

Electrochemical Investigations on PPV Model Compounds

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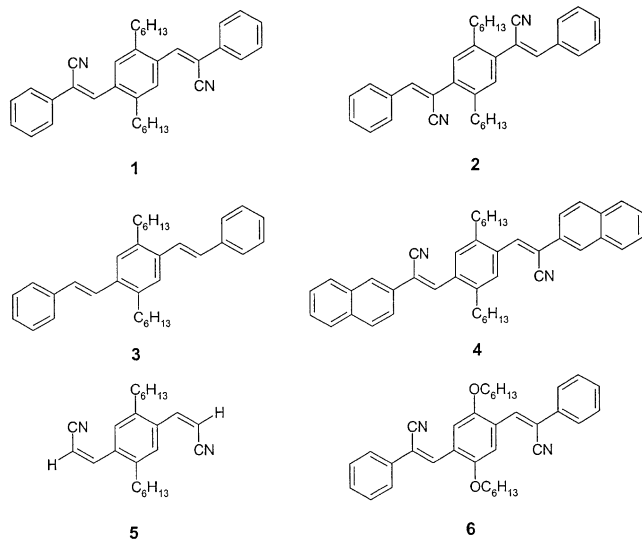
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To obtain more information on the redox behavior of poly(*para*-phenylenevinylene) (PPV) and its derivatives, electrochemical investigations were carried out on the short-chain PPV model compounds **1–6**. The effects of different substituents were investigated by determinations of the redox potentials by cyclic voltammetry.

1. Introduction

In 1970, Hörhold¹ reported on the optical, electronic, and photoelectric properties of poly(*para*-phenylenevinylene) (PPV). PPV is a high ohmic semiconductor with a conductivity of $\sigma \leq 10^{-15}$ S/cm. The band gap was evaluated at 2.4 eV using different experimental methods.¹ In accordance with the experiments, Brédas² calculated a theoretical value of 2.5 eV for the band gap of PPV. The redox behaviors of PPV and its derivatives were determined by differential pulse polarography (DPP) and cyclic voltammetry.^{3,4} The effects of substituents at the phenylene and vinylene subunits on the redox potentials and on the value of the energy gap were also reported.^{3,4} Electrochemical investigations of PPV by other research groups have mainly concentrated on its conjugation length.⁵ We report here on the redox potentials of the PPV analogous model compounds **1–6** determined by cyclic voltammetry. The preparation of compounds **1–6** is described in refs 6–11.



2. Experimental Section

Electrochemical measurements were performed in a three-electrode cell. A platinum disk electrode (Metrohm, area = 0.07

cm²) was used as the working electrode, a platinum foil as the counter electrode, and a silver wire as the quasireference electrode. The quasireference electrode was calibrated against ferrocene/ferrocenium ion.¹² Half-wave potentials were calculated according to the relation $E_{1/2} = (E_{pa} + E_{pc})/2$. The potentiostat was a computer-controlled PAR273 apparatus (EG & G). All measurements were performed in dry dichloromethane, acetonitrile, or tetrahydrofuran with *n*-Bu₄NPF₆ as the supporting electrolyte (Aldrich). All compounds, solvents, and supporting electrolyte were stored under inert gas (N₂, argon). Measurements were made in an inert gas atmosphere at room temperature. The concentration of the investigated compounds was about 1×10^{-3} mol/L. The supporting electrolyte used in the electrochemical measurements in 0.1 M concentration was recrystallized three times from ethanol. Dichloromethane and acetonitrile were each dried over calcium hydride and distilled twice in an inert atmosphere. Tetrahydrofuran was dried over sodium and distilled twice in an inert atmosphere.

