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Construction of well-defined butadiynylene-linked perylene bisimide arrays via cross-coupling

Hongwei Kang [a,b], Wei Jiang [a,*], Zhaohui Wang [a,*]

[a] Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
[b] Graduate School of the Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT

A homogeneous series of well-defined oligo-butadiynylene-PBIs have been efficiently synthesized in one pot by Hay Cross-Coupling. It is shocked that the rate of this oxidative coupling reaction is very fast, the whole process just takes a short time no more than 10 s. The four butadiynylene-linked oligomers having good solubility in common solvents show absorption spectra with broad absorption range (from 300 nm to 650 nm) and gradually increasing absorption coefficients (up to 1.4×10^5 mol^{-1} cm^{-1}). From the cyclic voltammentry data, we can see that the LUMO levels are effectively and precisely tuned by embedding butadiynylene linkage between PBI subunits. These compounds are promising for potential applications in molecular electronic devices such as conducting molecular wires and solar cells.

1. Introduction

The study of functional π-conjugated organic systems has long been of interest in context of conductive molecular wires that are key components for future circuits in molecular electronic devices [1–4]. Perylene bisimides (PBIs) have been attracted considerable attention in both academic and industrial research owing to their good photochemical and thermal stabilities, high fluorescence quantum efficiency, excellent electron transporting properties, and ability to self-assemble into ordered supramolecular structures [5–10]. In particular, they are broadly utilized in a variety of applications in the burgeoning field of organic electronics, including light emitting diodes (OLEDs) [11], field effect transistors (OFETs) [12–16] and organic solar cells (OSCs) [17–23] and molecular wires [24,25]. PBI derivatives with π-extended conjugated systems have been used as n-type [14] or ambipolar semiconductors [26–28], and near-infrared (NIR) dyes [29,30].

Conjugated dimeric and trimeric PBI oligomers that were covalently linked by a variety of bridges, such as phenylene, ethynylene, butadiynylene, thieno[3,2-*b*]thiophene unit etc. have been actively investigated [31–33]. In the course of our research on π-conjugated oligomeric PBIs, we have developed singly-, doubly- and triply-linked PBI oligomers by copper-mediated *Ullmann* coupling from either dibromo-PBIs or tetrahalo-PBIs, and investigated their photophysical properties and conformational structures systematically [34–41].

Oxidative acetylenic homo- and cross-coupling reactions of terminal and/or haloacetylenes (e.g., Hay coupling) are a well-established methodology of constructing π-conjugated oligomers with precisely defined length and constitution [42–47]. The copper-TMEDA (N,N,N′,N′-tetramethylethylene-diamine) complex was found to be the most versatile catalyst for achieving butadiynylene conjugated systems due to its high solubility in various of organic solvents [48–50]. In this contribution, we describe the one-pot synthesis of a homogeneous series of highly soluble and linearly conjugated butadiynylene-PBI oligomers of up to five PBI units by oxidative Hay cross-coupling reaction. Furthermore, the photophysical properties of these oligomers are systematically explored by spectroscopic and electrochemical measurements.

2. Experimental section

2.1. Materials and methods

All chemicals and solvents were purchased from commercial suppliers and used without further purification unless otherwise

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* Corresponding authors. Tel./fax: +86 010 6265 3617.
E-mail addresses: jiangwei@iccas.ac.cn (W. Jiang), wangzhaohui@iccas.ac.cn (Z. Wang).

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specified. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 or 150 MHz) spectra were recorded in deuterated solvents on a Bruker ADVANCE 400 NMR or 600 NMR Spectrometer. *J* values are expressed in Hz and quoted chemical shifts are in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. The signals have been designated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), and m (multiplets). Mass spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEX III Mass Spectrometer.

UV–vis spectra were measured with Hitachi (Model U-3010) UV–vis spectrophotometer in a 1-cm quartz cell. Cyclic voltammograms (CVs) were recorded on a Zahner IM6e electrochemical workstation at a scan rate of 100 mV s^{-1}, with using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode, and ferrocene/ferrocenium as an internal potential marker for the calibration of potential. 0.1 M tetrabutyl-ammoniumhexafluorophosphate (Bu_4NPF_6) dissolved in CH_2Cl_2 (HPLC grade) was employed as the supporting electrolyte.

