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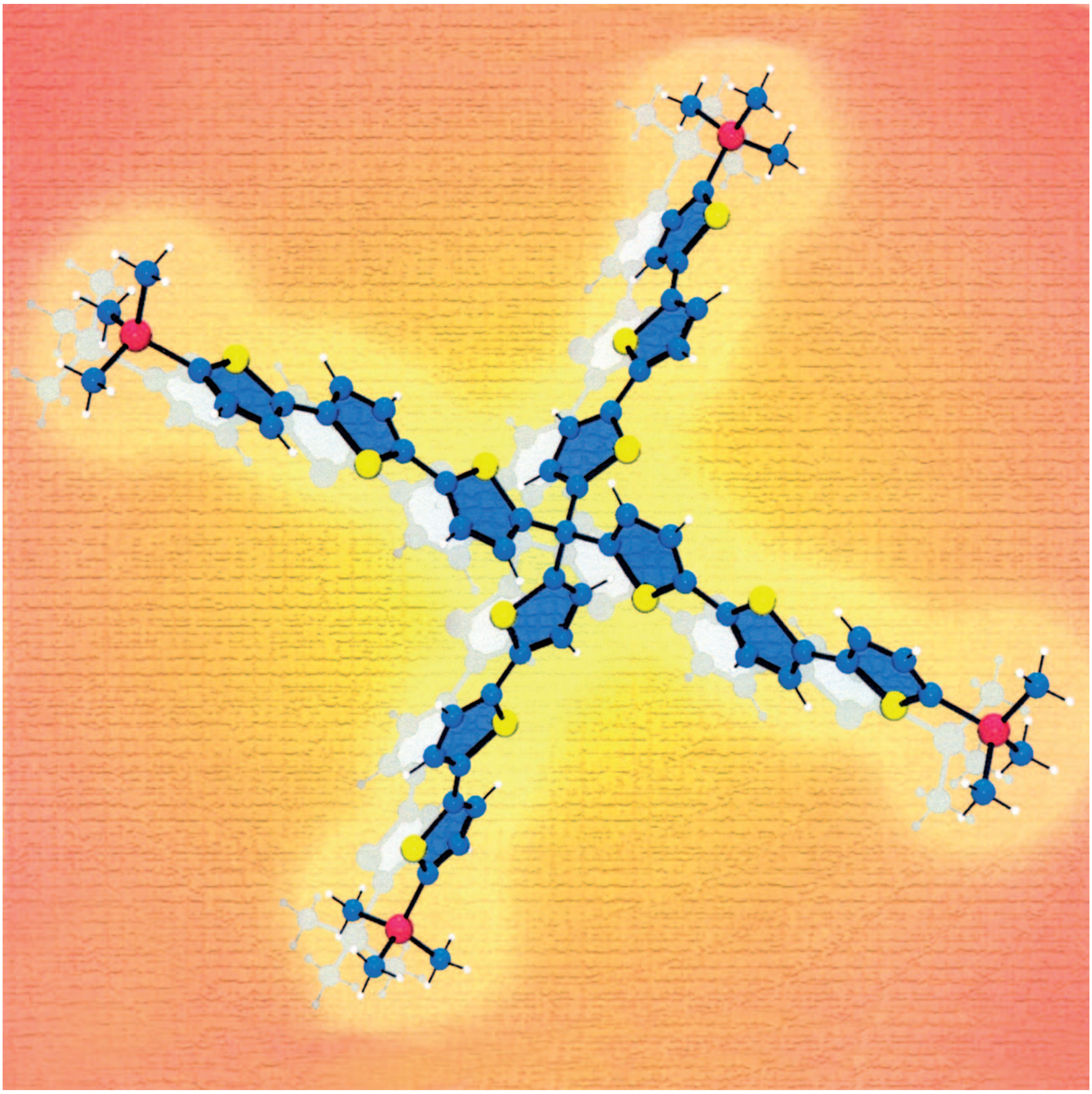
Tetrahedral Oligothiophenes; Synthesis, X-ray Analysis, and Optoelectronic Properties of Highly Symmetrical, 3D-Branched Oligothiophenes

Kouzou Matsumoto,* Toru Tanaka, Sota Kugo, Takuya Inagaki, Yoshikazu Hirao, Hiroyuki Kurata, Takeshi Kawase, and Takashi Kubo[a]



Abstract: Tetrakis(bithienyl)methane and tetrakis(terthienyl)methane have been synthesized from tetrakis(2-thienyl)methane by use of Suzuki–Miyaura coupling as a key reaction. Their trimethylsilyl (TMS) derivatives are also synthesized. X-ray analysis reveals that each oligothiophene moiety tends to adopt *anti*-conformations and show relatively small torsion angles between the adjacent thiophene rings. While the longest absorption maxima of these tetrakis(oligothienyl)methanes exhibit only a slight bathochromic shift compared to the corresponding linear oligothiophene derivative, tetrakis(bithienyl)methane and its TMS derivative exhibit an appreciable red-shift in their fluorescence spectra. The intramolecular interaction between thienyl groups of tetrakis(2-thienyl)methane is supported by DFT calculation.

Keywords: fluorescence spectroscopy • density functional calculations • Suzuki–Miyaura coupling • UV/Vis spectroscopy • X-ray diffraction

Introduction

Arising from their prominent optoelectronic properties, oligothiophenes are some of the most thoroughly studied π-conjugated oligomers.[1] In addition to the extraordinarily long oligothiophenes,[2] a number of hybrid systems with fullerene,[3] metal complex,[4] triarylamine,[5] heterocycle,[6] and polycyclic aromatic hydrocarbon[7] moieties have been studied with respect to a potential application in photovoltaic cells, light-emitting diodes, field effect transistors, and other optoelectronic devices. Furthermore, more complicated and well-defined oligothiophenes,[8] featuring macrocyclic,[9] interlocked,[10] helical (cross-conjugated),[11] or fused[12] systems, have been synthesized successfully in recent years. Considering the application of these extended oligothiophenes to various electronic devices, an efficient intermolecular interaction would be needed in the solid state in addition to an intramolecular interaction. From this viewpoint, 3D conjugated systems[13] (star-shaped[14] and dendritic[15] oligothiophenes) have been intensively studied in the last decade. We recently reported the synthesis of tetrakis(2-thienyl)methane (**1a**)[16] and some of its derivatives. **1a** would be a useful core unit for tetrahedrally extended oligothiophenes. These tetrahedral oligothiophenes would be expected to exhibit a number of useful characteristics. Firstly, they would have a solubility higher than those of the corresponding linear oligothiophenes because of the low planarity of the molecule. This is advantageous for their purification, crystallization for X-ray crystallographic analysis, further functionalization on terminal thienyl groups, and processability for application in optoelectronic devices. Secondly, an intramolecular interaction would be expected to exist between oligothiophene moieties through the central carbon atom, since X-ray analysis of tetrakis(5-bromo-2-thienyl)methane reveals that the average distance between *ipso*-carbons (ca. 2.47 Å)[16a] is much shorter than the van der Waals distance between sp^2 carbons. Thirdly, besides the intramolecular interaction, the efficient intermolecular interaction is also expected when the oligothiophene moieties become longer since more molecules can contact each other by intercalation. These structural features of tetrahedral oligothiophenes would improve the performance of the optoelectronic devices. In the course of our studies on tetrakis(heteroaryl)methanes,[17] we now report the synthesis, X-ray crystallographic analysis, and optoelectronic properties of tetrakis(oligothienyl)methanes **1a**–**3a**, and their trimethylsilyl (TMS) derivatives **1b**–**3b**.

Results and Discussion

We first examined functionalization of **1a** for the construction of tetrahedrally extended π-electron systems based on **1a**. Particularly, tetra-metallation and tetra-halogenation of **1a** will open the way to a number of derivatives of **1a**. Scheme 1 shows the tetra-lithiation and tetra-bromination of **1a**. It was found that tetralithiation of **1a** could be carried out by the treatment with 8 equiv of *n*BuLi at 0 °C. Quenching with trimethylsilyl chloride (TMSCl) or *N*,*N*-dimethylformamide (DMF) afforded tetrakis(trimethylsilyl) derivative **1b** or tetraaldehyde **1c**, respectively. Tetrabromide **1d** was synthesized by the bromination of **1a** with 5 equivalents of *N*-bromosuccinimide (NBS) in chloroform.

