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Synthesis and Characterization of Oligo(2,7-biphenylenylene-*(E)*-vinylene)s: Conjugated Oligomers Containing Antiaromatic 12-π Electron Units

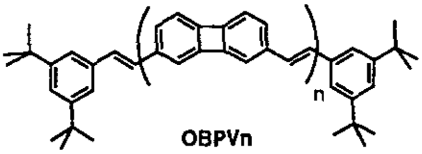
Chi-Yuen Kwong[b] (鄺志遠), Tze-Lock Chan[b] (陳子樂), Hak-Fun Chow[b] (周克勳),
Shi-Chun Lin[a] (林世崇) and Man-kit Leung*[a] (梁文傑)
[a]*Department of Chemistry, National Taiwan University, Taipei, Taiwan, R.O.C.*
[b]*Department of Chemistry, The Chinese University of Hong Kong, Shatin, Hong Kong*

The syntheses and the electronic properties of oligo(2,7-biphenylenylene-(*E*)-vinylene)s are reported. According to our spectral analysis, a limit of 2.5 ev for the peak band-gap of poly(2,7-biphenylenylene-(*E*)-vinylene)s is estimated. In addition, we discovered that oligo(2,7-biphenylenylene-(*E*)-vinylene)s are amphoteric and can be either oxidized or reduced electrochemically.

INTRODUCTION

Due to their unusual electrical and optical properties, conjugated polymers containing aromatic 6π-electron units as the fundamental building blocks have intrigued polymer and organic chemists during the past few decades.[1-9] Many other conjugated oligomers or polymers containing aromatic $(4n+2)\pi$-electron systems, such as naphthalene, anthracene, and fused-ring heterocycles have also been developed. However, conjugated polymers based on $(4n)\pi$-electron systems are surprisingly rare.[9,10] To exploit the potential of applying the unusual electrochemical properties of antiaromatic $(4n)\pi$-electron units to conjugated polymer systems, we are interested in developing a series of novel polymers that contain biphenylene or its derivatives as the building blocks.

Biphenylene[11] is a planer, radialene-like molecule that contains 12π-electrons. Unlike cyclobutadiene and benzocyclobutadiene, biphenylene is thermally and chemically stable. Spectroscopic evidence and the chemical behavior of biphenylene suggest that the two 6π-electron systems interact with each other in a special way. For example, the HOMO-LUMO gap of biphenylene is far smaller than that of biphenyl. The UV spectrum of biphenylene shows two main bands at 235-260 nm and 330-370 nm, which resembles the spectrum of anthracene more than that of biphenyl. Biphenylene can be either oxidized to form monocation-radical or dication, or reduced to form monoanion-radical or dianion.[12] These electrochemical properties are suitable for charge-storage purposes. In addition, biphenylene photochemically dimerizes to provide a three dimensional conjugated structure.[13] This interesting photochemical behavior may provide an entry for chemists to synthesize three dimensional conjugated polymeric networks. In our effort to develop different kinds of novel conjugated polymers,[14] we have chosen oligo(2,7-biphenylenylenevinylene)s (**OBPVn**) as the models for poly(2,7-biphenylenylenevinylene)s (**PBPV**) to explore.[14b]



OBPVn

RESULTS AND DISCUSSION

Since our target molecules require connection points at the 2 and 7 positions of the biphenylene units, we began our syntheses with dialkyl 2,7-biphenylenedicarboxylates such as **5a** and **5b** (Scheme I). To prepare **5a** or **5b** on a large-scale, a modified Marvel's approach was adopted in our studies.[15] Nickel(0)-catalyzed homocoupling of aryl halide **1** led to biphenyl **2** in high yield.[16,17] Since the reaction requires anhydrous conditions, the synthesis works best on a medium scale. Nevertheless, we successfully carried out the reaction using up to 100 g of the starting methyl *p*-chlorobenzoate (**1**) to give the desired **2** in 80% yield. Iodination at the $2,2'$-positions was facilitated by Ag_2SO_4 with I_2 in concentrated H_2SO_4. The procedures in the literature work well in this case except that the reaction actually gives diacid **3** as the product. Because of its low solubility and high polarity, formation of the diacid **3** is hard to monitor by TLC analysis during the course of reaction. Therefore, the reaction conditions had to be pre-optimized in order to minimize the extent of incomplete or excessive iodination. The

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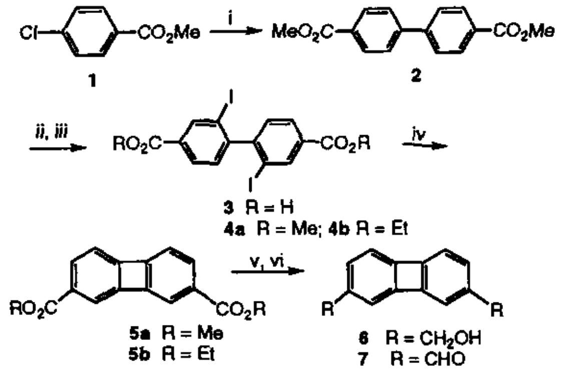
Dedicated to Professor Yu-Shia Cheng on the occasion of her 65th birthday.

Scheme I



Reagents: i, $Ni(PPh_3)_2Cl_2$, Zn, Bu_4NI; ii, Ag_2SO_4, I_2; iii, MeOH or EtOH, H^+; iv, Cu, 250 °C; v, $LiAlH_4$; vi, PDC

diacid was then esterified to diesters **4a** and **4b** respectively, using methanol or ethanol in acidic conditions.

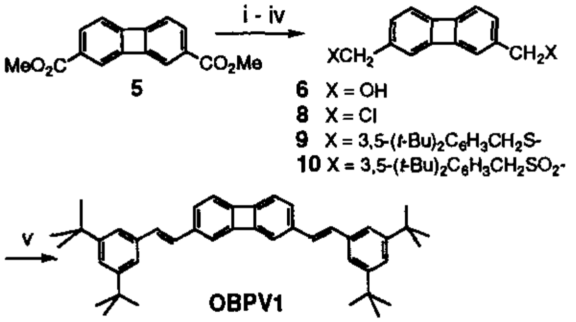
The key-step in synthesizing **5a** and **5b** is the Ullman coupling reaction. In Marvel's route, this intramolecular coupling reaction was effected by refluxing **4a** with copper powder in dry pyridine. However, the reported procedure failed to give any desired product in our experiments. Modification of the procedures by changing the solvent to DMF, DMSO, or DMA only led to **5a** in poor yields (< 15%). In addition, ultrasound irradiation is ineffective in our reaction conditions.[18] Fortunately, we discovered that the Ullman reaction proceeds smoothly at high temperature in neat conditions. Heating of a mixture of copper powder and **4a** or **4b** at 250 °C for 10 hours under dry nitrogen led to the corresponding **5a** or **5b** in satisfactory yields (~50%). Commercially available copper powder can also be used on condition that the copper powder has been prewashed with acetone and dried under vacuum for at least 24 hours. Otherwise, protio-deiodination of the diiodo esters **4** occurs, giving back significant amounts of the deiodinated esters as side products. LAH reduction of **5**, followed by PCC oxidation led to dialdehyde **7**.

Synthesis of OBPV1

OBPV1 serves as the prototype of poly(2,7-biphenylenylene-(*E*)-vinylene)s. It is an important basis for establishing a structure-properties relationship with its higher homologues by comparison. The 3,5-di-*tert*-butylphenyl group serves as the solubilization appendage for the system since the desired conjugated biphenylene oligomers are anticipated to have low solubility in most organic solvents. It also acts as a stable terminal group of the system, which is adequately inert to most reactions involved.

OBPV1 was first prepared by Wittig olefination of biphenylene-2,7-dicarbaldehyde **7**, affording a mixture of *cis-trans* isomers. In an effort to obtain **OBPV1** with all trans double bonds, we adopted the recently reported modified Ramberg-Bäcklund reaction[19] as the key synthetic tool (Scheme II). LAH reduction of **5**, followed by dehydroxychlorination of alcohol **6** led to dichloride **8**, which was converted to the desired **OBPV1** in a three-step reaction sequence of sulfide formation, oxidation, and Ramberg-Bäcklund olefination.

Scheme II



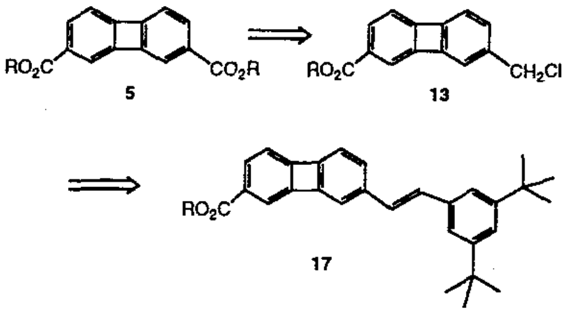
Reagents: i, $LiAlH_4$; ii, $SOCl_2$; iii, 3,5-(t-Bu)$_2C_6H_3CH_2SH$, Cs_2CO_3; iv, *m*CPBA; v, KOH/Al_2O_3, CBr_2F_2, 0 °C

The formation of bissulfide **9** was effected by heating the dichloride **8** and 3,5-di-*tert*-butylbenzylthiol with Cs_2CO_3 as the base. *m*CPBA oxidation of the bissulfide **9**, followed by Ramberg-Bäcklund olefination of the sulfone **10** led to **OBPV1**. Although Oxone® has been extensively used in our laboratory as the oxidant for thioethers,[19,20] oxidation by *m*CPBA is in this case superior for a shorter reaction time and higher yield compared to Oxone®. The modified Ramberg-Bäcklund procedure employing alumina-supported KOH and CBr_2F_2 has been extensively used in generating stilbenoid type compounds with excellent (*E*)-stereoselectivity.[14,19] In our cases, we found that the reaction is equally effective in generating an (*E*)-double bond between the biphenylene and the benzene units. The (*E*)-configurations of both newly formed double bonds were confirmed by ^{1}H NMR (J = 16.3 Hz). Conjugation throughout the phenyl rings and the biphenylene unit is also indicated by its greenish fluorescent properties.

