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Synthesis and Properties of a Series of Well-Defined and Polydisperse Benzo[1,2-*b*:4,3-*b*′]dithiophene Oligomers

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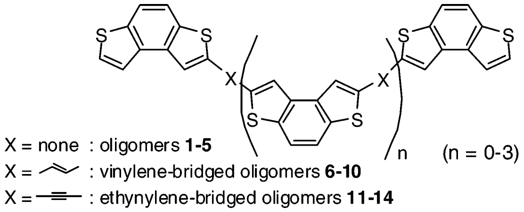

Monodisperse and polydisperse oligomers of benzo[1,2-*b*:4,3-*b*′]dithiophene (BDT) (**1**−**14**), including three types of oligomers with different spacers combining BDT units (direct linkage, vinylene spacers, and ethynylene spacers), were synthesized, and their thermal, optical, and electrochemical properties were investigated. The oligomers were synthesized using Suzuki, Stille, Wittig, and Sonogashira coupling reactions. All of the monodisperse oligomers showed high melting points and 5% weight loss temperatures (T_d > 400 °C). The fluorescence maxima of all oligomers were red-shifted, and the emission colors varied from blue to yellow as the chain lengths—and thus the conjugation lengths—increased. The vinylene-bridged oligomers emitted at longer wavelengths than the direct-linked and ethynylene-bridged oligomers. UV−vis absorption spectra in toluene solution indicated an effective conjugation length of about six BDT units for polydisperse oligomer **5**. Cyclic voltammetry measurement indicated that tetramer **3** had high electrochemical stability. Although tetramer **3** and vinylene-bridged tetramer **8** exhibited reversible oxidation waves, ethynylene-bridged tetramer **13** showed an irreversible oxidation process. Each type of monodisperse oligomer exhibited higher HOMO levels with increasing chain length.

Introduction

Monodisperse well-defined π-conjugated oligomers have recently become the subject of intense research in materials science.[1] They can be used as undefected materials for electronic devices, such as organic light-emitting diodes (OLEDs),[2] solar cells,[3] and field-effect transistors (OFETs),[4] and as models[1c] for investigating the fundamental properties of analogous polydisperse polymers. The development of a synthetic methodology has made it possible to design a variety of soluble monodisperse oligomers which allow tuning of emission color and charge injection ability via control of their conjugation

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(1) For an extensive review, see: (a) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537−554. (b) Pu, L. *Chem. Rev.* **1998**, *98*, 2405−2494. (c) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350−1377. (d) Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747−1786. (e) Roncali, J. *Acc. Chem. Res.* **2000**, *33*, 147−156. (f) Cunningham, G. B.; Li, Y.; Liu, S.; Schanze, K. S. *J. Phys. Chem. B* **2003**, *107*, 12569−12572. (g) Gaylord, B. S.; Wang, S.; Heeger, A. J.; Bazan, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 6417−6418. (h) Ng, M.-K.; Lee, D.-C., Yu, L. *J. Am. Chem. Soc.* **2002**, *124*, 11862−11863. (i) Shimizu, H.; Fujimoto, K.; Furusyo, M.; Maeda, H.; Nanai, Y.; Mizuno, K.; Inouye, M. *J. Org. Chem.* **2007**, *72*, 1530−1533. (j) Panda, P.; Veldman, D.; Sweelssen, J.; Bastiaansen, J. J. A. M.; Langeveld-Voss, B. M. W.; Meskers, S. C. J. *J. Phys. Chem. B* **2007**, *111*, 5076−5081. (k) Yin, J.; Elsenbaumer, R. L. *J. Org. Chem.* **2005**, *70*, 9436−9446. (l) Guldi, D. M.; Luo, C.; Swartz, A. *J. Org. Chem.* **2002**, *67*, 1141−1152.

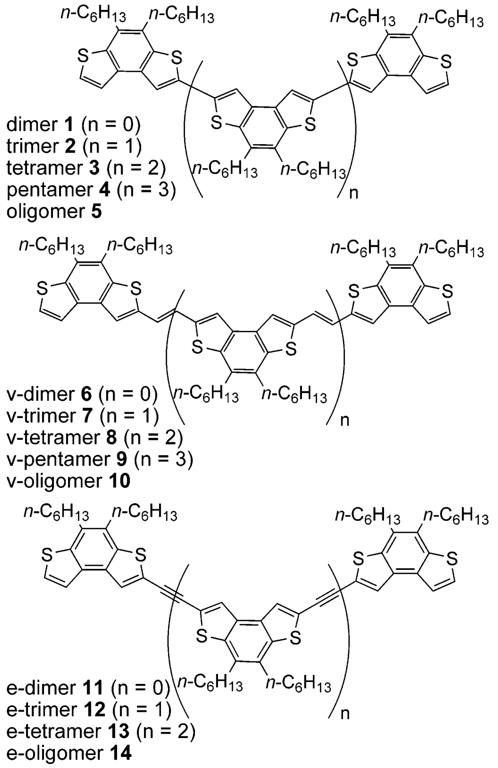
(2) (a) Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Müllen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc.* **2001**, *123*, 946−953. (b) Wu, C.-W.; Lin, H.-C. *Macromolecules* **2006**, *39*, 7232−7240. (c) Schulz, G. L.; Chen, X.; Chen, S.-A.; Holdcroft, S. *Macromolecules* **2006**, *39*, 9157−9165. (d) Kulkarni, A. P.; Kong, X.; Jenekhe, S. A. *Macromolecules* **2006**, *39*, 8699−8711. (e) Zhu, Y.; Gibbons, K. M.; Kulkarni, A. P.; Jenekhe, S. A. *Macromolecules* **2007**, *40*, 804−813.

(3) (a) Jung, I.; Lee, J. K.; Song, K. H.; Song, K.; Kang, S. O.; Ko, J. *J. Org. Chem.* **2007**, *72*, 3652−3658. (b) Eckert, J.-F.; Nicoud, J.-F.; Nierengarten, J.-F.; Liu, S.-G.; Echegoyen, L.; Barigelletti, F.; Armaroli, N.; Ouali, L.; Krasnikov, V.; Hadziioannou, G. *J. Am. Chem. Soc.* **2000**, *122*, 7467−7479. (c) Colladet, K.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Gelan, J.; Vanderzande, D.; Nguyen, L. H.; Neugebauer, H.; Sariciftci, S.; Aguirre, A.; Janssen, G.; Goovaerts, E. *Macromolecules* **2007**, *40*, 65−72.

(4) Murphy, A. R.; Fréchet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066−1096.

10.1021/jo071062b CCC: $37.00

SCHEME 1. Structures of Oligomers



length, as well as the introduction of electron-donating or electron-withdrawing groups to the parent π-conjugated systems.[5]

Since the discovery of multilayered OLEDs by Tang et al.,[6] electroluminescent devices have shown potential as materials for low-cost, full-color, flat panel displays due to their merits of high brightness and easy fabrication and the availability of a wide range of emission colors.[7] Over the past decade, significant progress has been made in both device fabrication techniques and material development.[5c,8] However, further improvement in both the efficiency and durability of OLEDs is still necessary.

We previously reported the fabrication of OLEDs using 1,2-dithienylethylene derivatives, including the *ortho*-fused heterocyclic compound benzo[1,2-*b*:4,3-*b*′]dithiophene (BDT).[9] This device was shown to give strong emissions (25 000 cd/m^2), with CIE (Commission International de l'Eclairage) chromaticity coordinates at 0.19 and 0.27, in the greenish-blue region. However, because pure color emission is necessary for application to full-color displays, we found that it was necessary to reconsider the structures of the emitting compounds and the construction of the devices. In the course of our reinvestigation of the structures of emitting materials, we have prepared a series of well-defined and polydisperse BDT oligomers with characteristic properties.

We report herein the synthesis and properties of monodisperse and polydisperse oligomers of BDT. The purpose of this study was to achieve tuning of emission color via control of the extended conjugation length by varying the number of BDT units used. We also determined the effective conjugation length of the resulting polydisperse oligomers. One important step in this process was the introduction of hexyl groups into the benzene ring of BDT to increase its solubility in organic solvents; when unsubstituted BDT was used, only dimer and vinylene-bridged dimer compounds were obtained, and higher analogues could not be prepared. In addition, we examined the thermal, optical, and electrochemical properties obtained by varying the spacer between the BDT units to obtain oligomers with direct linkage (oligomers **1**−**5**) or with linkage of the units by vinylene (vinylene-bridged oligomers, v-oligomers, **6**−**10**) or ethynylene spacers (ethynylene-bridged oligomers, e-oligomers, **11**−**14**). The BDT oligomers synthesized in this work are shown in Scheme 1.

Results and Discussion

Synthesis of BDT Oligomers. Four types of well-defined monodisperse benzodithiophene oligomers, **1**−**4** (n = 0, 1, 2, 3), and polydisperse oligomer **5** were synthesized according to Schemes 2−4. As shown in Scheme 2, the precursors **16** and **17** were prepared by mono- and dibromination of **15** with NBS, respectively.[10] Lithiation of **15** using n-butyllithium and subsequent treatment with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane or tributylstannyl chloride gave the precursors **18**−**20**. As shown in Scheme 3, dimer **1** and trimer **2** were obtained in 77% and 84% yield via a Suzuki coupling reaction between borolane **18** and monobromo- (**16**) or dibromobenzodithiophene (**17**).[11] To synthesize the tetramer **3**, we initially attempted to carry out bromination of dimer **1** by NBS to obtain the dibromo dimer **21**; however, only starting material was recovered because of the poor solubility of **1** in organic solvents such as THF, CH$_2$Cl$_2$, and DMF. Eventually, **21** was obtained in 37% yield by monolithiation of **17** and subsequent oxidative homocoupling using Fe(acac)$_3$.[12] A Suzuki coupling reaction was initially attempted to obtain tetramer **3** under conditions similar to the syntheses of **1** and **2**, but the reaction did not progress. However, the desired tetramer **3** was obtained in 63% yield by palladium(0)-catalyzed Stille coupling between monostannyl derivatives **19** and **21**.[13] This difference in reactivity was thought to be due to problems with hydrolytic deboronation of thiophene boronic derivatives[14] in the Suzuki reaction and acceleration of the transmetalation step[15] in the Stille reaction due to the electron-donating property of the thiophene rings. The monobromo dimer **22** was prepared in 40% yield via Suzuki coupling between **17** (1 equiv) and **18** (1 equiv). Although this

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[5] (a) Geng, Y.; Chen, A. C. A.; Ou, J. J.; Chen, S. H. *Chem. Mater.* **2003**, *15*, 4352−4360. (b) Detert, H.; Sugiono, E. *Synth. Met.* **2000**, *115*, 89−92. (c) Mitschke, U.; Bäuerle, P. *J. Mater. Chem.* **2000**, *10*, 1471−1507.

