Extension of Conjugation Leading to Bathochromic or Hypsochromic Effects in OPV Series

Herbert Meier,* Jürgen Gerold, Heinz Kolshorn, and Bastian Mühling[a]

Abstract: Four OPV series **1**–**4** (**a**–**d**) with a terminal dialkylamino group as electron donor were prepared by Wittig–Horner reactions. To study the influence of the push–pull effect on the long-wavelength absorption, three of the four series contained terminal acceptor groups (CN, CHO, NO_2). The length of the chromophores strongly affects the intramolecular charge transfer (ICT)—an effect which superimposes upon the extension of the conjugation. Increasing numbers *n* of repeat units cause an overall bathochromic shift for the purely donor-substituted series **1a**–**4a** and the series **1b**–**4b** with CN as weak acceptor. The two effects annihilate each other in the series **1c**–**4c** with terminal CHO groups, so that the absorption maxima are almost independent of the length of the chromophore. A hypsochromic shift is observed for the series **1d**–**4d**, which contains the strong acceptor group NO_2. This anomaly disappears on protonation of the dialkylamino group because the push–pull effect disappears in the ammonium salts. The results can be explained by semiempirical quantum mechanics (AM1, INDO/S). The HOMO–LUMO transition, which is mainly responsible for the ICT, becomes less important in the electron transitions $S_0 \rightarrow S_1$ when the distance between donor and acceptor is increased. The commonly used VB model, which contains an electroneutral and a zwitterionic resonance structure, is contrasted with a MO model with dipole segments at both ends of the OPV chains. The latter model turned out to be more appropriate—at least for donor–acceptor-substituted OPVs with $n \geq 2$.

Keywords: absorption · conjugation · intramolecular charge transfer · oligomers · push–pull effect

Introduction

In the previous two decades a lot of research work was focussed on investigation of donor–acceptor-substituted conjugated compounds (D-π-A). The π-electron "spacer" between the terminal position of D and A can consist of double or triple bonds and/or aromatic or heteroaromatic ring systems.

The major work was done on polyenes and polyenynes,[1–20] but stilbenes,[21–27] tolanes,[28] biphenyls[29] and oligothiophenes[30–32] represent further examples. Among the interesting electrical, optical and optoelectronic properties of such compounds, the outstanding hyperpolarizabilities β in the field of nonlinear optics (NLO) should be mentioned here.[23,33–36]

Normally conjugated compounds such as the oligo(1,4-phenylenevinylene)s (OPVs) exhibit a monotonous and convergent bathochromic shift for the long-wavelength absorption when the conjugation is extended by an increasing number of repeat units.[36–39] However, we recently observed an unexpected hypsochromic effect for some OPV series with strong donor and strong acceptor groups in the terminal positions (D-OPV-A).[25–27] Altogether, as far as the effect of extended conjugation on the electron transition is concerned, there are three different types of D-π-A systems. Figure 1 demonstrates the dependence of the long-wavelength absorption on the number of repeat units: $\lambda_{max}(n)$. Cyanines exhibit a linear relationship (constant increment $\Delta\lambda$ for $\Delta n = 1$), whereas the merocyanines show a regular increase in $\lambda_{max}(n)$ with a decreasing slope, so that λ_{max} approaches a limiting value λ_{∞}.[19,40] The third type is illustrated in Figure 1 by the behaviour of an OPV chain with a dialkylamino group as strong donor and a 2,2-dicyanovinyl group as strong acceptor.[27]

This article reports a systematic study of the push–pull OPVs **1a**–**4a**, **1b**–**4b**, **1c**–**4c** and **1d**–**4d** shown in Scheme 1. We varied the number of repeat units ($n = 1, 2, 3, 4$) in these oligomers and the strengths of the terminal acceptor group. The bis(2-hexyloctyl)amino group, a strong donor, guarantees reasonable solubility of these compounds in organic solvents such as $CHCl_3$ or CH_2Cl_2.

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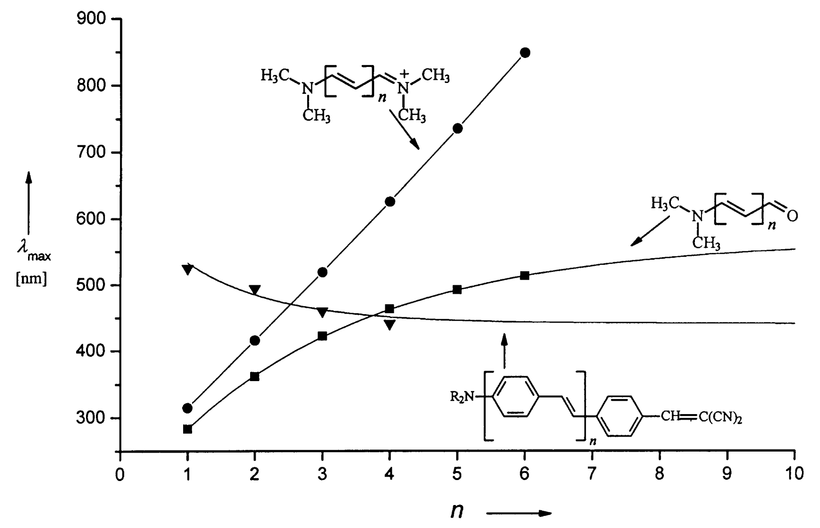
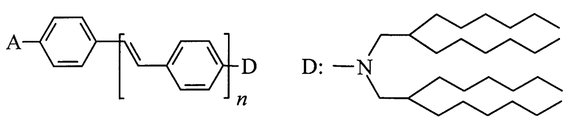


Figure 1. Different long-wavelength absorption behaviour of conjugated oligomers: λ_{max} as a function of the number n of repeat units.



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n A—	1	2	3	4
H—	**1a**	**2a**	**3a**	**4a**
N≡C—	**1b**	**2b**	**3b**	**4b**
O=HC—	**1c**	**2c**	**3c**	**4c**
O$_2$N—	**1d**	**2d**	**3d**	**4d**

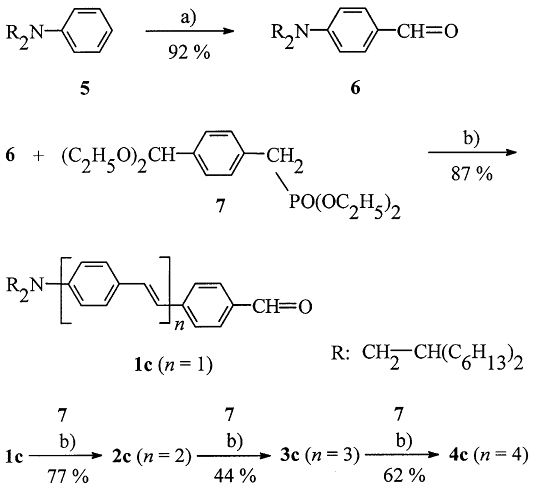
Scheme 1. Donor-substituted oligo(1,4-phenylenevinylene)s **1a**–**4a** and donor–acceptor-substituted OPV series **1b**–**4b**, **1c**–**4c** and **1d**–**4d**.

Results and Discussion

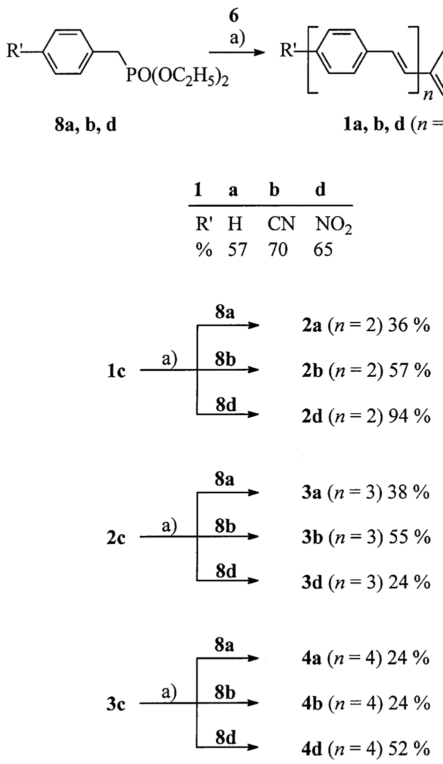
Synthesis: The synthetic strategy for the preparation of the compounds **1**–**4** (**a**–**d**) was based on the series of the aldehydes **6** and **1c**–**4c** (Scheme 2). The parent 4-dialkylaminobenzaldehyde **6** was obtained in high yields by Vilsmeier formylation of the corresponding aniline **5**. The phosphonate **7** then served for the stepwise extension of the conjugated chain by application of the Wittig–Horner reaction: **6**→**1c**→**2c**→**3c**→**4c**; for this purpose phosphonate **7** contains a protected formyl group, which is deprotected in the acidic workup of the PO-activated olefination, so that the compound can be directly used for the subsequent reaction step.The OPV series **1a**–**4a**, **1b**–**4b** and **1d**–**4d** were then obtained in convergent syntheses by treatment of the corresponding aldehydes **1c**–**3c** with the corresponding phosphonates **8a**, **8b** or **8d** (Scheme 3). Phosphonate **8a**, without a p-substituent, afforded the purely donor-substituted systems **1a**, **2a**, **3a** and **4a**. The cyano- or nitro-substituted compounds **1b**–**4b** and **1d**–**4d**, respectively, were obtained in an analogous way (Scheme 3). The individual yields differ between 24 and 94%.

The Wittig–Horner reaction shows a high *trans* selectivity; the usual *trans*/*cis* ratio for stilbenoid compounds is in the range of 95:5. Recrystallization, wherever possible, is the simplest way to get rid of the 5% *cis* isomers, because the solubility of the *trans* products is always much lower in this series. Waxy or oily products were purified by column chromatography on silica gel.

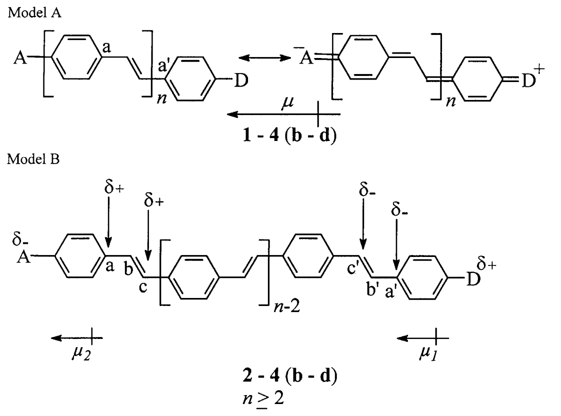
Push–pull effect: The push–pull character of the compounds **1b**–**1d** can be explained by considering dipolar resonance structures (Scheme 4). The longer the distance between A and D, the higher is the energy for the charge separation, which is represented by the participation of the quinoid resonance structure (Model A). As an alternative to an extended quinoid chain, we suggest a Model B, with two terminal partial dipole moments μ_1 and μ_2, which have the same direction and add to the overall dipole moment μ. It is important to notice that the experimentally determined μ for the ground state S_0 decreases with increasing distance between A and D (increasing numbers n).[26] In terms of Model A that would mean that the dipolar canonical structures become less important with growing length of the chain, and in terms of Model B that the mutual amplification of the terminal dipoles is reduced with growing distance between A and D.^{13}C NMR spectroscopy is a suitable tool for the confirmation of partial positive or negative charges on certain carbon atoms. In particular, the p-position (position a) to an electron-withdrawing substituent A in a benzene ring and



Scheme 2. Preparation of the aldehyde series **1c**–**4c**: a) POCl$_3$, DMF; b) 1) KOC(CH$_3$)$_3$/THF, 2) HCl.



Scheme 3. Preparation of the OPVs **1a**, **1b**, **1d**, **2a**, **2b**, **2d**, **3a**, **3b**, **3d** and **4a**, **4b**, **4d** by Wittig–Horner reactions: a) NaH, DME or $KOC(CH_3)_3$ in DMF or THF.



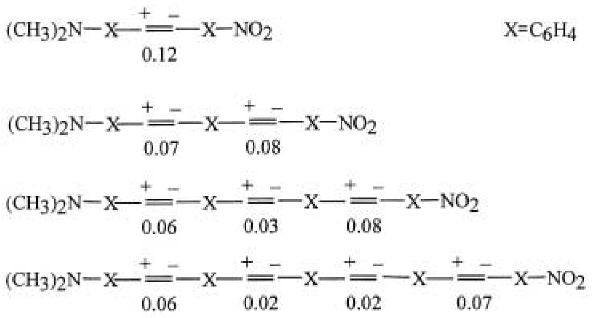
Scheme 4. Models for the push–pull character of the compounds **1**–**4** (**b**–**d**): A) VB model indicating the resonance of an electroneutral and a zwitterionic canonical structure; B) MO model with dipolar segments at the chain ends.

the *p*-position (position a′) to an electron-releasing substituent D provide a good indication of the charge distribution.[41,42] Moreover, the polarisation of the adjacent olefinic double bonds should be important. In Model A the polarisation effect should go through the whole chain from D to A, in Model B it should decline from both ends of the chain to the centre.

The ^{13}C chemical shifts of the selected positions a(′), b(′) and c(′) (Scheme 4) of unsubstituted *trans*-stilbene and the compounds **1a**–**3a**, **1b**–**3b**, **1c**–**3c** and **1d**–**3d** are listed in Table 1. The assignment of the signals is based on normal and long-range $^1H,^{13}C$ shift correlation measurements. (The solubility of **4a**–**4d** in $CDCl_3$ at room temperature was too low for exact chemical shifts to be obtained.) Table 1 reveals that the presence of the dialkylamino group as electron donor in **1a**–**3a** leads to a significant high-field shift of 13.2 ppm for position a′ in comparison to the quaternary carbon atom in *trans*-stilbene and to a polarisation of the olefinic double bond ($\delta_{b'}$–$\delta_{c'}$ = 5.6 ± 0.2 ppm). The latter effect is due to an upfield shift in position c′, which is induced by a high electron density in this position. The additional presence of an electron-withdrawing substituent in the other terminal position of **1b**–**1d** accordingly provokes a downfield shift of 6–8 ppm for position a (Scheme 4 and Table 1) and a polarisation of the olefinic double bond, which corresponds to $\Delta\delta = \delta_{b'}-\delta_{c'}$ of 10–13 ppm. The enhanced $\Delta\delta$ value is caused by a high electron density in position c′ and a low electron density in position b′. The OPVs with longer chains **2b**–**2d** and **3b**–**3d** show on the acceptor side (a, b, c) the typical effect of the electron-withdrawing substituents: namely high δ values—that is, low electron densities—for the positions a and c and a low δ value—which means a high electron density—for position b. On the donor side (a′, b′, c′), **2b**–**2d** and **3b**–**3d** have δ values very close to the δ values of **1a**–**3a**. Evidently, the donor side is only influenced by the presence of an acceptor when the conjugated "spacer" is short (**1b**–**1d** with $n = 1$), and not when the distance between donor and acceptor group is longer ($n \geq 2$). Moreover, the δ values of positions a and c or their mean can be taken in each series with equal numbers *n* for a rough scale of the acceptor strength. This argument furnishes an increasing acceptor strength in the sequence CN < CHO < NO_2. The ^{13}C data are in good accordance with charge densities calculated by the AM1 method. Scheme 5 shows the polarisation of the olefinic double bonds for the series **1d**–**4d**. The highest difference Δq in partial charges was found for **1d**. An increase in the

Table 1. Selected ^{13}C NMR data of the OPV series **1a**–**3a**, **1b**–**3b**, **1c**–**3c** and **1d**–**3d**; δ values in $CDCl_3$ for the positions a′, b′ and c′ shown in Scheme 4, TMS as internal standard.

Compound	A	*n*	a	b	c	c′	b′	a′
(*E*)-stilbene			137.6	129.0	129.0			
1a	H	1	138.4			123.6	129.0	124.4
2a	H	2	137.5	127.8	128.5	123.2	129.0	124.4
3a	H	3	137.4	128.3	128.4	123.2	129.0	124.4
1b	CN	1	143.1			121.4	132.8	123.2
2b	CN	2	141.9	125.5	132.1	122.7	129.5	124.1
3b	CN	3	141.9	126.3	132.0	123.1	129.2	124.3
1c	CHO	1	144.8			122.1	132.7	123.7
2c	CHO	2	143.6	126.3	132.0	122.9	129.6	124.3
3c	CHO	3	143.4	126.9	131.8	123.1	129.0	124.4
1d	NO_2	1	145.3			120.9	133.9	123.3
2d	NO_2	2	144.1	125.3	133.2	122.9	129.9	124.3
3d	NO_2	3	143.9	125.8	132.9	123.1	129.2	124.4



Scheme 5. Polarization of the double bonds in the series $(H_3C)_2N$-OPV(n)-NO_2: Charge differences Δq between the olefinic carbon atoms calculated by AM1 (Δq in fractions of the elemental charge, positive and negative signs are related to unsubstituted *trans*-stilbene).

D–A distance results in fairly constant charge distributions in both terminal double bonds and very small effects for the inner double bonds.

Concerning the ground state S_0, the dipolar quinoid resonance structure in Model A (Scheme 4) seems to be appropriate for the compounds **1b**–**1 d** ($n = 1$), whereas for the longer chains ($n \geq 2$), Model B, containing the terminal dipoles μ_1 and μ_2, is better.

Table 3. Long-wavelength absorption maxima of the OPV series **1a**–**4a**, **1b**–**4b**, **1c**–**4c** and **1d**–**4d** ($\tilde{\nu}_{max}$ [cm^{-1}] and ε [cm^{2}mmol^{-1}] in $CHCl_3$).[a]

Series		1	2	3	4
a	$\tilde{\nu}_{max}$	27248	24814	23866	23474
	$10^{-3}\varepsilon$	19.5	29.7	68.9	85
b	$\tilde{\nu}_{max}$	24691	23529	23364	23256
	$10^{-3}\varepsilon$	21.7	48.1	63.3	86.2
c	$\tilde{\nu}_{max}$	23641	23256	23256	23256
	$10^{-3}\varepsilon$	20.5	46.8	67.3	84.9
d	$\tilde{\nu}_{max}$	21645	22321	22936	23148
	$10^{-3}\varepsilon$	28.8	35.4	58.8	95.9

[a] The accuracy of the $\tilde{\nu}_{max}$ values is about 50 cm^{-1}; the accuracy of the ε values is in the range of 10^3—only for **4a** is it somewhat higher—because of the low solubilities of these compounds.

