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Band Gap Engineering of Poly(*p*-phenyleneethynylene)s: Cross-Conjugated PPE−PPV Hybrids

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We report novel, luminescent, cross-conjugated poly(*p*-phenyleneethynylene) (PPE) derivatives (**5**) with unsaturated side chains.[1−4] The synthetic scheme allows the facile appendage of substituents to PPE monomers via a *trans*-configured alkene formed in a double Horner[5] reaction of **2** with aldehydes.

The PPEs,[4] dehydrogenated congeners of the poly(*p*-phenylenevinylene)s (PPV), are a class of conjugated polymers with demonstrated sensory and device applications.[6−9] Their superb photophysical properties combined with their high stability and high electron affinity make them attractive and in many ways complementary to the PPVs. Compared to the PPVs, the PPEs are however at a disadvantage for applications in OLEDs: Their poor hole injection capability witnesses the electron-withdrawing nature of the alkyne groupings and PPEs lowered HOMO.[8,9] It would be of interest to have materials that combine the stability, electron affinity, and high emissive quantum yield of the PPEs with the excellent hole injection capabilities of the PPVs.[10] Cross-conjugated PPE−PPV hybrids **5**, in which styryl side chains decorate a PPE main chain, are presently unknown and combine PPE and PPV motifs.

We present a simple approach for the synthesis of the monomers **4a**−**f** and their novel cross-conjugated polymers **5a**−**f** (Figure 1). 2,5-Bis(bromomethyl)-1,4-diiodobenzene (1)[11] combines quantitatively with triethyl phosphite to the bisphosphonate **2**. Reaction of **2** with the aldehydes **3a**−**f** in the presence of sodium hydride in THF furnishes the diiodides **4** (Table 1) in excellent yields (70−95%) as yellow, crystalline, air- and water-stable materials. In the monomers **4** the stilbenoid double bond is exclusively *trans*-configured according to ^{1}H NMR spectroscopy, as expected for a Horner olefination.[5] The synthetic access to the monomers **4** seems to be general and depends only upon availability and reactivity of a suitable aldehyde **3**.

While the monomers **4** are soluble in dichloromethane, chloroform, and toluene, their alkyne-bridged homopolymers would expected to be insoluble. Consequently, we coupled **4a**−**f** with 1,4-diethynyl-2,5-bis(ethylhexyl)-benzene utilizing $(Ph_3P)_2PdCl_2$/CuI as the catalyst system in a mixture of toluene/dichloromethane/piperidine. The cross-conjugated PPE derivatives **5a**−**f** were obtained in fair to good yields after aqueous workup and 3-fold precipitation into methanol. They appear as fluorescent, yellow or orange, moderately to well organosoluble powders/films after drying in high vacuum. ^{1}H NMR and ^{13}C NMR spectroscopy confirmed the proposed structures (Supporting Information) of **5a**−**f** unequivocally. The degree of polymerization (P_n) of the PPEs **5** was determined by gel permeation chromatography (GPC, Table 1). As expected, the number of repeating units (P_n) in these polymers is moderate and ranges from $P_n = 38$ to $P_n = 55$. Exceptions are **5b** and **5f**. The GPC values of several different samples of **5b** and **5f** were spuriously high ($M_w = 3 \times 10^8$); dilute solutions of **5f** are strongly gelating. We assume that aggregate formation is the reason for the extremely high *apparent* molecular weight of these two polymers. According to powder diffraction, the polymers **5** are amorphous, probably due to the introduction of the styrene side chains that induce a step in the polymer and inhibit efficient solid-state packing/ordering. While some of the polymers form gels in organic solvents, spin-cast films of **5a**−**f** of good quality are obtained from toluene or chloroform. Differential scanning calorimetry measurements did show the presence of a glass transition or other thermal processes in some of the polymers (Table 1).

To elucidate the effect of the substituents on the electronic properties of **5,** we recorded their UV−vis and emission spectra in solution and in the solid state (Table 1). In solution, the cross-conjugated PPEs show absorption between 355 and 390 nm with an additional shoulder at 410−430 nm. Their solid-state absorption is broad and featureless with a λ_{max} that ranges from 360 to 455 nm. There are only moderate differences between solution and solid-state spectra.[12] The emission spectra of **5a**−**f** display relatively broad and red-shifted features with respect to that of the PPEs and show a Stokes shift that is considerably larger than those of the PPEs. Their strong solid-state emission ($\lambda_{max} = 521$, 551 nm) is red-shifted compared to that of the PPEs ($\lambda_{max} = 480$ nm). Figure 2 shows the absorption and emission spectra of **5e** and **5f**. Both polymers display broad and featureless absorption in solution and in the solid state. Planarization of the chains in the solid state, so significant in the dialkyl-PPEs,[9] is not very distinct in the polymers **5** because of their bulky side chains. The loss of conformational order probably leads to the broader absorption and emission spectra.

