

(*E,E,E*)-4,4'-Distyrylstilbenes – Synthesis, Photophysics, Photochemistry and Phase Behavior

Herbert Meier,^{*,[a]} Thorsten Lifka,^[a] Ulf Stalmach,^[a] Annette Oehlhof,^[a] and Sabine Prehl^[a]**Keywords:** Condensation reaction / Fluorescence quantum yields / Liquid crystals / Oligo(phenylenevinylene)s / Photo-reaction

The fluorescence quantum yields $\phi_F(n)$ of oligo[2,5-bis(prop-yloxy)-1,4-phenylenevinylene]s (**1b**) reach for the trimer ($n = 3$) in solution a maximum of 86 %, which is almost twice as high as for the monomer ($n = 1$) and the octamer or undecamer ($n = 8, 11$). The latter represent the convergence limit of 46 %. 4-Mono-, 3,4-di- or 3,4,5-trisubstituted terminal phenyl rings in the trimers **6a–f** do not lead to calamitic or phasmodic liquid crystals; however, 2,3,4-trisubstitution with

hexyloxy groups (**6h**) and even with OCH₃ groups (**6g**) effects LC formation. Irradiation with energy-rich UV light provokes a crosslinking of the originally conjugated chains. In the case of **6c**, a chemo- and stereoselective $[2\pi + 2\pi]$ photocycloaddition could be established as well.

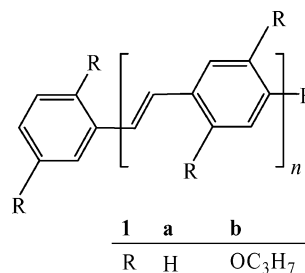
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Introduction

Due to their interesting electrical, optical and optoelectronic properties, oligo- and poly(1,4-phenylenevinylene)s [OPV and PPV] are a highly attractive class of compounds in organic chemistry and materials science.^[1] Already with $n > 3$, the parent system **1a** is insoluble in organic solvents, so solubilizing alkyl or better alkoxy side chains have to be introduced. Some time ago we prepared the series **1b** ($n = 1–8, 11, 15$) with 2,5-dipropoxy-substituted phenyl rings (Scheme 1).^[2–4] Increasing numbers n of repeating units in conjugated oligomers lead for various properties P to limiting values which can be matched by the corresponding polymer. This approach can be monotonous, as for the $\lambda_{\max}$ values of absorption and fluorescence of **1b**,^[2–4] but the approach $P(n) \rightarrow P_\infty$ can also pass for a certain number n' through a maximum and/or a minimum.^[11]

An important example is given for the electroluminescence efficiency of **1b** which reaches a maximum for $n = 3$.^[5]

Earlier studies indicated that the photoluminescence quantum yields ϕ_F should also have a maximum for a certain repeat number n of **1b** since $\phi_F = 0.82$ for the dimer $n = 2$ measured in CH₂Cl₂ is much higher than ϕ_F of a long oligomer chain ($\phi_F \approx 0.5$ for $n = 11$).^[6,7] We determined now the fluorescence quantum yields $\phi_F(n)$ for the whole series **1b** ($n = 1–8, 11$) and tried to obtain liquid crystals (LC) for those oligomers that have the highest ϕ_F value.



Scheme 1. Oligo(1,4-phenylenevinylene)s.

Results and Discussion

Fluorescence Quantum Yields of the OPV Series 1b

Measurements of the fluorescence quantum yields of **1b** ($n = 1–8, 11$) in CH₂Cl₂ gave the results shown in Figure 1. (*E*)-2,2',5,5'-Tetrakis(propyloxy)stilbene, the monomer with $n = 1$, has a ϕ_F value of 45 %. Increasing length of the conjugated OPV chain leads to an increase of ϕ_F via 82 ($n = 2$) to a maximum of 86 % for the trimer ($n = 3$). Further extension of the chain results in a strong decrease of ϕ_F and finally to an approach to 46 %. The flat minimum for $n = 6$ ($\phi_F = 43 %$) may be an artefact due to the margins of error of $\pm 5 %$. However, the signal intensity of the electroluminescence of the series **1b** measured at a current density of 1.0 mA cm⁻² has also a flat minimum before it approaches to a limiting value.^[5]

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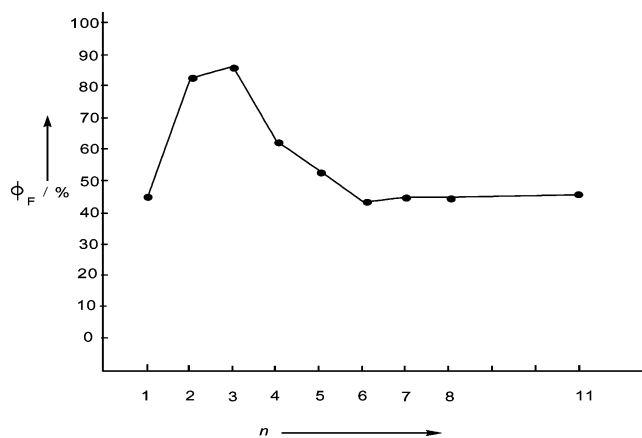


Figure 1. Fluorescence quantum yields of **1b** ($n = 1-8, 11$) measured in CH_2Cl_2 at room temperature.

The wavelengths of the absorption maxima λ_{max} were used as excitation wavelengths λ_{exc} and 1,4-distyrylstilbene^[6] served as standard 1. Table 1 contains the corresponding $\phi_{\text{F}}(n)$ values of the series **1b**. Comparable values were obtained by applying quinine sulfate/ H_2SO_4 as standard 2.

Table 1. Fluorescence quantum yields of the OPVs **1b**.

