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[16] ^{1}H NMR experiments were acquired on 3 mM samples in 9:1 (v:v) H_2O/D_2O at 500 MHz (Bruker DRX500 spectrometer) as described in reference [15b,c] with water suppression achieved by presaturation or WATERGATE technique (V. Sklenár, M. Piotto, R. Leppik, V. Saudek, *J. Magn. Reson. A* **1993**, *102*, 241–245). Conversion of NMR data to geometrical constraints and structure calculations (100 structures) were performed as described in reference [15b,c].

[17] The linear peptide precursors were synthesized on chlorotrityl resin by using the 9-fluorenylmethoxycarbonyl (Fmoc)/*t*Bu chemistry as described in reference [14]. Cyclization of the resulting side chain protected peptides was performed in DMF at a concentration of 0.5 mM by PyBOP/HOBt (benzotriazolyl-1-oxy-tris(pyrrolidino)phophonium hexafluorophosphate/1-hydroxybenzotriazole), and deprotection was carried out with trifluoroacetic acid/CH_2Cl_2 (95:5) containing triethylsilane as scavenger. Oxidation of the cyclic bis(cysteinyl)peptide was performed by air-oxygen in ammonium acetate buffer (pH 8) at a concentration of 10^{-4} M. **1**: ESI-MS: *m*/*z*: 1113.6 [M+H$^+$]; $M_r = 1112.4$ calcd for $C_{49}H_{72}N_{14}O_{12}S_2$; amino acid analysis (6 M HCl, 110 °C, 24 h): Asp 1.00 (1), Thr 0.90 (1), Ala 0.97 (1), Cys 1.46 (2), Lys 2.95 (3); peptide content: 71 %. **2**: ESI-MS: *m*/*z*: 1085.8 [M+H$^+$]; $M_r = 1082.6$ calcd for $C_{49}H_{74}N_{14}O_{14}$; amino acid analysis (6 M HCl, 110 °C, 24 h): Asp 1.00 (1), Thr 0.99 (1), Ser 1.98 (2), Ala 0.98 (1), Lys 2.90 (3); peptide content: 75 %.

[18] For the determination of the K_{ox} values, the *trans* isomer and mixtures of the *cis*/*trans* isomers of **1** (0.1 mM) in argon-saturated 0.1 M phosphate buffer (pH 7) containing 0.1 M NaCl and 1 mM EDTA were equilibrated at 25 °C for 3–4 h under argon with 100-fold excess glutathione at varying GSH/GSSG ratios. Aliquots of the equilibrated redox mixtures were quenched with 1 M phosphoric acid and analyzed by HPLC. Baseline separation of all components was achieved and these were identified as the two sets of the *cis* and *trans* isomer species by ESI-MS and by comparison with the redox mixture obtained for the pure *trans* isomer (see Figure 2). The concentrations of the oxidized and reduced forms of **1** at equilibrium were obtained by integration of the corresponding HPLC peak areas.

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[20] Fully reduced and denatured RNase A was prepared from bovine pancreatic RNase A (Aldrich, approximately 100 Kunitz units mg^{-1} protein) and refolding assays were performed following essentially the protocols previously described (Y. Konishi, T. Ooi, H. A. Sheraga, *Biochemistry* **1982**, *21*, 4734–4740). Reoxidation of the reduced RNase A (24 μM) in 0.1 M Tris-HCl buffer, 1 mM EDTA, pH 7.4, was carried out at 30 °C under argon in the glutathione redox buffer at an RNase A/GSH/GSSG molar ratio of 1:20:4 and in the presence of **1** at an RNase A/GSH/GSSG/**1** molar ratio of 1:20:3:1 and 1:20:2:2. Compound **1** was used as *trans* isomer (100 % after thermal relaxation at 50 °C overnight) and, upon irradiation at 360 nm, in the *cis*-azo configuration, that is in the photostationary state (*cis*/*trans* ratio: 80:20 ± 3). The reactivation reactions were initiated by addition of RNase A to the preequilibrated (at least 2 h at room temperature) refolding mixtures. The samples with the *cis* isomer were irradiated at 360 nm for 4 min every 2 h over 14 h and for a further 4 min after 21 h and 28 h. The time course of correctly folded RNase A was determined by measuring on aliquots of the refolding mixtures the initial rates of enzymatic cCMP hydrolysis (432 μM in 0.1 M MOPS buffer, pH 7.0) at 284 nm and at a final RNase A concentration of 1.7 μM.

