Organic LETTERS
Letter
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Synthesis and Properties of Ethene-Bridged Terthiophenes

Koichi Mitsudo,[*,†] Hidehiko Sato,[†] Arata Yamasaki,[†] Natsuyo Kamimoto,[†] Jun Goto,[†] Hiroki Mandai,[†] and Seiji Suga[*,†,‡,§]

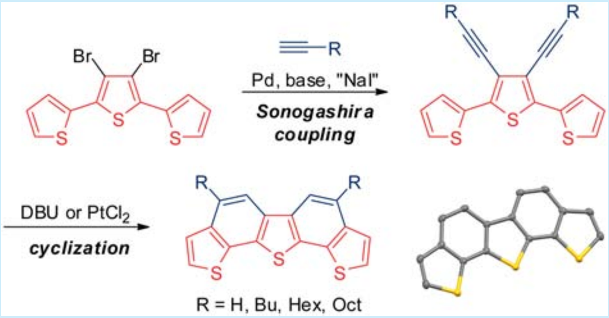
[†]Division of Applied Chemistry, Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-naka, Kita-ku, Okayama 700-8530, Japan

[‡]Research Center of New Functional Materials for Energy Production, Storage and Transport, Okayama University, 3-1-1 Tsushima-naka, Kita-ku, Okayama 700-8530, Japan

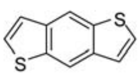
[§]JST, ACT-C, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

Supporting Information

ABSTRACT: A method for the facile synthesis of ethene-bridged terthiophenes (EBTTs) in two steps has been developed. The first step is a double Sonogashira coupling between 3′,4′-dibromo-2,2′:5′,2″-terthiophene and terminal alkynes to give dialkynylated terthiophenes, and the second step is a cyclization reaction to afford EBTTs. The fundamental physical properties of EBTTs were also studied.



Thienoacenes, which are acene derivatives that contain sulfur atoms, have received considerable attention as potential components for use in organic materials such as organic field effect transistors (OFETs), and the syntheses and properties of numerous thienoacenes have been reported.[1] One of the key skeletons of these thienoacenes is benzodithiophene (BDT). Several kinds of thienoacenes containing BDT skeletons, especially benzo[1,2-*b*:4,5-*b*′]dithiophene (**A**)[2] and benzo[1,2-*b*:6,5-*b*′]dithiophene (**B**),[3] have been reported. While there have been many reports on such thienoacenes, to realize an efficient organic semiconductor, the development of synthetic methodologies for a novel type of thienoacene is significant.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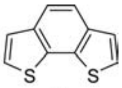
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Meanwhile, we recently reported the first synthesis of tetrabromoterthiophene and its conversion to nitrogen-bridged terthiophenes by tandem Buchwald–Hartwig coupling reactions.[4,5] During the course of this study, we also developed an efficient synthetic method for preparing multibrominated terthiophenes by regioselective Negishi coupling.[4] We next turned our attention to the use of these brominated terthiophenes for the synthesis of thienoacenes bearing a BDT unit. At the start of this study, we focused on ethene-bridged terthiophene (EBTT, **1**). To the best of our knowledge, there has been only one previous report on the synthesis of EBTT by flash vacuum pyrolysis[6] and there is no convenient approach to EBTT skeletons under mild conditions. Moreover, their electrochemical and optical properties have not been characterized. First, we carried out density functional theory (DFT) calculations for EBTT at the B3LYP/6-31G(d) level of theory and found that EBTT has its HOMO orbital on all atoms except the center S atom and LUMO orbitals on all atoms (Figure 1).

