VIS/NIR Absorption Spectra of Positively Charged Oligo(phenylenevinylene)s and Comparison with Time-Dependent Density Functional Theory Calculations

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A combined experimental and theoretical study of the optical properties of positively charged unsubstituted and dialkoxy-substituted phenylenevinylene (PV) oligomers in solution is presented. Cations of PV oligomers were produced by irradiation of a solution with high-energy electron pulses. The optical absorption spectra were measured using time-resolved visible/near-infrared (VIS/NIR) spectroscopy in the range of 500−2100 nm (0.6−2.5 eV). The optical absorption spectra of positively charged PVs are compared with results from time-dependent density functional theory (TDDFT) calculations and previous semiempirical calculations. The experimental spectra of cations of partially dialkoxy-substituted PVs indicate the presence of a transition with a maximum below 0.6 eV. According to earlier semiempirical calculations, the energy of this transition exhibits an oscillating behavior as a function of the length of the oligomer. This was not observed experimentally. However, the monotonic decrease of the low-energy absorption band, as obtained from TDDFT calculations, is in agreement with the experimental findings.

1. Introduction

Conjugated polymers are polyunsaturated compounds, in which the backbone C atoms are sp or sp^2 hybridized. In their pure state, conjugated polymers are wide band-gap semiconductors, which can become conducting by injection of charges from electrodes, photoexcitation, or chemical doping.[1] Poly(*p*-phenylenevinylene) (PPV) and its derivatives have received considerable attention during the last two decades, because of potential applications in light-emitting diodes (LEDs),[2−4] solid-state lasers,[5−7] field-effect transistors,[8] optical waveguides,[9,10] and photovoltaics.[11−13] The properties that make them suitable for such applications include efficient luminescence,[14−16] low weight, flexibility, and low cost. The presence of alkyl or alkoxy substituents provides soluble polymers, which can be easily processed, e.g., by spin coating. The introduction of such substituents also modifies the electronic properties of the polymers, leading to changes in the optical absorption and emission spectra[17,18] and an increase of the luminescence yield in LEDs.[19,20]

The performance of PPV derivatives in optoelectronic devices is dependent on the properties of the excess charges. Optical absorption spectra of excess charges can provide valuable information about their spatial extent along the polymer chain. Therefore, both experimental and theoretical studies of the optical absorption spectra of charged phenylenevinylene (PV) oligomers have been performed. Sakamoto et al.[21] reported ultraviolet to infrared absorption measurements of positively charged unsubstituted PV oligomers. van Hal et al.[22] measured cation spectra of fully dialkoxy-substituted PVs by photoinduced absorption spectroscopy. Using pulse radiolysis with time-resolved spectrophotometric detection, Grozema et al.[23] measured the optical absorption spectra of radical cations of partially dialkoxy-substituted PV oligomers.

Quantum chemical calculations have been performed, to gain insight into the nature of the electronic transitions. Cornil et al.[24] performed semiempirical calculations on neutral and positively charged unsubstituted PV oligomers. The geometries of the cations were optimized using the Austin Model 1 (AM1). The optical absorption spectra were calculated using the Hartree−Fock intermediate neglect of differential overlap (INDO) method, combined with configuration interaction of singly excited states (CIS). According to the calculations by Cornil et al.,[24] two subgap absorption peaks are induced by the generation of singly charged PVs. For doubly charged PVs, the absorption spectrum is characterized by a single strong transition. Grozema et al.[23] calculated the spectra of positively charged unsubstituted and dialkoxy-substituted PVs, using the INDO/s-CIS method with geometries obtained from density functional theory (DFT) calculations. It was shown that this combination of methods gives a good description of the optical absorption spectra of short derivatives of PV oligomers. For longer chains, Grozema et al.[23] found that the charge distributions obtained from DFT calculations are more delocalized than those calculated using the INDO/s Hartree−Fock method. The differences between the two methods are also reflected in the effect of alkoxy side chains. The INDO/s-CIS method predicts an oscillating behavior of the low absorption energy (RC1) of partially dialkoxy-substituted PVs, as a function of chain length. This odd−even effect was determined to be consistent with the degree of charge delocalization as obtained from semiempirical INDO/s Hartree−Fock calculations. The odd−even effect could not be verified experimentally, because of the limited accessible energy range of the optical absorption setup.

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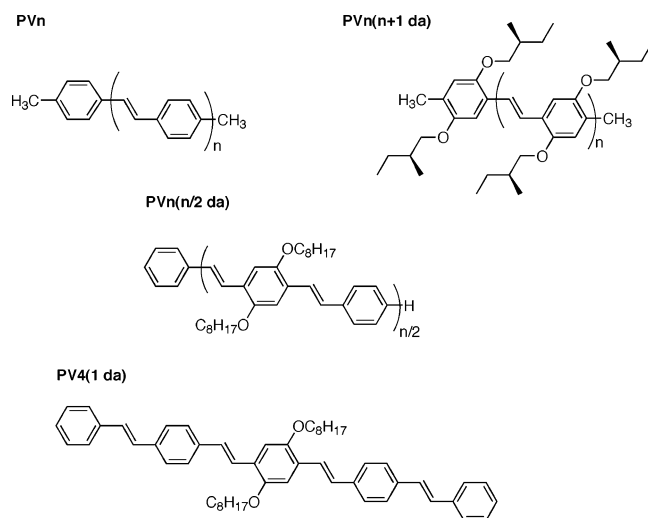
Figure 1. Chemical structures of phenylenevinylene (PV) oligomers (*n* is the number of phenylenevinylene units).

The odd−even effect could be an artifact in the INDO/s-CIS calculations. Therefore, we have extended the measurements of the optical absorption spectra of cations of partially dialkoxy-substituted PVs to low absorption energies, and we performed time-dependent density functional theory (TDDFT) calculations. The latter method is promising, because Hirata et al.[25] have shown that TDDFT provides a good description of the lowest excitation energies of polycyclic aromatic hydrocarbon radical ions. Until now, only a few TDDFT calculations on open-shell systems have been performed.[25,26] To gain further insight into the performance of this method, we also calculated optical absorption spectra of unsubstituted and fully dialkoxy-substituted PV oligomers. The results of the TDDFT calculations are compared with those from experiments and INDO/s-CIS calculations. The structures of the PV oligomers investigated in the present work are presented in Figure 1.

2. Experimental Section

The PV*n*(*n*/2 da) and PV4(1 da) oligomers, shown in Figure 1, were synthesized and purified as reported earlier.[27] Solutions of PV*n*(*n*/2 da) oligomers in UV-spectroscopic-grade benzene with concentrations in the range of 10^{-4}−10^{-3} M were prepared. The solutions were bubbled with benzene-saturated oxygen for ~30 min and maintained under a slight overpressure of the gas during the experiments. Experiments were also performed on oligomer solutions (with concentrations of the order of 10^{-5}−10^{-4} M) in UV-spectroscopic-grade chloroform. The chloroform solutions were bubbled with chloroform-saturated argon. All experiments were performed at room temperature.

The pulse radiolysis technique[28] was used to generate positive charges on isolated PV oligomers in solution. The solutions were irradiated with 20 ns pulses of 3 MeV electrons from a Van de Graaff accelerator. PV cations were detected, using time-resolved visible/near-infrared (VIS/NIR) spectroscopy measurements. The detection light source was an Osram XBO high-pressure xenon lamp (450 W). To avoid photolysis of the solution by the analyzing light, a slow shutter, a suitable cut-off filter, and a fast shutter were placed between the light source and the sample. The solution was flowed continuously through a quartz cell (optical path length of 12.5 mm), using a switch overpressure system. For detection up to 1000 nm, a silicon photodiode was used. Between 1000 and 1600 nm, a short-wavelength enhanced InGaAs PIN photodiode (model G5125-10, Hamamatsu, Japan) was used, whereas, for NIR analysis,

this was replaced by a long-wavelength enhanced InGaAs PIN photodiode (model G5853-01, Hamamatsu, Japan). Transient changes in the optical absorption spectrum were recorded by a Tektronix model TDS680 digitizer.

The absorption spectra of the PV radical cations were measured by following the transient changes in absorbance of the solution at different wavelengths. The initial concentration of charge carriers is determined by the amount of energy that is transferred from the incident 3 MeV electrons to the solution. The radiation dose (in units of Gy, where 1 Gy = 1 J/kg) is defined as the amount of energy transferred per unit mass.[29] The change in optical absorbance is related to the radiation dose, the yield of free charge carriers per unit dose (*G*), and the molar absorption coefficient (ϵ). The radiation dose per pulse was determined by dosimetry, using KSCN solution (10 mM) in N_2O-saturated water. For such a solution, *G* and ϵ are accurately known ($G\epsilon(SCN)_2^- = 5.18 \times 10^{-4}$ m^2/J at 475 nm).[30] In the optical absorption spectra shown in Figures 2, 4, and 5 (shown later in the work), the absorbance changes upon irradiation are normalized to the radiation dose.

3. Computational Methodology

The geometries of the positively charged PV oligomers were optimized using the Amsterdam Density Functional (ADF) theory program.[31] The geometry optimizations were performed using the local density approximation (LDA) with exchange and correlation functionals based on Vosko−Wilk−Nusair (VWN) parametrization of electron gas data.[32] The generalized gradient approximation (GGA)[33] corrections by Becke[34] (exchange) and Perdew[35] (correlation) were included. For optimizing the geometries, a triple-zeta plus double polarization (TZ2P) basis set was used. The geometries were restricted to C_{2h} symmetry.

The electronic absorption spectra of the positively charged PVs were calculated with TDDFT,[36,37] as implemented in the Q-Chem program.[38] The excitation energies were computed using a correlation consistent[39] polarized valence double zeta (cc-pVDZ) basis set. The Becke (exchange) and the Lee−Yang−Parr (correlation)[40] functional (BLYP) or the Becke3 (exchange) and the Lee−Yang−Parr (correlation) hybrid functional (B3LYP)[41] were used. The TDDFT results for the positively charged PV oligomers are compared with INDO/s-CIS calculations published previously.[23]

4. Results and Discussion

Three different series of PV oligomers were studied. The first series, PV*n*, consists of PV oligomers that have been para-substituted with methyl groups on the first and last phenyl ring (see Figure 1). The experimental optical absorption spectra of the PV*n* cations, up to *n* = 3, are available in the literature.[21] The experimental and calculated optical absorption energies are presented in Table 1. The second series, PV*n*(*n* + 1 da), contains two alkoxy substituents on each phenyl ring. The experimental optical absorption spectra of PV*n*(*n* + 1 da) cations were published previously,[22] and the energies of the maxima in the spectra are given in Table 2, together with theoretical results. The third series, PV*n*(*n*/2 da), has two alkoxy substituents on every second phenyl ring. The optical absorption spectra of the PV*n*(*n*/2 da) cations were measured using pulse radiolysis, as described below. To obtain additional insight into the effects of substituents, experiments and calculations were also performed on PV4(1 da), which is dialkoxy-substituted only on the central phenyl ring. The experimental and calculated results obtained for the third series of PV oligomers are presented in Table 3.

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TABLE 1: Calculated and Experimental Transition Energies (ΔE), and Calculated Oscillator Strengths (*f*) for Radical Cations of PV*n* Oligomers[a]

| | | TDDFT | | | | | |
| | | BLYP | | B3LYP | | INDO/s-CIS[c] | |
band	Exp.[b] ΔE	ΔE	f	ΔE	f	ΔE	f
			Oligomer PV1				
RC1	1.54	1.91	0.11	1.99	0.15	1.71	0.04
RC2	2.45	3.08	0.88	3.11	0.90	2.20	0.80
			Oligomer PV2				
RC1	1.03	1.28	0.26	1.32	0.39	1.13	0.36
RC2	1.95	2.34	1.58	2.43	1.56	1.89	1.01
			Oligomer PV3				
RC1	0.80	0.98	0.50	1.01	0.74	0.87	0.62
RC2	1.74	1.94	1.90	2.07	1.94	1.69	1.14
			Oligomer PV4				
RC1		0.80	0.79	0.81	1.12	0.71	0.89
RC2		1.74	1.04	1.85	1.44	1.65	1.03
RC3		2.60	0.67	1.92	0.48	1.91	0.22
			Oligomer PV6				
RC1		0.58	1.34	0.56	1.76	0.55	1.13
RC2		1.46	1.84	1.67	1.81	1.44	0.14
RC3		2.08	1.68	2.39	1.09	1.58	1.00
			Oligomer PV8				
RC1		0.43	1.73	0.41	2.11	0.49	1.29
RC2		1.36	1.58	1.57	1.13	1.57	0.80
RC3						1.81	0.38
			Oligomer PV10				
RC1		0.37	2.15	0.35	2.65	0.46	1.33
RC2						1.47	0.23
RC3						1.60	0.27
			Oligomer PV12				
RC1		0.30	2.31	0.27	2.51	0.45	1.39
RC2						1.60	0.43
RC3						1.72	0.34

[a] Only the transitions with an oscillator strength of >0.1 are presented. [b] Experimental data were taken from ref 21. [c] Theoretical data were taken from ref 23.