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[a] Dr. K. Matsumoto, T. Tanaka, S. Kugo, T. Inagaki, Dr. Y. Hirao, Dr. H. Kurata, Dr. T. Kawase, Dr. T. Kubo
Graduate School of Science
Osaka University
1-1 Machikaneyamacho, Toyonaka, Osaka 560-0043 (Japan)
Fax: (+81) 6-6850-5387
E-mail: kmatsu@chem.sci.osaka-u.ac.jp

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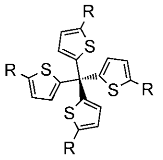
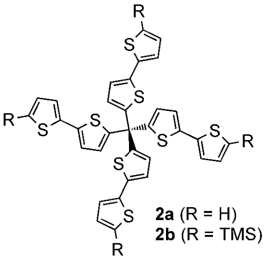
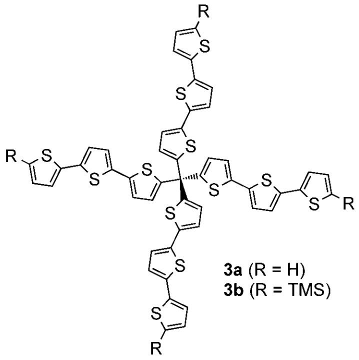


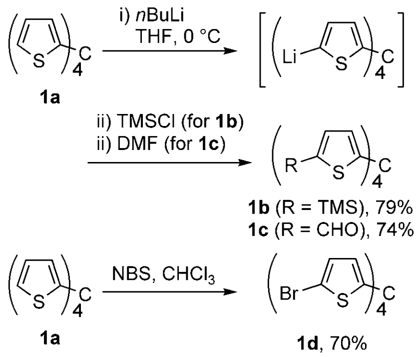
1a (R = H)
1b (R = TMS)



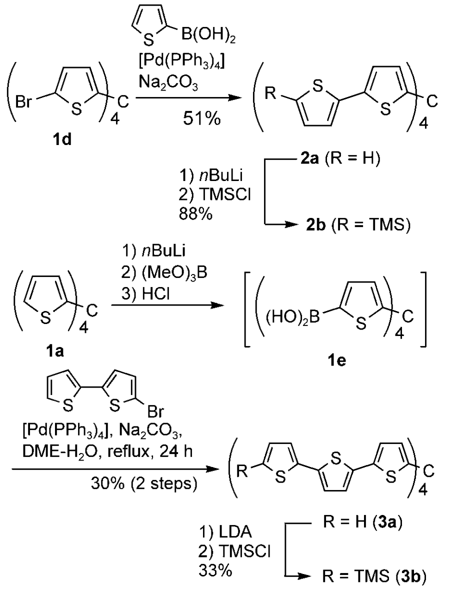
2a (R = H)
2b (R = TMS)



3a (R = H)
3b (R = TMS)



Scheme 1. Lithiation and bromination of **1a**.



Scheme 2. Synthesis of tetrakis(oligothienyl)methanes **2** and **3**.

The synthesis of tetrakis(oligothienyl)methanes is illustrated in Scheme 2. Compounds **2a** and **3a** were synthesized by Suzuki–Miyaura coupling as a key reaction. The reaction of **1d** with 2-thienylboronic acid[18] in the presence of [Pd(PPh_3)$_4$] gave **2a** in 51% yield as colorless needles. **2a** exhibited the prominent clathrate property for CH_2Cl_2; CH_2Cl_2 molecules are included in the crystals of **2a** obtained both by crystallization from CH_2Cl_2–hexane and by concentration of a solution in CH_2Cl_2–hexane. The ratio of **2a** and CH_2Cl_2 was 2:1. This suggested that the size and shape of the CH_2Cl_2 molecule matched well with the vacant space of the crystal of **2a**. Although it was expected that **3a** could be synthesized from **1d** and 2,2′-bithiophene-5-boronic acid, we could not synthesize this boronic acid despite several attempts. Hence, we decided to synthesize **3a** by the coupling of tetrakis(boronic acid) **1e** and 5-bromo-2,2′-bithienyl.[19] **1e** was obtained by tetra-lithiation of **1a** followed by the treatment with trimethyl borate. Suzuki–Miyaura coupling of **1e** and 5-bromo-2,2′-bithienyl afforded **3a** in 30% yield. Although partial coupling products were also produced, pure crystals of **3a** appeared from the fractions during column chromatography on silica gel. **2a** and **3a** show satisfactory solubility in CH_2Cl_2, $CHCl_3$, and THF. This solubility helps further transformation of **2a** and **3a**. As is the case of **1a**, tetra-lithiation of **2a** could be also achieved with 8 equivalents of *n*BuLi, and **2b** was obtained in 88% yield by quenching with TMSCl. However, the tetra-lithiation of **3a** did not proceed effectively under similar conditions, and only resulted in the partially substituted products. Therefore, tetra-lithiation of **3a** had to be carried out under more severe conditions. Thus, a treatment of **3a** with 20 equivalents of lithium diisopropylamide (LDA) followed by the addition of TMSCl afforded **3b** in 33% yield with a small amount of partially TMS substituted compounds.

X-ray crystallographic analysis is the most powerful method to obtain the characteristics of the molecular structure and molecular packing in the solid state.[20] The single crystals of **1a**–**3a** and **1b**–**3b** were obtained from CH_2Cl_2 or $CHCl_3$ solution by the technique of slow vapor diffusion with *n*-pentane. Their crystallographic parameters are listed in Table 1.[21] In these tetrahedral oligothiophenes, the oligothiophene moieties take-up an *anti* conformation except in the case of unsubstituted terminal thiophene rings of **1a**–**3a**, which show the rotational disorder of *syn* and *anti* conformations. Since oligothiophenes often adopt a *syn* conformation in the solid state, the tendency to adopt an *anti* conformation may arise from the demand for effective molecular

Abstract in Japanese:

テトラキス(5-(2-チエニル)-2-チエニル)メタンおよびテトラキス(5-(5-(2-チエニル)-2-チエニル)-2-チエニル)メタンとそれらのトリメチルシリル誘導体を合成した。結晶中でオリゴチオフェン部位は比較的平面性が高く、隣接するチオフェン環はアンチ配座をとる傾向が見られた。吸収スペクトルにおける吸収極大波長は相当するオリゴチオフェン誘導体と比較してわずかに長波長シフトするのみであるが、蛍光波長はテトラキス(5-(2-チエニル)-2-チエニル)メタンについては大きな長波長シフトが見られた。

Table 1. Crystallographic data and some characteristic structural features of tetrahedral oligothiophenes.

	1a	**1b**	**2a**·0.5 CH_2Cl_2	**2b**	**3a**·1.5 $CHCl_3$	**3b**
Formula	$C_{17}H_{12}S_4$	$C_{29}H_{44}S_4Si_4$	$C_{33.5}H_{21}S_8Cl$	$C_{45}H_{52}S_8Si_4$	$C_{50.5}H_{29.5}S_{12}Cl_{4.5}$	$C_{61}H_{60}S_{12}Si_4$
M_r [g mol^{-1}]	344.52	633.25	715.47	961.73	1180.55	1290.21
Color	colorless	colorless	yellow	yellow	yellow	yellow
Habit	prism	prism	plate	block	plate	needle
Crystal size [mm]	0.3×0.2×0.2	0.5×0.3×0.3	0.5×0.3×0.1	0.4×0.2×0.2	0.5×0.3×0.1	0.3×0.2×0.2
T [K]	200	200	200	200	200	200
Crystal system	monoclinic	tetragonal	monoclinic	monoclinic	monoclinic	tetragonal
Space group	$P2_1/n$ (No. 14)	I-4 (No. 82)	$P2_1/c$ (No. 14)	$P2/n$ (No. 13)	$P2_1/a$ (No. 14)	P-4 (No. 81)
a [Å]	9.8227(7)	22.895(7)	10.596(3)	18.126(7)	26.012(5)	23.578(7)
b [Å]	16.103(2)	22.895(7)	13.611(4)	7.739(3)	14.685(3)	23.578(7)
c [Å]	10.3426(9)	6.990(4)	21.802(6)	18.171(7)	26.610(6)	6.489(2)
α [°]	90	90	90	90	90	90
β [°]	106.041(2)	90	91.66(1)	91.91(2)	94.134(9)	90
γ [°]	90	90	90	90	90	90
V [Å^3]	1572.2(2)	3664(2)	3143(5)	2547(5)	10137(11)	3607(6)
Z	4	4	4	2	8	2
ρ_{calcd} [g cm^{-3}]	1.455	2.247	1.512	1.254	1.547	1.188
μ [mm^{-1}]	0.593	8.703	0.678	0.474	0.791	0.463
Reflections measured	3572	13393	30470	23508	94133	32159
R_{int}	0.077	0.023	0.045	0.079	0.225	0.069
Reflections in refinement for $R1$	3000	3260	6214	3606	9188	5501
Parameters	190	167	388	258	1147	347
$R1$[a]	0.056	0.033	0.051	0.078	0.144	0.068
$wR2$[b]	0.177	0.096	0.157	0.240	0.422	0.223
S	0.95	1.03	1.07	1.04	1.13	0.96
d(C1-*ipso*C) [Å][c]	1.53[f]	1.52	1.53[f]	1.54[f]	1.53[f]	1.53[f]
d(C1···C1) [Å][d]	6.24	7.36	6.88	7.74	7.40	6.49
ϕ(Th–Th) [°][e]	–	–	18.0	13.6	13.8	16.1

[a] For data of $I > 2\sigma(I)$. [b] For all data. [c] Bond length of the central carbon atom. [d] Short atom distance between the central carbon atoms. [e] Averaged torsion angle between the adjacent thiophene rings. [f] Averaged value.