Absorption: Table 2 shows the absorption maxima of **1d**–**4d** in different organic solvents. The stilbene derivative **1d** exhibits principally a positive solvatochromic effect. A linear correlation with typical solvent parameters[43] such as π^* or $E_T(30)$, however, fails. In contrast to the ground state S_0, the first excited singlet state S_1 should show a stronger interaction of the donor and the acceptor side because of the *intramolecular charge transfer* (ICT) involved in the long-wavelength transition. However, the donor–acceptor-substituted compounds **2d**, **3d** and **4d**, with longer chains (n = 2, 3, 4), do not show a uniform solvatochromic trend. The absorption maxima in chloroform (or in dioxane), for example, are at higher λ values than in acetone.Table 3 summarises the UV/Vis data for the OPV series **1**–**4** (**a**–**d**). Figure 2 illustrates the absorption maxima.[26] All four series converge to $\tilde{\nu}_\infty$ = 23231 cm^{-1} for increasing numbers n of repeat units.

Table 2. Absorption maxima λ_{max} [nm] of the long-wavelength bands of the OPV series **1d**–**4d** in different solvents.

Solvent	1d	2d	3d	4d
cyclohexane	436	433	429	[a]
dioxane	443	441	435	433
chloroform	462	448	436	432
dichloromethane	460	449	436	430
acetone	450	436	429	429
acetonitrile	451	432	[a]	[a]
dimethyl sulfoxide	465	[a]	[a]	[a]

[a] Too low solubility.

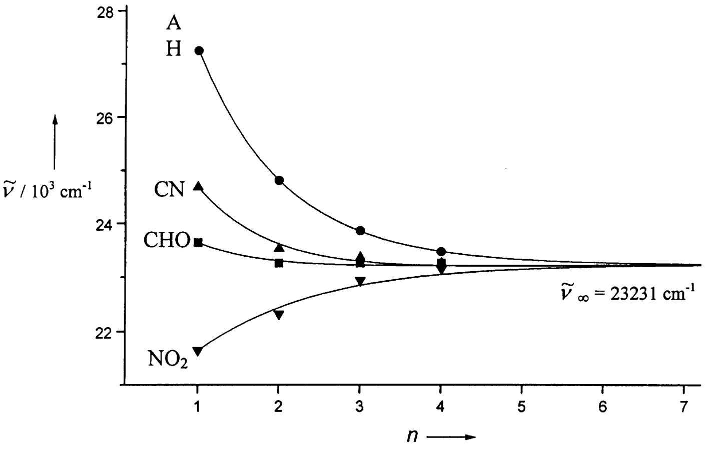


Figure 2. Long-wavelength absorption maxima of the OPV series **1a**–**4a** (●) **1b**–**4b** (▲), **1c**–**4c** (■) and **1d**–**4d** (▼) in chloroform. The fitted curves correspond to Equation (1).

The donor-substituted series **1a**–**4a** exhibits a bathochromic shift in comparison to normal OPV series;[37] this substituent effect decreases with increasing n. In the donor–acceptor OPVs **1**–**4** (**b**–**d**), the intramolecular charge transfer also has to be considered. The convergence behaviour[26,37] of the transition energy $E_{DA}(n)$ of these series can be split into two terms. The first term, $E_D(n)$, which relates to all four series **1**–**4** (**a**–**d**), comprises the extension of the conjugation with increasing numbers n of repeat units. It also contains the substitution effect of the donor group. The second term, $\Delta E_{DA}(n)$, takes the effect of the ICT on the transition energies in the three push–pull series **1**–**4** (**b**–**d**) into account; this effect decreases with increasing n. The exponents a and Δa characterise the rate of the convergence[26] [Eq. (1) and Eq. (2)].

$$E_{DA}(n) = E_D(n) - \Delta E_{DA}(n) \tag{1}$$

$$E_{DA}(n) = E_\infty + [E_D(1) - E_\infty]e^{-a(n-1)} - [E_D(1) - E_{DA}(1)]e^{-\Delta a(n-1)} \tag{2}$$

The extension of the conjugation in the series of conjugated oligomers leads to the usual bathochromic shift. The effect of the ICT, however, is diminished by the growing extension of the chromophores. The two effects are thus opposite to each other and the crucial question is, which effect predominates? Table 3 and Figure 2 give the answer. Relatively weak acceptors such as the CN group in this case lead to an *overall bathochromic shift* for **1b**–**4b**. In the formyl series **1c**–**4c**, the two effects annihilate each other almost completely; this means that the extension of the conjugated chromophores has almost no influence on the energy of the electron transition (Figure 2 and Figure 3)! Strong acceptors such as NO_2 in **1d**–**4d** provoke an *overall hypsochromic effect*, because the reduced effect of the ICT with growing *n* [second term in Equation (1)] cannot be compensated by the "conjugation effect" [first term in Equation (1)].

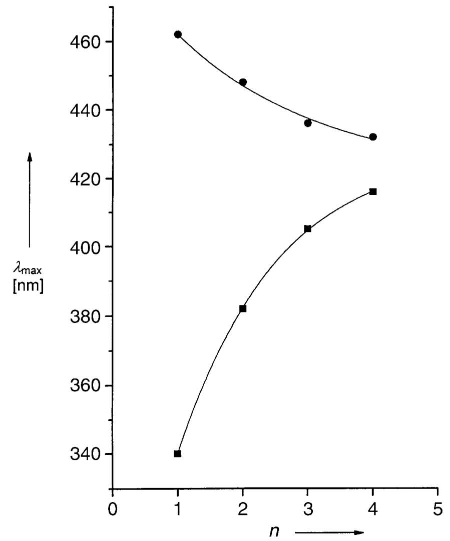


Figure 4. Reversal of the hypsochromic effect by protonation: absorption maxima of the series **1d**–**4d** (n = 1–4) in $CHCl_3$ (——●——) and in $CHCl_3/CF_3COOH$ 10:1 (——■——).

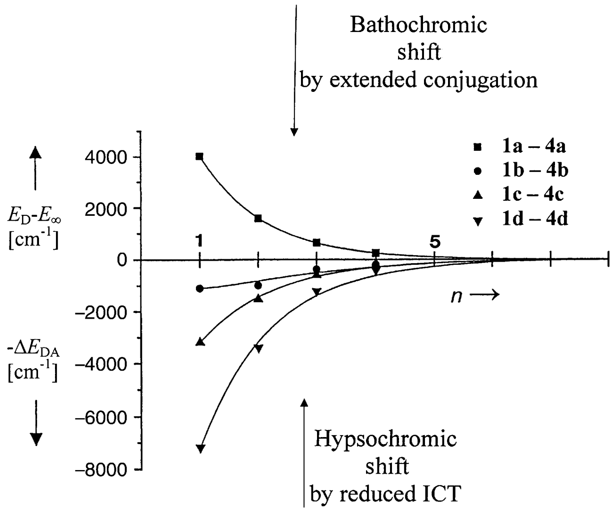


Figure 3. Bathochromic term $E_D(n)$ and hypsochromic term $E_{DA}(n)$ according to Equation (1). [The exponential fitting of the curves is based on the parameters $E_\infty = 23231\pm12\,\text{cm}^{-1}$, $a = 0.93\pm0.01$ and $\Delta a = 0.76\pm0.04$ for **1b**–**4b**, 0.87 ± 0.02 for **1c**–**4c** and 0.86 ± 0.03 for **1d**–**4d**.]

The push–pull character of the compounds **1**–**4** (**b**–**d**) disappears as soon as the dialkylamino groups are protonated. UV measurements in $CHCl_3/CF_3COOH$ (10:1) showed a hypsochromic shift for the long-wavelength absorptions of all systems. The most interesting result was obtained for the series **1d**–**4d** (Figure 4), in which the "abnormal" hypsochromic effect for increasing *n* is reversed by protonation. In terms of Model B, two opposite terminal dipoles μ_1 and μ_2 are present in the ammonium structure; therefore, the "conjugation effect" prevails.

The common limiting value E_∞ (in $CHCl_3$) of all four series **1**–**4** (**a**–**d**) is $\tilde{\nu}_\infty = 23231\pm12\,\text{cm}^{-1}$ (Figure 2), which corresponds to $\lambda_\infty = 430.5\pm0.5$ nm. The effective conjugation length[37,44] n_{ECL} amounts to 6 for the series **1a**–**4a** and to 5 for **1d**–**4d**. Because the opposite effects $E_D(n)$ and $\Delta E_{DA}(n)$ are comparable in size, the n_{ECL} values for **1b**–**4b** and particularly for **1c**–**4c** are extremely low: namely 4 and 2, respectively. The convergence parameters of the four series are listed in Table 4.