3. Results and Discussion

The multicycle voltammogram (CV) of 1,4-bis(2-cyano-2-phenylethenyl)-2,5-dihexylbenzene (**1**) measured in dichloromethane shows three reduction waves and one

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Table 1. Redox Potentials $E_{1/2}$ of 1,4-Bis(2-cyano-2-phenylethenyl)-2,5-dihexylbenzene (1) Determined by Cyclic Voltammetry^a

solvent	$E_{1/2}(\text{Ox}_1)$ (V) (ΔE_p [mV])	$E_{1/2}(\text{Red}_1)$ (V) (ΔE_p [mV])	$E_{1/2}(\text{Red}_2)$ (V) (ΔE_p [mV])	$E_{1/2}(\text{Red}_3)$ (V) (ΔE_p [mV])	$E_{1/2}(\text{Red}_4)$ (V) (ΔE_p [mV])
dichloromethane	1.87 (160)	-1.31 (315)	-1.39 (100)		
tetrahydrofuran		-1.27 (135)	-1.43 (120)	-1.66 (95)	-2.11 ^c

^a Scan rate = 100 mV/s. ^b $\Delta E_p = |E_{pa} - E_{pc}|$. ^c Cathodic peak only.

Table 2. Redox Potentials $E_{1/2}$ of 2 Determined by Cyclic Voltammetry in Different Solvents^a

solvent	$E_{1/2}(\text{Ox}_1)$ (V) (ΔE_p [mV])	$E_{1/2}(\text{Red}_1)$ (V) (ΔE_p [mV])	$E_{1/2}(\text{Red}_2)$ (V) (ΔE_p [mV])	$E_{1/2}(\text{Red}_3)$ (V) (ΔE_p [mV])
dichloromethane	1.98 (70)	-1.61 (130)	-1.66 (240)	
acetonitrile	1.98 (220)	-1.61 (120)	-1.66 (145)	-1.90 (160)
tetrahydrofuran		-1.58 (140)	-1.72 (100)	-1.94 (200)

^a Scan rate = 100 mV/s.

Table 3. HOMO–LUMO Distances ΔE_{CV} Determined by Different Methods^a

compd	ΔE_{CV} (eV)	ref	ΔE_{PL} (eV)	ref	ΔE_{UV} (eV)	ref
1	2.86	this work	2.72	7, 13, 15	3.51	7, 8, 15
2	3.28	this work	3.04	7, 8, 10, 15	4.13	7, 15
3	3.02	this work	2.97	7, 8, 10	3.62	7
4	2.76	this work	2.53	14	3.33	9
5	3.1 ^b	this work	3.32/3.47	15	4.08	9
6	2.42	this work	2.35	8	2.88	8, 11

^a CV (onset), PL, and UV/vis measurements carried out in dichloromethane. ^b Measured in acetonitrile.

oxidation wave. The redox potentials are listed in Table 1. The first and second reduction waves are not well-resolved, but in the differential pulse voltammogram (DPV), the reduction wave splits into two peaks. If tetrahydrofuran (see Figure 1) is used as the solvent, the peaks are well-resolved, because the radical anion is better stabilized in this solvent. The first and second reductive electron transfers are quasireversible. The third reduction wave is broadened but also quasireversible. The oxidation wave appears at +1.87 V vs SCE.

We have reported on the crystal structures of **1** and 1,4-bis(1-cyano-2-phenylethenyl)-2,5-dihexylbenzene (**2**) in a previous paper⁶ in this journal, which showed that compound **2** exhibits a stronger torsion of the phenylene subunits than compound **1**. This causes a shorter conjugation length and, consequently, a larger HOMO–LUMO distance for **2**, as confirmed by the electrochemical results (see Tables 2 and 3). For compound **2**, we measured a band gap of 3.59 eV, whereas compound **1** has an electrochemically determined band gap of 3.18 eV. The band gap is electrochemically estimated as the distance between the onset of the first oxidation peak and the onset of first reduction peak (ΔE_{PL}). To determine the band gap via optical methods, UV and photoluminescence spectroscopies were utilized. The peak maxima of optical spectra are caused by the HOMO–LUMO transitions. Consequently, the HOMO–LUMO gap can easily be determined from the wavelength of the peak maximum. Compound **2** is also more difficult to reduce and to oxidize than **1**. Electrochemical measurements in dichloromethane show one oxidative and two reductive electron transfers for **2**. In tetrahydrofuran (see Figure 2), the multicycle CV shows three poorly resolved reduction waves but no oxidation wave. The second reductive electron transfer is followed by a chemical reaction, and a new wave for the oxidation of the subsequent product appears at 0.43 V vs SCE.

