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

Kenji Hara,§ Masashi Hasegawa,§ Yoshiyuki Kuwatani,§ Hideo Enozawa,‡ and Masahiko Iyoda*

Department of Chemistry, Graduate School of Science and Engineering, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan; iyoda@tmu.ac.jp

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)tetrathiafulvalene 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.

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 procedure6 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(PPh$_3$)$_4$ (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. For the synthesis of 1, almost stoichiometric amounts of Pd(PPh$_3$)$_4$ 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 CS$_2$ but bright green in CH$_2$Cl$_2$. 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 [[$\lambda_{\text{max}}$ (CS$_2$) 656 nm and $\lambda_{\text{max}}$ (CH$_2$Cl$_2$) 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
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\(^{1+}\), and 1\(^{5+}\), or 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.\(^1\) In contrast, the oxidation potentials of 1 and 2 seemed to be similar. However, the first oxidation potential of 1 was split into two (\( E^{\text{ox}1/2} \) = 0.12 V; \( E^{\text{ox}1/2} \) = 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.\(^2\) Consequently, the oxidation potential of the TTF units decreases in the order 2 ≥ 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^{\text{red}2/1/2} )</th>
<th>( E^{\text{red}1/1/2} )</th>
<th>( E^{\text{ox}1/1/2} )</th>
<th>( E^{\text{ox}2/1/2} )</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 \(^6\)Bu\(4\)NCIO\(_4\) (0.1 M), glassy carbon (working electrode), Pt (counter electrode), and 100 mVs\(^{-1}\), whereas oxidation potential was measured in benzonitrile using \(^6\)Bu\(4\)NCIO\(_4\) (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.

ACKNOWLEDGEMENTS

This work was supported in part by a Grant-in-Aid for Scientific Research from JSPS and CREST of JST. KH would like to acknowledge a research fellowship for young scientists from JSPS. We are grateful to Prof. Masato Yoshida (Shimane University) and Prof. Haruo Matsuyama (Muroran Institute of Technology) for their helpful discussions.

REFERENCES AND NOTES

# Present Address: Department of Chemistry, School of Science, Kitasato University, Sagamihara, Kanagawa 228-8555, Japan
† Present Address: VSN Inc., Nishimiyahara 2-1-3, Yodogawa-Ku, Osaka 532-0004, Japan
‡ Present Address: Functional Soft Matter Engineering Laboratory, Advanced Science Institute, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

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 11.5+ as shown in Figure 2. Although the formation of a mixed valence dimer (123+) was expected, the electronic spectrum of 11.5+ showed only a weak absorption at ca. 2000 nm and hence almost no formation of a mixed valence dimer (123+) 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, see:

