Preparation, Structure, and Spectral Properties of Cyclophanes Consisting of Oligothiophene Units

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Small-sized cyclophanes consisting of oligothiophene units as a component have been prepared. Correlation between the cyclophane structure and fluorescence spectral properties has been examined. It has been found that emission from intramolecular excimer-formation is confirmed for the cyclophanes having two or three thiophene units, but not for those having four or five thiophene units with the β-hexyl chain.

Over the past decades well-defined π-conjugated oligothiophenes have gained great importance as advanced molecular electronic materials, including for example, organic field effect transistors (OFETs)[1] and organic light-emitting diodes (OLEDs)[2] because of the feasibility in manipulation of their chemical structures. Indeed, in order to improve electronic and optical properties of oligothiophenes, introduction of end-capping groups,[3] insertion of various functional groups,[4] and changing oligomer lengths[5] have been carried out. These strategies mainly involve creation of novel π systems.

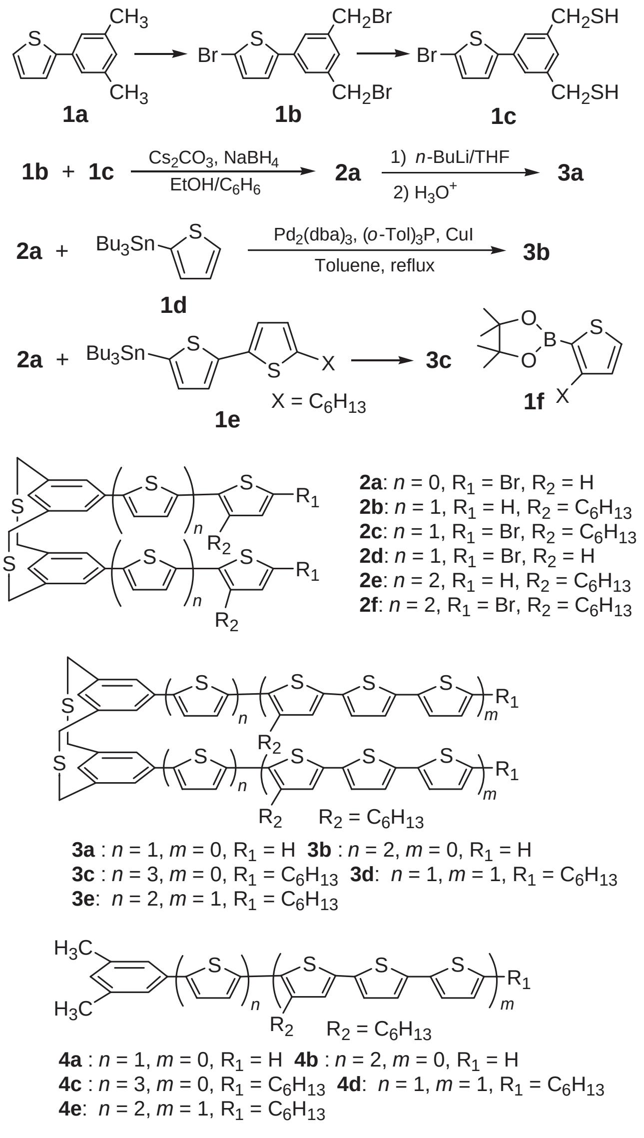
Meanwhile, we have reported that π systems based on the cyclophane skeleton give rise to specific electronic properties owing to strong transannular π-electronic interactions.[6] Some cyclophane-derived oligothiophenes consisting of a [2.2]metacyclophane skeleton have been reported.[3a,7] Cyclophane-type compounds in which two oligothiophene units are bridged with alkylene chains have been also reported.[8] Among a number of cyclophanes, the [3.3]dithiametacyclophane skeleton seems to provide an appropriate platform to arrange two oligomer chains side by side in stacked form since it is known[9] that this kind of cyclophane assumes a syn structure.

Thus, we describe the preparation of metacyclophanes to which two oligothiophene units are introduced, their structure and spectral properties.

Bromination of compound **1a** gave bromomethyl compound **1b** in 65% yield. The sulfanylmethyl compound **1c** was obtained by the reaction of **1b** and thiourea in 95% yield.

Cyclization of **1b** and **1c** using Cs_2CO_3 as a base under highly dilute conditions afforded the corresponding dithiacyclophane **2a** in 57% yield. Treatment of **2a** with *n*-butyllithium followed by quenching with hydrochloric acid afforded the desired cyclophane **3a** in 83% yield. The cyclophane having two thiophene units **3b** was obtained from **2a** and 2-tributylstannylthiophene (**1d**) in 43% yield. Although the cyclophane having three thiophene units was prepared by similar reaction, the product showed poor solubility in conventional organic solvents.