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Oligo(phenylenevinylene)s with Terminal Donor–Acceptor Substitution**

Herbert Meier,* Jürgen Gerold, Heinz Kolshorn, Wolfram Baumann,* and Michael Bletz

Conjugated oligomers[1] such as the oligo(phenylenevinylene)s (OPV)s have been extensively investigated for a number of years because they exhibit properties of interest to materials science in regard to application in nonlinear optics (NLO) and as photoconductors and electroluminophores. Typical of such a class of compounds is the convergence of absorption and fluorescence with the increasing number *n* of repeating units.[2] The determination of the effective conjugation length (ECL)[1q] is important for the characterization of the oligomers, as well as for their function as model compounds for the corresponding polymers. A simple algorithm, based upon exponential functions as natural growth functions, has been demonstrated to be effective for the determination of convergence and ECL in more than 20 series of conjugated compounds.[3]

We recently demonstrated that with a terminal push–pull substitution of conjugated oligomers the expected monotonic bathochromic shifts of absorption and fluorescence with increasing number *n* of repeating units need not necessarily be present.[4] Since such series are very important, especially for NLO materials, we have investigated the effect more thoroughly. OPV systems were prepared which have solubilizing bis(2-hexyloctyl)amino residues as the donor (D). Different acceptors (A) were introduced at the other end of the OPV chain (Scheme 1). The involvement of zwitterionic resonance structures should have a decisive influence upon

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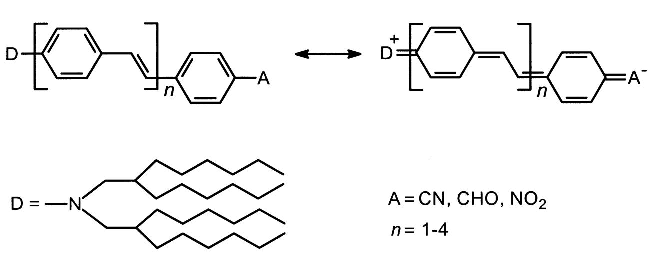
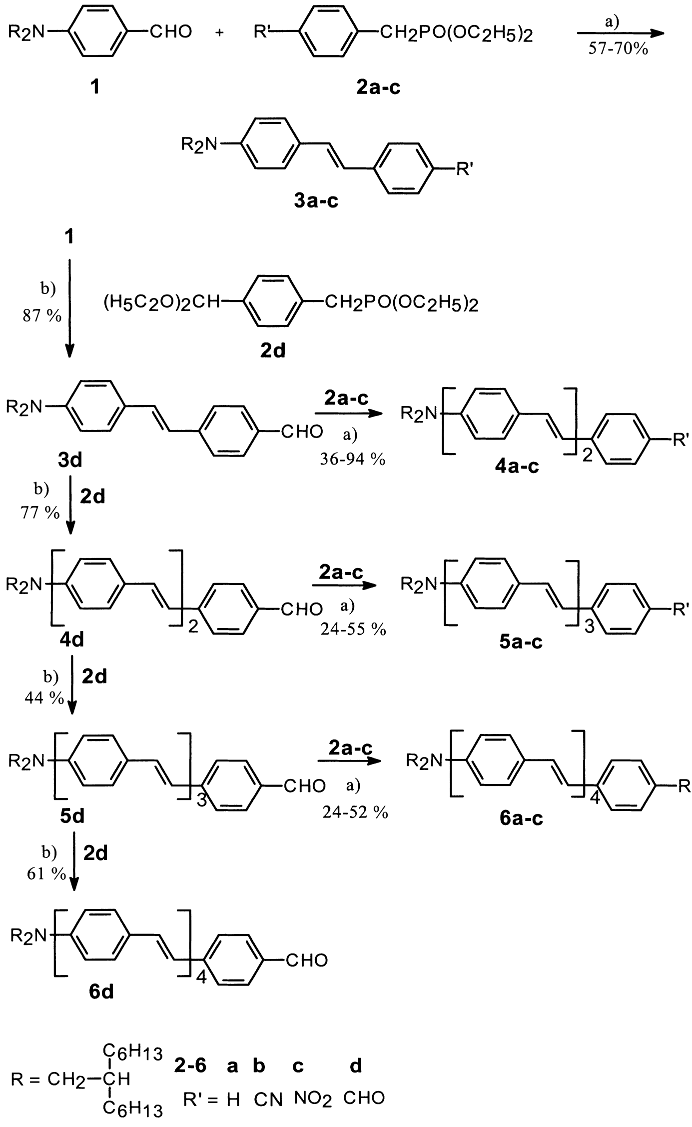


Scheme 1. Donor–acceptor substituted OPV systems

the electronic transitions; the solely donor substituted series (A = H) serves as a reference series.

The preparation of monodisperse, configurationally pure oligomers was carried out by a convergent-synthesis strategy outlined in Scheme 2. 4-Bis(2-hexyloctyl)aminobenzaldehyde (**1**) was converted into the monostilbenes **3a–c** with the phosphonates **2a–c**, and also used for the construction of the "styrylogous" aldehydes **3d–6d**, the latter was by a repetitive Wittig–Horner reaction with the phosphonate **2d** and a simple protecting-group technique.[5] Each new aldehyde stage **3d–5d** was then converted into the target compounds **4a–c**, **5a–c**, and **6a–c** with **2a–c**.



Scheme 2. Preparation of the OPV series **3–6**. a) NaH, DME; b) 1) KOC(CH$_3$)$_3$, THF; 2) HCl.

Figure 1 shows the long-wavelength maxima of the donor-substituted series **3a–6a** and the donor–acceptor substituted series **3b–6b**, **3c–6c**, and **3d–6d**. With each additional *n* the terminal acceptors lead to a marked bathochromic shift of the push–pull systems relative to the purely donor-substituted series **3a–6a**. Most pronounced is the effect of the nitro group, the strongest acceptor. In contrast to the OPV series previously investigated,[2, 6] with terminal push–pull substituents a charge transfer occurs during the electron transition. The monotonic reduction in excitation energies (bathochromic effect) with increasing *n* is in line with expectations in the two series **3a–6a** and **3b–6b**; in the series **3d–6d** $\tilde{\nu}_{max}$ is surprisingly almost independent of *n*, and in the series **3c–6c** the effect is even reversed: with **3c–6c** an increase in conjugation leads to a pronounced hypsochromic shift. With increasing *n* all four series converge towards the convergence limit E_∞ of the donor-substituted series **3a–6a**.

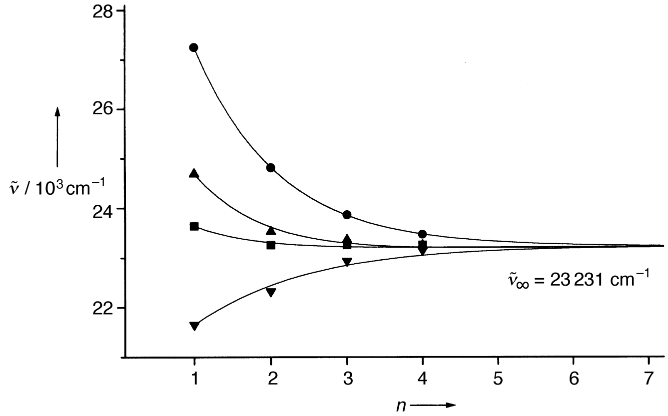


Figure 1. Long-wavelength absorption maxima of the OPV series **3a–6a** (●), **3b–6b** (▲), **3c–6c** (▼), and **3d–6d** (■) in CHCl$_3$ and fitting of the Equation (1).[7] $\tilde{\nu}_\infty$ = common convergence limit.

