SYNTHESIS AND \(\pi\)-AMPHOTERIC PROPERTIES OF TRIS(TETRATHIAFULVALENO)HEXADEHYDRO[12]ANNULENE

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Abstract – The Sonogashira coupling reaction of the diiodide 6 of 1,2-[4,5-bis(butylthio)tetrathiafulvalenyl]ethyne with 4,5-bis(ethynyl)-4',5'-bis(butylthio)tetrathiafulvane 5 produced the corresponding tris(tetrathiafulvaleno)hexadehydro[12]annulene 1 in moderate yield. The [12]annulene 1 exhibits multi-redox behavior and solvatochromism in the neutral state.

INTRODUCTION

Hexadehydro[12]annulene has received considerable attention, because its tribenzo-analogue is regarded as a structural unit of graphyne,\(^1\) and because various unique transition-metal complexes have been constructed using the [12]annulene frame.\(^2,3\) Furthermore, tribenzohexadehydro[12]annulene (TBA) has been employed as a starting material for the synthesis of cage molecules and polyethers.\(^4,5\) Recently, we have reported the synthesis and \(\pi\)-amphoteric properties of bis(tetrathiafulvaleno)hexadehydro[12]-annulene 2 and related compounds based on the tetrathiafulvalene (TTF) and [12]annulene moieties.\(^6,7\) The annulene 2 exhibited multi-redox potentials, solvatochromism, and the formation of a large sandwich complex. Based on these results, we next synthesized tris(tetrathiafulvaleno)hexadehydro[12]annulene 1. We report here the synthesis, unique redox behavior, and solvatochromic properties of 1.

RESULTS AND DISCUSSION

The synthesis of 1 is summarized in Scheme 1. Although various synthetic methods of accessing hexadehydro[12]annulenes have been reported to date,\(^8,9\) we employed the Sonogashira coupling of the bis(ethynyl)-TTF 5 with the diiodo-bi-TTF 6 similar to our previously reported procedure\(^6\) owing to the instability of 1 to light, atmospheric oxygen, and acidic condition. Thus, the reaction of the diiodo-TTF 3 with trimethylsilylacetylene (4 equiv) in the presence of Pd(PPh\(_3\))\(_4\) (15 mol\%), CuI (30 mol\%), and Et\(_3\)N...
in benzene at 50 °C for 12 h produced the bis(trimethylsilylethynyl)-TTF 4 in 74% yield. The treatment of 4 with KOH (excess) in THF-methanol (1:1) at room temperature for 3 min yielded 5 to remove the trimethylsilyl groups. Since 5 was unstable and readily polymerized after removal of the solvent, a solution of 5 in benzene was employed for the following reaction without further purification. The Sonogashira coupling of 6 with 5 (1.65 equiv based on 100% conversion of 4) in the presence of Pd(PPh3)4 (50 mol%) and CuI (100 mol%) in benzene-triethylamine (10:3) at room temperature for 5 h produced the desired 1 in 36% yield based on 6.10 For the synthesis of 1, almost stoichiometric amounts of Pd(PPh3)4 and CuI were required to complete the reaction.

Interestingly, the tris(TTF)annulene 1 shows solvatochromism, and a solution of 1 is deep green in CS2 but bright green in CH2Cl2. As shown in Figure 1, the UV-Vis-NIR spectrum of 1 shows strong (322 nm, $\varepsilon = 90,000$) and weak (623-656 nm, $\varepsilon = 3500-4000$) absorptions. The strong absorption is unchanged with the type of solvent, whereas the weak absorption varies with the type of solvent used [$\lambda_{\text{max}}$ (CS2) 656 nm and $\lambda_{\text{max}}$ (CH2Cl2) 623 nm]. Since the longest absorption is assigned to the charge-transfer (CT) band from the TTF ($\pi$-donor) to [12]annulene ($\pi$-acceptor) moieties, this transition is sensitive to the polarity of the solvent.