2.2. Synthesis and characterization of compounds **1–7**

2.2.1. Compound **1**

A Schlenk flask was charged with a mixture of 1,7-dibromo-PBI (868.7 mg, 1.0 mmol), trimethylsilyl acetylene (0.5 ml, 3.0 mmol), $Pd(PPh_3)_4$ (30 mg, 0.26 mmol), CuI (5 mg, 0.026 mmol), and diisopropylamine (20 ml) under argon. The mixture was stirred for 30 min at 40 °C. After the solvent was evaporated in vacuum, 150 ml THF was added to the residue, the catalysts were filtered out. The organic layer was condensed in vacuo and the crude product was purified with column chromatography on silica gel eluted with CH_2Cl_2/petroleum ether (from 1:1 to 2:1, v/v) to afford **1** as a red solid (810 mg, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) $\delta = 10.31$ (d, $J = 8.0$ Hz, 2H), 8.94 (s, 2H), 8.76 (d, $J = 8.0$ Hz, 2H), 7.52 (t, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 4H), 2.72–2.79 (m, 4H), 1.18–1.20 (m, 24H), 0.40 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) $\delta = 163.60$, 163.40, 146.01, 138.95, 135.14, 134.87, 131.41, 130.70, 130.11, 128.79, 128.25, 124.47, 123.67, 122.51, 120.54, 106.93, 105.81, 29.60, 24.36, 24.33, 1.37. MS (MALDI-TOF): cacld for $[M + H]^+$, $[M + Na]^+$, 904.3, 926.3; found 904.6, 926.6.

2.2.2. Compound **6**

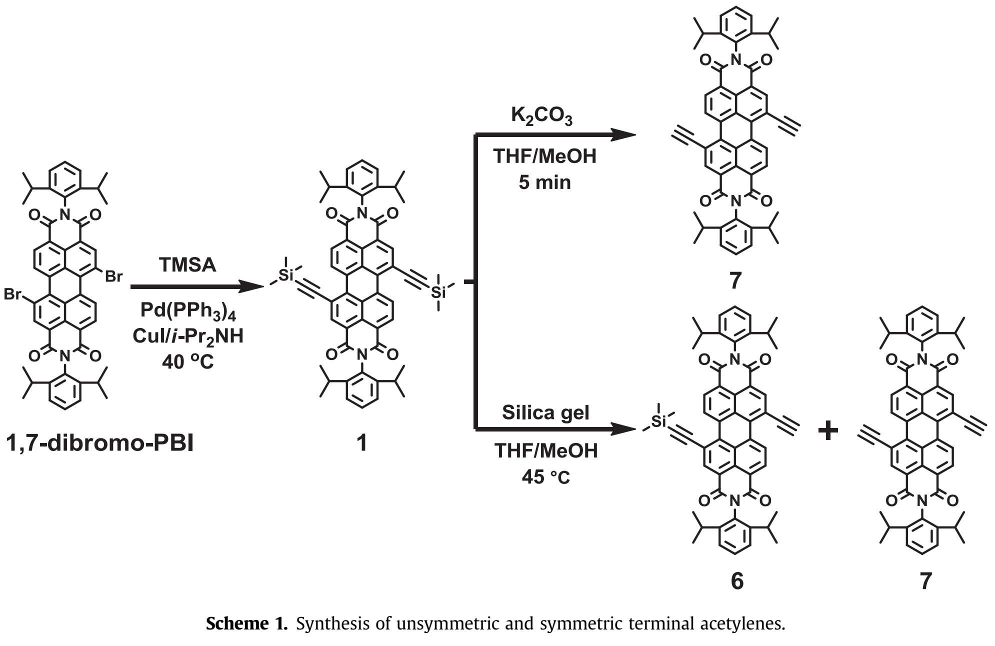
To a 250 ml bottle, compound **1** (500 mg, 0.55 mmol), silica gel (2.5 g), THF (50 ml), methanol (50 ml) were added, the mixture was stirred for 5 h at 45 °C. Then the solvent was removed under reduced pressure after purification by column chromatography on silica gel with CH_2Cl_2/petroleum ether (2:1, v/v) to give a mixture of **6** and **7** with a ratio of about 4:1 to 5:1 detected by ^{1}H NMR analysis. And the compound **6** can be separated from the mixture by column chromatography. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) $\delta = 10.29$ (d, $J = 8.0$ Hz, 1H), 10.13 (d, $J = 8.0$ Hz, 1H), 8.96 (d, $J = 8.0$ Hz, 2H), 8.76–8.82 (dd, 2H), 7.52 (t, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 4H), 3.83 (s, 1H), 2.75 (m, 4H), 1.18–1.20 (m, 24H), 0.40 (s, 9H). MS (MALDI-TOF): cacld for $[M + H]^+$, $[M + Na]^+$, 832.1, 854.1; found, 832.5, 854.5.