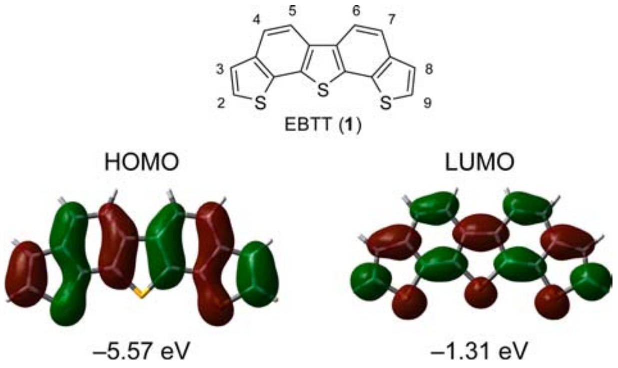


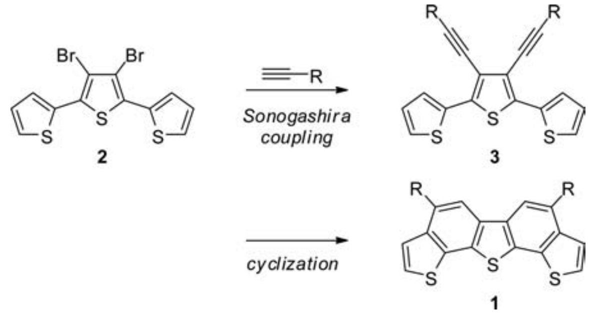
Figure 1. Kohn–Sham HOMO and LUMO energy levels of ethene-bridged terthiophene (EBTT) at the B3LYP/6-31G(d) level of theory.

Our synthetic strategy for EBTT is illustrated in Scheme 1. The first step is Sonogashira coupling between 3′,4′-dibromo-2,2′:5′,2″-terthiophene (**2**) and terminal alkynes to give a 3′,4′-dialkynyl-2,2′:5′,2″-terthiophene (**3**), and the next step is cyclization to construct an EBTT (**1**). The advantages of this strategy are (i) EBTT is obtained in two step reactions and (ii)

Received: August 21, 2015
Published: September 18, 2015

DOI: 10.1021/acs.orglett.5b02417
Org. Lett. 2015, 17, 4858–4861

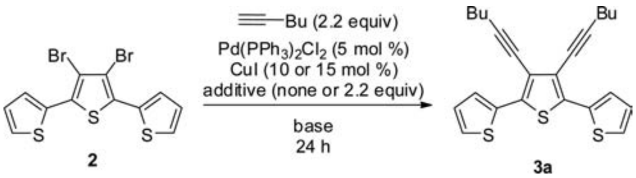
Scheme 1. Synthetic Strategy for EBTT



several alkyl groups can be introduced by the use of the corresponding alkynes. We report here a novel and facile method for synthesizing **1** and its derivatives, along with their fundamental properties.

First, we synthesized **3a**, a terthiophene bearing two hexyne moieties, by Sonogashira coupling between **2** and 1-hexyne (Table 1). Surprisingly, Sonogashira coupling did not proceed under typical conditions, and monoalkynylated products were obtained predominantly. For example, in the presence of $Pd(PPh_3)_2Cl_2$ (5 mol %) and CuI (10 mol %), the treatment of **2** and 1-hexyne in triethylamine (Et_3N) or diisopropylamine (DIPA) did not give the desired dialkynylated product **3a** (entries 1 and 2). When piperidine (pip) was used as a base, a trace amount of **3a** was obtained (2%, entry 3).[7]

Table 1. Sonogashira Coupling between 2 and 1-Hexyne under Various Conditions[a]



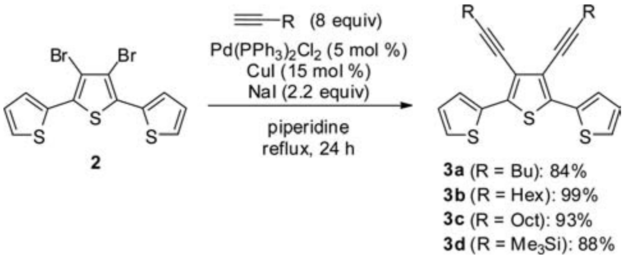
entry	CuI (mol %)	additive	base	temp (°C)	yield (%)[b]
1	10	none	Et_3N	90	N.D.[c]
2	10	none	DIPA	90	N.D.
3	10	none	pip	125	2
4	10	NaI	pip	125	41
5	15	NaI	pip	125	58 (59)[d]
6[e]	15	NaI	pip	125	76
7[f]	15	NaI	pip	125	84 (89)[g]

[a] Reaction conditions: **2** (0.2 mmol), 1-hexyne (2.2−8.0 equiv), $Pd(PPh_3)_2Cl_2$ (5 mol %), CuI (10 or 15 mol %), additive (none or 2.2 equiv), base (2 mL), 90−125 °C, 24 h. [b] Isolated yield. [c] Not detected. [d] Performed for 48 h. [e] Performed with 6.0 equiv of hexyne. [f] Performed with 8.0 equiv of hexyne. [g] Performed with 5.0 mmol scale of **2** in 50 mL of piperidine.