However, the oxidation wave of the following product appears only in cyclic voltammograms measured with scan rates faster than 20 mV/s, which demonstrates that the subsequent product is instable. The third reduction wave is quasireversible.

To investigate the effects of the electron-withdrawing cyano groups on the C–C double bonds in **1** and **2**, we also examined compound **3** without cyano groups for comparison. (See Table 4.) In dichloromethane, **3** exhibits a band gap of 3.28 eV as determined by cyclic voltammetry. The voltammogram shows one reduction and two oxidation peaks. At fast scan rates, the first oxidative electron transfer at +1.27 V vs SCE (≥ 5000 mV/s) is quasireversible, but at lower scan rates (20–500 mV/s), the peak current of the reverse transfer decreases. This result corresponds with observations that reversible oxidations can only be achieved if the reactive α and/or β positions are blocked with a substituent or if fast scanning methods are employed.¹³ The first reductive electron transfer is followed by a chemical reaction that forms a subsequent product with an oxidation potential of +1.20 V vs SCE. In the cyclic voltammogram of **3** in tetrahydrofuran, no further product of the first reduction is observed. Therefore, in this solvent, the first reductive electron transfer is quasireversible. The second and third reduction waves are broadened and not well-resolved.

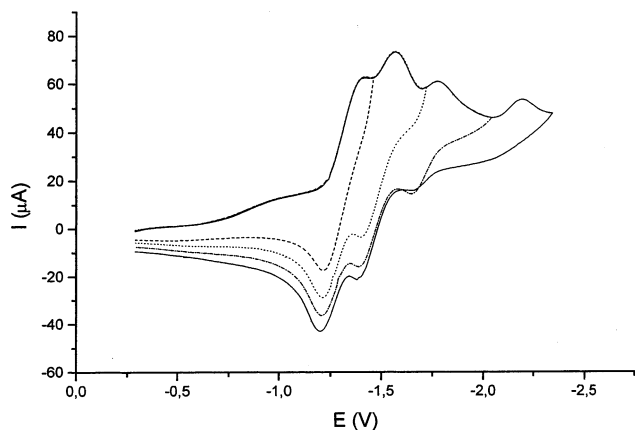
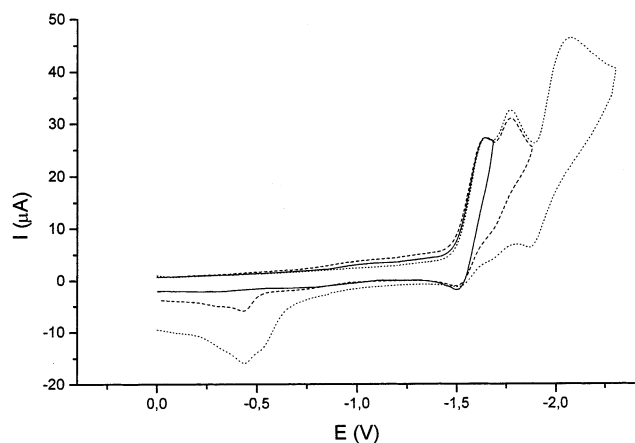
To study the effect of phenyl and naphthyl substituents, compounds **1** and **4** were compared with the unsubstituted compound **5**. Already in 1948, Kuhn¹⁴ had reported that the HOMO–LUMO distances of PPV-analogous compounds increase linearly with the reciprocal number of their π -electron pairs, which means the influence of the conjugation length on the HOMO–LUMO distance is very strong. As mentioned above, all measurements were performed in solution, whereas the determination of HOMO–LUMO distances of materials is also quite frequently carried out in the solid state. Nevertheless, to study the influence of different substituents and side chains, measurements in solution are quite significant. Electrochemical measurements lead to band gaps of 3.08, 3.18, and 3.49 eV for compounds **4**, **1**, and **5** respectively (see Table 3), in accordance with the early calculations by Kuhn.¹⁴ The cyclic voltammogram of 1,4-bis(1-cyano-2-naphthylethenyl)-2,5-dihexyl-