How may the different behavior of the donor–acceptor substituted series be explained? It may be concluded from the common convergence limit that with longer OPV chains the acceptor group plays no role in the absorption. Therefore, we have split the energy values of the electron transitions $E_{DA}(n)$ into two components. The first term $E_D(n)$ corresponds to the normal behavior of the purely donor-substituted series **3a–6a**, that is, to the expected bathochromic shift with increase in conjugation. The second term $\Delta E_{DA}(n)$ is a correction term for the superimposition of the intramolecular charge transfer (ICT) in the push–pull substituted series. Both terms can be described by exponential functions[2] [Eq. (1)].

$$E_{DA}(n) = E_D(n) - \Delta E_{DA}(n) = E_\infty + [E_D(1) - E_\infty]e^{-a(n-1)} - [E_D(1) - E_{DA}(1)]e^{-\Delta a(n-1)} \quad (1)$$

Table 1 gives an overview of the measured absorption maxima and the parameters from the fitting for convergence with increasing *n*. The charge-transfer correction term $\Delta E_{DA}(n)$ is always greatest at $n = 1$. With increasing separa-

Table 1. Long-wave absorption maxima ($\tilde{\nu}_{max}$ [cm^{-1}], ε_{max} [cm^2 mmol^{-1}]) of the OPV series **3a**–**6a**, **3b**–**6b**, **3c**–**6c**, and **3d**–**6d** in $CHCl_3$ and parameters from the fitting of Equation (1).[a]

Compound	n	Series **a**		Series **b**		Series **c**		Series **d**	
		$\tilde{\nu}_{max}$	ε_{max}	$\tilde{\nu}_{max}$	ε_{max}	$\tilde{\nu}_{max}$	ε_{max}	$\tilde{\nu}_{max}$	ε_{max}
3	1	27248	19483	24691	21711	21645	28789	23641	20462
4	2	24814	29711	23529	48107	22321	35425	23256	46822
5	3	23866	68944	23364	63341	22936	58760	23256	67320
6	4	23474	–	23256	86164	23148	95860	23256	84882
Parameters									
E_∞ [cm^{-1}]		23231 ± 12		23231 ± 12		23231 ± 12		23231 ± 12	
$E_D(1) - E_{DA}(1)$ [cm^{-1}]		–		2557		5603		3607	
a		0.93 ± 0.01		0.93 ± 0.01		0.93 ± 0.01		0.93 ± 0.01	
Δa		–		0.76 ± 0.04		0.86 ± 0.03		0.87 ± 0.02	

[a] Curve fitting was carried out with the program Origin 5.0.

tion of donor and acceptor it falls exponentially towards zero, for example, from 5603 cm^{-1} for **3c**, through 2493 and 930 to 326 cm^{-1} for **6c** in the NO_2 substituted series. This reduction cannot be offset by the opposing effect which is a result of the extension of conjugation and is represented by $E_D(n)$. The nitro-substituted series consequently shows a hypsochromic shift for increasing n. In contrast the cyano-substituted series exhibits significantly smaller correction terms $\Delta E_{DA}(n)$, which moreover decrease more slowly with increasing n, from 2557 cm^{-1} at $n = 1$ to 218 cm^{-1} at $n = 4$. In this case the bathochromic effect on extending conjugation can overcompensate the decreasing charge-transfer term and in the summation the expected bathochromic shift is observed. In the series **3d**–**6d** the conjugation effect and the charge-transfer effect offset each other almost completely so that $\tilde{\nu}_{max}$ is almost independent of n.

How may this theory, on the basis of empirical fit functions, be supported quantum mechanically? We have calculated the frontier orbitals of **3a**–**c**, **4a**–**c**, **5a**–**c**, and **6a**–**c** by AM1 and INDO/S methods.[8, 9]. A selection of these is reproduced in Figure 2. The long-wavelength electron transitions of the OPV systems are essentially HOMO→LUMO transitions for $n = 1$. The HOMO→LUMO energy difference decreases for $n = 1$ (and also for each higher n) in the sequence **a** > **b** > **c**. Since the exchange integral for the electron correlation also decreases in this sequence because of the decreasing transition density, a bathochromic shift in the absorption for every n in the change from A = H, through A = CN, to A = NO_2 results. Within the series **a**, **b**, and **c** the HOMO→LUMO energy difference decreases with increasing n. However, the electron correlation leads then to smaller Coulomb integrals for the repulsion with increasing size of the chromophore, and therefore, to an opposing tendency. Thus, in principle, with increasing n in the oligomer series either a bathochromic or a hypsochromic shift of the absorption can occur.