[6] Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913−915.

[7] Shen, Z.; Burrows, P. E.; Bulović, V.; Forrest, S. R.; Thompson, M. E. *Science* **1997**, *276*, 2009−2011.

[8] (a) *Organic Electroluminescent Materials and Devices*; Miyata, S., Nalwa, H. S., Eds.; Cordon and Breach: New York, 1997. (b) Chen, C. H.; Shi, J.; Tang, C. W. *Coord. Chem. Rev.* **1998**, *171*, 161−174.

[9] Tanaka, K.; Osuga, H.; Tsujiuchi, N.; Hisamoto, M.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 551−557.

[10] Sumi, N.; Nakanishi, H.; Ueno, S.; Takimiya, K.; Aso, Y.; Otsubo, T. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 979−988.

[11] Zhang, F.-J.; Cortez, C.; Harvey, R. G. *J. Org. Chem.* **2000**, *65*, 3952−3960.

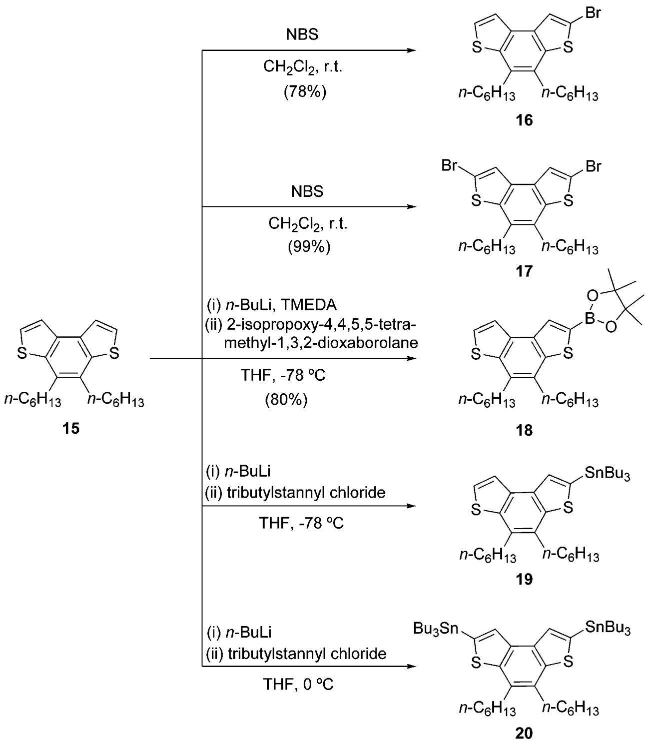
[12] (a) Baran, P. S.; Hafensteiner, B. D.; Ambhaikar, N. B.; Guerrero, C. A.; Gallagher, J. D. *J. Am. Chem. Soc.* **2006**, *128*, 8678−8693. (b) Zhang, Z.; Matzger, A. J. *J. Org. Chem.* **2003**, *68*, 9813−9815. (c) Nagano, T.; Hayashi, T. *Org. Lett.* **2004**, *6*, 1297−1299.

[13] Heller, M.; Schubert, U. S. *J. Org. Chem.* **2002**, *67*, 8269−8272.

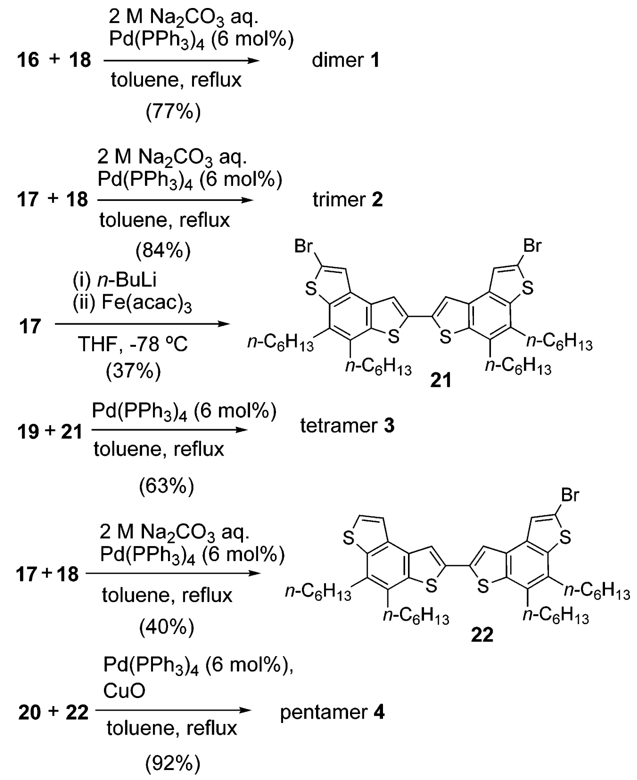
[14] (a) Jayakannan, M.; Joost, L.; van Dongen, J. L. J.; Janssen, R. A. J. *Macromolecules* **2001**, *34*, 5386−5393. (b) McCulloch, I.; Bailey, C.; Giles, M.; Heeney, M.; Love, I.; Shkunov, M.; Sparrowe, D.; Tierney, S. *Chem. Mater.* **2005**, *17*, 1381−1385.

[15] Bao, Z.; Chan, W. K.; Yu, L. *J. Am. Chem. Soc.* **1995**, *117*, 12426−12435.

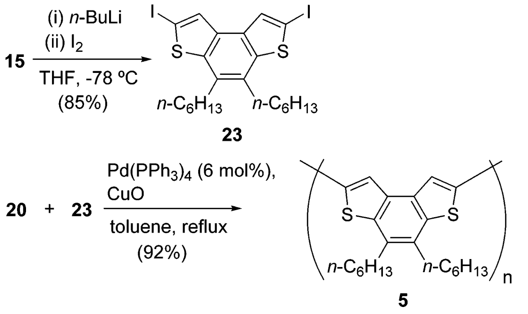
SCHEME 2. Synthesis of Precursors for Coupling Reactions



SCHEME 3. Synthesis of Monodisperse Oligomers 1−4



SCHEME 4. Synthesis of Polydisperse Oligomer 5



Suzuki coupling reaction also affords the trimer **3** as a byproduct, the yield is somewhat better than that obtained by lithiation of dimer **1** and subsequent halogenation. Pentamer **4** was obtained in 92% yield by palladium-catalyzed Stille coupling between **20** and **22**, using copper(II) oxide, which has been reported to enhance the reactivity of Stille coupling reactions, as an additive.[16] As shown in Scheme 4, diiodide **23** was synthesized by dilithiation of BDT **15**, with addition of an excess of *n*-BuLi followed by reaction with I$_2$. A Stille coupling reaction between the distannyl derivative **20** and diiodide **23** using CuO gave polydisperse oligomer **5** ($M_\mathrm{n} = 2.1 \times 10^3$ g/mol; PDI = 1.4, determined by GPC). The solubility of **5** in common organic solvents such as chloroform was improved compared to those of monodisperse oligomers **1**−**4**. The overall yields of oligomers from starting material **15** were 48% (**1**), 67% (**2**), 23% (**3**), and 29% (**4**).

Synthesis of Vinylene-Bridged Oligomers. Four well-defined vinylene-bridged monodisperse oligomers, **6**−**9** (n = 0, 1, 2, 3), were prepared according to Schemes 5−7. As shown in Scheme 5, lithiation of **15**, subsequent reaction with DMF, and reduction of the resulting monoaldehyde **24** afforded monoalcohol **25** (80% overall yield in two steps). Monoalcohol **25** was then converted to phosphonium salt **26** by reaction with triphenylphosphonium bromide in refluxing CH$_3$CN.[17] A Wittig reaction between **24** and **26** in the presence of *t*-BuOK gave vinylene-bridged dimer **6** in 90% yield.[18] Although vinylene-bridged trimer **7** was obtained from **26** and dialdehyde **27** only in low yield under similar conditions, a Wittig reaction with the phosphonium ylide obtained by treatment of phosphonium salt **26** with *n*-BuLi in THF gave **7** in 87% yield.

For synthesis of higher analogues such as vinylene-bridged tetramer **8** and pentamer **9**, the solubility of the intermediates was very important. Several derivatives of vinylene-bridged dimer **6** were difficult to obtain due to the poor solubility of the starting materials in organic solvents such as THF, CH$_2$Cl$_2$, and DMF. Therefore, we introduced a triisopropylsilyl group to increase their solubility. As shown in Scheme 6, after protection of alcohol **25** with a triisopropylsilyl group,[19] formylation of silylether **28** afforded aldehyde **29** (94% overall yield in two steps). A Wittig reaction between **29** and phosphonium salt **26** in the presence of *t*-BuOK gave silyl-protected vinylene-bridged dimer **30** in 74% yield. Desilylation of **30** with tetra-*n*-butylammonium fluoride (TBAF) gave alcohol **31** in 81% yield. Aldehyde **32** was prepared by oxidation of **31** with PDC,[20] and phosphonium salt **33** was obtained by refluxing a solution of alcohol **31** with triphenylphosphonium bromide in a mixture of CH$_3$CN and toluene, due to the poor solubility of **31** in CH$_3$CN. Monosubstituted vinylene-bridged dimer intermediates **32**

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(16) Clapham, B.; Sutherland, A. J. *J. Org. Chem.* **2001**, *66*, 9033−9037.

