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Synthesis, optical, and electrochemical properties of conjugated oligomers derived from 4-bromo-4′-(*n*-butyl)-2,2′-biphenyl ☆

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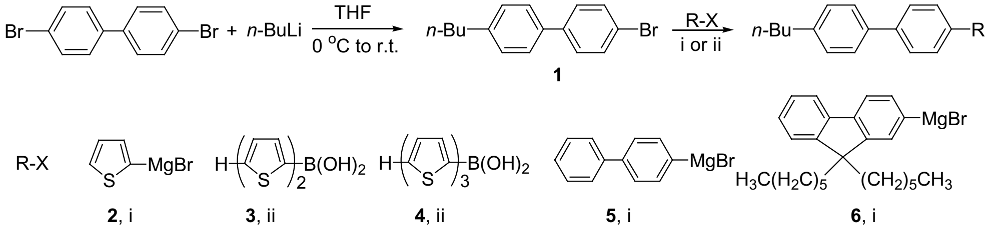
Abstract—The synthesis, optical, and electrochemical properties of semi-conducting co-oligomers of biphenyl/oligothiophenes and homo-oligophenylenes derived from a precursor 4-bromo-4′-(*n*-butyl)-2,2′-biphenyl, which was synthesized by a direct alkylation from 4,4′-dibromo-2,2′-biphenyl using *n*-butyl lithium, are reported.

During the last two decades, conducting oligomers and polymers have attracted tremendous attention in a variety of areas such as organic light-emitting diodes, field-effect transistors, solar cells, and photocopiers.[1] Among various conducting polymers, oligothiophene-based materials and polyphenylenes have been intensively investigated.[2] Interest in the former derives from their well-defined structures, and the feasibility of tuning their processability, optical, and electrochemical properties by simple structural modifications.[3] For example, extension of the π-conjugation length with other aromatic rings,[4] introduction of different terminal groups into the backbones[5] and bridging oligothiophene arms with different linkers[6] have greatly influenced the optical, electrochemical, and thermal properties of oligothiophenes. Polyphenylenes, on the other hand, have attracted much attention because of their liquid crystalline properties, light-emitting properties and superior thermal stability.[7] Thiophene/phenylene co-oligomers have been shown to be potential solid-state lasing materials.[8] In this communication, we report the synthesis, optical, and electrochemical properties of several biphenyl-oligothiophene co-oligomers and their homo-oligophenylene analogues.

The synthesis of the oligomers is shown in Scheme 1. Compound **1** was prepared previously by a two-step method, however, no characterization data was reported.[9] By using the commercially available *n*-BuLi as an alkylating agent, **1** was synthesized in 63% yield more efficiently. We anticipated that replacement of one bromo group in the starting compound by an *n*-butyl group would minimize the formation of byproducts in subsequent reactions and improve the solubility of its



Scheme 1. Reagents and conditions: (i) [NiCl$_2$(dppp)], THF, refluxing; (ii) [Pd(PPh$_3$)$_4$], toluene/2 M K$_2$CO$_3$ (3:2, v/v), refluxing.

Keywords: Oligothiophene; Oligophenylene; Semi-conducting oligomers; Light emitting; Electrochemical properties.

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oligomeric derivatives in organic solvents. Compounds **2**, **5**, and **6** were prepared by the Grignard coupling method using [NiCl$_2$(dppp)] as a catalyst, and were obtained in 45%, 42%, and 62% yields, respectively. Suzuki couplings of 4-bromo-4′-(*n*-butyl)-2,2′-biphenyl with 2,2′-bithiophene-5-boronic acid and 2,2′:5′,2″-terthiophene-5-boronic acid yielded **3** and **4** in 31% and 28% yields, respectively. Compounds **1**–**6** were fully characterized by ^{1}H NMR, ^{13}C NMR, MS, and microanalysis.[10]

