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SYNTHESES, STRUCTURES, AND PROPERTIES OF BITHIOPHENOPHANES BRIDGED AT 1,8-POSITIONS OF NAPHTHALENES

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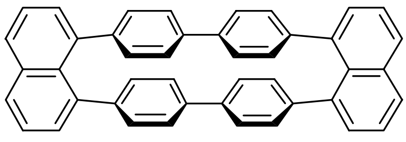
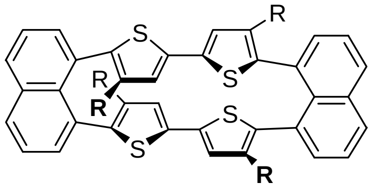
Abstract – The 2,2'-bithiophenophanes **2** and **3** bridged at the 1,8-positions of naphthalenes together with the linear dimers **4** and **6**, the trimers **5** and **7**, and the tetramer **8** were synthesized by the homo-coupling of 1,8-di(5-lithio-2-thienyl)naphthalenes with $CuCl_2$. The cyclophane **2**, which has no alkyl substituents, shows a hindered rotation of its bithiophene units to give two isomers, of which the major isomer easily isomerized photochemically to produce the minor isomer. In contrast, **3**, which has ethyl substituents, shows a rapid rotation of its bithiophene units in solution to afford a mixture of four conformational isomers, although an X-ray analysis of **3** revealed the existence of only one isomer in crystals. The redox and fluorescence behaviors of **2** and **3** show either a face-to-face interaction of the 2,2'-bithiophene units or deformation of the naphthalene moieties. Furthermore, the linear oligomers **4**, **5**, **6**, **7**, and **8** show fairly low oxidation potentials and clear emission owing to the π-π interaction of the face-to-face-stacked thiophene rings.

INTRODUCTION

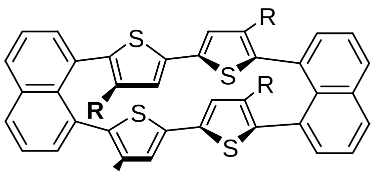
Cyclophanes, cyclic oligophenylenes, and their heterocyclic counterparts have attracted much attention because of their unique structures, molecular strain, π-π interactions in neutral and cation radical states, enhanced π-donor ability, and aromaticity, as well as the synthetic challenges they present.[1] Among these compounds, cyclic oligophenylenes are a unique π-conjugated system with highly fluorescent and extremely stable frameworks, although only a limited number of fully conjugated compounds have been reported to date.[2,3] We previously reported the synthesis and X-ray structure of the cyclic oligophenylene **1**.[4] Although it bears a fairly large internal ring strain with a strong π-π interaction between its two biphenyls, **1** is extremely stable to light, atmospheric oxygen, and prolonged heating. By considering these results as well as general knowledge of 1,8-diarylnaphthalenes,[5] the 2,2'-bithiophenophanes **2** and **3** bridged at the 1,8-positions of naphthalenes can be regarded as a model system for examining the face-to-face interaction between two 2,2'-bithiophene units. Since 1,8-diarylnaphthalenes show a strong π-π interaction between two aryl rings separated by a distance smaller than the sum of van der Waals radii (3.4 Å), the stabilities of the *syn*- and *anti*-conformations of 1,8-bis(2-thienyl)naphthalene may control the most favorable structures of **2** and **3**.[6]



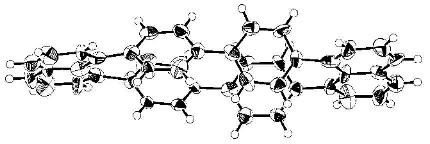
1



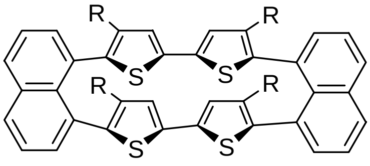
2a: R = H
3a: R = Et



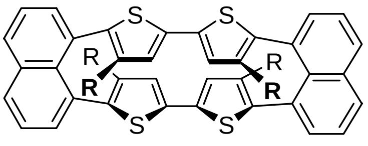
2b: R = H
3b: R = Et



X-ray structure of **1**

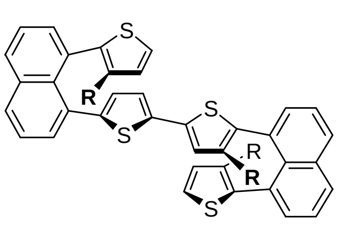


2c: R = H
3c: R = Et

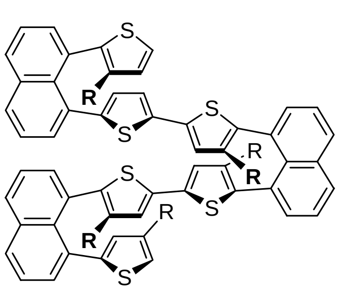


2d: R = H
3d: R = Et

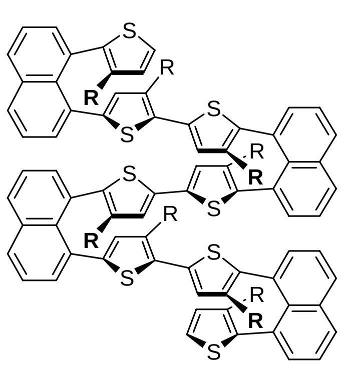
In addition to synthesizing **2** and **3**, we also synthesized their corresponding linear dimers **4** and **6**, trimers **5** and **7**, and tetramer **8** because of the multilayered π-π interactions. The linear oligomers **4**-**8** bear a reduced internal strain but stack face to face owing to their closely located thiophene rings. Therefore, these molecules should show an enhanced π-π interaction of multilayered thiophene rings.



4: R = H
6: R = Et



5: R = H
7: R = Et

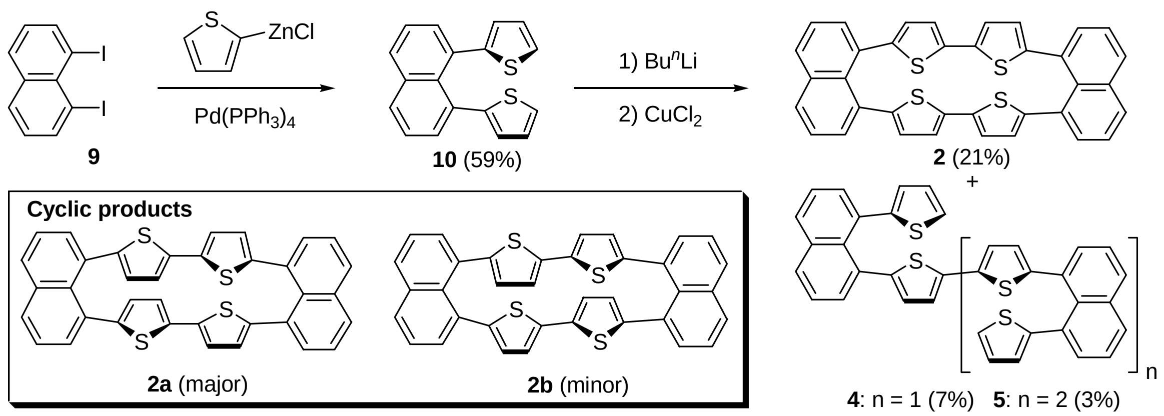


8: R = Et

In preliminary form, we reported the synthesis of the thiophenophane **2** together with **4** and **5**.[7] In this paper, we describe the details of the synthesis of the thiophenophanes **2** and **3** and the linear oligomers **4-8** together with the crystal structure of **3** and the calculated molecular structures of **2** and **3**. The redox and emission properties of **2-8** clearly reflect the π-π interactions between face-to-face-stacked thiophene rings.

