Red- and Blue-Shifts in Oligo(1,4-phenyleneethynylene)s Having Terminal Donor−Acceptor Substitutions

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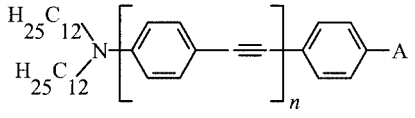
Four series of oligo(1,4-phenyleneethynylene)s (OPEs), **1**–**4** (**a**–**d**), each having a terminal dialkylamino group as their electron donor, were prepared by applying Sonogashira–Hagihara reactions and a protecting group strategy. To study the influence that the push–pull effect has on the long-wavelength absorption, three of the four series of OPEs contain terminal acceptor groups (CN, CHO, NO_2). Extending the conjugation (increasing the number of repeat units, *n*) lowers the energy *E*(*n*) of the electron transition in the purely donor-substituted series **1a**–**4a** (bathochromic shift). This effect is superimposed in the push–pull series **1**–**4** (**b**–**d**) by the effect of the intramolecular charge transfer (ICT), which decreases with increasing the distance between the donor and acceptor groups. In the case of the relatively weak acceptor CN, both effects annihilate one another, whereas the reduction of the ICT predominates in the CHO and NO_2 series. Therefore, *E*(*n*) is virtually independent of *n* in the CN series **1b**–**4b** and shows a hypsochromic effect in the CHO and NO_2 series (**1c**–**4c** and **1d**–**4d**, respectively). We rationalize these results based on AM1–INDO/S calculations. The results of the commonly used intuitive VB model having electroneutral and zwitterionic resonance structures are compared with those of a more appropriate MO model having dipole segments at both chain ends.

Introduction

Conjugated oligomers and polymers, such as the 1,4-phenyleneethenylenes (OPVs and PPVs) and the corresponding 1,4-phenyleneethynylenes (OPEs and PPEs), attract a lot of attention in organic chemistry and materials science.[1] Recently we reported the preparation and nonlinear optical properties of a series of eight oligo(2,5-dipropoxy-1,4-phenyleneethynylene)s.[2,3] Because of the presence of a center of symmetry in these molecules, we studied the third harmonic generation (THG)/second hyperpolarizability, γ. In this paper, we deal with the preparation of donor−acceptor-substituted OPEs. These molecules do not have a center of symmetry; moreover, they should exhibit a large intramolecular charge transfer (ICT) upon $S_0 \rightarrow S_1$ excitation. Thus, these compounds should have high values of the second harmonic generation (SHG)/hyperpolarizability (β). We chose the solubilizing didodecylamino groups as the electron donors, D, and CN (series **1b**−**4b**), CHO (series **1c**−**4c**), and NO_2 groups (series **1d**−**4d**) as the electron acceptors (A, Scheme 1). The series **1a**−**4a** lacking the terminal acceptor (A = H) was prepared for the sake of comparing the push−pull series **1**−**4** (**b**−**d**) with "normal" OPEs.



—A \ *n*	1	2	3	4
—H	**1a**	**2a**	**3a**	**4a**
—C≡N	**1b**	**2b**	**3b**	**4b**
—CH=O	**1c**	**2c**	**3c**	**4c**
—NO_2	**1d**	**2d**	**3d**	**4d**

Scheme 1. Donor-substituted oligo(1,4-phenyleneethynylene)s **1a**−**4a** and donor−acceptor-substituted oligo(1,4-phenyleneethynylene)s **1b**−**4b**, **1c**−**4c**, and **1d**−**4d**

Conjugated oligomers usually exhibit a convergent *bathochromic shift* of both the absorption and fluorescence when the number of repeat units, *n*, is increased.[4] Recently, however, we found some D−OPV(*n*)−A series (OPV = oligo-*p*-phenylenevinylene) that display the opposite behavior: a *hypsochromic shift* is induced upon extending the length of the chromophores.[5−8] These results stimulated us to investigate also the OPEs **1**−**4** (**a**−**d**).

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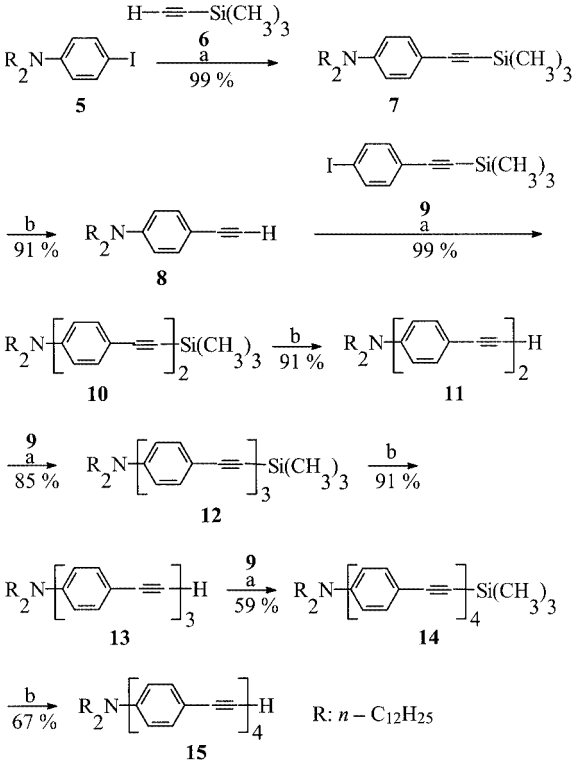
Results and Discussion

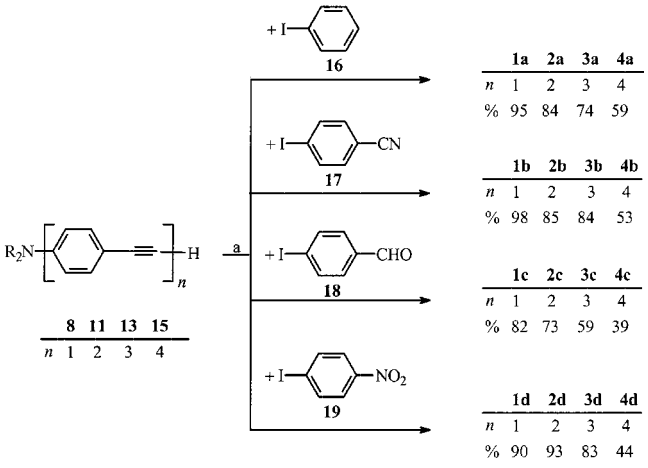
Synthesis

For a coupled synthesis of the 16 compounds **1**−**4** (**a**−**d**), we started with *N*,*N*-didodecyl-4-iodoaniline (**5**) and first prepared the OPE series **7**, **10**, **12**, and **14** having terminal trimethylsilylethynyl groups and the corresponding deprotected OPE series, **8**, **11**, **13**, and **15** (Scheme 2). The Sonogashira−Hagihara reaction[9] of **5** and trimethylsilylacetylene (**6**) gave *N*,*N*-didodecyl-4-(trimethylsilylethynyl)aniline (**7**) in quantitative yield. After deprotection with K_2CO_3, the alkyne **8** was transformed to the next higher, protected OPE **10**, again by applying a quantitative Pd-catalyzed C(sp^2)−C(sp) coupling reaction (**8** + **9** → **10**). The process was repeated twice, i.e., **10** was deprotected to give **11**, which was coupled with **9** to give **12**, which was deprotected to give **13**, which was coupled again with **9** to give **14**, which was deprotected to give **15**. The yields of these steps are high (91−59%), although they are somewhat lower than those for the shorter-chain compounds (Scheme 2). The two series of OPEs have good solubilities because the didodecylamino group is present in every one of these compounds.



Scheme 2. Preparation of the donor-substituted oligo(1,4-phenyleneethynylene) series **7**, **10**, **12**, and **14** and **8**, **11**, **13**, and **15**: (a) Pd^0, PPh_3, CuI, piperidine, (b) K_2CO_3, CH_2Cl_2/CH_3OH

The final step toward obtaining the target compounds **1**−**4** (**a**−**d**) was Sonogashira−Hagihara coupling of the deprotected members of the OPE series [**8**, **11**, **13**, and **15** (*n* = 1−4)] with the corresponding iodo compounds **16**−**19** (Scheme 3). Again, the yields of these 16 C−C coupling reactions are high (98−73%) for the shorter systems (*n* = 1,2) and somewhat lower (84−39%) for the longer ones (*n* = 3,4).

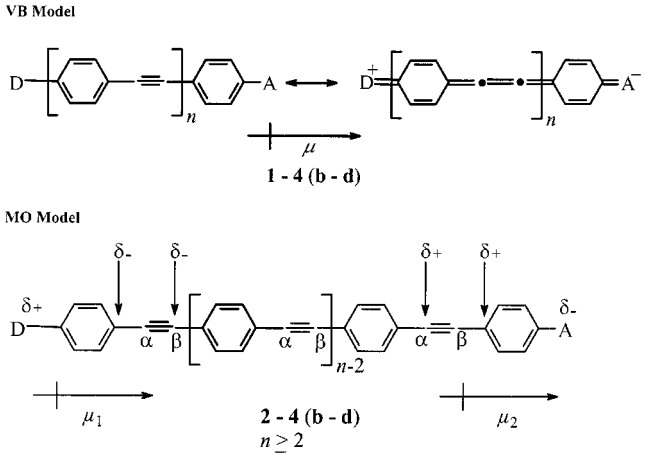


Scheme 3. Synthesis of the donor-substituted series **1a**−**4a** and the donor−acceptor-substituted series **1b**−**4b**, **1c**−**4c**, and **1d**−**4d**: (a) Pd^0, CuI, piperidine, Ar

Our synthetic principle was based on a construction set of compounds (coupled synthesis) and relying, from the very beginning, on the presence of the solubilizing didodecylamino groups.