Normal OPV series without terminal donor and acceptor groups have much longer effective conjugation lengths: namely n_{ECL} of 10 and 11.[37] Compounds with $n > n_{ECL}$ in a certain series exhibit absorption intensities $\varepsilon_{max}(n) > \varepsilon_{max}(n_{ECL})$, but their bands are at the limiting value: $\lambda_{max}(n) = \lambda_{max}(n_{ECL})$. Recently, confirmation in the OPV series was provided by the synthesis of a monodisperse pentadecamer.[38,45]

Quantum mechanics: The remaining question now is, why is the effect of the ICT on the transition energies of the D-OPV-A compounds **1**–**4** (**b**–**d**) reduced by increasing length of the chromophores (increasing numbers (*n*) of repeat units)? The answer is given by quantum chemical calculation (AM1, INDO/S)[46] of the ground states S_0 and their electronic transitions (Model B, Scheme 4).[48] For increasing *n*, other π orbitals approach the π (HOMO) and other π^* orbitals π^* (LUMO). The HOMO–LUMO transition is combined with a large ICT, but the participation of the HOMO→LUMO transition in the electronic excitation of the long-wavelength transition decreases with increasing *n*. Figure 5a demonstrates this effect for the unsubstituted OPV series and for the push–pull OPVs with dimethylamino groups and cyano or nitro groups in the terminal positions.

Table 4. Convergence parameters in Equation (2) for the OPV series **1a**–**4a**, **1b**–**4b**, **1c**–**4c** and **1d**–**4d** (the limits of error of about ±1 nm relate to the fitting and not to inaccuracy of the spectrometer).

Series	a	Δa	$E_D(1)-E_{DA}(1)$	n_{ECL}
1a–**4a**	0.93±0.01	–	0	6
1b–**4b**	0.93±0.01	0.76±0.04	2557	4
1c–**4c**	0.93±0.01	0.87±0.02	3607	2
1d–**4d**	0.93±0.01	0.86±0.03	5603	5

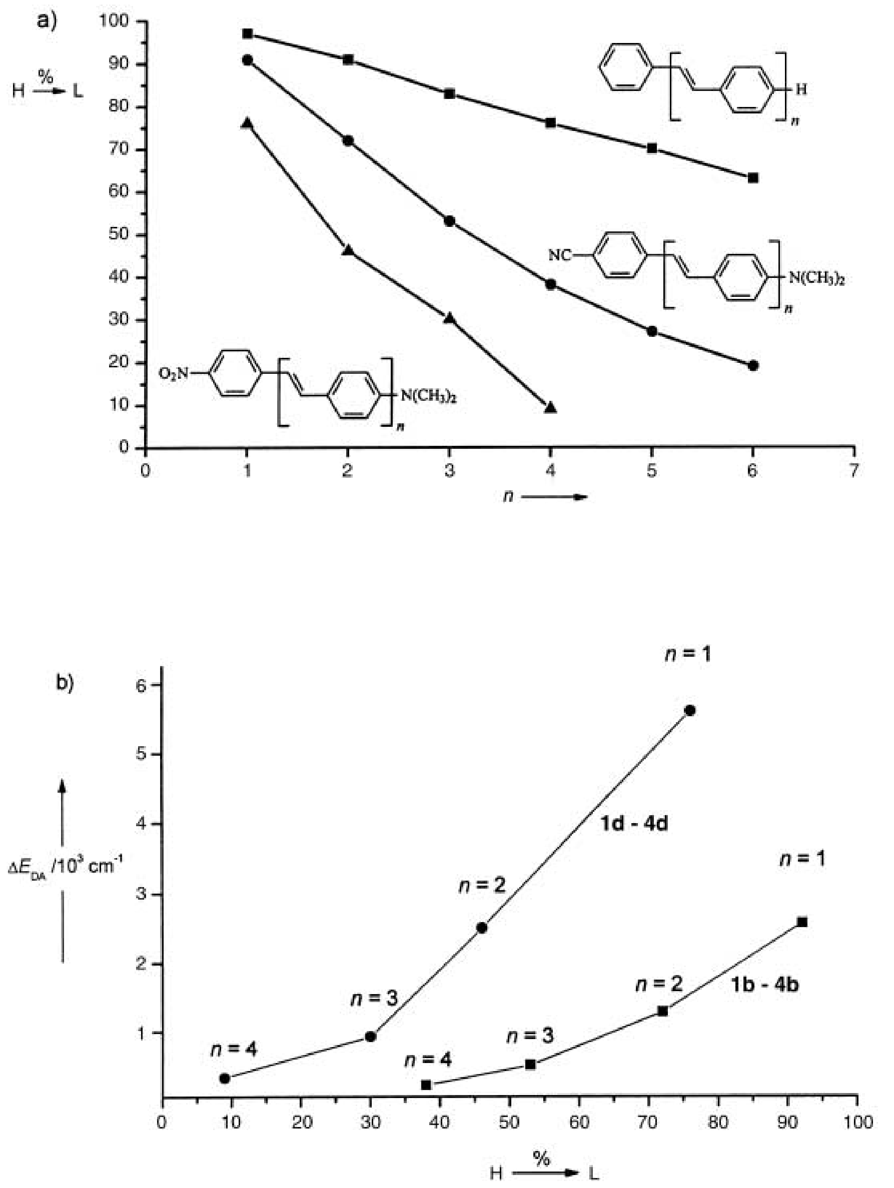


Figure 5. a) Decreasing participation of the HOMO→LUMO transition in the long-wavelength absorption (calculated by AM1, INDO/S) with increasing numbers (*n*) of repeat units; b) dependence of the ICT term ΔE_{DA} on the fraction of the HOMO–LUMO transition in the long-wavelength transition of the oligomer series **1b**–**4b** and **1d**–**4d**.

Figure 5b shows the dependence of ΔE_{DA}, the term based on the ICT, on the percentage of the HOMO–LUMO participation; ΔE_{DA} approaches 0 with decreasing HOMO–LUMO involvement (increasing *n*). In accordance with Model B in Scheme 4, the interaction of the acceptor side and the donor side is getting smaller and smaller, the longer the chain is. The influence of the acceptor on the electron transition can be completely neglected for $n > 4$. The long-wavelength absorption of the three D-OPV-A series approaches the absorption of the purely donor-substituted series **1a**–**4a**.[49]

A direct illustration of the decrease in the intramolecular charge transfer is given in Figure 6. This shows the orbitals mainly involved in the long-wavelength transition of $(CH_3)_2N$-OPV($n = 4$)-NO_2. The HOMO→LUMO transition is characterized by the greatest ICT, but its participation—at 9%—is very low. The other, more involved, transitions are combined with a smaller intramolecular charge transfer (HOMO−1→LUMO and HOMO→LUMO+1) or almost none (HOMO−1→LUMO+1).

The ICT associated with the electronic excitation $S_0 \rightarrow S_1$ leads to a considerable increase in the dipole moments μ. Figure 7 shows $\Delta\mu = \mu(S_1) - \mu(S_0)$ in relation to the number *m* of π electrons in the calculated series with dimethylamino groups as donors and CN or NO_2 groups as acceptors. The diagram confirms the decrease in the ICT with increasing *m*—directly related to the numbers *n* of repeat units ($m = 6 + 8n$)—for the OPV systems. For comparison we performed an AM1/INDO/S calculation of the polyene series with terminal dimethylamino and nitro groups; Δμ increases first with growing $m = 2n$, reaches its maximum for $n = 7$, and then steadily decreases. Interestingly, the decrease in Δμ starts in the polyene series at 14 π electrons, which is exactly the number of π electrons in the OPV chains with $n = 1$.[50]

Of course, it would be very interesting to compare the calculated Δμ values with experimental data. Related push–pull-substituted polyene series show growing Δμ values with increasing *n*,[19,51] but $n = 7$ has not so far been experimentally reached in these series. Nevertheless, one should be careful in comparing calculated dipole moments of the neat molecules with measured dipole moments in a solvent.

In contrast to Model B (Scheme 4), which is an MO description, Model A is a valence bond model.[52] Equation (3) and Equation (4) describe the wave functions for the ground state S_0 and the electronically excited state S_1 on the basis of an electroneutral and a zwitterionic resonance structure. Several proposals for the experimental determination of the "weight" of the two resonance structures have been made. R. Wortmann et al. proposed Equation (5) for the parameter c^2, which characterises the mixing depending on the transition moment μ_{01} and the difference Δμ in the dipole moments.[53–55]

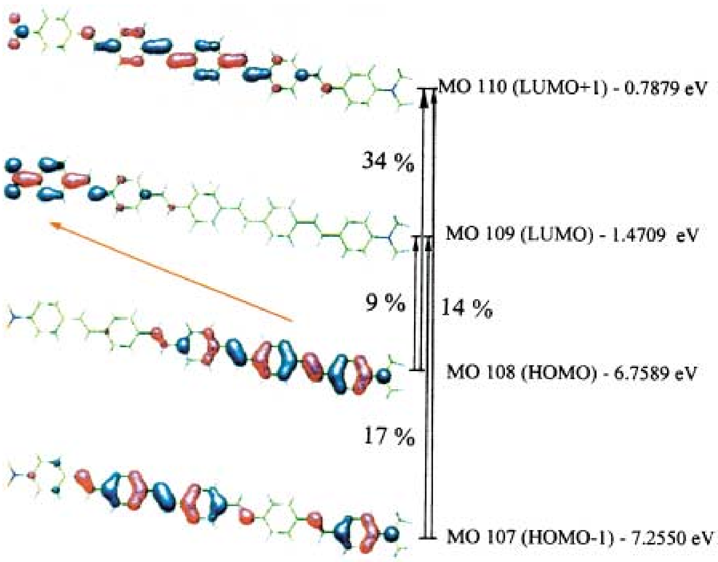


Figure 6. Participation (%) of the two highest occupied π orbitals and the two lowest unoccupied π^* orbitals in the long-wavelength absorption of $(CH_3)_2N$-OPV(n = 4)-NO_2.