PPE is relatively difficult to oxidize[8b] (1.3 V) and to reduce (−2.5 V). It was of interest to evaluate how the substituted styryl side chains would modulate the electrochemical behavior of **5**. Thin film samples of the styryl-substituted derivatives **5** are irreversibly oxidized at peak potentials (with exception of **5d**) that range from 0.4 to 1.5 V (Table 1). As expected, the two derivatives **5e** and **5f** are particularly easily oxidized due to their strongly electron-donating side chains. Interestingly enough, the reduction potential of the derivatives of **5** is in the range of −1.6−1.7 V; an exception is **5e**, which does not show a reduction peak to −2.5 V. However, **5e** does show a reduction *onset* above −1.3 V.

From these data (see Figure 3) one can obtain two series of band gaps that correspond either to the *onset* of oxidation and reduction (small values) or to the peak-to-peak distances (larger values). Janietz et al.[13] suggest

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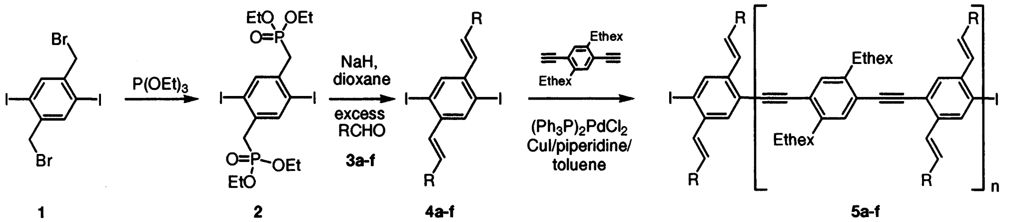
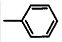
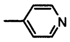
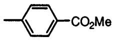
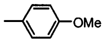
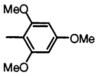
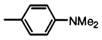


Figure 1. Synthetic routes to monomers **4** and cross-conjugated PPE derivatives **5**.

Table 1. Yields, Substitution Pattern Properties for 3–5, and Electrochemical Properties of Thin Films of Polymers 5a–f

3-5	a	b	c	d	e	f	PPE
Substi- tuent							-
Yield 4	97%	70%	95%	95%	93%	91%	-
Yield 5	80%	25%	81%	38%	55%	56%	-
P_n of 5	55	-	38	50	52	-	-
M_w/M_n of 5	2.8	-	3.2	2.0	3.2	-	-
Tg (°C)	-	119	123	183	-	79	-
$\lambda_{max,sol}$ 5 (nm)	354	350	366	389	374	386	385
	417 sh	410 sh	414 sh	414 s	-	432 sh	-
$\lambda_{max,film}$ 5 (nm)	450	420	448	442	380	390	439
Emission $\lambda_{max,sol}$ 5 (nm)	442	450	451	436	496	530	425
Emission $\lambda_{max,film}$ 5 (nm)	527	476	504	522	511	550	450 480
Φ (PL) solution	0.58	0.02	0.24	0.21	0.08	0.09	0.99
Peak E^{ox} peak (V vs. Fc/Fc$^+$)	1.25	1.55	1.40	1.87	0.83	0.72	1.3
E^{OX} (V) onset	0.9	0.8	0.6	1.1	0.15	0.25	1.1
Peak E^{RED} (V)	-1.68	-1.61	-1.75, -2.26	-2.3	-	-1.7	-2.5
E^{RED} (V) onset	-1.55	-1.3	-1.5	-1.3	-1.3	-1.3	-2.3
Maximum electochemical bandgap (eV)	2.93	3.16	3.15	4.21	>3.3	2.43	3.80
Minimum electochemical bandgap (eV)	2.45	2.10	2.10	2.60	1.50	1.50	3.40
Midpoint electrochemical bandgap (eV)	2.69	2.63	2.63	3.40	2.40	2.00	3.60
Thin film optical bandgap from Abs/Em intercept (eV)	2.64	2.78	2.67	2.72	2.64	2.49	2.82

that the difference in the onset of reduction and oxidation is a good measure for the band gap given an ideal sample (monodisperse, defect free). Our materials are polydisperse and amorphous and have multiple degrees of rotational freedom with respect to both the main and side chains. A significant distribution of electrochemical/electronic and optical properties results in broad bands in absorption and emission. We estimate the optical band gaps of **5** as the point where normalized emission and absorption intersect. These values are shown in Table 1 and fall between the two extremal values for the electrochemical band gap.