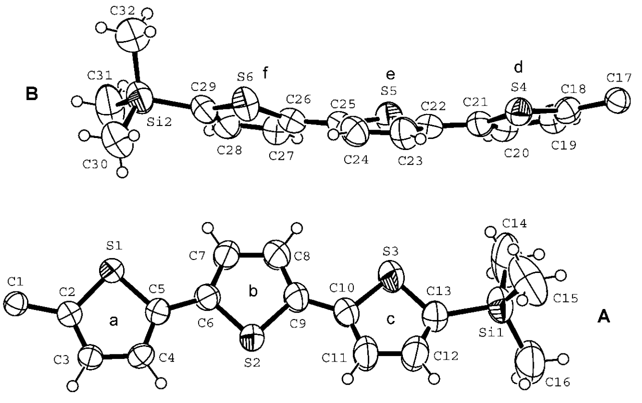


Figure 1. ORTEP drawing of the asymmetric unit of **3b** (50% probability). The atomic numbering, ring, and molecular representations are also given.

packing. The bond lengths of the central carbon atom, d(C1–*ipso*-C), are not affected by the extension with thiophene units. The short atom distance between the central atoms (d(C1···C1)), which would allow the possibility of intermolecular interaction between oligothiophene moieties, is lengthened by the bulky TMS groups which prevent the molecules from close contact with each other (**1b** and **2b**). However, d(C1···C1) of **3b** is considerably short in spite of the terminal bulky TMS groups, suggesting an effective intermolecular interaction between oligothiophenes. The inclusion of the solvent molecules also prevents the close contact of molecules (**2a** and **3a**). The averaged torsion angles between the adjacent thiophene rings, ϕ(Th–Th), are relatively small (around 15°).

The crystal structure of **3b** exhibits the highest symmetry and most interesting features which should be characteristic of tetrakis(oligothienyl)methanes. The crystal of **3b** shows a tetragonal crystal system reflecting the high symmetry of the molecule. Figure 1 shows the asymmetric unit of **3b**. Although there are two crystallographically independent molecules of **3b** (represented as conformer **A** and **B** in Figure 1), both conformers have $S4$ symmetry. The terthienyl moieties of the conformer **A** show high coplanarity; each thiophene ring is almost planar and the torsion angles between adjacent thiophene rings are less than 10° (ring a–ring b 8.7°, ring b–ring c 8.7°). On the other hand, the torsion angles between the corresponding thiophene rings in conformer **B** are larger than those of the conformer **A** (ring d–ring e 20.7°, ring e–ring f 26.0°). The intramolecular atomic distances between the *ipso*-carbon atoms (C2···C2′, or C18···C18′) are in the range of 2.44–2.52 Å, indicating the close contact between the oligothiophene moieties. The expected orbital overlap between the oligothiophenes is supported by UV/Vis spectroscopy, cyclic voltammetry, and DFT calculation (see below). Figure 2 shows the crystal structure of **3b** along the c axis. The central carbon atoms of **3b** are located both at the vertices, and at the center of the ab plane in the unit cell. Conformer **A** and **B** are stacked separately along the c

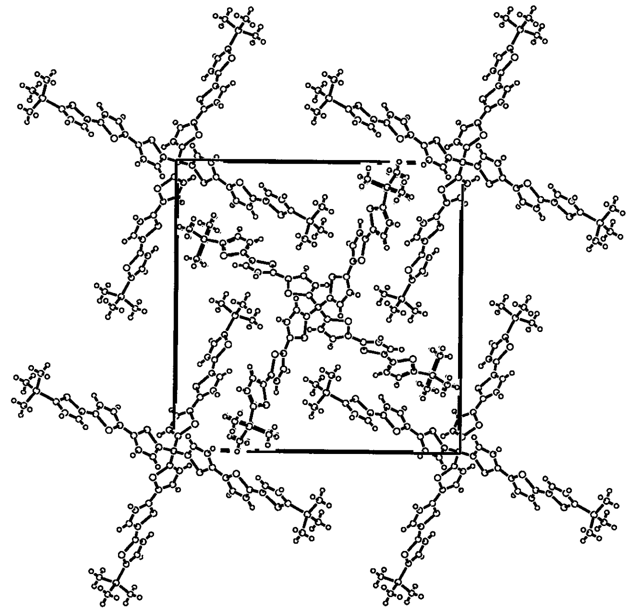


Figure 2. Crystal structure viewed along the *c* axis with conformer representations. Selected atom distances (Å): C3···C4$^{1)}$ 3.471(7), C3···C3$^{1)}$ 3.568(8), C3···C3$^{2)}$ 3.568(8), C19···C20$^{3)}$ 3.554(8), C23···C27$^{4)}$ 3.512(9), C23···C27$^{4)}$ 3.513(9), C24···C28$^{4)}$ 3.415(9). Symmetry operations: 1) $-y+2$, x, $-z+1$; 2) y, $-x+2$, $-z+1$; 3) y, $-x+1$, $-z+1$, 4) x, *y*, $z-1$.

axis to form two kinds of columnar structures; [···–**A**–**A**–**A**–···] and [···–**B**–**B**–**B**–···]. The atom distances between the central carbon atoms in both columns are 6.49 Å. In these columnar structures, there are several intermolecular atom distances which are nearly twice the van der Waals radius of carbon. In addition, each molecule contacts the four neighboring molecules in the face-to-edge fashion (Figure 1). This face-to-edge contact between the neighboring molecules is often observed in crystals of oligothiophenes or their derivatives to form the herringbone arrangement.[20] There are no appreciable S···S contacts and the shortest S···S distance is 4.49 Å (S3···S5). The shortest atom distance in the face-to-edge contact of **3b** is 3.55 Å (C8···C27), which is also nearly twice the van der Waals radius of carbon. Pentacene, one of the most applicable molecules to organic field-effect transistors (OFETs),[22] also forms a herringbone structure as a crystal. The shortest intermolecular C···C distance of pentacene is in the range of 3.58–3.69 Å.[23] Therefore, **3b** is expected to be a promising compound of electro-conductive material because of the relatively close packing of the herringbone structure and intramolecular interaction because of the short $d_{\text{ipso}}\cdots d_{\text{ipso}}$ distances.

The crystal structure of **2b** is similar to that of **3b**. The cell parameters of **2b** are close to tetragonal with shorter *a* and *c* values. The molecules of **2b** are stacked along the *b* axis (see Figure S10 of the Supporting Information). However, the most important difference between the crystal structure of **2b** and **3b** is the distance between the adjacent molecules. The distance between the central carbon atoms in adjacent molecules along the *b* axis is approximately 7.74 Å (vs 6.49 Å for **3b**). Consequently, the distance between the molecules is longer and no close contact is observed (the shortest atom distance is 3.71 Å (C3···C8)). There is also no short contact between the adjacent columns. As a consequence of the shorter oligothiophene backbones compared to **3b**, the bulky terminal TMS groups observed prevent the adjacent molecules coming into contact with each other in the case of **2b**. The torsion angles between the adjacent thiophene rings are comparatively small (about 14°).