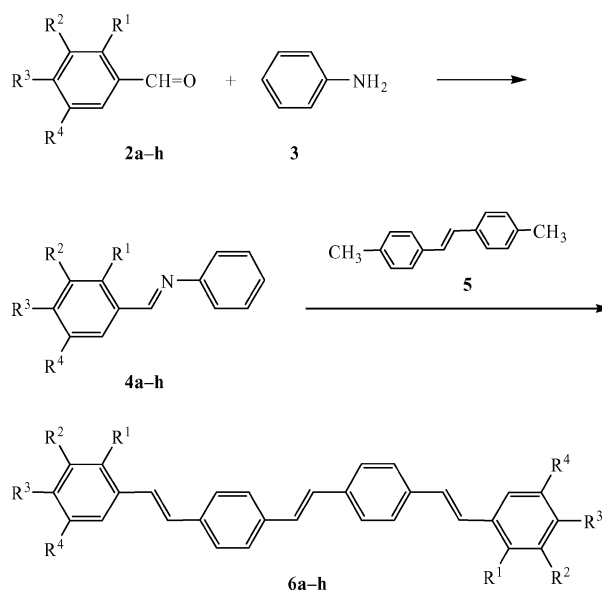
1b n	Absorption λ_{max} [nm]	Emission λ_{max} [nm]	Fluorescence quantum yields ϕ_{F} (%) Standard 1	ϕ_{F} (%) Standard 2
1	358	413	45	45
2	404	460	82	79
3	435	496	86	81
4	454	521	62	57
5	460	534	53	[a]
6	470	543	43	40
7	475	547	45	40
8	478	550	45	[a]
11	481	552	46	41

[a] Not measured.

We interpret the behavior of $\phi_{\text{F}}(n)$ in Figure 1 in terms of two opposite effects. Increasing length of the relatively rigid OPV chain leads first up to $n = 3$ to increasing ϕ_{F} values. Radiationless deactivation becomes then more and more efficient – not only due to the strongly increasing number of vibration modes but predominantly by the increasing tendency of photodissociation to polarons, whose stability (average lifetime) increases with increasing numbers n of repeat units.^[8,9] The saturation value obtained here corresponds fairly well to the value $\phi_{\text{F}} = 35 \pm 5\%$, which was found for poly[5-(2-ethylhexyloxy)-2-methoxy-1,4-phenylenevinylene].^[10] The ϕ_{F} value of polymers as this PPV chain certainly depends on the number of defects, the OPVs studied here are free of defects.^[11] Aggregates of OPVs have much lower ϕ_{F} values. The energy transfer to fluorescence traps leads to ϕ_{F} values of OPVs of about one tenth of the values in solution.^[6] Therefore it is even more interesting to apply compounds with high “molecular” ϕ_{F} values. Consequently we tried to obtain LC systems of 4,4'-distyrylstilbenes, analogues of the trimer **1b** ($n = 3$).

Synthesis of Terminally Substituted (E,E,E)-4,4'-Distyrylstilbenes

The preparation of the 4,4'-distyrylstilbenes **6a-h** was started with the corresponding aldehydes **2a-h** (Scheme 2). Their condensation reaction with aniline (**3**) afforded the azomethines (Schiff bases) **4a-h**. Almost quantitative yields could be obtained, when the process **2** + **3** was performed without solvent at low pressure, so that the generated water was continuously distilled off. The azomethines **4a-h** were then subjected to a Siegrist reaction^[12,13] with (E)-4,4'-dimethylstilbene (**5**). Compared to other condensation reactions, as for example Knoevenagel, Wittig or Wittig–Horner reactions, the yields of Siegrist reactions are often lower, but the major advantage of the Siegrist reaction is given by the extremely high *trans* selectivity of the aniline elimination – provided that the reaction conditions guarantee kinetic control.^[14] Thus, the target compounds **6a-h** were obtained as pure (E,E,E)-isomers^[15] in yields between 51 and 71%, except for the *ortho*-substituted compounds **6g** and **6h**. Their low yields of 23 and 18%, respectively, were attributed to the steric shielding of the electrophilic carbon atom of the imino group in **4g,h**.



6	R ¹	R ²	R ³	R ⁴	% Yield
a	H	H	OC ₁₂ H ₂₅	H	60
b	H	OC ₁₂ H ₂₅	OC ₁₂ H ₂₅	H	66
c	H	OCH ₃	OCH ₃	OCH ₃	71
d	H	OCH ₃	OC ₁₂ H ₂₅	OCH ₃	55
e	H	OC ₆ H ₁₃	OC ₆ H ₁₃	OC ₆ H ₁₃	51
f	H	OC ₁₂ H ₂₅	OC ₁₂ H ₂₅	OC ₁₂ H ₂₅	65
g	OCH ₃	OCH ₃	OCH ₃	H	23
h	OC ₆ H ₁₃	OC ₆ H ₁₃	OC ₆ H ₁₃	H	18

Scheme 2. Preparation of the distyrylstilbenes **6a-h**.