4.1. Measurement of Cation Spectra of Partially Dialkoxy-Substituted Phenylvinylenes. Irradiation of benzene (bz) leads to the generation of radical cations (bz$^{\bullet+}$), excited states (bz*), and solvated electrons (e^{-})[42−44] (see eq 1).

$$bz \rightarrow bz^{\bullet+}, bz^*, e^- \qquad (1)$$

The radiolytic processes that result in the formation of positively charged PVs were discussed in detail elsewhere.[45] The most important reactions are described below. In oxygen-saturated solutions ([O$_2$] = 11.9 mM at 1 atm and 25 °C), the excess electrons are rapidly scavenged, according to eq 2.

$$e^- + O_2 \rightarrow O_2^- \qquad (2)$$

The excited states are quenched by O$_2$ within a few nanoseconds to yield O$_2$ in the $^1\Delta$ excited state[46] (see eq 3).

$$bz^* + O_2 \rightarrow O_2(^1\Delta) + bz \qquad (3)$$
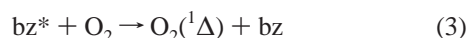
The radical cations of benzene transfer their charge to the PV oligomers, because these compounds have a lower ionization potential than benzene (see eq 4).

$$bz^{\bullet+} + PV \rightarrow bz + PV^{\bullet+} \qquad (4)$$

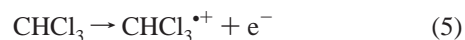Candeias et al.[47] have shown that the radical cations of PV oligomers are unaffected by O$_2$.

TABLE 2: Calculated and Experimental Transition Energies (ΔE), and Calculated Oscillator Strengths (*f*) for Radical Cations of PV*n*(*n* + 1 da) Oligomers[a]

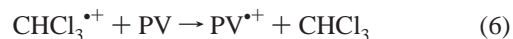| | | TDDFT | | | | | |
| | | BLYP | | B3LYP | | INDO/s-CIS[c] | |
band	Exp.[b] ΔE	ΔE	f	ΔE	f	ΔE	f
			Oligomer PV2(3 da)				
RC1	0.76	0.77	0.20	0.86	0.33	0.90	0.30
RC2	1.71	1.89	0.87	2.12	1.21	1.66	0.64
RC3	∼2.0[d]	2.47	0.22	3.58	0.21	1.99	0.23
			Oligomer PV3(4 da)				
RC1	0.66	0.67	0.38	0.76	0.64	0.71	0.43
RC2	1.52	1.66	1.07	1.92	1.57	1.34	0.34
RC3	∼1.7[d]	2.17	0.37			1.56	0.61
			Oligomer PV4(5 da)				
RC1	0.59	0.62	0.53	0.69	0.90	0.68	0.58
RC2	1.43	1.30	0.24	1.58	1.42	1.35	0.96
RC3	∼1.6[d]	1.42	1.59	1.70	0.74	1.61	0.11
			Oligomer PV5(6 da)				
RC1	0.54	0.62	0.52	0.69	0.88	0.57	0.74
RC2	1.40	1.30	0.33	1.57	1.63	1.24	0.31
RC3	∼1.6[d]	1.42	1.57	1.71	0.60	1.40	0.85

[a] Only the transitions with an oscillator strength of >0.1 are presented. [b] Experimental data were taken from ref 22. [c] Theoretical data were taken from ref 23. [d] The estimated absorption energies of RC3 were extracted from the spectra in ref 22.

The measured radical cation absorption spectra of PV*n*(*n*/2 da) oligomers are shown in Figure 2. The energies corresponding to the absorption maxima can be found in Table 3. For the PV2-(1 da) radical cation, two bands are observed. The first band appears at 1.27 eV and is denoted RC1. The second band (denoted as RC2) has a maximum at 2.08 eV and exhibits two vibrational transitions, in agreement with previous measurements.[23] The shape of the RC2 band between 1.8 eV and 2.4 eV differs from that in ref 23, because of improvement of the spectral resolution of the optical setup. For the longer oligomers in the PV*n*(*n*/2 da) series, the maximum of the low-energy band (RC1) shifts to <0.6 eV. At energies of <0.6 eV, optical absorption measurements could not be performed, because of absorption by the benzene solvent. In Figure 3, the optical absorption spectra of the positively charged, partially dialkoxy-substituted oligomers are superposed. The RC2 band of the PV*n*(*n*/2 da) radical cations (with *n* > 2) exhibits no observable shift to lower energies with increasing chain length. The absorption maxima of the RC1 band could not be determined for PVs other than PV2(1 da); however, the onset of the RC1 band in Figure 3 suggests that there is not a large shift, as a function of the chain length.

Additional measurements were performed in chloroform. Irradiation of chloroform (CHCl$_3$) with 3 MeV electrons leads to the formation of radical cations (CHCl$_3^{\bullet+}$) and excess electrons (e^{-}),[48,49] according to eq 5.

$$CHCl_3 \rightarrow CHCl_3^{\bullet+} + e^- \qquad (5)$$

The CHCl$_3^{\bullet+}$ ions transfer their charge to the PV oligomers, which have a lower ionization potential. This leads to the formation of PV radical cations (see eq 6).