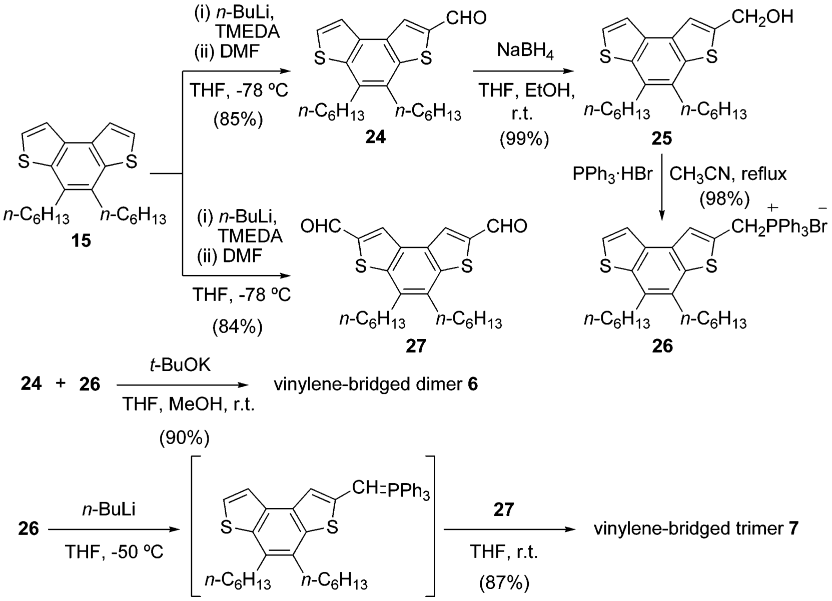
(17) Nakayama, J.; Fujimori, T. *Heterocycles* **1991**, *32*, 991−1002.

(18) (a) Wynberg, H.; Groen, M. B.; Schadenberg, H. *J. Org. Chem.* **1971**, *36*, 2797−2809. (b) Maryanoff, B. E.; Reitz, A. B. *Chem, Rev.* **1989**, *89*, 863−927.

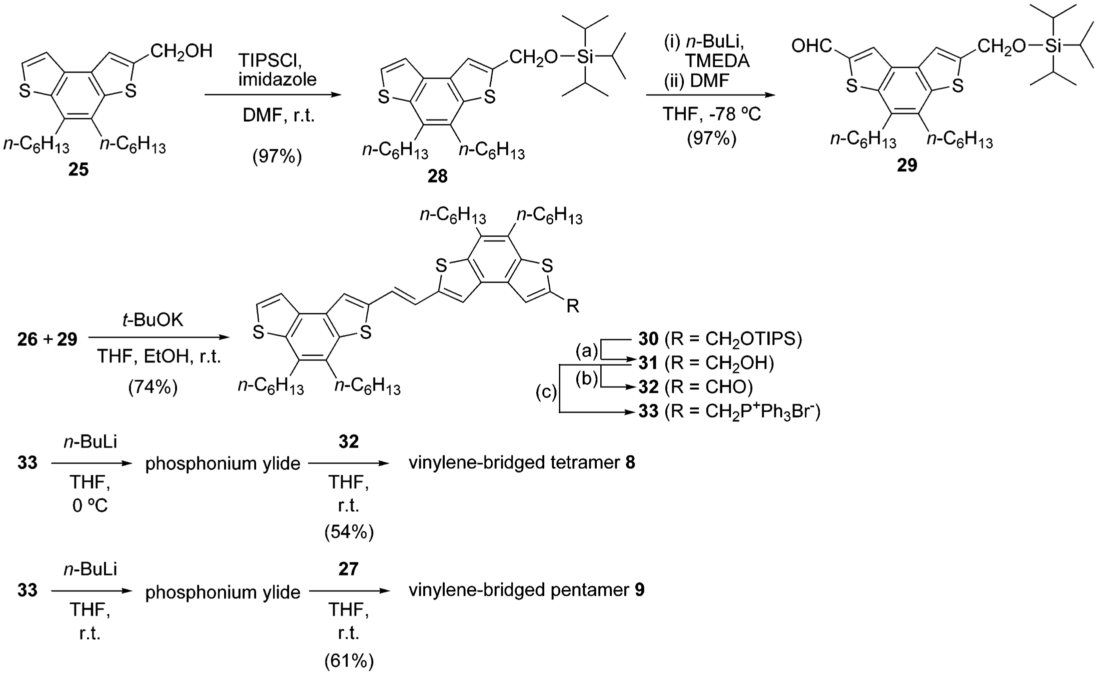
(19) Tanaka, K.; Osuga, H.; Tsujiuchi, N.; Hisamoto, M.; Sakaki, Y. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 551−557.

(20) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, *20*, 399−402.

SCHEME 5. Synthesis of Vinylene-Bridged Dimer 6 and Trimer 7



SCHEME 6. Synthesis of Vinylene-Bridged Tetramer 8 and Pentamer 9[a]



[a] Reagents and conditions: (a) TBAF (1.5 equiv), THF, room temperature, 81%; (b) PDC (1.5 equiv), DMF, room temperature, 59%; (c) PPh_3·HBr (1.2 equiv), CH_3CN, toluene, reflux, 73%.

and **33** showed higher solubility than the nonsubstituted dimer **6**; thus, the prepared aldehyde **32** and phosphonium salt **33** were used in a Wittig reaction, under conditions similar to the preparation of vinylene-bridged trimer **7**, affording the desired vinylene-bridged tetramer **8** in 54% yield. Similarly, vinylene-bridged pentamer **9** (61%) was obtained from a Wittig reaction between dialdehyde **27** and phosphonium salt **33**. The synthetic route for polydisperse vinylene-bridged oligomer **10** is shown in Scheme 7. Bromination of monoaldehyde **24** with NBS gave bromide **34** in 67% yield. A Wittig reaction between **34** and the phosphonium ylide obtained from methyltriphenylphosphonium bromide and *n*-BuLi afforded compound **35** (85%). Polydisperse vinylene-bridged oligomer **10** was obtained by palladium(II)-catalyzed Heck reaction of compound **35**.[21] The progress of this reaction was confirmed by gel permeation chromatography (GPC), and the reaction was terminated when the molecular weight showed no further increase. The number average molecular weight (M_n) was 4.2 × 10^3, with a polydispersity index (PDI) of 2.0; higher molecular weight compounds could not be obtained, probably because the solubility of the

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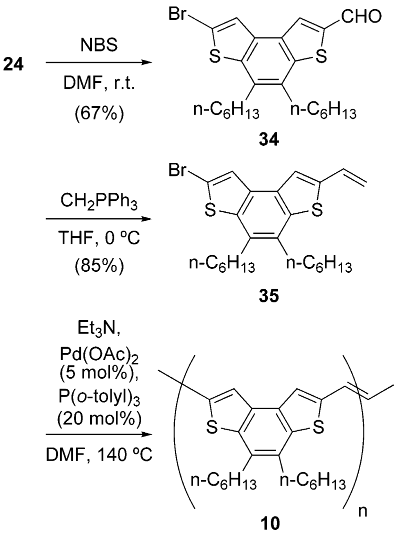
(21) (a) Jin, S.-H.; Kim, M.-Y.; Koo, D.-S.; Kim, Y.-I.; Park, S.-H.; Lee, K.; Gal, Y.-S. *Chem. Mater.* **2004**, *16*, 3299−3307. (b) Peng, Z.; Galvin, M. E. *Chem. Mater.* **1998**, *10*, 1785−1788.

SCHEME 7. Synthesis of Polydisperse Vinylene-Bridged Oligomer 10



oligomer decreased with polymerization. The overall yields of vinylene-bridged oligomers from starting material **15** were 74% (**6**), 60% (**7**), 11% (**8**), and 17% (**9**), respectively.

Although the configurations of all double bonds in vinylene-bridged oligomers **6**−**8** were determined as *trans* by ^{1}H NMR, probably as a result of purification by recrystallization from $CHCl_3$ and/or toluene, the geometries of vinylene-bridged pentamer **9** and oligomer **10** could not be identified.

Synthesis of Ethynylene-Bridged Oligomers. Three well-defined monodisperse ethynylene-bridged oligomers, **11**−**13** (n = 0, 1, 2), and polydisperse oligomer **14** were prepared according to Schemes 8 and 9. As shown in Scheme 8, monoiodo derivative **36** was prepared by monolithiation of BDT **15** with *n*-BuLi, followed by treatment with I_2. A Pd/Cu-catalyzed Sonogashira coupling reaction between **36** and trimethylsilyl acetylene provided **37** (96%),[22] which was then converted to monoethynyl derivative **38** by base-promoted desilylation in 76% yield. Diethynyl derivative **40** was also prepared from BDT **15** by a similar procedure. As shown in Scheme 9, a Pd/Cu-catalyzed cross-coupling reaction of iodide **36** with **38** afforded ethynylene-bridged dimer **11** in 65% yield, and ethynylene-bridged trimer **12** was obtained from **36** and **40** in 74% yield. Diiodo dimer **41**, an important precursor for the ethynylene-bridged tetramer **13**, was prepared in 60% yield by dilithiation of **11** followed by treatment with iodine; compared to dimer **1** and vinylene-bridged dimer **6**, **11** possesses much higher solubility in organic solvents such as AcOEt, THF, and $CHCl_3$. A Sonogashira coupling reaction between **38** and **41** gave the desired ethynylene-bridged tetramer **13** in 73% yield. Unfortunately, an ethynylene-bridged pentamer could not be obtained due to difficulties in preparing the monoethynyl-substituted dimer. The polydisperse ethynylene-bridged oligomer **14** was also obtained by Pd/Cu-catalyzed cross-coupling of **23** and **40**, Its number average molecular weight (M_n) was 1.5 × 10^4, and the polydispersity index (PDI) was 1.8. The molecular weight of this compound was high compared with those of the other polydisperse oligomers, probably due to its excellent solubility. The overall yields of ethynylene-bridged oligomers from the starting material **15** were 38% (**11**), 40% (**12**), and 17% (**13**), respectively.