Synthesis of OBPV2 and OBPV3

After having **OBPV1** in hand, we started to synthesize **OBPV2** and **OBPV3**. In order to obtain these two compounds, we have to first secure the synthesis of the bifunctional intermediate **13** (Scheme III), an important building block for higher homologues of **OBPVn**. The $-CH_2Cl$ group on **13** could then be converted to a styryl component using our previously described Ramberg-Bäcklund olefina-

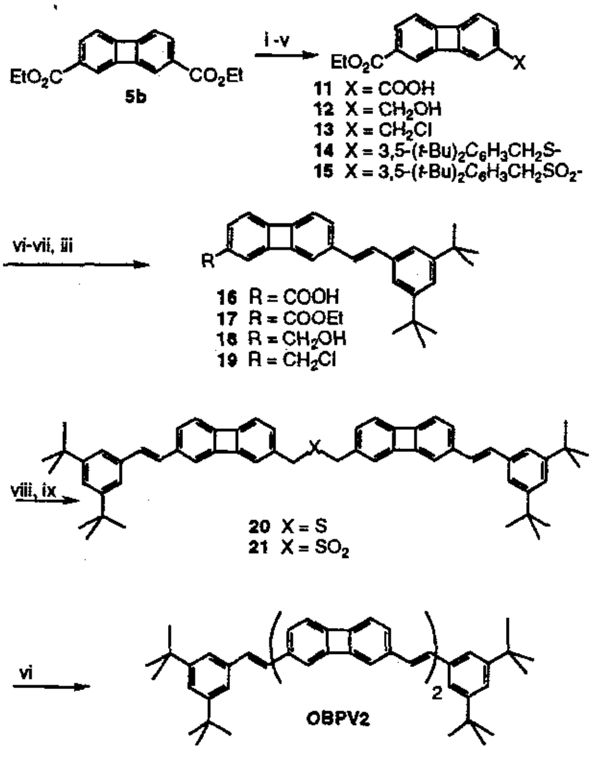
Scheme III



tion strategy.

The synthesis of **OBPV2** is summarized in Scheme IV. Selective hydrolysis of diester **5b**, using KOH in EtOH/THF at 40 °C, afforded the potassium salt of monoacid-ester **11**. The use of diethyl ester **5b** is preferred in this case because of its superior solubility in EtOH/THF. Due to the low solubility of the potassium salt of **11**, it precipitated from the solution during hydrolysis and hence prevented **11** from further hydrolysis. Neutralization of the potassium salt gave **11** in good yield. Chemoselective reduction of the -COOH group was achieved by using excess amounts of BH_3·THF complex at 0 °C, yielding **12** in moderate yield. The use of excess BH_3·THF complex greatly accelerates the reduction rate of the -COOH functionality, leaving the ester group untouched.

Scheme IV



Reagents: i, KOH in THF-EtOH; ii, BH_3-THF; iii, $SOCl_2$; iv, 3,5-(*t*-Bu)$_2C_6H_3CH_2SH$, Cs_2CO_3; v, *m*CPBA; vi, KOH/Al_2O_3, CBr_2F_2, 0 °C; vii, $LiAlH_4$; viii, Na_2S; ix, Oxone®

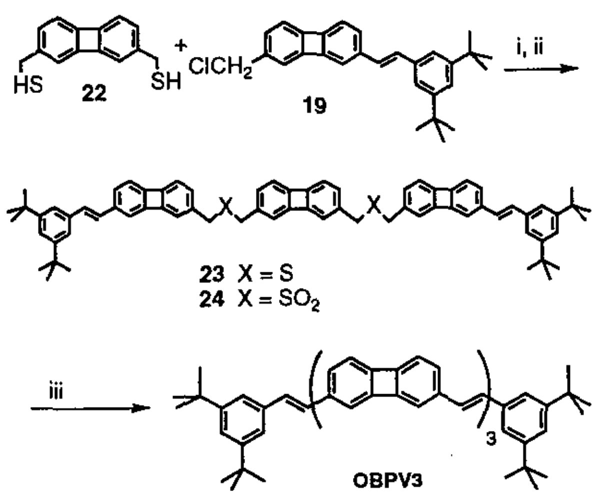
The -CH_2OH functionality was then converted to a styryl component through a dehydroxy-chlorination, sulfide formation, oxidation, and Ramberg-Bäcklund olefination sequence. Since the Ramberg-Bäcklund reaction was performed under basic conditions, the desired ester **17** was found to be partially hydrolysed during the course of olefin formation, affording a mixture of **16** and **17** as the final products. Fortunately, both products could be directly reduced to alcohol **18** by $LiAlH_4$. The presence of an (*E*)-carbon-carbon double bond was clearly demonstrated by the coupling constant of the vinylic protons ($J = 16.2$ Hz) of **18**.

Alcohol **18** is highly acid sensitive and decomposes quickly even in the presence of trace amounts of acetic acid, giving a complicated mixture of unidentified compounds. Although the mechanism is uncertain, decomposition has not been observed in alcohols **6** and **12**. Therefore, we tentatively attribute the decomposition to the extended conjugation of this alcohol. Chlorination of alcohol **18** was effected by $SOCl_2$ at 0 °C. Because of the similar conjugation effects, chloride **19** also decomposes in basic medium as well as on silica gel. Thus **19** could only be partially purified by flash chromatography through a short column of silica gel. Since the alcohol **18** and the chloride **19** slowly decompose even at -20 °C, they were freshly prepared before use in our studies.

Making use of chloride **19** as the building block, **OBPV2** and **OBPV3** were constructed on the basis of our Ramberg-Bäcklund olefination strategy (Scheme IV and Scheme V). In the synthesis of **OBPV2**, sulfide **20** was obtained through a coupling reaction of chloride **19** with Na_2S in THF/EtOH. In the synthesis of **OBPV3**, bissulfide **23** was obtained through a coupling reaction of chloride **19** with dithiol **22** in benzene, using DBU as the base. Chemoselective oxidations of sulfides **20** and **23** to the corresponding sulfones **21** and **24** were achieved by Oxone® in CH_2Cl_2-MeOH, with the styryl groups remaining unreacted. Although these sulfones are much less soluble than the sulfide precursors, they are still soluble enough for chromatographic purifications. Finally, olefination of these sulfones gave the corresponding fully conjugated **OBPV2** and **OBPV3**.

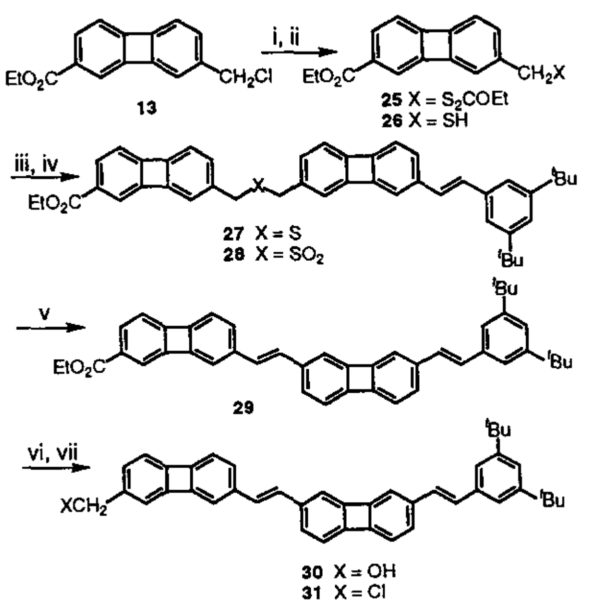
For **OBPV2**, the olefinic protons of the newly formed double bond are chemically equivalent ($\delta = 6.84$ ppm); while for **OBPV3**, the ^1H NMR resonances of the newly formed olefinic protons appeared coincidentally as a singlet at 6.83 ppm. As a consequence, the stereochemical configu-

Scheme V



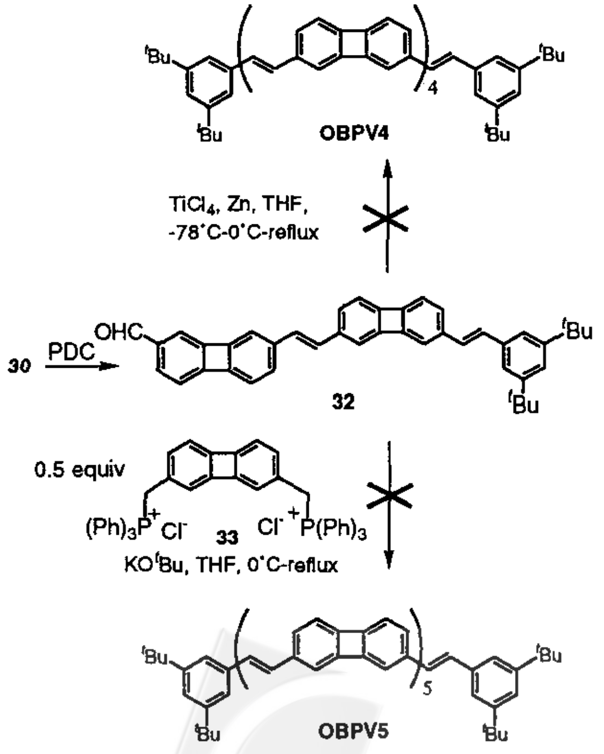
Reagents: i, DBU; ii, Oxone®; iii, KOH/Al_2O_3, CBr_2F_2, 0 °C