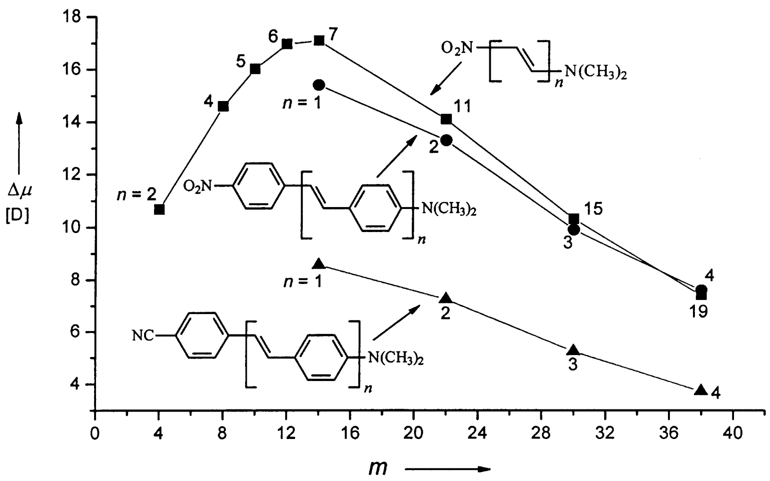


Figure 7. Calculated changes in the dipole moments $\Delta\mu = \mu(S_1)-\mu(S_0)$ on electron excitation in the three series of conjugated oligomers indicated. The numbers m represent the numbers of π electrons in the chain between donor and acceptor.

$$\Psi(S_0) = c\Psi_Z-\sqrt{1-c^2}\Psi_n \tag{3}$$

$$\Psi(S_1) = \sqrt{1-c^2}\Psi_z+c\Psi_n \tag{4}$$

$$c^2 = \frac{1}{2}\left[1-\frac{\Delta\mu}{\sqrt{4\mu_{01}^2+\Delta\mu^2}}\right] \tag{5}$$

Apart from Δμ, which can be obtained from, for example, electrooptical absorption measurements, the transition moment μ_{01} has to be evaluated from the absorption intensity. The ratio of Δμ and the difference Δ in the dipole moments of the zwitterionic and the electroneutral resonance structure is expressed in Equation (6).

$$\frac{\Delta\mu}{\Delta} = 1-2c^2 \tag{6}$$

The negative value of this ratio was taken by Barzoukas et al.[56] as a parameter MIX for the characterization of the "mixing" of the two resonance structures.[57] Finally, Marder et al.[58–61] introduced the parameter BLA (bond length alternation), which is related to the π bond order alternation and empirically related to MIX by Equation (7).[56]

$$\text{BLA (in Å)} = 0.11\ \text{MIX} \tag{7}$$

Increasing numbers n of repeat units in the oligomer series produce an increasing distance between D and A and should therefore lead to increasing Δ values. Electrooptical absorption measurements[26] gave an almost constant value[62] of $1-2c^2 = 0.80 \pm 0.07$ for the series **1d**–**3d**. Therefore, as to Equation (6), Δμ should grow with Δ for increasing n. This was not found, either experimentally[26] or by the INDO/S calculation. The calculation illustrated in Figure 7 even reveals a decrease in Δμ with increasing n in the series R_2N-OPV(n = 1–4)-NO_2.

The valence bond (VB) concept with a certain "mixture" of an electroneutral and a zwitterionic resonance structure for the ground state S_0 and the "reversed mixture" for the first excited singlet state S_1 is obviously not appropriate for D-OPV(n)-A series with very low c^2 values ($c^2 < 0.1$) and corresponding MIX values. The VB concept is certainly much better for systems close to the so-called cyanine limit (c^2 = 0.5, MIX = 0). The BLA value is also problematic for stilbenoid compounds, because it is restricted to very small bond length changes in the olefinic segments; the benzene rings try to keep their equalised bond lengths.

It was stated in the Introduction that D-π-A systems deserve their attention mainly because of their NLO properties. It therefore remains here to discuss the second order hyperpolarizabilities β_0. Although Equation (8) is based on a two-state level,[63] it is useful for prediction of the β_0 values.

$$\beta_0 = \frac{6\mu_{01}^2\Delta\mu\lambda_{\max}^2}{h^2c_0^2} \tag{8}$$

For many D-π-A systems, the transition moment μ_{01}, the difference of the dipole moments Δμ and $\lambda_{\max}$ increase with increasing numbers n of repeat units; this means that β_0 increases with n too. For the series **1d**–**3d**, however, $\mu_{01}^2 \cdot \Delta\mu$ increases with increasing n, but $\lambda_{\max}^2$ decreases.[26] Nevertheless, $\beta_0(n)$ should show an enhancement with the extension of the chromophore. On the basis of Equation (8) and the obtained values of μ and Δμ[26] for **1d**, **2d** and **3d** we calculated β_0 values of 198, 287 and 346×10^{-50} Cm^3V^{-2}, respectively.

Conclusion

The D-OPV-A series **1b**–**4b**, **1c**–**4c** and **1d**–**4d** (with n = 1–4 each) and terminal donor–acceptor substitution were prepared by application of Wittig–Horner reactions and compared to the purely donor-substituted series **1a**–**4a** (n = 1–4). Solubilizing bis(2-hexyloctyl)amino groups served as electron donors, cyano (**b**), formyl (**c**) and nitro (**d**) groups as acceptors. The long-wavelength absorption ($S_0 \rightarrow S_1$) shows a bathochromic effect for **1a**–**4a** and **1b**–**4b**, almost no influence of the extension of the chromophore for **1c**–**4c** and a hypsochromic shift in the series **1d**–**4d**. The $\lambda_{\max}$ values of the four series approach the same limiting value λ_∞. The absorption intensity grows with increasing numbers n of repeat units in all four series. Extension of the conjugation leads in **1a**–**4a** to a bathochromic shift, which is enhanced in the push–pull systems **1**–**4** (**b**–**d**) by the effect of an intramolecular charge transfer (ICT). However, the effect of the ICT on the transition energy is strongly reduced by increasing distance between D and A. For A = CN the "conjugation effect" dominates over the "ICT-induced reduction", for A = CHO the two effects annihilate each other, and for the strongest acceptor, the nitro group, an overall hypsochromic effect results. (Apart from the donor and acceptor strengths, the connecting "π spacer" has an important influence on the question of which of the two effects prevails. A polyene chain permits a better D–A interaction than an OPV chain). Protonation of the dialkylamino group leads to the disappearance of the push–pull effect; consequently, the protonated series **1**–**4** (**b**–**d**) all exhibit a normal bathochromic effect with extension of the conjugation.

The empirical separation into two opposite effects (quantified by exponential functions) can be justified by semiempirical quantum mechanics (AM1, INDO/S). It turned out that the fraction of HOMO→LUMO transition in $S_0 \rightarrow S_1$ is strongly reduced with increasing n. The percentage of the involved HOMO–LUMO transition correlates with the term ΔE_{DA} of the ICT effect. Moreover, the calculations predict that the enhancement of the dipole moments $\Delta\mu = \mu(S_1) - \mu(S_0)$ should also be reduced with growing n. An interesting comparison with push–pull-substituted polyenes, concerning the dependence of $\Delta\mu$ on the number m of π electrons in the chain, was made.

The absorption behaviour of the D-OPV-A systems is discussed in terms of the usual VB model with an electroneutral (Ψ_n) and a zwitterionic (Ψ_z) resonance structure. As an alternative, an MO model with terminal dipole moments is suggested. The charge distribution in the ground state S_0, checked by ^{13}C NMR measurements, as well as the ICT, involved in the transition to the first excited singlet state S_1, reveal that the VB model is suitable for the stilbenes (n = 1); for the higher OPVs (n = 2–4), the MO model is much better.

Experimental Section

General remarks: The melting points were measured on a Büchi melting point apparatus and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM 400 and AC 200 spectrometers with $CDCl_3$ as solvent unless otherwise stated, with TMS as internal standard. The FD mass spectra were obtained on a Finnigan MAT 95 instrument. The UV/Vis absorption spectra were taken on a Zeiss MCS 320/340 machine. Silica gel (E. Merck 60, 70–230 mesh ASTM) was used for column chromatography. Elemental analyses were performed in the microanalytical laboratory of the Institute of Organic Chemistry of the University of Mainz, Germany.