Figures 1 and 2 show the UV and emission spectra of **1**–**6** in THF, respectively. A summary on their optical data is given in Table 1. The thiophene/phenylene co-oligomers **2**–**4** exhibit two absorption bands, the strong absorption band at longer wavelength being assigned to the $\pi \rightarrow \pi^*$ electron transfer of the entire chromophore, and the less intense band to the $\pi \rightarrow \pi^*$ local excitation of the hetero-nucleus.[11] The absorption maxima of **2**–**4** are red shifted significantly relative to their parent oligothiophene chromophores,[11] due to the conjugation with the biphenyl unit. The absorption maxima of **2**–**4** show a significant red shift with increase in conjugation length, as expected. In contrast, all the three homo-oligophenylenes **1**, **5**, and **6** exhibit one major strong structureless peak, associated with the $\pi \rightarrow \pi^*$ electron transfer of the entire chromophores. Compounds **2**–**4** emitted indigo to blue light with their maximum emission wavelengths being red shifted with increase in conjugation length. The starting compound **1** is virtually nonemissive, whereas the emission spectra of **5** and **6** center in the UV range. The absorption and emission wavelength maxima of **6** are red shifted significantly relative to **5**, with its quantum efficiency being significantly higher, due to a higher degree of conjugation.[12] A comparison of the optical properties of **3** and **5**, both of which have four aromatic rings, but with the former being a co-oligomer of biphenyl–bithienyl whereas the latter is a homo-oligomer of phenylene, shows that both the absorption and emission maxima of **3** red shift dramatically compared to those of **5**. Furthermore, **3** exhibits a significantly higher quantum yield than **5**.

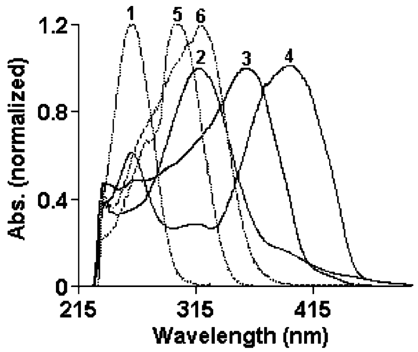

Figure 1. The UV spectra of compounds **1**–**6** in THF (1×10^{-5} M).

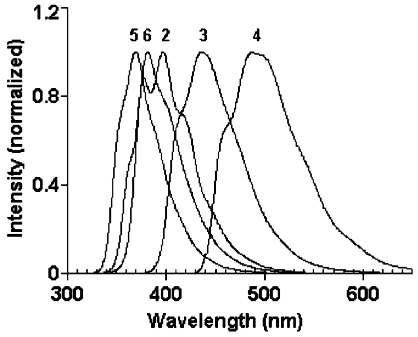

Figure 2. The FL emission spectra of compounds **2**–**6** in THF (1×10^{-5} M).

Table 1. Photophysical data for compounds **1**–**6**[a]

	Absorption		Emission (λ_{max}) (fwhm)	Quantum yield (%)[b]
	λ_{max} (nm)	$\varepsilon \times 10^4$ M^{-1} cm^{-1}		
1	263	8.1	—	—
2	318, 237	4.2, 1.8	396 (63)	25
3	359, 238	7.6, 2.6	435 (66)	20.8
4	403, 260	11.9, 7.2	487 (88)	20.7
5	299	4.9	370 (49)	5.5
6	321	3.8	382 (53)	17.5

[a] Determined in THF solutions, sample solutions are around 1×10^{-5} M. The emission spectra were taken by excitation at their longest wavelength absorption maxima.

[b] Determined in THF solutions ($A < 0.2$) at room temperature using quinine sulfate solution (*ca.* 1.0×10^{-5} M) in 0.01 M H$_2$SO$_4$ (quantum yield, 55%) as a standard.

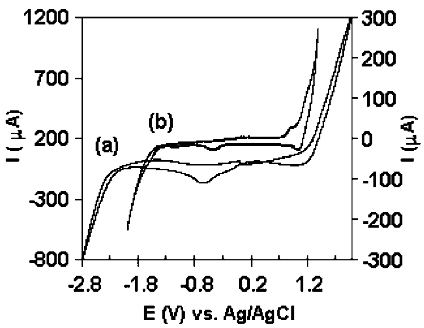

Figure 3. Single-scan cyclic voltammograms in 0.1 M Bu$_4$NBF$_4$–CH$_2$Cl$_2$, scan rate 100 mV/s: (a) **1**, 6.0×10^{-4} M; (b) **6**, about 1.0×10^{-4} M.