Push−Pull Effect and Intramolecular Charge Transfer

Conjugated oligomers bearing donor and acceptor groups in their terminal positions are often described by a valence bond model, which consists of resonance between an electroneutral and a zwitterionic structure. Such a model in the OPE series requires quinoid segments connected by cumulene units (Scheme 4): the longer the chain, the higher the energy for the charge separation in the quinoid form. Alternatively, an MO model can be conceived. It contains two dipolar segments, one at each end of the chain. The partial dipole moments μ_i (*i* = 1,2) consist of intrinsic and induced parts and sum to the total dipole moment $\mu(n)$ =



Scheme 4. VB and MO models of the donor−acceptor-substituted OPEs **1**−**4** (**b**−**d**)

$\mu_1(n) + \mu_2(n)$. The intrinsic fraction is due to the polar group at the chain end; the induced fraction is caused by the dipole moment on the opposite chain end and should decrease upon increasing the number of repeat units, *n*.

The ^{13}C NMR spectroscopy of **1**−**4** (**b**−**d**) not only permits a statement to be made about the charge distribution in these compounds, but it should also indicate the degree of participation of the cumulene substructures because the chemical shifts for the acetylene and cumulene carbon atoms differ by more than 100 ppm. Table 1 summarizes selected δ (^{13}C) values of tolane and the series **1**−**3** (**a**−**d**). The solubility of **4a**−**4d** was too low to for us to obtain exact δ (^{13}C) data for these compounds. The correlation of the signals with certain carbon atoms is based on 2D measurements (HMQC and HMBC). Figure 1 shows an example for compound **3b** and the assignment of the six acetylenic carbon atoms by making use of the ^3J (^{13}C,^1H) couplings.

Table 1. Selected ^{13}C NMR spectroscopic data (sp-C) of tolane and OPEs **1**−**3** (**a**−**d**): δ values in $CDCl_3$, TMS as internal standard

Compound	D side			Middle			A side		
	—C_α≡C_β—		Δδ	—C_α≡C_β—		Δδ	—C_α≡C_β—		Δδ
Ph—C≡C—Ph				89.4	89.4	0.0			
1a (A=H)				90.9	87.1	3.8			
2a (A=H)	93.1	87.0	6.1				89.4	90.7	-1.3
3a (A=H)	93.3	87.0	6.3	91.3	89.1	2.2	90.5	91.3	-0.8
1b (A=CN)				96.2	86.2	10.0			
2b (A=CN)	93.8	86.9	6.9				93.8	89.0	4.8
3b (A=CN)	93.4	86.9	6.5	91.9	90.2	1.7	93.4	89.5	3.9
1c (A=CHO)				95.9	86.9	9.0			
2c (A=CHO)	93.7	86.9	6.8				93.5	89.8	3.7
3c (A=CHO)	93.4	86.9	6.5	91.8	90.3	1.5	93.4	90.3	2.9
1d (A=NO_2)				97.6	86.3	11.3			
2d (A=NO_2)	94.0	86.9	7.1				94.8	88.8	6.0
3d (A=NO_2)	93.4	86.9	6.5	92.0	90.2	1.8	94.3	89.3	5.0

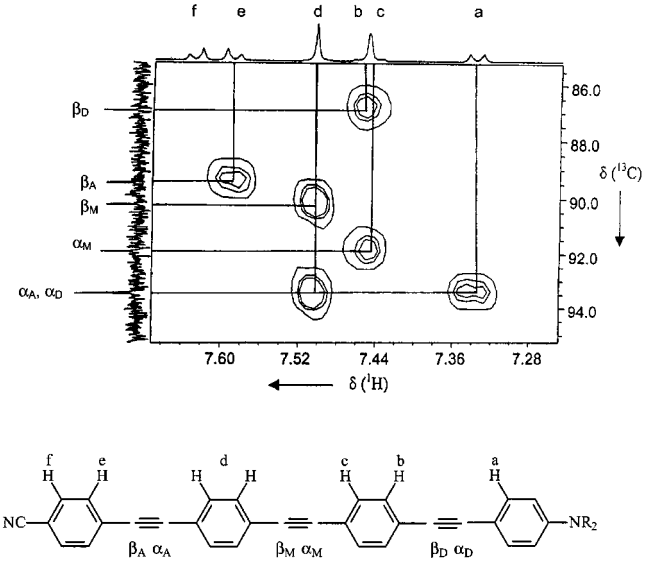


Figure 1. HMBC measurements of **3b** in $CDCl_3$: correlation of the six sp-hybridized C atoms with aromatic protons by making use of ^3J (^1H,^{13}C) couplings. ^1H NMR: (a) low-field portion of the AA′XX′ pattern of the donor-substituted benzene ring; (b,c) narrow AA′BB′ pattern; (d) pseudo-singlet (collapsed AA′BB′); (e,f) AA′BB′ pattern of the acceptor-substituted benzene ring.

All compounds exhibit values of δ (^{13}C-sp) that are between δ = 86.9 and 94.8 ppm, which are close to the chemical shift of tolane (δ = 89.4 ppm). Thus, any discernible contribution of a cumulene structure can be excluded. Moreover, the data in Table 1 reveal the polarization of the C=C bonds, which is expressed by the Δδ values. The polarization of the longer chains (*n* = 2) is particularly high at the chain ends. This result corresponds exactly to the polarization obtained by an AM1 calculation.[10] Figure 2 shows the calculated charge differences on the sp-hybridized C atoms of **1d**−**4d** and the corresponding Δδ values from Table 1.

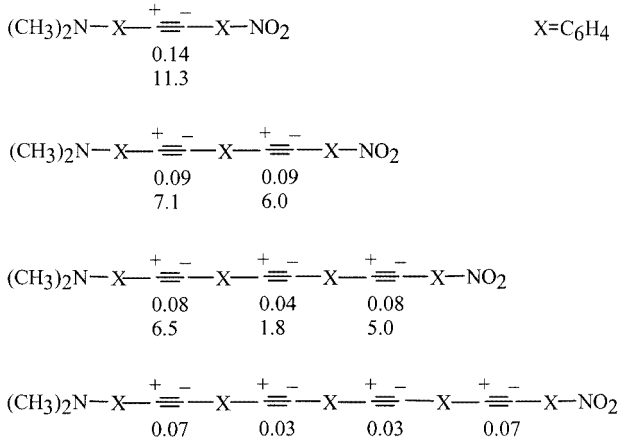


Figure 2. Charge differences (upper values) of the acetylenic carbon atoms calculated for the push−pull oligomers **1d**−**4d**;[10] the positive and negative signs relate to the partial charge in tolane. Below them are the Δδ values measured from the ^{13}C NMR spectrum recorded in $CDCl_3$

Table 2 summarizes the long-wavelength absorption maxima of **1**−**4** (**a**−**d**) in $CHCl_3$. Apart from the inaccuracy of the spectrometer (Δλ = ± 1 nm, which corresponds to a value of $\Delta\tilde{\nu}$ of 60−70 cm^{-1}), the longer chromophores give overlapping bands, which cause the $\lambda_{max.}$ values to have somewhat higher intervals $\Delta\tilde{\nu}$. A separation of two overlapping absorption bands is feasible by an algorithm based on Gauss functions.[11] However, even the bands that are not overlapping for $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ are slightly unsymmetrical. Therefore, we suggest the following modified exponential function for the analysis of these spectra. Figure 3 illustrates the separation of the bands for **2d**.

$$\varepsilon(\tilde{\nu}) = \varepsilon_{max} \bullet e^{-\left[\frac{\tilde{\nu}_{max}\,(\tilde{\nu}-\tilde{\nu}_{max})}{\tilde{\nu} \bullet \Delta\tilde{\nu}}\right]^2} \quad (1)$$

The parameters $\Delta\tilde{\nu}$ for compounds having *m* repeat units were evaluated from the corresponding bands of the shorter compounds in which *n* = *m* − 1.

$$\Delta\tilde{\nu} = 0.5(\tilde{\nu}_2 - \tilde{\nu}_1) \quad (2)$$

whereby

$$\varepsilon(\tilde{\nu}_1) = \varepsilon(\tilde{\nu}_2) = \varepsilon_{max.} \cdot e^{-1} \quad (3)$$

This algorithm has its advantages for slightly unsymmetrical bands with

$$\tilde{\nu}_2 - \tilde{\nu}_{max.} \neq \tilde{\nu}_{max.} - \tilde{\nu}_1 \quad (4)$$