The corresponding α-unsubstituted derivatives **2a** and **3a** are expected to have more effective intermolecular contacts than **2b** and **3b** because of the lack of bulky TMS groups. However, these compounds show the tendency for the inclusion of solvent molecules in their crystal. The crystal of **2a** includes one CH_2Cl_2 molecule for every two molecules of **2a**. This high affinity of **2a** for CH_2Cl_2 was also observed in the preparation and characterization of **2a** (described above). Short contacts between **2a** and CH_2Cl_2, smaller than the sum of the van der Waals radii, are observed (S2···Cl1 3.54 Å, S8···Cl1 3.46 Å). The intermolecular contacts between oligothiophene moieties are also observed (see the Supporting Information). The crystal of **3a** includes three $CHCl_3$ molecules for every two molecules of **3a**. Contrary to **2a**, specific interaction between **3a** and $CHCl_3$ is observed.

Figure 3 shows the absorption and emission spectra of **2** and **4**. Table 2 summarizes the optical properties of **1**–**3**. The data of the corresponding linear oligothiophenes (2,2′-bithienyl (**4a**), 5,5′-bis(trimethylsilyl)-2,2′-bithienyl (**4b**),

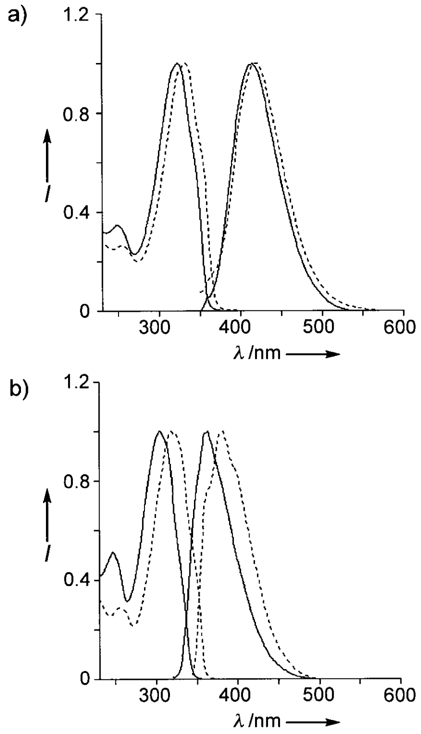


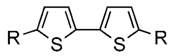
Figure 3. Absorption and fluorescence spectra of a) **2a** (solid lines) and **2b** (dashed lines); b) **4a** (solid lines) and **4b** (dashed lines). Both absorption and fluorescence intensities (*I*) are normalized.

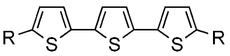
Table 2. Optical properties of **1**–**3** and those of the corresponding oligothiophenes in CH_2Cl_2.

Compound	λ_{abs} [nm][a] (log ε)	λ_{em} [nm][b]	Stokes shift [nm]	E^{ox} [V][c,d]
1a	241 (4.44)	none	–	+1.77
1b	252 (4.61)	none	–	+1.73
2a	344 (4.59)	415	71	+1.13
2b	353 (4.70)	419	66	+1.08
3a	400 (4.81)	446	46	+0.93
3b	407 (4.89)	453	46	+0.88
4a	330 (3.88)	364	34	–[e]
4b	343 (4.05)	382	39	+1.24
5a	389 (4.00)	432	43	+1.05
5b	401 (4.17)	446	45	+0.98

[a] Only the longest absorption maxima are shown. [b] Excited at the longer absorption maxima. [c] V vs Ag/Ag^+ in 0.1 M $n\mathrm{Bu_4NClO_4}$ (Fc/Fc^+ = +0.22 V), 100 mV sec^{-1}. [d] peak potentials. [e] not observed as a peak potential in 0 ± 1.5 V.

2,2′;5′,2″-terthienyl (**5a**), and 5,5″-bis(trimethylsilyl)-2,2′;5′,2″-terthienyl (**5b**) are also listed in Table 2.


4a (R = H)
4b (R = TMS)


5a (R = H)
5b (R = TMS)

Similar to the series of linear oligothiophenes, bathochromic shifts are observed by the extension with thienyl groups. The difference of the longest absorption maximum (λ_{abs}) of **2** and **3** are compatible with that of the corresponding linear oligothiophenes; **4** and **5** (about 60 nm). The longest absorption maxima of **2** and **3** exhibit an appreciable red-shift (6–14 nm) compared to their corresponding linear analogues **4** and **5**, respectively, as a result of tetrahedral extension of the oligothiophene moieties. These red-shifts of the absorption maxima should be attributable to the homoconjugation between oligothiophene moieties through the central carbon.[24] In order to elucidate the intramolecular interaction between the oligothiophene moieties in these tetrakis(oligothienyl)methanes, a DFT study of **1a** was carried out. According to the DFT calculation at the RB3LYP/6-31G-(d,p) level, LUMO of **1a** is constructed by four LUMOs of thiophene, among which there are bonding through-space interactions (Figure 4). On the other hand, an anti-bonding through-bond interaction is suggested in the doubly degenerate HOMOs of **1a**. Compared with thiophene, the stabilization energy of the LUMO and destabilization energy of the HOMO are 0.261 and 0.258 eV, respectively, which account for the red-shift of the longest absorption maximum of these tetrakis(oligothienyl)methane derivatives.

In the fluorescence spectra, the Stokes shifts of **2** (66–71 nm) are larger than those of **4** (34–39 nm). The fluorescence spectra of **2** show only a broad band without the vibrational structure whereas those of **4** display vibrational structure (Figure 3). These fluorescence properties in **2** might be attributable to the intramolecular interaction between the bithienyl moieties. On the other hand, the Stokes shifts of **3** (46 nm) are similar to those of **5** (43–45 nm). The shape of the fluorescence spectra of **3**, exhibiting vibrational structure, are quite similar to those of **5** (see Figure S16 of the Supporting Information). It is suggested that the behavior of each terthiophene moiety is predominant over the intramolecular interaction between terthiophenes.

Upon cyclic voltammetry (see Figure S17 of the Supporting Information), all oxidation potentials were observed as irreversible waves, which indicated the oxidative oligomerization. The oxidation potentials of **2** and **3** were observed at lower potentials than the corresponding linear oligothiophene derivatives **4** and **5**, respectively (Table 1). This result would be also attributable to the destabilization of the HOMO in the tetrakis(2-thienyl)methane framework by intramolecular interaction between the oligothiophene moieties.

Conclusions

In summary, we have synthesized a series of tetrakis(oligothienyl)methanes **1a**–**3a** and their TMS derivatives **1b**–**3b**. The crystal structure of **3b** shows a well-regulated arrangement of molecules, reflecting the highly symmetric molecular structure. Large Stokes shifts, attributable to the intramolecular interaction between the bithiophene moieties, are observed in **2a** and **2b**. The intramolecular interaction between thiophenes in **1a** is also suggested by DFT calculation. The tetrahedrally extended oligothiophene derivatives described here show promise for application as organic semiconductors because of both the intramolecular and intermolecular interaction between the oligothiophene moieties. Furthermore, rational structural modification can be done easily through the lithiation and bromination of **1a**. Synthe-

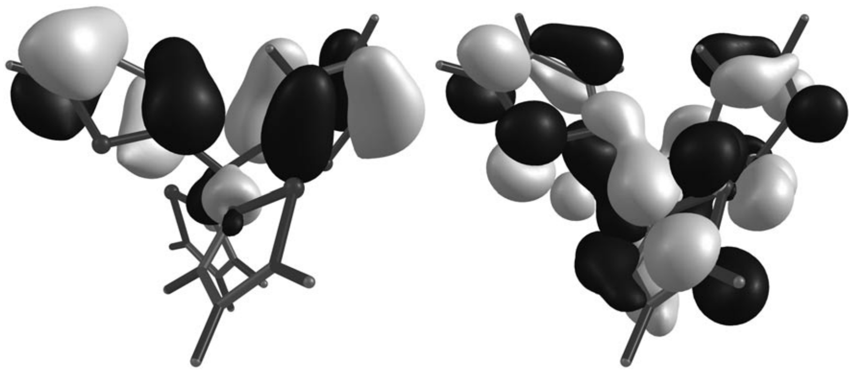


Figure 4. HOMO (left, one of the degenerate orbitals is shown) and LUMO (right) of **1a** (RB3LYP/6-31G-(d,p) method).

sis of longer homologues and application to optoelectronic devices are now under investigation.