TABLE 1. Melting Points, DSC Thermal Transitions and TGA Decomposition Temperatures for Oligomers 1−14

compd	mp^a (°C)	T_m^{b} (°C)	T_d^{c} (°C)
dimer **1**	233−234	224	424
trimer **2**	242−244	234	458
tetramer **3**	246−248	231	468
pentamer **4**	224−228	224	436
oligomer **5**	−	−	357
v-dimer **6**	252−254	247	400
v-trimer **7**	207−212	211	402
v-tetramer **8**	254−258	256	431
v-pentamer **9**	247−250	243	421
v-oligomer **10**	−	−	347
e-dimer **11**	151−153	151	408
e-trimer **12**	140−142	130	444
e-tetramer **13**	161−163	150	420
e-oligomer **14**	−	−	330

[a] Melting point determined by hot stage apparatus. [b] Highest endothermic peak observed by DSC analysis. [c] Temperature of 5% weight loss, determined by TGA.

Thermal Properties. The thermal properties of the BDT oligomers were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. Table 1 summarizes the melting points (T_m) and 5% weight loss temperatures (T_d), characterized by DSC and TGA, of compounds **1**−**14**. All of the monodisperse oligomers showed high 5% weight loss temperatures (T_d > 400 °C). This result indicates that volatilization and decomposition processes that result in weight change do not occur at under 400 °C. On the basis of the TGA analysis, these compounds may be judged to have high thermal stability. Oligomers **1**−**4** and vinylene-bridged oligomers **6**−**9** melted at considerably higher temperatures than ethynylene-bridged oligomers **11**−**13**, but polydisperse oligomers **5**, **10**, and **14** did not show distinct melting points and/or glass transition phenomena (T_g). Figure 1 shows DSC thermograms of dimers **1**, **6**, and **11** with sequential heating and cooling at a scan rate of 10 and −20 °C/min. Endothermic peaks indicating the melting points (T_m) of dimer **1** and vinylene-bridged dimer **6** were observed at 224 and 247 °C, respectively, in the first heating process. Interestingly, the thermogram of ethynylene-bridged dimer **11** showed two endothermic peaks, at 99 and 151 °C. The first peak, which disappeared when a ground sample was used, probably resulted from a crystal−crystal transition, and the second peak represents the melting point.[23] Exothermic peaks due to crystallization were observed at 183 and 219 °C, respectively, for **1** and **6** during the cooling process, but no exothermic peak was observed for **11**. In contrast, when the DSC thermogram was measured up to 200 °C, an exothermic peak for **11** was observed at 138 °C in the cooling process (Figure 2). Close investigation of the DSC thermogram in the area between 200 and 300 °C revealed a broad and weak exothermic peak above 250 °C (Figure 1, inset). In the GPC chromatogram of **11** after heating for 1 h at 250 °C, a broad peak appeared at a range of high molecular weights (see Figure S1 in Supporting Information). A similar phenomenon was observed for ethynylene-bridged tetramer **13**.

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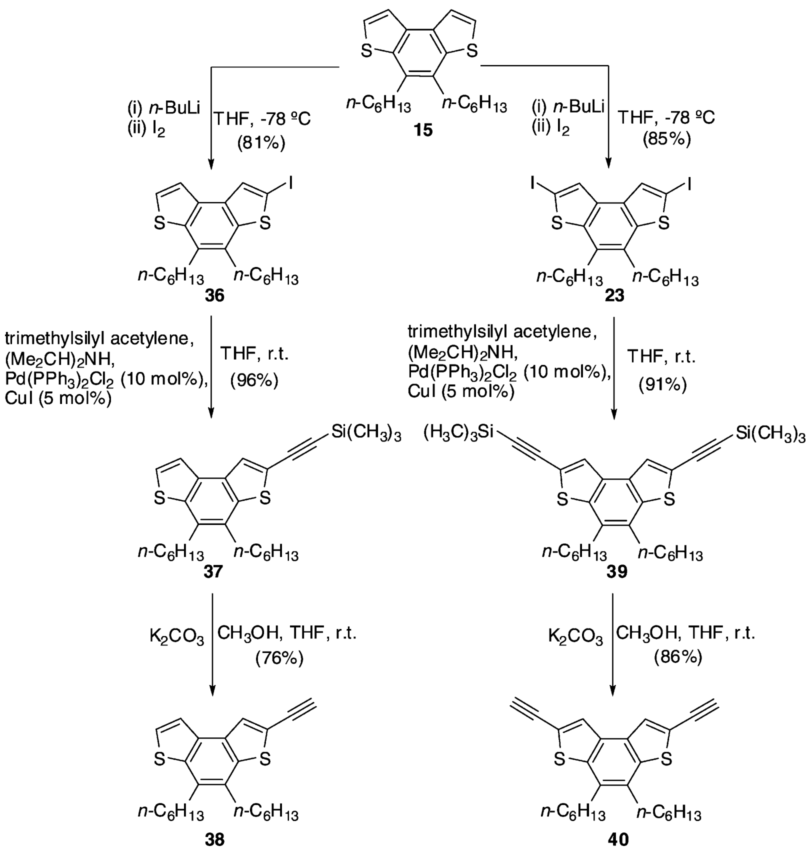
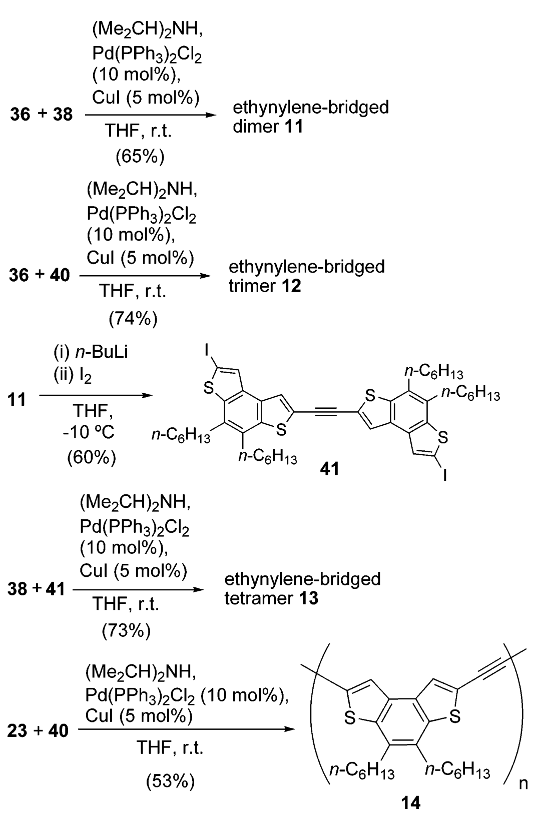
(22) (a) Liu, C.-Y.; Luh, T.-Y. *Org. Lett.* **2002**, *4*, 4305−4307. (b) Novák, Z.; Nemes, P.; Kotschy, A. *Org. Lett.* **2004**, *6*, 4917−4920. (c) Nicolaou, K. C.; Smith, A. L.; Wendeborn, S. V.; Hwang, C. K. *J. Am. Chem. Soc.* **1991**, *113*, 3106−3114.

(23) van Breeman, A. J. J. M.; Herwig, P. T.; Chlon, C. H. T.; Sweelssen, J.; Schoo, H. F. M.; Setayesh, S.; Hardeman, W. M.; Martin, C. A.; de Leeuw, D. M.; Valeton, J. J. P.; Bastiaansen, C. W. M.; Broer, D. J.; Popa-Merticaru, A. R.; Meskers, S. C. J. *J. Am. Chem. Soc.* **2006**, *128*, 2336−2345.

SCHEME 8. Synthesis of Precursors for Ethynylene-Bridged Oligomers



SCHEME 9. Synthesis of Monodisperse Ethynylene-Bridged Oligomers 11−13 and Polydisperse Ethynylene-Bridged Oligomer 14



These results suggest that intermolecular reactions or decomposition processes which do not involve a weight change take place at the ethynylene spacer at around 250 °C, and **11** and **13** have lower thermal stabilities despite their high T_d values.

UV−Vis and Photoluminescence (PL) Properties. To investigate the electronic properties of each type of oligomer, the UV−vis absorption and fluorescence spectra of compounds **1**−**14** were measured in toluene solution (1×10^{-5} M) and in thin films deposited on glass substrates. Table 2 summarizes the absorption and fluorescence properties of compounds **1**−**14**. Figure 3 presents the absorption spectra of oligomers **1**−**4** in dilute toluene solution; these exhibit distinct red-shifts of the absorption maxima and enhancement of the absorption coef-

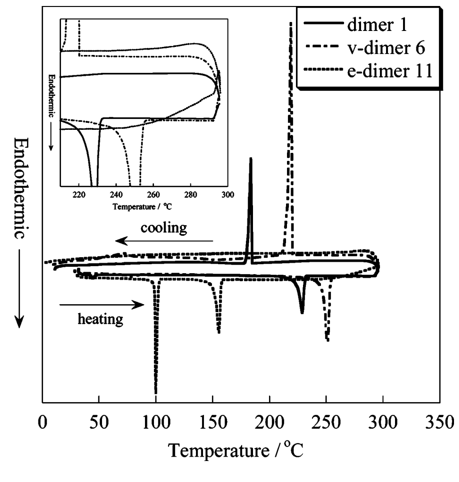


FIGURE 1. DSC curves of dimers **1**, **6**, and **11** upon continuous heating (10 °C/min) and cooling (−20 °C/min).

