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# Poly(propylene imine) dendrimers functionalized with stilbene or 1,4-distyrylbenzene chromophores

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**Abstract**—Two generations of dendritic nanoparticles were prepared, which contain (*E*)-stilbene or (*E*,*E*)-1,4-distyrylbenzene chromophores in the 4 or 8 terminal positions of the propylene imine dendrons. The compounds show a highly efficient photoreactivity. On prolonged irradiation all stilbenoid chromophores were destroyed by oligomerization (crosslinking) and the typical absorption and fluorescence of the chromophores disappeared completely.

## 1. Introduction

Dendrimers are particularly suitable for the attachment of chromophores in the peripheral positions of the dendrons.[1] Thus, a high absorption cross-section can be obtained. We selected poly(propylene imine) [PPI] systems because the terminal $NH_2$ groups permit various functionalizations, which lead to higher amines, amides, sulfonamides, carbamates, ureas or azomethines. In fact all these functional links have been used for the attachment of aromatics,[2] heteroaromatics,[3] crown ethers and complexes,[2b,4] polycycles,[5] etc.

Stilbenes belong to the best studied class of compounds from a photophysical and photochemical viewpoint.[6] They exhibit *E*/*Z* isomerizations, cyclizations, dimerizations, and polymerization reactions on irradiation and can be used for manifold applications in material science.[6e,7]

Therefore dendrimers with stilbenoid building blocks represent an attractive area of research.[8] The Refs. 9–11 demonstrate the increasing interest in these systems during the recent years. Stilbene units can represent the core,[9] or can be a part of the dendrons[2a,10] or both.[11] We decided to study poly(propylene imine) dendrimers [PPI] with (*E*)-stilbene or (*E*,*E*)-1,4-distyrylbenzene chromophores attached to the four $NH_2$ groups of the first generation PPI and to the eight $NH_2$ groups of the second generation PPI. Apart from our own newly synthesized compounds of this type, there exists—to our best knowledge—only a single such dendrimer, which was investigated by Balzani et al.[2d] Meijer et al. studied oligo(1,4-phenylenevinylene) [OPV] terminated PPIs.[12]

## 2. Results and discussion

### 2.1. Synthesis

For the preparation of the target dendrimers we used the condensation reaction of aldehydes with the amino groups of PPIs of first and second generation. Scheme 1 shows the formation of stilbene aldehyde **3a** by applying the Wittig–Horner reaction of phosphonate **1** and unilaterally protected terephthalaldehyde **2a**. The deprotection occurred directly in the acidic work-up. The analogous Wittig–Horner reaction of **1** and methyl 4-formylbenzoate **2b** yielded stilbene derivative **3b**, which was reduced to the 4-styrylbenzyl alcohol **4**. Bromination and Arbuzov reaction with $P(OEt)_3$ yielded **5** and the phosphonate **6**. The final Wittig–Horner reaction of **6** and **2a** afforded the 4-(stilbenylvinyl)benzaldehyde **7**.[11k,13–15] The three propoxy groups in **3a** and **7** serve for the enhancement of the solubility. Wittig–Horner reactions in the stilbenoid series exhibit *E*/*Z* selectivities of about 95:5. Purification of the raw products by crystallization furnishes pure (*E*)-configured products, whereby the detection limit in the $^1$H NMR spectroscopy is 2% or lower for the (*Z*)-isomers.[16]

PPI **8** (first generation) was then reacted with aldehyde **3a** to the four-fold azomethine **9** (Scheme 2). It turned out that the conjugated Schiff bases are light-sensitive (UV component of the daylight). This sensitivity is remarkably diminished when the C═N double bonds are hydrogenated by the reaction with $LiAlH_4$ (**9**→**10**). Accordingly aldehyde **7** was reacted with PPI **8** and in situ reduced to dendrimer **11**.

Without isolation of the intermediate azomethines the dendrimers **13** and **14** were obtained (Scheme 3) by the reaction of PPI **12** (second generation) and aldehyde **3a** and **7**, respectively, and subsequent hydrogenation with $LiAlH_4$.

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*Keywords*: Crosslinking; Dendrimers; Photochemistry.