4-[Bis(2-hexyloctyl)amino]benzaldehyde (6): This compound was prepared according to the literature.[64]

Diethyl 4-(diethoxymethyl)benzylphosphonate (7): This compound was prepared according to the literature.[65]

General procedure for the Wittig–Horner reactions

Method A: Equimolar amounts of the appropriate aldehyde and the corresponding phosphonate, dissolved in dry DMF or THF, were dropped into a solution of potassium *tert*-butoxide (slight excess) in the same solvent. The mixture was stirred at room temperature for 1 h and then poured onto crushed ice. The aqueous phase was extracted three times with dichloromethane and the combined organic phases were dried over Na_2SO_4. After removal of the solvent, the residue was purified either by silica gel column chromatography or by recrystallization or both.

Method B: A solution of the phosphonate in dry dimethoxyethane (DME) was added dropwise to a suspension of NaH (slight excess) in the same solvent. After the system had been stirred for 15 min at room temperature, a solution of an equimolar amount of the corresponding aldehyde in DME was added. The reaction mixture was heated at reflux for 3 h and carefully quenched with $MeOH/H_2O$ 1:1. The purification was performed as described for Method A.

4-(*E*)-2-{4-[Bis(2-hexyloctyl)amino]phenyl}ethenyl)benzaldehyde (1c): This compound was prepared from **6** and **7** as described in the General Procedure (Method A) described above. The crude material was chromatographed on silica gel (50×3 cm) with petroleum ether (b.p. 40–70 °C)/ethyl acetate 2:1 to give 87% of an orange oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.87 (t, 12H; CH_3), 1.25 (m, 40H; CH_2), 1.84 (m, 2H; CH), 3.23 (d, 4H; NCH_2), 6.63 (AA′ of AA′MM′, 2H; aromat. H), 6.88 (d, ^3J = 16.1 Hz, 1H; olefin. H), 7.18 (d, ^3J = 16.1 Hz, 1H; olefin. H), 7.38 (MM′, 2H; aromat. H), 7.56 (m, 2H; aromat. H), 7.80 (m, 2H; aromat. H), 9.94 (s, 1H; CHO) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.6–31.8 (CH_2, superimposed), 35.7 (CH), 56.7 (NCH_2), 112.8, 126.1, 128.2, 130.2 (aromat. CH), 122.1, 132.7 (olefin. CH), 123.7, 134.5, 144.8, 148.9 (aromat. C_q), 191.0 (CHO) ppm; FD MS: m/z (%): 616 (100) $[M]^+$; elemental analysis calcd (%) for $C_{43}H_{69}NO$ (616.0): C. 83.84, H 11.29, N 2.27; found: C 83.98, H 10.90, N 2.46.

4-{(*E*)-2-[4-((*E*)-2-{4-[Bis(2-hexyloctyl)amino]phenyl}ethenyl)phenyl]-ethenyl}benzaldehyde (2c): This compound was prepared from **1c** and **7** as described in Method A. Recrystallization from ethyl acetate gave 77% of orange crystals; m.p. 98 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, 12H; CH_3), 1.25 (m, 40H; CH_2), 1.84 (m, 2H; CH), 3.21 (d, 4H; NCH_2), 6.63 (m, 2H; aromat. H), 6.86 (d, ^3J = 16.1 Hz, 1H; olefin. H), 7.06 (d, ^3J = 16.1 Hz, 1H; olefin. H), 7.10 (d, ^3J = 16.4 Hz, 1H; olefin. H), 7.24 (d, ^3J = 16.4 Hz, 1H; olefin. H), 7.36 (m, 2H; aromat. H), 7.45 (m, 2H; aromat. H), 7.49 (m, 2H; aromat. H), 7.63 (m, 2H; aromat. H), 7.84 (m, 2H; aromat. H), 9.97 (s, 1H; CHO) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.6–31.8 (CH_2, superimposed), 35.6 (CH), 56.6 (NCH_2), 112.8, 126.2, 126.7, 127.1, 127.6, 130.1 (aromat. CH), 122.9, 126.3, 129.6, 132.0 (olefin. CH), 124.3, 134.6, 135.2, 138.8, 143.6, 148.3 (aromat. C_q), 191.3 (CHO) ppm; FD MS: m/z (%): 718 (100) $[M]^+$; elemental analysis calcd (%) for $C_{51}H_{75}NO$ (717.9): C 85.30, H 10.53, N 1.95; found: C 85.29, H 10.51, N 1.65.

4-[(*E*)-2-(4-{(*E*)-2-[4-((*E*)-2-{4-[Bis(2-hexyloctyl)amino]phenyl}ethenyl)-phenyl]ethenyl}phenyl)ethenyl]benzaldehyde (3c): This compound was prepared from **2c** and **7** as described in Method A. The crude product was purified by column chromatography on silica gel with toluene/petroleum ether (b.p. 40–70 °C) 2:1, yielding orange crystals; m.p. 165 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 12H; CH_3), 1.26 (m, 40H; CH_2), 1.84 (m, 2H; CH), 3.21 (d, 4H; NCH_2), 6.63 (m, 2H; aromat. H), 6.86 (d, ^3J = 16.1 Hz, 1H; olefin. H), 7.06 (d, ^3J = 16.1 Hz, 1H; olefin. H), 7.10, 7.13 (m, 3H; olefin. H), 7.26 (d, ^3J = 16.6 Hz, 1H; olefin. H), 7.36 (m, 2 H; aromat. H), 7.46 ("s", 4H; aromat. H), 7.51 ("s", 4H; aromat. H), 7.63 (m, 2H; aromat. H), 7.85 (m, 2H; aromat. H), 9.98 (s, 1H;

CHO) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 14.0$ (CH_3), 22.6–31.8 (CH_2, superimposed), 35.6 (CH), 56.7 (NCH_2), 112.8, 126.2, 126.8, 126.8, 126.8, 127.2, 127.5, 130.1 (aromat. CH), 123.1, 126.9, 127.1, 129.0, 129.1, 131.8 (olefin. CH), 124.4, 135.4, 135.4, 135.6, 137.8, 138.1, 143.4, 148.2 (aromat. C_q) ppm; FD MS: *m/z* (%): 820 (100) $[M]^+$; elemental analysis calcd (%) for $C_{59}H_{81}NO$ (820.3): calcd. C 86.39, H 9.95, N 1.71; found: C 86.39, H 9.84, N 1.77.

4-((*E*)-2-{4-[(*E*)-2-(4-{(*E*)-2-[4-((*E*)-2-{4-[Bis(2-hexyloctyl)amino]phenyl}ethenyl)phenyl]ethenyl}phenyl)ethenyl]phenyl}ethenyl)benzaldehyde (4c): This compound was prepared from **3c** and **7** as described in Method A. The crude product was purified by column chromatography on silica gel with CH_2Cl_2 as eluent, yielding 62% orange crystals; m.p. 195 °C; ^{1}H NMR (400 MHz, $CHCl_3$): $\delta = 0.87$ (t, 12H; CH_3), 1.24 (m, 40H; CH_2), 1.83 (m, 2H; CH), 3.20 (d, 4H; NCH_2), 6.61 (m, 2H; aromat. H), 6.86 (d, $^3J = 16.4$ Hz, 1H; olefin. H), 7.03 (d, $^3J = 16.3$ Hz, 1H; olefin. H), 7.09, 7.12, 7.24, (3 m, 6H; olefin. H), 7.35 (m, 2H; aromat. H), 7.45 (m, 4H; aromat. H), 7.50 (“s”, 4H; aromat. H), 7.52 (“s”, 4H; aromat. H), 7.64 (m, 2H; aromat. H), 7.85 (m, 2H; aromat. H), 9.97 (s, 1H; CHO) ppm; FD MS: *m/z* (%): 923 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{67}H_{87}NO$ (922.4): C 87.24, H 9.51, N 1.52; found: C 87.18, H 9.38, N 1.69.

Diethyl benzylphosphonate (8a), diethyl 4-cyanobenzylphosphonate (8b) and diethyl 4-nitro-benzylphosphonate (8d): These compounds were prepared according to the literature: **8a**,[66] **8b**,[67,68] **8d**.[69]

***N,N*-Bis(2-hexyloctyl)-4-[(*E*)-2-phenylethenyl]aniline (1a)**: This compound was prepared from **6** and **8a** as described in Method B. The crude product was purified by column chromatography on silica gel with petroleum ether (b.p. 40–70 °C), yielding 57% of a yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.89$ (t, 12H; CH_3), 1.27 (m, 40H; CH_2), 1.85 (m, 2H; CH), 3.22 (d, 4H; NCH_2), 6.64 (d, 2H; aromat. H), 6.88 (d, $^3J = 16.4$ Hz, 1H; olefin. H), 7.04 (d, $^3J = 16.4$ Hz, 1H; olefin. H), 7.18 (m, 1H; aromat. H), 7.35 (m, 4H; aromat. H), 7.47 (m, 2H; aromat. H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 14.1$ (CH_3), 22.7–31.9 (CH_2, superimposed), 35.6 (CH), 56.8 (NCH_2), 112.8, 126.0, 126.5, 127.6, 128.6 (aromat. CH), 123.6, 129.0 (olefin. CH), 124.5, 138.5, 148.1 (aromat. C_q) ppm; FD MS: *m/z* (%): 588 (100) $[M]^+$; elemental analysis calcd (%) for $C_{42}H_{69}N$ (588.0): C 85.79, H 11.83, N 2.38; found: C 85.88, H 12.16, N 2.66.