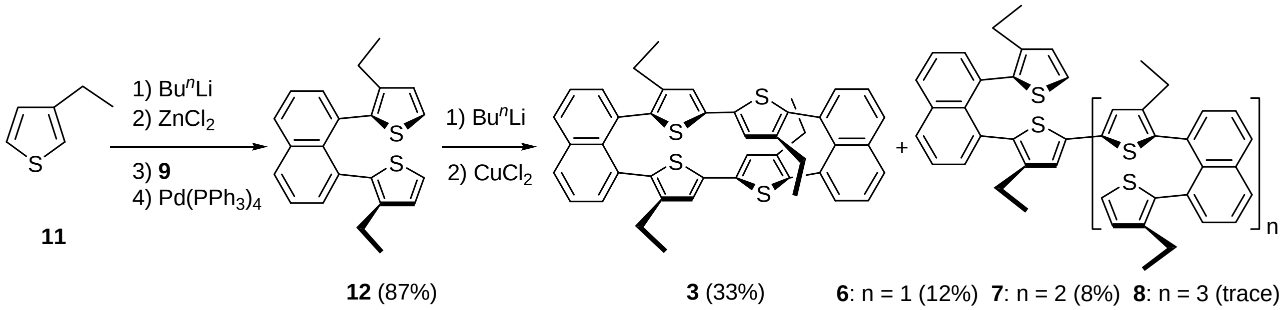
RESULTS AND DISCUSSION

Synthesis. To the synthesize 1,8-di(2-thienyl)naphthalene and its derivatives, Nakayama and coworkers developed a nickel-catalyzed cross-coupling reaction of 1,8-diiodonaphthalene **9** with 2-thienylmagnesium bromide.[8,9] However, the yield of the cross-coupling product was not satisfactorily high because of the reduction of **9** to 1-iodonaphthalene. Therefore, the palladium-catalyzed cross-coupling of **9** with 2-thienylzinc chloride was employed for the preparation of **10** (Scheme 1).[10,11] The reaction of **9** with 2-thienylzinc chloride in the presence of $Pd(PPh_3)_4$ proceeded smoothly to afford **10** in 59% yield. The reaction of **10** with butyllithium (3 equiv.) at 0 °C, followed by treatment with copper(II) chloride (3.4 equiv.)[12] at room temperature produced **2** (21%), **4** (7%), and **5** (3%), together with the starting material **10** (22%). On the basis of its ^{1}H NMR spectrum, **2** was found to be a mixture of **2a** and **2b** (5 : 1). Pure **2a** was obtained by the recrystallization of the reaction product from carbon disulfide. Interestingly, **2a** gradually isomerized to **2b** in refluxing toluene or chlorobenzene. Although the thermal isomerization of **2a** proceeded very slowly to produce **2b** in moderate yield, the photochemical transformation of **2a** into **2b** was effective. A solution of **2a** in chlorobenzene was irradiated with a metal halide lamp[13] in a Pyrex tube at room temperature for 30 min to give only the *syn*-anti isomer **2b** in 77% yield. The dilute conditions (0.75 mmol/L) and short irradiation (30 min) yielded better results, and a higher concentration and a longer reaction time decreased the yield of **2b**.



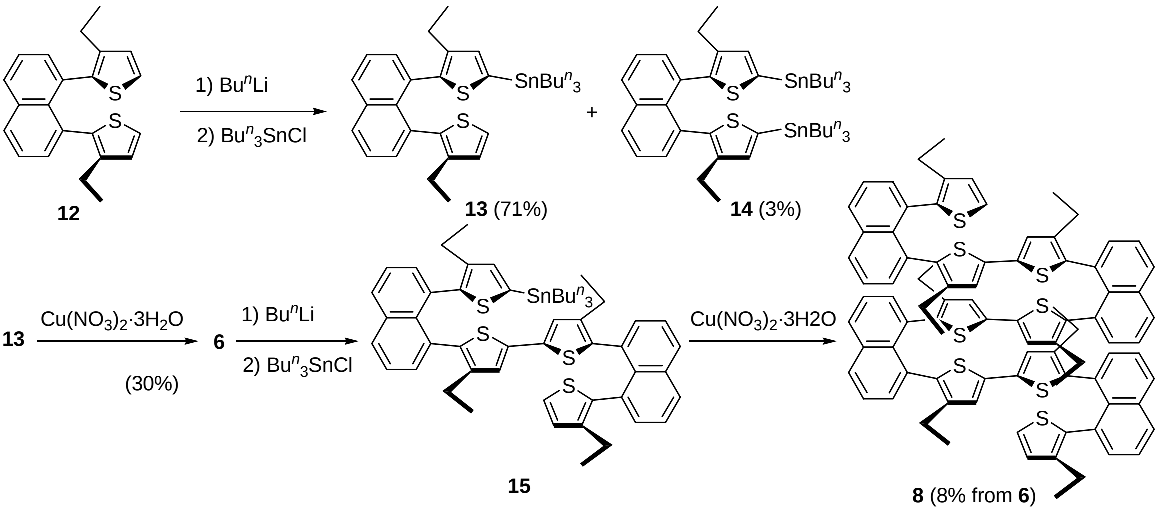
Scheme 1. Synthesis of **2**, **4**, and **5**.

Since the solubility of **2** was very low in common organic solvents, ethyl groups were introduced in the 3-position of the thiophene rings. First, the cross-coupling reaction of the zinc derivative of **11**[14] with **9** in the presence of a palladium catalyst was carried out similarly to the synthesis of **10** to produce **12** in 87% yield together with a trace amount of monosubstituted product (Scheme 2). To synthesize tetraethylbithiophenophane **3**, the halogenation of **12** was first planned. However, the direct lithiation of the thiophene protons at the 5-position seemed to have proceeded smoothly to give a dilithiated product in good yield. Therefore, the reaction of **12** with butyllithium, followed by treatment with copper(II) chloride was performed to produce the desired cyclic bithiophenophane **3** in 33% yield together with the acyclic oligomers **6** (12%) and **7** (8%) and the recovered **12** (18%). Fortunately, the bithiophenophane **3** was easily separated from the crude products owing to its relatively poor solubility. The bithiophenophane **3** possesses higher solubility in organic solvents than **2**.



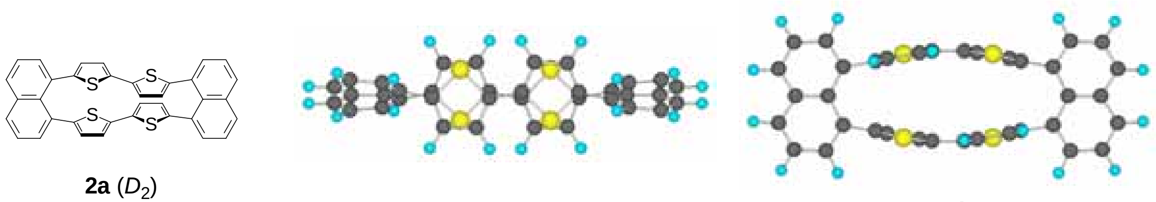
Scheme 2. Synthesis of **3**, **6**, **7**, and **8**.

As for the other approaches to the synthesis of **8**, a stepwise coupling reaction based on the corresponding monostannanes was also carried out. Thus, introduction of a tributylstannyl group was performed by the reaction of **12** with butyllithium, followed by the addition of tributyltin chloride (Scheme 3).[7] Since considerable decomposition of the stannanes **13** and **14** was observed during chromatographic separation on silica gel, **13** from **14** were separated by GPC using chloroform as the eluent to give **13** (71%) and **14** (3%). Note that **13** and **14** are stable after purification and can be stored at room temperature. The monostannane **13** was subjected to a coupling reaction using $Cu(NO_3)_2 \cdot 3H_2O$[15-20] to afford the linear dimer **6** (30%) with **12** (70%). Similarly, a tributylstannyl group was introduced into **6** by successive treatment with butyllithium and tributyltin chloride to produce **15**. The coupling reaction of the monostannane **15** with $Cu(NO_3)_2 \cdot 3H_2O$ afforded the linear tetramer **8** in 8% overall yield together with **6** (90%) (Scheme 3).



Scheme 3. Stepwise synthesis of **6** and **8**.