TABLE 2. Absorption Maxima (λ_{max}, nm) and Fluorescence Maxima (λ_{max}, nm) for Oligomers 1−14

compd	absorption[a,b] (solution)		emission[a,b,c] (solution)	absorption[b,d] (film)	emission[b,c,d] (film)
	λ_{max} (nm)	ϵ_{max}	λ_{max} (nm)	λ_{max} (nm)	λ_{max} (nm)
1	$\underline{380}$, 403	54260	$\underline{413}$, 437, 465	$\underline{370}$, 388, 416	$\underline{463}$, 494
2	$\underline{405}$, 427	72670	443, $\underline{471}$, 502	399, $\underline{423}$, 453	511
3	$\underline{417}$, 440	91490	458, $\underline{486}$	410, $\underline{434}$, 464	522
4	$\underline{420}$, 445	97660	462, $\underline{490}$	411, $\underline{435}$, 468	529
5	410	−	$\underline{466}$, 489	411	540
6	381, $\underline{403}$, 429	78920	440, $\underline{467}$, 496	$\underline{396}$, 418, 449	502
7	411, $\underline{435}$, 463	115250	476, $\underline{505}$	423, $\underline{453}$, 485	535
8	423, $\underline{448}$, 478	145260	490, $\underline{520}$	436, $\underline{466}$, 499	550
9	431, $\underline{453}$, 484	113870	495, $\underline{528}$	438, $\underline{469}$, 504	558
10	$\underline{409}$, 435	−	506, $\underline{527}$	415	544
11	$\underline{383}$, 405	48140	$\underline{412}$, 435	$\underline{387}$, 397, 418	461, $\underline{493}$
12	394	85770	$\underline{439}$, 464	392	$\underline{498}$, 524
13	394	102030	$\underline{448}$, 476	400	517
14	400	−	454	398	534

[a] Measured in toluene. [b] Absolute maxima are denoted by an underline. [c] Excited at the absorption maximum. [d] Measured for deposited thin film.

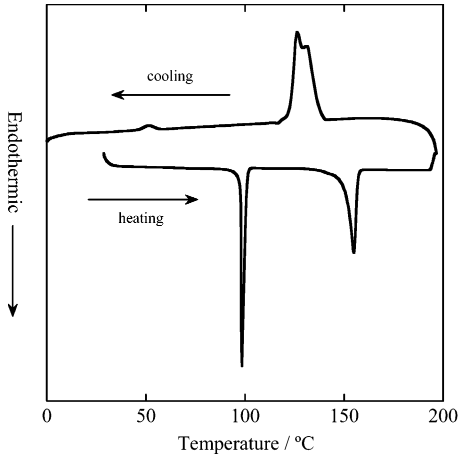


FIGURE 2. DSC curve of dimer **11** upon continuous heating (10 °C/min) and cooling (−20 °C/min).

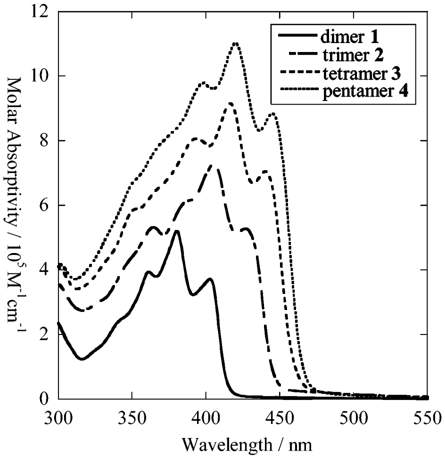


FIGURE 3. Absorption spectra of oligomers **1**−**4** in toluene solution (1×10^{-5} M).

ficient as their chain lengths increase.[10] This result indicates that the probability of a $\pi-\pi^*$ transition to excited states was enhanced by extension of the conjugation length. Similarly, vinylene-bridged oligomers **6**−**9** and ethynylene-bridged oligomers **11**−**13** also show convergent shifts in their absorption maxima (Table 2). However, the amount of red-shift depends on the structure of the oligomer, because each spacer provides a different degree of conjugation: e.g., dimer **1** to trimer **2** = 25 nm, vinylene-bridged dimer **6** to trimer **7** = 32 nm, and ethynylene-bridged dimer **11** to trimer **12** = 11 nm. The HOMO−LUMO energy gaps, estimated from the absorption edges in the spectra,[24] were plotted as a function of oligomer length (Figure 4). This curve clearly indicates that the prepared oligomers are well defined. The effective conjugation length of the polydisperse oligomer **5** is about six BDT units, which corresponds to 18 aromatic rings. This result is consistent with that of oligothiophene, whose effective conjugation length is 13−20 thiophene rings.[10]

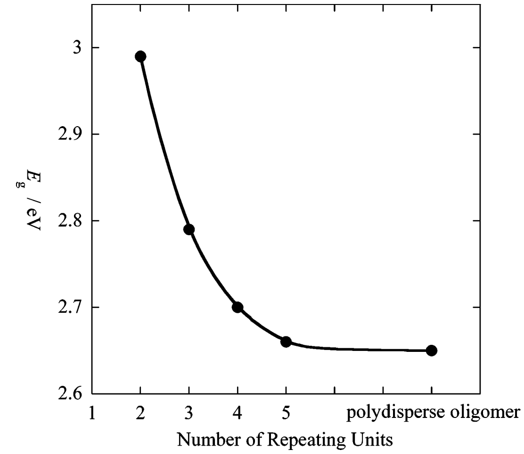


FIGURE 4. Plot of HOMO−LUMO energy gap (E_g) versus number of BDT units (n) for oligomers **1**−**4** and polydisperse oligomer **5**: E_g = 1240/(wavelength of the absorption edge) (eV).

Figure 5 shows the fluorescence spectra of oligomers **1**−**4** in dilute toluene solution. As observed for the absorption spectra, these exhibit distinct red-shifts in their fluorescence maxima. To investigate the electronic properties of each type of oligomer, the fluorescence spectra of tetramers **3**, **8**, and **13** were obtained in dilute toluene solution. These are shown in Figure 6. All of the compounds show similar vibronic structures in their fluorescence spectra and thus have similar vibrational modes. Vinylene-bridged tetramer **8** (λ^{em} = 520 nm) exhibits emission

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(24) Hou, J.; Tan, Z.; He, Y.; Yang, C.; Li, Y. *Macromolecules* **2006**, *39*, 4657−4662.

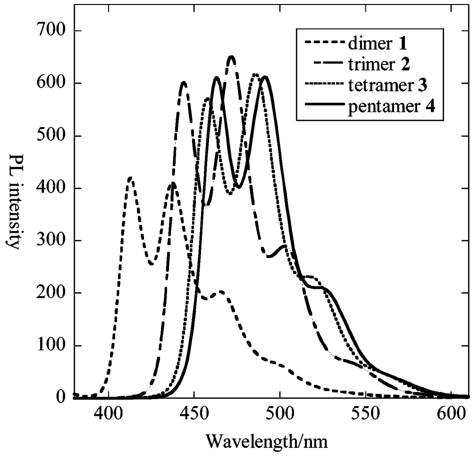

FIGURE 5. Photoluminescence spectra of oligomers **1**−**4** in toluene solution (1 × 10^{-5} M).

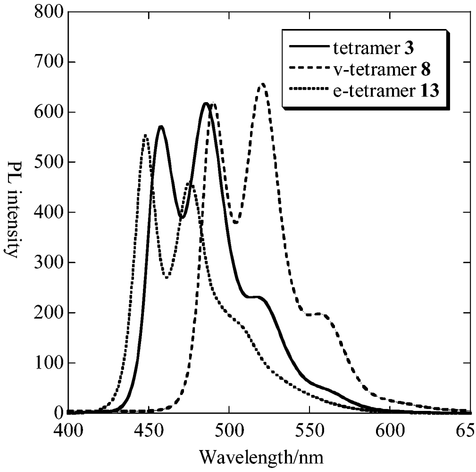

FIGURE 6. Photoluminescence spectra of tetramers **3**, **8**, and **13** in toluene solution (1 × 10^{-5} M).

at a longer wavelength than tetramer **3** (λ^{em} = 490 nm), and ethynylene-bridged tetramer **13** (λ^{em} = 476 nm) exhibits emission at a shorter wavelength than **3**. Figure 7 shows the fluorescence spectra of tetramers **3**, **8**, and **13** in thin films deposited on glass substrates. Changing from dilute solution to the solid state, the fluorescence maxima of tetramers **3**, **8**, and **13** exhibit significant red-shifts of 36, 30, and 69 nm, respectively. Ethynylene-bridged tetramer **13** exhibits the largest red-shift, which suggests that the introduction of an ethynylene spacer results in stronger excited-state $\pi-\pi$ intermolecular interactions compared to the other oligomers. This may be due to a change in structure, such as the adoption of a more planar shape.[25]

The fluorescence maxima of all the oligomers are red-shifted, and the emission colors vary from blue to yellow as their chain lengths—and thus their conjugation lengths—increase. However, the polydisperse oligomers **5**, **10**, and **14** exhibit almost the same emission colors as pentamer **4**, vinylene-bridged pentamer **9**, and ethynylene-bridged tetramer **13**, respectively, because their effective conjugation lengths are limited to about six BDT units. Minute color tuning can also be achieved by changing the spacers combining BDT units. The vinylene-bridged oligomers emit at longer wavelengths than the direct-linked and ethynylene-bridged oligomers.