Experimental Section

General

Melting points were obtained on a Yanako MP500D apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-270 (270 MHz) or JEOL LA-500 (500 MHz) spectrometer. Chemical shifts were recorded in units of per million downfield from tetramethylsilane as an internal standard, and all coupling constants are reported in Hertz. UV/Vis spectra were recorded in CH_2Cl_2 on a JASCO J-720W spectrophotometer. Fluorescence spectra were recorded in CH_2Cl_2 on a JASCO FP-6300 spectrofluorometer. Mass spectra were recorded using a Shimadzu GCMS-QP5050 spectrometer (by EI method) or a JEOL JMS-SX102 spectrometer (by FAB method). Cyclic voltammetry was performed in THF on a BAS CV-50W voltammetric analyser using nBu$_4$NClO$_4$ as an electrolyte. If necessary, the compound was purified by a recycle HPLC (LC-9201, Japan Analytical Industry Co., Ltd) on GPC columns (JAIGEL 1H and JAIGEL 2H) after purification by column chromatography on silica gel. Elemental analysis was performed at the Elemental Analysis Center at the Faculty of Science, Osaka University.

Materials

Diisopropylamine, methylene chloride, and dimethylformamide (DMF) were distilled from calcium hydride and stocked under nitrogen with dried molecular sieves (4 Å). Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were distilled from sodium benzophenone ketyl under nitrogen before use. Other commercially available reagents and solvents were used without further purification. Synthetic procedure and spectroscopic data for **1a** was already reported.[16] 2-Thienylboronic acid[18] and 5-bromo-2,2′-bithienyl[19] were prepared according to literature procedures.

Tetrakis(5-trimethylsilyl-2-thienyl)methane (**1b**): A 1.4 M solution of nBuLi in hexane (2.9 mL, 4.0 mmol) was added to a solution of **1a** (172 mg, 0.50 mmol) in THF (40 mL) over 3 min at −70 °C under nitrogen atmosphere. The resulting red solution was stirred at 0 °C for an hour. The reaction mixture turned into an orange suspension. The reaction mixture was cooled at −70 °C again, then TMSCl (1.2 mL, 8.0 mmol) was added over 5 min. The reaction mixture turned into a red solution during the addition of TMSCl. The reaction mixture was stirred for 30 min at −70 °C, then allowed to warm to room temperature. After stirring for 2 h, water (50 mL) was added to the reaction mixture. The aqueous layer was extracted with hexane–ethyl acetate (3:1 v/v, 50 mL × 3). The combined organic layers were washed with water and brine, then dried over anhydrous Na_2SO_4. After filtration and evaporation, the pale yellow residue was purified by column chromatography on silica gel (30 g) eluted with hexane. Recrystallization with hexane gave 250 mg (79 %) of **1b** as colorless needles (m.p. 189–190 °C, hexane); UV/Vis (in CH_2Cl_2) λ_{max}/nm (log ε) 252 (4.61); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.09$ (d, $J = 3.3$ Hz, 4H), 7.07 (d, $J = 3.3$ Hz, 4H), 0.28 ppm (s, 36H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 158.1$, 139.7, 133.2, 129.1, 53.7, 0.0 ppm; MS (EI): m/z (rel intensity) 632 [M^+, 58], 559 ([$M-C_3H_9Si$]$^+$, 100), 477 ([$M-C_7H_{11}SSi$]$^+$, 21), 322 ([$M-C_{14}H_{22}S_2Si_2$]$^+$, 26); elemental analysis: calcd (%) for $C_{29}H_{44}S_4Si_4$: C 55.00, H 7.00; found C 54.95, H 7.03.

Tetrakis(5-formyl-2-thienyl)methane (**1c**): A 1.4 M solution of nBuLi in hexane (5.8 mL, 4.0 mmol) was added to a solution of **1a** (344 mg, 1.0 mmol) in THF (80 mL) over 5 min at −70 °C under nitrogen atmosphere. The resulting red solution was stirred at 0 °C for an hour followed by the addition of DMF (0.62 mL, 8.0 mmol). The reaction mixture was stirred at 0 °C for an hour and then room temperature for an hour. Saturated aqueous ammonium chloride solution (80 mL) was added, and the solution was stirred for 30 min. The aqueous layer was extracted with ethyl acetate (100 mL × 3). The combined organic layers were washed with water and brine, and then dried over anhydrous Na_2SO_4. After filtration and evaporation, the yellow residue was purified by column chromatography on silica gel (40 g) eluted with ethyl acetate–chloroform (1:5 v/v). The desired tetraaldehyde **1c** (337 mg, 74 %) was obtained as pale yellow crystals. M.p. 253–254 °C; UV/Vis (in CH_2Cl_2) λ_{max}/nm (log ε) 296 (4.68), 274 sh (4.57); ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 9.90$ (s, 4H), 7.72 (d, $J = 4.1$ Hz, 4H), 7.22 ppm (d, $J = 4.1$ Hz, 4H), ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 182.5$, 157.9, 143.6, 135.4, 129.5, 55.0 ppm; MS (FAB) m/z 457.0 [$M+H$]$^+$; elemental analysis: calcd (%) for $C_{21}H_{12}O_4S_4$: C 55.24, H 2.65; found C 54.22, H 2.82.

Tetrakis(5-bromo-2-thienyl)methane (**1d**): NBS (0.22 g, 1.2 mmol) was added to a solution of **1a** (103 mg, 0.3 mmol) in 10 mL of chloroform in the dark. The reaction mixture was stirred overnight at room temperature. After the addition of water (10 mL), the reaction mixture was extracted with chloroform (25 mL × 2). The combined organic layers were washed with water, and dried over anhydrous Na_2SO_4. After filtration and evaporation, the yellow residue was purified by recrystallization with chloroform. Tetrabromide **1d** was obtained as colorless crystals (140 mg, 70 %). M.p. 249.5–250.5 °C; UV/Vis (in CH_2Cl_2) λ_{max}/nm (log ε) 277 (4.41); ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 6.94$ (d, $J = 4.0$ Hz, 4H), 6.78 ppm (d, $J = 4.0$ Hz, 4H); ^{13}C NMR (67.8 MHz, [D$_8$]THF): $\delta = 151.3$, 129.9, 128.5, 112.8, 53.8 ppm; MS (EI) m/z (rel intensity) 662 [M^+, $^{81}Br_3\cdot{}^{79}Br$, 34], 660 [M^+, $^{81}Br_2\cdot{}^{79}Br_2$, 47], 658 [$M^+$, $^{81}Br\cdot{}^{79}Br_3$, 25], 583 ([$M-Br$]$^+$, $^{81}Br_3$, 34), 581 ([$M-Br$]$^+$, $^{81}Br_2\cdot{}^{79}Br$, 63), 579 ([$M-Br$]$^+$, $^{81}Br\cdot{}^{79}Br_2$, 69), 577 ([$M-Br$]$^+$, $^{79}Br_3$, 25), 502 ([$M-2Br$]$^+$, $^{81}Br_2$, 69), 500 ([$M-2Br$]$^+$, $^{81}Br\cdot{}^{79}Br$, 100), 498 ([$M-2Br$]$^+$, $^{79}Br_2$, 53), 421 ([$M-3Br$]$^+$, ^{81}Br, 53), 419 ([$M-3Br$]$^+$, ^{79}Br, 50), 340 ([$M-4Br$]$^+$, 28); elemental analysis: calcd for $C_{17}H_8S_4Br_4$: C 30.93, H 1.22, found C 31.22, H 1.20.