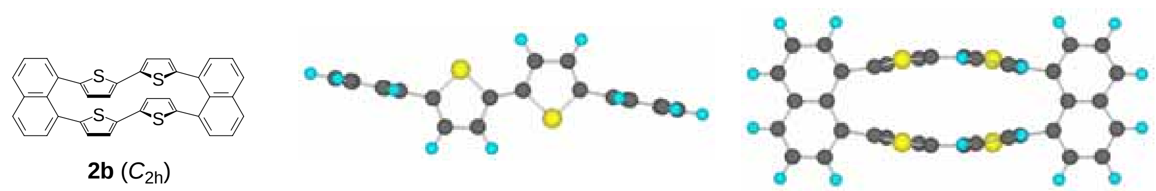
Structures and conformational stabilities. The structures of **2a** and **2b** were assigned based on the ^{1}H NMR spectral data and the result of MO calculations. The thiophene protons in the *all-anti* form **2a** show signals at δ 6.42 (d, J = 3.4 Hz) and 6.72 (d, J = 3.4 Hz), whereas the corresponding thiophene protons in the *syn-anti* form **2b** show signals at δ 6.36 (d, J = 3.7 Hz) and 6.66 (d, J = 3.7 Hz). The *syn*-stacked thiophenophane shows an upper-field shift of thiophene protons compared with the *anti*-stacked one, and the reported chemical shifts of the *syn*- and *anti*-isomers are similar to those of **2a** and **2b**.[21] The B3LYP/6-31G* calculations of D_2-**2a** and C_{2h}-**2b** revealed that **2a** adopts an optimized structure with two slipped thiophene rings as shown in Figure 1. In contrast, **2b** adopts a closely stacked structure with two thiophene rings. The face-to-face distances (3.00-3.87 Å) of the bithiophene units in **2b** are slightly longer than those (2.95-3.77 Å) in **2a**. In the four isomers of **2**, the energies of **2a** and **2b** are close and more stable by 5-9 kcal/mol than those of C_{2v}-**2c** and C_{2h}-**2d** in calculations at the B3LYP/6-31G* level.



2a (D_2)
(relative enegy: 0.00)

Side view

Top view



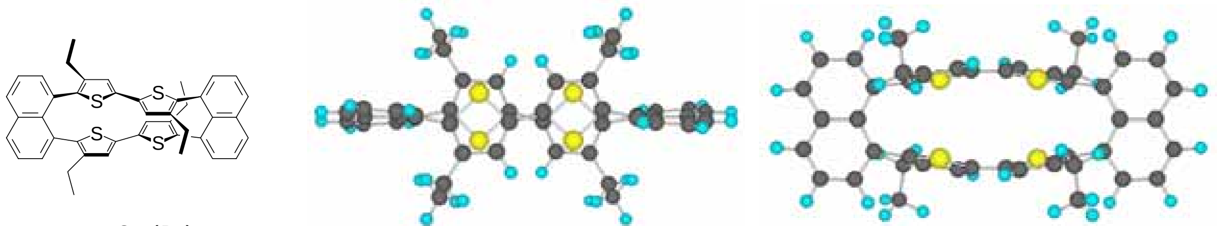
2b (C_{2h})
(relative energy: 2.00 kca/mol)

Side view

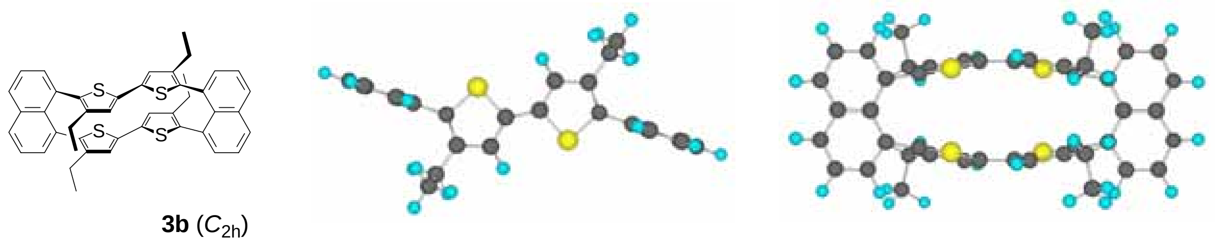
Top view

Figure 1. B3LYP/6-31G* optimized structures of **2a** and **2b**.

Although **2** has a rigid structure, the tetraethyl derivative **3** shows a conformational mobility in the VT-^{1}H NMR spectra. The calculated energies of D_2-**3a**, C_{2h}-**3b**, C_{2v}-**3c**, and C_1-**3e** based on the B3LYP/6-31G* optimized structures showed that the D_2-structure **3a** has the lowest energy (Figure 3). Thus, the most stable conformer **3a** has a similar structure to **2**. However, the energy differences between **3a** and C_{2h}-**3b**, C_{2v}-**3c** and C_1-**3e** are 1.50, 3.67, and 1.98, respectively, which are smaller than the energy differences between **2a** and **2b**-**2e**. Thus, all conformers may contribute to the conformation of **3**, except for **3d**, which has a very high energy level.[22]

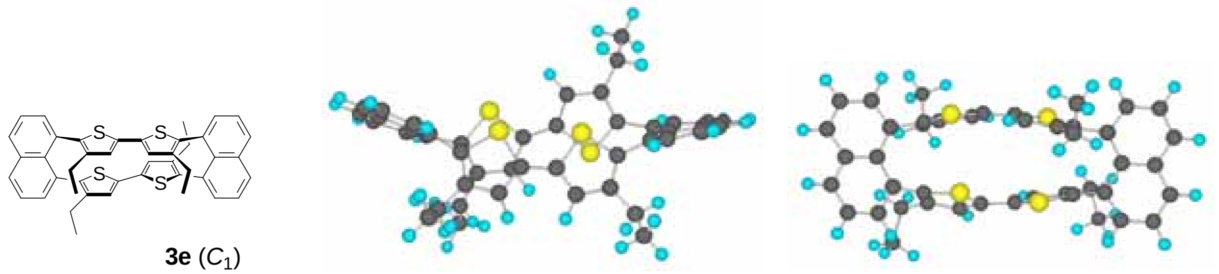


3a (D_2)
(relative enegy: 0.00)
Side view
Top view



3b (C_{2h})
(relative energy: 1.50 kca/mol)
Side view
Top view

3c (C_{2v})
(relative enegy: 3.67 kcal/mol)
Side view
Top view



3e (C_1)
(relative enegy: 1.98 kcal/mol)
Side view
Top view

Figure 2. B3LYP/6-31G* optimized structures of **3a**, **3b**, **3c**, and **3e**

As shown in Figure 3, the ^{1}H NMR spectrum of **3** in $CDCl_2CDCl_2$ at 30 °C indicates the four **3** isomers (**3a**, **3b**, **3c**, and **3e**). The signals of **3a** (δ 6.71), **3b** (δ 6.67), **3c** (δ 6.75), and **3e** (δ 6.95-6.56) were assigned by comparing them with the calculated ^{1}H NMR chemical shifts of **3a** (δ 6.88), **3b** (δ 6.87), **3c** (δ 7.23), and **3e** (δ 7.22-6.71), respectively, estimated at the GIAO/HF/6-31G*//B3LYP/6-31G* level. Nakayama and coworkers also reported an increased conformational mobility of 1,8-bis(3-methyl-2-thienyl)naphthalene with the introduction of methyl groups into 1,8-bis(2-thienyl)naphthalene.[9]

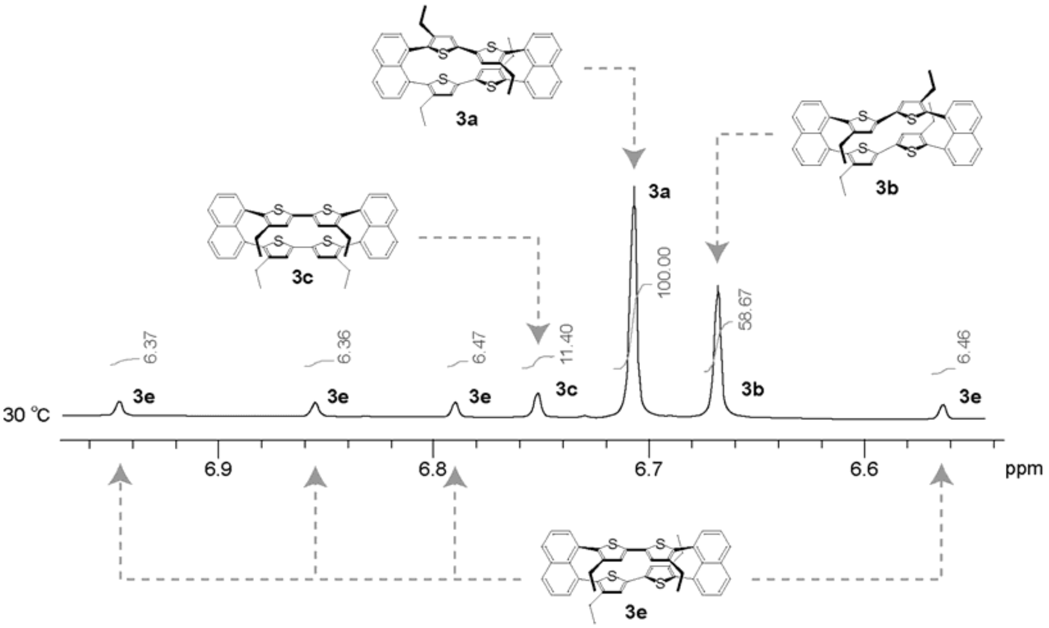
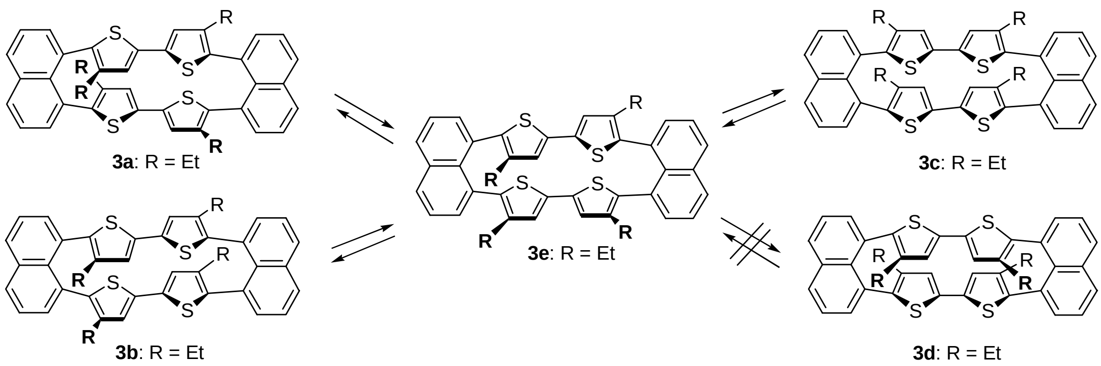