The compounds **6a–h** were carefully characterized by one- and two-dimensional NMR spectroscopy. Figure 2 shows as an example the ^1H and ^{13}C chemical shifts of the conjugated chain of **6f**. The molecule exists at room temperature in solution – as usual for such OPV trimers^[1m] – in a fast equilibrium between two C_{2v} and two C_s conformations with a de facto C_{2v} symmetry, so that it is sufficient to depict here the half molecule. The electron releasing dodecyloxy groups induce small polarizations of the terminal olefinic double bonds [$\Delta\delta(^{13}\text{C}) = 1.7$ ppm, $\Delta\delta(^1\text{H}) = 0.08$ ppm, $^3J(^1\text{H}, ^1\text{H}) = 16.3$ Hz].^[16] The effect is much lower than for related push-pull systems.^[11]

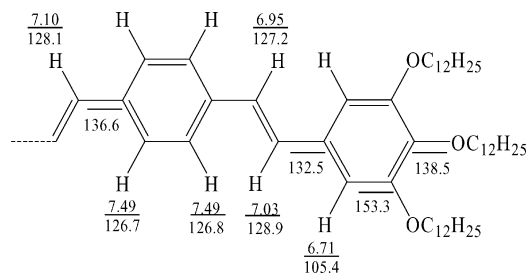


Figure 2. ^1H and ^{13}C NMR spectroscopic data of **6f** (solvent CDCl_3 , TMS internal standard). Dodecyloxy chains: ^1H NMR: 0.88 (t, 18 H, CH_3), 1.20–1.38 (m, 96 H, CH_2), 1.50 (m, 12 H, $\gamma\text{-CH}_2$), 1.75 (m, 4 H, $\beta\text{-CH}_2$), 1.83 (m, 8 H, $\beta\text{-CH}_2$), 3.95 (t, 4 H, $\alpha\text{-CH}_2$), 4.02 (t, 8 H, $\alpha\text{-CH}_2$). ^{13}C NMR: 14.1 (CH_3), 22.7, 26.1, 29.4, 29.4, 29.5, 29.6, 29.7, 29.7, 30.4, 31.9 (CH_2 , partly superimposed), 69.3 ($m\text{-OCH}_2$), 73.6 ($p\text{-OCH}_2$).

Phase Behavior of the (E,E,E)-4,4'-Distyrylstilbenes **6a–h**

All compounds **6a–h** form yellow crystals. One or two alkoxy chains, even dodecyloxy chains (**6a,b**) are not sufficient to obtain meltable compounds; **6a** and **6b** decompose on heating to temperatures above 330 °C. The phasemic systems **6c–f** with six alkoxy groups show melting points between 229 and 91 °C.

Differential scanning calorimetry (DSC) and polarization microscopy reveal different crystalline but no liquid crystalline (LC) phases. Heating of **6e**, for example, leads in the DSC diagram (rate: 10 K min^{−1}) to a crystal → crystal phase transition at an onset temperature of 333 K ($\Delta H = 3.4$ kJ mol^{−1}) and to the isotropic melt at an onset temperature of 359 K ($\Delta H = 39.0$ kJ mol^{−1}). In contrast to 4-styrylstilbene,^[17,18] the rigid, conjugated π system of 4,4'-distyrylstilbene is too long for the formation of a mesogenic building block for calamitic or phasemic LC structures.

The situation changes if one of the three alkoxy groups is fixed in *ortho* position of the terminal phenyl rings. Even the hexamethoxy compound **6g** generates above 513 K (240 °C) a nematic phase *N*. Heating above 330 °C again provokes decomposition. Six hexyloxy chains, present in **6h**, lower significantly the temperature range of the *N* phase, which then exists between 381 and 461 K (108 and 188 °C). Figure 3 exhibits the typical “schlieren” texture of the nematic phase of **6h**, which was measured close to the clearing point. The situation resembles the behaviour of conjugated

π systems in which the outer olefinic double bonds of **6** are replaced by CN double bonds (and the central CC double bond eventually by a N=N bond).^[19]

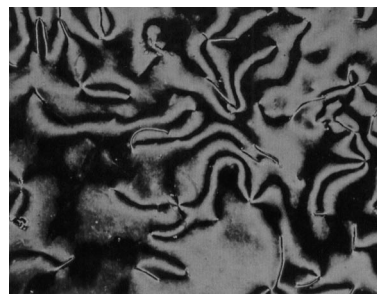


Figure 3. Texture of **6h** measured at 173 °C in the polarization microscope (scale 1:340).

The model established by Praefcke^[19] for the (azo)diimine mentioned above describes a biaxial nematic phase N_b . In contrast to the results found for the diimines, extension of the length of the alkoxy chains leads in our compounds to a broadening of the temperature intervals, in which the mesophases exist.

Because of the high temperature range of the LC phases of **6g** and **6h**, we could not measure directly the fluorescence quantum yields ϕ_F of these phases, but we determined ϕ_F of a precipitated aggregate of **6g**. An emission efficiency of 26% was found, which is a remarkably high value compared to related aggregates.^[6] One cannot expect values of about 80% as in diluted solutions, where the Förster energy transfer cannot work.

Photophysics and Photochemistry of the (E,E,E)-4,4'-Distyrylstilbenes **6**

Absorption and fluorescence maxima of the (E,E,E)-4,4'-distyrylstilbenes **6** depend on the number of alkoxy chains and to a minor extent on the position of the OR groups. Table 2 summarizes a selection of λ_{max} values, which were measured in CH_2Cl_2 . The absorption and emission maxima of **6** are blue-shifted compared to **1b** ($n = 3$) and exhibit a higher Stokes shift.

Table 2. Absorption and fluorescence maxima of **6a**, **6b**, **6f** and **6h** (10^{-5} M solutions in CH_2Cl_2).

Compd.	Alkoxy groups	Absorption ^[a] λ_{max} [nm]	Fluorescence λ_{max} [nm]
6a	4-OC ₁₂ H ₂₅	373	469
6b	3-OC ₁₂ H ₂₅		
	4-OC ₁₂ H ₂₅	395	471, 485
6f	3-OC ₁₂ H ₂₅		
	4-OC ₁₂ H ₂₅	399	469
6h	5-OC ₁₂ H ₂₅		
	2-OC ₆ H ₁₃		
	3-OC ₆ H ₁₃		
	4-OC ₆ H ₁₃	397	469

[a] ϵ values between 79 and 104×10^5 L cm^{−1} mol^{−1}.