Scheme VI



Reagents: i, CS_2, KOH, EtOH in THF, reflux; ii, NaOEt, 0 °C; iii, **19**, DBU, rt; iv, Oxone®; v, KOH/Al_2O_3, CBr_2F_2, 0 °C; vi, $LiAlH_4$; vii, $SOCl_2$

Scheme VII



rations of these newly formed double bonds are difficult to confirm. Nevertheless, both **OBPV2** and **OBPV3** were isolated as a single component from the reaction mixture. Since the modified Ramberg-Bäcklund olefination usually results in *trans* olefins,[14,19] we tentatively assign (*E*)-configurations to the newly formed double bonds in **OBPV2** and **OBPV3**.

Synthesis of the building block 26 and 31

To synthesize the higher homologues of **OBPVn**, a building block **26** bearing both of a mercapto functionality and an ester group is desired (Scheme VI). On treatment of chloride **13** with potassium ethyl xanthate followed by ethanolysis of the resulting xanthate ester **25**, thiol **26** was obtained in reasonable yields. With thiol **26** in hand, we extended the conjugation of **19** by addition of one more biphenylenylenevinylene unit, providing **31** through a five-step iterative sequence. After the reactions of sulfide formation, oxidation, Ramberg-Bäcklund olefination, LAH reduction and $SOCl_2$ chlorination, the crude chloride **31** was obtained in 43% yield. Again, alcohol **30** and chloride **31** are unstable and were used immediately after preparations.

Attempted synthesis of OBPV4 and OBPV5

By following the previous routes, we attempted to couple chloride **31** by Na_2S and dithiol **22** but failed (Scheme VII). TLC showed slow conversion of **31** to a complicated mixture which could not be separated by chromatography. More frustrating are the facts that other types of thiolation were also unsuccessful. For example, similar results were obtained in its reaction with thiourea. After a number of unsuccessful trials, the route of thiolation of **31** was abandoned. Attracted by the smooth PDC oxidation of the alcohol **30** to the corresponding aldehyde **32**, two methods utilizing carbonyl compounds for generating olefins were attempted. They were the reductive coupling of **32** by the

McMurry procedure[21,22] and the Wittig reaction with the bisphosphonium salt **33**.[9,23-26] Unfortunately, though performed under nitrogen and dark conditions, both reactions were unsuccessful. In the case of the reductive coupling using $TiCl_4$ with Zn as the reducing agent, the reaction proceeded very slowly to give a very complicated mixture whereas in the Wittig reaction, the aldehyde **32** remained unreacted even at refluxing temperature for 2 days. The unusual chemical behaviors of **30** and **32** are perplexing. Whatever electronic effects are conferred on them by the extended conjugation of two biphenylene units and one benzene unit are puzzling to us. Further investigation is necessary for unveiling this mystery.

Electronic properties of OBPVn's

OBPVn's (n = 1-3) show two major bands at 310-330 nm (Band I) and 450-500 nm (Band II) in the UV-VIS spectra (Fig. 1). While the absorption maxima of the first band do not shift in respect to the extent of conjugation, significant bathochromic shifts are observed in the second band from **OBPV1** (λ_{max} = 414 nm) to **OBPV2** (λ_{max} = 455 nm), and to **OBPV3** (λ_{max} = 466 nm). Although the bathochromic shift in the second absorption band from **OBPV2** to **OBPV3** is not as significant as from **OBPV1** to **OBPV2**, it is strong evidence of the effective electron delocalization between the biphenylene chromophores. More interesting is the linear relationship between the parameter $E_n = hc/\lambda_{max}$ and 1/n,[26] where n is the number of the biphenylene units in the **OBPVn** molecule and λ_{max} is the corresponding absorption maxima in band II (Fig. 2). This observation is consistent with the prediction based on the empirical equation $E_n = E_\infty + E/n$. Accordingly, the λ_{max} for poly(2,7-biphenylenylene-(*E*)-vinylene) (*PBPV*, n = ∞) can be estimated by extrapolating of the results from **OBPVn**'s. Thus, a peak band-gap of 2.5 eV (~ 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).[27,28] This result implies that **PBPV** could be a new class of organic conducting materials.

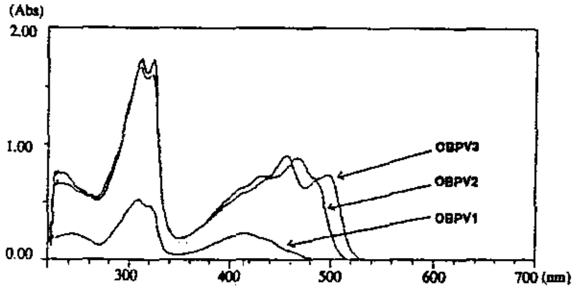


Fig. 1. UV-Visible spectra of **OBPVn** in CH_2Cl_2.

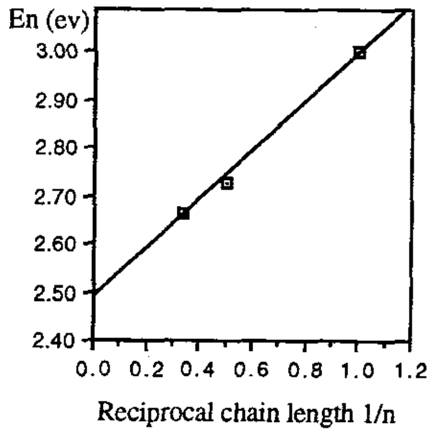


Fig. 2. Reciprocal chain length versus E_n for **OBPV1**, **OBPV2** and **OBPV3**.

Red shifts are also observed in the colors of solid **OBPVn**'s (Table 1). The red shifts from solution samples to solid samples could be attributed either to the restricted rotational and vibrational movements of the molecular framework in the solid state, creating a more effective π-overlapping between the chromophores in the chains which enhances the conjugation in the system,[29] or intermolecular ground-state interactions of the conjugated systems which may lead to absorption band broadening.[28]

Redox activities of **OBPVn**'s are demonstrated by cyclic voltammetry and the redox data obtained are shown in Table 2. The electrochemical studies of **OBPV1** to **OBPV3** revealed that all three oligomers can either be oxidized or reduced quasi-reversibly in solution. More interestingly, the potential difference between subsequent oxidations ($\Delta E_{oxid.} = E_4 - E_3$ in Table 2) decreases dramatically from **OBPV1** to **OBPV2**, and for **OBPV3**, the first and the second oxidation potentials merge to a single oxidation potential (Fig. 3). This can be explained by the delocalization of the positive charges over the conjugative π 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.[30]

Table 1. Comparison of the Color of **OBPVn** in Solution and in Solid State

	Solution[a]	Solid State
OBPV1	yellow	yellow
OBPV2	yellow	orange
OBPV3	orange	red

[a] in CH_2Cl_2

Table 2. Oxidation and Reduction Potentials (V)[a] of **1**, **2** and **3**

	Reduction potential[b]			Oxidation potential[c]		
	E_1	E_2	$\Delta E_{red.} = E_2 - E_1$	E_3	E_4	$\Delta E_{oxid.} = E_4 - E_3$
OBPV1	-2.16	-1.96	0.20	0.82	1.23	0.41
OBPV2	-2.20	-1.90	0.30	0.73	0.96	0.20
OBPV3	-2.10	-1.80	0.30	0.72	-	-

[a] vs Ag/AgCl electrode, scan rate = 100 mV/s, calibration vs ferrocene, in CH_2Cl_2 containing $TBABF_4$ (0.1 M) as the supporting electrolyte. [b] Measured at -78 °C. [c] Measured at 20 °C.

On the other hand, the reduction potential differences ($\Delta E_{red.} = E_2 - E_1$ in Table 2) of **OBPV1** to **OBPV3** 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.