Figure 3. ^{1}H NMR spectrum of **3** in $CDCl_2CDCl_2$ at 30 °C.

To examine the equilibrium among the conformers **3a**, **3b**, **3c**, and **3e**, the VT-^{1}H NMR spectra of **3** were measured. Between 30 ºC and 80 ºC, the ^{1}H NMR spectra of **3** show seven signals of thiophene protons due to the four isomers. At 90 ºC, each spectrum becomes broad, and finally at 140 ºC the spectrum shows only one thiophene signal. The character of VT-NMR spectra clearly shows a conformational change of **3** on the NMR time scale. As shown in Scheme 4, the rotation of one thiophene ring in **3a**-**3c** produces **3e**, which can be converted into **3a**-**3c** by the rotation of the same or a different thiophene ring.



Scheme 4. Possible conformational change of **3**.

Interestingly, the ^{1}H NMR spectrum of **6** is temperature-dependent. As shown in Figure 4, such a spectrum in $CDCl_2CDCl_2$ at 30 ºC shows several broad signals, presumably owing to the equilibrium of the conformational isomers of **6**. At 60 ºC, the spectrum changes to three broad signals corresponding to thiophene protons. At 140 ºC, the spectrum exhibits a very simple pattern owing to a rapid conformational change.

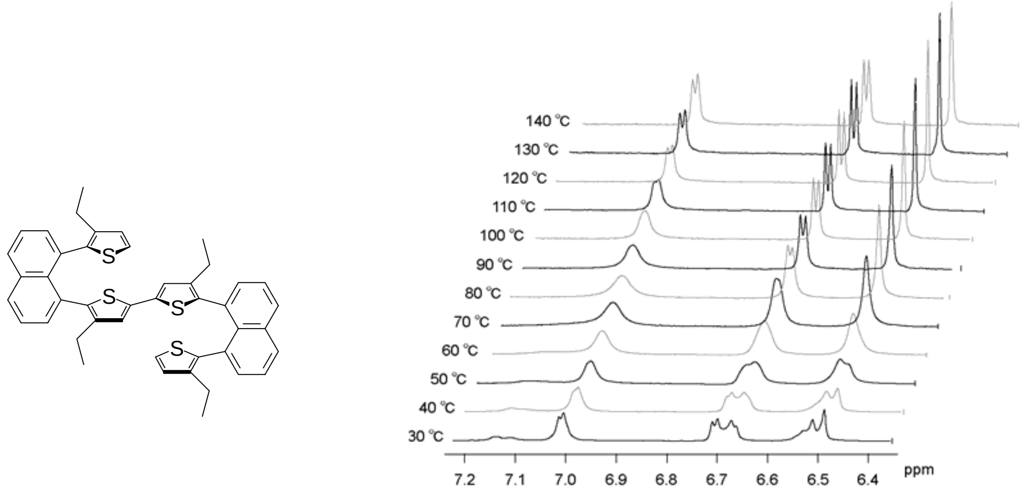


Figure 4. VT-^{1}H NMR spectra of **6** in $CDCl_2CDCl_2$.

X-ray crystal structure of 3. The ^{1}H NMR spectra of **3** show a rapid conformational change of **3** in solution. Fortunately, single crystals of **3** were obtained from benzene, and the crystal structure of **3** was clearly determined by X-ray crystallographic analysis. A single crystal of **3** contains two benzene molecules. As shown in Figure 5, the crystal structure of **3** has a crystallographic S_2 symmetry, and its two bithiophene units are stacked face to face. The intramolecular distances between thiophene rings of **3** are 3.03-3.77 Å. Thus, the thiophene rings exist nearly parallel to each other (Figure 5b) similarly to those of 1,8-[1,8-naphthalenediylbis(4',4-biphenyldiyl)]naphthalene.[4]

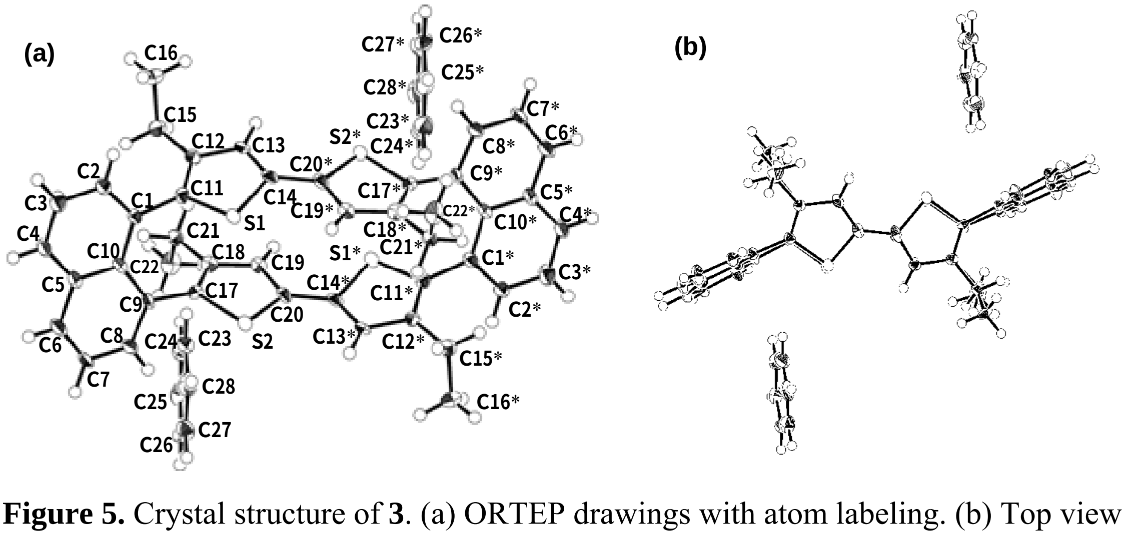


Figure 5. Crystal structure of **3**. (a) ORTEP drawings with atom labeling. (b) Top view.

Since the four thiophene rings in **3** show a planar structure (Figure 5), the ring strain of the thiophene units is considered small. Although the crystal structure adopts the C_{2h} structure **3b**, which is not the most stable conformation, the four ethyl groups and two benzene molecules appear to control the crystal packing to form **3b** as the most stable crystal structure.

Absorption and emission spectra. The bithiophenophanes **2a** and **2b** and their related compounds **10**, **4**, and **5** showed fluorescence in solution and in solid state. UV-vis absorption and fluorescence emission spectral data are summarized in Table 1; **2a**, **2b**, **4**, and **5** have similar absorption maxima except for the shoulder absorption (428 nm) of **2a**, reflecting the existence of a 5,5'-di(1-naphthyl)-2,2'-bithiophene chromophore, whereas **10** shows an absorption at shorter wavelength (313 nm) owing to its small π-frame. Similarly, **2a**, **2b**, **4**, and **5** show emission in the narrow wavelength region (478-497 nm), except for **10** (Table 1). The bithiophenophanes **2a** and **2b** show large Stokes shifts (139-141 nm), presumably owing to the stacking structure of the two bithiophene moieties. Interestingly, **10** shows a much lower fluorescence quantum yield than **2a**, **2b**, **4**, and **5**, probably owing to the mobility of the two thiophene rings. Although **2a** and **2b** seem to have smaller conformational mobility than **4**, they have lower fluorescence quantum yields than **4**.