$$CHCl_3^{\bullet+} + PV \rightarrow PV^{\bullet+} + CHCl_3 \qquad (6)$$

TABLE 3: Calculated and Experimental Transition Energies (ΔE), and Calculated Oscillator Strengths (f) for Radical Cations of PVn(n/2 da) Oligomers

| | | TDDFT | | | | | |
| | | BLYP | | B3LYP | | INDO/s-CIS[b] | |
band	Exp.[b] ΔE	ΔE	f	ΔE	f	ΔE	f
			Oligomer PV2(1 da)				
RC1	1.27	1.25	0.24	1.33	0.38	1.26	0.04
RC2	2.08	2.27	1.07	2.45	1.20	2.02	1.08
			Oligomer PV4(2 da)				
RC1	<0.6	0.74	0.52	0.76	0.88	0.51	0.75
RC2	1.52	1.55	2.02	1.74	2.10	1.49	0.56
RC3	1.71	2.41	0.33	2.69	0.12	1.74	0.53
			Oligomer PV6(3 da)				
RC1	<0.6	0.54	1.07	0.54	1.59	0.75	0.86
RC2	1.45	1.22	0.20	1.52	1.98	1.47	0.44
RC3	1.63	1.31	1.82			1.56	0.72
RC4						1.91	0.30
			Oligomer PV8(4 da)				
RC1	<0.6	0.44	1.56	0.41	2.03	0.38	1.03
RC2	1.59					1.41	0.77
RC3						1.56	0.10
						1.72	0.29
			Oligomer PV10(5 da)				
RC1		0.36	3.28	0.33	2.38	0.66	1.08
RC2						1.47	0.30
RC3						1.65	0.81
RC4						1.92	0.49
			Oligomer PV12(6 da)				
RC1	<0.6	0.29	2.31	0.27	2.58	0.34	1.15
RC2	1.51					1.51	0.56
RC3						1.59	1.19
RC4						1.72	0.38
			Oligomer PV16(8 da)				
RC1	<0.6						
RC2	1.50						
			Oligomer PV4(1 da)				
RC1	0.77	0.79	0.78	0.82	1.07	1.03	0.44
RC2	1.63	1.62	0.52	1.82	0.47	1.77	1.47
RC3		1.77	1.33	1.98	1.39	1.94	0.14

[a] Experimental data obtained from spectra in Figures 2 and 5. [b] Theoretical data were taken from ref 23.

The excess electrons react with neutral chloroform and form the methylene chloride radical and the chloride anion[50] (see eq 7).

$$e^- + CHCl_3 \rightarrow {}^\bullet CHCl_2 + Cl^- \qquad (7)$$

The methylene chloride radical can react with neutral PV oligomers, leading to the formation of PV radical cations and methylene chloride anions (eq 8).

$$^\bullet CHCl_2 + PV \rightarrow PV^{\bullet+} + CHCl_2{}^- \qquad (8)$$
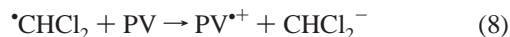
In Figure 4, the optical absorption spectra of PV2(1 da) and PV16(8 da) radical cations in chloroform are compared with the spectra in benzene. For PV2(1 da), the absorption maxima in chloroform appear at an energy, which is ∼0.1 eV higher than that in benzene. The effect of the solvent on the cation spectrum of PV16(8 da) is much smaller. Apparently, for the longer oligomer, the solvent effect is reduced as a consequence of a larger extent of delocalization of the charge.

Figure 5 shows a comparison of the absorption spectra for the radical cations of PV4(1 da) and PV4(2 da). The number and position of the substituents clearly influence the optical absorption spectra of these PV tetramers. The low-energy band
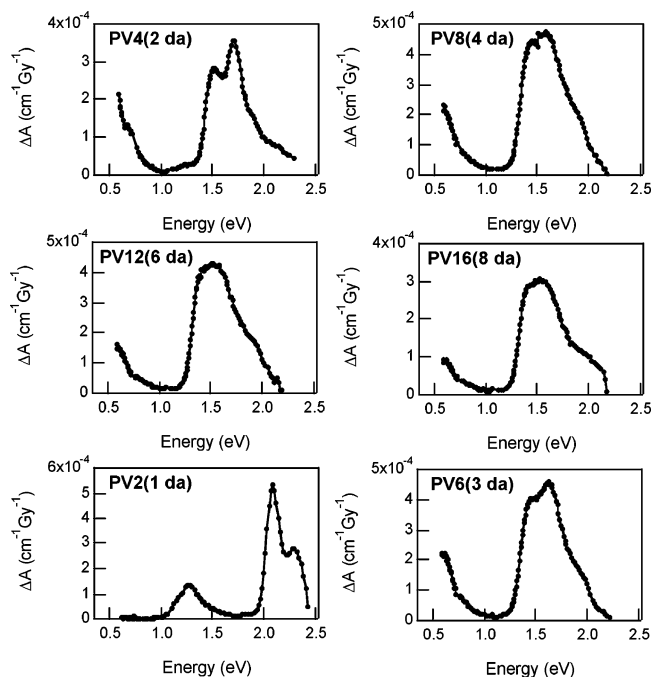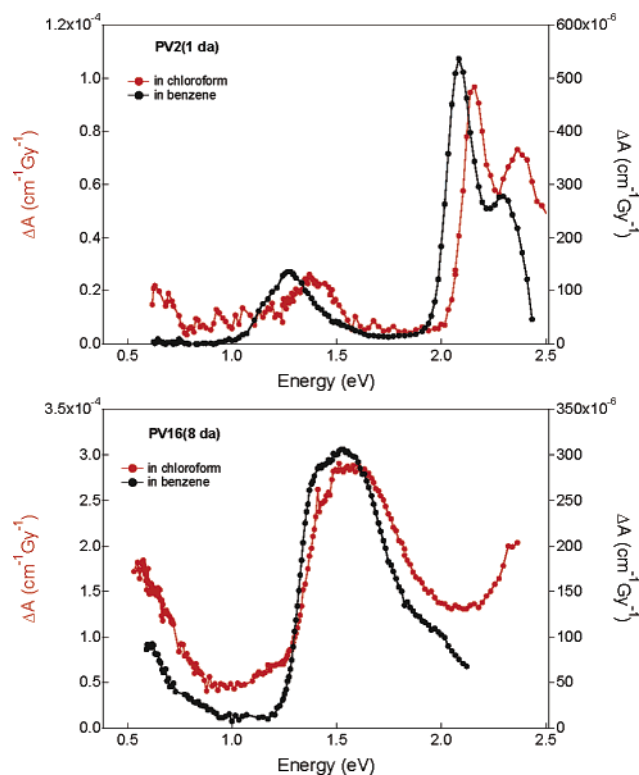

Figure 2. Optical absorption spectra of the radical cations of the PVn(n/2 da) series in benzene.
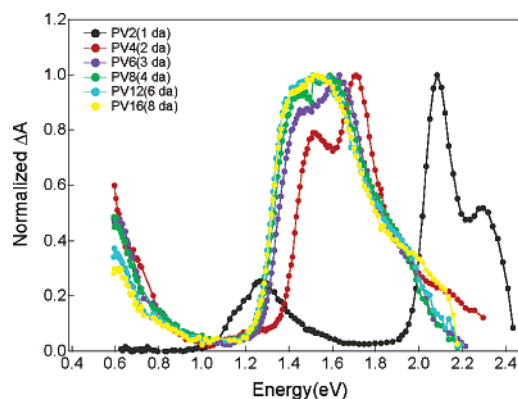
Figure 3. Superposed optical absorption spectra of the radical cations of the PVn(n/2 da) series in benzene. (The spectra were normalized to the maximum absorbance.)