Table 2. UV/Vis absorption of the oligomer series **1**−**4** (**a**−**d**) in $CHCl_3$

Compound	n	$\tilde{\nu}_{max.}$ [$10^3 \cdot cm^{-1}$]	$\lambda_{max.}$ [nm]	ε [$cm^2 \cdot mmol^{-1}$]
1a	1	29.33 ± 0.07	341	25000
2a	2	26.74 ± 0.07	374	44900
3a	3	26.28 ± 0.18	379[a]	57800
4a	4	26.16 ± 0.30	378[a]	77100
1b	1	25.84 ± 0.07	387	38900
2b	2	25.84 ± 0.07	387	45300
3b	3	25.97 ± 0.18	384[a]	56800
4b	4	26.09 ± 0.30	379[a]	86000
1c	1	25.00 ± 0.06	400	26300
2c	2	25.64 ± 0.06	390	37700
3c	3	26.00 ± 0.20	382[a]	56300
4c	4	26.02 ± 0.25	388[a]	78600
1d	1	23.15 ± 0.06	432	23700
2d	2	24.81 ± 0.06	403	30100
3d	3	26.15 ± 0.30	380[a]	57500
4d	4	26.15 ± 0.30	382[a]	81700

[a] Because of the overlap of bands, the measured values of $\lambda_{max.}$ differ somewhat in these cases from the $1/\tilde{\nu}_{max.}$ values of the separated long-wavelength band.

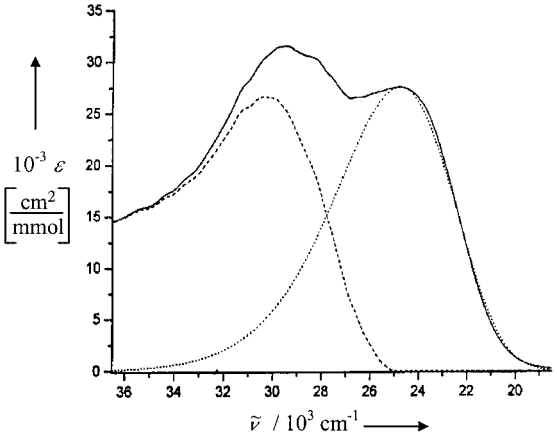


Figure 3. UV/Vis absorption of **2d** in $CHCl_3$ (−) and separation of the long-wavelength band (···) according to Equations (1)−(3)

The merely donor-substituted oligomer series **1a**−**4a** shows a bathochromic shift upon extension of the chromophore. The push−pull series **1c**−**4c** and **1d**−**4d** exhibit distinct hypsochromic effects upon increasing the number of repeat units, *n*, but extending the length of the chromophore in the series **1b**−**4b**, which has the CN group as its relatively weak acceptor, does not have an appreciable influence on the long-wavelength band; the slight increase of $\tilde{\nu}_{max.}$ from $n = 1$ to $n = 4$ is within the limits of error.

Apart from the extension of conjugation, the intramolecular charge transfer (ICT) also must be considered. The transition energy, $E_{DA}(n)$, of the donor−acceptor-substituted oligomers can be split into two terms.[5,8] The first term, $E_D(n)$, refers to the extension of conjugation and takes the substituent effect of the donor group into account. This term, which is derived from the series **1a**−**4a**, causes a pronounced bathochromic effect. The second term, $\Delta E_{DA}(n)$, refers to the effect of the ICT in the three push−pull series **1**−**4** (**b**−**d**); ΔE_{DA} decreases with decreasing ICT (increasing *n*). The convergence limit of all four series is located at 25840 ± 100 cm^{-1}.

$$E_{DA}(n) = E_D(n) - \Delta E_{DA}(n) \quad (5)$$

$$E_{DA}(n) = E_\infty + [E_D(1) - E_\infty]e^{-a(n-1)} - [E_D(1) - E_{DA}(1)]e^{\Delta a(n-1)} \quad (6)$$

Thus, Equations (5) and (6) show that the conjugation effect and the effect of the ICT are opposite to one another. The decrease of the ICT effect with increasing *n* prevails in series **1c**−**4c** and **1d**−**4d**; the result is an overall hypsochromic shift. In the oligomer series **1b**−**4b**, however, both effects annihilate one another. Obviously, it depends on the acceptor strength in **1**−**4** (**b**−**d**) as to which of the two effects predominates. The change of $\tilde{\nu}_{max.}$ from $n = 1$ to $n = 2$ (Table 2) already indicates the dominating influence in all four series. Figure 4 illustrates the two contrary effects. Series having weak donors or weak acceptors, or both, always exhibit bathochromic shifts.[12]

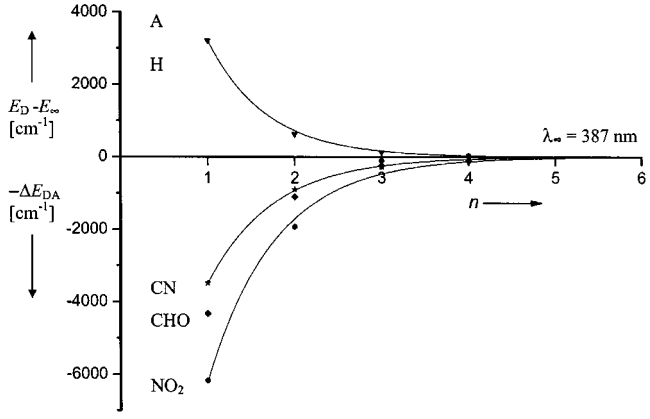


Figure 4. Bathochromic effect [$E_D - E_\infty$] owing to the extension of the conjugation (triangles) and opposite hypsochromic effects ($-\Delta E_{DA}$) caused by the decrease of the ICT upon increasing the number of repeat units, *n*, in the push−pull series **1b**−**4b** (∗), **1c**−**4c** (filled diamond) and **1d**−**4d** (filled circles). The wavenumbers correspond to the absorption maxima $\tilde{\nu}_{max.}$ listed in Table 2.

Müllen and coworkers[13] have studied a series of $(CH_3)_2N-OPE-NO_2$ compounds that were separated by

HPLC; they found a hypsochromic effect from $n = 1$ to $n = 2$, but bathochromic effects from there on ($n = 3$, 4, etc.). It is difficult to compare that series of compounds with our series **1d**−**4d** because of the 2,5-dihexyl substitution of the inner, but not outer, benzene rings in the former series.[13] Even the $\lambda_{max.}$ values for the first two members of the series differ significantly from the values found for **1d** and **2d**.

It is interesting to note that the "competition" between the extension of the chromophores and the decrease of the ICT upon increasing the number of repeat units, n, is also influenced by the π system present between the donor D and acceptor A. Not surprisingly, in pure polyene systems, D−PE−A, a hypsochromic shift has never been established ($n \rightarrow \infty$).[14]

Quantum chemical calculations allow for a rationalization of the obtained effects. We used the AM1 method to optimize the geometries and the INDO/S method to calculate the electron transitions. Figure 5 shows a comparison of the long-wavelength electron transitions of **1d** and **4d**.[10] The $S_0 \rightarrow S_1$ transition of **1d** consists predominantly (67%) of the excitation of an electron from the HOMO to the LUMO. This transition is connected with a strong intramolecular charge transfer (ICT) from the donor side to the acceptor side. Accordingly, the dipole moment of **1d** increases from $\mu(S_0) = 9.6$ D to $\mu(S_1) = 25.4$ D (Table 3). On proceeding to longer chromophores, the participation of the HOMO → LUMO transition for $S_0 \rightarrow S_1$ decreases and approaches zero for $n = 4$. The other fractions, HOMO-1 → LUMO, HOMO → LUMO+1, and HOMO-1 → LUMO+1, however, have either a small ICT or no ICT at all, as demonstrated for **4d** in Figure 5.