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Table 4. Redox Potentials $E_{1/2}$ of **3 Determined by Cyclic Voltammetry in Different Solvents^a**

solvent	$E_{1/2}(\text{Ox}_1)$ (V) (ΔE_p [mV])	$E_{1/2}(\text{Ox}_2)$ (V) (ΔE_p [mV])	$E_{1/2}(\text{Red}_1)$ (V) (ΔE_p [mV])	$E_{1/2}(\text{Red}_2)$ (V) (ΔE_p [mV])
dichloromethane	1.27 (125)	-1.47 (150)	-2.00 (315)	
tetrahydrofuran			-2.13 (315)	-2.30 (170)

**Figure 1.** Cyclic voltammograms of **1** carried out in THF/*n*-Bu₄NPF₆ at a scan rate of 500 mV/s.**Figure 2.** Cyclic voltammograms of **2** carried out in THF/*n*-Bu₄NPF₆ at a scan rate of 500 mV/s.**Table 5. Redox Potentials $E_{1/2}$ of **4** Determined by Cyclic Voltammetry in Different Solvents^a**

solvent	$E_{1/2}(\text{Ox}_1)$ (V) (ΔE_p [mV])	$E_{1/2}(\text{Red}_1)$ (V) (ΔE_p [mV])	$E_{1/2}(\text{Red}_2)$ (V) (ΔE_p [mV])
dichloromethane	1.78 (190)	-1.29 (110)	
tetrahydrofuran		-1.30 (130)	-1.40 (125)

^a Scan rate = 100 mV/s.

benzene (**4**) measured in dichloromethane shows one reduction and one oxidation waves. The reduction takes place in THF at -1.30 V vs SCE (see Table 5) with a quasireversible electron transfer. In the first reductive step, two electrons are transferred. This was determined by combined chronoamperometric and cyclovoltammetric measurements. This result corresponds to the two-electron transfer determined for compound **1**. 1,4-Bis(1-cyanoethenyl)-2,5-dihexylbenzene (**5**) has a larger HOMO-LUMO distance than **1** or **4**, because of the short conjugation length (see Table 3). Thus, by cyclovoltammetric measurements in dichloromethane and tetrahydrofuran, only reductive electron transfers can be determined. For this reason, acetonitrile was used as the solvent because of its wider potential range. In this solvent, the cyclic voltammogram shows three

reduction waves and one oxidation wave (see Table 6), from which the band gap can be calculated (see Table 3). The first reduction at -1.4 V vs SCE is well-resolved and quasireversible. The second reductive electron transfer is followed by a chemical reaction and forms a subsequent product, which is oxidized at -0.01 V vs SCE. The third reduction is again quasireversible.

Because of the two alkyloxy groups in the central phenylene unit, 1,4-bis(2-cyano-2-phenylethenyl)-2,5-bis(hexyloxy)benzene (**6**) is expected to have decreased oxidation and reduction potentials and a decreased band gap.⁴ In the cyclic voltammogram of **6** carried out in dichloromethane, three reduction waves appear at -1.24, -1.38, and -1.67 V vs SCE and one oxidation wave appears at +1.47 V vs SCE (see Table 7); in the differential pulse voltammogram, one more oxidative electron transfer at -1.82 V is observed. The first and second reductions are well-resolved and quasireversible, just as the first oxidation. Confirming the earlier reported results in comparison with **1-5**, a smaller HOMO-LUMO distance of 2.71 eV was determined for **6**.⁴

The PPV model compounds **1**, **2**, **4**, and **5** were also investigated by UV/vis/NIR spectroelectrochemistry (SEC) in tetrahydrofuran and Bu₄NPF₆ at different potentials vs Ag/Ag⁺. The data for **1** point to the fact that, at -1.5 V (vs Ag/Ag⁺), the monoradical anion is formed.¹⁵ The subsequent formation of a di- or trianion was not confirmed by SEC.

For the bis(cyano) compound **2**, despite the fact that different potentials were applied, no notable changes in the UV/vis/NIR absorptions could be observed. The HOMO-LUMO distance of **2**, as pointed out before, is too large, so **2** could not be reduced or oxidized under the applied conditions.

