Pergamon

Tetrahedron Letters 43 (2002) 3373–3376

TETRAHEDRON
LETTERS

Synthesis and properties of a new ethyne-linked donor/acceptor pentamer

Chitoshi Kitamura,[a,]* Kakuya Saito,[a] Masaki Nakagawa,[a] Mikio Ouchi,[a] Akio Yoneda[a] and Yoshiro Yamashita[b]

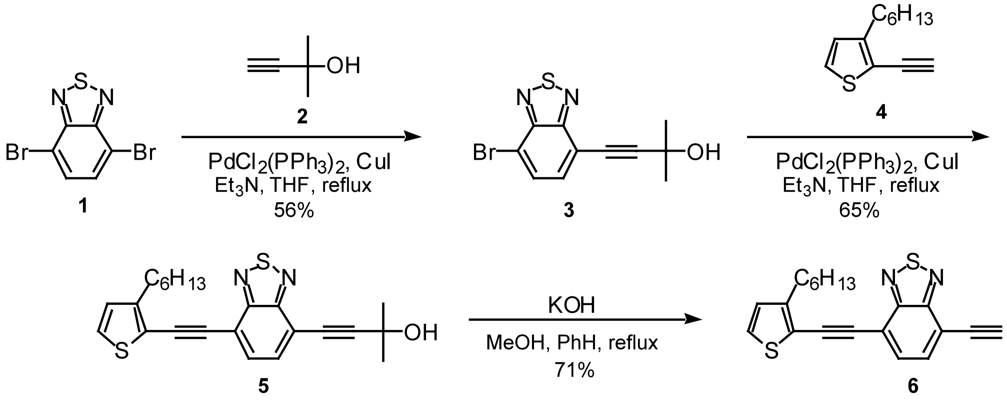
[a]*Department of Applied Chemistry, Himeji Institute of Technology, Shosha 2167, Himeji, Hyogo 671-2201, Japan*
[b]*Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8502, Japan*

Received 12 February 2002; revised 8 March 2002; accepted 11 March 2002

Abstract—A new alternating π-donor/π-acceptor pentamer with ethyne linkage was synthesized by a bi-directional method using Sonogashira reactions. The pentamer showed small HOMO–LUMO gap compared with other π-conjugated oligomers. © 2002 Elsevier Science Ltd. All rights reserved.

Synthesis of well-defined linear conjugated oligomers such as oligo(1,4-phenylene ethynylene)s has attracted considerable interest due to their potential use in molecule-based electronics, e.g. molecular wires.[1] Such compounds are easily accessed via Sonogashira cross-coupling[2] and protection/deprotection technique of functional groups such as a terminal ethyne. However, oligo(1,4-phenylene ethynylene)s are insufficient as molecular wires owing to their relatively large HOMO–LUMO gaps, which may lead to unsatisfactory electric conduction. To tune electronic characteristics of the π-system, modification of the conjugated backbone is most effective. The literature on the study about oligo(arylene ethynylne)s with a combination of different heterocyclic units has been rarely reported. In order to gain smaller HOMO–LUMO gap molecules,[3] we decided to substitute π-donor and π-acceptor heterocycles for 1,4-phenylene moieties on the oligomers stated above. Recently we have described reduction of HOMO–LUMO gaps of conjugated oligomers and polymers due to intramolecular charge transfer.[4] In this paper we report synthesis of a new alternating π-donor (thiophene; D)/π-acceptor (2,1,3-benzothiadiazole; A) D-A-D-A-D-type pentamer with ethyne linkage.

In our synthetic strategy, bi-directional synthesis from a central starting ring, thus [2+1+2] method, was adopted as shown in Schemes 1 and 2. Sonogashira coupling of

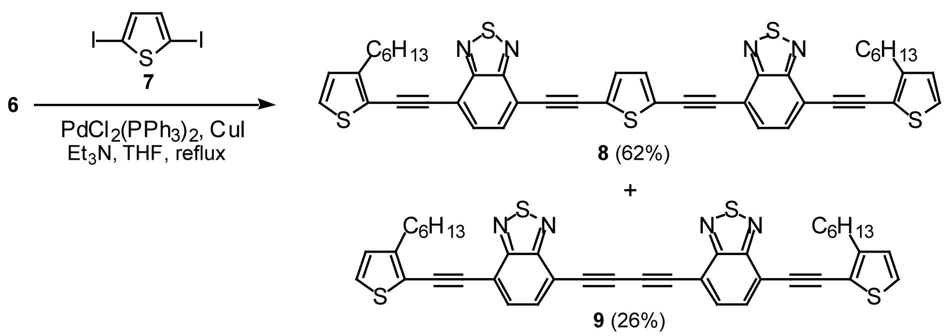


Scheme 1.