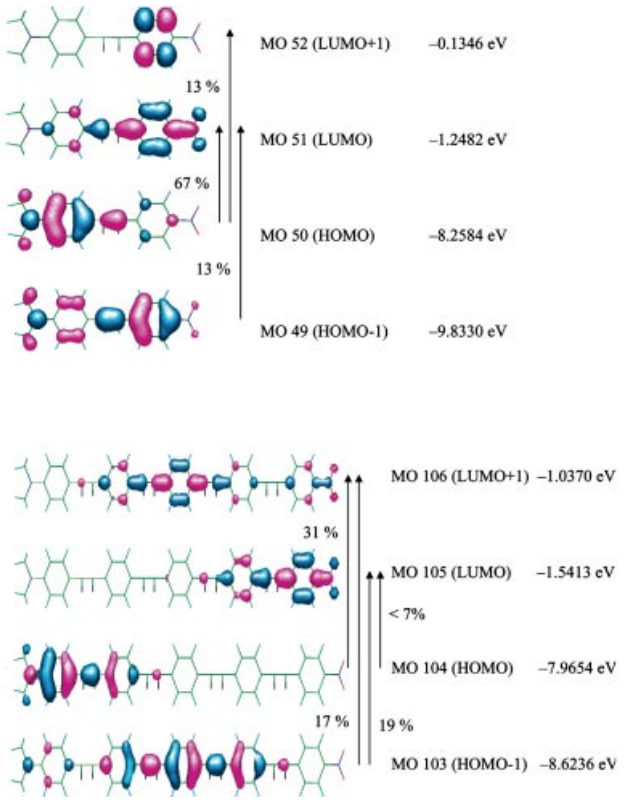


Figure 5. Orbitals that are involved predominantly in the $S_0 \rightarrow S_1$ transition of **1d** (upper part) and **4d** (lower part); calculations were performed by applying the AM1−INDO/S method[10]

Table 3. Dipole moments (in Debye) of **1d**−**4d**,[10] calculated by AM1−INDO/S methods for the ground state, S_0, and the first excited singlet state, S_1

Series	d	n	$\mu(S_0)$	$\mu(S_1)$	$\Delta\mu$
	1	1	9.6	25.4	15.8
	2	2	9.9	25.0	15.1
	3	3	10.0	22.1	12.1
	4	4	10.1	19.4	9.3

The term ΔE_{DA} in the Equations (5) and (6) is responsible for the effect of the ICT on the transition energy E_{DA}; ΔE_{DA} correlates with the HOMO−LUMO participation in $S_0 \rightarrow S_1$. Figure 6 illustrates, for the series **1d**−**4d**, the dependence of the HOMO → LUMO fraction on the number of repeat units, n, and the corresponding decrease of $|\Delta E_{DA}|$. In accordance with the MO model (Scheme 4), the mutual interaction of the acceptor group and the donor group gets smaller with the longer distance between them.

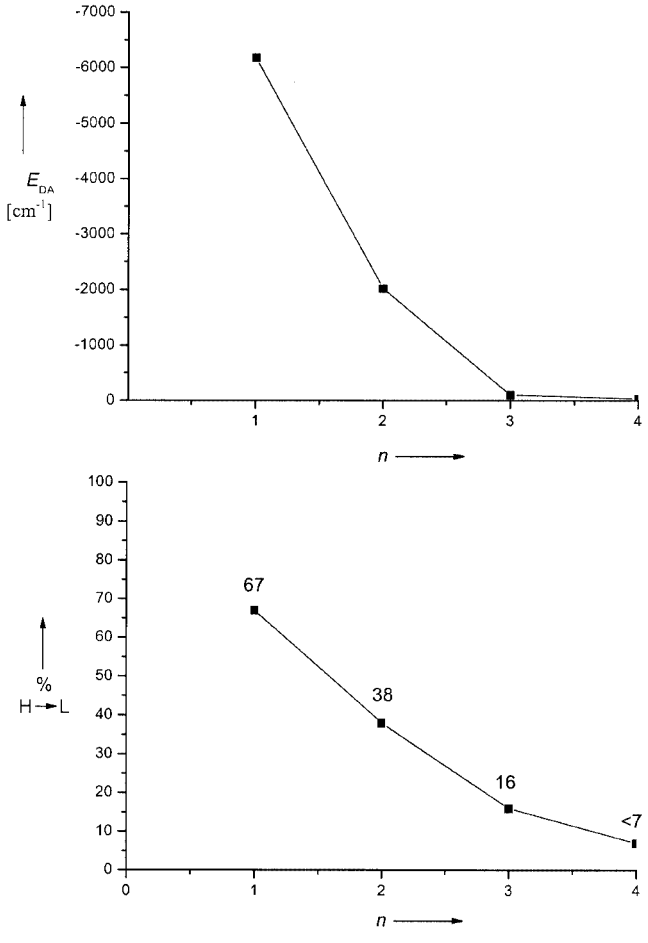


Figure 6. Decrease of the push−pull correction term E_{DA} upon increasing the number of repeat units, n (upper part), and corresponding decrease of the fraction of the HOMO → LUMO transition in $S_0 \rightarrow S_1$ (lower part)

The influence of the acceptor on the electron transition $S_0 \rightarrow S_1$ can be neglected for $n > 3$. The long-wavelength absorptions of **1**−**4** (**b**−**d**) approach the absorption of the purely donor-substituted series **1a**−**4a** (λ_∞ = 387 ± 2 nm).

The decrease of the ICT upon increasing the number of repeat units (i.e., increasing the extension of the chromophores) should also be documented in the dipole moments, μ. Table 3 contains the calculated values of μ of the ground state, S_0, and the first excited singlet state, S_1, of **1d**−**4d**; $\Delta\mu = \mu(S_1) - \mu(S_0)$ is reduced in this series from 15.8 to 9.3 D.

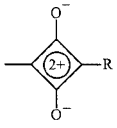
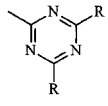
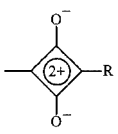
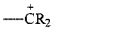
Conclusion

We prepared the donor-substituted oligomers D−OPE (**1a**−**4a**) and the three D−OPE−A series **1**−**4** (**b**−**d**) having n = 1−4 repeat units by applying the Sonogashira−Hagihara reaction and a protection/deprotection strategy. Solubilizing didodecylamino groups served as electron donors (D) and cyano, formyl, and nitro groups as electron acceptors (A). The push−pull systems are best described by an MO model having partial dipole moments at the chains' ends. The polarization of the chain, which is characterized by the polarization of the C−C triple bonds, decreases from both chain ends to the center. The long-wavelength absorption ($S_0 \rightarrow S_1$) shows a bathochromic shift from n = 1 to n = 4 for **1a**−**4a**, virtually no effect for **1b**−**4b** (A = CN), and hypsochromic shifts for **1c**−**4c** (A = CHO) and **1d**−**4d** (A = NO_2). The $\lambda_{max.}$ values of all four series approach to the same limiting value, λ_∞ = 387 ± 2 nm ($n \rightarrow \infty$).

A rationalization of these results is provided by semiempirical quantum mechanics (AM1−INDO/S). Extending the conjugation and decreasing the intramolecular charge transfer (ICT) upon increasing n are opposite effects. The acceptor strength decides which of these effects prevails, but the π electron system between D and A also has a considerable influence. The OPE chain is somewhat more prone to overall hypsochromic effects than the related OPV chain. Table 4 provides a survey of the absorption behavior of OPEs and OPVs having donor−acceptor substitution.

The theory regarding the color of π systems having push−pull substitution, which is more than 80 years old,[18,19] has obtained a new facet. Apart from the donor and acceptor strength, the extension of the π system (OPV, OPE) can be a decisive feature for bathochromic, as well as hypsochromic, effects.[20]

Table 4. Bathochromic or hypsochromic effects on the long-wavelength absorption of conjugated oligomers (OPVs and OPEs) upon increasing the lengths of the chromophores (increasing the number of repeat units, n)

Oligomer series	Effect caused by the acceptor group A: bathochromic	none	hypsochromic	Literature
R_2N—OPV—A	C≡N	CH=O	NO_2	[5,8]
			$CH=C(CN)_2$	[7]
				[6]
R_2N—OPE—A	C≡CH	C≡N	CH=O	this work
			NO_2	this work
			$CH=C(CN)_2$	[15]
RO—OPV—A	CH=O			[16]
				[17]
				[15]
				[16]

Experimental Section

General Remarks: Melting points (uncorrected): Stuart Scientific apparatus SMP/3. NMR: Bruker AMX 400, ARX 400, Avance 600, $CDCl_3$ as solvent unless otherwise stated, TMS as internal standard. MS: Varian MAT CH7A and Finnigan MAT 95. UV−Vis: Zeiss MCS 320/340.

Starting Compounds: *N*,*N*-Didodecyl-4-iodoaniline (**5**) was prepared according to a literature procedure.[21] The yield could be more than doubled by extracting the organic layer three times with the equivalent amount of water instead of filtration of the residue. **5**: Colorless oil, obtained in 79% yield. ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, 6 H, CH_3), 1.25 (m, 36 H, CH_2), 1.53 (m, 4 H, CH_2), 3.20 (t, H, NCH_2), 6.39 (AA′ part of AA′MM′, 2 H, 2-H, 6-H), 7.40 (MM′, 2 H, 3-H, 5-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.1, 27.2, 29.3, 29.5, 31.9 (CH_2, partly superimposed), 51.0 (NCH_2), 75.3 (C-4), 114.0 (C-2, C-6), 137.6 (C-3, C-5), 147.1 (C-1) ppm.

