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Mono- and bis(tetrathiafulvaleno)hexadehydro[12]annulenes†

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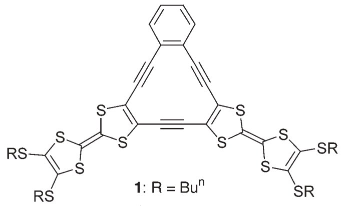
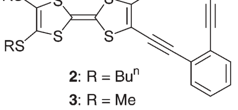
Hexadehydro[12]annulenes annelated with one or two TTF units have been synthesized to investigate their π-amphoteric properties based on the TTF and [12]annulene moieties; these compounds show multi-redox potentials, solvatochromism and the formation of large sandwich complexes.

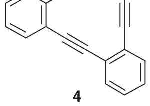
Tetrathiafulvalenes (TTFs) have attracted much attention because of their unique electronic properties,[1] and have been used for the synthesis of new organic metals and superconductors.[2] Furthermore, there is considerable current interest in the supramolecular chemistry based on TTFs.[3] Thus, TTF-containing oligomers, polymers and dendrimers have been synthesized to realize redox-active supramolecular systems. Since TTF is a stable and reversible two-electron donor, supramolecular systems having TTF moieties may act as nanometer-sized chemical sensors, molecular switches and molecular devices in neutral, radical cationic and polycationic states. Mono- and bis(tetrathiafulvaleno)hexadehydro[12]annulenes **1–3** can be regarded as π-amphoteric host molecules with TTF donor and [12]annulene acceptor parts. We report here the synthesis, intra- and intermolecular donor–donor interactions, solvatochromic properties, and formation of large sandwich complexes of **1** and **2**, together with the X-ray analysis of **3**.



1: R = Bu^n



2: R = Bu^n
3: R = Me



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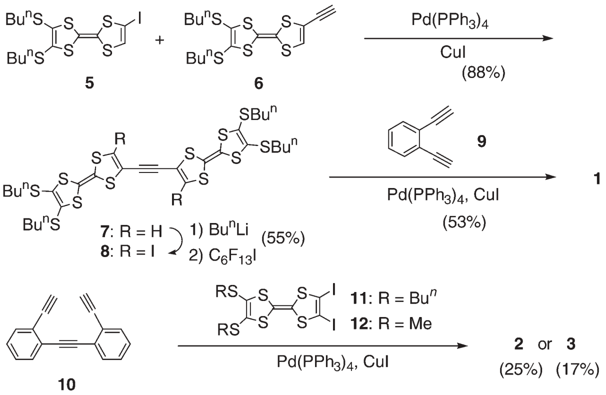
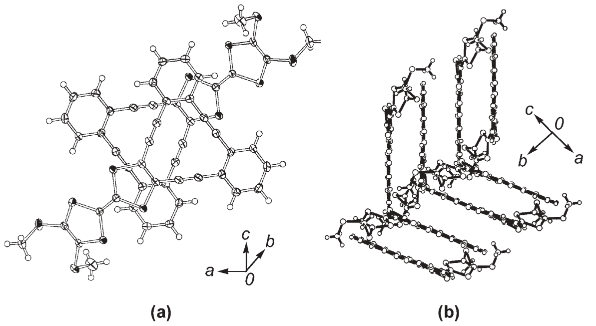
Tribenzohexadehydro[12]annulene **4** is a structural unit of graphyne,[4] and a variety of synthetic methods for **4** have been developed.[5,6] However, synthesis of **1–3** using the normal reported procedures was unsuccessful. Therefore, we improved the Sonogashira reaction for the synthesis of **1–3** (Scheme 1). First, the cross-coupling of **5** with **6** under normal Sonogashira conditions afforded **7**, which was converted into the diiodide **8**. For the construction of the [12]annulene framework, the Sonogashira coupling of **8** with **9** using almost stoichiometric amounts of Pd(PPh$_3$)$_4$ and CuI under improved Krause's conditions[7] was employed to produce **1** in 53% yield. Similarly, the coupling of **10** with **11** or **12** using almost stoichiometric amounts of reagents in benzene–triethylamine produced **2** and **3** in 25 and 17% yields, respectively. Interestingly, the reactions using catalytic amounts of palladium and copper reagents in benzene–triethylamine led to small amounts of **1–3**.