(RC1) for the PV4(1 da) radical cation has a maximum at 0.77 eV. Although the low-energy band for PV4(2 da) could not be measured completely, the data in Figure 5 show that the maximum of this band appears at <0.6 eV. This reduction of the transition energy suggests that the charge is more delocalized when more dialkoxy substituents are present. The RC2 bands for PV4(1 da) and PV4(2 da) appear at similar energies in the cation spectra.

4.2. Calculated Absorption Spectra of PV Cations. The calculated electronic transitions of the three series of PV radical cations are listed in Tables 1–3, together with the experimental data from the present measurements and literature. In the calculations, the alkoxy substituents were taken to be methoxy groups. This simplification is not expected to influence the results significantly, with regard to electronic effects of the substituents.[23] The results from the TDDFT calculations are discussed and compared with INDO/s-CIS results and with the experimental data below.

4.2.1. PVn Radical Cations. The calculated and experimental transition energies (ΔE) and the calculated oscillator strengths (f) for radical cations of PVn oligomers are given in Table 1. The electronic configurations that dominate the allowed transi-

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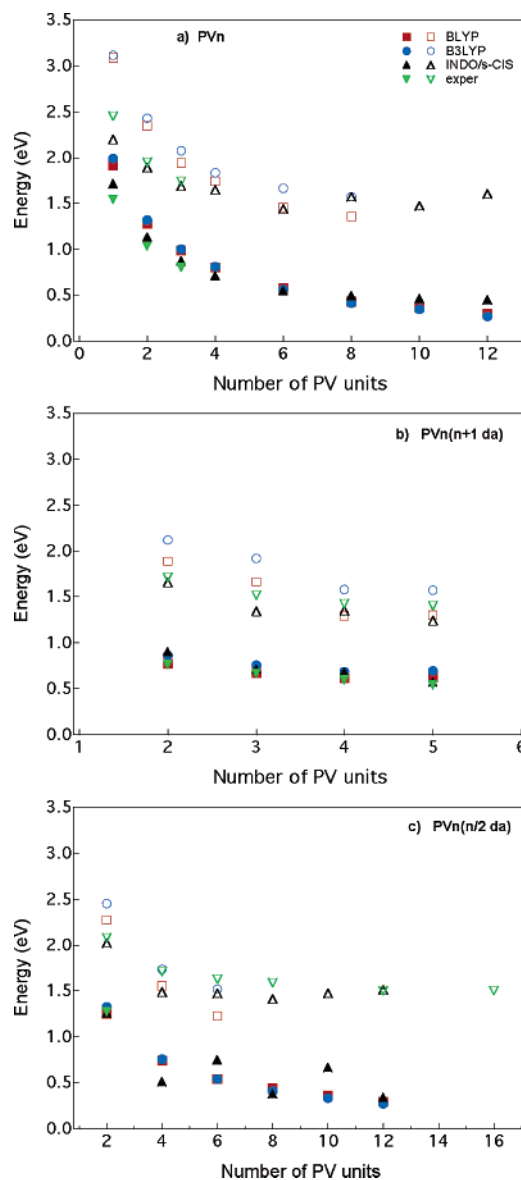*J. Phys. Chem. B, Vol. 108, No. 52, 2004* **19971**

Figure 4. Comparison of the optical absorption spectra of radical cations of PV2(1 da) and PV16(8 da) in chloroform and benzene.
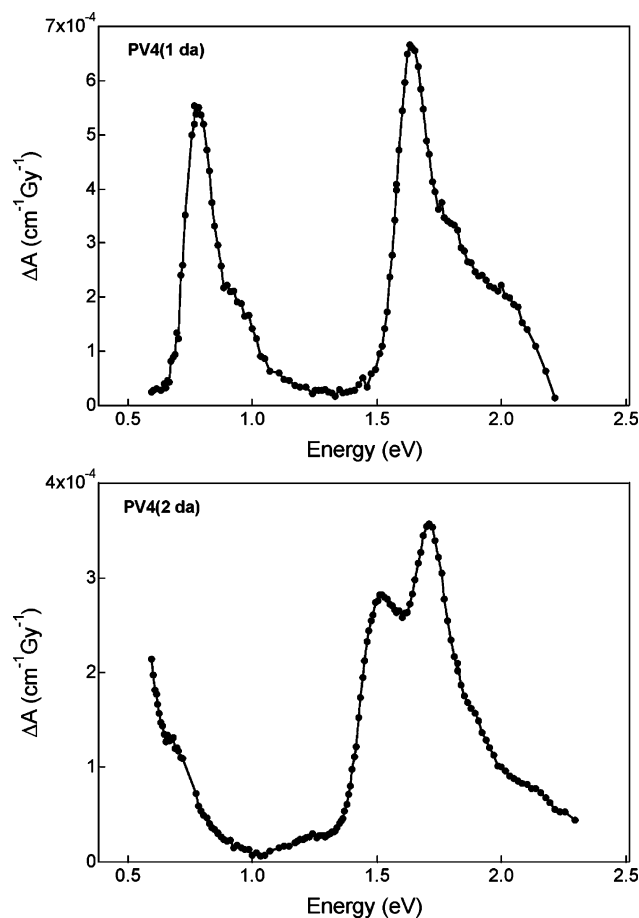
Figure 5. Optical absorption spectra of radical cations of PV4(1 da) and PV4(2 da) in benzene.

Figure 6. Chain-length dependence of the absorption energies for PV cations ((a) PV*n*, (b) PV*n*(*n* + 1 da), and (c) PV*n*(*n*/2 da)). Filled markers correspond to the lowest energy band (RC1), and open markers correspond to the second energy band (RC2)).

the lowest transition (RC1) is dominated by excitation of an electron from the highest doubly occupied molecular orbital to the singly occupied molecular orbital. The second (RC2) and third (RC3) transition correspond mainly to excitation of an electron from the singly occupied molecular orbital to the lowest unoccupied molecular orbital with a different contribution of other excitations involving lower-lying orbitals.