Scheme 1. Synthesis of tris(TTF)[12]annulene 1
Figure 1. UV-Vis-NIR spectra of 1. (a) Entire spectrum in CH$_2$Cl$_2$. (b) Expansion of the weak absorptions in CH$_2$Cl$_2$ and CS$_2$.

The cyclic voltammetric (CV) analysis of 1 shows unique redox properties owing to the $\pi$-amphoteric nature of 1. As shown in Table 1, 1 and 2 indicated 4-step redox processes; namely, the formation of 1$^{2-}$, 1$^-$, 1$^{3+}$, and 1$^{6+}$, or 2$^{2-}$, 2$^-$, 2$^{2+}$, and 2$^{4+}$. Since tribenzohexadehydro[12]annulene (TBA) shows two reduction waves at -2.50 and -2.19 V vs Fc/Fc$^+$ under the same conditions, the reduction potential of the [12]annulene unit increases in the order 1 > 2 > TBA, reflecting the increase in the degree of cyclic conjugation. In contrast, the oxidation potentials of 1 and 2 seemed to be similar. However, the first oxidation potential of 1 was split into two ($E^{ox1/2}(1) = 0.12$ V; $E^{ox1/2}(2) = 0.26$ V vs Fc/Fc$^+$) when measured at a very slow rate (3 mV s$^{-1}$), while the first oxidation potential of 2 showed a broad oxidation even when measured at a very low rate. Consequently, the oxidation potential of the TTF units decreases in the order 2 $\geq$ 1 > TTF, reflecting the increase in donor ability.

Table 1. Redox potentials of 1, 2, and TTF vs Fc/Fc$^+$ at room temperature.$^a$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E^{red2}_{1/2}$</th>
<th>$E^{red1}_{1/2}$</th>
<th>$E^{ox1}_{1/2}$</th>
<th>$E^{ox2}_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTF</td>
<td>—</td>
<td>—</td>
<td>-0.08</td>
<td>0.30</td>
</tr>
<tr>
<td>1</td>
<td>-1.78</td>
<td>-1.41</td>
<td>0.21 (0.12, 0.26)$^b$</td>
<td>0.49</td>
</tr>
<tr>
<td>2</td>
<td>-1.87</td>
<td>-1.50</td>
<td>0.19</td>
<td>0.46</td>
</tr>
</tbody>
</table>

$^a$Reduction potential was measured in THF using $^{n}$Bu$_4$NClO$_4$ (0.1 M), glassy carbon (working electrode), Pt (counter electrode), and 100 mVs$^{-1}$, whereas oxidation potential was measured in benzonitrile using $^{n}$Bu$_4$NClO$_4$ (0.1 M), Pt (working and counter electrodes) and 100 mV s$^{-1}$. The potential was measured against a Ag/Ag$^+$ reference electrode and converted to the value vs Fc/Fc$^+$. $^b$Measured at 3 mV s$^{-1}$. 
The CV analysis of 1 showed three oxidation potentials (Table 1). Accordingly, the chemical oxidation of 1 with Fe(ClO₄)₃ revealed characteristic changes in color and electronic spectra. As shown in Figure 2, the oxidation of 1 with 1, 2, 3, and 6 equiv of Fe(ClO₄)₃ in CH₂Cl₂–CH₃CN (v/v 4:1) resulted in the formation of 1⁺ (859 and ca. 2000 nm), 1²⁺ (872 nm), 1³⁺ (860 nm), and 1⁶⁺ (694 nm), respectively. The solutions changed from green (1) to dark orange (1⁺), greenish orange (1²⁺), dark green (1³⁺), and blue (1⁶⁺). The cation radical 1⁺ shows a very broad absorption at approximately 2000 nm probably owing to the strong intermolecular interaction between the TTF and TTF⁺ units. However, the possible formation of a mixed valence dimer (1₂³⁺) was ruled out, because 1₂³⁺ (i.e., 1¹.₅⁺ in Figure 2) exhibited a weak absorption at approximately 2000 nm as shown in Figure 2. Regarding 1³⁺, no π-dimer formation was observed based on its electronic spectra, and the absorption of 1³⁺ (860 nm) appeared almost the same as that of 1⁺ (859 nm). However, the absorption of 1²⁺ (872 nm) showed a red shift corresponding to the intramolecular head-to-tail interaction of two TTF⁺ units. In contrast to the preferable π-dimer formation of tris(TTF)[18]annulene trications, the absence of the π-dimer formation of 1³⁺ might have been due to the difficulty in stacking the [4n] π-electron system.

