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SYNTHESIS AND π -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

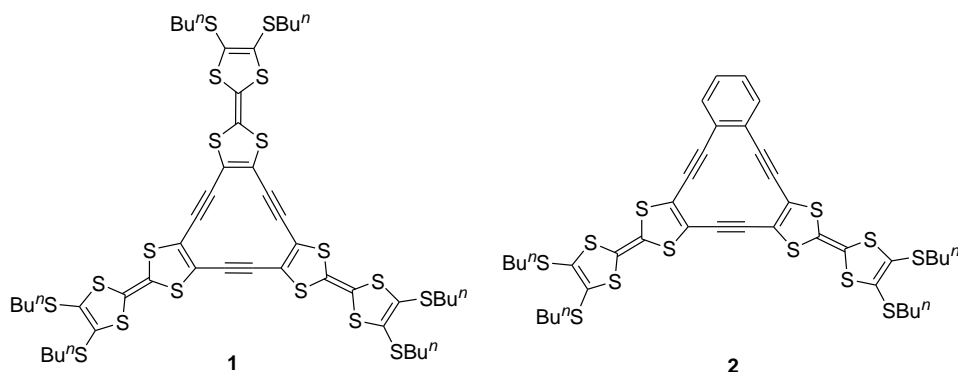
Abstract – The Sonogashira coupling reaction of the diiodide **6** of 1,2-[4,5-bis(butylthio)tetrathiafulvalenyl]ethyne with 4,5-bis(ethynyl)-4',5'-bis(butylthio)tetrathiafulvanene **5** produced the corresponding tris(tetrathiafulvaleno)hexadecahydro[12]annulene **1** in moderate yield. The [12]annulene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

INTRODUCTION

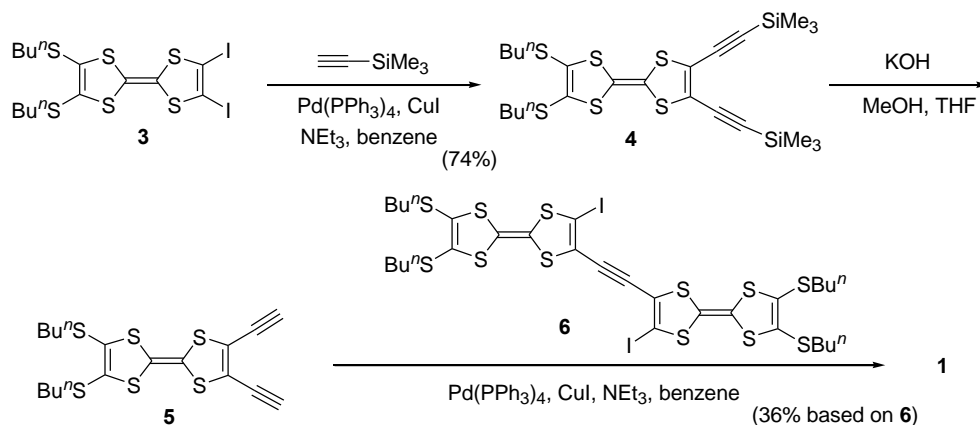
Hexadecahydro[12]annulene has received considerable attention, because its tribenzo-analogue is regarded as a structural unit of graphyne,¹ and because various unique transition-metal complexes have been constructed using the [12]annulene frame.^{2,3} Furthermore, tribenzohexadecahydro[12]annulene (TBA) has been employed as a starting material for the synthesis of cage molecules and polyethers.^{4,5} Recently, we have reported the synthesis and π -amphoteric properties of bis(tetrathiafulvaleno)hexadecahydro[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)hexadecahydro[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 hexadecahydro[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(PPh₃)₄ (15 mol%), CuI (30 mol%), and Et₃N



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.



Scheme 1. Synthesis of tris(TTF)[12]annulene **1**

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, ε = 90,000) and weak (623-656 nm, ε = 3500-4000) absorptions. The strong absorption is unchanged with the type of solvent, whereas the weak absorption varies with the type of solvent used [λ_{max} (CS₂) 656 nm and λ_{max} (CH₂Cl₂) 623 nm]. Since the longest absorption is assigned to the charge-transfer (CT) band from the TTF (π -donor) to [12]annulene (π -acceptor) moieties, this transition is sensitive to the polarity of the solvent.