2.2.3. Compound **7**

Compound **1** (300 mg, 0.33 mmol), K_2CO_3(50 mg, 0.36 mmol), THF (20 ml), methanol (20 ml) were added to a 100 ml bottle, the mixture was stirred for 5 min at room temperature. Then the solvent was removed under reduced pressure after purification by column chromatography on silica gel with CH_2Cl_2/petroleum ether (2:1 to 3:1, v/v) to give **7** as an orange solid (200 mg, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) $\delta = 10.12$ (d, $J = 8.0$ Hz, 2H), 8.96 (s, 1H), 8.84 (d, $J = 8.0$ Hz, 2H), 7.53 (t, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 4H), 3.83 (s, 2H), 2.71–2.78 (m, 4H), 1.18–1.20 (m, 24H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) $\delta = 163.54$, 163.23, 145.98, 138.95, 138.47, 135.81, 134.54, 131.99, 130.62, 130.18, 128.89, 128.46, 128.17, 124.53, 123.72, 122.78, 119.61, 84.48, 29.63, 24.34, 1.36. MS (MALDI-TOF): cacld for $[M]^+$, 758.9; found, 758.1.

2.2.4. Conjugated butadiynylene-PBI oligomers

To a 100 ml bottle exposed to air, CuCl (50 mg, 0.51 mmol), TMEDA (1.5 ml), CH_2Cl_2 (30 ml) were added orderly at ambient temperature, then a mixture of compound **6** and**7** (415 mg, a ratio of 4.69/1 analyzed by H NMR, and the mol ratio were 0.418 mmol and 0.089 mmol, respectively) were poured into the mixture system with the color changed from blue to purple instantly. Then the solvent was removed under reduced pressure, purified by column chromatography on silica gel with CH_2Cl_2/petroleum ether (1:2 to 3:1, v/v) to give the four oligomers: dimer (**2**, 135 mg, 32.2%), trimer (**3**, 50 mg, 12.3%), tetramer (**4**, 21.6 mg, 5.2%), pentamer (**5**, 15 mg, 3.8%).