Keywords: donor/acceptor; Sonogashira coupling; oligomer; effective conjugation length.

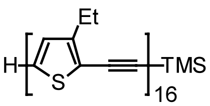
* Corresponding author. Tel.: +81-792-67-4888; fax: +81-792-67-4888; e-mail: kitamura@chem.eng.himeji-tech.ac.jp

PII: S0040-4039(02)00478-1

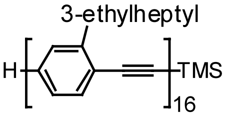


Scheme 2.

4,7-dibromo-2,1,3-benzothiadiazole **1**[5] (3 equiv.) with a mono-protecting ethyne **2** in refluxing Et_3N and THF[6] for 2 h afforded a mono-coupling product **3** and a bis-coupling product 4,7-bis(3-hydroxy-3-methyl-1-butynyl)-2,1,3-benzothiadiazole in 56 and 6%, yields, respectively, and unreacted **1** was able to be recovered readily. Although the most popular protecting groups for ethyne are non-polar silyl groups such as trimethylsilyl (TMS), polar 1-hydroxy-1-methylethyl (HME) protecting group appeared to be suitable for rapid isolation of mono- and bis-coupling molecules using column chromatography.[7] Thus, when trimethylsilylethyne was applied to the above reaction, the R_f values of the corresponding mono- and bis-coupling were too close to separate them. Sonogashira coupling of **3** with 3-hexyl-2-ethynylthiophene **4**,[8] whose alkyl chain was introduced to solubilize the desired oligomer, using $PdCl_2(PPh_3)_2$/CuI for 2 h gave HME-protected ethynyl D-A dimer **5** in 65% yield. Deproptection of **5** with KOH in refluxing methanol and benzene for 3 h afforded ethynyl D-A dimer **6** in 71% yield. We first attempted the synthesis of a D-A-D-A-D pentamer by Sonogashira coupling of the dimer **6** with 2,5-dibromothiophene as a central donor unit. However, the reaction under an inert atmosphere led to exclusive generation of homo-coupling product **9** in moderate yields. Finally it was found that by changing the substrate from 2,5-dibromothiophene to diiodothiophene **7**, reaction of **6** (2.4 equiv.) with **7** in the presence of $PdCl_2(PPh_3)_2$, CuI and Et_3N in refluxing THF for 4 h yielded a cross-coupling pentamer **8** and a homo-coupling molecule **9** in 62 and 26% yields, respectively.[9]



16Th



16Ph

As expected, **8** showed good solubility against organic solvents. For example, the solubility of **8** in $CHCl_3$ was 50 mg mL^{-1}, on the other hand that of **9** was 25 mg mL^{-1}. Table 1 lists optical and cyclic voltammetric data for **8** and **9**. Literature data for 16-mer oligomers of thiophene and benzene (**16Th**[10] and **16Ph**[11]) are included for comparison. The physical properties of **8** and **9** exhibited unique characteristics. Thus, the absorption maximum of **8** in $CHCl_3$ was 473 nm, indicating that our molecule is a small HOMO–LUMO gap system compared with 16-mer oligomers **16Th** and **16Ph**. Interestingly, **9** showed almost the same absorption maximum at 471 nm. This fact means that **8** and **9** have a similar conjugation length in that solution although, based on the structure, we expected **8** to have a longer conjugation length compared with that of **9**. The relatively free rotation about alkyne–aryl and alkyne–alkyne single bonds would lead to the coexistence and rapid equilibration of coplanar and non-coplanar conformations in solutions,[12] therefore we thought that there was no difference in conjugation length between **8** and **9**. Redox potentials were also measured from the cyclic voltammetry. The cyclic voltammograms of **8** and **9**, as shown in Figs. 1 and 2, indicated both an irreversible oxidation wave[13] and a quasi-reversible reduction wave, reflecting the combination of donor-thiophene and acceptor-2,1,4-benzothiadiazole. The oxidation and reduction peak potentials of **8** were observed at 1.66 and −1.09 V versus SCE, respectively. Moreover, a shoulder peak in the oxidation region was observed at 1.48 V. On the other hand, **9** exhibited two oxidation steps at 1.59 and 1.79 V and two reduction steps at −0.93 and −1.10 V. It is thought that the clear reduction behavior of **9** would result from the stabilization of reduction species by connecting two π-acceptor units with diyne.