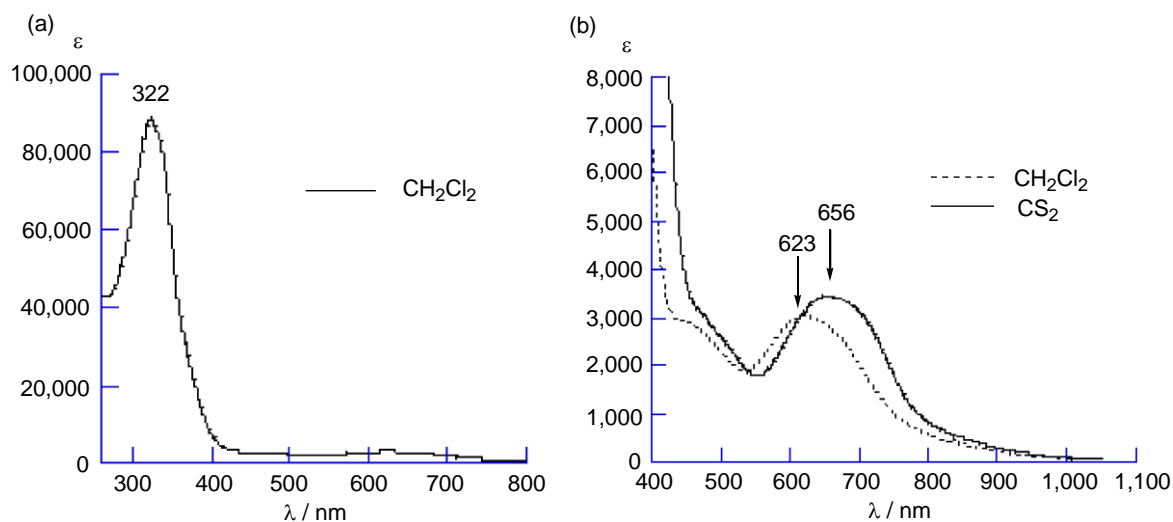


Figure 1. UV-Vis-NIR spectra of **1**. (a) Entire spectrum in CH₂Cl₂. (b) Expansion of the weak absorptions in CH₂Cl₂ and CS₂.

The cyclic voltammetric (CV) analysis of **1** shows unique redox properties owing to the π -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.¹¹ In contrast, the oxidation potentials of **1** and **2** seemed to be similar. However, the first oxidation potential of **1** was split into two ($E^{\text{ox}1}_{1/2}(\mathbf{1}) = 0.12$ V; $E^{\text{ox}1}_{1/2}(\mathbf{2}) = 0.26$ 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.¹² 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

Compound	$E^{\text{red}2}_{1/2}$	$E^{\text{red}1}_{1/2}$	$E^{\text{ox}1}_{1/2}$	$E^{\text{ox}2}_{1/2}$
TTF	—	—	-0.08	0.30
1	-1.78	-1.41	0.21 (0.12, 0.26) ^b	0.49
2	-1.87	-1.50	0.19	0.46

^aReduction potential was measured in THF using ⁿBu₄NClO₄ (0.1 M), glassy carbon (working electrode), Pt (counter electrode), and 100 mV s⁻¹, whereas oxidation potential was measured in benzonitrile using ⁿBu₄NClO₄ (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⁺.

^bMeasured at 3 mV s⁻¹.

The CV analysis of **1** showed three oxidation potentials (Table 1). Accordingly, the chemical oxidation of **1** with $\text{Fe}(\text{ClO}_4)_3$ revealed characteristic changes in color and electronic spectra.¹³ As shown in Figure 2, the oxidation of **1** with 1, 2, 3, and 6 equiv of $\text{Fe}(\text{ClO}_4)_3$ in $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{CN}$ (v/v 4:1) resulted in the formation of $\mathbf{1}^{+\cdot}$ (859 and ca. 2000 nm), $\mathbf{1}^{2+}$ (872 nm), $\mathbf{1}^{3+}$ (860 nm), and $\mathbf{1}^{6+}$ (694 nm), respectively. The solutions changed from green (**1**) to dark orange ($\mathbf{1}^{+\cdot}$), greenish orange ($\mathbf{1}^{2+}$), dark green ($\mathbf{1}^{3+}$), and blue ($\mathbf{1}^{6+}$). The cation radical $\mathbf{1}^{+\cdot}$ shows a very broad absorption at approximately 2000 nm probably owing to the strong intermolecular interaction between the TTF and $\text{TTF}^{+\cdot}$ units. However, the possible formation of a mixed valence dimer ($\mathbf{1}_2^{3+}$) was ruled out, because $\mathbf{1}_2^{3+}$ (*i.e.*, $\mathbf{1}^{1.5+}$ in Figure 2)¹⁴ exhibited a weak absorption at approximately 2000 nm as shown in Figure 2. Regarding $\mathbf{1}^{3+}$, no π -dimer formation was observed based on its electronic spectra, and the absorption of $\mathbf{1}^{3+}$ (860 nm) appeared almost the same as that of $\mathbf{1}^{+\cdot}$ (859 nm).¹⁵ However, the absorption of $\mathbf{1}^{2+}$ (872 nm) showed a red shift corresponding to the intramolecular head-to-tail interaction of two $\text{TTF}^{+\cdot}$ units.¹⁶ In contrast to the preferable π -dimer formation of tris(TTF)[18]annulene trications,¹⁷ the absence of the π -dimer formation of $\mathbf{1}^{3+}$ might have been due to the difficulty in stacking the $[4n]$ π -electron system.¹⁸