The aggregation tendency of **6a–h** in solvents like CHCl_3 or CH_2Cl_2 is low. We could not find a concentration dependence of the absorption coefficient $\varepsilon(\lambda)$. However, the tailing of the fluorescence band can be taken as a hint for the existence of some aggregates (Figure 4).

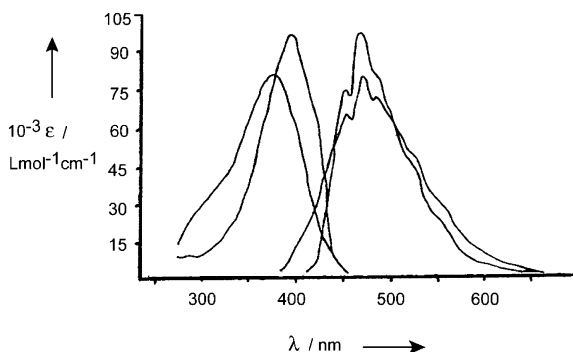
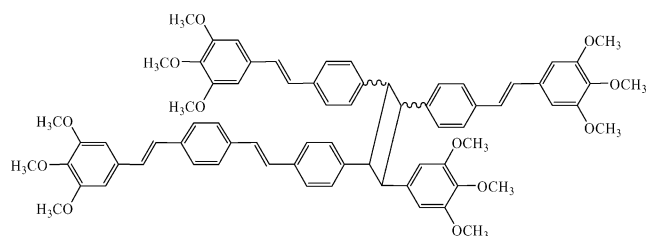


Figure 4. Lower curves: absorption $\varepsilon(\lambda)$ and fluorescence (normalized intensity) of **6a**. Upper curves: absorption $\varepsilon(\lambda)$ and fluorescence (normalized intensity) of **6d**. Measurements in CH_2Cl_2 , $\lambda_{\text{exc}} = 366 \text{ nm}$.

On irradiation with energy-rich UV light, all OPV systems undergo photoreactions. Apart from the monomers ($n = 1$), these oligomers have extremely low quantum yields for $E \rightarrow Z$ isomerization reactions.^[14] However, CC bond formations can be observed with high efficiency.^[14,20,21] Two different reaction types have to be considered, concerted $[\pi^2s + \pi^2s]$ cycloadditions leading to four-membered rings and statistical crosslinking processes.

A preparative photolysis of **6c** ($\lambda_{\text{max}} = 395 \text{ nm}$) with $\lambda \geq 290 \text{ nm}$ in a $1.77 \times 10^{-3} \text{ M}$ solution in benzene led – according to NMR and mass spectroscopical measurements – to a mixture of dimers, trimers and higher oligomers. Cyclo-dimer **7** (Scheme 3) could be isolated in a pure state by a combination of thin-layer and column chromatography. The ^1H NMR spectrum of **7** shows four AA'BB' spin patterns and four singlets in the aromatic region, additionally four olefinic AB spin systems ($^3J = 16.3 \text{ Hz}$) and an ABCD spin pattern for a cyclobutane ring. Mass spectroscopic fragmentation of **7** led not only to the starting compound, the trimer **6c**, but also to 1,4-bis(3,4,5-trimethoxystyryl)-benzene, a dimer, and the corresponding tetramer. These two “perpendicular” cleavage routes for the cyclobutane ring and the ^1H NMR spectrum of **7** prove that an unsymmetrical dimer was formed by a $[2 + 2]$ cycloaddition of a central and a terminal C=C bond. The strong high-field



Scheme 3. Photocyclodimer **7** formed by a $[2\pi + 2\pi]$ cycloaddition of a central and a terminal olefinic double bond of **6c**.

shift of the *ortho* protons of the 1-phenyl group provides moreover a proof for the *1r,2c,3t,4t* stereochemistry of **7**, which corresponds to the major stereochemistry of (*E*)-stilbene photodimers.^[22]

According to UV/Vis reaction spectra, the other trimers exhibit analogous photooligomerization reactions. The crosslinking processes are particularly fast when 254 nm light is used. Longer side chains render the isolation of pure dimers extremely difficult. Therefore we refrained from further oligomer separations.

Conclusions

The fluorescence quantum yield increases in the OPV series **1b** ($n = 1–8, 11$) from the monomer ($\phi_F = 45\%$) to the trimer ($\phi_F = 86\%$ for $n = 3$) and decreases then to a limiting value of 46% for higher oligomers ($n \geq 6$). Based on this result we tried to obtain highly fluorescent liquid crystals of (*E,E,E*)-4,4'-distyrylstilbenes **6**. It turned out that usual calamitic or phasmidic structure concepts realized in **6a–f**, which have alkoxy chains in 4-, 3,4- or 3,4,5-position of the terminal phenyl rings, are not successful for the rather long, conjugated mesogen of the trimer. Only the special 2,3,4-trisubstitution of the terminal phenyl rings with alkoxy groups (OCH_3 , OC_6H_{13}), present in the compounds **6g** and **6h**, led to fluorescent liquid-crystalline compounds.

Experimental Section

General Remarks: UV/Vis: Zeiss MCS 320/340; CH_2Cl_2 as solvent. Fluorescence: Perkin–Elmer LS 50B. IR: Beckman Acculab (reaction spectra as film). ^1H and ^{13}C NMR: Bruker AC 300, AMX 400, Avance 600, CDCl_3 as solvent, if not otherwise stated; TMS as internal standard. MS: Finnigan MAT 95 (EI and FD). DSC: Perkin–Elmer DSC 7. Melting points: Büchi apparatus and Stuart Scientific SMP/3; uncorrected. Elemental analyses: Microanalytical laboratory of the Institute of Organic Chemistry, University of Mainz.