Table 1. Absorption and emission data of **2a**, **2b**, **10**, **4**, and **5** in benzene

	Absorption		Fluorescence	
	λ_{max} [nm]	ε [$M^{-1}cm^{-1}$]	λ_{max} [nm]	Φ_F [10^{-2}]
2a	356, 428sh	37500, 2790	497	1.0
2b	347	21700	486	5.4
10	313	12800	420	0.5
4	327, 374	23600, 19500	478	15
5	346	41000	486	6.6

The ethyl-substituted **3** and its corresponding linear oligomers **6-8** exhibit UV-visible absorptions tailing up to 450 nm, whereas the 1,8-di-(2-thienyl)naphthalene derivative **12** shows only a short-wavelength absorption (Table 2 and Figure 6). Thus, the long-wavelength absorptions of **3** and **6-8** can be assigned to that of the $S_0 \rightarrow S_1$ transition of bithiophene units.

Table 2. Absorption and emission data of **3**, **12**, **6**, **7**, and **8** in benzene

	Absorption		Fluorescence	
	λ_{max} [nm]	ε [$M^{-1}cm^{-1}$]	λ_{max} [nm]	Φ_F [10^{-2}]
3	337	37600	broad	0.1
12	305	9100	415	0.4
6	325	24400	471	3.3
7	330	38300	481	2.1
8	333	50000	485	0.7

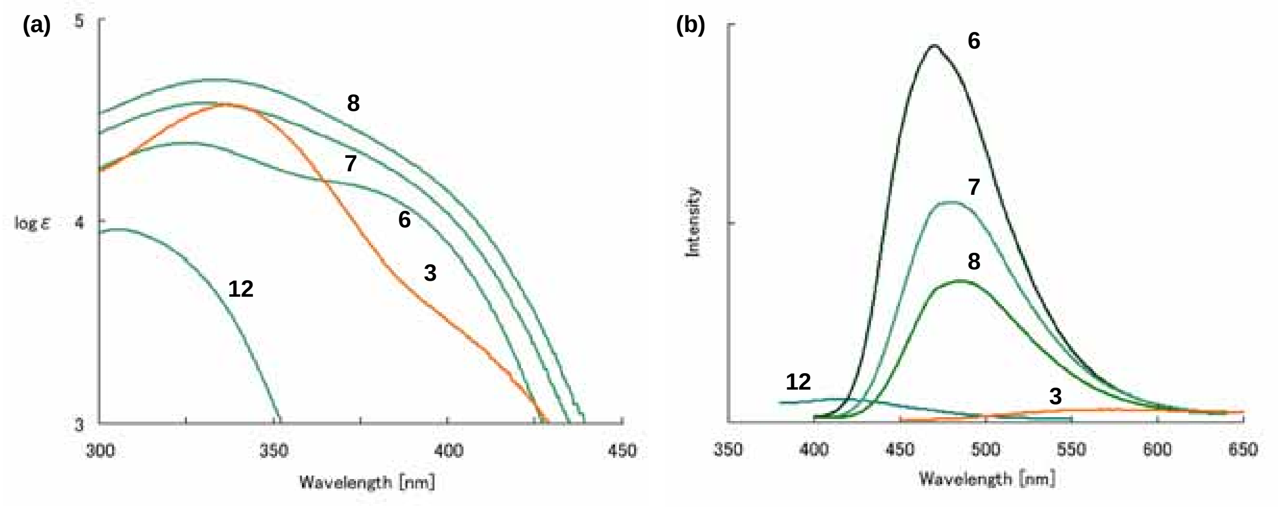


Figure 6. UV-vis absorption spectra (a) and emission spectra (b) of **3**, **6-8**, and **12** in benzene.

The linear oligomers **6-8** exhibit fluorescent spectra with slightly high quantum yields, whereas **3** shows a weak broad emission with a low quantum yield, reflecting the molecular strain in addition to its rapid mobility in solution.

Chemical and electrochemical oxidations. 1,8-Di(2-thienyl)naphthalene **10** and its dimer **4** are oxidized to give stable radical cations.[6,8,9] Therefore, **2a**, **2b**, and **5** are expected to produce more stable radical cations, namely $\mathbf{2a}^{\bullet+}$, $\mathbf{2b}^{\bullet+}$, and $\mathbf{5}^{\bullet+}$, and to show lower oxidation potentials. As shown in Table 3, the oxidation potentials of **2a**, **2b**, **4**, **5**, and **10** measured by cyclic voltammetry are irreversible but fairly low. Interestingly, **2b** and **5** show second oxidations corresponding to the formation of the dications $\mathbf{2b}^{2+}$ and $\mathbf{5}^{2+}$. These dications may be stabilized by π-dimer formation or the separation of the two charges.

Table 3. Oxidation potentials in *o*-dichlorobenzene[a)]

	E_{ox}^1 [V]	E_{ox}^2 [V]
2a	0.42	
2b	0.47	0.58
10	1.10	
4	0.70	
5	0.52	0.74

a) V vs. Fc/Fc$^+$, 0.1 M Bu_4NClO_4, Ag/Ag$^+$ reference electrode, Pt counter electrode, glassy carbon working electrode.

The bithiophenophane **3** and its corresponding linear oligomers **6-8** exhibit redox properties as π-donors. As shown in Figure 7, **3** shows reversible two-step one-electron redox waves corresponding to the formation of $\mathbf{2}^{\bullet+}$ and $\mathbf{2}^{2+}$. Since the linear trimer **7** and the tetramer **8** have a stacked bithiophene structure, **7** and **8** show a two-step one-electron oxidation wave (Table 4). However, **6** with one bithiophene unit and **12** without a bithiophene unit exhibit only a one-step oxidation wave.

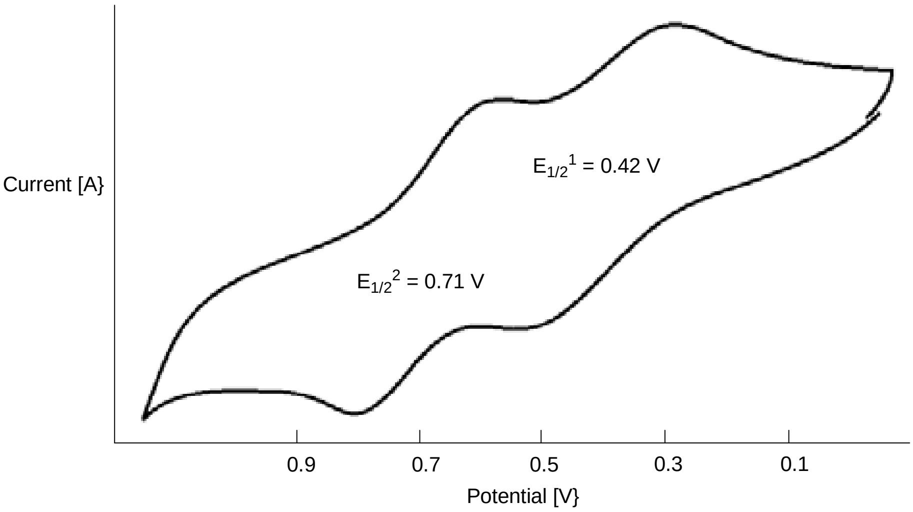


Figure 7. Cyclic voltammogram of **3**.