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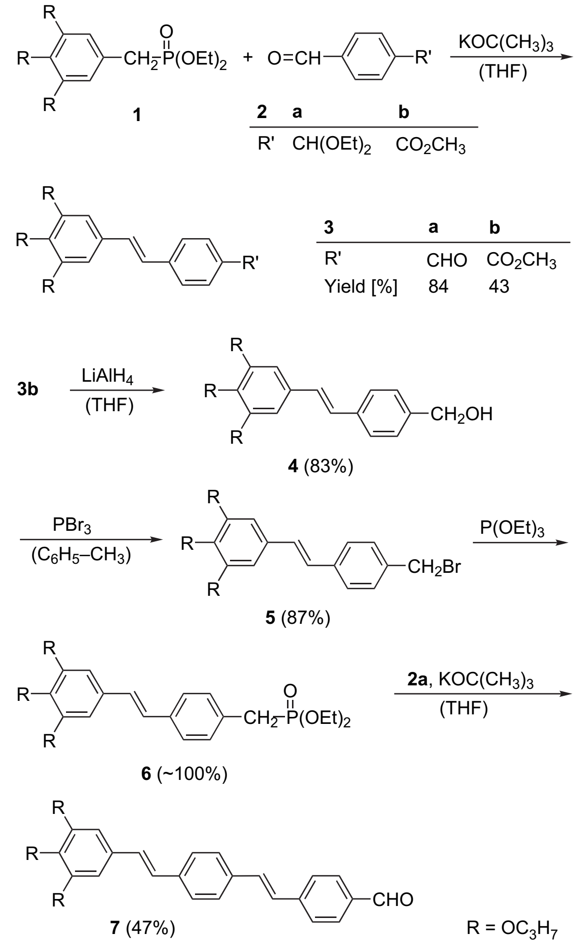
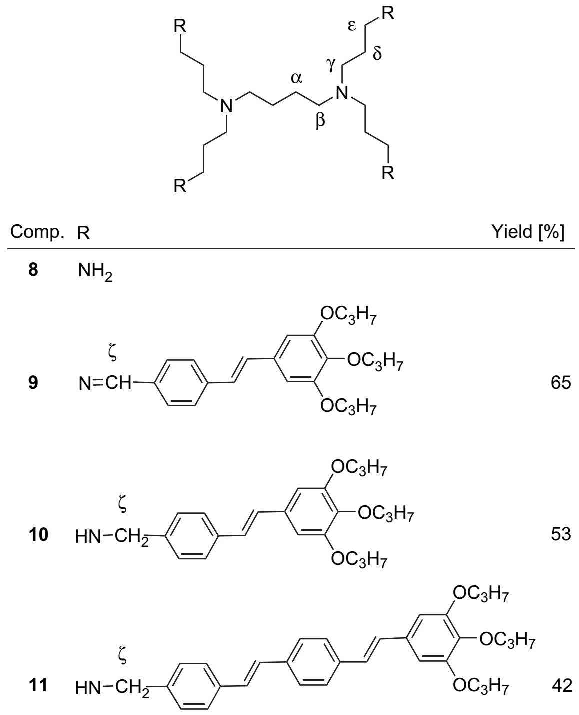
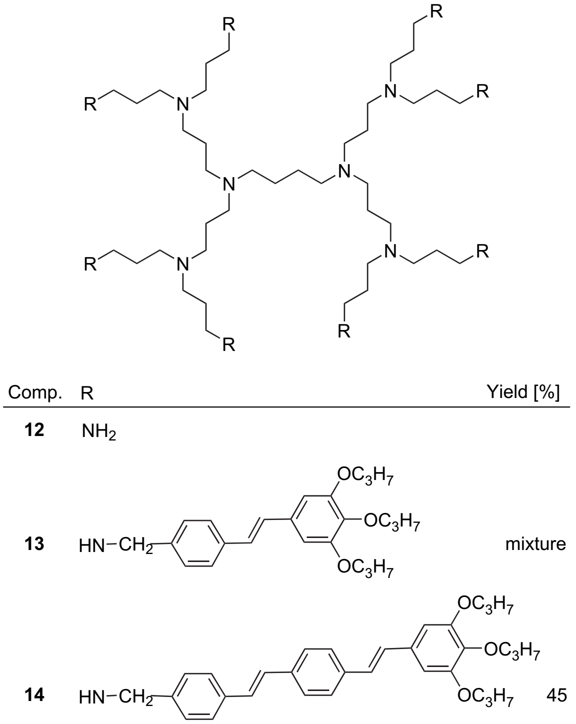