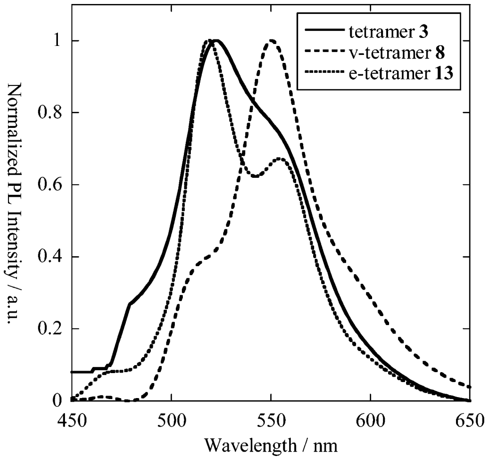

FIGURE 7. Photoluminescence spectra of tetramers **3**, **8**, and **13** in thin films.

Electrochemical Properties. To evaluate the electrochemical stability of each type of oligomer, cyclic voltammetry measurement was carried out for 10 cycles at a scan rate of 100 mV/s in benzonitrile or CH_2Cl_2, using tetrabutylammonium perchlorate as an electrolyte. The cyclic voltammograms of tetramers **3**, **8**, and **13** are shown in Figure 8a−c, and the electrochemical properties of all oligomers are summarized in Table 3. Although tetramer **3** and vinylene-bridged tetramer **8** exhibit reversible oxidation waves, ethynylene-bridged tetramer **13** shows an irreversible oxidation process. It is likely that extensive decomposition during electrochemical analysis resulted in the production of unidentifiable materials, mostly resulting from alkyne degradation.[26] The oxidation potential of vinylene-bridged tetramer **8** was found to be slightly lower than that of oligomer **3**. This is because the π-conjugated system is extended by the presence of vinylene groups. Each type of monodisperse oligomer exhibited higher HOMO levels as its chain length increased.[27] The HOMOs of tetramer **3** and vinylene-bridged tetramer **8** were estimated to be −5.29 and −5.25 eV, respectively; these values are slightly higher than that of the HOMO of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) (PEDOT:PSS) (−5.0 eV), and thus hole injection from PEDOT:PSS to these compounds is expected to be comparatively easy.[28]

Conclusions

We synthesized three types of BDT oligomers, direct-linked oligomers **1**−**5**, vinylene-bridged oligomers **6**−**10**, and ethynylene-bridged oligomers **11**−**14**, via Suzuki, Stille, Wittig, and Sonogashira coupling reactions. All of the monodisperse oligomers showed high T_d values, and tetramer **3** showed higher thermal and electrochemical stability than any of the other oligomers. The ethynylene-bridged oligomers had lower melting points and showed lower electrochemical stability than the other

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[25] Li, J.; Pang, Y. *Macromolecules* **1997**, *30*, 7487−7492.

[26] Tovar, J. D.; Rose, A.; Swager, T. M. *J. Am. Chem. Soc.* **2002**, *124*, 7762−7769.

[27] Noh, Y. Y.; Azumi, R.; Goto, M.; Jung, B.-J.; Lim, E.; Shim, H.-K.; Yoshida, Y.; Yase, K.; Kim, D.-Y. *Chem. Mater.* **2005**, *17*, 3861−3870. HOMO = $-4.8 - (E_{ox} - E_{ox}^{fer})$ (eV).

[28] Tang, R.; Tan, Z.; Li, Y.; Xi, F. *Chem. Mater.* **2006**, *18*, 1053−1061.

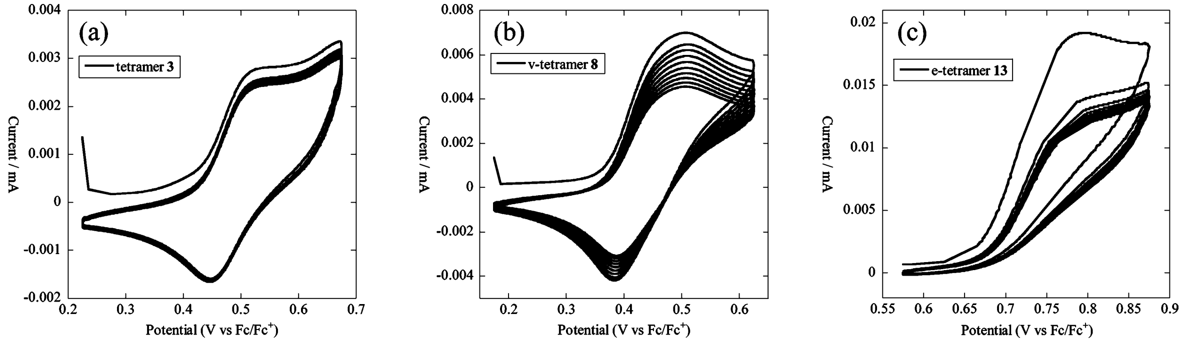

FIGURE 8. CV curves (10 cycles) of (a) tetramer **3**, (b) vinylene-bridged tetramer **8**, and (c) ethynylene-bridged tetramer **13**, at a scan rate of 100 mV/s in benzonitrile with tetrabutylammonium perchlorate (0.1 mol/L).

TABLE 3. Electrochemical Properties of Oligomers 1−14

compound	$E_{1/2}^{ox}$ [a] (V)	E_{HOMO} [b] (eV)	E_{LUMO} [c] (eV)	E_g [d] (eV)
1	0.63	5.43	2.44	2.99
2	0.55	5.35	2.56	2.79
3	0.49	5.29	2.59	2.70
4	0.42	5.22	2.55	2.67
5	0.40[e]	5.20	2.56	2.64
6	0.62	5.42	2.61	2.81
7	0.53[e]	5.33	2.73	2.60
8	0.45	5.25	2.73	2.52
9	0.52[e]	5.32	2.84	2.48
10	0.41[e]	5.21	2.75	2.46
11	0.74[e]	5.54	2.55	2.99
12	0.68[e]	5.48	2.69	2.79
13	0.65[e]	5.45	2.70	2.75
14	0.60[e]	5.40	2.77	2.63

[a] $E_{1/2}^{ox}$ potential (vs Fc/Fc$^+$ couple) was determined by cyclic voltammetry in benzonitrile (compounds **1−10**, 1.0×10^{-4} M) or CH_2Cl_2 (compounds **11−14**, 1.0×10^{-4} M) containing tetrabutylammonium perchlorate (0.1 M) as a supporting electrolyte. [b] E_{HOMO} was estimated from $E_{1/2}^{ox}$ using a Fc/Fc$^+$ couple ($E_{1/2}^{ox} = 0.53$) as an internal standard. $E_{HOMO} = E_{1/2}^{ox} + 4.8$. [c] E_{LUMO} was calculated approximately by subtracting E_g from E_{HOMO}. [d] E_g was determined from the optical absorption edge in toluene solution. [e] E_{onset}^{ox} potential vs Fc/Fc$^+$ couple ($E_{onset}^{ox} = 0.39$).

types of oligomer. The fluorescence maxima of all of the oligomers were red-shifted, and the emission colors varied from blue to yellow as their chain lengths, and thus their conjugation lengths, increased. However, the polydisperse oligomers **5**, **10**, and **14** exhibited almost the same emission colors as pentamer **4**, vinylene-bridged pentamer **9**, and ethynylene-bridged tetramer **13**, respectively, because their effective conjugation lengths are limited to about six BDT units.

Experimental Section

Dimer 1. To a stirred solution of bromide **16** (0.73 g, 1.7 mmol) and borolane **18** (1.06 g, 2.18 mmol) in toluene (60 mL) were added $Pd(PPh_3)_4$ (60 mg, 0.050 mmol) and 2 M aqueous Na_2CO_3 (30 mL) under argon, and the mixture was refluxed for 15 h. The residue was purified by silica gel column chromatography (chloroform) and recrystallized from toluene to give **1** (0.93 g, 77%) as a yellow solid. Mp 233−234 °C; $T_{d5\%}$ 424 °C; ^1H NMR ($CDCl_3$) δ 0.89−0.98 (m, 12H), 1.32−1.86 (m, 32H), 2.99 (t, $J = 8.2$ Hz, 8H), 7.49 (d, $J = 5.4$ Hz, 2H), 7.70 (d, $J = 5.4$ Hz, 2H), 7.89 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 29.8, 29.9, 31.7, 32.4, 119.6, 122.4, 125.2, 130.1, 131.2, 132.7, 133.5, 136.4, 138.3, 139.2; IR (KBr) 2955, 2924, 1465, 719 cm^{-1}; UV−vis, toluene, λ_{max}/nm (ϵ_{max}/L mol^{-1} cm^{-1}) 403 (3.72×10^4), 381 (5.20×10^4), 361 (3.93×10^4); MS (LDI-TOF) (*m/z*) found 714.9 (MH$^+$), calcd for $C_{44}H_{58}S_4$ 714.3 (M$^+$). Anal. Calcd for $C_{44}H_{58}S_4$: C, 73.89; H, 8.17. Found: C, 73.82; H, 8.24.

Trimer 2. This compound was prepared using a procedure similar to that of dimer **1** (0.17 g, 84%). Mp 242−244 °C; $T_{d5\%}$ 458 °C; ^1H NMR ($CDCl_3$) δ 0.88−0.98 (m, 18H), 1.32−1.62 (m, 36H), 1.71−1.87 (m, 12H), 2.94−3.05 (m, 12H), 7.50 (d, $J = 5.4$ Hz, 2H), 7.70 (d, $J = 5.4$ Hz, 2H), 7.90 (s, 2H), 7.92 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 14.0, 14.1, 22.6, 22.7, 22.8, 29.6, 29.7, 29.8, 29.9, 30.0, 30.1, 31.7, 31.8, 31.9, 32.5, 32.6, 119.6, 119.7, 125.3, 130.2, 130.9, 131.3, 132.8, 133.5, 133.6, 136.4, 136.8, 138.4, 138.7, 139.3; IR (KBr) 2956, 2924, 1468, 708 cm^{-1}; UV−vis, toluene, λ_{max}/nm (ϵ_{max}/L mol^{-1} cm^{-1}) 427 (4.78×10^4), 406 (6.53×10^4), 365 (4.67×10^4); MS (LDI-TOF) (*m/z*) found 1071.8 (MH$^+$), calcd for $C_{66}H_{86}S_6$ 1070.5 (M$^+$). Anal. Calcd for $C_{66}H_{86}S_6$: C, 73.96; H, 8.09. Found: C, 73.95; H, 8.20.