The RC1 and RC2 excitation energies of PV*n* cations calculated with TDDFT are compared with the INDO/s-CIS calculated energies[23] and with experimental data[21] in Figure 6a. The general observation is that all transition energies shift to lower values with increasing chain length, which can be understood in terms of increasing spatial delocalization of the charge. The TDDFT results obtained using BLYP and B3LYP functionals are similar. For short PV*n* oligomers (with *n* = 1−3), the TDDFT transition energies are higher than the INDO/s-CIS transition energies. The INDO/s-CIS excitation energies are generally more similar to the experimental values. For long PV*n* oligomers (with *n* > 3), the TDDFT results for the RC1 and RC2 bands are similar to those obtained with the INDO/s-CIS

tions, according to the INDO/s-CIS method for the PV*n* radical cations, were described in a previous study.[23] It was found that

method. The third absorption band (RC3) for longer PVn oligomers obtained from TDDFT calculations appears at a substantially higher energy than that observed by the INDO/s-CIS method (see Table 1). For PVn oligomers with $n \geq 8$, not all three transitions could be calculated, because of computer hardware limitations. The main conclusion is that both TDDFT and INDO/s-CIS methods reproduce the experimental data for the RC1 and RC2 transitions. To be able to distinguish the performance of the different theoretical methods, experimental results on the RC3 transition for longer oligomers are needed.

The data in Table 1 show that the calculated oscillator strength (f) of the RC1 transition increases with the chain length, in agreement with previous calculations.[24] For shorter chains, the oscillator strength of the RC1 transition is higher than that for RC2, whereas for longer chains, the RC2 transition is most intense. The oscillator strength obtained from TDDFT calculations generally is higher than that from INDO/s-CIS calculations, in particular for the RC2 band of the PV6 radical cation.

4.2.2. PVn(n + 1 da) Radical Cations. Table 2 shows the calculated and experimental transition energies (ΔE) and the calculated oscillator strengths (f) for the radical cations of PVn(n + 1 da) oligomers. Introduction of dialkoxy substitution at each phenyl ring reduces the absorption energies (cf. Tables 1 and 2). As can be seen in Figure 6b, both the TDDFT and INDO/s-CIS methods reproduce the experimental RC1 and RC2 transition energies reasonably well.[22] Note that the dependence of the RC1 energy on the chain length is much smaller than for the PVn series, both in the experiment and in the calculations. A possible explanation can be the delocalization of the charge into the alkoxy side chains. This means that, for the same chain length, the charge is always more delocalized in the PVn(n + 1 da) series than in the PVn series. As a consequence, the chain length at which the distance dependence becomes very small is reached already for shorter oligomers. The differences between the results obtained with the BLYP and B3LYP functionals are larger than for PVn radical cations. The transition energies obtained with the BLYP functional are more similar to the experimental data. According to both the TDDFT and the INDO/s-CIS calculations, a third absorption band (RC3) appears at higher energies (see Table 2). For the PV2(3 da) radical cation, a third absorption band is clearly present in the experimental spectrum of van Hal et al.[22] However, this band has not been assigned to a separate electronic transition by those authors. The energy of the RC3 band for PV2(3 da) is reproduced quite well by the INDO/s-CIS calculations, whereas TDDFT considerably overestimates the energy of this band. For longer PVn(n + 1 da) cations, a shoulder toward the high-energy side of the RC2 band can be distinguished in the experimental spectra of van Hal et al.[22] According to the present calculations, this shoulder could be due to the RC3 transition. The RC3 excitation energies as estimated from the experimental spectra in ref 22 are similar to the calculated values (see Table 2).

4.2.3. PVn(n/2 da) Radical Cations. The TDDFT transition energies (ΔE) for the cations of PVn(n/2 da) oligomers are compared with the INDO/s-CIS energies and with the experimental data from the present work in Figure 6c and Table 3. For the PV2(1 da) cation, the agreement between the calculated and the experimental energy of the RC1 band is excellent. The RC2 transition energy of the PV2(1 da) cation is better reproduced by the INDO/s-CIS method than by the TDDFT calculation.

The maximum of the low-energy band (RC1) in the measured spectrum of PV4(2 da) cation is <0.6 eV, in agreement with the results from INDO/s-CIS calculations.[23] TDDFT overesti-
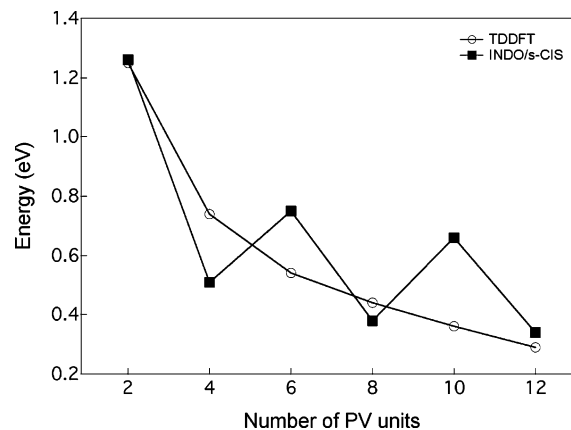
Figure 7. Chain-length dependence of the lowest transition energy (RC1) calculated for PVn(n/2 da) radical cations, using the TDDFT or INDO/s-CIS method.

mates the energy of the RC1 band by at least 0.15 eV. The double maximum of the high-energy band in the experimental spectrum of PV4(2 da) (see Figure 2) can be assigned to two separate electronic transitions, on the basis of INDO/s-CIS calculations (RC2 and RC3). In contrast, TDDFT does not predict two close-lying electronic transitions (see Table 3).

According to the experiments, the RC1 transition energy of the longer oligomers of the PVn(n/2 da) series is <0.6 eV, in agreement with the results from TDDFT calculations. The RC2 transition energies are reproduced quite well by both the INDO/s-CIS and the TDDFT calculations.