By examining numerous reaction conditions, we finally found that the addition of NaI was essential for the reaction. With NaI (2.2 equiv), the yield of **3a** increased to 41% (entry 4).[8] When we increased the amount of CuI to 15 mol %, the yield of **3a** increased to 58% (entry 5). Since some byproducts derived from 1-hexyne were observed under these conditions, we next optimized the amount of 1-hexyne. The yield increased when the amount of 1-hexyne increased. When 8.0 equiv of 1-hexyne were used, **3a** was obtained in 84% yield (entry 7). This reaction could also be carried out on a gram scale to give **3a** in high yield (89%).

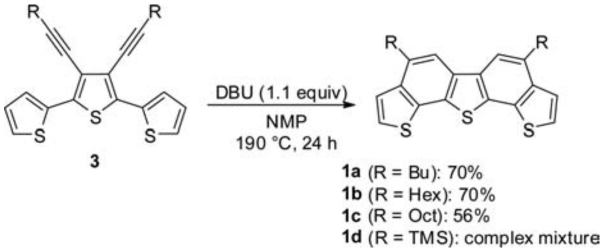
Under the optimized conditions, Sonogashira coupling was carried out between **2** and several alkynes, such as 1-octyne, 1-decyne, and trimethylsilylacetylene (Scheme 2). They also gave the corresponding dialkynylated terthiophenes **3b−d** in high yields.

Scheme 2. Sonogashira Coupling between 2 and Several Alkynes

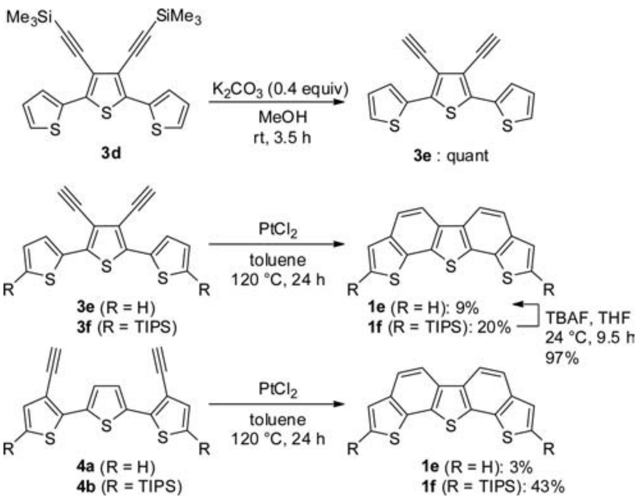


We next performed the cyclization of **3a−d** (Scheme 3). In the presence of DBU, **3a** was smoothly consumed and dibutyl-substituted EBTT **1a** was obtained in 70% yield.[9] Similarly, EBTT bearing two hexyl or octyl groups was respectively formed from **3b** and **3c** (**1b**: 70%, **1c**: 56%). Unfortunately, the attempt to cyclize **3d** gave a complex mixture under the reaction conditions, but **3d** could be used as a precursor for non-substituted EBTT (Scheme 4). The two trimethylsilyl groups of **3d** were readily removed with K_2CO_3/MeOH to give diethynyl terthiophene **3e** quantitatively, and subsequent $PtCl_2$-catalyzed cyclization gave nonsubstituted EBTT in 9% yield (**1e**).[10] The protection of the *α*-position of terminal thiophenes of **3e** by

Scheme 3. Cyclization of 3 Leading to 1



Scheme 4. Synthesis of EBTT from Several Precursors



TIPS (triisopropylsilyl) groups increased the yield of the cyclized product (from **3f** to **1f**, 20%). **1f** could be readily converted to **1e** in high yield by treatment with TBAF (tetra-*n*-butylammonium fluoride). Further study revealed that diethynyl terthiophene **4b**, a regioisomer of **3f**, was a better precursor than **3f**, and $PtCl_2$-catalyzed double cyclization of **4b** gave **1f** in 43% yield.[11]

The structures of **1a−c** and **1e** were confirmed by X-ray crystallography, and their skeletons are similar to that expected from DFT calculations. Among them, nonsubstituted EBTT **1e** exhibited a herringbone packing structure, which is known to be a suitable packing form for OFET (Figure 2).