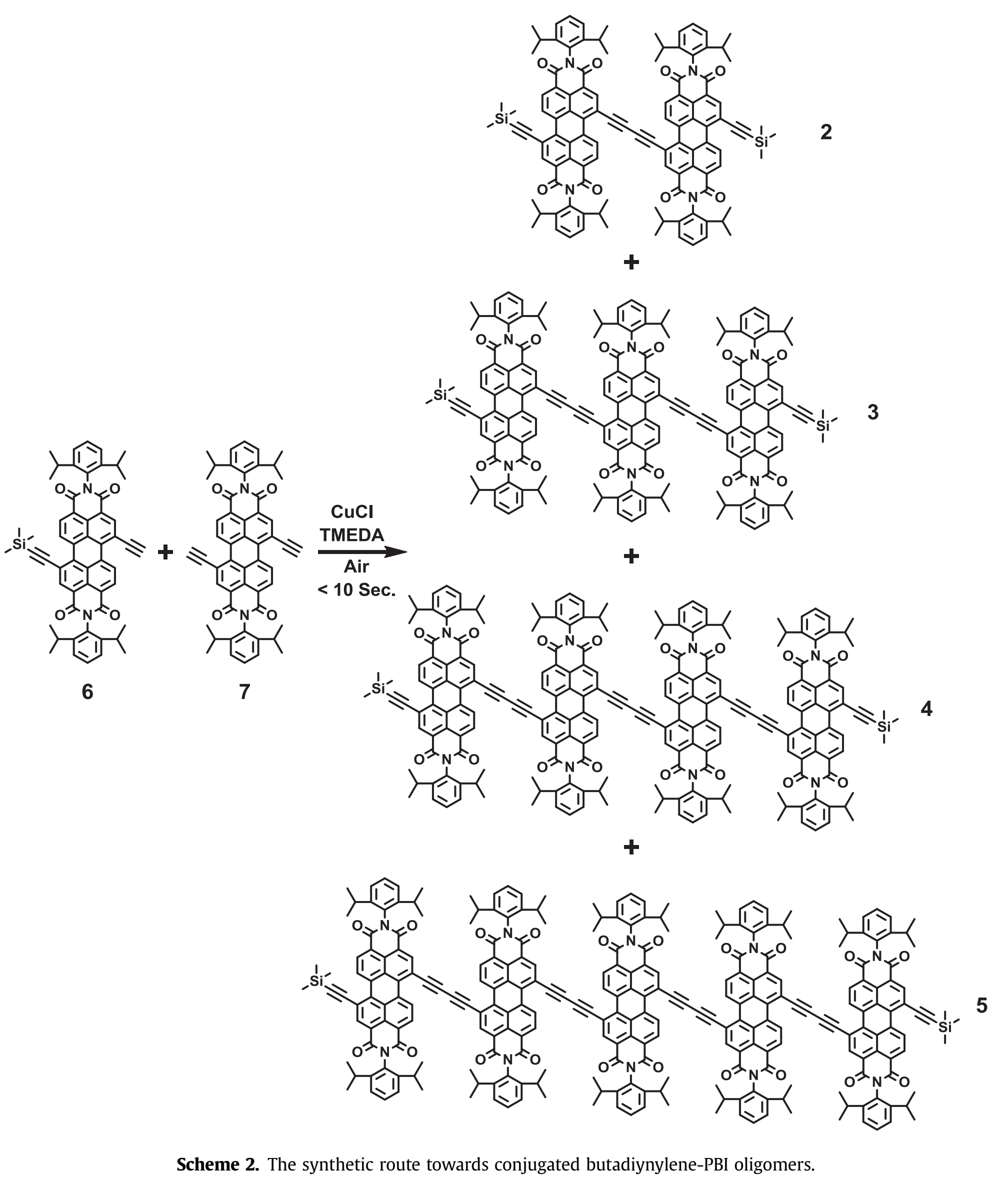
Scheme 1. Synthesis of unsymmetric and symmetric terminal acetylenes.

2.2.4.1. Compound ***2****(dimer).* ^{1}H NMR (CDCl$_3$, 400 MHz, ppm) $\delta = 10.35$ (d, $J = 8.0$ Hz, 2H), 10.02 (d, $J = 8.0$ Hz, 2H), 9.08 (s, 2H), 8.96 (s, 2H), 8.89 (d, $J = 8.0$ Hz, 2H), 8.82 (d, $J = 8.0$ Hz, 2H), 7.49–7.55 (m, 4H), 7.34–7.39 (m, 8H), 2.72–2.79 (m, 8H), 1.15–1.22 (m, 48H), 0.42 (s, 18H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm) $\delta = 163.51$, 163.44, 163.28, 163.09, 157.58, 145.94, 140.30, 139.10, 138.93, 138.63, 137.02, 134.91, 134.84, 134.33, 132.08, 131.98, 131.50, 130.54, 130.17, 129.20, 128.79, 128.43, 128.30, 128.07, 125.23, 124.50, 124.06, 123.68, 122.84, 122.64, 122.17, 121.01, 118.36, 113.76, 107.53, 105.64, 101.66, 86.33, 82.07, 29.61, 24.34, 1.37. MS (MALDI-TOF): cacld for [M]$^+$, 1660.1; found, 1660.2. HRMS (EI): cacld for [M + H]$^+$, 1660.7035; found, 1660.7007.