Table 4. Oxidation potentials in *o*-dichlorobenzene[a)]

	E_{ox}^1 [V]	E_{ox}^2 [V]
3	0.42	0.71
12	1.05	
6	0.67	
7	0.40	0.60
8	0.40	0.64

a) V vs. Fc/Fc$^+$, 0.1 M Bu_4NClO_4, Ag/Ag$^+$ reference electrode, Pt counter electrode, glassy carbon working electrode

The dication $\mathbf{3}^{2+}$ derived from **3** can be expected to behave as a π-dimer model,[23] because the two bithiophene moieties are fixed closely by naphthalene bridges to show a strong face-to-face interaction. As a result of one-electron oxidation with $Fe(ClO_4)_3$ in dichloromethane/acetonitrile (4 / 1),[24,25] the spectrum of $\mathbf{3}^{\bullet+}$ shows two absorption peaks in the visible region (Figure 8). The two low-energy bands (525 nm and 744 nm) in the spectrum of $\mathbf{3}^{\bullet+}$ due to the oxidized bithiophene exhibit a blue shift in comparison with those (564 nm and 924 nm) in the spectrum of $\mathbf{6}^{\bullet+}$ prepared by the one-electron oxidation of **6**. This suggests that there is a distinct H-type stacking interaction between the two bithiophene moieties of $\mathbf{3}^{\bullet+}$ in the one-electron oxidation state. In addition, the spectrum changes and gives three new bands at 510 nm, 704 nm, and 1016 nm in the two-electron oxidation state. The observation of the three bands indicates the formation of a π-dimer from the two monocationic species of $\mathbf{3}^{2+}$, because two π-π* transitions for cation radicals and three π-π* transitions for π-dimers are allowed according to the selection rule.[26] Although π-dimers can usually be observed by cooling a solution of cation radicals, $\mathbf{3}^{2+}$ only exhibits a spectrum of pure π-dimers.[27]

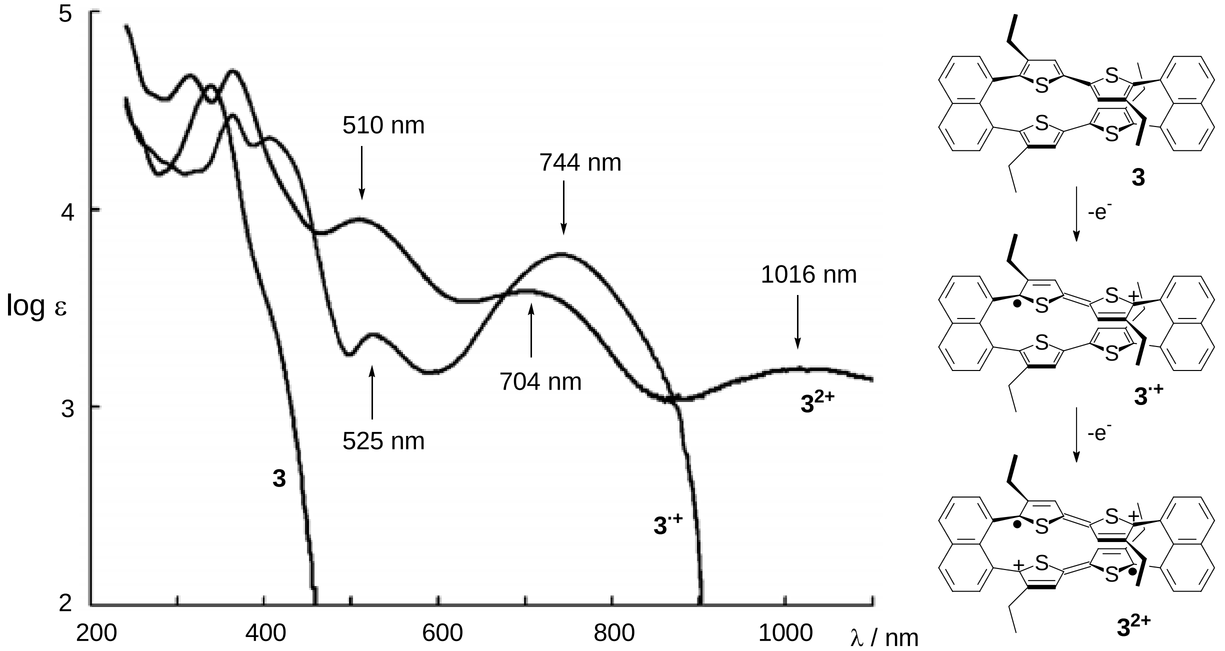


Figure 8. Electronic spectra of **3** and its cationic species $\mathbf{3}^{\cdot+}$ and $\mathbf{3}^{2+}$ in CH_2Cl_2-CH_3CN (4:1).

Conclusion. Extremely stable oligoheteroarylenes have been synthesized and their structures, conformation, redox properties, absorption and emission behaviors, and formation of cationic counterparts have been investigated. The bithiophenophane **2**, which have no substituents, has a rigid structure, and two conformers, *i.e.*, *anti*- and *syn*-isomers **2a** and **2b**, were isolated separately. In contrast, its tetraethyl derivative **3** exist as a mixture of four conformers that show a rapid interconversion on the time scale of ^{1}H NMR measurement. This conformational flexibility suggests that the molecular frames of the bithiophenophanes **2** and **3** have mobilities that permit the rotation of a thiophene ring, as shown in Scheme 4. The corresponding linear oligomers **4-8** also exist as a mixture of conformational isomers, although *anti*-conformation is the most stable one. All the bithiophenophanes and their linear counterparts **2-8** show relatively strong emission except for **3**, which show a rapid conformational change complying with thermal relaxation. The bithiophenophanes **2** and **3** together with the linear oligomers **4-8** show fairly low oxidation potentials to produce their corresponding cation radicals and dications. In agreement with these low oxidation potentials, the chemical oxidation of **3** with $Fe(ClO_4)_3$ producs the corresponding cation radical $\mathbf{3}^{\cdot+}$ and the dication $\mathbf{3}^{2+}$, and the formation of these cationic species is confirmed from their characteristic UV-vis-NIR spectra. The dication $\mathbf{3}^{2+}$ exists as a pure π-dimer owing to the its two closely located cation radicals. Since $\mathbf{3}^{2+}$ is very stable in spite of its short π-conjugation length, *i.e.*, two bithiophene radical cations, our results indicate possibilities of stabilizing bithiophene polarons and producing functional materials based on the bithiophene unit.

EXPERIMENTAL

All the chemicals and solvents used were of reagent grade. All reactions were carried out under a nitrogen atmosphere. Melting points are uncorrected. Nuclear magnetic resonance spectra were measured in deuteriochloroform at 400 or 500 MHz for ^{1}H and at 100 or 125 MHz for ^{13}C with TMS as internal standard, unless otherwise noted. Mass spectral data were obtained using an electron ionization procedure (70 eV), unless otherwise noted.

1,8-Di(2-thienyl)naphthalene (10): To a solution of 2-bromothiophene (7.83 g, 48 mmol) in THF (30 mL) was added dropwise butyllithium in hexane (1.57 M, 54 mmol) at -78 °C. This solution was stirred at -78 °C for 1 h, and then a suspension of anhydrous zinc chloride (8.18 g, 60 mmol) in THF (60 mL) was added. The mixture was stirred for 30 min at -78 °C and for 30 min at 0 °C. To the mixture was added 1,8-diiodonaphthalene **9** (4.56 g, 12 mmol) and $Pd(PPh_3)_4$ (693 mg, 0.60 mmol) at 0 °C. The mixture was then allowed to warm to rt. This solution was stirred overnight, and aqueous 2 N HCl (60 mL) and benzene (30 mL) were added at rt. The organic phase was washed with brine and dried over magnesium sulfate. The solvent was evaporated, and the residue was column chromatographed on silica gel using hexane as the eluent to afford **10** (2.08 g, 59%) together with 1-(2-thienyl)naphthalene (217 mg, 9%). **10**: colorless crystals; EI-MS *m/z* 292 (M^+); mp 108.5- 110 °C; ^{1}H NMR ($CDCl_3$ / TMS, 500 MHz) δ 7.93 (2H, dd, *J* = 8.2 and 1.2 Hz), 7.59 (2H, dd, *J* = 7.0 and 1.2 Hz), 7.53 (2H, dd, *J* = 8.2 and 7.0 Hz), 7.03 (2H, dd, *J* = 5.1 and 1.1 Hz), 6.63 (2H, dd, *J* = 5.1 and 3.6 Hz), 6.48 (2H, dd, *J* = 3.6 and 1.1 Hz); ^{13}C NMR ($CDCl_3$ / TMS, 125 MHz) δ 144.22, 135.45, 132.50, 132.40, 130.61, 129.24, 127.67, 126.76, 125.12, 124.00.

