

## Synthesis and Characterization of Oligo(2,7-biphenylenylene-(*E*)-vinylene)s

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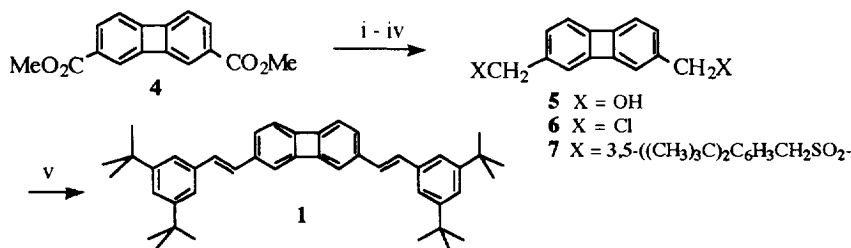
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**Abstract:** The syntheses, spectral behavior, and electrochemical properties of novel oligo(2,7-biphenylenylene-(*E*)-vinylene)s (OBPV's) **1** to **3** have been reported. On the basis of the spectral analysis of OBPV's, a band gap of 2.5 eV for poly(2,7-biphenylenylene-(*E*)-vinylene) was estimated.  
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Because of their unusual electrical and optical properties, conjugative polymers containing aromatic  $(4n+2)\pi$ -electron units as the fundamental building blocks have been extensively studied during the past few decades. However, conjugated polymers based on  $(4n)\pi$ -electron systems are surprisingly rare.<sup>1</sup> To exploit the potential of applying the anti-aromatic  $(4n)\pi$ -electron units to conjugated polymer systems, we have chosen oligo(2,7-biphenylenylene-(*E*)-vinylene)s (OBPV's) **1** to **3** as the models for poly(2,7-biphenylenylene-(*E*)-vinylene) to explore.<sup>2</sup>

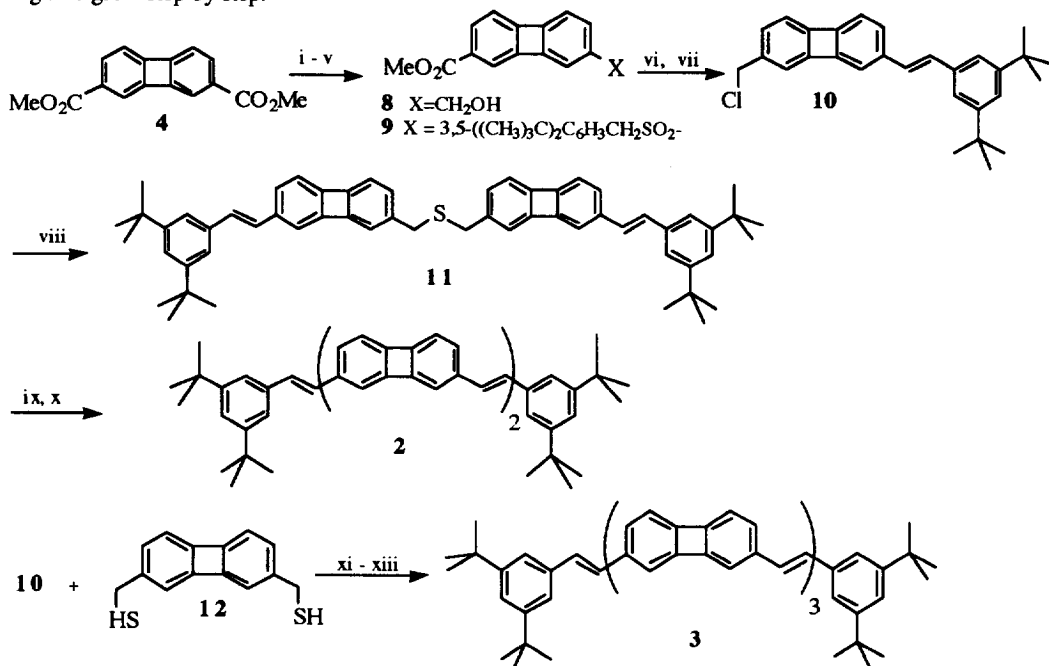
The synthetic sequences leading to OBPV's **1**, **2** and **3** are summarized in Schemes 1 and 2 respectively. Dimethyl(biphenylene-2,7-dicarboxylate) **4** was prepared by a modified Marvel's procedure.<sup>3</sup> LAH reduction of **4**, followed by PCC oxidation led to biphenylene-2,7-dialdehyde. However, Wittig olefination of the dialdehyde only afforded OBPV **1** as a mixture of cis-trans isomers. To obtain OBPV **1** with all trans double bonds, we adopted the recently reported modified Ramberg-Bäcklund reaction as the key synthetic tool.<sup>4,5</sup> Dehydroxy-chlorination of alcohol **5** led to bischloride **6** which was further converted to sulfone **7**, followed by Ramberg-Bäcklund olefination to provide OBPV **1** as a yellowish solid. The (*E*)-configurations of both newly formed double bonds were confirmed by <sup>1</sup>H NMR ( $J = 16.3$  Hz).<sup>6</sup>