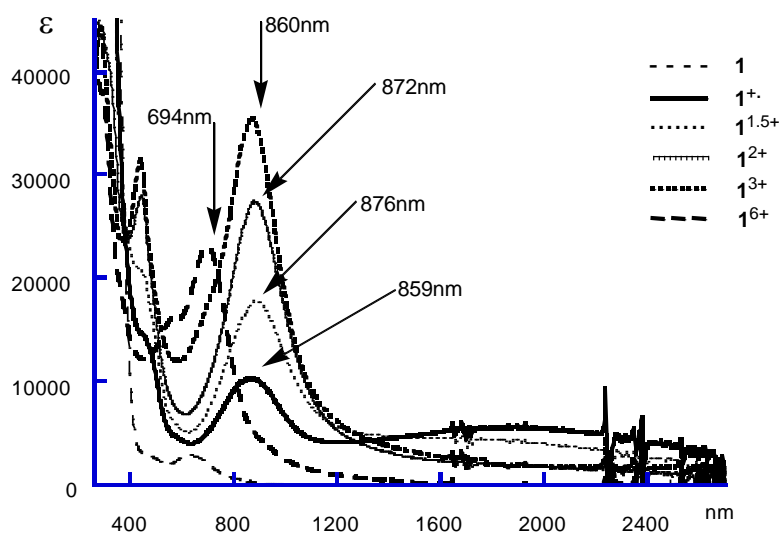


Figure 2. UV-Vis-NIR spectra of cationic species derived from **1** in $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{CN}$ (4:1)

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

§ Present Address: ADEKA Co., Higashi-Ogu 7-2-35, Arakawa-Ku, Tokyo 116-8553, Japan.

Present Address: Department of Chemistry, School of Science, Kitasato University, Sagami-hara, 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

1. R. H. Baughman, H. Eckhardt, and M. Kertesz, *J. Chem. Phys.*, 1987, **87**, 6687.
2. W. J. Youngs, C. A. Tessier, and J. D. Bradshaw, *Chem. Rev.*, 1999, **99**, 3153.
3. M. Iyoda, A. Vorasingha, Y. Kuwatani, and M. Yoshida, *Tetrahedron Lett.*, 1998, **39**, 4701.
4. (a) M. Iyoda, K. Fuchigami, A. Kusaka, T. Yoshida, M. Yoshida, H. Matsuyama, and Y. Kuwatani, *Chem. Lett.*, 2000, 860; (b) S. Sirinintasak, Y. Kuwatani, S. Hoshi, E. Isomura, T. Nishinaga, and M. Iyoda, *Tetrahedron Lett.*, 2007, **48**, 3433.
5. M. Ohkoshi, T. Horino, M. Yoshida, and M. Iyoda, *Chem. Commun.*, 2003, 2586.
6. K. Hara, M. Hasegawa, Y. Kuwatani, H. Enozawa, and M. Iyoda, *Chem. Commun.*, 2004, 2042.
7. For the TTF oligomers, see: (a) M. Iyoda, M. Hasegawa, and Y. Miyake, *Chem. Rev.*, 2004, **104**, 5085; (b) M. Iyoda, M. Hasegawa, and H. Enozawa, *Chem. Lett.*, 2007, **36**, 1402; (c) M. Hasegawa, H. Enozawa, and M. Iyoda, *J. Synth. Org. Chem. Jpn.*, 2008, **66**, 1211.
8. (a) I. D. Campbell, G. Eglinton, W. Henderson, and R. A. Raphael, *J. Chem. Soc., Chem. Commun.*, 1966, 87; (b) D. Solooki, J. D. Ferrara, D. Malaba, J. D. Bradshaw, C. A. Tessier, and W. J. Youngs, *Inorg. Synth.*, 1997, **31**, 122; (c) C. Huynh and G. Linstrumelle, *Tetrahedron*, 1988, **44**, 6337; (d) H. A. Staab and F. Graf, *Chem. Ber.*, 1970, **103**, 1107; (e) K. P. C. Vollhardt and G. D. Whitener, *Synlett*, 2003, 29.
9. M. Iyoda, S. Sirinintasak, Y. Nishiyama, A. Vorasingha, F. Sultana, K. Nakao, Y. Kuwatani,