Tetramer 3. To a stirred solution of dibromide **21** (0.42 g, 0.48 mmol) and stannyl compound **19** (0.78 g, 1.2 mmol) in toluene (20 mL) was added $Pd(PPh_3)_4$ (20 mg, 0.010 mmol) under argon, and the mixture was refluxed for 48 h. The reaction mixture was poured into hexane (20 mL), and the crude product which precipitated was purified by silica gel column chromatography (chloroform) and recrystallized from toluene to give **3** (0.43 g, 63%) as a yellow solid. Mp 246−248 °C; $T_{d5\%}$ 468 °C; ^1H NMR ($C_6D_5CD_3$) δ 0.93−0.98 (m, 24H), 1.38−1.61 (m, 48H), 1.85−1.96 (m, 16H), 3.05−3.14 (m, 16H), 7.17 (d, $J = 5.7$ Hz, 2H), 7.47 (d, $J = 5.7$ Hz, 2H), 7.92 (s, 2H), 7.92 (s, 2H), 7.93 (s, 2H); ^{13}C NMR ($C_6D_5CD_3$) δ 14.0, 23.1, 30.4, 30.5, 32.3, 33.1, 120.3, 120.5, 122.9, 130.7, 131.5, 131.6, 131.8, 133.8, 134.6, 138.8, 139.4, 139.7, 139.8, 140.1; IR (KBr) 2955, 2926, 2855, 1465 cm^{-1}; UV−vis, toluene, λ_{max}/nm (ϵ_{max}/L mol^{-1} cm^{-1}) 441 (6.13×10^4), 417 (7.91×10^4), 394 (6.74×10^4); MS (LDI-TOF) (*m/z*) found 1425.9 (M$^+$), calcd for $C_{88}H_{114}S_8$ 1426.7 (M$^+$). Anal. Calcd for $C_{88}H_{114}S_8$: C, 74.00; H, 8.04. Found: C, 74.04; H, 8.18.

Pentamer 4. To a stirred solution of bromide **22** (0.15 g, 0.19 mmol) and stannyl compound **20** (81 mg, 0.086 mmol) in toluene (2 mL) was added $Pd(PPh_3)_4$ (6 mg, 0.0052 mmol) and CuO (15 mg, 0.19 mmol) under argon, and the mixture was refluxed for 2 h. The reaction mixture was purified by silica gel column chromatography (chloroform). The crude product was washed with ethanol, hexane, and acetone and recrystallized from toluene to give **4** (0.14 g, 92%) as a green solid. Mp 224−228 °C; $T_{d5\%}$ 436 °C; ^1H NMR ($C_6D_5CD_3$) δ 0.92−0.99 (m, 30H), 1.33−1.49 (m, 40H), 1.52−1.68 (m, 20H), 1.82−2.02 (m, 20H), 305−3.17 (m, 20H), 7.18 (d, $J = 5.3$ Hz, 2H), 7.47 (d, $J = 5.3$ Hz, 2H), 7.91 (s, 2H), 7.92 (s, 2H), 7.93 (s, 2H), 7.95 (s, 2H); ^{13}C NMR ($C_6D_5CD_3$) δ 14.1, 23.1, 30.4, 30.5, 32.3, 33.2, 120.3, 120.5, 123.0, 130.7, 131.5, 131.6, 131.8, 133.8, 134.6, 139.4, 139.8, 140.2; IR (KBr) 2954, 2925, 2855, 1466 cm^{-1}; UV−vis, toluene, λ_{max}/nm (ϵ_{max}/L mol^{-1} cm^{-1}) 443 (7.68×10^4), 419 (9.93×10^4), 400 (9.08×10^4); MS (LDI-TOF) (*m/z*) found 1782.7 (M$^+$), calcd for $C_{110}H_{142}S_{10}$ 1782.8 (M$^+$). Anal. Calcd for $C_{110}H_{142}S_{10}$: C, 74.02; H, 8.02. Found: C, 74.30; H, 8.10.

Polydisperse Oligomer 5. To a stirred solution of diiodide **23** (0.23 g, 0.38 mmol) and distannyl compound **20** (0.56 mmol) in toluene (8 mL) was added $Pd(PPh_3)_4$ (39 mg, 0.034 mmol) and CuO (0.11 g, 1.4 mmol) under argon, and the mixture was refluxed for 39 h. After cooling, the reaction mixture was filtered through a celite pad. The filtrate was subjected to chromatography on silica gel (chloroform). The crude product was dissolved in a small amount of $CHCl_3$ and poured into 400 mL of methanol to give a precipitate which was collected by filtration, washed with methanol, and dried in vacuo to give **5** (0.16 g, 79%) as a yellow solid. $T_{d5\%}$ 357 °C; ^{1}H NMR ($CDCl_3$) δ 0.88−0.94 (m, 6H), 1.19−1.78 (m, 16H), 2.99 (m, 4H), 7.60−7.95 (m, 2H); IR(KBr) 1457, 2854, 2927, 2953 cm^{-1}; LDI-TOF mass spectrum is shown in Figure S2 in Supporting Information.

Vinylene-Bridged Dimer 6. Aldehyde **24** (0.18 g, 0.47 mmol) and phosphonium salt **26** (0.37 g, 0.52 mmol) were dissolved in a mixture of 2 mL of THF and 1 mL of methanol. To the resulting solution was added *t*-BuOK (0.08 g, 0.70 mmol) at room temperature, and the resulting yellow suspension was stirred for 3.5 h. The crude product was purified by silica gel column chromatography (chloroform) and recrystallized from toluene to give **6** (0.24 g, 90%) as a yellow solid. Mp 252−254 °C; $T_{d5\%}$ 400 °C; ^{1}H NMR ($CDCl_3$) δ 0.85−0.98 (m, 12H), 1.28−1.59 (m, 24H), 1.69−1.83 (m, 8H), 2.91−3.03 (m, 8H), 7.31 (s, 2H), 7.47 (d, J = 5.4 Hz, 2H), 7.62 (d, J = 5.4 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 14.0, 14.1, 22.6, 22.7, 29.8, 29.9, 30.0, 31.6, 31.7, 32.4, 32.5, 122.1, 122.4, 123.8, 125.2, 130.2, 131.4, 132.7, 133.5, 138.0, 139.1, 141.2; IR (KBr) 2925, 2858, 1466, 934, 713 cm^{-1}; UV−vis, toluene, λ_{max}/nm (ϵ_{max}/L mol^{-1} cm^{-1}) 429 (6.83×10^4), 403 (7.89×10^4), 382 (5.13×10^4); MS (LDI-TOF) (*m*/*z*) found 741.4 (MH$^+$), calcd for $C_{46}H_{60}S_4$ 740.4 (M$^+$). Anal. Calcd for $C_{46}H_{60}S_4$: C, 74.54; H, 8.16. Found: C, 74.32; H, 7.96.

Vinylene-Bridged Trimer 7. To a stirred solution of phosphonium salt **26** (0.42 g, 0.58 mmol) in THF (20 mL) was added *n*-BuLi (5.59 mmol, 0.40 mL of 1.40 M solution in hexane) at −50 °C, and the mixture was stirred for 20 min. To the resulting red solution was added a solution of dialdehyde **27** (0.10 g, 0.24 mmol) in THF (4 mL) at 0 °C. The reaction mixture was stirred at room temperature for 2 h and refluxed for 1.5 h. The crude product was purified by silica gel column chromatography (chloroform) and recrystallized from toluene to give **7** (0.31 g, 87%) as a yellow solid. Mp 207−212 °C; $T_{d5\%}$ 402 °C; ^{1}H NMR ($CDCl_3$) δ 0.89−0.97 (m, 18H), 1.27−1.62 (m, 36H), 1.66−1.85 (m, 12H), 2.87−3.02 (m, 12H), 7.30 (s, 4H), 7.46 (d, J = 5.4 Hz, 2H), 7.54 (s, 2H), 7.62 (d, J = 5.4 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 14.0, 14.1, 22.6, 22.7, 29.8, 29.9, 30.0, 31.7, 31.8, 32.4, 32.5, 122.0, 122.2, 122.4, 123.7, 124.0, 125.2, 130.2, 131.1, 131.4, 132.7, 132.8, 133.3, 133.4, 138.2, 139.1, 141.2, 141.5; IR (KBr) 2924, 2856, 1467, 930, 709 cm^{-1}; UV−vis, toluene, λ_{max}/nm (ϵ_{max}/L mol^{-1} cm^{-1}) 463 (1.03×10^5), 435 (1.15×10^5), 411 (7.98×10^4); MS (LDI-TOF) (*m*/*z*) found 1123.4 (MH$^+$), calcd for $C_{70}H_{90}S_6$ 1122.5 (M$^+$). Anal. Calcd for $C_{70}H_{90}S_6$: C, 74.81; H, 8.07. Found: C, 74.53; H, 7.89.