Although we cannot explain the above phenomena on a theoretical basis, the above explanations are consistent with the behavior of the biphenylene dication and dianion. Previous experiments demonstrated that the positive charges on the biphenylene dication are delocalized relatively evenly over the structure[31] while the negative charges on the biphenylene dianion are more localized on the central four membered ring unit because of the counter-ion effects.[32] Similar negative charge localization effects also occur in the system of cyclooctatetraenylene vinylenes.[33]

EXPERIMENTAL SECTION

General Experimental

Melting points were measured on a Reichert Microscope apparatus and are uncorrected. UV-VIS spectra were recorded on a Hitachi U-3300 spectrophotometer using dichloromethane as the solvent. IR spectra were recorded on a Nicolet (205) FT-IR spectrophotometer as neat film or KBr plate. ^1H NMR spectra were recorded on a Bruker WM 250 (250 MHz) spectrometer. Chemical shifts (δ) are reported in ppm downfield from internal standard tetramethylsilane and coupling constants (J) are reported in hertz (Hz). ^{13}C spectra were either obtained on a Bruker WM 250 (62.9 MHz) or a Bruker ARX 500 (125 MHz) spectrometer. Cyclic voltammetry was performed on a EG&G PAR Model 173 Potentiostat, Model 175 Universal Programmer, and Model RE0089 X-Y Recorder. Mass spectra were determined using a VG Micromass 7070F instrument. Elemental analyses were carried out at MEDAC Ltd., Department of Chemistry, Brunel University, United Kingdom. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Bis(triphenylphosphine)nickel(II) chloride,[16] dimethyl 4,4′-biphenyldicarboxylate,[17] 3,5-di-*tert*-butylbenzylthiol,[14] and KOH/Al_2O_3 (1:2, *w/w*) catalyst[19] for Ramberg Bäcklund reactions were prepared according to methods in the literature. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. Dichloromethane and benzene were distilled over phosphorous pentaoxide and stored over 4Å molecular sieves.

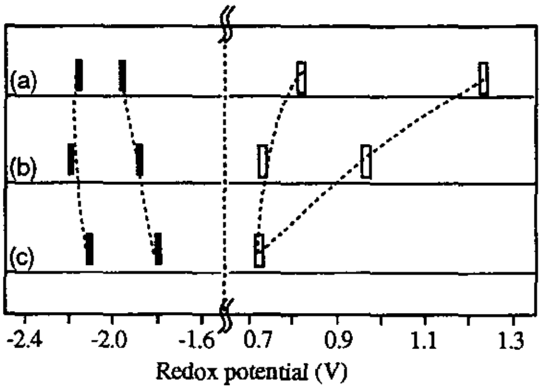


Fig. 3. Redox potential diagram for **OBPVn**: (a) **OBPV1**; (b) **OBPV2**; (c) **OBPV3**.

Representative Synthetic Procedure for Dialkyl diiodobiphenyl-4,4′-dicarboxylates

Dimethyl 2,2′-diiodobiphenyl-4,4′-dicarboxylate (4a)[15b]

To a vigorously stirred solution of dimethyl biphenyl-4,4′-dicarboxylate (**2**) (46.9 g, 0.17 mol) and Ag_2SO_4 (159.5 g, 0.51 mol) in H_2SO_4 (98%, 570 mL) was added I_2 (103.2 g, 0.41 mol) in one lot. With the flask stoppered, the mixture was heated at 80 °C for 36 h. The resulting purple reaction mixture was poured into diluted Na_2SO_3 solution (2 L) at 0 °C, and the yellow suspension was extracted with ethyl acetate. The combined organic extract was washed with water, dried over Na_2SO_4, and concentrated to give a white solid which was esterified in refluxing methanol (600 mL) for 24 h, using conc. sulfuric acid (20 mL) as a catalyst. After removal of methanol (400 mL), subsequent work-up of the crude mixture by extraction with CH_2Cl_2, washing with aqueous $NaHCO_3$, drying over anhydrous Na_2SO_4, and concentration under reduced pressure gave essentially pure **4a** (80.0 g, 86%) as a white crystals: mp 155-156 °C (methanol) [lit.[35d] 152-153 °C (methanol)]; ^1H NMR ($CDCl_3$, 250 MHz) δ 3.95 (s, 6H), 7.29 (d, 2H, J = 8.0 Hz), 8.13 (dd, 2H, *J* = 1.6, 8.0 Hz), 8.64 (d, 2H, *J* = 1.6 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 52.4, 98.3, 129.3, 129.5, 131.5, 140.2, 152.4, 165.2.

Diethyl 2,2′-diiodobiphenyl-4,4′-dicarboxylate (4b)

By the representative procedure, dimethyl biphenyl-4,4′-dicarboxylate (**2**) (46.9 g, 0.17 mol), silver sulfate (159.5 g, 0.51 mol), iodine (103.2 g, 0.41 mol) in conc. sulfuric acid (570 mL), gave essentially pure **4b** (80.0 g, 86%) as white crystals: mp 72-75 °C (ethanol); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.35 (t, 6H, *J* = 7.2 Hz), 4.34 (q, 4H, *J* = 7.2 Hz), 7.17 (d, 2H, *J* = 7.9 Hz), 8.03 (dd, 2H, *J* = 1.6, 7.9 Hz), 8.53 (d, 2H, *J* = 1.6 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 14.3, 61.5, 98.3, 129.2, 129.5, 131.9, 140.1, 152.3, 164.7; MS (EI) 550 (M^+, 6), 423 (100), 395 (26), 367 (25); IR (KBr) 1722 cm^{-1}. Calcd. for $C_{18}H_{16}O_4I_2$: C, 39 29; H, 2.93. Found: C, 38.83; H, 2.82.

Representative Synthetic Procedure for Dialkyl 2,7-biphenylenedicarboxylates

Dimethyl 2,7-biphenylenedicarboxylate (5a)[15b]

A mixture of the diester **4a** (10.0 g 18.0 mmol) and copper powder (40.0 g, 630 mmol) was heated at 250 °C under nitrogen for 12 h. Upon cooling, the resulting mixture was extracted with CH_2Cl_2. The organic extract was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and flash chromatographed on silica gel, using hexane/CH_2Cl_2 (3:1) as eluent to yield a yellow solid. Further recrystallization of this material from toluene gave pure **5a** (3.2 g, 58%) as bright yellow crystals: mp 200-202 °C (toluene) [lit.* 190-193 °C (acetone)]; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.87 (s, 6H), 6.76 (dd, 2H, *J* = 0.75, 7.3 Hz), 7.25-7.27 (m, 2H), 7.61 (dd, 2H, *J* = 1.2, 7.3 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 52.0, 117.8, 118.0, 131.2, 132.3, 150.4, 154.6, 166.3; MS *m/e* (% relative intensity) (EI) 268 (M^+, 100), 237 (69), 209 (40), 178 (14), 150 (24).

Diethyl 2,7-biphenylenedicarboxylate (5b)

By the representative procedure, diester **4b** (10.0 g 18.0 mmol) and copper powder (40.0 g, 630 mmol) was reacted to gave **5b** (3.2 g, 56%) as bright yellow crystals: mp 105-107 °C (hexane); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.37 (t, 6H, *J* = 7.1 Hz), 4.33 (q, 4H, *J* = 7.1 Hz), 6.79 (dd, 2H, *J* = 0.9, 7.3 Hz), 7.31-7.32 (m, 2H), 7.64 (dd, 2H, *J* = 1.3, 7.3 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 15.0, 61.8, 118.6, 118.7, 132.1, 132.9, 151.0, 155.2, 166.6; MS *m/e* (% relative intensity) (EI) 296 (M^+, 100), 268 (25), 251 (42), 240 (29), 223 (49), 195 (18); IR (KBr) 1721, 1712 (C=O) cm^{-1}. Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.81; H, 5.44.

2,7-Bis(hydroxymethyl)biphenylene (6)

To a solution of the diester **4a** (500 mg, 1.9 mmol) in dry THF (100 mL) at 0 °C was added $LiAlH_4$ (300 mg, 7.9 mmol). After stirring for 5 h at r.t., the reaction mixture was quenched with water, and the aqueous mixture was extracted with ethyl acetate. The combined organic extract was dried over anhydrous Na_2SO_4 and concentrated to give a white solid which was purified by flash chromatography on silica gel, using hexane/EtOAc (1:2) as eluent to afford **4a** (380 mg, 95%) as colorless crystals: mp 174-175 °C; ^{1}H NMR (acetone-d_6, 250 MHz) δ 4.30 (t, 2H, *J* = 5.8 Hz), 4.55 (d, 4H, *J* = 5.8 Hz), 6.77 (d, 2H, *J* = 7.7 Hz), 6.89-6.91 (m, 4H); ^{13}C NMR (acetone-d_6, 125 MHz) δ 64.8, 117.4, 117.5, 126.7, 143.8, 150.3, 151.7; MS *m/e* (% relative intensity) (EI) 212 (M^+, 100), 195 (22), 181 (39), 165 (43), 152 (50); IR (KBr) 3600-3200 (-OH) cm^{-1}. Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70. Found: C, 78.94; H, 5.73.

2,7-Bis(chloromethyl)biphenylene (8)

With the content protected against atmospheric moisture by a $CaCl_2$ drying-tube, thionyl chloride (0.2 mL, 2.7 mmol) was added to a solution of diol **6** (100 mg, 0.48 mmol) in dry CH_2Cl_2 (20 mL) at 0 °C. After refluxing for 3 h, the reaction mixture was quenched with water and extracted with CH_2Cl_2. The combined organic extract was dried over anhydrous Na_2SO_4 and concentrated and flash chromatographed on silica gel, using hexane/CH_2Cl_2 (4:1) as eluent to afford **8** (100 mg, 83%) as white crystals: mp 104-107 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 4.38 (s, 4H), 6.54 (d, 2H, *J* = 7.0 Hz), 6.71 (s, 2H), 6.77 (d, 2H, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 46.9, 117.3, 118.1, 128.8, 137.9, 150.6, 151.1; MS *m/e* (% relative intensity) (EI) 252 ($M+4^+$, 3.5), 250 ($M+2^+$, 21), 248 (M^+, 31), 213 (100), 178 (70). Anal. Calcd. for $C_{14}H_{10}Cl_2$: C, 67.49; H, 4.05. Found: C, 66.97; H, 4.22.