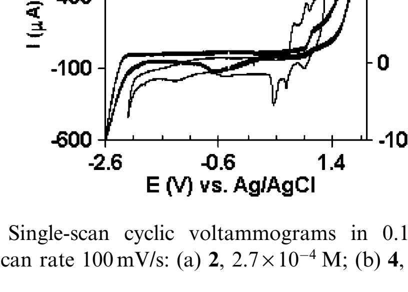

Figure 4. Single-scan cyclic voltammograms in 0.1 M Bu$_4$NBF$_4$–CH$_2$Cl$_2$, scan rate 100 mV/s: (a) **2**, 2.7×10^{-4} M; (b) **4**, saturated solution.

Table 2. Summary of the peak oxidation (E_{pa}) and re-reduction (E_{pc}) potentials from CV curves

Compound	**1**	**2**	**3**	**4**	**5**	**6**
E_{pa} (V)[a,b]	$\underline{1.60}$	1.06	0.96, $\underline{1.35}$	0.73, 0.93, $\underline{1.04}$	$\underline{1.26}$	0.88, 1.12
E_{pc} (V)[a,b]	1.07, −0.67	$\underline{0.88}$, −0.62	0.31, 0.66, $\underline{1.11}$, −0.52	0.36, 0.58, 0.91, −0.50, −1.33	1.10, $\underline{-0.50}$	1.07, −0.50

[a] E (V) versus Ag/AgCl.

[b] The underlined values are poorly resolved.

Cyclic voltammetry (CV) was employed to study the electrochemical properties of **1**–**6**. Figure 3 shows the solution state CV curves of **1** and **6**. The CV curve of **1** does not show a well-defined oxidation peak during the anodic scan, but it was oxidized as indicated by the dramatic increase of anodic current and the sharp color change from colorless to purple red (Fig. 3a). The CV curve of **5** (not shown) is similar to that of **1**, but that of **6** exhibits two ill-defined oxidation peaks (Fig. 3b). Continuous cathodic scan of **1**, **5**, and **6** up to −2.8 V produced one peak in the range −0.5 to −1.5 V, but after that, neither color change nor the detection of reduction peak were observed. The last observation indicates the unavailability of a reduction process for these compounds. The peaks in the range −0.5 to −1.5 V are attributable to the re-reduction of the oxidation state, which is not completed in the positive potential range. Large potential differences between anodic and cathodic peaks have been ascribed to the occurrence of chemical and/or structural changes after oxidation.[13]

Compounds **2**, **3**, and **4**, which contain both phenylene and thiophene rings in the oligomer chain, were more easily oxidized. Compound **4** is yellow in its neutral state. When the potential was scanned anodically to 1.3 V and then cathodically, the compound was oxidized and then re-reduced with three peaks detected in both the anodic and cathodic directions (Fig. 4b). During this process, blue colored material was produced at/near the electrode surface in the anodic scan and then the yellow color was recovered gradually in the back scan. The CV curve of **3** displayed two peaks in both anodic and cathodic scans, while that of **2** yielded only one (Fig. 4a). Reversibility of the redox processes also decreased on going from **4** to **2**. Like **1**, **5**, and **6**, a continuous scan of **2**–**4** to −2.2 V or even more negative potential produced only one or two peaks in the range −0.5 to −1.5 V, due to the re-reduction of the oxidation processes. This suggests that the reduction process of all the compounds is actually inaccessible in CH_2Cl_2 solution.

The peak oxidation (E_{pa}) and re-reduction (E_{pc}) potentials of all the compounds are compiled in Table 2. The results suggest that more phenylene or thiophene rings in the oligomer chain gives rise to a lower oxidation potential. This is in accordance with the longer conjugation length achieved.[14] The CV curves of **3**, **4**, and **6** display more than one peak in the anodic scan and the number of the accessible peaks increases with increase in the chain length. Similar observations were reported for high conjugated co- and homo-oligomers of thiophene and phenylene.[13c,14a,b,15] The multi-peaks are usually assigned to multi-electron processes, that is, the formation of radical cation, dication, radical trication, and even higher oxidation states of the oligomers.