Thus, the coupling of **2a** and tributylstannyl-2,2′-bithiophene carrying hexyl group **1e** gave cyclophane having three thiophene units **3c** in 35% yield. As expected **3c** showed good solubility. This result implies more than two alkyl groups should be necessary to obtain good solubility for cyclophanes carrying four or five thiophene units. Thus, cyclophane **2b** was prepared from **2a** and **1f** in 80% yield.



Scheme 1.

Bromination of **2b** gave cyclophane **2c** (89%), which reacted with **1e** to afford cyclophane having four thiophene units **3d** in 37% yield. After **3b** was brominated to give cyclophane **2d** (96%), followed by coupling with **1f**, cyclophane **2e** was obtained in 73% yield. The treatment of **2e** with NBS afforded

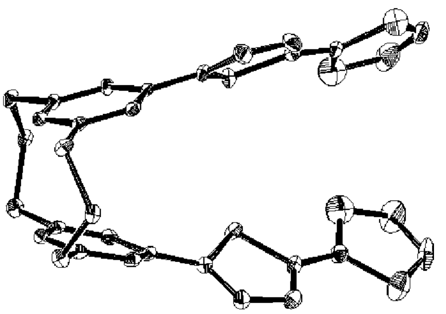


Figure 1. Perspective view of **3b**.

Table 1. Maximum wavelength (λ_{max}/nm)[a] of absorption and fluorescence spectra and quantum yields (Φ_f) of total fluorescence for **3a**–**3e** and **4a**–**4e**

Compound	Absorption	Fluorescence[b]	Φ_f
3a	284	342 (435)[c]	0.016
3b	341	418 (483)	0.094
3c	383	445 (508)	0.044
3d	409	506	0.068
3e	415	528	0.083
4a	284	337	0.083
4b	340	414	0.080
4c	384	445	0.120
4d	408	491	0.349
4e	423	513	0.431

[a] In cyclohexane, $T = 295$ K. [b] Excitation of the samples was performed at the wavelength of the corresponding absorption maximum. [c] Values in parentheses are for excimer fluorescence.

cyclophane **2f** (61%), which reacted with **1e** to give cyclophane having the five thiophene units **3e** in 44% yield. The corresponding referential oligothiophenes **4a**–**4e** were also prepared by similar methods (Scheme 1). All cyclophanes **3a**–**3e**[10] were identified by their ^{1}H NMR spectra, mass spectrometric measurements, and/or elemental analyses.

The protons of the bridges in cyclophanes **3a**–**3e** showed one singlet at room temperature in the ^{1}H NMR spectra. No significant signal changes were observed when the temperature was lowered to −80 °C, suggesting that they are basically a flexible structure.

The X-ray analysis of **3b**[11] shows the syn conformation (Figure 1). It has been reported[9,12] that these kinds of dithiacyclophanes tend to assume a syn conformation.

Obviously this syn structure could be essential for creating vertically stacked π-conjugated systems based on the cyclophane structure.

The electronic absorption and fluorescence spectral data of cyclophanes **3a**–**3e**, together with the corresponding oligothiophenes **4a**–**4e**, are summarized in Table 1. In the electronic absorption spectra the π–π^* transitions are shifted to longer wavelengths with increasing chain length. There were observed no essential differences in shape of the absorption spectra between the cyclophanes and the corresponding thiophenes. Cyclophane **3a** exhibits a weak excimer fluorescence band accompanied with a locally excited (LE) fluorescence band. For **3b** and **3c**, intense excimer fluorescence bands are observed together with the corresponding weak LE fluorescence bands. No such excimer fluorescence bands were obtained when increasing the concentrations of **4a**–**4c**. These results strongly suggest that thiophene moieties of **3a**–**3c** have a sandwich-like structure in the ground state, which corresponds to the syn conformation as seen for **3b**.

Conversely, cyclophanes **3d** and **3e** show fluorescence spectra with vibronic structures. These observations indicate that the fluorescence of **3d** and **3e** is not excimeric, but from the corresponding monomer moieties. In **3c** the α-hexyl chain seems to be no hindrance to excimer formation. From these results, it is inferred that elongation of thiophene units accompanied with introduction of a β-hexyl chain could hamper the conformation suitable for excimer formation.

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10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
11 Crystal data for **3b**: $C_{32}H_{24}S_6 \cdot C_6H_6$, $M_r = 679.01$, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.8263(3)$, $b = 13.5119(3)$, $c = 14.1160(4)$ Å, $\alpha = 104.9451(7)°$, $\beta = 101.9353(9)°$, $\gamma = 110.110(1)°$, $V = 1607.71(8)$ Å^3, $Z = 2$, $D_{calcd} = 1.403$ g cm^{-3}, Rigaku AFC7R diffractometer, $R_1 = 0.106$ (for 6356 reflections with $I > 3\sigma(I)$), $wR_2 = 0.214$ (for all data (15124 reflections)). CCDC reference No 664968.
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