2,7-Bis(3′,5′-di-*tert*-butylbenzylthiomethyl)biphenylene (9)

To a suspension of 3,5-di-*tert*-butylbenzylthiol (1.2 g, 5.0 mmol) and cesium carbonate (1.7 g, 5.1 mmol) in dry THF (10 mL) at 45 °C was added dichloride **8** (500 mg, 2.0 mmol) in dry THF (15 mL). After stirring for 20 h at 50 °C under N_2, the reaction mixture was quenched with water and the aqueous mixture was extracted with CH_2Cl_2. The combined organic extract was dried over anhydrous Na_2SO_4 and concentrated to give a thick oil which was purified by flash chromatography on silica gel, using hexane/ether (50:1) as eluent to afford bissulfide **9** (950 mg, 73%) as colorless oil: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.31 (s, 36H), 3.41 (s, 4H), 3.63 (s, 4H), 6.55 (d, 2H, *J* = 7.2 Hz), 6.59 (d, 2H, *J* = 7.2

Hz), 6.66 (s, 2H), 7.13 (d, 4H, J = 1.8 Hz), 7.30 (t, J = 1.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.5, 34.8, 36.2, 36.5, 116.7, 118.6, 120.9, 123.3, 128.6, 137.0, 138.6, 149.4, 150.9, 151.2; HRMS *m/e* (EI) Calcd. for $C_{44}H_{56}S_2$: 648.3824. Found: 648.3880.

2,7-Bis(3′,5′-di-*tert*-butylbenzylsulfonylmethyl)-biphenylene (10)

To a solution of bissulfide **9** (850 g, 1.3 mmol) in CH_2Cl_2 (20 mL) was added *m*CPBA (2.0 g, 5.8 mmol) at 0 °C. After stirring for 20 h at r.t. under nitrogen, the resulting solution was washed with NaOH solution (1 M, 25 mL × 2) and water. The organic solution was dried anhydrous Na_2SO_4 and concentrated to give a white solid which was purified by flash chromatography on silica gel, using hexane/EtOAc/CH_2Cl_2 (6:1:1) as eluent to afford bissulfone **10** (850 mg, 91%) as white crystals: mp > 245 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.34 (s, 36H), 3.91 (s, 4H), 4.19 (s, 4H), 6.70-6.73 (m, 6H), 7.23-7.24 (bs, 4H), 7.45 (bs, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.4, 34.9, 58.2, 58.9, 117.8, 120.1, 123.0, 125.1, 126.8, 128.3, 131.7, 151.0, 151.2, 151.6; MS *m/e* (% relative intensity) (EI) 712 (M^+, 1), 585 (6), 446 (18), 445 (54), 382 (31), 381 (95), 204 (17), 203 (100), 179 (22), 178 (85); IR (KBr) 1314, 1115 cm^{-1}. Anal. Calcd. for $C_{44}H_{56}O_4S_2$: C, 74.12; H, 7.92. Found: C, 74.25; H, 8.09.

2,7-Bis[(*E*)-3′,5′-di-*tert*-butylstyryl]biphenylene (OBPV1)

To a vigorously stirred solution of bissulfone **10** (300 mg, 0.4 mmol) in dry THF (10 mL) at 0 °C under nitrogen was added KOH/Al_2O_3 (1/2 w/w, 4.2 g). CBr_2F_2 (0.3 mL, 3.3 mmol) was then added in one portion. After stirring for 10 min, the reaction mixture was filtered, and the catalyst was washed thoroughly with CH_2Cl_2. The combined filtrate was washed with water, dried over anhydrous Na_2SO_4, concentrated, and flash chromatographed, using hexane/CH_2Cl_2 (10:1) as eluent to afford **OBPV1** (195 mg, 80%) as yellow crystals: mp 227-229 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.36 (s, 36H), 6.66 (d, 2H, J = 7.4 Hz), 6.87 (d, 2H, J = 7.4 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); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 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; MS *m/e* (% relative intensity) (EI) 581 (M^++1, 54), 580 (M^+, 100), 283 (11); UV-VIS [λ_{max}, nm (ε, Lmol^{-1}cm^{-1})] 309 (10.3 × 10^4), 414 (4.56 × 10^4). Anal. Calcd. for $C_{44}H_{52}$: C, 90.98; H, 9.02. Found: C, 91.15; H, 9.03.

Ethyl 7-hydroxymethyl-2-biphenylenecarboxylate (12)

A mixture of the diester **5b** (4.0 g, 13.5 mmol) and KOH (85%, 1.2 g, 18.9 mmol) in ethanol (80 mL) and dry THF (40 mL) was heated at 40 °C for 24 h under nitrogen. The solution was acidified with HCl (10%, 50 mL) and extracted with EtOAc. The combined organic extract was dried over anhydrous Na_2SO_4 and concentrated to give the crude monoacid **11** which was redissolved in dry THF (50 mL). To this solution at 0 °C was added borane in THF (1.0 M, 80.0 mL, 80.0 mmol). After stirring for 30 min under nitrogen, the reaction mixture was quenched with water, and the aqueous mixture was extracted with ethyl acetate. The combined organic extract was dried over anhydrous Na_2SO_4 and concentrated to give a yellowish solid which was purified by flash chromatography on silica gel, using hexane/EtOAc (3:1) as eluent to afford the product (2.8 g, 82%) as yellow crystals: mp 93-94 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.29 (t, 3H, J = 7.1 Hz), 1.78 (bs, 1H), 4.24 (q, 2H, J = 7.1 Hz), 4.42 (s, 2H), 6.60-6.73 (m, 4H), 7.15 (s, 1H), 7.52 (dd, 1H, J = 1.1, 7.3 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 14.3, 60.9, 65.5, 116.7, 117.2, 117.4, 118.3, 126.9, 130.3, 132.2, 142.6, 149.1, 150.7, 150.9, 155.8, 166.2; MS *m/e* (% relative intensity) (EI) 254 (M^+, 100), 225 (12), 209 (33), 181 (37), 152 (33); IR (KBr) 3600-3200 (-OH), 1710 (C=O) cm^{-1}. Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75 58; H, 5.55. Found: C, 75.71; H, 5.62.

Ethyl 7-chloromethyl-2-biphenylenecarboxylate (13)

Under a dry atmosphere thionyl chloride (0.4 mL, 5.3 mmol) was added to a solution of alcohol **12** (900 mg, 3.5 mmol) in dry CH_2Cl_2 (20 mL) at 0 °C. After stirring for 2 h, the reaction mixture was quenched with water and extracted with CH_2Cl_2. The combined organic extract was dried over anhydrous Na_2SO_4, concentrated, and purified by flash chromatography on silica gel, using hexane/CH_2Cl_2 (4:1) as eluent to afford **13** (830 mg, 86%) as yellow crystals: mp 129 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.37 (t, 3H, J = 7.2 Hz), 4.31 (q, 2H, J = 7.2 Hz), 4.39 (s, 2H), 6.65-6.81 (m, 4H), 7.24 (s, 1H), 7.61 (dd, 1H, J = 1.3, 7.3 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.0, 47.5, 61.7, 117.7, 118.3, 119.0, 119.2, 129.7, 131.3, 133.0, 139.5, 150.6, 151.1, 151.7, 156.0, 166.8; MS *m/e* (% relative intensity) (EI) 272 (M^+, 84), 237 (100), 209 (70), 163 (40); IR (KBr) 1706 cm^{-1}. Anal. Calcd. for $C_{16}H_{13}O_2Cl$: C, 70.46; H, 4.80. Found: C, 70.43; H, 4.89.

Ethyl 7-(3′,5′-di-*tert*-butylbenzylthiomethyl)biphenylene-2-carboxylate (14)

To a suspension of 3,5-di-*tert*-butylbenzylthiol (500 mg, 2.1 mmol) and Cs_2CO_3 (1.0 g, 3.17 mmol) in dry THF (10 mL) at 45 °C (bath temperature) was added chloride **13** (550 mg, 2.0 mmol) in dry THF (15 mL) dropwise over 3 min. After stirring for 20 h at 50 °C (bath temperature) under nitrogen, the reaction mixture was quenched with water and extracted with CH_2Cl_2. The combined organic extract

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was dried over anhydrous Na_2SO_4, concentrated, and flash chromatographed on silica gel, using hexane/ether (10:1) as eluent to afford **14** (750 mg, 79%) as yellow crystals: mp 85-88 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.32 (s, 18H), 1.37 (t, 3H, J = 7.2 Hz), 3.42 (s, 2H), 3.63 (s, 2H), 4.32 (q, 2H, J = 7.2 Hz), 6.64-6.71 (m, 4H), 7.12 (s, 2H), 7.21 (s, 1H), 7.30 (d, 1H, J = 1.5 Hz), 7.60 (d, 1H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.2, 31.3, 34.7, 35.8, 36.0, 60.6, 116.3, 117.0, 117.9, 119.1, 120.8, 123.1, 128.8, 129.9, 132.0, 136.7, 140.0, 148.0, 150.4, 150.6, 150.7, 155.6, 165.9; MS *m/e* (% relative intensity) (EI) 472 (M^+, 13), 269 (13), 237 (100), 209 (37); IR (KBr) 1714 cm^{-1}. Anal. Calcd. for $C_{31}H_{36}O_2S$: C, 78.77; H, 7.68. Found: C, 78.51; H, 7.81.