***N,N*-Bis(2-hexyloctyl)-4-((*E*)-2-{4-[(*E*)-2-phenylethenyl]phenyl}ethenyl)-aniline (2a)**: This compound was prepared from **1c** and **8a** as described in Method A. The crude product was purified by column chromatography on silica gel with petroleum ether (b.p. 40–70 °C), yielding 36% of a yellow wax. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.89$ (t, 12H; CH_3), 1.26 (m, 40H; CH_2), 1.84 (m, 2H; CH), 3.22 (d, 4H; NCH_2), 6.64 (m, 2H; aromat. H), 6.88 (d, $^3J = 16.4$ Hz, 1H; olefin. H), 7.05 (d, $^3J = 16.4$ Hz, 1H; olefin. H), 7.10 (“s”, 2H; olefin. H), 7.24 (m, 1H; aromat. H), 7.36 (m, 4H; aromat. H), 7.46 (m, 4H; aromat. H), 7.51 (m, 2H; aromat. H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 14.1$ (CH_3), 22.7–31.9 (CH_2, superimposed), 35.6 (CH), 56.8 (NCH_2), 112.7, 126.2, 126.4, 126.8, 127.4, 127.6, 128.7 (aromat. CH), 123.2, 127.8, 128.5, 129.0 (olefin. CH), 124.4, 135.5, 137.5, 137.9, 148.1 (aromat. C_q) ppm; FD MS: *m/z* (%): 691 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{50}H_{75}N$ (690.2): C 87.02, H 10.95, N 2.03; found: C 86.72, H 10.95, N 1.97.

***N,N*-Bis(2-hexyloctyl)-4-{(*E*)-2-[4-((*E*)-2-{4-[(*E*)-2-phenylethenyl]phenyl}ethenyl)phenyl]ethenyl}aniline (3a)**: This compound was prepared from **2c** and **8a** as described in Method B. The crude product was recrystallized from ethyl acetate, yielding 38% of yellow crystals; m.p. 158 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.88$ (t, 12H; CH_3), 1.26 (m, 40H; CH_2), 1.84 (m, 2H; CH), 3.22 (d, 4H; NCH_2), 6.64 (m, 2H; aromat. H), 6.87 (d, $^3J = 16.1$ Hz, 1H; olefin. H), 7.05 (d, $^3J = 16.1$ Hz, 1H; olefin. H), 7.10 (m, 2H; olefin. H), 7.11 (“s”, 2H; olefin. H), 7.25 (m, 1H; aromat. H), 7.36 (m, 4H; aromat. H), 7.46 (m, 4H; aromat. H), 7.50 (“s”, 4H; aromat. H), 7.51 (m, 2H; aromat. H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 14.1$ (4C; CH_3), 22.7–31.9 (CH_2, superimposed), 35.6 (CH), 56.7 (NCH_2), 112.7, 126.2, 126.5, 126.8, 126.8, 126.8, 127.6, 127.6, 128.7 (aromat. CH), 123.2, 127.4, 128.3, 128.4, 128.4, 129.0 (olefin. CH), 124.4, 135.5, 136.5, 136.9, 137.4, 137.9, 148.1 (aromat. C_q) ppm; FD MS: *m/z* (%): 793 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{58}H_{81}N$ (792.3): C 87.93, H 10.30, N 1.77; found: C 87.54, H 10.02, N 1.73.

***N,N*-Bis(2-hexyloctyl)-4-[(*E*)-2-(4-{(*E*)-2-[4-((*E*)-2-{4-[(*E*)-2-phenylethenyl]phenyl}ethenyl)phenyl]ethenyl}phenyl)ethenyl]aniline (4a)**: This compound was prepared from **3c** and **8a** as described in Method B. The crude product was purified by column chromatography on silica gel with $CHCl_3$, yielding 24% of a yellow wax. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.87$ (t, 12H; CH_3), 1.24 (m, 40H; CH_2), 1.83 (m, 2H; CH), 3.21 (d, 4H; NCH_2), 6.61 (m, 2H; aromat. H), 6.86 (d, $^3J = 16.0$ Hz, 1H; olefin. H), 7.04 (d, $^3J = 16.0$ Hz, 1H; olefin. H), 7.11 (m, 6H; olefin. H), 7.25 (m, 1H; aromat. H), 7.35 (m, 4H; aromat. H), 7.46 (m, 4H; aromat. H), 7.50 (m, 10H; aromat. H) ppm; FD MS: *m/z* (%): 894 (100) $[M]^+$; $C_{66}H_{87}N$ (894.4): after careful drying in vacuum the compound still contained some solvent; therefore a correct elemental analysis could not be obtained.

4-((*E*)-2-{4-[Bis(2-hexyloctyl)amino]phenyl}ethenyl)benzonitrile (1b): This compound was prepared from **6** and **8b** as described in Method A. The crude product was purified by column chromatography on silica gel with petroleum ether (b.p. 40–70 °C)/ethyl acetate 30:1, yielding 70% of yellow crystals; m.p. 60 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.87$ (t, 12H; CH_3), 1.25 (m, 40H; CH_2), 1.84 (m, 2H; CH), 3.23 (d, 4H; NCH_2), 6.63 (m, 2H; aromat. H), 6.82 (d, $^3J = 16.4$ Hz, 1H; olefin. H), 7.12 (d, $^3J = 16.4$ Hz, 1H; olefin. H), 7.36 (m, 2H; aromat. H), 7.48 (m, 2H; aromat. H), 7.56 (m, 2H; aromat. H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 14.1$ (CH_3), 22.7–31.9 (CH_2, superimposed), 35.6 (CH), 56.7 (NCH_2), 109.0, 123.2, 143.1, 148.8 (aromat. C_q), 119.5 (CN), 121.3, 132.8 (olefin. CH), 112.6, 126.1, 128.2, 132.4 (aromat. CH) ppm; FD MS: *m/z* (%): 613 (100) $[M]^+$; elemental analysis calcd (%) for $C_{43}H_{68}N_2$ (613.0): C 84.25, H 11.18, N 4.57; found: C 84.35, H 11.19, N 4.65.

4-{(*E*)-2-[4-((*E*)-2-{4-[Bis(2-hexyloctyl)amino]phenyl}ethenyl)phenyl]-ethenyl}benzonitrile (2b): This compound was prepared from **1c** and **8b** as described in Method A. The crude product was purified by column chromatography on silica gel with petroleum ether (b.p. 40–70 °C)/Et_2O 20:1, yielding 57% of yellow crystals; m.p. 103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.87$ (t, 12H; CH_3), 1.25 (m, 40H; CH_2), 1.84 (m, 2H; CH), 3.21 (d, 4H; NCH_2), 6.63 (m, 2H; aromat. H), 6.86 (d, $^3J = 16.1$ Hz, 1H; olefin. H), 7.05 (d, $^3J = 16.1$ Hz, 1H; olefin. H), 7.06 (d, $^3J = 16.1$ Hz, 1H; olefin. H), 7.18 (d, $^3J = 16.1$ Hz, 1H; olefin. H), 7.36 (m, 2H; aromat. H), 7.46 (“s”, 4H; aromat. H), 7.55 (m, 2H; aromat. H), 7.61 (m, 2H; aromat. H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 13.8$ (CH_3), 22.4–31.6 (CH_2, superimposed), 35.4 (CH), 56.5 (NCH_2), 110.1, 124.1, 134.2, 138.8, 141.9, 148.2 (aromat. C_q), 112.6, 126.1, 126.5, 127.0, 127.5, 132.2 (aromat. CH), 118.8 (CN), 122.7, 125.5, 129.5, 132.1 (olefin. CH) ppm; FD MS: *m/z* (%): 715 (100) $[M]^+$; elemental analysis calcd (%) for $C_{51}H_{74}N_2$ (715.2): C 85.65, H 10.43, N 3.92; found: C 85.56, H 10.48, N 3.90.

4-[(*E*)-2-(4-{(*E*)-2-[4-((*E*)-2-{4-[Bis(2-hexyloctyl)amino]phenyl}ethenyl)-phenyl]ethenyl}phenyl)ethenyl]benzonitrile (3b): This compound was prepared from **2c** and **8b** as described in Method B. Recrystallization from ethyl acetate gave 55% of orange crystals; m.p. 162 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.88$ (t, 12H; CH_3), 1.26 (m, 40H; CH_2), 1.84 (m, 2H; CH), 3.22 (d, 4H; NCH_2), 6.64 (m, 2H; aromat. H), 6.87 (d, $^3J = 16.1$ Hz, 1H; olefin. H), 7.05 (d, $^3J = 16.1$ Hz, 1H; olefin. H), 7.07 (d, $^3J = 16.2$ Hz, 2H; olefin. H), 7.13 (d, $^3J = 16.3$ Hz, 1H; olefin. H), 7.19 (d, $^3J = 16.2$ Hz, 1H; olefin. H), 7.36 (m, 2H; aromat. H), 7.46 (m, 4H; aromat. H), 7.51 (“s”, 4H; aromat. H), 7.56 (m, 2H; aromat. H), 7.61 (m, 2H; aromat. H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 14.1$ (CH_3), 22.7–31.9 (CH_2, superimposed), 35.6 (CH), 56.7 (NCH_2), 110.5, 124.1, 135.3, 135.3, 138.0, 138.2, 141.9, 148.2 (aromat. C_q), 112.7, 126.2, 126.8, 126.8, 126.8, 127.3, 127.6, 132.5 (aromat. CH), 119.0 (CN), 123.1, 126.3, 127.1, 129.1, 129.2, 132.0 (olefin. CH) ppm; FD MS: *m/z* (%): 817 (100) $[M]^+$; elemental analysis calcd (%) for $C_{59}H_{80}N_2$ (817.3): C 86.71, H 9.87, N 3.43; found: C 86.51, H. 9.71, N 3.18.

