic counteranions, and the charge−discharge performance of rechargeable batteries incorporating **2**−**4** as positive electrode materials, are actively in progress.

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Supporting Information Available. Detailed experimental procedures and spectra of all new compounds; plausible reaction processes for the formation of **7, 8,** and **11**; optimized structures, the HOMO and HOMO−*n* (*n* = 1−4) of **2**−**4**; UV−vis-NIR spectra of **2**, **3**, and their oxidative species. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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(9) Plausible reaction mechanisms are depicted in Schemes S1 and S2, Supporting Information.

(10) The clear redox waves were not observed at *ca.* 1 V in deconvoluted cyclic voltammogram of **4**.

(11) A simultaneous eight-electron (and more) transfer process was observed in the oligomeric TTF derivatives whose TTF units are linked by nonconjugated spacers with each other: (a) Bryce, M. R.; Devonport, W.; Moore, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1761–1763. (b) Christensen, C. A.; Goldenberg, L. M.; Bryce, M. R.; Becher, J. *Chem. Commun.* **1998**, 509–510.

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