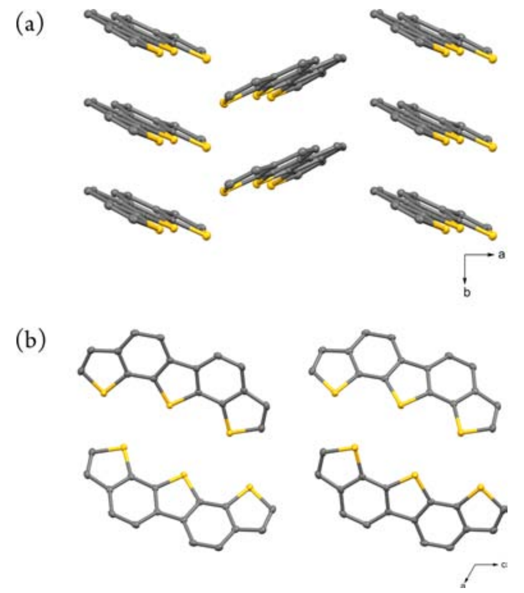


Figure 2. Crystal structures of **1e**: (a) *c*-axis projection and (b) *b*-axis projection (50% probability ellipsoids; hydrogen atoms omitted for clarity).

To clarify their physical properties, we next investigated the optical and electrochemical properties of EBTTs and compared them with those of picene derivatives, which have isoelectronic π-skeletons to EBTT, and nonfused terthiophene (2,2′:5′,2″-terthiophene). First, UV−vis absorption spectra of EBTTs were measured (Figure 3). **1a−c** exhibited λ_{max} at 264 nm and λ_{onset} at 357 nm. The spectrum of **1e** differed slightly from those of **1a−c**, and the wavelength of absorption of **1e** (λ_{max} at 260 nm, λ_{onset} at 350 nm) is shorter than those of **1a−c**. These wavelengths are shorter than those of picene derivatives[12] and that of terthiophene.[13] These results suggest that the substitution of the 4- and 7-position of EBTTs influences their optical properties and band gaps, and the band gaps of EBTTs are larger than those of picene derivatives and that of nonfused terthiophene. A similar tendency was observed in the TD-DFT calculations. Their band gaps calculated at B3LYP/6-31G(d) were 3.79 eV (**1a−c**), 3.87 eV (**1e**), 3.60 eV (picene), and 3.33 eV (terthiophene), respectively.

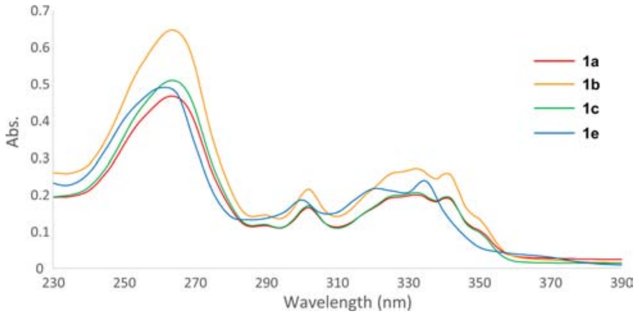


Figure 3. UV−vis absorption spectra of EBTTs measured in CH_2Cl_2 (1.0×10^{-5} M).