Tetrakis(5-(2-thienyl)-2-thienyl)methane (**2a**): A mixture of **1d** (400 mg, 0.60 mmol), 2-thienyl boronic acid (930 mg, 7.3 mmol), sodium carbonate (1.54 g, 14.5 mmol), and $(PPh_3)_4Pd$ (280 mg, 0.24 mmol) in DME (30 mL) and water (15 mL) was refluxed for 24 h under nitrogen atmosphere. The resultant reddish brown solution was diluted with water (50 mL), then extracted with CH_2Cl_2 (50 mL × 3). The combined organic layers were washed with water, and dried over anhydrous Na_2SO_4. After filtration and evaporation, the brown solid residue was adsorbed on silica gel (3 g), and purified by column chromatography on silica gel (25 g) eluted with hexane–CH_2Cl_2 (4:1 v/v, 500 mL), hexane–CH_2Cl_2 (1:1 v/v, 300 mL), then CH_2Cl_2 (200 mL). Although the greater part of **2a** was eluted with hexane–CH_2Cl_2 (4:1 v/v) or hexane–CH_2Cl_2 (1:1 v/v), a part of **2a** was eluted only with CH_2Cl_2. The **2a** in the fraction of CH_2Cl_2 was purified by column chromatography on silica gel again. Colorless crystals may appear from fractions in hexane–CH_2Cl_2 (4:1 v/v). According to elemental analysis and ^{1}H NMR spectroscopy, this crystals contain one CH_2Cl_2 molecule per two molecules of **2a** (**2a** $(CH_2Cl_2)_{0.5}$) as observed by X-ray crystallographic analysis.) Recrystallization with chloroform-hexane gave **2a** (260 mg, 63 %) as colorless crystals. M.p. 143–144 °C ($CHCl_3$-hexane); UV/Vis (in CH_2Cl_2) λ_{max}/nm (log ε) 344 sh (4.59), 323 (4.81), 249 (4.35), 228 (4.33); ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.19$ (dd, $J = 5.1$, 1.1 Hz, 4H), 7.13 (dd, $J = 3.5$, 1.1 Hz, 4H), 7.09 (d, $J = 3.8$ Hz, 4H), 7.06 (d, $J = 3.8$ Hz, 4H), 6.97 ppm (dd, $J = 5.1$, 3.5 Hz, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 149.9$, 137.3, 136.9, 128.4, 127.5, 124.3, 123.7, 122.8, 53.5 ppm; MS (EI) m/z (rel intensity) 672 [M^+, 78], 507 ([$M-C_8H_5S_2$]$^+$, 36), 342 ([$M-C_{16}H_{10}S_4$]$^+$, 100), 336 (M^{2+}, 19); elemental analysis: calcd (%) for $C_{33}H_{20}S_8\cdot 0.5CH_2Cl_2$: C 56.23, H 2.96; found C 56.05, H 2.90.

Tetrakis(5-(5-trimethylsilyl-2-thienyl)-2-thienyl)methane (**2b**): A 1.4 M solution of nBuLi in hexane (0.86 mL, 1.2 mmol) was added to a solution of **2a** (100 mg, 0.15 mmol) in THF (20 mL) over 5 min at −70 °C under nitrogen atmosphere. The reaction mixture (dark green solution) was allowed to warm up to 0 °C, and then stirred for an hour. Dark green precipitates appeared in a pale yellow solution. The reaction mixture was subsequently cooled to −70 °C, and trimethylsilyl chloride (370 mg, 3.0 mmol) was added. The green precipitates immediately dissolved and the reaction mixture turned into a yellow solution. The reaction mixture was stirred at room temperature overnight. The resulting green solution was diluted with water (20 mL) and extracted with CH_2Cl_2 (30 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4. After filtration and evaporation, the green solid residue was purified with column chromatography on silica gel (20 g) eluted with hexane–CH_2Cl_2 (5:1 v/v). **2b** (130 mg, 88 %) was obtained as pale yellow crystals. M.p. >

260 °C (dec.), (CH_2Cl_2–hexane); UV/Vis (in CH_2Cl_2) λ_{max}/nm (log ε) 353 sh (4.70), 332 (4.91), 254 (4.33), 228 (4.36); MS (FAB) m/z 961 $[M+H]^+$, 723 ($[M-C_{11}H_{13}S_2Si]^+$), 486 ($[M-C_{22}H_{26}S_4Si_2]^+$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.18 (d, J = 3.3 Hz, 4H), 7.09 (d, J = 3.3 Hz, 4H), 7.08 (d, J = 3.8 Hz, 4H), 7.04 (d, J = 3.8 Hz, 4H), 0.31 ppm (s, 36H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.3, 142.2, 140.0, 137.6, 134.7, 128.7, 125.1, 122.9, 53.6 ppm, −0.1; elemental analysis: calcd (%) for $C_{45}H_{52}S_8Si_4$: C 56.20, H 5.45; found C 55.87, H 5.36.

Tetrakis(5-(5-(2-thienyl)-2-thienyl)-2-thienyl)methane (**3a**): 1.4 M solution of nBuLi in hexane (1.7 mL, 2.4 mmol) was added to a solution of **1a** (100 mg, 0.29 mmol) in THF (25 mL) over 3 min at −70 °C under nitrogen atmosphere. The reaction mixture was stirred at −70 °C for 10 min and then at 0 °C for an hour. The resultant orange suspension was subsequently cooled to −70 °C, and then $(MeO)_3B$ (380 mg, 3.6 mmol) was added to the reaction mixture that turned into a yellow solution. The reaction mixture was stirred at room temperature for two hours. 2 M aqueous HCl (15 mL) was added at 0 °C and the reaction mixture was stirred at room temperature for 30 min, and extracted with ether (50 mL × 3). The organic layers were combined and concentrated to afford crude tetrakis(boronic acid) **1e** as yellow solid which was used for the next reaction without further purification. A mixture of crude **1e**, 5-bromo-2,2′-bithienyl (590 mg, 2.4 mmol), sodium carbonate (250 mg, 2.4 mmol), and $(PPh_3)_4Pd$ (67 mg, 0.058 mmol) in DME (30 mL) and water (15 mL) was refluxed for 24 h under nitrogen atmosphere. The reaction mixture was a yellow solution with black tar. (A large amount of **3a** was contained in this tar). This precipitate was purified with column chromatography on silica gel (40 g) eluted with hexane–CH_2Cl_2 (4:1 v/v, 500 mL) and hexane–CH_2Cl_2 (3:1 v/v, 600 mL). **3a** (80 mg, 27 %) was obtained as yellow needles. **3a** (10 mg, 3 %) was also obtained from a part of the yellow solution by the ordinary workup. Yellow needles; m.p. 142–143 °C ($CHCl_3$); UV/Vis (in CH_2Cl_2) λ_{max}/nm (log ε) 400 sh (4.81), 374 (5.03), 253 (4.50), 228 (4.55); ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.20 (dd, J = 5.1, 1.1 Hz, 4H), 7.16 (dd, J = 3.8, 1.1 Hz, 4H), 7.10 (d, J = 4.1 Hz, 4H), 7.07 (d, J = 4.1 Hz, 4H), 7.05 (s, 8H), 7.01 ppm (dd, J = 5.1, 3.8 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.1, 137.4, 137.1, 136.5, 135.8, 128.8, 127.9, 124.54, 124.53, 124.3, 123.8, 123.0, 53.7 ppm; MS (FAB) m/z 1000 $[M]^+$, 753 ($[M-C_{12}H_7S_3]^+$); elemental analysis calcd (%) for $C_{49}H_{28}S_{12}$: C 58.76, H 2.82; found C 58.63, H 2.80.

Tetrakis(5-(5-(5-trimethylsilyl-2-thienyl)-2-thienyl)-2-thienyl)methane (**3b**): A 1.4 M solution of nBuLi (1.0 mL, 1.4 mmol) was added to a solution of diisopropylamine (0.2 mL, 1.4 mmol) in THF (10 mL) over 3 min at −70 °C under nitrogen atmosphere. After stirring at 0 °C for 30 min, a solution of **3a** (70 mg, 0.070 mmol) in THF (15 mL) was added at −70 °C over 10 min. After stirring at 0 °C for an hour, trimethylsilyl chloride (0.51 mL, 3.5 mmol) was added to the resultant green fluorescent brown suspension at −70 °C. The reaction mixture was allowed to warm up to room temperature and turned light yellow. After stirring at room temperature overnight, the resultant green solution was diluted with water (40 mL). The mixture was extracted with CH_2Cl_2 (50 mL × 3) and the combined organic layers were dried over anhydrous Na_2SO_4. After filtration and evaporation, the green residue was purified by column chromatography on silica gel (20 g) eluted with hexane–CH_2Cl_2 (4:1 v/v) to afford **3b** (30 mg, 33 %) as yellow needles. Yellow needles, m.p. 177–178 °C ($CHCl_3$–hexane); UV/Vis (in CH_2Cl_2) λ_{max}/nm (log ε) 407 sh (4.89), 381 (5.11), 256 (4.53), 228 (4.65); ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.20 (d, J = 3.4 Hz, 4H), 7.12 (d, J = 3.4 Hz, 4H), 7.09 (d, J = 3.8 Hz, 4H), 7.07 (d, J = 3.8 Hz, 4H), 7.06 (d, J = 3.8 Hz, 4H), 7.04 (d, J = 3.8 Hz, 4H), 0.33 ppm (s, 36H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.9, 141.9, 139.9, 137.3, 136.4, 135.7, 134.6, 128.6, 124.8, 124.4, 124.2, 122.7, 53.6, −0.1 ppm; MS (FAB) m/z 1288 $[M^+]$, 969 ($[M-C_{15}H_{15}S_3Si]^+$), 650 ($[M-C_{30}H_{30}S_6Si_2]^+$); elemental analysis calcd (%) for $C_{61}H_{60}S_{12}Si_4$: C 56.78, H 4.69; found C 56.65, H 4.69.