Both the oxidation and the reduction potentials are affected by the attachment of the styryl side chain to the PPE main chain (Figure 3). The effect of the styryl side chains is twofold: they act as slightly electron-withdrawing substituents for the PPE main chain and thus decrease the reduction potential of all of the new

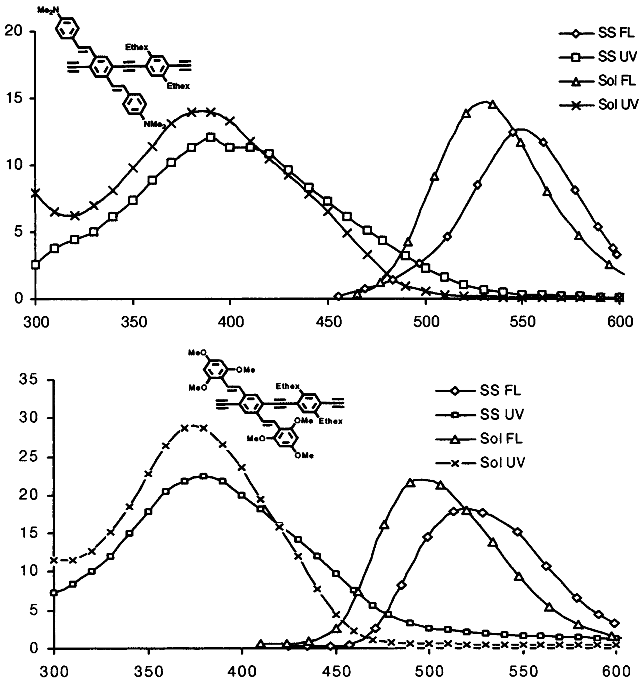


Figure 2. UV−vis and emission spectra of **5f** (top) and **5e** (bottom).

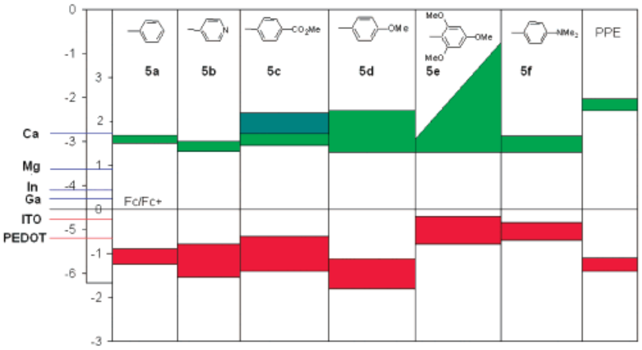


Figure 3. Schematic for relative band gaps of **5** and PPE obtained by cyclic voltammetry. Reduction potentials are shown in green, and oxidation potentials are shown in red. The dark green block indicates a second reduction wave. The lower absolute values indicate the onset of oxidation or reduction, while the higher absolute values indicate the peak potentials. In the case of **5e** there is an onset of the reduction, but no peak potential is reached. The oxidation and reduction values of dialkyl-PPEs are likewise shown. As comparison, the work functions of several common electrode materials (cathodes, anodes, and ferrocene) are shown.

polymers as compared to dialkyl-PPEs. This is almost independent of the nature of the arene on the side unit. On the other hand, the nature of the distyrylbenzene core largely determines the oxidation potential of the polymers **5**, suggesting that its HOMO has a significant electron density on the styryl sidearms. Whether the two crossed systems are electronically coupled or only topologically cross-conjugated is difficult to say, but attachement of styryl side chains significantly modulates the electronic properties of these PPE derivatives.

In conclusion, we have modified Bazan's oligomer concept to allow the synthesis of the hitherto unknown cross-conjugated PPV−PPE copolymers **5**. Because myriads of ketones and aldehydes are commercially available or easily made, their reaction with **2** bodes for the generation of libraries of distyrylbenzenes **4**. These monomers can be used in the synthesis of diversets[13] of cross-conjugated PPE−PPV derivatives with fine-tuned optical/electronic properties. We are continuing our studies of these materials to discern to what extent cross-conjugation exists as an electronic coupling of the PPV arms to the PPE backbone beyond the topological aspect.

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Supporting Information Available: Experimental details, spectroscopic data, and cyclic volatammograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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