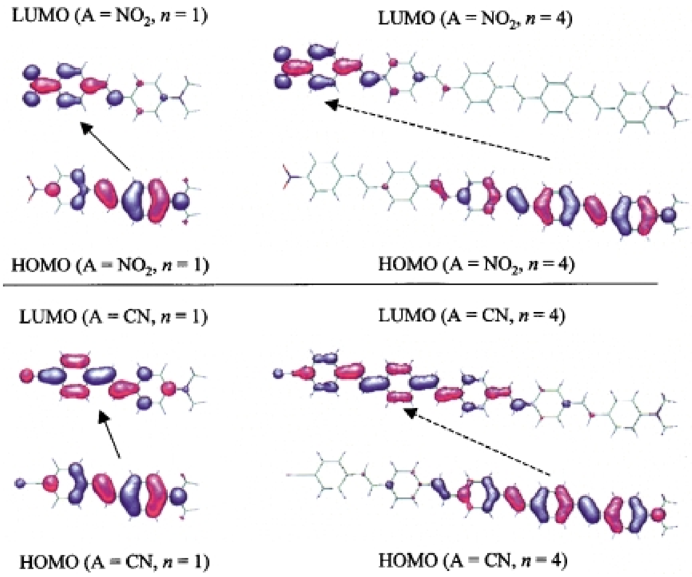


Figure 2. Frontier orbitals of compounds **3b** and **3c**, as well as **6b** and **6c** calculated by the INDO/S method. The arrows illustrate the shift of the electron densities during the HOMO→LUMO transition.

With increasing n the fraction of HOMO→LUMO transitions in the long-wavelength absorption falls drastically; above all the electron transitions NHOMO→LUMO, HOMO→NLUMO, and NHOMO→NLUMO intermix (where N = next-to-). However, as Figure 2 shows, the HOMO→LUMO fraction is essentially determinative for charge transfer. If the ICT correction term $\Delta E_{DA}(n)$ is now plotted against the involvement of the HOMO→LUMO transition calculated by the INDO/S method a simple correlation is recognized: the greater $\Delta E_{DA}(n)$ for the charge transfer is, the greater the HOMO→LUMO contribution to the long-wavelength electron transfer is (Figure 3). Thus semi-empirical quantum mechanics reproduces correctly the observed trend: with increasing n the HOMO→LUMO contribution decreases, and with it the ΔE_{DA}; this effect dominates in the nitro-substituted series **3c**–**6c** and hence leads to the hypsochromic shift—in contrast in the cyano-substituted series **3b**–**6b** the term $E_D(n)$, which expresses the extension of the conjugation, dominates such that a bathochromic shift occurs.

Since the nitro-substituted series clearly plays a special role we carried out electro-optical absorption measurements (EOAM) on the compounds **3c**–**5c**; a number of the results of these measurements are summarized in Table 2. Assuming that polarizabilities may be neglected with respect to dipole moments, and $\mu(S_0)$, $\mu(S_1)$, and the transition moment μ_{01} are parallel, EOAM[10, 11] gives μ_0 as well as the terms $\mu_0(\mu_1 - \mu_0)$ and $(\mu_1 - \mu_0)^2$, which are obtained as different regression coefficients from the first and second derivation of $\varepsilon(\tilde{\nu})$ according to the wavenumber $\tilde{\nu}$. Both statistically as well as by the EOAM model the first term $\mu_0(\mu_1 - \mu_0)$ leads to the more reliable values.

As expected, the intensity I, the oscillator strength f, and the transition moment μ_{01} increase with increasing n. Surprisingly

Table 2. Optical and electro-optical data of **3c**, **4c**, and **5c**.[a]

Compound	n	I [10^{10} cm mol^{-1}][b]	f	μ_{01} [10^{-30} C m]	$\mu_0(S_0)$ [10^{-30} Cm][c]	$\mu_1(S_1)$ [10^{-30} Cm][c,d]
3c	1	15.48	0.68	27.23	29.8	112.0
4c	2	19.70	0.86	30.30	26.4	128.8
5c	3	31.79	1.40	38.01	25.3	108.2

[a] Measurements in dioxan. [b] $I = \int \varepsilon(\tilde{\nu})d\tilde{\nu}$. [c] The statistical regression error is 1–5% for μ_0 and 2–6% for μ_1. [d] Determined from $d\varepsilon/d\nu$; $d^2\varepsilon/d\nu^2$ gives the less reliable values 106.6, 128.5, and 151.3 Cm for $10^{30}\mu_1$ with **3c**–**5c**.