Bithiophenophane 2: To a solution of 1,8-di(2-thienyl)naphthalene **10** (146 mg, 0.5 mmol) in Et_2O (5 mL) was added dropwise butyllithium in hexane (1.57 M, 1.5 mmol) at 0 °C. The solution was stirred at the same temperature for 1 h, and then anhydrous copper(II) chloride (229 mg, 1.7 mmol) was added. The mixture was stirred at 0 °C for 1 h and at rt overnight, then carbon disulfide (20 ml) was added. After stirring with carbon disulfide, the product was chromatographed on alumina, and then a fair amount of benzene was added. The resulting solution was concentrated and cooled to isolate **2** (30 mg, 21%) as yellow powders. The residue including linear products was purified by column chromatography on silica gel using a mixture of hexane and benzene (9:1, v/v) as the eluent to afford the starting material **10** (32 mg, 22%), the linear dimer **4** (11 mg, 7%), and the linear trimer **5** (3.7 mg, 3%). **2a**: yellow powder; EI-MS *m/z* 580 (M^+); mp 320-321 °C (decomp.); ^{1}H NMR ($CDCl_3 : CS_2$ = 1 : 3 / TMS, 500 MHz) δ 7.89 (4H, dd, *J* = 8.2 and 1.2 Hz), 7.57 (4H, dd, *J* = 7.1 and 1.2 Hz), 7.49 (4H, dd, *J* = 8.2 and 7.1 Hz), 6.72 (4H, d, *J* = 3.4 Hz), 6.42 (4H, d, *J* = 3.4 Hz); HR-MS *m/z* calcd for $C_{36}H_{20}S_4$ 580.0448, found 580.0497. **2b**: yellow powder; EI-MS *m/z* 580 (M^+); mp 322-323 °C (decomp.); ^{1}H NMR ($CDCl_3 : CS_2$ = 1 : 3 / TMS, 500 MHz) δ 7.87 (4H, dd, *J* = 8.2 and 1.2 Hz), 7.57 (4H, dd, *J* = 7.1 and 1.2 Hz), 7.50 (4H, dd, *J* =

8.2 and 7.1 Hz), 6.66 (4H, d, *J* = 3.7 Hz), 6.36 (4H, d, *J* = 3.7 Hz); ^{13}C NMR ($CDCl_3 : CS_2$ = 1 : 3 / TMS, 125 MHz) δ 142.77, 135.34, 135.29, 132.03, 131.55, 129.23, 128.16, 128.05, 125.04, 123.24; HR-MS *m/z* calcd for $C_{36}H_{20}S_4$ 580.0448, found 580.0463. **4**: yellow crystals; EI-MS *m/z* 582 (M^+); ^{1}H NMR ($CDCl_3$ / TMS, 500 MHz) δ 7.94 (4H, d, *J* = 8.3 Hz), 7.65-7.62 (4H, m), 7.55 (4H, t, *J* = 7.6 Hz), 7.10 (2H, d, *J* = 5.0 Hz), 6.71-6.70 (2H, m), 6.59 (2H, d, *J* = 3.7 Hz), 6.56 (2H, d, *J* = 3.5 Hz), 6.37 (2H, d, *J* = 3.7 Hz). **5**: yellow powder; FAB-MS (*m*-nitrobenzyl alcohol) *m/z* 873 (M^++1); mp 198-200 °C; ^{1}H NMR ($CDCl_3$ / TMS, 500 MHz) δ 7.96 (2H, dd, *J* = 8.2 and 1.2 Hz), 7.90 (4H, m), 7.67 (2H, dd, *J* = 7.1 and 1.2 Hz), 7.59-7.50 (8H, m), 7.40 (2H, dd, *J* = 8.2 and 7.1 Hz), 7.03 (2H, dd, *J* = 5.0 and 1.2 Hz), 6.68 (2H, d, *J* = 3.6 Hz), 6.65 (2H, dd, *J* = 5.0 and 3.4 Hz), 6.61 (2H, d, *J* = 3.6 Hz), 6.51 (2H, dd, *J* = 3.4 and 1.2 Hz), 6.46 (2H, d, *J* = 3.6 Hz), 6.32 (2H, d, *J* = 3.6 Hz); ^{13}C NMR ($CDCl_3$ / TMS, 125 MHz) δ 144.05, 143.20, 143.07, 136.51, 136.09, 135.54, 135.44, 132.38, 132.37, 132.11, 132.03, 132.01, 130.69, 130.57, 129.41, 129.27, 129.20, 128.50, 128.26, 127.87, 126.81, 125.22, 125.14, 125.11, 124.16, 123.39, 123.15.

1,8-Bis(3-ethylthien-2-yl)naphthalene 12: To a solution of 3-ethyl-2-iodothiophene **11** (1.91 g, 8.0 mmol) in THF (5 mL) was added dropwise butyllithium in hexane (1.57 M, 8.0 mmol) at -78 °C. This solution was stirred at -78 °C for 1 h before a suspension of anhydrous zinc chloride (1.15 g, 8.4 mmol) in THF (10 mL) was added. The mixture was stirred for 30 min at -78 °C and for 30 min at 0 °C. To the mixture was added 1,8-diiodonaphthalene **9** (760 mg, 2.0 mmol) and $Pd(PPh_3)_4$ (116 mg, 0.10 mmol) at 0 °C. The mixture was then allowed to warm to room temperature. This solution was stirred overnight before aqueous 2 N HCl (10 mL) and benzene (5 mL) were added at room temperature. The organic phase was washed with brine and dried over magnesium sulfate. The solvent was evaporated, and the residue was column chromatographed on silica gel using hexane as the eluent to afford **12** (608 mg, 87%). **12**: colorless crystals; EI-MS *m/z* 348 (M^+); mp 123-124 °C; ^{1}H NMR ($CDCl_3$ / TMS, 500 MHz) δ 7.88 (2H, dd, *J* = 7.9 and 1.2 Hz), 7.45 (2H, dd, *J* = 7.9 and 7.2 Hz), 7.39 (2H, dd, *J* = 7.2 and 1.2 Hz), 6.88 (2H, d, *J* = 5.2 Hz), 6.56 (2H, d, *J* = 5.2 Hz), 2.31 (2H, m), 2.00 (2H, m), 0.87 (6H, t, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$ / TMS, 125 MHz) δ 141.07, 137.22, 134.81, 132.67, 132.46, 132.00, 129.34, 126.94, 124.88, 122.52, 22.70, 14.49; Anal. Calcd for $C_{22}H_{20}S_2$: C, 75.82% ; H, 5.78%. Found : C, 75.78% ; H, 5.91%.

Tetraethylbithiophenophane 3: To a solution of 1,8-bis(3-ethylthien-2-yl)naphthalene **12** (174 mg, 0.5 mmol) in Et_2O (5 mL) was added dropwise butyllithium in hexane (1.57 M, 1.5 mmol) at 0 °C. The solution was stirred at this temperature for 1 h followed by the addition of anhydrous copper(II) chloride (229 mg, 1.7 mmol). The mixture was stirred at 0 °C for 1 h and at rt overnight, then carbon disulfide (20 mL) was added. After stirring with carbon disulfide, the product was chromatographed on alumina, and then a fairly amount of benzene was added. The resulting solution was concentrated and cooled to isolate **3** (57 mg, 33%) as yellow powder. The residue including linear products was purified by column chromatography on silica gel using a mixture of hexane and benzene (9:1, v/v) as the eluent to afford the starting material **12** (32 mg, 18%), the linear dimer **6** (21 mg, 12%), and the linear trimer **7** (14 mg, 8%) together with the linear tetramer **8** (trace). **3**: yellow crystals; LDI-MS *m/z* 692 (M^+); mp 302-303 °C (decomp.); ^{13}C NMR ($CDCl_2CDCl_2$ / TMS, 125 MHz, 120 °C) δ 142.67, 137.77, 136.82, 135.17, 134.47, 132.33, 131.95, 129.95, 124.75, 123.06, 22.10, 14.21; Anal. Calcd for $C_{44}H_{36}S_4$: C, 76.26% ; H, 5.24%, Found : C, 76.23% ; H, 5.41%. **6**: yellow crystals; LDI-MS *m/z* 694 (M^+); mp 220- 221 °C; ^{1}H NMR ($CDCl_3$ / TMS, 500 MHz, 120 °C) δ 7.90-7.88 (4H, m), 7.48-7.45 (4H, m), 7.41-7.39 (4H, m), 7.00 (2H, d, *J* = 5.2 Hz), 6.66 (2H, d, *J* = 5.2 Hz), 6.49 (2H, s), 2.30-2.04 (8H, m), 0.95 (6H, t, *J* = 7.6 Hz), 0.92 (6H, t, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$ / TMS, 125 MHz, 145 °C) δ 141.83, 141.40, 137.95, 136.91, 135.94, 135.40, 133.58, 132.87, 132.82, 132.63, 132.30, 129.55, 129.47, 127.11, 127.04, 124.95, 123.65, 123.57, 22.86, 22.83, 14.39, 14.30; Anal. Calcd for $C_{44}H_{38}S_4$: C, 76.04% ; H, 5.51%. Found : C, 75.74% ; H, 5.62%. **7**: yellow powder; LDI-MS *m/z* 1040 (M^+); mp 225-226 °C; ^{1}H NMR ($CDCl_3$ / TMS, 500 MHz, 120 °C) δ 7.90 (2H, dd, *J* = 7.8 and 1.5 Hz), 7.88-7.85 (4H, m), 7.50-7.35 (12H, m), 6.93 (2H, d, *J* = 5.2 Hz), 6.61 (2H, d, *J* = 5.2 Hz), 6.60 (2H, s), 6.51 (2H, s), 2.37-1.97 (12H, m), 1.01 (6H, t, *J* = 7.6 Hz), 0.90-0.85 (12H, m); Anal. Calcd for $C_{66}H_{56}S_6$: C, 76.11% ; H, 5.42%. Found : C, 76.07% ; H, 5.50%. **8**: yellow powder; LDI-MS *m/z* 1386 (M^+); mp 175-177 °C; ^{1}H NMR ($CDCl_3$ / TMS, 500 MHz, 120 °C) δ 7.89-7.85 (8H, m), 7.48-7.35 (16H, m), 6.87 (2H, d, *J* = 5.2 Hz), 6.61 (2H, s), 6.55 (2H, d, *J* = 5.2 Hz), 6.54 (2H, s), 6.45 (2H, s), 2.33-1.94 (16H, m), 0.97-0.80 (24H, m); Anal. Calcd for $C_{66}H_{56}S_6$: C, 76.15% ; H, 5.37%. Found : C, 76.35% ; H, 5.67%.