**Scheme 1**. Preparation of the aldehyde components.



**Scheme 2**. Functionalized poly(propylene imine) dendrimers: first generation.



**Scheme 3**. Functionalized poly(propylene imine) dendrimers: second generation.

The major problems of the synthetic procedures shown in Schemes 2 and 3 are firstly the complete reaction of all four or eight amino groups to generate uniform dendrimers and secondly the preservation of the (*E*)-configurations of the stilbene units. The latter point could be realized perfectly, but the complete reaction of all PPI amino groups turned out to be impossible in the divergent synthesis of **13** by reaction of **12** and **3a**. Even a high excess of aldehyde **3a** led to a mixture (MALDI-TOF measurement). Surprisingly, the analogous process with aldehyde **7** worked fairly well. After hydrogenation with $LiAlH_4$, the yield of uniform **14** amounted to 45%. The $^1H$ and $^{13}C$ NMR data of **3a**, **8**, and **9–11** are summarized in Tables 1 and 2.

## 2.2. Absorption, fluorescence, and photochemistry

Figure 1 illustrates the absorption of the dendrimers **9** and **10** and their emission. Compared to stilbenylmethanol **4**, ($\lambda_{max}$=330 nm) dendrimer **10** shows a small hypsochromic shift ($\lambda_{max}$=328 nm) in $CHCl_3$. Extension of the conjugation in the chromophore of dendrimer **9** causes a red shift ($\lambda_{max}$=345 nm), which is notably smaller than that of the aldehyde **3a** ($\lambda_{max}$=358 nm). However, **3a** has a stronger intramolecular charge transfer effect than **9**, which influences the long-wavelength absorption.[17] The fluorescence bands of **9** and **10** have their maxima at 500 and 412 nm. The Stokes shift of **9** (8986 $cm^{-1}$) is much larger than the Stokes shift of **10** (6316 $cm^{-1}$). The close arrangement of (*E*)-stilbene chromophores in the periphery of dendrimers can principally have different effects. Apart from excimer formation,[6e,18,19] exciplexes with the amino subunits can be formed.[20] However, corresponding bathochromically shifted emissions could not be detected. Despite the proximity of stilbene chromophores or stilbene and amine units, the steric

**Table 1**. $^1H$ NMR data of the components **3a** and **8** and the dendrimers **9–11** ($\delta$ values in $CDCl_3$, TMS as internal standard)

| Compd | $CH_2$ | | | | | CH/$CH_2$ | Aromat. H | | Olefin. H | $OC_3H_7$[a] | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | α | β | γ | δ | ε | ζ | $C_6H_4$ | $C_6H_2$ | CH=CH | $OCH_2$ | $CH_2$ | $CH_3$ |
| | (m) | (t) | (t) | (m) | (t) | (s) | (AA′BB′) | (s) | (AB, $^3J$=16.3±0.1 Hz) | (t) | (m) | (t) |
| **3a** | | | | | | 9.97 | 7.62 | 6.73 | 6.99 | 3.92 | 1.76 | 1.01 |
| | | | | | | | 7.83 | | 7.14 | 3.99 | 1.84 | 1.06 |
| **8** | 1.36 | 2.34 | 2.39 | 1.60 | 2.67 | | | | | | | |
| **9** | 1.48 | 2.41 | 2.50 | 1.77 | 3.61 | 8.23 | 7.48 | 6.69 | 6.93 | 3.93 | 1.76 | 1.02 |
| | | | | | | | 7.66 | | 7.05 | 3.96 | 1.82 | 1.04 |
| **10**[b] | 1.28 | 2.31 | 2.42 | 1.78 | 2.61 | 3.70 | 7.32 | 6.83 | 7.06 | 3.89 | 1.70 | 1.01 |
| | | | | | | | 7.46 | | 7.12 | 3.96 | 1.78 | 1.03 |
| **11** | 1.36 | 2.36 | 2.43 | 1.63 | 2.62 | 3.73 | 7.27 | 6.70 | 6.93 | 3.94 | 1.77 | 1.02 |
| | | | | | | | 7.43 | | 7.00 | 3.98 | 1.83 | 1.05 |
| | | | | | | | 7.44 | | 7.03 | | | |
| | | | | | | | 7.44 | | 7.07 | | | |