4-((*E*)-2-{4-[(*E*)-2-(4-{(*E*)-2-[4-((*E*)-2-{4-[Bis(2-hexyloctyl)amino]phenyl}ethenyl)phenyl]ethenyl}phenyl)ethenyl]phenyl}ethenyl)benzonitrile (4b): This compound was prepared from **3c** and **8b** as described in Method B. The crude product was recrystallized from ethyl acetate/MeOH 2:1, yielding 24% of orange crystals; m.p. >240 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.86$ (t, 12H; CH_3), 1.25 (m, 40H; CH_2), 1.81 (m, 2H; CH), 3.19 (d, 4H; NCH_2), 6.55 (m, 2H; aromat. H), 6.80 (d, $^3J = 16.1$ Hz, 1H; olefin. H), 6.96 (d, $^3J = 16.1$ Hz, 1H; olefin. H), 7.02 (m, 2H; olefin. H), 7.07 (m, 3H; olefin. H), 7.14 (d, $^3J = 16.3$ Hz, 1H; olefin. H), 7.29 (m, 2H; aromat. H), 7.40 (m, 4H; aromat. H), 7.46 (“s”, 4H; aromat. H), 7.48

(“s”, 4H; aromat. H), 7.52 (m, 2H; aromat. H), 7.57 (m, 2H; aromat. H) ppm; FD MS: m/z (%): 919 (100) $[M]^+$; elemental analysis calcd (%) for $C_{67}H_{86}N_2$ (919.4): C 87.53, H 9.43, N 3.05; found: C 87.16, H 9.21, N 2.83.

***N,N*-Bis(2-hexyloctyl)-4-[(*E*)-2-(4-nitrophenyl)ethenyl]aniline (1d)**: This compound was prepared from **6** and **8d** as described in Method A. Recrystallization from EtOH gave 65% of red crystals; m.p. 60–62°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.87$ (t, 12H; CH_3), 1.24 (m, 40H; CH_2), 1.83 (m, 2H; CH), 3.23 (d, 4H; NCH_2), 6.63 (m, 2H; aromat. H), 6.87 (d, $^3J = 16.0$ Hz, 1H; olefin. H), 7.17 (d, $^3J = 16.0$ Hz, 1H; olefin. H), 7.38 (m, 2H; aromat. H), 7.52 (m, 2H; aromat. H), 8.15 (m, 2H; aromat. H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 14.0$ (CH_3), 22.6–31.8 (CH_2, superimposed), 35.6 (CH), 56.6 (NCH_2), 112.7, 124.2, 125.9, 128.4 (aromat. CH), 120.9, 133.9 (olefin. CH), 123.3, 145.3, 145.8, 149.1 (aromat. C_q) ppm; FD MS: m/z (%): 633 (100) $[M]^+$; elemental analysis calcd (%) for $C_{42}H_{68}N_2O_2$ (633.0): C 79.69, H 10.83, N 4.43; found: C 80.02, H 10.66, N 4.18.

***N,N*-Bis(2-hexyloctyl)-4-((*E*)-2-{4-[(*E*)-2-(4-nitrophenyl)ethenyl]phenyl}ethenyl)aniline (2d)**: This compound was prepared from **1c** and **8d** as described in Method B. The residue was chromatographed on silica gel with CH_2Cl_2 to give 94% of orange crystals; m.p. 94°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.88$ (t, 12H; CH_3), 1.25 (m, 40H; CH_2), 1.84 (m, 2H; CH), 3.22 (d, 4H; NCH_2), 6.63 (m, 2H; aromat. H), 6.87 (d, $^3J = 16.1$ Hz, 1H; olefin. H), 7.08 (d, $^3J = 16.1$ Hz, 1H; olefin. H), 7.10 (d, $^3J = 16.1$ Hz, 1H; olefin. H), 7.26 (d, $^3J = 16.1$ Hz, 1H; olefin. H), 7.37 (m, 2H; aromat. H), 7.48 (“s”, 4H; aromat. H), 7.61 (m, 2H; aromat. H), 8.20 (m, 2H; aromat. H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 14.0$ (CH_3), 22.6–31.8 (CH_2, superimposed), 35.6 (CH), 56.7 (NCH_2), 112.8, 124.1, 126.3, 126.7, 127.4, 127.7 (aromat. CH), 122.9, 125.3, 129.9, 133.2 (olefin. CH), 124.3, 134.2, 139.2, 144.1, 146.6, 148.3 (aromat. C_q) ppm; FD MS: m/z (%): 735 (100) $[M]^+$; elemental analysis calcd (%) for $C_{50}H_{74}N_2O_2$ (735.2): C 81.69, H 10.15, N 3.81; found: C 81.68, H 10.03, N 3.66.

***N,N*-Bis(2-hexyloctyl)-4-{(*E*)-2-[4-((*E*)-2-[{4-[(*E*)-2-(4-nitrophenyl)ethenyl]phenyl}ethenyl)phenyl]ethenyl}aniline (3d)**:[70] This compound was prepared from **2c** and **8d** as described in Method A. The crude product was purified by column chromatography on silica gel with toluene/petroleum ether (b.p. 40–70°C) 1:2, yielding 24% of a red wax. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.87$ (t, 12H; CH_3), 1.24 (m, 40H; CH_2), 1.84 (m, 2H; CH), 3.23 (d, 4H; NCH_2), 6.63 (m, 2H; aromat. H), 6.87 (d, $^3J = 16.3$ Hz, 1H; olefin. H), 7.05 (d, $^3J = 16.3$ Hz, 1H; olefin. H), 7.07 (d, $^3J = 16.3$ Hz, 1H; olefin. H), 7.12 (d, $^3J = 16.3$ Hz, 1H; olefin. H), 7.14 (d, $^3J = 16.3$ Hz, 1H; olefin. H), 7.24 (d, $^3J = 16.3$ Hz, 1H; olefin. H), 7.36 (d, 2H; aromat. H), 7.46 (m, 4H; aromat. H), 7.52 (“s”, 4H; aromat. H), 7.61 (m, 2H; aromat. H), 8.20 (m, 2H; aromat. H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 14.0$ (CH_3), 22.6–31.8 (CH_2, superimposed), 35.6 (CH), 56.6 (NCH_2), 112.8, 124.1, 126.2, 126.7, 126.8, 126.8, 127.3, 127.5 (aromat. CH), 123.1, 125.8, 127.0, 129.2, 129.3, 132.9 (olefin. CH), 124.4, 135.2, 135.2, 138.2, 138.2, 143.9, 146.7, 148.3 (aromat. C_q) ppm; FD MS: m/z (%): 837 (100) $[M]^+$; elemental analysis calcd (%) for $C_{58}H_{80}N_2O_2$ (837.3): C 83,20, H 9.63, N 3.35; found: C 82.97, H 9.92, N 3.10.

***N,N*-Bis(2-hexyloctyl)-4-[(*E*)-2-(4-{(*E*)-2-[4-((*E*)-2-{4-[(*E*)-2-(4-nitrophenyl)ethenyl]phenyl}ethenyl)phenyl]ethenyl}phenyl)ethenyl]aniline (4d)**: This compound was prepared from **3c** and **8d** as described in Method B. The crude product was purified by column chromatography on silica gel with dichloromethane as eluent; yield 52% of a red viscous wax. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 0.89$ (t, 12H; CH_3), 1.27 (m, 40H; CH_2), 1.85 (m, 2H; CH), 3.25 (d, 4H; NCH_2), 6.66 (m, 2H; aromat. H), 6.88 (d, $^3J = 16.1$ Hz, 1H; olefin. H), 7.07 (d, $^3J = 16.1$ Hz, 1H; olefin. H), 7.15 (m, 2H; olefin. H), 7.19 (“s”, 2H; olefin. H), 7.21 (d, $^3J = 16.2$ Hz, 1H; olefin. H), 7.32 (d, $^3J = 16.2$ Hz, 1H; olefin. H), 7.36 (m, 2H; aromat. H), 7.49 (m, 4H; aromat. H), 7.55 (“s”, 4H; aromat. H), 7.59 (“s”, 4 H; aromat. H), 7.68 (m, 2H; aromat. H), 8.21 (m, 2H; aromat. H) ppm; FD MS: m/z (%): 939 (100) $[M]^+$. The compound $C_{66}H_{86}N_2O_2$ (939.4) contains H_2O even after careful drying in the vacuum; therefore we did not obtain a correct elemental analysis.

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