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[1] a) S. Hotta in *Handbook of Organic Conductive Molecules and Polymers Vol. 2* (Ed.: H. S. Nalwa) Wiley, Chichester, **1997**; b) P. Bäuerle in *Electronic Materials: The Oligomer Approach* (Eds.: K. Müllen, G. Wegner), Wiley-VCH, Weinheim, **1998**; c) *Handbook of Oligo- and Polythiophenes*, (Ed.: D. Fichou), Wiley-VCH, Weinheim, **1999**; d) P. F. H. Schwab, J. R. Smith, J. Michl, *Chem. Rev.* **2005**, *105*, 1197–1279.

[2] a) T. Otsubo, Y. Aso, K. Takimiya, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1789–1801; b) T. Izumi, S. Kobayashi, K. Takimiya, Y. Aso, T. Otsubo, *J. Am. Chem. Soc.* **2003**, *125*, 5286–5287.

[3] a) T. Nakamura, J. Ikemoto, M. Fujitsuka, Y. Araki, O. Ito, K. Takimiya, Y. Aso, T. Otsubo, *J. Phys. Chem. B* **2005**, *109*, 14365–14374; b) M. Sun, P. Song, Y. Chen, F. Ma, *Chem. Phys. Lett.* **2005**, *416*, 94–99; c) T. Otsubo, Y. Aso, K. Takimiya, *Pure Appl. Chem.* **2005**, *77*, 2003–2010; d) M. Narutaki, K. Takimiya, T. Otsubo, Y. Harima, H. Zhang, Y. Araki, O. Ito, *J. Org. Chem.* **2006**, *71*, 1761–1768; e) T. Nakamura, H. Kanato, Y. Araki, O. Ito, K. Takimiya, T. Otsubo, Y. Aso, *J. Phys. Chem. A* **2006**, *110*, 3471–3479; f) H. Kanato, M. Narutaki, K. Takimiya, T. Otsubo, Y. Harima, *Chem. Lett.* **2006**, *35*, 668–669; g) J.-L. Wang, X.-F. Duan, B. Jiang, L.-B. Gan, J. Pei, C. He, Y.-F. Li, *J. Org. Chem.* **2006**, *71*, 4400–4410.

[4] a) C. Moorlag, B. C. Sih, T. L. Stott, M. O. Wolf, *J. Mater. Chem.* **2005**, *15*, 2433–2436, and references cited therein; b) R. Ziessel, P. Bäuerle, M. Ammann, A. Barbieri, F. Barigelletti, *Chem. Commun.* **2005**, 802–804; c) C. Houarner, E. Blart, P. Buvat, F. Odobel, *Photochem. Photobiol. Sci.* **2005**, *4*, 200–204; d) M. H. Chisholm, A. J. Epstein, J. C. Gallucci, F. Feil, W. Pirkle, *Angew. Chem.* **2005**, *117*, 6695–6698; *Angew. Chem. Int. Ed.* **2005**, *44*, 6537–6540; e) F. Zhang, P. Bäuerle, *J. Am. Chem. Soc.* **2007**, *129*, 3090–3091.

[5] a) A. Petrella, J. Cremer, L. D. Cola, P. Bäuerle, R. M. Williams, *J. Phys. Chem. A* **2005**, *109*, 11687–11695; b) D. Rohde, L. Dunsch, A. Tabet, H. Hartmann, J. Fabian, *J. Phys. Chem. B* **2006**, *110*, 8223–8231; c) A. Cravino, S. Roquet, O. Alévêque, P. Leriche, P. Frère, J. Roncali, *Chem. Mater.* **2006**, *18*, 2584–2590; d) J. Lu, P. F. Xia, P. K. Lo, Y. Tao, M. S. Wong, *Chem. Mater.* **2006**, *18*, 6194–6203.

[6] a) J. Nishida, S. Murakami, H. Tada, Y. Yamashita, *Chem. Lett.* **2006**, *35*, 1236–1237; b) V. Promarak, A. Pankvuang, S. Ruchirawat, *Tetrahedron Lett.* **2007**, *48*, 1151–1154.

[7] a) J. Cremer, E. Mena-Osteritz, N. G. Pschierer, K. Müllen, P. Bäuerle, *Org. Biomol. Chem.* **2005**, *3*, 985–995; b) S. Chen, Y. Liu, W. Qiu, X. Sun, Y. Ma, D. Zhu, *Chem. Mater.* **2005**, *17*, 2208–2215; c) J. Cremer, P. Bäuerle, *Eur. J. Org. Chem.* **2005**, 3715–3723; d) F. Moggia, C. Videlot-Ackermann, J. Ackermann, P. Raynal, H. Brisset, F. Fages, *J. Mater. Chem.* **2006**, *16*, 2380–2386.

[8] T. Torroba, M. García-Valverde, *Angew. Chem.* **2006**, *118*, 8270–8274; *Angew. Chem. Int. Ed.* **2006**, *45*, 8092–8096, and references therein.

[9] a) J. Krömer, I. Rios-Carreras, G. Fuhrmann, C. Musch, M. Wunderlin, T. Debaerdemaeker, E. Mena-Osteritz, P. Bäuerle, *Angew. Chem.* **2000**, *112*, 3623–3628; *Angew. Chem. Int. Ed.* **2000**, *39*, 3481–3486; b) E. Mena-Osteritz, P. Bäuerle, *Adv. Mater.* **2001**, *13*, 243–246; c) G. Fuhrmann, T. Debaerdemaeker, P. Bäuerle, *Chem. Commun.* **2003**, 948–949; d) B. Jousselme, P. Blanchard, M. Allain, E. Levillain, M. Dias, J. Roncali, *J. Phys. Chem. A* **2006**, *110*, 3488–3494; e) S. S. Zade, M. Bendikov, *J. Org. Chem.* **2006**, *71*, 2972–2981; f) J. Casado, M. Z. Zgierski, G. Fuhrmann, P. Bäuerle, J. T. L. Navarrete, *J. Chem. Phys.* **2006**, *125*, 044518; g) K. Nakao, M. Nishimura, T. Tamachi, Y. Kuwatani, H. Miyasaka, T. Nishinaga, M. Iyoda, *J. Am. Chem. Soc.* **2006**, *128*, 16740–16747; h) A. Bhaskar, G. Ramakrishna, K. Hagedorn, O. Varnavski, E. Mena-Osteritz, P. Bäuerle, T. Goodson III, *J. Phys. Chem. B* **2007**, *111*, 946–954; i) M. Williams-Harry, A. Bhaskar, G. Ramakrishna, T. Goodson III, M.

Imamura, A. Mawatari, K. Nakao, H. Enozawa, T. Nishinaga, M. Iyoda, *J. Am. Chem. Soc.* **2008**, *130*, 3252–3253.

[10] a) M. Ammann, A. Rang, C. A. Schalley, P. Bäuerle, *Eur. J. Org. Chem.* **2006**, 1940–1948; b) S. Fomine, P. Guadarrama, *J. Phys. Chem. A* **2006**, *110*, 10098–10105; c) P. Bäuerle, M. Ammann, M. Wilde, G. Götz, E. Mena-Osteritz, A. Rang, C. A. Schalley, *Angew. Chem.* **2007**, *119*, 367–372; *Angew. Chem. Int. Ed.* **2007**, *46*, 363–368.

[11] a) A. Rajca, H. Wang, M. Pink, S. Rajca, *Angew. Chem.* **2000**, *112*, 4655–4657; *Angew. Chem. Int. Ed.* **2000**, *39*, 4481–4483; b) M. Miyasaka, A. Rajca, M. Pink, S. Rajca, *J. Am. Chem. Soc.* **2005**, *127*, 13806–13807; c) M. Miyasaka, A. Rajca, *J. Org. Chem.* **2006**, *71*, 3264–3266; d) R. M. Osuna, R. P. Ortiz, V. Hernández, J. T. L. Navarrete, M. Miyasaka, S. Rajca, A. Rajca, R. Glaser, *J. Phys. Chem. C* **2007**, *111*, 4854–4860.