Trimethylsilylethyne (**6**) is commercially available. 1-Iodo-4-trimethylsilylethynylbenzene (**9**) was prepared from 1,4-diodobenzene and **6** according to literature procedures.[22,23]

***N*,*N*-Didodecyl-4-trimethylsilylethynylaniline (7):** Compound **5** (16.5 g, 29.7 mmol) was dissolved under argon in oxygen-free piperidine (150 mL) and then $[Pd(PPh_3)_2Cl_2]$ (0.52 g, 0.74 mmol), CuI (0.28 g, 1.48 mmol), and PPh_3 (0.39 g, 1.48 mmol) were added. Trimethylsilylethyne (4.72 mL, 3.28 g, 33.4 mmol) was then slowly added dropwise to the orange solution. After stirring under argon overnight, the volatile parts were removed under vacuum and the residue was dissolved in $CHCl_3$ (100 mL). The solution was washed with saturated NH_4Cl, $NaHCO_3$, and NaCl solutions, dried (Na_2SO_4), and concentrated. Column chromatography (SiO_2, 4 × 50 cm; petroleum (b.p. 40−70 °C)/toluene, 7:1) yielded a colorless oil (15.5 g, 99%). UV ($CHCl_3$): $\lambda_{max.}$ = 311 nm, ε = 30460 $cm^2 \cdot mmol^{-1}$. ^{1}H NMR ($CDCl_3$): δ = 0.21 (s, 9 H, $SiCH_3$), 0.87 (t, 6 H, CH_3), 1.25 (m, 36 H, CH_2), 1.54 (m, 4 H, CH_2), 3.22 (t, 4 H, NCH_2), 6.48 (AA′ part of AA′MM′, 2 H, 2-H, 6-H), 7.27 (MM′, 2 H, 3-H, 5-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 0.3 ($SiCH_3$), 14.1 (CH_3), 22.7, 27.1, 27.2, 29.3, 29.5, 29.6, 31.9 (CH_2, partly superimposed), 50.9 (NCH_2), 90.7 (*C*≡*C*−Si), 106.8 (*C*≡C−Si), 108.6 (C-4), 111.0 (C-2, C-6), 133.3 (C-3, C-5), 148.0 (C-1) ppm. FD MS: *m*/*z* (%) = 526 (100) [M^+]. $C_{35}H_{63}NSi$ (526.0): calcd. C 79.92, H 12.07, N 2.66; found C 80.09, H 12.30, N 2.70.

***N*,*N*-Didodecyl-4-ethynylaniline (8):** A solution of **7** (4.0 g, 7.6 mmol) in CH_2Cl_2/CH_3OH (1:1, 60 mL) was treated with K_2CO_3

(1.16 g, 8.4 mmol). The mixture was stirred at room temperature until the reaction reached its end (TLC control: SiO_2, toluene). The solvent was evaporated and the residue was dissolved in $CHCl_3$ and extracted three times with an equivalent amount of water. The organic layer was dried (Na_2SO_4), concentrated, and purified by column chromatography (SiO_2, 5 × 15 cm; petroleum (b.p. 40−70 °C)/toluene, 7:1); an oily product was obtained (3.24 g, 94%). UV ($CHCl_3$): $\lambda_{max.}$ = 299 nm, ε = 23094 $cm^2 \cdot mmol^{-1}$. ^1H NMR ($CDCl_3$): δ = 0.86 (t, 6 H, CH_3), 1.25 (m, 36 H, CH_2), 1.54 (m, 4 H, CH_2), 2.94 (s, 1 H, acetylenic H), 3.22 (t, 4 H, NCH_2), 6.50 (AA′ part of AA′MM′, 2 H, 2-H, 6-H), 7.30 (MM′, 2 H, 3-H, 5-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.1, 27.2, 29.3, 29.5, 31.9 (CH_2, partly superimposed), 51.0 (NCH_2), 74.4 (C≡*C*H), 85.1 (C≡CH), 107.4 (C-4), 111.1 (C-2, C-6), 133.4 (C-3, C-5), 148.2 (C-1) ppm. FD MS: *m*/*z* (%) = 454 (100) [M^+]. $C_{32}H_{54}N$ (453.8): calcd. C 84.70, H 12.22, N 3.09; found C 84.73, H 12.47, N 3.12.

***N*,*N*-Didodecyl-4-[4-(trimethylsilylethynyl)phenylethynyl]aniline (10):** Prepared from **8** and **9** according to the procedure described for **7**. An oily product was obtained in 99% yield. UV/Vis ($CHCl_3$): $\lambda_{max.}$ = 372 nm, ε = 40641 $cm^2 \cdot mmol^{-1}$. ^1H NMR ($CDCl_3$): δ = 0.25 (s, 9 H, $SiCH_3$), 0.88 (t, 6 H, CH_3), 1.24 (m, 36 H, CH_2), 1.56 (m, 4 H, CH_2), 3.26 (t, 4 H, NCH_2), 6.55 (AA′ part of AA′MM′, 2 H, 2-H, 6-H), 7.34 (MM′, 2 H, 3-H, 5-H), 7.40 ("s", 4 H, aromat. H) ppm. ^{13}C NMR ($CDCl_3$): δ = −0.03 ($SiCH_3$), 14.1 (CH_3), 22.7, 27.1, 29.4, 29.6, 29.7, 31.9 (CH_2, partly superimposed), 50.9 (NCH_2), 86.9, 93.2, 95.6, 105.0 (C≡C), 108.3 (C-4), 111.2 (C-2, C-6), 121.7, 124.6 (aromat. C_q), 130.9, 131.8 (aromat. CH), 132.9 (C-3, C-5), 148.1 (C-1) ppm. FD MS: *m*/*z* (%) = 626 (100) [M^+]. $C_{43}H_{67}NSi$ (626.1): calcd. C 82.49, H 10.79, N 2.24; found C 82.58, H 10.85, N 2.28.

***N*,*N*-Didodecyl-4-[4-(ethynyl)phenylethynyl]aniline (11):** Prepared according to the procedure described for **7** → **8**. Yellow crystals were obtained in 91% yield, m.p. 50 °C. UV/Vis ($CHCl_3$): $\lambda_{max.}$ = 367 nm, ε = 28125 $cm^2 \cdot mmol^{-1}$. ^1H NMR ($CDCl_3$): δ = 0.88 (t, 6 H, CH_3), 1.24 (m, 36 H, CH_2), 1.56 (m, 4 H, CH_2), 3.13 (s, 1 H, acetylenic H), 3.26 (t, 4 H, NCH_2), 6.55 (AA′ part of AA′MM′, 2 H, 2-H, 6-H), 7.34 (MM′, 2 H, 3-H, 5-H), 7.42 ("s", 4 H, aromat. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.1, 29.4, 29.6, 29.7, 31.9 (CH_2, partly superimposed), 50.9 (NCH_2), 78.3, 83.6, 86.7, 93.2 (C≡C), 108.2 (C-4), 111.1 (C-2, C-6), 120.6, 124.9 (aromat. C_q), 130.9, 131.9 (aromat. CH), 132.9 (C-3, C-5), 148.1 (C-1) ppm. FD MS: *m*/*z* (%) = 554 (100) [M^+]. $C_{40}H_{59}N$ (553.9): calcd. C 86.74, H 10.74, N 2.53; found C 86.63, H 10.87, N 2.50.

***N*,*N*-Didodecyl-4-{4-[4-(trimethylsilylethynyl)phenylethynyl]-phenylethynyl}aniline (12):** Compound **12** was prepared by following the general procedure of the palladium-catalyzed coupling reaction described for **7**. Yellow crystals were obtained in 85% yield, m.p. 97 °C. UV/Vis ($CHCl_3$): $\lambda_{max.}$ = 381 nm, ε = 48660 $cm^2 \cdot mmol^{-1}$. ^1H NMR ($CDCl_3$): δ = 0.24 (s, 9 H, $SiCH_3$), 0.86 (t, 6 H, CH_3), 1.25 (m, 36 H, CH_2), 1.55 (m, 4 H, CH_2), 3.25 (t, 4 H, NCH_2), 6.54 (AA′ part of AA′MM′, 2 H, 2-H, 6-H), 7.34 (MM′, 2 H, 3-H, 5-H), 7.42 ("s", 4 H, aromat. H), 7.44 ("s", 4 H, aromat. H) ppm. ^{13}C NMR ($CDCl_3$): δ = −0.1 ($SiCH_3$), 14.1 (CH_3), 22.7, 27.1, 27.2, 29.4, 29.5, 29.6, 31.9 (CH_2, partly superimposed), 50.9 (NCH_2), 86.9, 90.4, 91.3, 93.3, 96.3, 104.6 (C≡C), 108.2 (C-4), 111.1 (C-2, C-6), 121.5, 122.9, 123.2, 124.5 (aromat. C_q), 131.1, 131.3, 131.4, 131.9 (aromat. CH), 132.9 (C-3, C-5), 148.1 (C-1) ppm. FD MS: *m*/*z* (%) = 726 (100) [M^+]. $C_{51}H_{71}NSi$ (726.2): calcd. C 84.35, H 9.85, N 1.93; found C 84.53, H 9.91, N 1.92.