In summary, several co-oligomers of biphenyl-oligothiophenes (**2**–**4**) and homo-oligophenylenes (**5**, **6**) were synthesized from a precursor compound 4-bromo-4′-(*n*-butyl)-2,2′-biphenyl **1**, which was synthesized by a direct alkylation using *n*-butyllithium. The oligomers were emissive of violet to blue light with their emission maxima being adjustable by the conjugation length and aromatic structures. The CV studies revealed that all the oligomers were oxidized in solution and some of them displayed multi-electron processes in anodic scan, suggesting the formation of more than one oxidation state.

Acknowledgements

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10. Physical data for compounds **1**–**6**. **1**: A white solid, mp 155 °C. Anal. calcd for $C_{16}H_{17}Br$: C, 66.45; H, 5.93; Br, 27.63. Found: C, 67.00; H, 5.50; Br, 27.18. ^1H NMR ($CDCl_3$): δ 0.98 (t, $^3J_{HH} = 7.2$ Hz, 3H), 1.42 (m, 2H), 1.67 (m, 2H), 2.68 (t, $^3J_{HH} = 7.2$ Hz, 2H), 7.27 (d, $^3J_{HH} = 8.0$ Hz, 2H), 7.49 (d, $^3J_{HH} = 8.8$ Hz, 2H), 7.52 (d, $^3J_{HH} = 8.0$ Hz, 2H), 7.56 (d, $^3J_{HH} = 8.8$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 14.50, 23.02, 34.03, 36.00, 127.36, 127.58, 127.81, 128.02, 128.19, 129.08, 129.40, 132.42. MS (EI) *m*/*z*: 290.0 (M^++1, 40%). **2**: A yellow solid, mp 221 °C. Anal. calcd for $C_{20}H_{20}S$: C, 82.14; H, 6.89; S, 10.96. Found: C, 81.92; H, 6.35; S, 10.40. ^1H NMR ($CDCl_3$): δ 0.96 (t, $^3J_{HH} = 7.2$ Hz, 3H), 1.40 (m, 2H), 1.65 (m, 2H), 2.66 (t, $^3J_{HH} = 7.2$ Hz, 2H), 7.10 (dd, $^3J_{HH} = {}^3J_{HH'} = 4.0$ Hz, 1H), 7.31 (d,

$^{3}J_{HH} = 4.0$ Hz, 1H), 7.37 (d, $^{3}J_{HH} = 3.6$ Hz, 1H), 7.53–7.61 (m, 4H), 7.64 (d, $^{3}J_{HH} = 8.4$ Hz, 2H), 7.70 (d, $^{3}J_{HH} = 8.0$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 14.02, 22.58, 33.89, 35.26, 123.19, 124.96, 126.36, 126.69, 126.91, 127.02, 127.29, 127.68, 127.96, 128.14, 128.93, 139.55. MS (EI) *m*/*z*: 292.5 (M^+, 45%). **3**: A yellow solid, mp 255 °C. Anal. calcd for $C_{24}H_{22}S_2$: C, 76.96; H, 5.92; S, 17.24. Found: C, 76.7; H, 5.6; S, 18.0. ^{1}H NMR ($CDCl_3$): δ 0.95 (t, $^{3}J_{HH} = 7.8$ Hz, 3H), 1.39 (m, 2H), 1.64 (m, 2H), 2.66 (t, $^{3}J_{HH} = 7.8$ Hz, 2H), 7.04 (dd, $^{3}J_{HH} = 4.0$ Hz, $^{3}J_{HH'} = 3.6$ Hz, 1H), 7.06–7.09 (m, 1H), 7.17 (d, $^{3}J_{HH} = 4.0$ Hz, 1H), 7.23 (d, $^{3}J_{HH} = 5.2$ Hz, 1H), 7.28 (d, $^{3}J_{HH} = 5.2$ Hz, 1H), 7.4–7.5 (m, 2H), 7.54 (d, $^{3}J_{HH} = 8.0$ Hz, 2H), 7.60 (d, $^{3}J_{HH} = 8.0$ Hz, 2H), 7.66 (d, $^{3}J_{HH} = 8.0$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 14.06, 22.50, 33.87, 35.06, 123.80, 124.39, 124.61, 126.83, 127.41, 127.80, 128.60, 128.79, 129.00, 131.81, 135.90, 136.35, 137.10, 137.44, 138.53, 141.75. MS (EI) *m*/*z*: 375.2 (M^+, 40%). **4**: A yellow solid, mp 276 °C. Anal. calcd for $C_{28}H_{24}S_3$: C, 73.64; H, 5.29; S, 21.06. Found: C, 73.70; H, 5.00; S, 20.60. ^{1}H NMR ($CDCl_3$): δ 0.95 (t, $^{3}J_{HH} = 7.2$ Hz, 3H), 1.40 (m, 2H), 1.64 (m, 2H), 2.66 (t, $^{3}J_{HH} = 7.2$ Hz, 2H), 7.04 (dd, $^{3}J_{HH} = 4.0$ Hz, $^{3}J_{HH'} = 4.8$ Hz, 1H), 6.8–7.4 (m, 3H), 7.16 (d, $^{3}J_{HH} = 3.6$ Hz, 1H), 7.19 (d, $^{3}J_{HH} = 3.2$ Hz, 1H), 7.23 (d, $^{3}J_{HH} = 5.2$ Hz, 1H), 7.25–7.32 (m, 2H), 7.54 (d, $^{3}J_{HH} = 8.0$ Hz, 2H), 7.61 (d, $^{3}J_{HH} = 8.4$ Hz, 2H), 7.66 (d, $^{3}J_{HH} = 8.0$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 14.12, 22.58, 33.80, 35.20, 124.14, 124.59, 124.81, 124.93, 125.02, 126.32, 127.12, 127.30, 127.80, 128.30, 128.31, 129.34, 133.07, 133.57, 135.26, 136.64, 138.11, 139.53, 140.79, 142.78. MS (EI) *m*/*z*: 456.7 (M^+, 35%). **5**: A white solid, mp 276 °C. Anal. calcd for $C_{28}H_{26}$: C, 92.77; H, 7.23. Found: C, 93.01; H, 7.05. ^{1}H NMR ($CDCl_3$): δ 0.96 (t, $^{3}J_{HH} = 7.2$ Hz, 3H), 1.40 (m, 2H), 1.64 (m, 2H), 2.66 (t, $^{3}J_{HH} = 7.2$ Hz, 2H), 7.29 (d, $^{3}J_{HH} = 8.0$ Hz, 2H), 7.37 (dd, $^{3}J_{HH} = {}^{3}J_{HH'} = 7.8$ Hz, 1H), 7.48 (dd, $^{3}J_{HH} = 8.0$ Hz, $^{3}J_{HH'} = 7.8$ Hz, 2H), 7.56 (d, $^{3}J_{HH} = 8.0$ Hz, 2H), 7.67 (d, $^{3}J_{HH} = 7.8$ Hz, 2H), 7.57–7.87 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 14.33, 22.77, 34.01, 35.64, 123.19, 124.96, 126.36, 126.69, 126.91, 127.02, 127.29, 127.68, 127.96, 128.14, 128.93, 139.55, 127–129 (m). MS (EI) *m*/*z*: 362.5 (M^+, 36%). **6**: A light-yellow semi-solid. Anal. calcd for $C_{41}H_{50}$: C, 90.72; H, 9.28. Found: C, 91.42; H, 9.05. ^{1}H NMR ($CDCl_3$): δ 0.85–0.94 (m, 9H), 1.15–1.28 (m, 16H), 1.53 (m, 2H), 1.78 (m, 2H), 2.09 (m, 2H), 2.16 (m, 2H), 2.79 (t, $^{3}J_{HH} = 7.2$ Hz, 2H), 7.37 (dd, $^{3}J_{HH} = 7.8$ Hz, 2H), 7.45 (d, $^{3}J_{HH} = 8.4$ Hz, 4H), 7.64 (d, $^{3}J_{HH} = 8.0$ Hz, 2H), 7.71–7.79 (m, 3H), 7.83 (d, $^{3}J_{HH} = 7.8$ Hz, 2H), 7.89–7.93 (m, $^{3}J_{HH} = 8.0$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 14.32, 22.76, 22.90, 24.04, 30.05, 31.82, 33.99, 35.63, 40.72, 55.33, 55.49, 119.95, 120.04, 123.16, 124.96, 126.99, 127.14, 127.29, 127.67, 127.80, 129.10, 129.25, 138.84, 141.43, 142.05, 126–128 (m). MS (EI) *m*/*z*: 543.0 (M^+, 30%).

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