In summary, we established a route for the ethyne-linked alternating π-donor and π-acceptor system, a new class of π-conjugated oligomer, by a bi-directional Sonogashira-coupling method. The physical properties

Table 1. Physical properties of oligomers

Compound	λ_{max}/nm (log ε)	E_{pa} (V)[a]	E_{pc} (V)[a]
8	473 (4.97)[d]	1.48 sh[g], 1.66	−1.09
9	471 (4.77)[d]	1.59, 1.79	−0.93, −1.10
16Th[b]	433[e]	Not reported	Not reported
16Ph[c]	376[f]	Not reported	Not reported

[a] 0.10 M Bu_4NClO_4 in PhCN, Pt electrode, scan rate 100 mV s^{-1}, V versus SCE.
[b] Ref. 10.
[c] Ref. 11.
[d] In $CHCl_3$.
[e] In THF.
[f] In CH_2Cl_2.
[g] sh = shoulder.

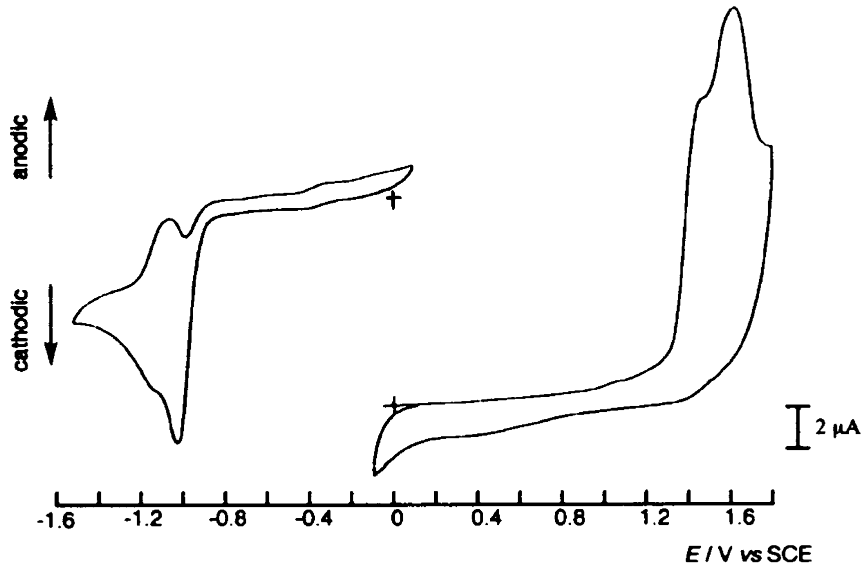


Figure 1. Cyclic voltammogram of **8** in 0.10 M Bu_4NClO_4/PhCN. Pt electrode, scan rate 100 mV s^{-1}.

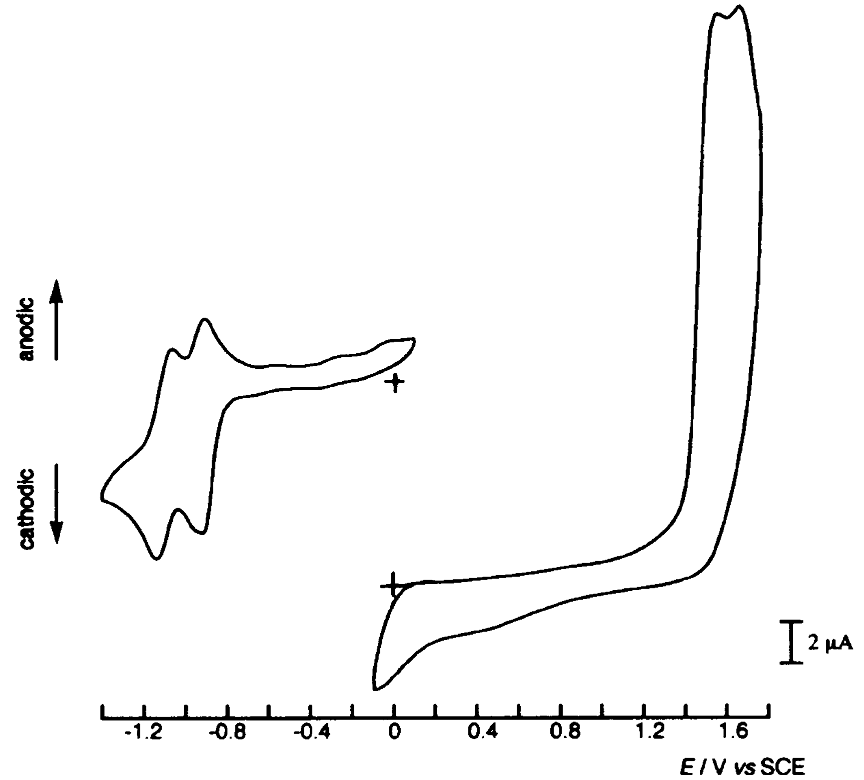


Figure 2. Cyclic voltammogram of **9** in 0.10 M Bu_4NClO_4/PhCN. Pt electrode, scan rate 100 mV s^{-1}.

reflected the small HOMO–LUMO gap system. However, the effective conjugation length of a D-A-D-A-D type of **8** was similar to that of a D-A-A-D type of **9**, indicating the importance of free rotation.