***N*,*N*-Didodecyl-4-{4-[4-(ethynyl)phenylethynyl]phenylethynyl}aniline (13):** Prepared according to the procedure described for **8.** Yellow crystals were obtained in 91% yield, m.p. 95 °C. UV/Vis ($CHCl_3$): $\lambda_{max.}$ = 380 nm, ε = 46034 $cm^2 \cdot mmol^{-1}$. ^1H NMR ($CDCl_3$): δ = 0.87 (t, 6 H, CH_3), 1.26 (m, 36 H, CH_2), 1.56 (m, 4 H, CH_2), 3.16 (s, 1 H, acetylenic H), 3.25 (t, 4 H, NCH_2), 6.54 (AA′ part of AA′MM′, 2 H, 2-H, 6-H), 7.34 (MM′, 2 H, 3-H, 5-H), 7.44 ("s", 4 H, aromat. H), 7.45 ("s", 4 H, aromat. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.1, 27.2, 29.3, 29.5, 29.6, 31.9 (CH_2, partly superimposed), 50.9 (NCH_2), 78.9, 83.2, 86.9, 90.1, 91.4, 93.3 (C≡C), 108.2 (C-4), 111.1 (C-2, C-6), 121.5, 121.8, 123.7, 124.6 (aromat. C_q), 131.1, 131.41, 131, 44 132.1 (aromat. CH), 132.9 (C-3, C-5), 148.1 (C-1) ppm. FD MS: *m*/*z* (%) = 654 (100) [M^+]. $C_{48}H_{63}N$ (654.0): calcd. C 88.51, H 9.71, N 2.14; found C 88.71, H 9.89, N 2.08.

***N*,*N*-Didodecyl-4-(4-{4-[4-(trimethylsilylethynyl)phenylethynyl]-phenylethynyl}phenylethynyl)aniline (14):** Compound **14** was prepared by following the general procedure of the palladium-catalyzed coupling reaction described for **7**. Yellow crystals were obtained in 59% yield, m.p. 153 °C. UV/Vis ($CHCl_3$): $\lambda_{max.}$ = 377 nm, ε = 78273 $cm^2 \cdot mmol^{-1}$. ^1H NMR ($CDCl_3$): δ = 0.23 (s, 9 H, $SiCH_3$), 0.86 (t, 6 H, CH_3), 1.24 (m, 36 H, CH_2), 1.56 (m, 4 H, CH_2), 3.25 (t, 4 H, NCH_2), 6.54 (AA′ part of AA′MM′, 2 H, 2-H, 6-H), 7.34 (MM′, 2 H, 3-H, 5-H), 7.43 ("s", 4 H, aromat. H), 7.45 ("s", 4 H, aromat. H), 7.48 ("s", 4 H, aromat. H) ppm. ^{13}C NMR ($CDCl_3$): δ = −0.1 ($SiCH_3$), 14.1 (CH_3), 22.7, 27.1, 27.2, 29.4, 29.6, 29.7, 31.9 (CH_2, partly superimposed), 50.9 (NCH_2), 87.0, 90.4, 90.9, 91.0, 91.5, 93.3, 96.4, 104.6 (C≡C), 108.3 (C-4), 111.2 (C-2, C-6), 121.6, 122.8, 123.0, 123.1, 123.3, 124.6 (aromat. C_q), 131.1, 131.4, 131.5, 131.6, 131.9 (aromat. CH, partly superimposed), 132.9 (C-3, C-5), 148.1 (C-1) ppm. FD MS: *m*/*z* (%) = 826 (100) [M^+]. $C_{59}H_{75}NSi$ (826.3): calcd. C 85.76, H 9.15, N 1.70; found C 85.62, H 9.04, N 1.68.

***N*,*N*-Didodecyl-4-(4-{4-[4-(ethynyl)phenylethynyl]phenylethynyl}-phenylethynyl)aniline (15):** Prepared according to the procedure described for **8**. Yellow crystals were obtained in 67% yield, m.p. 172 °C. UV/Vis ($CHCl_3$): $\lambda_{max.}$ = 377 nm, ε = 60879 $cm^2 \cdot mmol^{-1}$. ^1H NMR ($CDCl_3$): δ = 0.86 (t, 6 H, CH_3), 1.24 (m, 36 H, CH_2), 1.56 (m, 4 H, CH_2), 3.16 (s, 1 H, acetylenic H), 3.25 (t, 4 H, NCH_2), 6.54 (AA′ part of AA′MM′, 2 H, 2-H, 6-H), 7.34 (MM′, 2 H, 3-H, 5-H), 7.45 ("s", 4 H, aromat. H), 7.45 ("s", 4 H, aromat. H), 7.48 ("s", 4 H, aromat. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.1, 27.2, 29.4, 29.6, 29.7, 31.9 (CH_2, partly superimposed), 50.9 (NCH_2), 79.0, 83.2, 87.0, 90.4, 90.7, 91.1, 91.5, 93.3 (C≡C), 108.3 (C-4), 111.2 (C-2, C-6), 121.6, 122.1, 122.8, 123.4, 123.5, 124.6 (aromat. C_q), 131.1, 131.4, 131.5, 131.6, 132.1 (aromat. CH, partly superimposed), 133.0 (C-3, C-5), 148.1 (C-1) ppm. FD MS: *m*/*z* (%) = 754 (100) [M^+]. $C_{56}H_{67}N$ (754.2): calcd. C 89.19, H 8.95, N 1.86; found C 89.30, H 8.94, N 1.72.

***N*,*N*-Didodecyl-4-(phenylethynyl)aniline (la):** Compound **1a** was prepared by the general procedure of the palladium-catalyzed coupling reaction described for **7**. The almost-colorless oil was obtained in 95% yield. ^1H NMR ($CDCl_3$): δ = 0.88 (t, 6 H, CH_3), 1.26 (m, 36 H, CH_2), 1.54 (m, 4 H, CH_2), 3.25 (t, 4 H, NCH_2), 6.55 (AA′ part of AA′MM′, 2 H, 2-H, 6-H), 7.28 (m, 3 H, aromat. H), 7.34 (MM′, 2 H, 3-H, 5-H), 7.48 (m, 2 H, aromat. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.1, 27.2, 29.4, 29.5, 29.6, 31.9 (CH_2, partly superimposed), 50.9 (NCH_2), 87.1, 90.9 (C≡C), 108.7 (C-4), 111.2 (C-2, C-6), 124.4, 127.3 (aromat. C_q), 128.2, 131.2 (aromat. CH), 132.9 (C-3, C-5), 147.9 (C-1) ppm. FD MS: *m*/*z* (%) = 530 (100) [M^+]. $C_{38}H_{59}N$ (529.9): calcd. C 86.13, H 11.22, N 2.64; found C 86.02, H 11.10, N 2.57.

***N*,*N*-Didodecyl-4-[4-(phenylethynyl)phenylethynyl]aniline (2a):** Compound **2a** was prepared by following the general procedure of the

palladium-catalyzed coupling reaction described for **7**. Yellow crystals were obtained in 84% yield, m.p. 134 °C. ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, 6 H, CH_3), 1.25 (m, 36 H, CH_2), 1.54 (m, 4 H, CH_2), 3.25 (t, 4 H, NCH_2), 6.55 (AA′ part of AA′MM′, 2 H, 2-H, 6-H), 7.32 (m, 3 H, aromat. CH), 7.34 (MM′, 2 H, 3-H, 5-H), 7.45 (“s”, 4 H, aromat. H), 7.51 (m, 2 H, aromat. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.1, 27.2, 29.3, 29.5, 29.6, 29.7, 31.9 (CH_2, partly superimposed), 50.9 (NCH_2), 87.0, 89.4, 90.7, 93.1 (C≡C), 108.3 (C-4), 111.2 (C-2, C-6), 121.9, 123.2, 124.3, 128.3 (aromat. C_q), 128.3, 131.1, 131.4, 131.6, (aromat. CH), 132.9 (C-3, C-5), 148.1 (C-1) ppm. FD MS: *m*/*z* (%) = 630 (100) [M^+]. $C_{47}H_{62}N_2$ (630.0): calcd. C 87.70, H 10.08, 2.22; found C 87.56, H 9.97, N 2.15.

***N*,*N*-Didodecyl-4-{4-[4-(phenylethynyl)phenylethynyl]phenylethynyl}aniline (3a):** Compound **3a** was prepared by following the general procedure of the palladium-catalyzed coupling reaction described for **7**. Yellow crystals were obtained in 74% yield, m.p. 208 °C. ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, 6 H, CH_3), 1.25 (m, 36 H, CH_2), 1.53 (m, 4 H, CH_2), 3.25 (t, 4 H, NCH_2), 6.55 (AA′ part of AA′MM′, 2 H, 2-H, 6-H), 7.32 (m, 3 H, aromat. H), 7.34 (MM′, 2 H, 3-H, 5-H), 7.45 (“s”, 4 H, aromat. H), 7.48(“s”, 4 H, aromat. H), 7.51 (m, 2 H, aromat. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.1, 27.2, 29.3, 29.5, 29.6, 29.6, 31.9 (CH_2, partly superimposed), 50.9 (NCH_2), 87.0, 89.1, 90.5, 91.3, 91.3, 93.3 (C≡C), 108.3 (C-4), 111.2 (C-2, C-6), 121.6, 123.0, 123.1, 124.5, 128.4, (aromat. C_q), 128.4, 131.1, 131.4, 131.5, 131.5, 131.6, (aromat. CH), 132.9 (C-3, C-5), 148.1 (C-1) ppm. FD MS: *m*/*z* (%) = 730 (100) [M^+]. $C_{54}H_{67}N$ (730.13): calcd. C 88.83, H 9.25, N 1.92; found C 88.98, H 9.15, N 1.89.