Although the butylthio groups in **1** and **2** improved the solubility of these macrocyclic compounds in organic solvents, these compounds were obtained as amorphous dark brown solids. For the X-ray analysis, however, **3** with methylthio substituents gave single crystals.‡ As shown in Fig. 1, the [12]annulene ring in **3** is planar, whereas the TTF moiety has a boat conformation, forming a slipped-stack dimer with a staggered cofacial arrangement. The face-to-face distance of the aromatic and TTF rings is 3.42 Å. The dimeric unit forms a column structure along the *b* axis. There are two short intercolumn S···S contacts (3.54 and 3.62 Å), shorter than the sum of van der Waals radii (3.70 Å) between neighboring dimers; however, no intracolumn S···S contacts are observed in **3**. Although TTF derivatives tend to oligomerize to form a column structure in the crystals, the staggered cofacial stacking of the [12]annulene ring in **3** could be favored over the eclipsed structure with dimerization of the TTF moiety. In addition, **1–3** in CDCl$_3$ show no aggregation properties, because the ^{1}H NMR spectra of **1–3** in CDCl$_3$ and related solvents exhibit no concentration dependence at low and room temperatures.

Tetrathiafulvalenoannulenes **1–3** have π-amphoteric properties. Thus, the TTF units in **1–3** exhibit low oxidation potentials, while the [12]annulene moiety shows fairly high reduction potentials. As summarized in Table 1, oxidation and reduction potentials of **1** and



Scheme 1 Synthesis of **1–3**.



(a) (b)

Fig. 1 a) ORTEP (50% probability ellipsoids) diagram of the dimeric **3**. b) Packing structure of the dimeric **3**.

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† Electronic supplementary information (ESI) available: cyclic voltammograms of the annulenes **1** and **2**. See http://www.rsc.org/suppdata/cc/b4/b407200f/

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Table 1 Redox potentials of **1**, **2**, **4** and TTF[a]

Compound	$E^{\text{red2}b}$	$E^{\text{red1}b}$	$E^{\text{ox1}c}$	$E^{\text{ox2}c}$
1	−1.87	−1.50	0.19[d]	0.46[d]
2	−2.08	−1.80	0.16	0.43
4	−2.50	−2.19	—	—
TTF	—	—	−0.09	0.32

[a] Conditions: 0.1 M Bu_4NClO_4, Ag/Ag^+ reference electrode, Pt counter electrode, 100 mV s^{-1}; potentials referred to Fc/Fc^+. [b] In THF with glassy carbon working electrode. [c] In benzonitrile with Pt working electrode. [d] Two electrons' process.

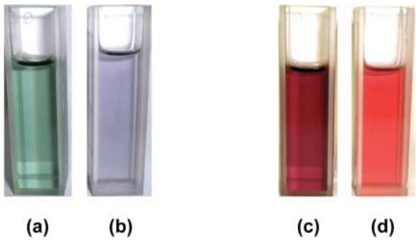
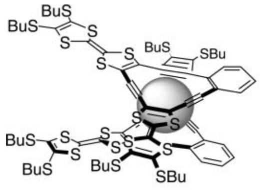


Fig. 2 Solutions of **1** in CS_2 (a) and CH_2Cl_2 (b) and of **2** in CS_2 (c) and CH_2Cl_2 (d).

2 were measured in benzonitrile and THF, respectively, at room temperature, and these indicated 4-step redox processes. Since the cyclic voltammogram of **1** shows a broad first oxidation, the overlap of two closely located oxidations is anticipated. Although the electron-withdrawing acetylenic substituents in **1** and **2** decrease the donor ability of TTF units, **1** and **2** possess oxidation potentials low enough to form conducting radical salts. On the contrary, the reduction potentials of the [12]annulene moiety increase in the order of **1** > **2** > **4**, reflecting the increase in cyclic conjugation, *i.e.*, paratropicity, of the annulene ring. The HOMO and LUMO energies of unsubstituted tetrathiafulvalenoannulenes calculated at the RHF/3-21G* level were in good agreement with the experimental redox potentials.

An interesting property of **1** and **2** is solvatochromism. As shown in Fig. 2, a solution of **1** exhibits deep green in CS_2 but purple in CH_2Cl_2. Similarly, solutions of **2** in CS_2 and CH_2Cl_2 are wine red and reddish orange, respectively. The UV-Vis spectra of **1** and **2** show strong (290–300 nm, log ε = *ca.* 5) and weak (550–650 nm, log ε = *ca.* 3.5) absorptions. Although the strong absorptions of **1–3** are independent of the solvent, the wavelengths of the weak absorptions vary with the solvent used [**1**: λ_{max} (CS_2) 608, λ_{max} (CH_2Cl_2) 577; **2**: λ_{max} (CS_2) 565, λ_{max} (CH_2Cl_2) 545 nm].