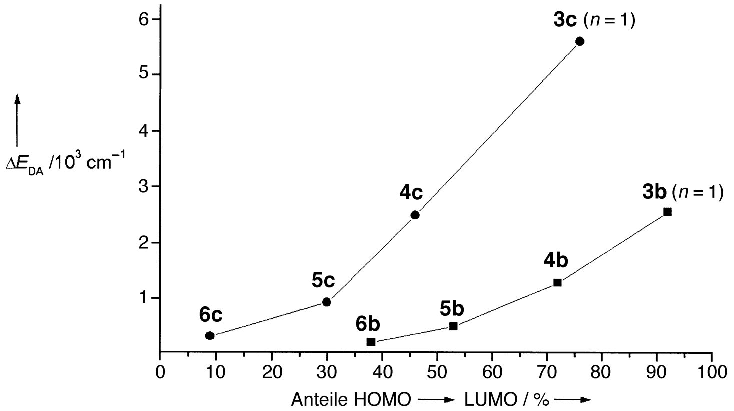


Figure 3. Charge-transfer terms ΔE_{DA} in relationship to the HOMO →LUMO fraction calculated by the INDO/S method for the long-wavelength electron transitions in the OPV series **3b**–**6b** (A = CN) and **3c**–**6c** (A = NO_2).

the experimental dipole moment μ_0 of the ground state S_0 decreases with the increasing distance between donor and acceptor. The dipole moments μ_1 of the electronically excited state S_1 are significantly higher. Clearly, a simple relationship with the benzenoid and quinoid (zwitterionic) resonance structures formulated in Scheme 1 does not exist. The calculation of resonance parameters known in the literature [12, 13] with the values for $\mu_0(S_0)$, $\mu_1 S_1$, and μ_{01} given in Table 2 shows that for the compounds **3c**–**5c** the zwitterionic structure—independent of n[14]—contributes modestly to the ground state at about 10%. The charge transfer on electronic excitation indeed does increase the dipole moment considerably ($\Delta\mu = 92.3(\pm 10.1) \times 10^{-30}$ Cm), it has, however, an increasingly smaller influence on the long-wavelength absorption with increasing n since with increasing distance between donor D and acceptor A at almost constant $\Delta\mu$, increasingly less negative charge is transferred to the acceptor part of the molecules. For the conjugated systems with large D–A distances described here the frequently used model of a dominating electrically neutral and a less involved terminal zwitterionic resonance structure is usable for the ground state S_0. The electronic excited state S_1 does have a significantly higher dipole moment, but the participation of resonance structures never reverses. The simple VB model is not consistent with this.[15]

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[8] Dimethylamino groups were used in the calculations in place of the branched dialkylamino groups. Differences in the frontier orbitals from the AM1 and INDO/S calculations were insignificant. For the INDO/S method see W. P. Anderson, W. D. Edwards, M. C. Zerner, *Inorg. Chem.* **1986**, *25*, 2728–2732. For the calculation of **3c** see M. Dekhtyar, W. Rettig, *Phys. Chem. Chem. Phys.* **2001**, *3*, 1602–1610.

[9] According to measurements and calculation the oscillator strengths f increases with increasing n for all series. However, as with the absolute values of λ_{max}, the absolute values of f can not be calculated satisfactorily by semi-empirical quantum mechanical methods.

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[14] With short push–pull substituted polyenes it was found that the participation of zwitterionic forms falls with increasing n.[13]

[15] The frequently used criterion for the convergence of bond lengths is also not suitable for the series investigated here. Neither semi-empirical quantum mechanics nor the experimental investigation show a change in bond lengths within a series. The experimental investigation was carried out with the coupling constants ^3J of the olefinic protons which are of the order of 16.2(±0.2) Hz.