The most interesting observation from the comparison of the TDDFT and the INDO/s-CIS results is that the former method predicts a monotonic decrease of the RC1 absorption energy with chain length (see Figure 7), in contrast with the latter. As shown earlier, the INDO/s-CIS calculations for PVn(n/2 da) radical cations predict the occurrence of a so-called odd−even effect.[23] The PVn(n/2 da) radical cations with an even number of dialkoxy-substituted phenyl rings were found to have the RC1 energy lower than that for the corresponding PVn radical cation. On the other hand, for PVn(n/2 da) radical cations with an odd number of dialkoxy-substituted phenyl rings, the RC1 energies are always higher than those of the unsubstituted analogue. This odd−even effect, as predicted by the INDO/s-CIS method, is not observed experimentally. In particular, the RC1 band for the PV6(3 da) radical cation is not higher than the RC1 band for the PV4(2 da) radical cation (see Figure 2). The INDO/s-CIS method seemingly overestimates the localization of charges, because of the presence of alkoxy side chains.

4.2.4. PV4(1 da) Radical Cation. To gain additional insight into the effect of the dialkoxy substitution on the optical properties of the PV radical cations, the compound PV4(1 da), which has substituents only at the central phenyl ring (see Figure 1) was also investigated. The optical absorption spectra of the PV4(1 da) and PV4(2 da) cations are shown in Figure 5. The RC1 and RC2 transition energies of the PV4(1 da) radical cation are reproduced very well by both the TDDFT and INDO/s-CIS methods (see Table 3). The RC2 band in the experimental spectrum of PV4(1 da) has a shoulder toward the high-energy side (see Figure 5). According to both theoretical methods, a third transition (RC3) occurs at higher energy, which may be the cause of this shoulder.

4.3. Effect of Substituents on the Charge Distribution. Insight into the effect of the substituents on the delocalization of a charge carrier on a PV oligomer can be obtained by analyzing the charge distribution along the chain. Charge

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distributions calculated with the INDO/s-CIS method have been discussed previously.[23] In the present study, the charge distribution is calculated with the DFT method and compared with the results from the INDO/s-CIS calculations. The charge distribution was obtained from a Mulliken population analysis performed on the same wave function used to calculate the absorption spectra. In the neutral molecules, the phenylene units carry some negative charge, whereas the vinylene units are positively charged. Therefore, the distribution of the excess positive charge was calculated as the difference between the charges of the atoms in the cations and in the neutral molecules. Hence, the calculated distribution corresponds to that of the excess positive charge. Figure 8 shows the distribution of an excess positive charge in PV tetramers with different dialkoxy substitution patterns.

The phenylene units in the unsubstituted oligomer (PV4) carry a similar amount of charge. The same holds for the vinylene units, even though the amount of charge on the latter is smaller than that on the phenylene units. Note that the charge per C atom is smaller for the phenylene units (which contain six C atoms) than for the vinylene units (which have two C atoms). However, because the atomic orbitals on the C atoms form molecular fragment orbitals on the phenylene and vinylene units, it is most appropriate to discuss the charge distribution in terms of these units. The higher amount of charge on the phenylene units is due to the lower ionization potential of these units, in comparison with that of the vinylene units. The introduction of methoxy substituents on the phenyl ring leads to a further reduction of the ionization potential of these units. As a consequence, the charge becomes more localized on the central methoxy-substituted phenyl ring in PV4(1 da) (see Figure 8). For PV4(2 da), the charge is mainly localized on the second and fourth phenyl ring, i.e., on the phenyl rings that contain methoxy substituents. When all phenyl rings are methoxy-substituted, which is the case for PV4(5 da), the charge is almost uniformly distributed over the phenylene units, with somewhat more charge on the outer phenyl rings. Figure 8 shows that the charge distribution for PV4(5 da) is almost the same as that for PV4.

The DFT charge distribution is different from that obtained with the INDO/s-CIS method. Grozema et al.[23] found, using the INDO/s-CIS method, that, for PV4, the maximum in the charge distribution is located at the central phenyl ring. For PV4-(1 da), the methoxy substituents localize the charge on the central phenyl ring, but to a larger extent than that according to the DFT calculations. In the PV4(2 da) oligomer, the charge is mainly localized on the substituted phenyl rings, according to the DFT calculations, whereas the charges calculated with the INDO/s-CIS method are distributed more evenly. The results also are different for the PV4(5 da) radical cation. According to INDO/s-CIS calculations, the amount of charge on the central phenylene unit is higher than on the other phenylene units, in contrast to the results obtained with DFT.

The degree of charge delocalization can be characterized in terms of the participation ratio, P (eq 9):

$$P = [\sum_{i=1}^{N} Q_i^2]^{-1} \qquad (9)$$

Note that the aforementioned expression represents the reciprocal value of the often-used inverse participation ratio. In eq 9, Q_i represents the amount of charge present on the ith unit and N is the number of units. If all the excess charge is localized on a single unit, P becomes 1. If the charge is evenly spread
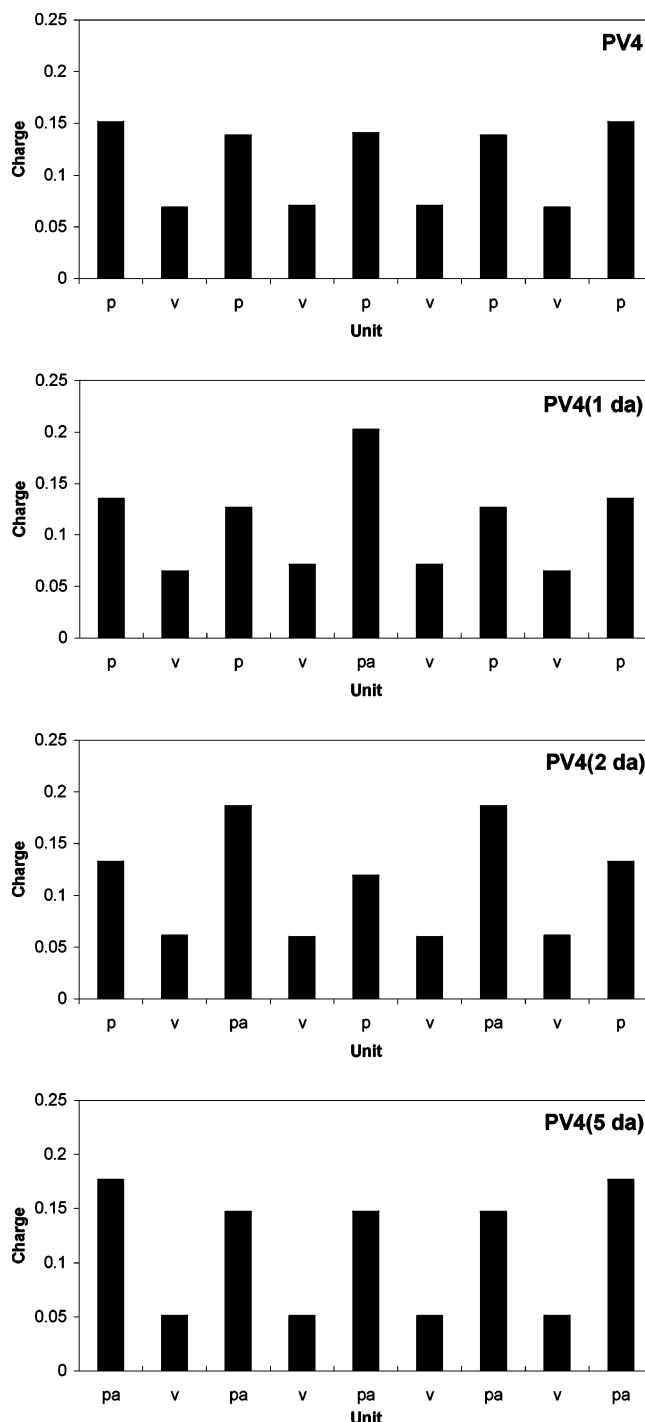
Figure 8. Distribution of an excess positive charge in PV tetramers with different dialkoxy substitution patterns (phenylene, vinylene, and dialkoxy-substituted phenylene units are indicated by p, v, and pa, respectively).