Cyclic voltammetry (CV) was carried out for **1a−c** and **1e**. In each cyclic voltammogram, an irreversible oxidation peak was observed at room temperature which became a quasi-reversible peak at −78 °C. To gain further insight into the characters of EBTTs, we synthesized 2,9-dimethylated **1b** and carried out CV measurements.[14] In contrast to nonprotected EBTTs, a reversible oxidation peak was observed even at room temperature. These results suggest that a cationic species generated from EBTTs under electro-oxidative conditions would be reacted or decomposed at the 2- or 9-position at room temperature. The comparison of CVs of EBTTs with the reported data of picene[12] and nonfused terthiophene[13] revealed that the E_{onset} of EBTTs and picene are similar, and nonfused terthiophene has the most negative oxidation potential among them, suggesting that the HOMO level of EBTT is similar to that of picene, and lower than that of nonfused terthiophene.

The combined electrochemical and optical data, and estimated HOMO−LUMO levels, for EBTTs are shown in Table 2. The E_{HOMO} of **1a−c** were quite similar, around −5.57 eV, suggesting that the length of their alkyl chains does not significantly influence their energy levels. In contrast, the HOMO−LUMO levels of **1e** (E_{HOMO}: − 5.62 eV, E_{LUMO}: − 2.08 eV) were slightly different from those of other EBTTs. The HOMO level of **1e** was lower than those of **1a−c**, and the band gaps (E_g^{opt}) of **1a−c** were slightly smaller than that of **1e**. These tendencies are also consistent with the results of DFT calculations. The low HOMO levels of **1** suggest that these compounds would be stable under air, and indeed, they were easy to handle under air. While all of the data indicate that **1e** would be the best candidate among them for use as an active material in OFET, a thermogravimetry-differential thermal analysis (TG-DTA) of **1e** suggested that it would decompose at around 170 °C. Therefore, we are currently trying to prepare a sheet of **1e** by a wet process in our laboratory.

Table 2. Electrochemical and Optical Data for EBTTs[a]

EBTT	λ_{max} (nm)	log ε	$\lambda_{onset}/E_g^{opt}$ (nm/eV)	E_{onset} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)
1a	264	4.7	357/3.47	0.76	−5.56	−2.09
1b	264	4.8	357/3.47	0.77	−5.57	−2.10
1c	264	4.7	357/3.47	0.78	−5.58	−2.11
1e	260	4.7	350/3.54	0.82	−5.62	−2.08

[a] E_{onset} values were determined by the onset of CV in CH_2Cl_2 at −78 °C. All the potentials were calibrated with the Fc/Fc^+ ($E^{1/2}$ = 0.02 V measured under identical conditions). E_{HOMO} values were determined with reference to ferrocene (4.8 eV vs vacuum).[15] Optical band gap: $E_g^{opt} = 1240/\lambda_{onset}$. $E_{LUMO} = E_{HOMO} + E_g^{opt}$.

In conclusion, we have developed a method for the facile synthesis of EBTTs, which belong to a new class of fused thiophenes. X-ray single-crystal analyses revealed that they have planar skeletons, and nonsubstituted EBTT exhibited a herringbone packing structure. Their fundamental characteristics were clarified by UV and CV analyses, and the results suggested that their HOMO−LUMO levels differed upon substitution with alkyl groups. Further studies on EBTTs and more π-extended derivatives are under investigation in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02417.

Experimental details, spectral data for all new compounds, results of UV and CV analyses, TG-DTA, theoretical calculations (PDF)
Crystallographic information for **1a** (CIF)
Crystallographic information for **1b** (CIF)
Crystallographic information for **1c**-1 (CIF)
Crystallographic information for **1c**-2 (CIF)
Crystallographic information for **1e** (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: mitsudo@cc.okayama-u.ac.jp.
*E-mail: suga@cc.okayama-u.ac.jp.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Prof. Yasushi Nishihara and Dr. Hiroki Mori (Okayama University) for their fruitful discussions. We also thank Prof. Tetsuya Uchida and Mr. Fumiaki Iwaguro (Okayama University) for TG-DTA measurement. This work was supported in part by a Grant-in-Aid for Scientific Research on Innovative Areas "Organic Synthesis based on Reaction Integration" (No. 2105) from MEXT (No. 24106730), Japan, a Grant-in-Aid for Scientific Research (C) (No. 25410042) from JSPS, Japan, and JST, ACT-C, Japan.

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