Stannanes 13 and 14: To a solution of 1,8-bis(3-ethylthien-2-yl)naphthalene **12** (348 mg, 1.0 mmol) in THF (10 mL) was added dropwise butyllithium in hexane (1.57 M, 1.0 mmol) at -30 °C. This solution was stirred at 0 °C for 1 h before a solution of tributyltin chloride (391 mg, 1.2 mmol) in THF (5 mLl) was added at -50 °C. The mixture was held at -50 °C with stirring for 1 h. The mixture was then allowed to warm to rt and stirred overnight. The product was chromatographed on alumina and further purified by GPC using $CHCl_3$ as the eluent to afford **13** (454 mg, 71%) together with **14** (27 mg, 3%). **13**: light blue oil; FAB-MS (*m*-nitrobenzyl alcohol) *m/z* 638 (M^++1); ^{1}H NMR ($CDCl_3$ / TMS, 500 MHz) δ 7.89 (2H, m), 7.48-7.45 (2H, m), 7.39 (2H, m), 6.83 (1H, d, *J* = 5.2 Hz), 6.59 (1H, s), 6.49 (1H, d, *J* = 5.2 Hz), 2.35-2.26 (2H, m), 2.02-1.94 (2H, m), 1.62-1.55 (6H, m), 1.41-1.34 (6H, m), 1.07-1.04 (6H, m), 0.94 (9H, t, *J* = 7.3 Hz), 0.89-0.86 (6H, m); ^{13}C NMR ($CDCl_3$ / TMS, 125 MHz) δ 142.90, 142.37, 141.10, 137.21, 135.59, 134.85, 133.12, 132.84, 132.56, 132.36, 132.30, 132.16, 129.32, 129.01, 126.93, 124.91, 124.79, 122.33, 29.02, 27.39, 22.75, 22.62, 14.57, 14.48, 13.74, 10.71. **14**: colorless oil; FAB-MS (*m*-nitrobenzyl alcohol) *m/z* 927 (M^++1); ^{1}H NMR ($CDCl_3$ / TMS, 500 MHz) δ 7.89 (2H, dd, *J* = 8.2 and 1.2 Hz), 7.47 (2H, dd, *J* = 8.2 and 7.0 Hz), 7.37 (2H, dd, *J* = 7.0 and 1.2 Hz), 6.53 (2H, s), 2.42-2.36 (2H, m), 2.17-2.10 (2H, m), 1.62-1.55 (12H, m), 1.41-1.33 (12H, m), 1.07-1.03 (12H, m), 0.95-0.92 (24H, m); ^{13}C NMR

($CDCl_3$ / TMS, 125 MHz) δ 143.48, 141.71, 135.30, 134.91, 132.90, 132.84, 132.31, 132.11, 128.99, 124.81, 29.07, 27.42, 22.77, 14.88, 13.72, 10.67.

Synthesis of the linear dimer 6 using copper-catalyzed coupling of 13: To a solution of the stannane **13** (255 mg, 0.4 mmol) in THF (0.8 mL) was added a solution of copper(II) nitrate trihydrate (145 mg, 0.6 mmol) in THF (1.0 mL) at 0 °C. The mixture was stirred at this temperature for 1 h, and then benzene (5 mL) was added at rt. After stirring with benzene, the product was chromatographed on alumina. The solvent was evaporated, and the residue was purified by a column of silica gel using a mixture of hexane and benzene (9:1, v/v) as the eluent to afford **6** (42 mg, 30%) together with the reduction product **12** (98 mg, 70%).

Synthesis of the linear tetramer 8 from the linear dimer 6: To a solution of the linear dimer **6** (209 mg, 0.30 mmol) in THF (15 mL) was added dropwise butyllithium in hexane (1.57 M, 0.48 mmol) at rt. The solution was stirred at this temperature for 1 h, and then a solution of tributyltin chloride (195 mg, 0.60 mmol) in THF (6 mL) was added at -50 °C. The mixture was stirred at -50 °C for 1 h, then allowed to warm to rt and stirred overnight. The product was chromatographed on alumina and the solvent was removed *in vacuo*. To a solution of the residue containing the mono-substituted stannane **15** in THF (3 mL) was added a solution of copper(II) nitrate trihydrate (116 mg, 0.48 mmol) in THF (3 mL) at 0 °C. The mixture was stirred at this temperature for 1 h, and then benzene (10 mL) was added at rt. After stirring with benzene, the product was chromatographed on alumina. The solvent was removed *in vacuo*, and the residue was purified by a column chromatography on silica gel using a mixture of hexane and benzene (4:1, v/v) as the eluent to afford **8** (16 mg, 8%) together with the starting material **6** (188 mg, 90%).

Fluorescence quantum yield: Fluorescence quantum yields were measured in an undegassed solution (ca. 10^{-6} M) using quinine sulfate in 0.5 M H_2SO_4 solution as standard, which absorbs at 350 nm and emits at 452 nm with a known quantum yield of $\Phi_F = 0.51$. The calculation of the fluorescence quantum yield of a sample solution (Φ_s), relative to the reference sample of known quantum yield (Φ_r), is given by $\Phi_s = \Phi_r(A_r/A_s)(I_s/I_r)(n_s/n_r)^2$ where A_s and A_r are the absorbances of the sample and the reference solutions, I_s and I_r are the corresponding relative integrated fluorescence intensities, and n_s and n_r are the measured refractive indexes of solvent and 0.5 M H_2SO_4 ($n_r = 1.3414$) at 296 K, respectively.

X-Ray Crystallographic Analysis of 3. X-Ray diffraction experiments were performed at -140˚C on a Rigaku AFC7R diffractometer with graphite-monochromated Mo K_α Radiation $\lambda = 0.71069$Å. The intensity data were measured using the ω-2θ scan techniques. The structures were solved by direct methods and refined by Full-matrix least-squares techniques with anisotropic temperature factor for non-hydrogen atoms. Crystal data for **3**: formula $C_{56}H_{48}S_4$; formula wt. 849.24; crystal system monoclinic; space group $P2_1/c$ (#14); $a = 11.298(9)$ Å; $b = 16.936(9)$ Å; $c = 11.411(7)$ Å; $\beta = 90.54(6)$˚;

$V = 2183(2)$ Å^3; $Z = 2$; $D_c = 1.292$ g cm^{-3}; No. of Observation ($I > 3.00\sigma(I)$, $2\theta < 55.12°$) = 1858; $R_1 = 0.069$, $R_w = 0.092$.

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