Acknowledgements

The authors thank the Research Center for Molecular Materials, the Institute for Molecular Science, for carrying out the measurement of MS spectra. This work was supported by the fund of Himeji Institute of Technology.

References

1. (a) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537; (b) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1350; (c) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791.

2. Sonogashira, K. In *Metal-catalyzed Cross-coupling Reactions*; Diederich, F.; Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998; p. 203.
3. For synthesis of small HOMO–LUMO gap molecules, see: (a) Roncali, J. *Chem. Rev.* **1997**, *97*, 173 and references cited therein; (b) van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Meijer, E. W. *Chem. Eur. J.* **1998**, *4*, 1235; (c) Raimundo, J.-M.; Blanchard, P.; Brisset, H.; Akoudad, S.; Roncali, J. *Chem. Commun.* **2000**, 939; (d) Mitschke, U.; Debaerdemaeker, T.; Bäuerle, P. *Eur. J. Org. Chem.* **2000**, 425; (e) Hay, C.; Fischmeister, C.; Hissler, M.; Toupet, L.; Réau, R. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 1812.
4. (a) Karikomi, M.; Kitamura, C.; Tanaka, S.; Yamashita, Y. *J. Am. Chem. Soc.* **1995**, *117*, 6791; (b) Kitamura, C.; Tanaka, S.; Yamashita, Y. *Chem. Mater.* **1996**, *8*, 570.
5. Pilgram, K.; Zupan, M.; Skiles, R. *J. Heterocycl. Chem.* **1970**, *7*, 629.
6. Thorand, S.; Krause, N. *J. Org. Chem.* **1998**, *63*, 8551.
7. For a practical standpoint, the importance of polar protecting groups for the terminal ethyne is pointed out, see: Ley, K. V.; Li, Y.; Johnson, J. V.; Powell, D. H.; Schanze, K. S. *Chem. Commun.* **1999**, 1749.
8. Higuchi, H.; Nishi, H.; Ojima, H.; Wada, T.; Sasabe, H. *Nonlinear Opt.* **1999**, *22*, 337.
9. New compounds gave satisfactory spectroscopic data. Selected data: Compound **8**: ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.87 (t, $J=7.6$ Hz, 6H), 1.25–1.45 (m, 12H), 1.72 (quintet, $J=7.6$ Hz, 4H), 2.90 (t, $J=7.6$ Hz, 4H), 6.95 (d, $J=5.1$ Hz, 2H), 7.29 (d, $J=5.1$ Hz, 2H), 7.38 (s, 2H), 7.74 (d, $J=7.4$ Hz, 2H), 7.80 (d, $J=7.4$ Hz, 2H); ^{13}C NMR (CDCl$_3$, 126 MHz) δ 14.10, 22.60, 28.98, 29.71, 30.30, 31.59, 89.87, 90.70, 91.48, 91.53, 115.79, 117.40, 117.75, 124.91, 127.56, 128.47, 131.27, 132.55, 133.18, 149.89, 153.93, 154.09; MS(EI) m/z 780 (M$^+$). Compound **9**: ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.87 (t, $J=7.6$ Hz, 6H), 1.31–1.43 (m, 12H), 1.72 (quintet, $J=7.6$ Hz, 4H), 2.90 (t, $J=7.6$ Hz, 4H), 6.96 (d, $J=5.1$ Hz, 2H), 7.31 (d, $J=5.1$ Hz, 2H), 7.72 (d, $J=7.4$ Hz, 2H), 7.85 (d, $J=7.4$ Hz, 2H); ^{13}C NMR (CDCl$_3$, 126 MHz) δ 14.14, 22.65, 29.03, 29.78, 30.35, 31.64, 80.47, 81.27, 91.53, 92.41, 114.85, 117.35, 118.91, 127.85, 128.56, 131.14, 134.36, 150.23, 154.09, 154.61; MS(EI) m/z 698 (M$^+$).
10. Sammuel, I. D. W.; Ledoux, I.; Delporte, C.; Pearson, D. L.; Tour, J. M. *Chem. Mater.* **1996**, *8*, 819.
11. Schumm, J. S.; Pearson, D. L.; Tour, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1360.
12. Levitus, M.; Schmieder, K.; Ricks, H.; Shimizu, K. D.; Bunz, U. H. F.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 4259.
13. Electrochemical oxidation of the oligomers did not bring about electropolymerization.