***N*,*N*-Didodecyl-4-(4-{4-[4-(phenylethynyl)phenylethynyl]phenylethynyl}phenylethynyl)aniline (4a):** Compound **4a** was prepared by following the general procedure of the palladium-catalyzed coupling reaction described for **7**. Yellow crystals were obtained in 59% yield, m.p. > 250 °C. ^{1}H NMR ($C_2Cl_4D_2$, 400 MHz, 333 K): δ = 0.84 (t, 6 H, CH_3), 1.26 (m, 36 H, CH_2), 1.56 (m, 4 H, CH_2), 3.23 (t, 4 H, NCH_2), 6.55 (AA′ part of AA′MM′, 2 H, 2-H, 6-H), 7.30 (m, 3 H, aromat. H), 7.35 (MM′, 2 H, 3-H, 5-H), 7.44 (“s”, 4 H, aromat. H), 7.48 (“s”, 4 H, aromat. H), 7.50 (“s”, 4 H, aromat. H), 7.52 (m, 2 H, aromat. H) ppm. FD MS: *m*/*z* (%) = 830 (100) [M^+]. $C_{63}H_{70}N_2$ (830.3): calcd. C 89.69, H 8.62, N 1.69; found C 89.78, H 8.47, N 1.55.

4-[4-(Didodecylamino)phenylethynyl]benzonitrile (1b): Compound **1b** was prepared by following the general procedure of the palladium-catalyzed coupling reaction described for **7**. The almost-colorless oily product was obtained in 98% yield. ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, 6 H, CH_3), 1.24 (m, 36 H, CH_2), 1.55 (m, 4 H, CH_2), 3.26 (t, 4 H, NCH_2), 6.55 (AA′ part of AA′MM′, 2 H, aromat. H), 7.34 (MM′, 2 H, aromat. H), 7.52/7.55 (AA′BB′, 4 H, 2-H, 3-H, 5-H, 6-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.1, 27.2, 29.4, 29.5, 29.6, 31.9 (CH_2, partly superimposed), 50.9 (NCH_2), 86.2, 96.2 (C≡C), 107.4, 110.2, 129.5, 148.5 (aromat. C_q), 111.2, 131.5, 131.9, 133.2 (aromat. CH), 118.9 (CN) ppm. FD MS: *m*/*z* (%) = 555 (100) [M^+]. $C_{39}H_{58}N_2$ (554.5): calcd. C 84.48, H 10.54, N 5.05; found C 84.28, H 10.23, N 5.01.

4-{4-[4-(Didodecylamino)phenylethynyl]phenylethynyl}benzonitrile (2b): Compound **2b** was prepared by following the general procedure of the palladium-catalyzed coupling reaction described for **7**. Yellow crystals were obtained in 85% yield, m.p. 134 °C. ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, 6 H, CH_3), 1.24 (m, 36 H, CH_2), 1.56 (m, 4 H, CH_2), 3.25 (t, 4 H, NCH_2), 6.55 (AA′ part of AA′MM′, 2 H, aromat. H), 7.34 (MM′, 2 H, aromat. H), 7.46 (“s”, 4 H, aromat. H), 7.52 (AA′ part of AA′MM′, 2 H, 3-H, 5-H), 7.61 (MM′, 2 H, 2-H, 6-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.1, 27.2, 29.4, 29.5, 29.7, 31.9 (CH_2, partly superimposed), 50.9 (NCH_2), 86.9, 89.0, 93.8, 93.8 (C≡C), 108.0, 111.4, 120.6, 125.3, 128.2, 148.1 (aromat. C_q), 111.1, 131.1, 131.6, 132.0, 132.1, 133.1 (aromat. CH), 118.5 (CN) ppm. FD MS: *m*/*z* (%) = 655 (100) [M^+]. $C_{47}H_{62}N_2$ (655.0): calcd. C 86.18, 9.54, 4.28; found C 86.27, H 9.57, N 4.25.

4-(4-{4-[4-(Didodecylamino)phenylethynyl]phenylethynyl}phenylethynyl)benzonitrile (3b): Compound **3b** was prepared by following the general procedure of the palladium-catalyzed coupling reaction described for **7**. Yellow crystals were obtained in 84% yield, m.p. 208 °C. ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, 6 H, CH_3), 1.24 (m, 36 H, CH_2), 1.56 (m, 4 H, CH_2), 3.25 (t, 4 H, NCH_2), 6.54 (AA′ part of AA′MM′, 2 H, aromat. H), 7.34 (MM′, 2 H, aromat. H), 7.45 (“s”, 4 H, aromat. H), 7.50 (“s”, 4 H, aromat. H), 7.60 (AA′ part of AA′ BB′, 2 H, 3-H, 5-H), 7.70 (BB′, 2 H, 2-H, 6-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.1, 27.2, 29.4, 29.6, 29.7, 31.9 (CH_2, partly superimposed), 50.9 (NCH_2), 86.9, 89.5, 90.2, 91.9, 93.4, 93.4 (C≡C), 108.2, 111.7, 121.4, 121.9, 124.1, 124.7, 128.0, 148.1 (aromat. C_q), 111.2, 131.1, 131.5, 131.6, 131.7, 132.1, 132.1, 132.9 (aromat. CH), 118.5 (CN) ppm. FD MS: *m*/*z* (%) = 755 (100) [M^+]. $C_{55}H_{66}N_2$ (755.1): calcd. C 87.48, H 8.81, N 3.71; found C 87.49, H 9.11, N 3.69.

4-[4-(4-{4-[4-(Didodecylamino)phenylethynyl]phenylethynyl}phenylethynyl)phenylethynyl]benzonitrile (4b): Compound **4b** was prepared by following the general procedure of the palladium-catalyzed coupling reaction described for **7**. Yellow crystals were obtained in 53% yield, m.p. > 250 °C. ^{1}H NMR ($C_2D_2Cl_4$, 333 K): δ = 0.85 (t, 6 H, CH_3), 1.26 (m, 36 H, CH_2), 1.55 (m, 4 H, CH_2), 3.24 (t, 4 H, NCH_2), 6.54 (AA′ part of AA′MM′, 2 H, aromat. H), 7.31 (MM′, 2 H, aromat. H), 7.42 (“s”, 4 H, aromat. H), 7.48 (“s”, 4 H, aromat. H), 7.50 (“s”, 4 H, aromat. H), 7.58 (AA′BB′, 4 H, 2-H, 3-H, 5-H, 6-H) ppm. The ^{13}C NMR spectrum could not be obtained because of poor solubility. FD MS: *m*/*z* (%) = 855 (100) [M^+]. $C_{63}H_{70}N_2$ (855.3): calcd. C 88.47, H 8.25, N 3.28; found C 88.28, H 8.97, N 2.90.

4-[4-(Didodecylamino)phenylethynyl]benzaldehyde (1c): Compound **1c** was prepared by following the general procedure of the palladium-catalyzed coupling reaction described for **7**. Yellow crystals were obtained in 82% yield, m.p. 41 °C. ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, 6 H, CH_3), 1.25 (m, 36 H, CH_2), 1.53 (m, 4 H, CH_2), 3.26 (t, 4 H, NCH_2), 6.55 (AA′ part of AA′MM′, 2 H, aromat. H), 7.36 (MM′, 2 H, aromat. H), 7.58 (AA′ part of AA′MM′, 2 H, 3-H, 5-H), 7.81 (MM′, 2 H, 2-H, 6-H), 9.97 (s, 1 H, CHO) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.1, 27.2, 29.3, 29.5, 29.6, 29.7, 31.9 (CH_2, partly superimposed), 50.9 (NCH_2), 86.9, 95.9 (C≡C), 107.6, 130.9, 134.5, 148.4 (aromat. C_q), 111.1, 129.5, 131.5, 133.2 (aromat. CH), 191.5 (CHO) ppm. FD MS: *m*/*z* (%) = 558 (100) [M^+]. $C_{39}H_{59}NO$ (557.90): calcd. C 83.96, H 10.66, N 2.51; found C 83.76, H 10.81, N 2.41.

4-{4-[4-(Didodecylamino)phenylethynyl]phenylethynyl}benzaldehyde (2c): Compound **2c** was prepared by following the general procedure of the palladium-catalyzed coupling reaction described for **7**. Yellow crystals were obtained in 73% yield, m.p. 134 °C. ^{1}H NMR ($CDCl_3$): δ = 0.87 (t, 6 H, CH_3), 1.27 (m, 36 H, CH_2), 1.53 (m, 4 H, CH_2), 3.26 (t, 4 H, NCH_2), 6.55 (AA′ part of AA′MM′, 2 H, aromat. H), 7.34 (MM′, 2 H, aromat. H), 7.47 (“s”, 4 H, aromat. H), 7.65 (AA′ part of AA′MM′, 2 H, 3-H, 5-H), 7.85 (MM′, 2 H, 2-H, 6-H), 10.00 (s, 1 H, CHO) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.1, 27.2, 29.3, 29.5, 29.6, 31.9

(CH_2, partly superimposed), 50.9 (NCH_2), 86.9, 89.8, 93.5, 93.7 (C≡C), 108.1, 120.9, 125.1, 129.5, 135.4, 148.1 (aromat. C_q), 111.1, 129.6, 131.1, 131.6, 132.1, 132.9 (aromat. CH), 191.4 (CHO) ppm. FD MS: *m/z* (%) = 658 (100) [M^+]. $C_{47}H_{63}NO$ (658.0): calcd. C 85.79, 9.65, 2.13; found C 85.68, H 9.63, N 2.04.