The compound series **1b** ($n = 1–8, 11, 15$) was prepared earlier.^[2–4]

General Procedure for the Preparation of the Aldimines 4: The condensation reaction of the substituted benzaldehydes **2a–h** and aniline (**3**) can be performed in many solvents (ethanol, chloroform, toluene, etc.), but we found that the solvent-free preparation is most convenient and normally gives quantitative yields. A mixture of 25 mmol aldehyde **2a–h** and 35 mmol aniline (**3**) was stirred at 80 °C and ca. 2 kPa. The reduced pressure served for the continuous removal of the generated water. The reaction came to an end after about 3 h (IR or TLC control). Excess aniline was then removed in a higher vacuum (0.1 kPa). The yellow residue was pure product and could directly be used for the subsequent reaction step. Solid products could be recrystallized from ethanol.

The Schiff bases **4e** and **4h**, which are new compounds, were isolated and additionally the deuterated compound **4c'**, which corresponds to the known compound **4c**.^[23]

(E)-N-[3,4,5-Tris(hexyloxy)benzylidene]aniline (4e): Yellowish oil, yield 12.0 g (100%). ^1H NMR (CDCl_3): $\delta = 0.89$ (t, 9 H, CH_3), 1.34 (m, 12 H, CH_2), 1.48 (m, 6 H, CH_2), 1.75 (m, 2 H, CH_2), 1.82 (m, 4 H, CH_2), 4.02 (t, 2 H, OCH_2), 4.04 (t, 4 H, OCH_2), 7.10 (s,

2 H, arom. H), 7.19 (m, 2 H, arom. H), 7.21 (m, 1 H, arom. H), 7.38 (m, 2 H, arom. H), 8.31 (s, 1 H, CHN) ppm. ^{13}C NMR (CDCl_3): δ = 13.9 (CH_3), 22.5, 25.7, 29.3, 31.5 (CH_2), 69.2 (OCH_2 , 3,5- OC_6H_{13}), 14.0 (CH_3), 22.6, 30.3, 31.7 (CH_2), 73.5 (OCH_2 , 4- OC_6H_{13}), 107.2, 120.8, 125.6, 129.0 (arom. CH), 131.1, 141.4, 152.2, 153.4 (arom. C_q), 160.1 (CHN) ppm. MS (EI): m/z (%) = 481 (61) [M^+], 43 (100). $\text{C}_{31}\text{H}_{47}\text{NO}_3$ (481.7): calcd. C 77.29, H 9.83, N 2.91; found C 77.08, H 10.05, N 2.85.

(*E,E,E*)-4,4'-Bis[2,3,4-Tris(hexyloxy)benzylidene]aniline (4h): Yellowish oil, yield 12.0 g (100%). ^1H NMR (CDCl_3): δ = 0.89 (m, 9 H, CH_3), 1.10–1.55 (m, 18 H, CH_2), 1.78 (m, 6 H, CH_2), 3.99 (t, 2 H, OCH_2), 4.03 (t, 2 H, OCH_2), 4.11 (t, 2 H, OCH_2), 6.74/7.85 (AB, 3J = 8.8 Hz, 2 H, arom. H), 7.21 (m, 3 H, arom. H), 7.39 (m, 2 H, arom. H), 8.78 (s, 1 H, CHN) ppm. ^{13}C NMR (CDCl_3): δ = 14.0 (CH_3 , superimposed), 22.6, 25.8, 29.2, 29.3, 29.7, 30.2, 30.3, 31.5, 31.6, 31.7 (CH_2 , partly superimposed), 68.8, 73.7, 74.9 (OCH_2), 108.5, 121.0, 122.3, 125.4, 129.0 (arom. CH), 122.9, 141.2, 152.8, 154.3, 156.4 (arom. C_q), 156.4 (CHN) ppm. MS (EI): m/z (%) = 481 (3) [M^+], 390 (100) $\text{C}_{31}\text{H}_{47}\text{NO}_3$ (481.7): calcd. C 77.29, H 9.83, N 2.91; found C 77.59, H 9.66, N 2.94.

(*E,E,E*)-4,4'-Bis[2,3,4-Tris(methoxy)phenyl]methylidene]aniline (4c'): The general procedure was applied to 3,4,5-[D₁]trimethoxybenzaldehyde^[24] (5.0 g, 25.4 mmol) and aniline (3) (3.0 g, 32.3 mmol). The yellow product (6.8 g, 98%) melted after recrystallization from ethanol at 109 °C. ^1H NMR (CDCl_3): δ = 3.91, 3.94 (2s, 9 H, OCH_3), 7.12 (s, 2 H, arom. H), 7.18 (m, 2 H, arom. H), 7.20 (m, 1 H, arom. H), 7.39 (m, 2 H, arom. H) ppm. ^{13}C NMR (CDCl_3): δ = 56.2, 60.9 (OCH_3), 106.2, 120.8, 125.8, 129.1 (arom. CH), 131.6, 141.2, 152.0, 153.5 (arom. C_q), 159.5 [t, 1J (C,D) = 25.0 Hz, CDN] ppm. MS (EI): m/z (%) = 272 (100) [M^+], 257 (58), 77 (24). $\text{C}_{16}\text{H}_{16}\text{DNO}_3$ (272.3): calcd. C 70.57, H 6.66, N 5.14; found C 70.19, H 6.31, N 4.85.

General Procedure for the Preparation of the (*E,E,E*)-4,4'-Distyryl-stilbenes 6a–h: A dry, oxygen-free stream of N_2 was purged for 30 min through a solution of (*E*)-4,4'-dimethylstilbene (5) (1.03 g, 5.0 mmol) in 150 mL DMF, then 2.24 g (20.0 mmol) $\text{KOC}(\text{CH}_3)_3$ was added. After 10 min vigorous stirring 10.0 mmol of the crude (or recrystallized) aldimine 4a–h was added and the temperature was raised to 90 °C. After 1 h the mixture was cooled to 0–5 °C and 150 mL H_2O was added dropwise. The precipitated product was filtered off and washed with cold methanol. The products 6c–h were then subjected to a column filtration (20 × 7 cm SiO_2 , CH_2Cl_2) and recrystallized. The products 6a and 6b have a low solubility and were directly recrystallized.