Ethyl 7-[(3′,5′-di-*tert*-butylbenzyl)sulfonylmethyl)-biphenylene-2-carboxylate (15)

To a solution of sulfide **14** (7.5 g, 15.9 mmol) in CH_2Cl_2 (120 mL) was added *m*CPBA (12.4 g, 71.9 mmol) in three portions. After stirring for 9 h at r.t. under nitrogen, the reaction mixture was washed with NaOH solution (1 M, 50 mL × 2) and water. The organic solution was dried over anhydrous Na_2SO_4 and concentrated to give a yellowish solid which was purified by flash chromatography on silica gel, using hexane/ethyl acetate (3:1) as eluent to afford **15** (7.4 g, 92%) as yellow crystals: mp 188-189 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.33 (s, 18H), 1.37 (t, 3H, J = 7.0 Hz), 3.91 (s, 2H), 4.20 (s, 2H), 4.33 (q, 2H, J = 7.0 Hz), 6.72-6.79 (m, 4H), 7.24 (m, 3H), 7.45 (t, 1H, J = 1.8 Hz), 7.60 (dd, 1H, J = 1.1, 7.3 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 14.3, 31.4, 34.9, 58.1, 58.9, 60.9, 117.2, 117.8, 118.4, 120.3, 123.0, 125.0, 126.7, 128.9, 130.8, 131.7, 132.3, 150.37, 150.44, 151.0, 151.5, 155.1, 165.9; MS *m/e* (% relative intensity) (EI) 504 (M^+, 2), 440 (11), 237 (100), 209 (25), 203 (26); IR (KBr) 1713, 1316, 1116 cm^{-1}. Anal. Calcd. for $C_{31}H_{36}O_4S$: C, 73.78; H, 7.19. Found: C, 73.63; H, 7.28.

2-[(*E*)-3′,5′-di-*tert*-butylstyryl]-7-hydroxymethyl-biphenylene (18)

To a vigorously stirred solution of sulfone **15** (7.4 g, 15.0 mmol) in dry THF (300 mL) at 0 °C under nitrogen was added KOH/Al_2O_3 (1/2 w/w, 130 g), followed by CBr_2F_2 (6.4 mL, 70.0 mmol). After stirring for 3 min, the reaction mixture was filtered and the catalyst was washed thoroughly with EtOAc. The combined organic solution was washed with water, dried over anhydrous Na_2SO_4, and evaporated to give 9.0 g of a mixture of the crude acid **16** and ester **17** which was reduced without further purification in the next step. To a solution of the crude mixture **16** and **17** (100 mg) in dry THF (5 mL) at 0 °C was added $LiAlH_4$ (16 mg, 0.42 mmol). After stirring for 2 h under N_2, the reaction mixture was quenched with water and the aqueous mixture was extracted with EtOAc. The combined organic extract was dried over Na_2SO_4, concentrated, and flash chromatographed on silica gel, using hexane/EtOAc (6:1) as eluent to afford **18** (70 mg, 100% from sulfone **15**) as yellow crystals: mp 126-127 °C; ^{1} NMR ($CDCl_3$, 250 MHz) δ 1.35 (s, 18H), 4.49 (s, 2H), 6.62 (d, 1H, J = 7.2 Hz), 6.65 (d, 1H, J = 7.2 Hz), 6.74 (s, 1H), 6.76 (d, 1H, J = 7.2 Hz), 6.85 (d, 1H, J = 7.2 Hz), 6.92 (d, 1H, J = 16.2 Hz), 7.00 (s, 1H), 7.05 (d, 1H, J = 16.2 Hz), 7.32-7.34 (m, 3H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.4, 34.8, 65.5, 114.0, 116.8, 117.0, 117.4, 120.7, 122.0, 126.8, 128.1, 128.2, 128.8, 136.5, 138.0, 141.2, 149.7, 150.2, 150.9, 151.0 (only 20 carbon signals are observed); MS *m/e* (% relative intensity) (EI) 397 (M^++1, 31), 396 (M^+, 100); IR (KBr) 3500-3200 cm^{-1}. Anal. Calcd. for $C_{29}H_{32}O$: C, 87.83; H, 8.13. Found: C, 87.67; H, 8.14.

Bis{7-[(*E*)-3′,5′-di-*tert*-butylstyryl]biphenylen-2-yl-methyl}sulfide (20)

With the content protected against atmospheric moisture by a $CaCl_2$ drying-tube, thionyl chloride (88 μL, 0.11 mmol) was added to a solution of the alcohol **18** (40 mg, 0.09 mmol) in dry dichloromethane (5 mL) at 0 °C. After stirring for 2 h, the reaction mixture was quenched with water and extracted with CH_2Cl_2. The organic extract was washed with water, dried over anhydrous Na_2SO_4, concentrated, and flash chromatographed through a short silica gel column, using hexane/EtOAc (6:1) as eluent to afford the crude chloride **19** (37 mg, ≤ 100%). Since this material underwent extensive decomposition on standing at r.t., **30** was used immediately for the next step.

To a solution of the crude chloride **19** (106 mg, 0.26 mmol) in dry THF (10 mL) under nitrogen was added a solution of Na_2S (60%, 17 mg, 0.13 mmol) in EtOH (1 mL). After stirring for 12 h, water was added and the mixture was extracted with CH_2Cl_2. The combined organic extract was washed with water, dried over anhydrous Na_2SO_4, and concentrated to give a yellowish solid which was flash chromatographed on silica gel, using hexane/CH_2Cl_2 (4:1) as eluent to afford the monosulfide **20** (68 mg, 67%) as yellow crystals: mp 136-138 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.35 (s, 36H), 3.46 (s, 4H), 6.58 (d, 2H, J = 7.1 Hz), 6.62-6.65 (m, 4H), 6.72 (s, 2H), 6.84 (d, 2H, J = 7.2 Hz), 6.92 (d, 2H, J = 16.8 Hz), 6.99 (s, 2H), 7.01 (d, 2H, J = 16.8 Hz), 7.33 (bs, 6H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.5, 34.9, 36.3, 114.3, 116.9, 117.4, 118.6, 120.8, 122.1, 128.2, 128.3, 128.8, 128.9, 136.6, 138.1, 138.4, 149.6, 149.8, 151.1 (only 19 carbon signals were observed); MS *m/e* (% relative intensity) (FAB) 791 (M^++1, 11), 379 (100); HRMS *m/e* (EI)

Calcd. for $C_{58}H_{62}S$: 790.4572. Found: 790.4537.

Bis{7-[(*E*)-3′,5′-di-*tert*-butylstyryl]biphenylen-2-ylmethyl}sulfone (21)

A mixture of the sulfide **20** (44 mg, 0.06 mmol) and Oxone®) (100 mg, 0.16 mmol) in CH_2Cl_2 (4 mL) and methanol (2 mL) was stirred under N_2 for 24 h. The reaction mixture was then filtered through a short bed of silica gel with thorough washing with CH_2Cl_2. The combined filtrate was washed with water, dried over anhydrous Na_2SO_4, and concentrated to give a yellowish solid which was flash chromatographed on silica gel, using hexane/EtOAc (4:1) as eluent to afford the monosulfone **21** (37 mg, 82%) as yellow crystals: mp 186-188 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.36 (s, 36H), 4.03 (s, 4H), 6.65-6.69 (m, 4H), 6.75-6.76 (m, 4H), 6.87 (d, 2H, *J* = 7.3 Hz), 6.93 (d, 2H, *J* = 16.8 Hz), 7.01 (s, 2H), 7.03 (d, 2H, *J* = 16.8 Hz), 7.33 (s, 6H); due to the low solubility of **21**, high quality ^{13}C NMR could not be obtained; MS *m/e* (% relative intensity) (FAB) 823 (M$^+$, 4), 759 (7), 379 (100). Anal. Calcd. for $C_{58}H_{62}O_2S$: C, 84.63; H, 7.59. Found: C, 83.88; H, 8.01.

(*E*)-1,2-Bis{7′-[(*E*)-3″,5″-di-*tert*-butylstyryl]biphenylen-2′-yl}ethene (OBPV2)

By the representative synthetic procedure reported for **OBPV1**, sulfone **21** (20 mg, 0.02 mmol), KOH/Al_2O_3[32] (1/2 w/w, 20 mg), and CBr_2F_2 (0.3 mL, 3.28 mmol) in dry THF (5 mL) gave an orange solid crude product which was purified by flash chromatography on silica gel, using hexane/CH_2Cl_2 (6:1) as eluent to afford **OBPV2** (15 mg, 83%) as orange crystals: mp > 245 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 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); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 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; MS *m/e* (% relative intensity) (FAB) 756 (M$^+$, 34), 307 (22), 154 (100), 136 (70); HRMS *m/e* (EI) Calcd. for $C_{58}H_{60}$: 756.4695. Found: 756.4736; UV-VIS [λ_{max}, nm (ε, Lmol^{-1}cm^{-1})] 310 (34.8×10^4), 323 (34.6×10^4), 455 (18.1×10^4), 485 (14.0×10^4).