2.2.4.2. Compound ***3*** *(trimer).* ^{1}H NMR (CDCl$_3$, 400 MHz, ppm) $\delta = 10.34$ (d, $J = 8.0$ Hz, 2H), 9.98–10.04 (dd, 4H), 9.07 (d, $J = 4.0$ Hz, 4H), 8.95 (s, 2H), 8.86–8.92 (dd, 4H), 8.81 (d, $J = 8.0$ Hz, 2H), 7.47–7.54 (m, 6H), 7.33–7.38 (m, 12H), 2.70–2.77 (m, 12H), 1.14–1.20 (m, 72H), 0.40 (s, 18H). ^{13}C NMR (CDCl$_3$, 100 MHz, ppm) $\delta = 163.51$, 163.44, 163.28, 163.09, 162.98, 158.54, 145.96, 139.12, 138.92, 137.09, 136.71, 134.94, 134.83, 134.32, 132.65, 130.57, 130.46, 130.19, 129.24, 128.81, 128.33, 128.16, 128.02, 124.53, 124.13, 123.71, 122.89, 122.69, 121.06, 118.87, 118.28, 107.59, 105.66, 86.70, 86.16, 82.63, 81.99, 29.63, 24.35, 1.37. MS (MALDI-TOF): cacld for [M]$^+$, 2417.0; found, 2417.6. HRMS (EI): cacld for [M + H]$^+$, 2417.0023; found, 2417.0083.

2.2.4.3. Compound ***4*** *(tetramer).* ^{1}H NMR (CDCl$_3$, 400 MHz, ppm) $\delta = 10.34$ (d, $J = 8.0$ Hz, 2H), 9.98–10.04 (dd, 6H), 9.07 (d, $J = 4.0$ Hz, 6H), 8.86–8.95 (m, 8H), 8.81 (d, $J = 8.0$ Hz, 2H), 7.48–7.52 (m, 8H), 7.33–7.38 (m, 16H), 2.69–2.77 (m, 16H), 1.14–1.18 (m, 96H), 0.41 (s, 18H). ^{13}C NMR (CDCl$_3$, 150 MHz, ppm) $\delta = 163.45$, 163.35, 162.98, 145.96, 139.12, 137.09, 136.70, 134.94, 134.37, 132.65, 132.12, 131.98, 130.57, 130.45, 130.19, 129.25, 128.81, 128.33, 128.17, 124.54, 124.14, 123.71, 123.04, 122.89, 122.70, 121.07, 118.90, 118.28, 107.60, 105.66, 86.72, 86.48, 86.15, 82.65, 82.51, 81.98, 29.63, 24.35, 1.37. MS (MALDI-TOF): cacld for [M + H]$^+$, 3174.9; found, 3174.4. HRMS (EI): cacld for [M + Na]$^+$, 3196.2864; found, 3196.2844.

2.2.4.4. Compound ***5*** *(pentamer).* ^{1}H NMR (CDCl$_3$, 400 MHz, ppm) $\delta = 10.34$ (d, $J = 8.0$ Hz, 2H), 9.98–10.04 (m, 8H), 9.07 (d, $J = 4.0$ Hz, 8H), 8.95 (s, 8H), 8.90 (t, $J = 8.0$ Hz, 2H), 8.81 (s, 2H), 7.47–7.54 (m,



Scheme 2. The synthetic route towards conjugated butadiynylene-PBI oligomers.

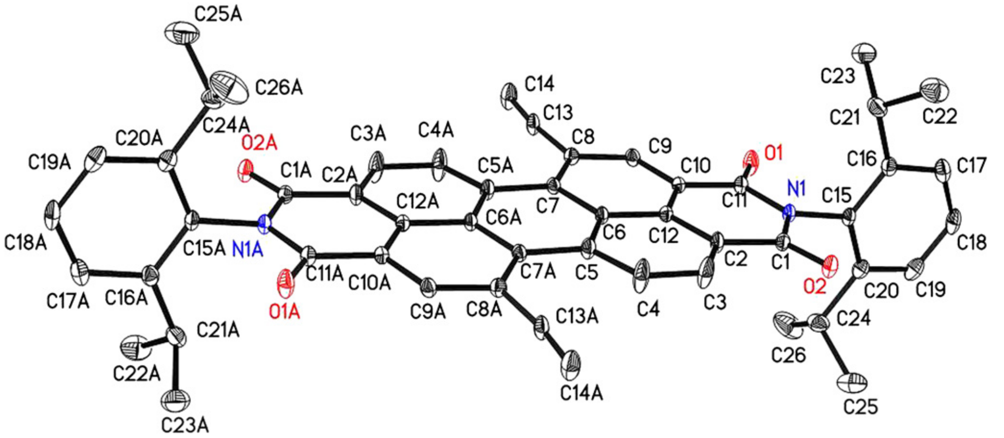


Fig. 1. ORTEP drawing of the molecular structure of compound **7** (top view). The solvent molecules are omitted for clarity.