(*E,E,E*)-4,4'-Bis[2-(4-dodecyloxyphenyl)vinyl]stilbene (6a): Yield 2.26 g, 60%, yellow crystals which after recrystallization from CHBr_3 decompose above 330 °C. ^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, T = 373 K): δ = 0.88 (t, 6 H, CH_3), 1.20–1.55 (m, 40 H, CH_2), 1.77 (m, 4 H, CH_2), 3.93 (t, 4 H, OCH_2), 6.85/7.38 (AA'BB', 8 H, arom. H, outer phenyl rings), 6.91/7.02 (AB, 3J = 16.3 Hz, 4 H, outer olefin. H), 7.08 (s, 2 H, inner olefin. H), 7.43 ("s", 8 H, inner phenyl rings) ppm.^[25] MS (FD): m/z (%) = 754 (100) [$\text{M} + \text{H}^+$]. $\text{C}_{54}\text{H}_{72}\text{O}_2$ (753.2): calcd. C 86.12, H 9.64; found C 86.09, H 9.42.

(*E,E,E*)-4,4'-Bis[2-[3,4-bis(dodecyloxy)phenyl]vinyl]stilbene (6b): Yield 3.70 g, 66%, yellow crystals which decompose after recrystallization from CHCl_3 above 330 °C. ^1H NMR (CDCl_3 , T = 333 K): δ = 0.88 (t, 12 H, CH_3), 1.20–1.60 (m, 72 H, CH_2), 1.80 (m, 8 H, CH_2), 4.02 (t, 4 H, OCH_2), 4.05 (t, 4 H, OCH_2), 6.83–7.15 (m, 6 H, arom. H, outer phenyl rings), 6.94/7.02 (AB, 3J = 16.4 Hz, 4 H, outer olefin. H), 7.10 (s, 2 H, inner olefin. H), 7.47 ("s", 8 H, arom. H, inner phenyl rings) ppm.^[25] MS (FD): m/z (%) = 1123

(100) [$\text{M} + \text{H}^+$]. $\text{C}_{78}\text{H}_{120}\text{O}_4$ (1121.8): calcd. C 83.51, H 10.78; found C 83.17, H 10.41.

(*E,E,E*)-4,4'-Bis[2-[3,4,5-tris(methoxy)phenyl]vinyl]stilbene (6c): Yield 2.00 g, 71%, yellow crystals, m.p. 229 °C after recrystallization from toluene. ^1H NMR (CDCl_3): δ = 3.86 (s, 6 H, OCH_3), 3.90 (s, 12 H, OCH_3), 6.74 (s, 4 H, arom. H, outer phenyl rings), 6.99/7.05 (AB, 3J = 16.4 Hz, 4 H, outer olefin. H), 7.11 (s, 2 H, inner olefin. H), 7.50 ("s", 8 H, inner phenyl rings) ppm. ^{13}C NMR (CDCl_3): δ = 56.2 (*m*- OCH_3), 60.9 (*p*- OCH_3), 103.9 (arom. CH, outer phenyl rings), 126.8, 126.9 (arom. CH, inner phenyl rings), 127.7, 128.2, 128.8 (olefin. CH), 133.0, 136.6, 136.7, 138.3, 153.5 (arom. C_q) ppm. MS (EI): m/z (%) = 564 (100) [M^+], 549 (14). $\text{C}_{36}\text{H}_{36}\text{O}_6$ (564.7): calcd. C 76.57, H 6.43; found C 76.68, H 6.53.

(*E,E,E*)-4,4'-Bis[2-deuterio-2-[3,4,5-tris(methoxy)phenyl]vinyl]-stilbene (6c'): Yield 1.59 g, 56%, yellow crystals, m.p. 228 °C after recrystallization from toluene. ^1H NMR (CDCl_3): δ = 3.86 (s, 6 H, OCH_3), 3.91 (s, 12 H, OCH_3), 6.74 (s, 4 H, arom. H, outer phenyl rings), 6.99 (s, 2 H, outer olefin. H), 7.11 (s, 2 H, inner olefin. H), 7.50 ("s", 8 H, arom. H, inner phenyl rings) ppm. ^{13}C NMR (CDCl_3): δ = 56.2 (*m*- OCH_3), 60.9 (*p*- OCH_3), 103.9 (arom. CH, outer phenyl rings), 126.8, 126.9 (arom. CH, inner phenyl rings), 127.7, 128.2 (olefin. CH), 133.0, 136.6, 136.7, 138.3, 153.5 (arom. C_q) ppm. MS (EI): m/z (%) = 566 (100) [M^+], 551 (13). $\text{C}_{36}\text{H}_{34}\text{D}_2\text{O}_6$ (566.7): calcd. C 76.30, H/D 6.76; found C 76.42, H/D 6.82.