During the SEC investigations, the UV/vis/NIR absorptions of compound **4** exhibited a decrease of the absorption maximum at 362 nm resulting from the reductive process. The first reductive electron transfer at -1.3 V (vs Ag/Ag⁺) leads to new absorption maxima at 615, 686, and 1.050 nm. The maximum at 1.050 nm disappears with the second electron transfer at -1.5 V (vs Ag/Ag⁺). Both results point to the formation of a radical anion and to the subsequent formation of a dianion.

During measurements of the cyclic voltammetry of **5**, it was observed that the solution of **5** is red in color at the first reduction potential. The spectroelectrochemical investigations of **5** were carried out during the reduction to correlate the potential and the time. It could be shown that the UV/vis/NIR absorptions are time-dependent. The UV/vis/NIR spectra are almost the same after the reduction process as well as after the oxidation process. The change that occurs with compound **5** at a longer constant reduction potential therefore must be reversible. This points to a reversible dimerization as de-

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Table 6. Redox Potentials $E_{1/2}$ of 5 Determined by Cyclic Voltammetry in Different Solvents^a

solvent	$E_{1/2}(\text{Ox}_1)$ (V) (ΔE_p [mV])	$E_{1/2}(\text{Red}_1)$ (V) (ΔE_p [mV])	$E_{1/2}(\text{Red}_2)$ (V) (ΔE_p [mV])	$E_{1/2}(\text{Red}_3)$ (V) (ΔE_p [mV])
dichloromethane	2.04 (205)	-1.40 (165)	-1.58 (110)	-1.86 (380)
acetonitrile		-1.40 (105)	-1.59 (120)	-1.84 (125)
tetrahydrofuran		-1.39 (120)	-1.68 (150)	-1.86 (130)

^a Scan rate = 100 mV/s.**Table 7. Redox Potentials $E_{1/2}$ of 6 Determined by Cyclic Voltammetry in Different Solvents^a**

solvent	$E_{1/2}(\text{Ox}_1)$ (V) (ΔE_p [mV])	$E_{1/2}(\text{Red}_1)$ (V) (ΔE_p [mV])	$E_{1/2}(\text{Red}_2)$ (V) (ΔE_p [mV])	$E_{1/2}(\text{Red}_3)$ (V) (ΔE_p [mV])
dichloromethane	1.47 (110)	-1.24 (100)	-1.38 (110)	-1.67 (130)
dichloromethane/acetonitrile (1:1) ^b	0.93 (110)	-1.70 (160)	-1.90 (200)	

^a Scan rate = 100 mV/s. ^b Scan rate = 20 mV/s.**Table 8. Comparison of Substituent Effects on the Resonance Orbitals and the Band Gap**

compd	compared with compd	effect on HOMO (eV)	effect on LUMO (eV)	effect on band gap (eV)	caused by
1	3	+0.60	+0.70	-0.10	electron acceptor
6	1	-0.40	+0.07	-0.47	electron donor
1	5	-0.22	+0.09	-0.31	larger π system
1	4	+0.09	-0.01	+0.10	smaller π system
2	1	+0.11	-0.30	+0.41	torsion

scribed by Heinze et al.,^{5a,b} which could occur through the formation of a σ bond or through aggregation of the charged particles.

4. Conclusion

The electrochemically determined redox potentials are in conformity with the ab initio calculations (semi-

empirical Hartree–Fock calculations, VEH).^{2,15} The results show an asymmetric stabilization and a decrease of the resonance orbitals by introduction of electron-withdrawing groups (e.g., cyano groups) in PPV. An enlargement of the conjugated system is caused by insertion of phenyl rings at the periphery, leading to a reduction of the HOMO–LUMO distance. By substitution of PPV model compounds with electron-donating groups at the central phenylene ring, an increase and asymmetric destabilization of the resonance orbitals occurs. A comparison of the electrochemically determined substituent effects in our PPV model compounds on the resonance orbitals and the HOMO–LUMO distances is presented in Table 8.

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