10H), 7.33–7.38 (m, 20H), 2.69–2.77 (m, 20H), 1.14–1.20 (m, 120H), 0.40 (s, 18H). ^{13}C NMR (CDCl$_3$, 150 MHz, ppm) $\delta = 165.95$, 163.34, 162.98, 154.78, 145.96, 142.35, 139.12, 136.77, 134.94, 134.37, 132.68, 131.97, 130.57, 130.45, 130.25, 129.26, 128.17, 124.55, 124.17, 123.71, 123.52, 123.05, 121.07, 118.91, 107.61, 86.48, 86.15, 83.15, 82.53, 81.99, 29.64, 24.36, 1.37. MS (MALDI-TOF): cacld for $[M + H]^+$, 3931.8, found, 3931.3. HRMS (EI): cacld for $[M + Na]^+$, 3952.5852; found, 3952.5834.

3. Results and discussion

While oligo-butadiynylene-NDIs were prepared in one pot by oxidative homocoupling of di((trimethylsilyl)ethynyl)-NDIs [51], our efforts at direct homocoupling of di((trimethylsilyl)-ethynyl)-PBIs, which was readily prepared from 1,7-dibromo-PBI [52,53] and trimethylsilylacetylene (TMSA) by a standard Sonogashira coupling, to produce the desired well-defined butadiynylene-PBI oligomers were not successful. Unexpectedly, we found that elimination of the TMS protecting group(s) of 1,7-di((trimethylsilyl) ethynyl)-PBI (**1**) with silica gel could lead to the formation of both unsymmetric and symmetric terminal acetylenes (Scheme 1, the ratio of **6** and **7** is from 4/1 to 5/1). Subsequently, the Hay coupling reaction between the mixture of terminal alkynes **6** and **7** was carried out in ambient air to give the desired butadiynylene-PBI oligomers in good yields: **2** (32.2%), **3** (12.3%), **4** (5.2%), and **5** (3.8%) (Scheme 2). It should be noted that the whole process terminated within a few seconds, and these novel oligomers bearing TMS protecting group could be further endowed with functionality for attractive molecular wires.

Desilylation of the TMS groups of compound **1** with potassium carbonate in THF/MeOH solely provided symmetric terminal alkyne **7** in quantitative yield. A single crystal of compound **7** suitable for X-ray crystallographic analysis was obtained from a solution in CDCl$_3$ by slow evaporation at room temperature. The crystal structure reveals that compound **7** has crystallographically imposed inversion symmetry, and the perylene core is almost planar with a torsion angle of 1.78°. The terminal acetylene units are slightly flipping up and down with respect to the perylene core (Fig. 1).

All of the butadiynylene-PBI oligomers are red-violet solids and show high solubility in common organic solvents such as dichloromethane, chloroform, toluene, and tetrahydrofuran. Their structures are unambiguously identified by mass spectrometry and NMR spectroscopy. Room-temperature absorption spectra of these homogeneous butadiynylene-PBI oligomers in chloroform are shown in Fig. 2. The UV–vis absorption spectra showed that they all exhibit well-defined vibronic π-π^* transition absorption bands with high absorption coefficients in the region of visible light, which show much broader and more complicated absorption bands that shifted bathochromically upon the increase in the number of PBI units. Their spectra are more alike and show a pronounced red-shift of the onset of absorption at 571, 618, 637, 645, 648 nm for monomer (**1**), dimer (**2**), trimer (**3**), tetramer (**4**), and pentamer (**5**), respectively, due to extensive conjugation by the electronic coupling of the PBI units. However, a degree of saturation behavior is observed for these butadiynylene-PBI oligomers asa result of their decreasing interval value of the bathochromicbathochromic shifts (Fig. 2).

Cyclic voltammentry (CV) of these oligomers in CH$_2$Cl$_2$ has been investigated to assess their electrochemical properties (Fig. 3). The onset reduction potentials are shifted toward less negative potential value from monomer to pentamer at −0.76, −0.71, −0.67, −0.65 and −0.64 V for **1**, **2**, **3**, **4**, and **5** respectively vs Fc/Fc$^+$, indicating that the LUMO level can be effectively and precisely tuned by embedding butadiynylene linkage between PBI subunits because of the electronic coupling among them through butadiynylene spacers and the conjugation saturation behavior as proven by UV–vis absorption.