(*E,E,E*)-4,4'-Bis[2-[4-dodecyloxy-3,5-bis(methoxy)phenyl]vinyl]-stilbene (6d): Yield 2.40 g, 55%, yellowish crystals, m.p. 148 °C after recrystallization from acetone melt. ^1H NMR (CDCl_3): δ = 0.88 (t, 6 H, CH_3), 1.20–1.34 (m, 32 H, CH_2), 1.45 (m, 4 H, CH_2), 1.75 (m, 4 H, CH_2), 3.89 (s, 12 H, OCH_3), 3.97 (t, 4 H, OCH_2), 6.72 (s, 4 H, arom. H, outer phenyl rings), 6.98/7.04 (AB, 3J = 16.2 Hz, 4 H, outer olefin. H), 7.12 (s, 2 H, inner olefin. H), 7.49 ("s", arom. H, inner phenyl rings) ppm. ^{13}C NMR (CDCl_3): δ = 14.1 (CH_3), 22.7, 25.9, 29.3, 29.5, 29.6, 29.6, 29.6, 29.7, 30.1, 31.9 (CH_2), 56.2 (OCH_3), 73.7 (OCH_2), 103.9 (arom. CH, outer phenyl rings), 126.7, 126.8 (arom. CH, inner phenyl rings), 127.5, 128.1, 128.7 (olefin. CH), 132.8, 136.6, 136.7, 137.6, 153.7 (arom. C_q) ppm. MS (FD): m/z (%) = 873 (100) [M^+]. $\text{C}_{58}\text{H}_{80}\text{O}_6$ (873.3): calcd. C 79.77, H 9.23; found C 79.65, H 9.29.

(*E,E,E*)-4,4'-Bis[2-[3,4,5-tris(hexyloxy)phenyl]vinyl]stilbene (6e): Yield 2.51 g (51%), yellowish crystals, m.p. 91 °C after recrystallization from 2-propanol. ^1H NMR (CDCl_3): δ = 0.88 (t, 6 H, CH_3), 0.89 (t, 12 H, CH_3), 1.35 (m, 24 H, CH_2), 1.49 (m, 12 H, CH_2), 1.75 (m, 4 H, CH_2), 1.85 (m, 8 H, CH_2), 3.97 (t, 4 H, OCH_2), 4.02 (t, 8 H, OCH_2), 6.71 (s, 4 H, arom. H, outer phenyl rings), 6.95/7.02 (AB, 3J = 16.2 Hz, 4 H, outer olefin. H), 7.10 (s, 2 H, inner olefin. H), 7.48 ("s", 8 H, inner arom. H) ppm. ^{13}C NMR (CDCl_3): δ = 14.0, 14.0 (CH_3), 22.6, 22.7, 25.8, 25.8, 29.4, 30.3, 31.6, 31.8 (CH_2), 69.3, 73.5 (OCH_2), 105.4 (arom. CH, outer phenyl rings), 126.7, 126.8 (arom. CH, inner phenyl rings), 127.3, 128.1, 128.9 (olefin. CH), 132.5, 136.5, 136.8, 138.6, 153.5 (arom. C_q) ppm. MS (FD): m/z (%) = 985 (100) [M^+]. $\text{C}_{66}\text{H}_{96}\text{O}_6$ (985.5): calcd. C 80.44, H 9.82; found C 80.59, H 9.75.

(*E,E,E*)-4,4'-Bis[2-[3,4,5-tris(dodecyloxy)phenyl]vinyl]stilbene (6f): Yield 4.84 g (65%), yellowish crystals, m.p. 92 °C after recrystallization from 2-propanol. MS (FD): m/z (%) = 1490 (100) [M^+]. $\text{C}_{102}\text{H}_{168}\text{O}_6$ (1490.4): calcd. C 82.20, H 11.36; found C 82.29, H 11.42.

(*E,E,E*)-4,4'-Bis[2-[2,3,4-tris(methoxy)phenyl]vinyl]stilbene (6g): Yield 0.65 g (23%), yellow crystals, m.p. 240 °C after recrystallization from 2-propanol (a nematic phase is formed which decomposes above 330 °C). ^1H NMR (CDCl_3): δ = 3.87 (s, 3 H, OCH_3),

3.89 (s, 3 H, OCH₃), 3.91 (s, 3 H, OCH₃), 6.69/7.31 (AB, ³J = 8.6 Hz, 4 H, arom. H, outer phenyl rings), 7.02/7.34 (AB, ³J = 16.4 Hz, 4 H, outer olefin. H), 7.10 (s, 2 H, inner olefin. H), 7.49 ("s", 8 H, arom. H, inner phenyl rings) ppm. ¹³C NMR (CDCl₃): δ = 56.2, 60.9, 61.3 (OCH₃), 108.0, 120.8, 123.0, 126.7, 126.8, 127.6, 128.1 (arom. and olefin. CH), 124.6, 136.5, 137.4, 142.6, 151.8, 153.4 (arom. C_q) ppm. MS (EI): m/z (%) = 564 (100) [M⁺], 475 (89). C₃₆H₃₆O₆ (564.7): calcd. C 76.57, H 6.43; found 76.62, H 6.75.

(E,E,E)-4,4'-Bis[2-[2,3,4-tris(hexyloxy)phenyl]vinyl]stilbene (6h): Yield 0.89 g (18%), yellow crystals, m.p. 108 °C after recrystallization from 2-propanol (a nematic phase is formed, clearing point at 188 °C). ¹H NMR (CDCl₃): δ = 0.88 (t, 18 H, CH₃), 1.34 (m, 24 H, CH₂), 1.50 (m, 12 H, CH₂), 1.80 (m, 12 H, CH₂), 3.96 (t, 4 H, OCH₂), 3.97 (t, 4 H, OCH₂), 4.03 (t, 4 H, OCH₂), 6.66/7.28 (AB, ³J = 8.2 Hz, arom. H, outer phenyl rings), 6.98/7.39 (AB, ³J = 16.4 Hz, 4 H, outer olefin. H), 7.10 (s, 2 H, inner olefin. H), 7.48 ("s", 8 H, arom. H, inner phenyl rings) ppm. ¹³C NMR (CDCl₃): δ = 14.0, 14.0, 14.1 (CH₃), 22.6, 22.7, 22.7, 25.8, 25.8, 26.0, 29.4, 30.3, 30.4, 31.6, 31.8, 31.8 (CH₂), 68.9, 73.7, 74.2 (OCH₂), 108.8, 120.3, 123.4, 126.8, 127.0, 128.0 (arom. and olefin. CH), 124.6, 136.3, 137.6, 142.1, 151.4, 153.2 (arom. C_q) ppm. MS (FD): m/z (%) = 985 (100) [M⁺]. C₆₆H₉₆O₆ (985.5): calcd. C 80.44, H 9.82; found C 80.53, H 9.79.