Reagents: (i) LiAlH<sub>4</sub>, rt., 95%; (ii) SOCl<sub>2</sub>, rt., 85%; (iii) Cs<sub>2</sub>CO<sub>3</sub>, 3,5-di-*tert*-butylbenzylthiol, 50°C, 73%; (iv) mCPBA, rt., 91%; (v) KOH/Al<sub>2</sub>O<sub>3</sub>, CBr<sub>2</sub>F<sub>2</sub>, 0°C, 80%.

Scheme 1

On the other hand, selective hydrolysis of **4**, followed by  $\text{BH}_3$  reduction gave unsymmetrical methyl 7-hydroxymethylbiphenylene-2-carboxylate **8** (Scheme 2). By using a similar synthetic strategy described for OBPV **1**, alcohol **8** was transformed to sulfone **9** which was further subjected to the modified Ramberg-Bäcklund olefination, during which the carboxylic ester was partially hydrolysed, to provide a mixture of carboxylic acid and methyl ester. The mixture was then converted to chloride **10** via a LAH reduction and  $\text{SOCl}_2$  chlorination sequence. The (*E*)-configuration of the double bond of **10** was again confirmed by  $^1\text{H}$  NMR ( $J = 16.4$  Hz). The successful synthesis of **10** allows us to prepare OBPV **2** and OBPV **3**. In addition, compounds **8** and **10** are important precursors for the iterative approach which may allow the conjugation length to grow step by step.<sup>5</sup>



Reagents : (i)  $\text{KOH}$ ,  $\text{EtOH}$ ,  $40^\circ\text{C}$ ; (ii)  $\text{BH}_3\text{-THF}$ ,  $0^\circ\text{C}$ , 82%; (iii)  $\text{SOCl}_2$ , rt., 85%; (iv)  $\text{Cs}_2\text{CO}_3$ , 3,5-di-*tert*-butylbenzylthiol,  $50^\circ\text{C}$ , 79%; (v) mCPBA, rt., 92%; (vi)  $\text{KOH}/\text{Al}_2\text{O}_3$ ,  $\text{CBr}_2\text{F}_2$ ,  $0^\circ\text{C}$ , (vii) LAH,  $0^\circ\text{C}$ , followed by  $\text{SOCl}_2$ , rt., 75 % from the sulfone **9**; (viii)  $\text{Na}_2\text{S}$ ,  $\text{EtOH}$ , rt., 55%; (ix) Oxone<sup>®</sup>,  $\text{MeOH}$ ,  $\text{CH}_2\text{Cl}_2$ , 82%; (x)  $\text{KOH}/\text{Al}_2\text{O}_3$ ,  $\text{CBr}_2\text{F}_2$ ,  $0^\circ\text{C}$ , 83%; (xi)  $\text{KOH}$ ,  $\text{EtOH}$ ,  $\text{THF}$ , rt., 51%; (xii) Oxone<sup>®</sup>,  $\text{MeOH}$ ,  $\text{CH}_2\text{Cl}_2$ , rt., 51%; (xiii)  $\text{KOH}/\text{Al}_2\text{O}_3$ ,  $\text{CBr}_2\text{F}_2$ ,  $0^\circ\text{C}$ , 93%..