Vinylene-Bridged Tetramer 8. To a stirred solution of phosphonium salt **33** (0.07 g, 0.06 mmol) in THF (1.5 mL) was added *n*-BuLi (0.06 mmol, 0.04 mL of a 1.4 M solution in hexane) at 0 °C, and the mixture was stirred for 30 min. To the resulting red solution was added aldehyde **32** (0.05 g, 0.06 mmol) in THF (1.5 mL) at room temperature. A precipitate was formed slowly, and the mixture was stirred at room temperature for 2 h. The reaction was then quenched with water, and the reaction mixture was filtered. The solid precipitate was washed with ethanol and hexane, dried in vacuo, and recrystallized from toluene to give **8** (50 mg, 54%) as an orange solid. Mp 254−258 °C; $T_{d5\%}$ 431 °C; ^{1}H NMR (C_6D_5-CD_3) δ 0.91−0.95 (m, 24H), 1.35−1.44 (m, 32H), 1.53−1.63 (m, 16H), 1.85−1.94 (m, 16H), 3.04−3.11 (m, 16H), 7.18 (d, J = 5.7 Hz, 2H), 7.38 (s, 2H), 7.39 (s, 4H), 7.40 (s, 2H), 7.43 (s, 2H), 7.44 (s, 2H), 7.46 (d, J = 5.7 Hz, 2H); IR (KBr) 2955, 2924, 2857, 1677, 1466, 1146, 1094, 1016, 827 cm^{-1}; UV−vis, toluene, λ_{max}/nm (ϵ_{max}/L mol^{-1} cm^{-1}) 478 (1.43×10^5), 448 (1.45×10^5), 423 (1.03×10^5); MS (LDI-TOF) (*m*/*z*) found 1504.9 (M$^+$), calcd for $C_{94}H_{120}S_8$ 1504.7 (M$^+$). Anal. Calcd for $C_{94}H_{120}S_8$: C, 74.94; H, 8.03. Found: C, 75.17; H, 7.80.

Vinylene-Bridged Pentamer 9. This compound was prepared using a procedure similar to that of vinylene-bridged tetramer **8** (0.22 g, 61%). Mp 247−250 °C; $T_{d5\%}$ 421 °C; ^{1}H NMR (C_6D_5-CD_3) δ 0.87−0.99 (m, 30H), 1.28−1.67 (m, 60H), 1.80−1.99 (m, 20H), 3.04−3.13 (m, 20H), 7.18 (d, J = 6.0 Hz, 2H), 7.39 (s, 8H), 7.40 (s, 2H), 7.42 (s, 2H), 7.44 (s, 4H), 7.46 (d, J = 6.0 Hz, 2H); IR (KBr) 2953, 2924, 2854, 1457, 1158, 1098, 928, 819 cm^{-1}; UV−vis, toluene, λ_{max}/nm (ϵ_{max}/L mol^{-1} cm^{-1}) 484 (1.03×10^5), 453 (1.14×10^5), 431 (1.04×10^5); MS (LDI-TOF) (*m*/*z*) found 1885.9 (M$^+$), calcd for $C_{118}H_{150}S_{10}$ 1886.9 (M$^+$).

Polydisperse Vinylene-Bridged Oligomer 10. A mixture of **35** (0.20 g, 0.43 mmol), $Pd(OAc)_2$ (4.8 mg, 0.022 mmol), tri-*o*-tolylphosphine (26 mg, 0.086 mmol), and triethylamine (0.18 mL) in 1.5 mL of DMF was stirred at 140 °C for 24 h. The hot reaction mixture was then poured into 500 mL of MeOH to precipitate the polymer product, which was collected by filtration and purified by silica gel column chromatography (chloroform). The polymer was redissolved in a small amount of chloroform and then poured into MeOH to give a precipitate, which was collected by filtration and dried in vacuo to give **10** (0.10 g, 50%) as a yellow solid. $T_{d5\%}$ 347 °C; ^{1}H NMR ($CDCl_3$) δ 0.93−0.95 (m, 6H), 1.25−1.74 (m, 16H), 2.95 (m, 4H), 7.46−7.62 (m, 4H); IR(KBr) 930, 1159, 1463, 1625, 2854, 2924, 2954 cm^{-1}; LDI-TOF mass spectrum is shown in Figure S3 in Supporting Information.

Ethynylene-Bridged Dimer 11. To a stirred solution of **36** (0.11 g, 0.23 mmol) and **38** (90 mg, 0.24 mmol) in THF (5.0 mL) were successively added diisopropylamine (0.15 mL, 0.46 mmol), bis(triphenylphosphine)palladium(II) dichloride (10 mg, 0.020 mmol), and copper(I) iodide (3 mg, 0.01 mmol). This mixture was stirred for 6 h at room temperature. The crude product was chromatographed on silica gel (dichloromethane) and recrystallized from dichloromethane to give **11** (0.11 g, 65%) as a yellow powder. Mp 151−153 °C; $T_{d5\%}$ 408 °C; ^{1}H NMR ($CDCl_3$) δ 0.91−0.95 (m, 12H), 1.37−1.38 (m, 16H), 1.48−1.53 (m, 8H), 1.70−1.75 (m, 8H), 2.93−3.02 (m, 8H), 7.51 (d, J = 5.4 Hz, 2H), 7.66 (d, J = 5.4 Hz, 2H), 7.89 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 29.7, 29.9, 31.6, 32.4, 88.7, 121.2, 122.4, 125.6, 127.6, 129.9, 132.0, 132.3, 132.6, 139.2, 139.7; IR (KBr) 2956, 2926, 2854, 1457, 1212, 830 cm^{-1}; UV−vis, toluene, λ_{max}/nm (ϵ_{max}/L mol^{-1} cm^{-1}) 405 (4.43×10^4), 383 (4.81×10^4); MS (LDI-TOF) (*m*/*z*) found 738.6 (MH$^+$), calcd for $C_{46}H_{58}S_4$ 738.3 (M$^+$). Anal. Calcd for $C_{46}H_{58}S_4$: C, 74.74; H, 7.91. Found: C, 74.98; H, 7.94.

Ethynylene-Bridged Trimer 12. This compound was prepared using a procedure similar to that of ethynylene-bridged dimer **11** (0.10 g, 74%). Mp 140−142 °C; $T_{d5\%}$ 444 °C; ^{1}H NMR ($CDCl_3$) δ 0.93−0.96 (m, 18H), 1.37−1.38 (m, 24H), 1.51−1.56 (m, 12H), 1.73−1.75 (m, 12H), 2.96−3.02 (m, 12H), 7.51 (d, J = 5.4 Hz, 2H), 7.66 (d, J = 5.4 Hz, 2H), 7.85 (s, 2H), 7.91 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 29.7, 29.9, 31.6, 32.4, 88.4, 89.1, 121.0, 121.9, 122.4, 125.6, 127.4, 127.8, 129.9, 131.5, 132.1, 132.2, 132.3, 132.6, 139.2, 139.7, 140.1; IR (KBr) 2953, 2925, 2853, 1457, 829 cm^{-1}; UV−vis, toluene, λ_{max}/nm (ϵ_{max}/L mol^{-1} cm^{-1}) 394 (8.58×10^4); MS (LDI-TOF) (*m*/*z*) found 1119.2 (MH$^+$), calcd for $C_{70}H_{86}S_6$ 1118.5 (M$^+$). Anal. Calcd for $C_{70}H_{86}S_6$: C, 75.08; H, 7.74. Found: C, 74.98; H, 7.99.

Ethynylene-Bridged Tetramer 13. This compound was prepared using a procedure similar to that of ethynylene-bridged dimer **11** (0.11 g, 73%). Mp 161−163 °C; $T_{d5\%}$ 420 °C; ^{1}H NMR ($CDCl_3$) δ 0.92−0.96 (m, 24H), 1.37−1.39 (m, 32H), 1.48−1.57 (m, 16H), 1.71−1.81 (m, 16H), 2.94−3.02 (m, 16H), 7.51 (d, J = 5.4 Hz, 2H), 7.66 (d, J = 5.4 Hz, 2H), 7.85 (s, 2H), 7.87 (s, 2H), 7.91 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 29.7, 29.9, 31.6, 32.4, 88.5, 89.2, 89.7, 121.0, 121.8, 122.5, 125.6, 127.4, 127.6, 127.8, 129.9, 131.5, 132.3, 132.6, 139.2, 139.7, 140.1; IR (KBr) 2953, 2925, 2852, 1456, 828 cm^{-1}; UV−vis, toluene, λ_{max}/nm (ϵ_{max}/L mol^{-1} cm^{-1}) 394 (1.02×10^5); MS (LDI-TOF) (*m*/*z*) found 1498.2 (MH$^+$), calcd for $C_{94}H_{114}S_8$ 1498.7 (M^+). Anal. Calcd for $C_{94}H_{114}S_8$: C, 75.25; H, 7.66. Found: C, 75.34; H, 7.74.

Polydisperse Ethynylene-Bridged Oligomer (14). To a stirred solution of **23** (0.10 g, 0.17 mmol) and **40** (70 mg, 0.20 mmol) in THF (5 mL) were successively added diisopropylamine (0.07 mL, 0.5 mmol), bis(triphenylphosphine)palladium(II) dichloride (10 mg, 0.020 mmol), and copper(I) iodide (2 mg, 0.01 mmol). This mixture was stirred for 45 h at room temperature. The reaction mixture was chromatographed on silica gel ($CHCl_3$), and the crude product was reprecipitated from hexane to give **14** (90 mg, 53%) as a black powder. Further reprecipitation of this powder from ethanol gave **14** as an orange powder. $T_{d5\%}$ 330 °C; T_g 111 °C; ^{1}H NMR ($CDCl_3$) δ 0.80−1.96 (m, 6H), 1.20−1.30 (m, 8H), 1.30−1.45 (m, 4H), 1.60−1.80 (m, 4H), 2.80−3.00 (m, 4H), 7.80−7.88 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 29.7, 29.9, 31.6, 32.3, 121.7, 127.4, 131.5, 132.0, 140.1; IR (KBr) 2953, 2923, 2852, 1457, 1199, 826 cm^{-1}. Anal. Calcd for $C_{24}H_{30}S_2$: C, 75.34; H, 7.90. Found: C, 73.62; H, 7.21.

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Supporting Information Available: Detailed experimental procedures and compound characterization data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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