over all N units, than P will be equal to N. Table 4 shows the calculated participation ratio for the unsubstituted and dimethoxy-substituted PV radical cations. The participation ratio for the unsubstituted PV oligomers increases smoothly with chain length, which reflects that the charge becomes more delocalized for longer oligomers. Table 1 shows a decrease of the low-energy band, RC1 for PVn oligomers, with increasing chain length. This decrease coincides with the increased charge delocalization. The same behavior is found for PV$n(n/2$ da) oligomers. The participation ratio substantiates the fact that DFT does not predict the odd−even trend in the RC1 transition energies for the PV$n(n/2$ da) series. As can be observed in Table

TABLE 4: Participation Ratio from the DFT Mulliken Population Analysis

unsubstituted oligomer	participation ratio, P	dimethoxy-substituted oligomer	participation ratio, P
PV2	4.5	PV2(1 da)	4.3
PV4	8.1	PV4(2 da)	7.5
PV6	11.7	PV6(3 da)	10.8
PV8	15.3	PV8(4 da)	14.1
PV10	18.9	PV10(5 da)	17.4
PV12	22.6	PV12(6 da)	20.7
		PV4(1 da)	5.4
		PV4(5 da)	7.2

4, the P values for unsubstituted oligomers are higher than those for the methoxy-substituted oligomers, which means that the charge is more localized when the substituents are present. The calculated degree of charge delocalization correlates with the calculated energy of the lowest absorption band. The only exception is PV4(1 da), which has a lower participation ratio than PV4, whereas the RC1 absorption energies are similar.

The differences between results obtained from INDO/s and DFT calculations were noticed previously. According to DFT calculations on singly and doubly charged thiophene oligomers,[51-53] the charge distribution and the geometry deformations are fully delocalized over the entire length of the oligomer. There are indications that the delocalization of charge is overestimated in DFT.[54] In contrast, the charge distribution obtained from INDO/s-CIS calculations of charged oligo(phenylenevinylene)-s[23,24] and oligothiophenes[55] has a rather localized character. Moreover, the comparison of experimental[56] and theoretical[55] results for thiophene oligomers indicates that semiempirical INDO/s calculations underestimate the spatial extent of charge carriers on conjugated chains. The difference between DFT and semiempirical INDO/s results is attributed to the fact that the two methods are developed from different monoelectronic operators with different theoretical frameworks.[57] DFT includes the electron correlation, whereas, in INDO/s-CIS calculations, the dynamic correlation is not taken into consideration. The extent to which electron correlation is taken into consideration has a large effect on the delocalization of an excess charge.

5. Conclusions

Cations of partially dialkoxy-substituted phenylenevinylene (PV) oligomers were produced in solution using pulse radiolysis with nanosecond pulses of 3 MeV electrons. The cations were detected using time-resolved visible/near-infrared (VIS/NIR) optical absorption measurements.

Quantum chemical calculations were performed for unsubstituted and dialkoxy-substituted PV oligomers. The geometries of the positively charged PV oligomers were optimized using the Amsterdam Density Functional (ADF) theory program. The electronic absorption spectra of the charged PVs were calculated with time-dependent density functional theory (TDDFT) and compared with those obtained earlier from intermediate negelct of differential overlap combined with configuration interaction of singly excited states (INDO/s-CIS) calculations.

The calculated absorption energies for transition bands RC1 and RC2 for the unsubstituted PVn and fully dialkoxy-substituted PV$n(n + 1$ da) cations were determined to be in agreement with experiments. For the shortest PV$n(n + 1$ da) cations, TDDFT overestimates the energy of the third RC3 transition.

The experimental spectra of partially dialkoxy-substituted PV$n(n/2$ da) radical cations show that the maximum of the lowest optical absorption band (RC1) is <0.6 eV. This is in agreement with the TDDFT calculations, which predict a monotonic decrease of the lowest transition energy (RC1) with chain length. INDO/s-CIS calculations predict an oscillating behavior (odd−even effect) of the RC1 transition energy with the length of the oligomer chain, which is in disagreement with the current experimental findings. The decrease of the RC1 absorption energy with chain length is consistent with the degree of charge delocalization, as calculated with density functional theory (DFT).

The presence of alkoxy substituents reduces the transition energies, which is most pronounced for fully dialkoxy-substituted PV oligomers. In partially dialkoxy-substituted PV oligomers, more positive charge is present on the substituted phenylene units than on the unsubstituted ones.

DFT calculations lead to a more-delocalized charge distribution than the INDO/s-CIS method. It is of interest to establish whether the relatively localized charge distributions from INDO/s-CIS calculations and the odd−even effect are caused by the absence of dynamic electron correlation or by an artifact in the semiempirical INDO/s calculations. This issue could be solved by performing correlated quantum mechanics calculations, e.g., using second-order Møller−Plesset (MP2) methods. Such calculations should be performed on PV oligomers of at least eight repeat units, which requires high computational power.

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