**Scheme 2**

To synthesize OBPV **2**, two equivalents of **10** were coupled together to one equivalent of  $\text{Na}_2\text{S}$  to give disulfide **11**. By employing the aforementioned oxidation and Ramberg-Bäcklund olefination protocol, OBPV **2** was obtained in good yield.<sup>6</sup> It is worth mentioning that Oxone<sup>®</sup> was used, instead of MCPBA as the oxidizing agent in order to prevent from epoxidation of the existent double bonds.<sup>7</sup>

OBPV **3** was assembled in a [1+1+1] coupling fashion (Scheme 2). Thus, two equivalents of **10** were coupled to one equivalent of dithiol **12** to give the corresponding disulfide which was further transformed in a similar way to OBPV **3** as an orange solid.<sup>6</sup>

For OBPV **2**, the olefinic protons of the newly formed double bond are chemically equivalent ( $\delta = 6.84$  ppm); while for OBPV **3**, the  $^1\text{H}$  NMR resonances of the newly formed olefinic protons appeared coincidentally as a singlet at 6.83 ppm. As a consequence, the stereochemical configurations of these newly formed double bonds are difficult to confirm. Nevertheless, both OBPV **2** and OBPV **3** were isolated as a single component from the reaction mixture. Since the modified Ramberg-Bäcklund olefination usually results in *trans* olefins,<sup>4</sup> we tentatively assign (*E*)-configurations to the newly formed double bonds in OBPV **2** and OBPV **3**.

OBPV's **1**, **2** and **3** exhibit a major UV absorption band with the  $\lambda_{\text{max}}$  at 414, 455, and 466 nm, respectively. These absorption maxima show a linear correlation between  $E_n = hc/\lambda_{\text{max}}$  and  $1/n$ ,<sup>9</sup> where  $n$  is the number of the biphenylenylene units in the molecule (Figure 1). It is noteworthy that the  $\lambda_{\text{max}}$  for poly(2,7-biphenylenylene-(*E*)-vinylene) (PBPV,  $n = \infty$ ) can be estimated by extrapolating of the results from OBPV's. Thus, a peak band-gap of 2.5 eV ( $\sim 500$  nm) for PBPV was obtained on the basis of our spectral analysis. This band gap is far smaller than that of poly(*para*-phenylene-(*E*)-vinylene) (3.1 eV).<sup>10</sup> This result implies that PBPV will be a new class of organic conducting materials.

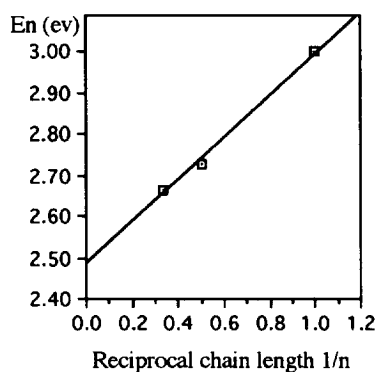


Figure 1: Reciprocal chain length versus absorption maxima for OBPV's **1**, **2**, and **3**.

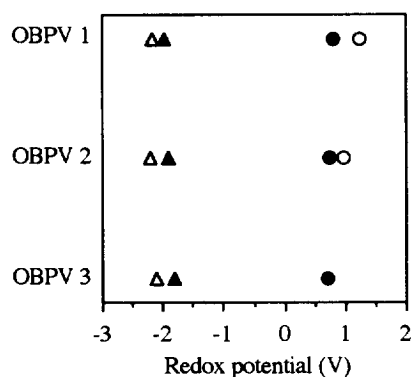


Figure 2: Redox potential diagram for OBPV's **1**, **2**, and **3** ( $\Delta$ : 1st red. potential;  $\Delta$ : 2nd red. potential;  $\circ$ : 1st oxid. potential;  $\circ$ : 2nd oxid. potential).

The electrochemical studies of OBPV's **1** to **3** by cyclic voltammetry suggest that all three oligomers can either be oxidized or reduced reversibly in solution. More interestingly, the potential difference between subsequent oxidations ( $\Delta E_{\text{oxid.}} = E_4 - E_3$  in Table 1)<sup>11</sup> decreases dramatically from OBPV **1** to OBPV **2**, and for OBPV **3**, the first and the second oxidation potentials merge to a single oxidation potential (Figure 2). This can be explained by the delocalization of the positive charges over the conjugative  $\pi$  systems which reduces the Coulombic repulsion between the charges. This observation is complementary to the electrochemical reduction behavior of oligo(*p*-phenylenevinylene)s (OPPV's) of which the potential difference between the first two reduction waves vanishes at a certain conjugation length.<sup>12</sup>

On the other hand, the reduction potential differences ( $\Delta E_{\text{red.}} = E_2 - E_1$  in Table 1)<sup>11</sup> of OBPV's **1** to **3** remain almost unchanged with increasing the conjugation-length. We tentatively interpret these effects as due to the localization of the negative charges of which the electrostatic repulsion could not be relaxed simply by increasing the chain length.