2,7-Bis(mercaptomethyl)biphenylene (22)

A mixture of the dichloride **8** (50 mg, 0.2 mmol) and thiourea (30 mg, 0.4 mmol) in dry THF (2 mL) was refluxed for 5 h under nitrogen. Water (1 mL) was added to the hot reaction mixture to dissolve all the solids which had formed. NaOH (160 mg, 40 mmol) in water (2 mL) was then added and the solution was kept at 70 °C (bath temperature) for 15 min under nitrogen. Upon cooling, the solution was acidified with HCl (10%, 20 mL) and was extracted with CH_2Cl_2. The combined organic extract was dried over anhydrous Na_2SO_4, concentrated, and purified by flash chromatography on silica gel, using hexane/CH_2Cl_2 (2:1) as eluent to afford **22** (39 mg, 79%) as pale yellow crystals: mp 84-87 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.71 (t, 2H, *J* = 7.6 Hz), 3.54 (d, 4H, *J* = 7.6 Hz), 6.55 (d, 2H, *J* = 7.5 Hz), 6.56-6.68 (m, 4H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 29.6, 117.1, 117.8, 127.4, 141.4, 149.4, 151.1; MS *m/e* (% relative intensity) (EI) 244 (M$^+$, 40), 211 (91), 178 (100), 165 (25). Anal. Calcd. for $C_{14}H_{12}S_2$: C, 68.81; H, 4.95. Found: C, 68.30; H, 5.26.

2,7-Bis{7′-[(*E*)-3″,5″-di-*tert*-butylstyryl]biphenylen-2′-ylmethylthiomethyl}biphenylene (23)

To a solution of dithiol **22** (50 mg, 0.20 mmol) and the crude chloride **19** (160 mg, ≤ 0.39 mmol) in dry benzene (2 mL) was added DBU (72 μL, 0.48 mmol). After stirring for 2 h under N_2, HCl (10%, *ca.* 10 mL) was added, and the aqueous mixture was extracted with CH_2Cl_2. The combined organic extract was dried over anhydrous Na_2SO_4, concentrated, and purified by flash chromatography on silica gel, using hexane/CH_2Cl_2 (5:1) as eluent to afford bissulfide **23** (104 mg, 52%) as yellow crystals: mp 155-157 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.36 (s, 36H), 3.43 (s, 4H), 3.44 (s, 4H), 6.55 (d, 2H, *J* = 7.0 Hz), 6.56 (d, 2H, *J* = 7.0 Hz), 6.61 (d, 2H, *J* = 7.0 Hz), 6.62 (d, 4H, *J* = 7.0 Hz), 6.67 (s, 2H), 6.70 (s, 2H), 6.83 (d, 2H, *J* = 7.3 Hz), 6.92 (d, 2H, *J* = 16.3 Hz), 6.97 (s, 2H), 7.01 (d, 2H, *J* = 16.3 Hz), 7.33-7.34 (m, 6H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.5, 34.8, 36.3, 114.3, 116.76, 116.82, 117.4, 118.6, 120.8, 122.1, 128.2, 128.3, 128.6, 128.7, 128.9, 136.6, 138.1, 138.3, 138.4, 149.46, 149.51, 149.8, 151.0, 151.2 (only 24 carbon signals are observed); MS *m/e* (% relative intensity) (FAB) 1001 (M$^+$, 22), 589 (14), 379 (100). Anal. Calcd. for $C_{72}H_{72}S_2$: C, 86.35; H, 7.25. Found: C, 85.26; H, 7.33.

2,7-Bis{7′-[(*E*)-3″,5″-di-*tert*-butylstyryl]biphenylen-2′-ylmethylsulfonylmethyl}biphenylene (24)

A mixture of bissulfide **23** (43 mg, 0.04 mmol) and Oxone® (160 mg, 0.26 mmol) in CH_2Cl_2 (4 mL) and methanol (2 mL) was stirred under N_2 at r.t. for 24 h. The reaction mixture was then filtered through a short bed of silica gel with thorough washing with CH_2Cl_2. The combined filtrate was washed with water, dried over anhydrous Na_2SO_4, concentrated, and purified by flash chromatography on silica gel, using hexane/EtOAc/CH_2Cl_2 (6:1:1) as eluent to afford bissulfone **24** (37 mg, 81%) as yellow crystals: mp > 245 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.36 (s, 36H), 4.00 (s, 4H), 4.02 (s, 4H), 6.64-6.74 (m, 14H), 6.87 (d, 2H, *J* = 6.7 Hz), 6.92 (d, 2H, *J* = 16.9 Hz), 7.00 (s, 2H), 7.02 (d, 2H, *J* = 16.9

Hz), 7.33-7.34 (m, 6H); due to the low solubility of **24**, high quality ^{13}C NMR could not be obtained; MS *m/e* (% relative intensity) (FAB) 1065 (M$^+$, 20), 936 (17), 379 (100).

(*E,E*)-2,7-Bis{2-[7′-[(*E*)-3″,5±-di-*tert*-butylstyryl]-biphenylen-2′-yl]ethenyl}biphenylene (OBPV3)

By the representative synthetic procedure reported for **OBPV1**, bissulfone **24** (35 mg, 0.03 mmol), KOH/Al_2O_3 (1/2 w/w, 650 mg), CBr_2F_2 (0.3 mL, 3.28 mmol) in dry THF (5 mL) gave a reddish crude solid which was purified by flash chromatography on silica gel, using hexane/dichloromethane (6:1) as eluent to afford the **OBPV3** (29 mg, 93%) as red crystals: mp > 245 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 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* = 16.4 Hz), 6.96 (s, 2H), 6.97 (s, 2H), 7.03 (s, 2H), 7.04 (d, 2H, *J* = 16.4 Hz), 7.33 (s, 4H), 7.34 (s, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.48, 34.89, 114.21, 114.26, 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; MS *m/e* (% relative intensity) (FAB) 933 (M$^+$, 2), 467 (2), 380 (2), 207 (10), 71 (10), 83 (11), 91 (12), 69 (12), 55 (20), 57 (21), 43 (24), 44 (100); UV-VIS [λ_{max}, nm (ε, Lmol^{-1}cm^{-1})] 310 (33.3×10^4), 321 (32.0×10^4), 466 (17.7×10^4), 497 (15.0×10^4).

Ethyl 7-(ethoxythiocarbonylthiomethyl)-2-biphenylenecarboxylate (25)

A mixture of KOH (85%, 620 mg, 11.0 mol), ethanol (0.65 mL, 11.0 mmol), and dry THF (10 mL) was refluxed under nitrogen for 1 h. After that, the mixture was cooled to 0 °C and carbon disulfide (0.66 mL, 11.0 mmol) was added. The resulting suspension was further refluxed for 2 h and upon cooling, was added to a precooled (0 °C) solution of chloride **13** (1.5 g, 5.5 mmol) in dry THF (5 mL). After stirring for 12 h at r.t. under nitrogen, the reaction mixture was quenched with water and extracted with CH_2Cl_2. The organic extract was dried over anhydrous Na_2SO_4 and concentrated to give a yellowish wax which was purified by flash chromatography on silica gel, using hexane/CH_2Cl_2 (4:1) as eluent to afford **25** (2.0 g, 100%) as yellow crystals: mp 89-90 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.36 (t, 3H, *J* = 7.1 Hz), 1.42 (t, 3H, *J* = 7.1 Hz), 4.18 (s, 2H), 4.31 (q, 2H, *J* = 7.1 Hz), 4.65 (q, 2H, *J* = 7.1 Hz), 6.62-6.79 (m, 4H), 7.22 (s, 1H), 7.59 (d, 1H, *J* = 1.1, 7.3 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 13.7, 14.3, 41.0, 60.8, 70.1, 116.7, 117.3, 118.3, 119.0, 129.2, 130.5, 132.2, 137.4, 149.0, 150.6, 150.9, 155.5, 166.0, 193.9; MS *m/e* (% relative intensity) (EI) 358 (M$^+$, 6), 237 (100), 209 (31). Calcd. for $C_{19}H_{18}O_3S_2$: C, 63.66; H, 5.06. Found: C, 63.68; H, 5.11.

7′-Ethoxycarbonylbiphenylen-2′-ylmethyl 7-[(*E*)-3″,5″-di-*tert*-butylstyryl]biphenylen-2-ylmethyl sulfide (27)

Sodium metal (400 mg, 18.0 mmol) was added to ethanol (20 mL) under nitrogen. After all the sodium had reacted, a solution of the xanthate ester **25** (550 mg, 1.5 mmol) in dry THF (10 mL) was added to the sodium ethoxide solution. After stirring for 7 h, the reaction mixture was acidified with 10% hydrochloric acid until red with litmus. The acidic aqueous solution was extracted with dichloromethane, and the combined organic extract was dried over anhydrous Na_2SO_4. Rotavaporation left the crude thiol **26** (405 mg, ≤ 100%) as a yellowish solid. To a solution of this crude thiol **26** (220 mg, 0.81 mmol) and the crude chloride **19** (310 mg, 0.74 mmol) in dry benzene (10 mL) was added DBU (0.13 mL, 0.89 mmol). After stirring for 5 h under nitrogen, the reaction mixture was quenched with water and extracted with CH_2Cl_2. The combined organic extract was dried over anhydrous Na_2SO_4 and concentrated to give a yellow solid which was purified by flash chromatography on silica gel, using hexane/CH_2Cl_2 (3:1) as eluent to afford **27** (320 mg, 67%) as yellow crystals: mp 157-159 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.36 (m, 21H), 3.46 (s, 4H), 4.31 (q, 2H, *J* = 7.1 Hz), 6.56-6.75 (m, 8H), 6.84 (d, 1H, *J* = 7.4 Hz), 6.92 (d, 1H, *J* = 16.3 Hz), 6.98 (s, 1H), 7.01 (d, 1H, *J* = 16.3 Hz), 7.23 (s, 1H), 7.33-7.34 (m, 3H), 7.66 (dd, 1H, *J* = 1.1, 7.3 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 14.3, 31.5, 34.9, 36.3, 36.4, 60.8, 114.3, 116.5, 116.8, 117.3, 117.4, 118.1, 118.5, 119.2, 120.8, 122.1, 128.2, 128.3, 128.8, 129.0, 130.3, 132.2, 136.6, 138.1, 138.3, 139.9, 148.5, 149.6, 149.8, 150.8, 151.1, 155.8, 166.1 (only 33 carbon signals are observed); MS *m/e* (% relative intensity) (EI) 648 (M$^+$, 16), 380 (53), 379 (100); IR (KBr) 1750 cm^{-1}. Anal. Calcd. for $C_{45}H_{44}O_2S$: C, 83.29; H, 6.83. Found: C, 83.04; 6.93.