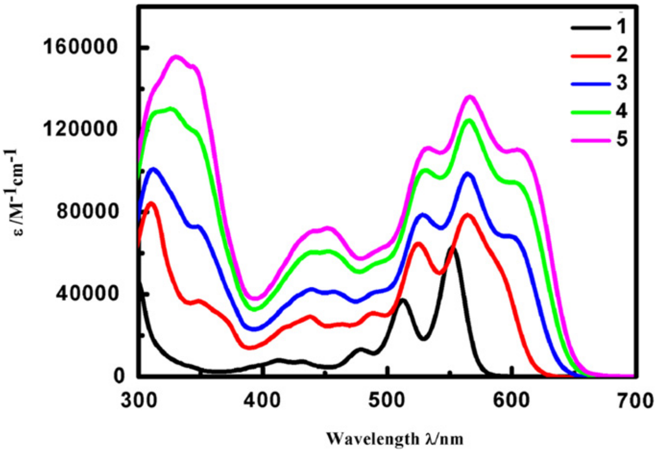


Fig. 2. UV–vis absorption spectra of compounds **1** (black), **2** (red), **3** (blue), **4** (green), and **5** (magenta) in chloroform at room temperature. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

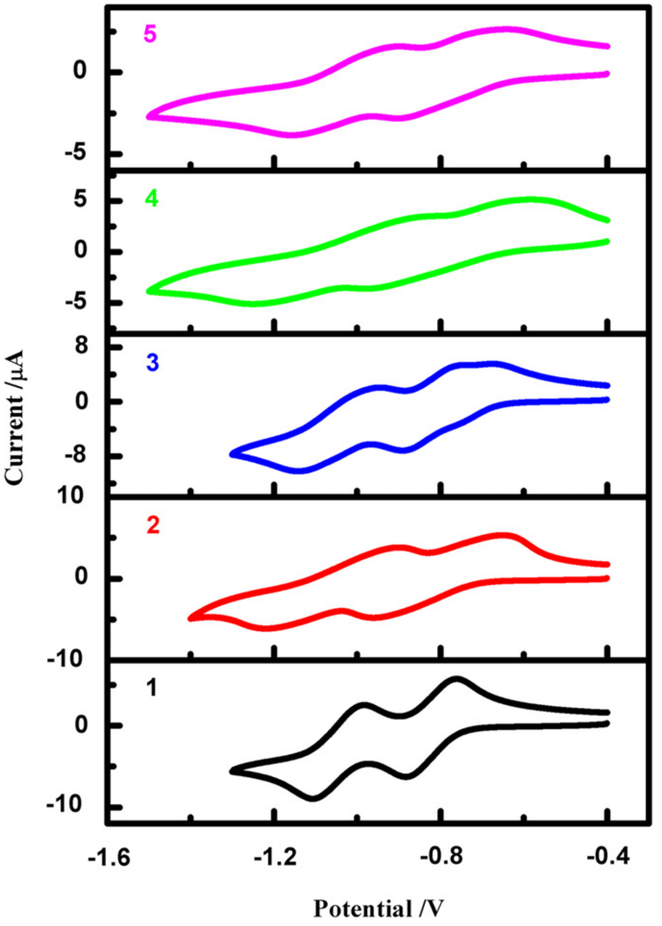


Fig. 3. Reductive cyclic voltammograms of butadiynylene-PBI oligomers in CH_2Cl_2 (electrolyte, 0.1 M Bu_4NPF_6) with a scan rate of 100 mV s^{-1} vs Fc/Fc^+.

4. Conclusions

In summary, we have presented the one-pot synthesis of well-defined of highly soluble and linearly conjugated butadiynylene-PBI oligomers containing up to five PBI units by an efficient oxidative Hay cross-coupling in less than 10 s. In light of the broad absorption with high absorption coefficients in the region of visible light and precisely controllable LUMO energy evidenced by UV–vis absorption and gradually less negative reduction potentials, these butadiynylene-linked oligomers are promising for potential applications as conducting molecular wires and in molecular electronic devices such as solar cells. Extension of this synthetic strategy to highly ordered butadiynylene-linked oligomers as well as further construction of molecular electronics is currently underway.

Acknowledgment

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Appendix A. Supplementary material

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2012.12.015.

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