The detailed discussion about the preparation, theoretical studies, electrochemical behavior and fluorescence properties of OBPV's will be reported in due course. Potential applications of these materials for electroluminescent devices are under investigation.

### Acknowledgements

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- All new compounds were characterized on the basis of  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, mass spectral data and elemental analyses, for satisfactory results were obtained. Physical and selected spectral data for: OBPV **1**: yellow crystals: mp 227-229°C;  $\delta_{\text{H}}$  1.36 (s, 36H), 6.66 (d, 2H,  $J = 7.4$  Hz), 6.87 (d, 2H,  $J = 7.5$  Hz), 6.94 (d, 2H,  $J = 16.3$  Hz), 7.01 (s, 2H), 7.03 (d, 2H,  $J = 16.3$  Hz), 7.33 (s, 6H);  $\delta_{\text{C}}$  31.5, 34.9, 114.4, 117.5, 120.9, 122.1, 128.3, 128.4, 129.0, 136.6, 138.2, 149.9, 150.9, 151.1; OBPV **2**: orange crystals, mp > 245°C;  $\delta_{\text{H}}$  1.36 (s, 36H), 6.66 (d, 2H,  $J = 7.2$  Hz), 6.67 (d, 2H,  $J = 7.2$  Hz), 6.84 (d, 2H,  $J = 7.2$  Hz), 6.84 (s, 2H), 6.88 (d, 2H,  $J = 7.2$  Hz), 6.93 (d, 2H,  $J = 16.4$  Hz), 6.96 (s, 2H), 7.04 (s, 2H), 7.05 (d, 2H,  $J = 16.4$  Hz), 7.34 (bs, 6H);  $\delta_{\text{C}}$  31.48, 34.88, 114.19, 114.41, 117.53, 117.62, 120.84, 122.14, 128.09, 128.35, 128.42, 128.55, 129.05, 136.56, 137.87, 138.28, 149.82, 150.16, 150.82, 150.96, 151.11; OBPV **3**: red crystals, mp > 245°C;  $\delta_{\text{H}}$  1.36 (s, 36H), 6.66 (d, 4H,  $J = 7.2$  Hz), 6.68 (d, 2H,  $J = 7.2$  Hz), 6.83 (d, 4H,  $J = 7.2$  Hz), 6.83 (s, 4H), 6.88 (d, 2H,  $J = 7.2$  Hz), 6.93 (d, 2H,  $J = 16.2$  Hz), 6.95 (s, 2H), 6.83 (s, 2H), 7.04 (d, 2H,  $J = 16.2$  Hz), 7.04 (s, 2H), 7.33 (s, 4H), 7.34 (s, 2H);  $\delta_{\text{C}}$  (only 26 carbon signals were observed for OBPV **3**) 31.48, 34.89, 114.26, 114.31, 114.43, 117.52, 117.61, 120.84, 122.14, 128.05, 128.16, 128.34, 128.44, 128.59, 128.64, 129.08, 136.57, 137.84, 137.96, 138.31, 149.81, 150.08, 150.19, 150.81, 150.90, 151.13.
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- Table 1.** Oxidation and reduction potentials (V) of **1**, **2**, and **3** vs Ag/AgCl electrode, scan rate = 100 mV/s, calibration vs ferrocene, in  $\text{CH}_2\text{Cl}_2$  containing TBABF<sub>4</sub> (0.1M) as the supporting electrolyte.

	Reduction			Oxidation	
	$E_1$	$E_2$	$\Delta E_{\text{red.}} = E_2 - E_1$	$E_4$	$\Delta E_{\text{oxid.}} = E_4 - E_3$
OBPV <b>1</b>	-2.16	-1.96	0.20	0.82	0.41
OBPV <b>2</b>	-2.20	-1.90	0.30	0.73	0.20
OBPV <b>3</b>	-2.10	-1.80	0.30	-	-

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