Tribenzohexadehydro[12]annulene **4** and its derivatives form sandwich complexes with silver salts both in solution and in the solid state.[6,8] Although silver salts are sometimes employed for complexation with sulfur atoms and for oxidation of TTF derivatives,[9] we expected that **1** and **2** might form sandwich complexes with silver salts because of their reduced oxidation potentials (Table 1). Thus, $AgOCOCF_3$ was used to form sandwich complexes **13** and **14** from **1** and **2** in $CDCl_3$, whereas partial oxidation of **1** and **2** took place with $AgClO_4$. The ^1H NMR chemical shifts of aromatic protons in **1** revealed an upfield shift of 0.14–0.21 ppm on addition of 0.5 equiv. of $AgOCOCF_3$, indicating the formation of **13**, though the attempted measurements of electronic and MS spectra of **13** were unsuccessful due to its instability. Similarly, the aromatic protons in the ^1H NMR spectra of **2** shifted upfield by 0.04–0.06 ppm on addition of 0.5 equiv. of $AgOCOCF_3$. Since the upfield shift of the aromatic protons in **2** is small, we assume a partial formation of the sandwich complex **14** in an equilibrium state.



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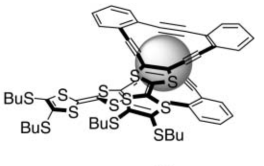

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Tetrathiafulvalenoannulenes **1** and **2** exhibit two oxidation potentials (Table 1). Accordingly, chemical oxidation of **1** and **2** with $Fe(ClO_4)_3$ revealed characteristic changes in color and electronic spectra. The oxidation of **1** with 1, 2 and 4 equiv. of $Fe(ClO_4)_3$ in CH_2Cl_2–CH_3CN (v/v 4 : 1) resulted in the formation of $\mathbf{1}^{\bullet+}$ (λ_{max} = 881 and 2000 nm), $\mathbf{1}^{2+}$ (λ_{max} = 889 nm) and $\mathbf{1}^{4+}$ (λ_{max} = 732 nm). Consequently, the color of the solutions changed from purple (**1**) to orange ($\mathbf{1}^{\bullet+}$), deep orange ($\mathbf{1}^{2+}$) and blue ($\mathbf{1}^{4+}$). Since $\mathbf{1}^{\bullet+}$ shows a very broad absorption around 2000 nm, intramolecular interaction between the TTF and $TTF^{\bullet+}$ units can be expected.[10] In the case of $\mathbf{1}^{2+}$, no π-dimer formation was detected based on the electronic spectra, and the longer absorption of $\mathbf{1}^{2+}$ at 889 nm than that of $\mathbf{1}^{\bullet+}$ at 881 nm may reflect a head-to-tail interaction of the two $TTF^{\bullet+}$ units.[10] Similarly, **2** shows a drastic change in the electronic spectra and color of the solutions upon oxidation with $Fe(ClO_4)_3$ in CH_2Cl_2–CH_3CN [**2**: 545 nm, reddish orange; $\mathbf{2}^{\bullet+}$: 926 nm, orange; $\mathbf{2}^{2+}$: 769 nm, blue].

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Notes and references

‡ Crystal data for **3**: $C_{26}H_{14}S_6$, M_W 518.76, monoclinic, space group $P2_1/n$ (# 14), a = 14.262(2), b = 7.965(4), c = 20.160(3) Å, β = 94.64(1)°, V = 2282(1) Å^3, Z = 4, D_c = 1.509 g cm^{-3}, μ(MoKα) = 6.13 cm^{-1}, R = 0.038, Rw = 0.049, GOF = 1.13. All measurements were performed on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα (λ = 0.71069 Å) radiation at 23 °C. Among a total of 5854 reflections measured, 5252 were unique and the observed ($I > 3.00\sigma(I)$) 3009 reflections were used for the refinement. The crystal structure was solved by the direct method and refined by the full matrix least-squares method. CCDC 239107. See http://www.rsc.org/suppdata/cc/b4/b407200f/ for crystallographic data in .cif or other electronic format.

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