[12] a) Y. Mazaki, K. Kobayashi, *Tetrahedron Lett.* **1989**, *30*, 3315–3318; b) X. Zhang, A. P. Côté, A. J. Matzger, *J. Am. Chem. Soc.* **2005**, *127*, 10502–10503; c) Y. Nicolas, P. Blanchard, J. Roncali, M. Allain, N. Mercier, A.-L. Deman, J. Tardy, *Org. Lett.* **2005**, *7*, 3513–3516; d) K. R. Radke, K. Ogawa, S. C. Rasmussen, *Org. Lett.* **2005**, *7*, 5253–5256; e) T. Okamoto, K. Kudoh, A. Wakamiya, S. Yamaguchi, *Chem. Eur. J.* **2007**, *13*, 548–556; f) T. Okamoto, K. Kudoh, A. Wakamiya, S. Yamaguchi, *Appl. Phys. Lett.* **2007**, *90*, 072102; g) L. S. Miguel, W. W. Porter III, A. J. Matzger, *Org. Lett.* **2007**, *9*, 1005–1008; h) M. He, F. Zhang, *J. Org. Chem.* **2007**, *72*, 442–451.

[13] J. Roncali, P. Leriche, A. Cravino, *Adv. Mater.* **2007**, *19*, 2045–2060, and references therein.

[14] a) S. A. Ponomarenko, S. Kirchmeyer, A. Elschner, B.-H. Huisman, A. Karbach, D. Drechsler, *Adv. Funct. Mater.* **2003**, *13*, 591–596; b) J. Pei, J.-L. Wang, X.-Y. Cao, X.-H. Zhou, W.-B. Zhang, *J. Am. Chem. Soc.* **2003**, *125*, 9944–9945; c) R. de Bettignies, Y. Nicolas, P. Blanchard, E. Levillain, J.-M. Nunzi, J. Roncali, *Adv. Mater.* **2003**, *15*, 1939–1943; d) Y. Nicolas, P. Blanchard, E. Levillian, M. Allain, N. Mercier, J. Roncali, *Org. Lett.* **2004**, *6*, 273–276; e) Y. Sun, K. Xiao, Y. Liu, J. Wang, J. Pei, G. Yu, D. Zhu, *Adv. Funct. Mater.* **2005**, *15*, 818–822; f) S. A. Ponomarenko, E. A. Tatarinova, A. M. Muzafarov, S. Kirchmeyer, L. Brassat, A. Mourran, M. Moeller, S. Setayesh, D. de Leeuw, *Chem. Mater.* **2006**, *18*, 4101–4108; g) X. Sun, Y. Liu, S. Chen, W. Qiu, G. Yu, Y. Ma, T. Qi, H. Zhang, X. Xu, D. Zhu, *Adv. Funct. Mater.* **2006**, *16*, 917–925; h) J. Cremer, P. Bäuerle, *J. Mater. Chem.* **2006**, *16*, 874–884.

[15] a) C. Xia, X. Fan, J. Locklin, R. C. Advincula, *Org. Lett.* **2002**, *4*, 2067–2070; b) M.-H. Xu, L. Pu, *Tetrahedron Lett.* **2002**, *43*, 6347–6350; c) X.-M. Liu, C. He, J. Huang, *Tetrahedron Lett.* **2004**, *45*, 6173–6177; d) C. Xia, X. Fan, J. Locklin, R. C. Advincula, A. Gies, W. Nonidez, *J. Am. Chem. Soc.* **2004**, *126*, 8735–8743; e) S. Deng, J. Locklin, D. Patton, A. Baba, R. C. Advincula, *J. Am. Chem. Soc.* **2005**, *127*, 1744–1751; f) W. J. Mitchell, N. Kopidakis, G. Rumbles, D. S. Ginley, S. E. Shaheen, *J. Mater. Chem.* **2005**, *15*, 4518–4528; g) S. Roquet, R. de Bettignies, P. Leriche, A. Cravino, J. Roncali, *J. Mater. Chem.* **2006**, *16*, 3040–3045; h) Y. Zhang, C. Zhao, J. Yang, M. Kapiamba, O. Haze, L. J. Rothberg, M.-K. Ng, *J. Org. Chem.* **2006**, *71*, 9475–9483; i) E. A. Shumilkina, O. V. Borshchev, S. A. Ponomarenko, N. M. Surin, A. P. Pleshkova, A. M. Muzafarov, *Mendeleev Commun.* **2007**, *17*, 34–36; j) N. Negishi, Y. Ie, M. Taniguchi, T. Kawai, H. Tada, T. Kaneda, Y. Aso, *Org. Lett.* **2007**, *9*, 829–832; k) C.-Q. Ma, E. Mena-Osteritz, T. Debaerdemaeker, M. M. Wienk, R. A. J. Janssen, P. Bäuerle, *Angew. Chem.* **2007**, *119*, 1709–1713; *Angew. Chem. Int. Ed.* **2007**, *46*, 1679–1683; l) N. Negishi, Y. Ie, H. Tada, T. Kaneda, Y. Aso, *Chem. Lett.* **2007**, *36*, 544–545; m) Y. Zhang, Z. Wang, M.-K. Ng, L. J. Rothberg, *J. Phys. Chem. B* **2007**, *111*, 13211–13216; n) G. Ramakrishna, A. Bhaskar, P. Bäuerle, T. Goodson III, *J. Phys. Chem. A* **2008**, *112*, 2018–2026.

[16] a) K. Matsumoto, H. Nakaminami, M. Sogabe, H. Kurata, M. Oda, *Tetrahedron Lett.* **2002**, *43*, 3049–3052; b) K. Matsumoto, T. Tanaka, M. Oda, *Synth. Commun.* **2004**, *34*, 4037–4042.

[17] a) K. Matsumoto, M. Kannami, M. Oda, *Tetrahedron Lett.* **2003**, *44*, 2861–2864; b) K. Matsumoto, M. Kannami, M. Oda, *Chem. Lett.* **2004**, *33*, 1096–1097; c) H. Kurata, Y. Oki, K. Matsumoto, T. Kawase, M. Oda, *Chem. Lett.* **2005**, *34*, 910–911; d) K. Matsumoto, T. Inagaki, T. Nehira, M. Kannami, D. Inokuchi, H. Kurata, T. Kawase, G. Pescitelli, M. Oda, *Chem. Asian J.* **2007**, *2*, 1031–1036; e) K. Matsumoto, M. Kannami, D. Inokuchi, H. Kurata, T. Kawase, M. Oda, *Org. Lett.* **2007**, *9*, 2903–2906.

[18] G. E. Collis, A. K. Burell, S. M. Scott, D. L. Officer, *J. Org. Chem.* **2003**, *68*, 8974–8983.

[19] P. Bäuerle, F. Wünthner, G. Götz, F. Effenberger, *Synthesis* **1993**, 1099–1103.

[20] a) S. Hotta, K. Waragai, *Adv. Mater.* **1993**, *5*, 896–908; b) D. Fichou, *J. Mater. Chem.* **2000**, *10*, 571–588; c) R. Azumi, E. Mena-Osteritz, R. Boese, J. Benet-Buchholz, P. Bäuerle, *J. Mater. Chem.* **2006**, *16*, 728–735.

[21] CCDC 688433 (**1a**), CCDC 688434 (**1b**), CCDC 688435 (**2a**), CCDC 688436 (**2b**), CCDC 688437 (**3a**), and CCDC 688438 (**3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

[22] M. Bendikov, F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, *104*, 4891–4945, and references therein.

[23] a) R. B. Campbell, J. M. Robertson, J. Trotter, *Acta Crystallogr.* **1961**, *14*, 705–711; b) D. Holmes, S. Kumaraswamy, A. J. Matzger, K. P. C. Vollhardt, *Chem. Eur. J.* **1999**, *5*, 3399–3412; c) C. C. Mattheus, A. B. Dros, J. Baas, A. Meetsma, J. L. de Boer, T. T. M. Palstra, *Acta Crystallogr. Sect. C* **2001**, *57*, 939–941.

[24] a) W. J. Oldham, Jr., R. J. Lachicotte, G. C. Bazan, *J. Am. Chem. Soc.* **1998**, *120*, 2987–2988; b) S. Sengupta, N. Pal, *Tetrahedron Lett.* **2002**, *43*, 3517–3520; c) S. Sengupta, S. K. Sadhukhan, S. Muhuri, *Tetrahedron Lett.* **2002**, *43*, 3521–3524.

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