H. Matsuyama, M. Yoshida, and Y. Miyake, [Synthesis, 2004, 1527](#).

10. Data for **1**: dark green powder, mp (measured by DSC) 91.2 °C (decomp.); LDI-MS m/z 1206 (M^+); $^1\text{H-NMR}$ (500 MHz, CDCl_3) 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); $^{13}\text{C-NMR}$ (125MHz, CDCl_3) δ 13.6, 21.6, 29.7, 36.1, 92.9, 106.7, 114.4, 123.2, 127.8; UV-Vis (CH_2Cl_2 , ϵ) 322 (90000), 623 (3800) nm. Anal. Calcd for $\text{C}_{48}\text{H}_{54}\text{S}_{18}$: 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 $\text{TBA} < \mathbf{2} < \mathbf{1}$, reflecting the increase in the degree of cyclic conjugation. The LUMO levels of **1**, **2**, and TBA are $\mathbf{1} < \mathbf{2} < \text{TBA}$, 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}
13. For the chemical oxidation of TTFs with $\text{Fe}(\text{ClO}_4)_3$, see: M. Iyoda, M. Hasegawa, Y. Kuwatani, H. Nishikawa, K. Fukami, S. Nagase, and G. Yamamoto, [Chem Lett., 2001, 1146](#).
14. The oxidation of **1** with 1.5 equiv of $\text{Fe}(\text{ClO}_4)_3$ in CH_2Cl_2 - CH_3CN (v/v 4:1) resulted in the formal formation of $\mathbf{1}^{1.5+}$ as shown in Figure 2. Although the formation of a mixed valence dimer ($\mathbf{1}_2^{3+}$) was expected, the electronic spectrum of $\mathbf{1}^{1.5+}$ showed only a weak absorption at *ca.* 2000 nm and hence almost no formation of a mixed valence dimer ($\mathbf{1}_2^{3+}$) 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](#).
15. (a) M. Iyoda, K. Hara, Y. Kuwatani, and S. Nagase, [Org. Lett., 2000, 2, 2217](#); (b) M. Iyoda, M. Hasegawa, K. Hara, J. Takano, E. Ogura, and Y. Kuwatani, [J. Phys. IV France, 2004, 114, 455](#); (c) M. Hasegawa, Y. Kuwatani, and M. Iyoda, [J. Phys. IV France, 2004, 114, 505](#); (d) M. Hasegawa, H. Enozawa, Y. Kawabata, and M. Iyoda, [J. Am. Chem. Soc., 2007, 129, 3072](#); (e) M. Hasegawa, Y. Kobayashi, K. Hara, H. Enozawa, and M. Iyoda, [Heterocycles, 2009, 77, 837](#).
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:

- (a) M. Iyoda, M. Hasegawa, J. Takano, K. Hara, and Y. Kuwatani, [Chem. Lett., 2002, 590](#);
- (b) M. Iyoda, H. Enozawa, and Y. Miyake, [Chem. Lett., 2004, 1098](#).
17. (a) H. Enozawa, M. Hasegawa, D. Takamatsu, K. Fukui, and M. Iyoda, [Org. Lett., 2006, 8, 1917](#); (b) H. Enozawa, M. Hasegawa, E. Isomura, T. Nishinaga, T. Kato, M. Yamato, T. Kimura, and M. Iyoda, *ChemPhysChem*, in press [[DOI: 10.1002/cphc.200900545](#)].
18. Although terminal benzene rings of helicenes tend to stack on top of each other, terminal biphenylene rings of heliphenes tend to separate from each other, see: S. Han, D. R. Anderson, A. D. Bond, H. V. Chu, R. L. Disch, D. Holmes, J. M. Schulman, S. J. Teat, K. P. C. Vollhardt, and G. D. Whitener, [Angew. Chem. Int. Ed., 2002, 41, 3227](#).
19. (a) J. B. Torrance, B. A. Scott, B. Welber, F. B. Kaufman, and P. E. Seiden, [Phys. Rev. B, 1979, 19, 730](#); (b) M. E. Kozlov, Y. Tanaka, M. Tokumoto, and T. Tani, [Synth. Metal., 1995, 70, 987](#).