Figure 2. UV-Vis-NIR spectra of cationic species derived from 1 in CH₂Cl₂–CH₃CN (4:1)

In summary, the synthesis of the tris(TTF)[12]annulene 1 was successfully carried out using the nearly stoichiometric Sonogashira coupling of the diiodo-biTTF 6 with the diethynyl-TTF 5. The TTF-annulene 1 exhibits solvatochromism, electrochromism, and multi-redox behavior owing to the π-amphoteric nature of 1. Although 1 is unstable in the solid state, presumably owing to the combination of the [4n] π-electron system with π-donors, the introduction of electron-withdrawing groups into the TTF units in 1.
can stabilize the molecule.

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REFERENCES AND NOTES

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9. M. Iyoda, S. Sirinintasak, Y. Nishiyama, A. Vorasingha, F. Sultana, K. Nakao, Y. Kuwatani,
10. Data for 1: dark green powder, mp (measured by DSC) 91.2 °C (decomp.); LDI-MS m/z 1206 (M⁺); ¹H-NMR (500 MHz, CDCl₃) δ 2.78 (t, J = 7.4 Hz, 12H), 1.59 (quint, J = 7.4 Hz, 12H), 1.42 (sext, J = 7.4 Hz, 12H), 0.93 (t, J = 7.4 Hz, 18H); ¹³C-NMR (125MHz, CDCl₃) δ 13.6, 21.6, 29.7, 36.1, 92.9, 106.7, 114.4, 123.2, 127.8; UV-Vis (CH₂Cl₂, ε) 322 (90000), 623 (3800) nm. Anal. Calcd for C₄₈H₅₄S₁₈: C, 47.72; H, 4.51. Found: C, 47.61; H, 4.58.

11. Since the double bonds of TTFs have an olefinic character, the [12]annulene ring in 1 is more paratropic than that in 2. Similarly, the paratropicity of 2 is much more stronger than that of tribenzohexadehydro[12]annulene (TBA). Therefore, the first reduction potential of the [12]annulene unit increases in the order TBA < 2 < 1, reflecting the increase in the degree of cyclic conjugation. The LUMO levels of 1, 2, and TBA are 1 < 2 < TBA, reflecting the decrease in the degree of cyclic conjugation, see: M. Iyoda, Y. Onishi, and M. Nakagawa, *Tetrahedron Lett.*, 1981, 22, 3645.

12. The CV analysis of 1 and 2 in benzonitrile at room temperature revealed that these compounds show only weak intra- and intermolecular interactions in the cationic states, although some TTF oligomers show fairly strong intra- and intermolecular interactions owing to mixed valence dimer and π-dimer formations.⁷a


14. The oxidation of 1 with 1.5 equiv of Fe(ClO₄)₃ in CH₂Cl₂–CH₃CN (v/v 4:1) resulted in the formal formation of 1¹⁵⁺ as shown in Figure 2. Although the formation of a mixed valence dimer (1²⁺⁺ı) was expected, the electronic spectrum of 1¹⁵⁺ showed only a weak absorption at ca. 2000 nm and hence almost no formation of a mixed valence dimer (1²⁺⁺ı) in solution. For the formation of a mixed valence dimer from the tris-TTF system, see: M. Hasegawa, J. Takano, H. Enozawa, Y. Kuwatani, and M. Iyoda, *Tetrahedron Lett.*, 2004, 45, 4109.


16. The intramolecular head-to-tail (or side-by-side) interaction of the two cation-radicals shows a bathochromic shift of the longest absorption maximum owing to Davydov red shift,¹⁹ see:

