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Development of β-linked quaterthiophene and tetrathiafulvalene dimers as new organic semiconductors

Minoru Ashizawa *, Yan Yu, Takuro Niimura, Kazuma Tsuboi, Hidetoshi Matsumoto, Akihiko Tanioka, Takehiko Mori

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, 152-8552, Tokyo, Japan

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ABSTRACT

A series of β-linked quaterthiophene and tetrathiafulvalene dimers **1**–**4** has been prepared. Their redox and optical properties are almost the same as the parent monomers indicative of very little interaction between the monomers. Crystal structures of **1**, **2**, and **4** are highly one-dimensional, in which molecular structure of **1** is planar whereas those of **2** and **4** are in a bent form.

1. Introduction

High performance organic semiconductors have been widely investigated in recent years because of their practical use for flexible, low-cost, and large-area coverage electronic devices [1]. In organic field effect transistors (OFETs), linear π-conjugated molecules are considered to be desirable to make densely packed molecular arrangement [2–4]. The best charge carrier mobility of OFETs has already approached and even surpassed that of amorphous Si devices. However, a simple increase in the π-conjugation length in, for example, linear oligothiophenes reduces the solubility considerably. In order to improve the solubility by maintaining the desirable molecular packing, a solution of a processable swivel cruciform oligothiophene has been investigated to show excellent OFET performance [5].

In order to investigate electronic properties and molecular packing motifs of twisted molecules, we have developed new soluble quaterthiophene dimers linked at the β-position of the thiophene rings and tetrathiafulvalene (TTF) dimer whose TTF units are linked at the β-position of thiophene ring with ethynyl spacer. Molecular flexibility based on rotational freedom at the β-linkage of thiophene rings would be advantageous for solubility in common organic solvents. In this study, we report syntheses, redox and optical properties, and crystal structures of quaterthiophene and TTF dimers **1**–**4** (Scheme 1).

2. Experimental detail

All chemicals and solvents are of reagent grade unless otherwise indicated. All reactions were carried out under an argon atmosphere. THF was purified by distillation over sodium benzophenone kethyl under argon prior to use. NMR data were obtained on a JEOL JNN-AL300 spectrometer. The melting points were determined with a Yanako MP micromelting point apparatus. Microanalyses were performed at Microanalysis Center, Tokyo Institute of Technology. Cyclic voltammetry (CV) was performed with a Yanako electrochemistry analyzer VMA-010. MS spectra were obtained with a SHIMADZU/KRATOS AXIMA-CFR for MALDI-TOF MS. UV-vis spectra were collected on a HITACHI U2800, and photoluminescence spectra were collected on a JASCO FP-750. Crystal structures were determined with single-crystal X-ray diffraction data. Measurements were made on a RIGAKU Mercury CCD system with for **1** and **4** and a RIGAKU Vari Max RAPID-II system for **2**. Thermal gravimetric analysis (TGA) was conducted on a Seiko instruments TG/DTA6200 (temperature rate 10 °C min^{-1} under N_2).

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[*] Corresponding author. Tel.:+81357342426; fax: +8135734876.
E-mail address: ashizawa.m.aa@m.titech.ac.jp (M. Ashizawa).

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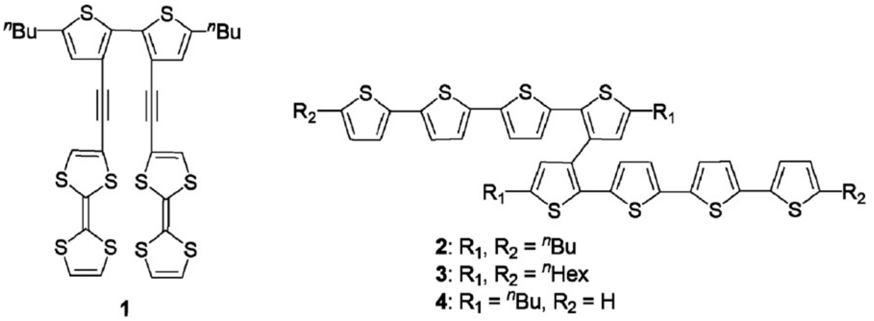


Scheme 1. Dimeric TTF and quaterthiophene molecules.

2.1. *Material Syntheses*

2.1.1. *TTF dimer 1*

Into a solution of TTF iodide **9** (0.50 g, 1.51 mmol), $Pd(PPh_3)_4$ (0.10 g, 0.08 mmol), and copper (I) iodide (0.03 g, 0.15 mmol) in toluene (15 ml) was added triethylamine (15 ml). After the mixture was stirred at room temperature for 5 min, diethynylbithiophene **8** (0.25 g, 0.77 mmol) in toluene (10 ml) was added dropwise. The resulting mixture was stirred at 60 °C overnight and poured into 2 M HCl (50 ml). After the insoluble materials were removed by filtration through celite, the filtrate was extracted with CS_2. The extract was successively washed with a saturated $NaHCO_3$ solution and water, and dried over $MgSO_4$. After evaporation, the residue was purified by column chromatography on silica gel with CS_2-hexane (1:1, v/v), and recrystallization from toluene gave a red solid (0.14 g, 33%). Mp=176–177 °C (decomp.). Ms (MALDI-TOF) *m/z* 731.5 (M^++H); ^{1}H NMR (300 MHz, CS_2-$CDCl_3$) δ 1.00 (t, *J*=6.9 Hz 6 H), 1.40–1.50 (m, 4 H), 1.71–1.76 (m, 4 H), 2.81 (t, *J*=6.9 Hz, 4 H), 6.32 (s, 4 H), 6.49 (s, 2 H), 6.70 (s, 2 H).

2.1.2. *Quaterthiophene dimers 2 and 3*

Quaterthiophene dimer 2: Dibromo-dibutylbithiophene **14** (0.25 g, 0.58 mmol), tri(*n*-butyl)stannyl-butylterthiophene **15** (0.71 g, 1.20 mmol), and $Pd(PPh_3)_4$ (0.05 g, 0.04 mmol) were dissolved in 20 ml of toluene. The mixture was refluxed for 48 h. The reaction mixture was poured into 1 M HCl (50 ml) and extracted with CS_2. The organic phase was subsequently washed with a saturated $NaHCO_3$ solution and water, and dried over $MgSO_4$. After evaporation, the residue was purified by column chromatography on silica gel with CS_2-hexane (1:1, v/v), and recrystallization from toluene afforded a yellow solid (0.13 g, 33%). Mp=202–203 °C. Ms (MALDI-TOF) *m/z* 882.7 (M^+); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, *J*=7.2 Hz, 12 H), 1.36–1.47 (m, 8 H), 1.60–1.72 (m, 8 H), 2.75–2.83 (m, 8 H), 6.57 (s, 2 H), 6.62(d, *J*=3.5 Hz, 2 H), 6.81 (d, *J*=3.9 Hz 2 H), 6.84–6.89 (m, 8 H). Anal. Calcd for $C_{48}H_{50}S_8$: C, 65.26; H: 5.70; S: 29.04. Found: C, 64.99; H: 5.51; S: 29.13.

Quaterthiophene dimer 3 was prepared in a similar manner as described for **2**. Mp=186, 187 °C. Ms (MALDI-TOF) *m/z* 995.8 (M^+); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (m, 12 H), 1.30 (m, 24 H), 1.61–1.73 (m, 8 H), 2.69–2.83 (m, 8 H), 6.60 (s, 2 H), 6.64(d, *J*=3.0 Hz, 2 H), 6.84 (d, *J*=3.9 Hz, 2 H), 6.84–6.93 (m, 8 H). Anal. Calcd for $C_{56}H_{66}S_8$: C, 67.55; H: 6.68; S: 25.76. Found: C, 67.46; H: 6.40; S: 26.04.

2.1.3. *Quaterthiophene dimer 4*

A mixture of dibromo-dibutylbithiophene **14** (0.39 g, 0.90 mmol), Na_2CO_3 (0.5 g), and $Pd(PPh_3)_4$ (0.12 g, 0.11 mmol) in 1,2-dimethoxyethane (20 ml) and water (30 ml) was heated under reflux. A solution of terthiopheneboronic acid **15** (0.64 g 2.2 mmol) in 1,2-dimethoxyethane (15 ml) was added dropwise. The mixture was heated under reflux overnight. The reaction mixture was poured into water and extracted with CS_2. After evaporation, the residue was purified by column chromatography on silica gel with CS_2-hexane (1:1, v/v), and recrystallization from toluene afforded a yellow solid **4** (0.05 g, 8%). Mp=216–217 °C. Ms (MALDI-TOF) *m/z* 768.0(M^+); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, *J*=7.3 Hz 6 H), 1.41–1.51(m, 4 H), 1.66–1.73 (m, 4 H), 2.82 (t, *J*=7.3 Hz, 4 H), 6.61 (s, 2 H), 6.62 (d, *J*=3.5 Hz, 2 H), 6.92 (d, *J*=4.6 Hz, 2 H), 7.13 (d, *J*=3.5 Hz, 2 H), 7.16 (d, *J*=4.4 Hz, 2 H). Anal. Calcd for $C_{40}H_{34}S_8$: C, 62.29; H: 4.44; S: 33.26. Found: C, 62.07; H: 4.37; S: 33.57.

2.1.4. *Single-crystal structure analyses*

Slow evaporation of a CS_2-hexane (1:1, v/v) solution of **1** gave red rods for X-ray structure analysis. Crystal data: $C_{32}H_{26}S_{10}$, Mw=729.92, monoclinic, space group $P2_1/c$, a=14.420(6), b=5.235(2), c=21.850(9) Å, β=99.163(11)°, V=1628.3(12) Å^3, Z=2, 17219 reflections measured, 4396 unique (R_{int}=0.248). Final R indices [$I > 2\sigma(I)$]: R_1=0.0708, wR_2=0.0986.

Vapor diffusion of hexane into a CS_2 solution of **2** afforded yellow needles for X-ray structure analysis. Crystal data: $C_{48}H_{50}S_8$, Mw=883.40, orthorhomic, space group Aea2, a=16.4463(3), b=49.9261(9), c=5.35235(10) Å, V=4394.82(14) Å^3, Z=4, 11780 reflections measured, 4011 unique (R_{int}=0.160). Final R indices [$I > 2\sigma(I)$]: R_1=0.1101, wR_2=0.1759.

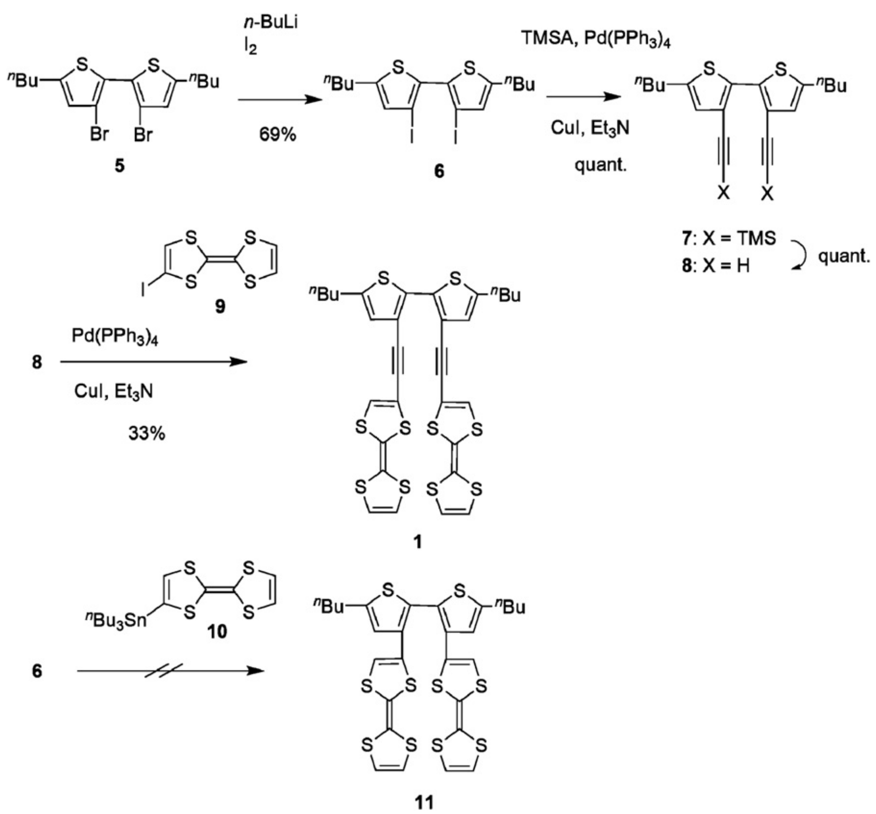
Vapor diffusion of hexane into a CS_2 solution of **4** afforded yellow needles for X-ray structure analysis. The obtained crystal was basically isostructural to **2**. Crystal data: $C_{40}H_{40}S_8$, a=16.433(18), b=39.68(4), c=5.475(6) Å, V=3570(7) Å^3, Z=4.

As for the single crystal of **3**, vapor diffusion of hexane into a CS_2 solution of **3** afforded very thin yellow needles, which were not suitable for X-ray structure analysis.

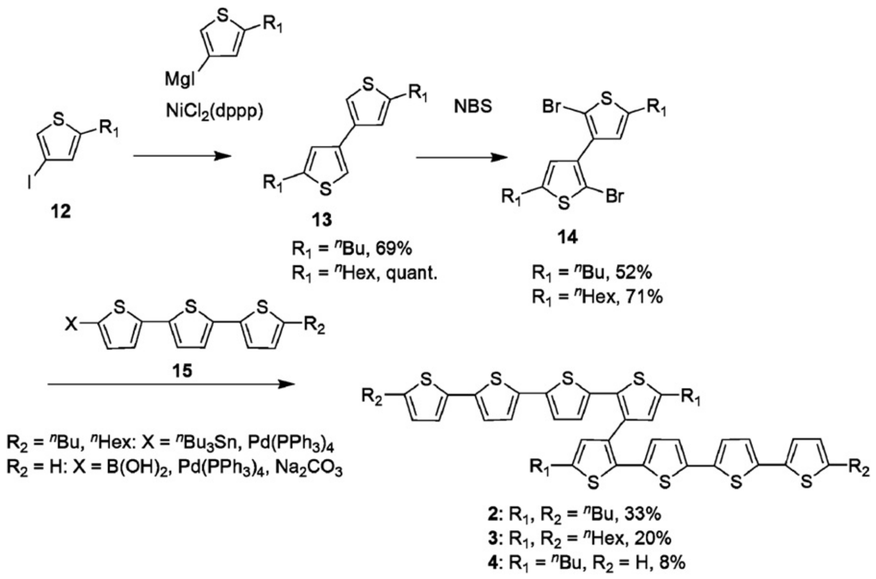
3. Results and discussions

3.1. *Synthesis of TTF dimer 1*

The synthesis of TTF dimer **1** is outlined in Scheme 2. Dibromide **5** is readily accessible by three steps from the starting α-butylthiophene [6]. The conversion of dibromide **5** to diiodide **6** is accomplished via lithium–halogen exchange, followed by quenching with iodine. Subsequent Sonogashira coupling of **6** with (trimethylsilyl)acetylene (TMSA), followed by removal of the TMS groups, and then the cross-coupling with TTF iodide **9**, affords **1** by three steps in 16% yield. Unfortunately, we have failed to prepare directly β-linked dimer **11** by Stille coupling to date, in which an unidentified byproduct was obtained.



Scheme 2. Synthesis of dimeric TTF.



Scheme 3. Synthesis of dimeric quaterthiophenes.

In the cyclic voltammetry measurement, **1** shows two pairs of reversible waves like the parent TTF under the same condition: $E^1_{1/2} = 0.231\,\mathrm{V}$, $E^2_{1/2} = 0.57\,\mathrm{V}$ for **1** and $E^1_{1/2} = -0.07\,\mathrm{V}$, $E^2_{1/2} = -0.48\,\mathrm{V}$ for TTF (vs Ag/AgNO$_3$ in PhCN with 0.1 M n-Bu$_4$NPF$_6$, grassy carbon working electrode, and scan rate 100 mV s^{-1}), indicating that two TTF units of **1** are practically independent. The first redox potential of **1** is significantly larger than that of TTF because an electron-withdrawing acetylene unit is attached to the TTF moiety. The $E^2_{1/2}$-$E^1_{1/2}$ value (0.34 V) for **1**, which is electrochemical estimation of the on-site Coulomb repulsion, is smaller than 0.55 V for TTF, reflecting the extended π-conjugation of **1**.

3.2. Syntheses of quaterthiophene dimers *2*–*4*

Scheme 3 illustrates syntheses of quaterthiophene dimers **2–4**. The key compounds **13** were obtained by the Kumada coupling of β-iodothiophene **12** which was prepared via lithium–halogen dance reaction of α-iodothiophene [7]. The NBS bromination of **13** gave dibromide **14**, in which treatment with 1 equiv. and 2 equiv. of NBS afforded mono- and dibromide, respectively. The Stille coupling of **14** with tributylstannyl butyl- and hexylterthiophenes **15** gave quaterthiophene dimers **2** in 33% yield and **3** in 20% yield, respectively. On the other hand, **4** was prepared by the Suzuki

Table 1
Redox[a] and optical properties[b]

	E^1_{ox}	E^2_{ox}	$\lambda_{abs,\ max}$ (nm)	$\lambda_{em,\ max}$ (nm)
2	0.58	0.79	418	511
3	0.56	0.74	418	510
4	0.61	0.80	408	507
DB4T	0.58	0.83	400	494
Ferrocene	0.31			

[a] vs. Ag/AgNO$_3$ in PhCN with 0.1 M n-Bu$_4$NPF$_6$, grassy carbon working electrode, scan rate 100 mV s^{-1}.

[b] 10^{-5} M in CHCl$_3$.

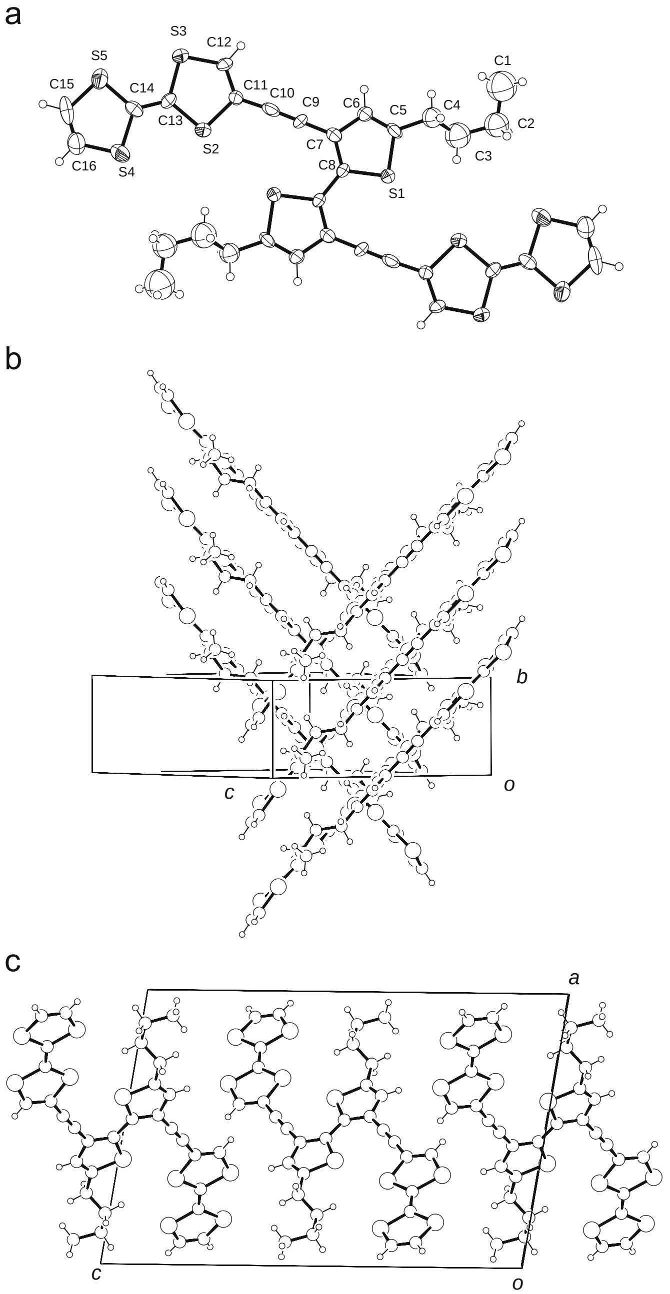


Fig. 1. Crystal structure of **1**. (a) Molecular structure and (b) (c) molecular packing.

coupling because the Stille coupling gave only a trace of the product. Dimers **2**–**4** are moderately soluble in common organic solvents.

Redox and optical properties of dimers **2**–**4** are summarized in Table 1. Quaterthiophene dimers **2**–**4** show two irreversible oxidation waves, which are almost the same as those of the parent monomer α,ω-dibuthylquaterthiophene (DB4T). The HOMO levels of **2**–**4** are estimated to be $-5.20\sim-5.29$ eV from the onset oxidation potentials. Dimers **2**–**4** exhibit UV-Vis absorption maxima at 408–418 nm and photoluminescence (PL) maxima at 507–511 nm. Compared with DB4T, these values are slightly red shifted. These results indicate that there is very little interaction between the monomers. The thermogravimetric analysis (TGA) in nitrogen of **2** shows the onset decomposition temperature of 425 °C. In contrast, an analogous oligothiophene α,ω-dihexylsexythiophene (DH6T) decomposes at 320 °C under similar conditions [8].

3.3. *Crystal structure of TTF dimer 1*

TTF dimer **1** crystallizes in the monoclinic system with the space group P2$_1$/c. The molecular and crystal structures of **1** are shown in Fig. 1. A half molecule of **1** is crystallographically independent, and a unit cell contains two molecules. In contrast to the chair form of the neutral TTF [9], the whole molecule of **1** is almost planar. In the unit cell, TTF dimer **1** makes two kinds of uniform stacks along the *b* axis (5.325 Å), and the molecular planes are nearly perpendicular to each other (Fig. 1(b)). Therefore the packing motif of **1** is one-dimensional.

3.4. *Crystal structure of quaterthiophene dimers 2 and 4*

Quaterthiophene dimer **2** crystallizes in the orthorhombic system with the space group Aea2. Although the crystal quality of **4** is poor, compound **4** seems to be also isostructural to **2**. A half molecule of **2** is crystallographically independent, and a unit cell contains four molecules (Fig. 2). The molecule has a twisted V-form centered at the β-linked bithiophene part. The twisted form agrees with the electronically independent redox and optical properties. The quaterthiophene groups form uniform stacks along the *c* axis embedded in the herringbone-like molecular packing (Fig. 2(b)). There are some intermolecular CH-π contacts shorter than the van der Waals distance in the stack. However, the largely twisted form of **2** breaks the electronic through-bond and through-space interactions between the quaterthiophene units. The calculated intrastack transfer integrals are by one order magnitude larger than the interstack integrals. Accordingly, the molecular packing is highly one-dimensional.

FET devices of **2**–**4** were fabricated by spin-coating from chloroform solutions, although **2**–**4** were not vacuum evaporated. However, the FET performance is not observed. This may be related to the one-dimensional molecular packing of these molecules.

4. Conclusions

We have prepared a series of β-linked quaterthiophene and TTF dimers. Their redox and optical properties reflect the inherent properties of the parent monomers, indicating that these monomers work independently, and the β-linkage does not connect the two units electronically. The crystal structures of **1**, **2**, and **4** are highly one-dimensional, in which **1** is in the planar form while **2** and **4** are in the twisted V-form. The present synthetic approach allows stepwise introduction of functional groups such as electron-donating and withdrawing units into the twisted bithiophene part. Along with this line, development of

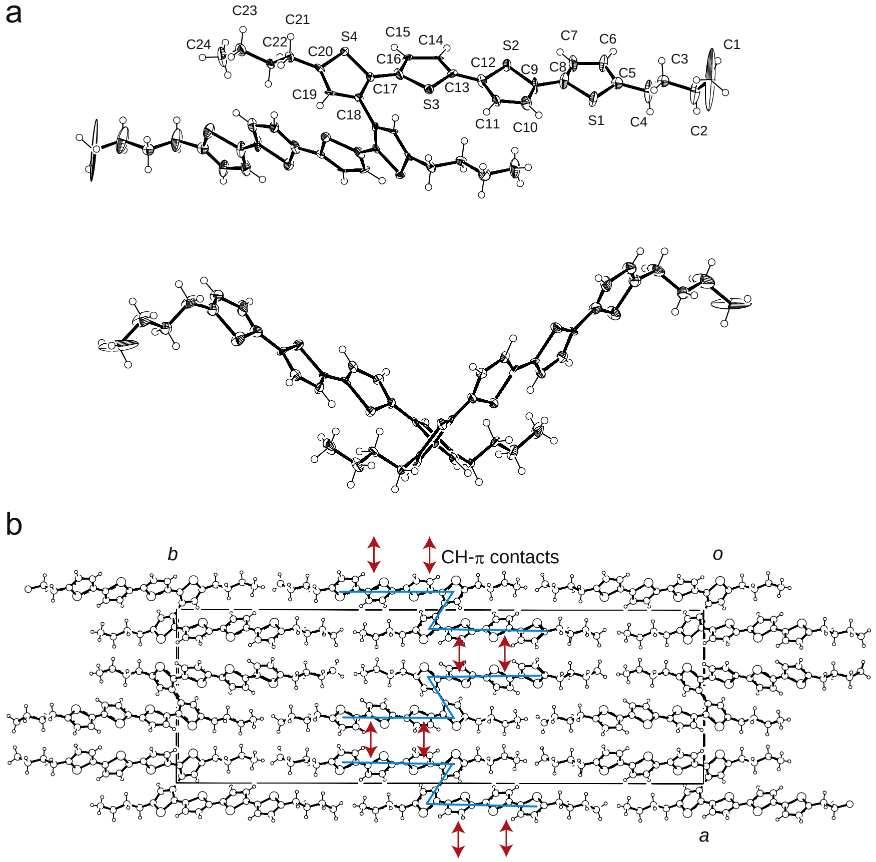


Fig. 2. Crystal structure of **2**. (a) Molecular structure and (b) molecular packing viewed along the *c* axis. Arrows indicate short CH-**π** intermolecular contacts.

new class of functional organic semiconductors is currently in progress.

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