7′-Ethoxycarbonylbiphenylen-2′-ylmethyl 7-[(*E*)-3″,5″-di-*tert*-butylstyryl]biphenylen-2-ylmethyl sulfone (28)

A mixture of sulfide **27** (300 mg, 0.46 mmol) and Oxone® (850 mg, 1.39 mmol) in CH_2Cl_2 (10 mL) and ethanol (5 mL) was stirred for 24 h under nitrogen. The resulting solution was filtered through a short bed of silica gel with thorough washing with CH_2Cl_2. The combined filtrate was washed with water, dried over anhydrous Na_2SO_4 and concentrated to give a yellowish solid which was purified by flash chromatography on silica gel, using hexane/EtOAc/CH_2Cl_2 (4:1:1) as eluent to afford the product (250 mg, 81%) as yellow crystals: mp 232 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.30-1.40 (m, 21H), 4.02 (s, 2H), 4.03 (s, 2H), 4.31 (q, 2H, *J* = 7.0 Hz), 6.62-6.87 (m, 9H), 6.92 (d, 1H, *J* = 16.3 Hz), 6.98 (s, 1H), 7.01 (d, 1H, *J* = 16.3 Hz), 7.24 (s, 1H), 7.33-7.35, (m, 3H), 7.61 (d, 1H, *J* = 7.4 Hz); ^{13}C NMR

($CDCl_3$, 62.9 MHz) δ 14.2, 31.4, 34.8, 58.6, 59.2, 60.8, 114.8, 117.1, 117.7, 118.1, 118.4, 119.4, 120.1, 120.8, 122.1, 127.2, 128.0, 128.3, 128.5, 129.3, 130.8, 131.5, 131.7, 132.2, 136.3, 138.6, 149.0, 150.3, 150.46, 150.54, 151.0, 151.3, 151.7, 155.0, 165.8 (only 35 carbon signals are observed); MS *m/e* (% relative intensity) (EI) 680 (M^+, 3), 616 (4), 380 (45), 379 (100); IR (KBr) 1713 cm^{-1}. Anal. Calcd. for $C_{45}H_{44}O_4S$: C, 79.38; H, 6.51. Found: C, 79.38; H, 6.58.

7-{2-[7′-(3″,5″-di-*tert*-butylstyryl)biphenylen-2′-yl]-ethenyl}-2-biphenylenecarbaldehyde (32)

To a vigorously stirred solution of sulfone **28** (220 mg, 0.32 mmol) in dry THF (10 mL) at 0 °C under nitrogen was added KOH/Al_2O_3[32] (1/2 w/w, 3.3 g). CBr_2F_2 (0.3 mL, 3.28 mmol) was then added in one portion. After stirring for 10 min, the reaction mixture was filtered, and the catalyst was washed thoroughly with CH_2Cl_2 followed by EtOAc. The combined organic filtrate was washed with water, dried over anhydrous Na_2SO_4, and concentrated to give the crude ester **29** (197 mg, ≤ 100%) which was redissolved in dry THF (10 mL) and cooled to 0 °C. $LiAlH_4$ (200 mg, 5.25 mmol) was then added to this solution. After stirring for 2 h under nitrogen, the reaction mixture was quenched with water, and the aqueous was extracted with CH_2Cl_2. The organic extract was dried over anhydrous Na_2SO_4, concentrated, and purified by flash chromatography on silica gel, using hexane/ethyl acetate (8:1) as eluent to afford alcohol **30** (195 mg, 80%) as yellow crystals: mp > 245 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.36 (s, 18H), 4.49 (s, 2H), 6.63-6.68 (m, 4H), 6.76 (d, 2H, J = 7.6 Hz), 6.81 (d, 1H, J = 7.6 Hz), 6.82 (s, 2H), 6.88 (d, 1H, J = 7.6 Hz), 6.93 (d, 1H, J = 16.2 Hz), 6.94 (s, 1H), 6.95 (s, 1H), 7.03 (s, 2H), 7.04 (d, 1H, J = 16.2 Hz), 7.34 (m, 3H); MS *m/e* (% relative intensity) (EI) 573 (M^+ + 1), 51), 572 (M^+, 100).

A mixture of alcohol **30** (37 mg, 0.07 mmol), PDC (37 mg, 0.10 mmol) and powdered 4Å molecular sieve (50 mg) in CH_2Cl_2 (5 mL) was stirred under N_2 for 1 h. The reaction mixture was filtered through a short bed of silica gel with thorough washing with CH_2Cl_2. The combined filtrate was concentrated to give an orange solid which was flash chromatographed on silica gel using hexane/CH_2Cl_2 (4:1) as eluent to afford aldehyde **32** (32 mg, 85%) as orange crystals: mp > 245 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.36 (s, 18H), 6.65-6.69 (m, 2H), 6.78-6.96 (m, 9H), 7.02-7.08 (m, 3H), 7.15 (s, 1H), 7.32-7.34 (m, 4H), 9.72 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.5, 34.9, 114.2, 114.5, 115.5, 116.7, 117.5, 117.7, 119.4, 120.9, 122.2, 127.1, 127.5, 128.3, 128.4, 128.9, 129.2, 129.4, 136.6, 136.8, 137.4, 137.5, 138.5, 139.9, 148.4, 149.7, 150.3, 150.6, 150.8, 151.1, 151.2, 151.4, 157.8, 190.8 (only 34 carbon signals are observed); MS *m/e* (% relative intensity) (EI) 573 (M^+ + 1, 49), 570 (M^+, 100); IR (KBr) 1730 cm^{-1}.

2,7-Bis(triphenylphosphoniomethyl)biphenylene dichloride (33)

A solution of the dichoride **8** (100 mg, 0.40 mmol) and triphenylphosphine (1.0 g, 4.0 mmol) was refluxed in THF (5 mL) and ethanol (1 mL) under nitrogen for 7 days. The reaction mixture was concentrated to give a residue which was purified by flash chromatography on silica gel, using hexane/$CHCl_3$/EtOH (2:1:1) as the eluent to afford the product (280 mg, 90%) as pale yellow crystals: mp 230-235 °C (dec.); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 5.31 (d, 4H, J_{HP} = 14.9 Hz), 6.17-6.21 (m, 4H), 6.41 (dd, 2H, J = 3.2, 6.9 Hz), 7.58-7.82 (m, 30H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 30.8 (d, J_{cp} = 45.9 Hz), 117.4, 117.7, 119.0, 120.8, 127.7, 127.9, 129.9, 130.1, 132.7, 134.6, 134.7, 150.20, 150.85; MS *m/e* (% relative intensity) (FAB) 702 (M^+ - $2Cl^-$ + 1, 4) 440 (M^+ - $2Cl^-$ - PPh_3 + 1, 29), 439 (M^+ - $2Cl^-$ -PPh_3, 50), 178 (M^+ - $2Cl^-$ - $2PPh_3$ + 1), 149 (M^+ - $2Cl^-$ -$2PPh_3$ - $2CH_2$, 100); IR (KBr) 2950, 2860, 1438, 1112, 747, 719, 690, 509 cm^{-1}.

Cyclic Voltammetric Experiments for OBPVn's

^{n}Bu_4NBF_4 used as the supporting electrolyte (0.1 M) for the cyclic voltammetry studies was dried at r.t. under vacuum for 1 day prior to use. Dichloromethane, the solvent, was dried and distilled over phosphorous pentaoxide before use. The CV studies were performed, using Ag/AgCl electrode as the reference electrode and ferrocene as the standard. The scan rate was 100 mv/s. The electrochemical oxidation studies of **OBPVn's** were performed at room temperature while the reduction studies were performed at dry ice-acetone temperature under agron. In our case, we have attempted to carry out the reduction experiments at room temperature or 0 °C, but unsuccessfully, and only the background current of CH_2Cl_2 was obtained. Although it is known that CH_2Cl_2 is not a good solvent for reductive electrochemistry, we decided to use it because of the low solubilities of **OBPVn's** in other solvents.

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Biphenylene; Oligo(2,7-biphenylenylene-*(E)*-vinylene)s; Poly(2,7-biphenylenylene-*(E)*-vinylene); Antiaromatic compounds; Conjugated oligomers; Conjugated polymers.

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