4-(4-{4-[4-(Didodecylamino)phenylethynyl]phenylethynyl}phenylethynyl)benzaldehyde (3c): Compound **3c** was prepared by following the general procedure of the palladium-catalyzed coupling reaction described for **7**. Yellow crystals were obtained in 59% yield, m.p. 208 °C. ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, 6 H, CH_3), 1.27 (m, 36 H, CH_2), 1.53 (m, 4 H, CH_2), 3.25 (t, 4 H, NCH_2), 6.55 (AA′ part of AA′MM′, 2 H, aromat. H), 7.34 (MM′, 2 H, aromat. H), 7.45 ("s", 4 H, aromat. H), 7.51 ("s", 4 H, aromat. H), 7.66 (AA′ part of AA′MM′, 2 H, 3-H, 5-H), 7.86 (MM′, 2 H, 2-H, 6-H), 10.00 (s, 1 H, CHO) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.1, 27.2, 29.3, 29.5, 29.6, 29.7, 31.9 (CH_2, partly superimposed), 50.9 (NCH_2), 86.9, 90.3, 91.8, 93.1, 93.4, 93.4 (C≡C), 108.2, 121.4, 122.2, 123.8, 124.7, 129.3, 135.5, 148.1 (aromat. C_q), 111.1, 129.6, 131.1, 131.4, 131.6, 131.7, 132.1, 132.9 (aromat. CH), 191.3 (CHO) ppm. FD MS: *m/z* (%) = 758 (100) [M^+]. $C_{55}H_{67}NO$ (758.1): calcd. C 87.13, H 8.91, N 1.85; found C 86.97, H 8.79, N 1.79.

4-[4-(4-{4-[4-(Didodecylamino)phenylethynyl]phenylethynyl}phenylethynyl)phenylethynyl]benzaldehyde (4c): Compound **4c** was prepared by following the general procedure of the palladium-catalyzed coupling reaction described for **7**. Yellow crystals were obtained in 39% yield, m.p. > 250 °C. ^{1}H NMR ($C_2D_2Cl_4$, 333 K): δ = 0.84 (t, 6 H, CH_3), 1.26 (m, 36 H, CH_2), 1.56 (m, 4 H, CH_2), 3.24 (t, 4 H, NCH_2), 6.53 (AA′ part of AA′MM′, 2 H, aromat. H), 7.34 (MM′, 2 H, aromat. H), 7.41 ("s", 4 H, aromat. H), 7.47 ("s", 4 H, aromat. H), 7.52 ("s", 4 H, aromat. H), 7.67 (AA′ part of AA′MM′, 2 H, C-3, C-5), 7.85 (MM′, 2 H, C-2, C-6), 10.00 (s, 1 H, CHO) ppm. The ^{13}C NMR spectrum could not be obtained because of poor solubility. FD MS: *m/z* (%) = 858 (100) [M^+]. $C_{63}H_{71}NO$ (858.3): calcd. C 88.17, H 8.34, N 1.63; found C 87.97, H 8.20, N 1.51.

***N,N*-Didodecyl-4-(4-nitrophenylethynyl)aniline (1d):** Compound **1d** was prepared by following the general procedure of the palladium-catalyzed coupling reaction described for **7**. Red crystals were obtained in 90% yield, m.p. 41 °C. ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, 6 H, CH_3), 1.25 (m, 36 H, CH_2), 1.56 (m, 4 H, CH_2), 3.26 (t, 4 H, NCH_2), 6.56 (AA′ part of AA′MM′, 2 H, 2-H, 6-H), 7.36 (MM′, 2 H, 3-H, 5-H), 7.56 (AA′ part of AA′MM′, 2 H, aromat. H), 8.15 (MM′, 2 H, aromat. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.1, 27.2, 29.3, 29.5, 29.6, 29.7, 31.9 (CH_2, partly superimposed), 50.9 (NCH_2), 86.3, 97.6 (C≡C), 107.2 (C-4), 111.2 (C-2, C-6), 123.6, 133.4 (aromat. CH), 131.5 (C-3, C-5), 131.6, 146.1 (aromat. C_q), 148.7 (C-1) ppm. FD MS: *m/z* (%) = 575 (100) [M^+]. $C_{38}H_{58}N_2O_2$ (574.9): calcd. C 79.39, H 10.17, N 4.87; found C 79.06, H 10.34, N 4.83.

***N,N*-Didodecyl-4-[4-(4-nitrophenylethynyl)phenylethynyl]aniline (2d):** Compound **2d** was prepared by following the general procedure of the palladium-catalyzed coupling reaction described for **7**. Orange crystals were obtained in 93% yield, m.p. 111 °C. ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, 6 H, CH_3), 1.24 (m, 36 H, CH_2), 1.56 (m, 4 H, CH_2), 3.25 (t, 4 H, NCH_2), 6.55 (AA′ part of AA′MM′, 2 H, 2-H, 6-H), 7.34 (MM′, 2 H, 3-H, 5-H), 7.47 ("s", 4 H, aromat. H), 7.64 (AA′ part of AA′MM′, 2 H, aromat. H), 8.21 (MM′, 2 H, aromat. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.1, 27.2, 29.4, 29.6, 29.7, 31.9 (CH_2, partly superimposed), 50.9 (NCH_2), 86.9, 88.8, 94.0, 94.8 (C≡C), 108.1 (C-4), 111.2 (C-2, C-6), 120.6, 125.5, 130.2, 146.9 (aromat. C_q), 123.6, 131.2, 131.7, 132.2 (aromat. CH), 133.0 (C-3, C-5), 148.2 (C-1) ppm. FD MS: *m/z* (%) = 675 (100) [M^+]. $C_{46}H_{62}N_2O_2$ (675.0): calcd. C 81.85, H 9.26, N 4.15; found C 81.80, H 9.53, N 4.12.

***N,N*-Didodecyl-4-{4-[4-(4-nitrophenylethynyl)phenylethynyl]phenylethynyl}aniline (3d):** Compound **3d** was prepared by following the general procedure of the palladium-catalyzed coupling reaction described for **7**. Orange crystals were obtained in 93% yield, m.p. 226 °C. ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, 6 H, CH_3), 1.24 (m, 36 H, CH_2), 1.56 (m, 4 H, CH_2), 3.25 (t, 4 H, NCH_2), 6.54 (AA′ part of AA′MM′, 2 H, 2-H, 6-H), 7.33 (MM′, 2 H, 3-H, 5-H), 7.45 ("s", 4 H, aromat. H), 7.52 ("s", 4 H, aromat. H), 7.65 (AA′ part of AA′MM′, 2 H, aromat. H), 8.21 (MM′, 2 H, aromat. H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 27.1, 27.2, 29.4, 29.6, 29.7, 31.9 (CH_2, partly superimposed), 50.9 (NCH_2), 86.9, 89.3, 90.2, 92.0, 93.4, 94.3 (C≡C), 108.2 (C-4), 111.2 (C-2, C-6), 121.4, 121.8, 124.2, 124.8, 130.0, 147.1 (aromat. C_q), 123.7, 131.1, 131.5, 131.6, 131.8, 132.3 (aromat. CH), 132.9 (C-3, C-5), 148.1 (C-1) ppm. FD MS: *m/z* (%) = 775 (100) [M^+]. $C_{54}H_{66}N_2O_2$ (775.1): calcd. C 83.68, H 8.58, N 3.61; found C 83.69, H 8.54, N 3.45.

***N,N*-Didodecyl-4-(4-{4-[4-(4-nitrophenylethynyl)phenylethynyl]-phenylethynyl}phenylethynyl)aniline (4d):** Compound **4d** was prepared by following the general procedure of the palladium-catalyzed coupling reaction described for **7**. Yellow crystals were obtained in 59% yield, m.p. > 250 °C. ^{1}H NMR ($C_2Cl_4D_2$, 333 K): δ = 0.84 (t, 6 H, CH_3), 1.26 (m, 36 H, CH_2), 1.55 (m, 4 H, CH_2), 3.23 (t, 4 H, NCH_2), 6.53 (AA′ part of AA′MM′, 2 H, 2-H, 6-H), 7.30 (MM′, 2 H, 3-H, 5-H), 7.42 ("s", 4 H, aromat. H), 7.48 ("s", 4 H, aromat. H), 7.50 ("s", 4 H, aromat. H), 7.63 (AA′ part of AA′MM′, 2 H, aromat. H), 8.15 (MM′, 2 H, aromat. H) ppm. The ^{13}C NMR spectrum could not be obtained because of poor solubility. FD MS: *m/z* (%) = 875 (100) [M^+]. $C_{62}H_{70}N_2O_2$ (875.3): After careful drying under vacuum, the compound still contained some water; therefore, we could not obtain a correct elemental analysis.

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