Irradiation of 4,4'-Distyrylstilbenes 6: Irradiation of **6** in diluted, oxygen-free solution (5.10⁻⁴ M) in C₆H₆ with energy-rich UV light (λ = 254 nm) led to photo-crosslinking by CC bond formation. According to ¹H and ¹³C NMR reaction spectra, E → Z isomerizations could be excluded.^[26,27] The long-wavelength band of **6** decreased steadily. Statistical CC bond formation and [2π + 2π] cycloadditions took place and yielded a complex mixture of oligomers. In the case of **6c** we isolated the cyclodimer **7** in a preparative photolysis: a solution of 50 mg (0.089 mmol) **6c** in 195 mL benzene was irradiated at 25 °C with a 450 W Hanovia medium-pressure lamp equipped with a Pyrex filter (λ ≥ 290 nm). The ¹H NMR spectrum of the reaction mixture showed after 3.5 h a turnover of 35%. The mixture was first separated by preparative TLC [SiO₂ (thickness d = 5 mm), toluene/ethyl acetate, 2:1]. The fractions between R_F = 0.22 and 0.43 were then chromatographed on a column (30 × 1 cm SiO₂, toluene/ethyl acetate gradient). The first fraction contains open-chain dimers and trimers (mass spectroscopy). Yellowish crystals of the cyclodimer **7** (6.5 mg, 13%) were obtained as second fraction.

Cyclodimer 7: rac-[1r-[3,4,5-Tris(methoxy)phenyl]-2c,3r-bis[4-[2-[3,4,5-tris(methoxy)phenyl]vinyl]phenyl]-4t-[4-(2-[4-[2-(3,4,5-tris(methoxy)phenyl]vinyl]phenyl]vinyl]phenyl]cyclobutane (7): M.p. 270 °C (dec.) ¹H NMR (CDCl₃):^[28] δ = 3.63 (s, 6 H), 3.73 (s, 3 H), 3.82 (s, 3 H), 3.84 (s, 6 H), 3.85 (s, 6 H), 3.90 (s, 12 H) [12 OCH₃], 4.35–4.49 (m, 4 H, typical ABCD spin pattern, four-membered ring protons), 6.26 (s, 2 H), 6.66 (s, 2 H), 6.69 (s, 2 H), 6.72 (s, 2 H) [arom. H, trimethoxy-substituted phenyl rings], 6.88/6.93 (AB, ³J = 16.3 Hz, 2 H), 6.91/6.94 (AB, ³J = 16.3 Hz, 2 H), 6.97/7.02 (AB, ³J = 16.3 Hz, 2 H), 7.00 ("s", 2 H) [olefin. H], 7.11/7.32 (AA'BB', 4 H), 7.12/7.32 (AA'BB', 4 H), 7.14/7.30 (AA'BB', 4 H), 7.43/7.46 (AA'BB', 4 H) [arom. H] ppm. ¹³C NMR (CDCl₃): δ = 47.3, 47.6, 48.1, 48.2 (CH, cyclobutane), 56.1, 56.2, 56.2, 56.2 (m-OCH₃), 60.8, 60.9, 60.9, 60.9 (p-OCH₃), 103.8, 103.9, 104.0, 105.9 (arom. CH, trimethoxy-substituted phenyl rings), 126.2, 126.3, 126.7, 127.7, 127.8, 127.9, 128.0, 128.1, 128.3, 128.4, 128.5, 128.6 (arom. and olefin. CH, partly superimposed), 133.1, 133.1, 133.2, 135.1, 135.2, 135.3, 136.2, 136.6, 136.7, 136.8, 138.2, 138.3 (arom. C_q), 140.1, 140.3, 140.3, 140.3, 152.9, 153.4, 153.5, 153.5 (arom. C_qO) ppm. MS (EI): m/z (%) = 667 (22) [M⁺ - C₂₈H₂₉O₆], 556 (100) [M/2]⁺, 462 (18), [M⁺ - C₄₄H₄₂O₆].^[29]

Measurement of the Fluorescence Quantum Yields: Solutions of each **1b** (n = 1–8, 11) in CH₂Cl₂ were prepared which had the same absorbance for the λ_{max} values as solutions of the standard (E,E)-1,4-distyrylbenzene in CH₂Cl₂. The individual λ_{max} values served as excitation wavelengths λ_{exc}. The intensities of the fluorescence bands, determined by using the software of the fluorimeter, were then related to the fluorescence intensity of the standard. The fluorescence quantum yield of the standard amounts in CH₂Cl₂ at room temperature to 90% (φ_F = 0.90).^[6] In addition, quinine sulfate in 1 M H₂SO₄ (φ_F = 0.55) was used as second standard.^[30,31] The results of both measurements agree within the margins of error (± 5%).

Preparation and measurement of aggregates of **6g** were performed according to the literature.^[6]

Acknowledgments

We are grateful to the Deutsche Forschungsgemeinschaft (DFG), the Fonds der Chemischen Industrie and the Center of Materials Science of the University of Mainz for financial support. We thank Prof. D. Oelkrug, University of Tübingen, and his research group for some of the fluorescence measurements.

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Received: November 6, 2007

Published Online: February 5, 2008