[a] The upper values belong to the *p*-$OC_3H_7$ chains.
[b] Measurement in $(CD_3)_2CO$.

**Table 2**. $^{13}C$ NMR data of the components **3a** and **8** and the dendrimers **9–11** ($\delta$ values in $CDCl_3$, TMS as internal standard)

| Compd | $CH_2$ | | | | | CH/$CH_2$ | $C_6H_4$ | | $C_6H_2$ | | | C=C | $OC_3H_7$[a] | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | α | β | γ | δ | ε | ζ | CH | $C_q$ | CH | $C_q$ | $C_qO$ | CH | $OCH_2$ | $CH_2$ | $CH_3$ |
| **3a** | | | | | | 191.5 | 126.7 | 135.1 | 105.7 | 131.7 | 139.1 | 126.3 | 70.9 | 22.7 | 10.5 |
| | | | | | | | 130.2 | 143.5 | | | 153.4 | 132.4 | 75.1 | 23.5 | 10.6 |
| **8** | 24.9 | 54.0 | 51.8 | 30.8 | 40.7 | | | | | | | | | | |
| **9** | 25.1 | 54.0 | 51.6 | 28.3 | 59.8 | 160.7 | 126.5 | 135.3 | 105.3 | 130.1 | 139.5 | 127.0 | 70.7 | 22.7 | 10.5 |
| | | | | | | | 128.4 | 138.5 | | | 153.3 | 132.2 | 75.1 | 23.5 | 10.6 |
| **10**[b] | 25.9 | 54.8 | 48.5 | 28.3 | 54.1 | 54.8 | 126.9 | 133.6 | 105.9 | 129.1 | 138.8 | 129.0 | 71.0 | 23.4 | 10.8 |
| | | | | | | | 128.2 | 136.7 | | | 154.1 | 129.1 | 75.1 | 24.2 | 10.9 |
| **11** | 25.1 | 54.1 | 48.2 | 27.5 | 53.9 | 52.4 | 126.5 | 136.0 | 105.3 | 132.5 | 138.4 | 127.3 | 70.7 | 22.8 | 10.6 |
| | | | | | | | 126.7 | 136.5 | | | 153.3 | 127.8 | 75.1 | 23.5 | 10.6 |
| | | | | | | | 126.8 | 136.7 | | | | 128.2 | | | |
| | | | | | | | 128.5 | 140.1 | | | | 128.7 | | | |

[a] The upper values belong to the two *m*-$OC_3H_7$ chains.
[b] Measurement in $(CD_3)_2CO$.

situation seems to be not very suitable for the generation of excimers and exciplexes. The dendrimer generation does not affect the absorption and emission range. Monochromatic irradiation ($\lambda$=340 nm) of **9** in $10^{-5}$ M solution in $CHCl_3$ leads to a decrease of the long-wavelength absorption and the fluorescence. Using the light of a Xenon high-pressure lamp, the process becomes very fast (Fig. 2). After 1 min the absorbance at $\lambda_{max}$=345 nm is reduced to almost one third. A new absorption arises at about 425 nm, which disappears slowly in 75 min. Dendrimer **10** behaves in the same way. Figure 3 shows the corresponding photodegradation of **11**. The extended (*E*,*E*)-distyrylbenzene chromophore ($\lambda_{max}$=366 nm) is fast destroyed and a new low-intensity absorption appears at 425 nm, which then disappears slowly. A novel maximum around 260 nm arises on extended irradiation. All three photoprocesses of **9**, **10**, and **11** are

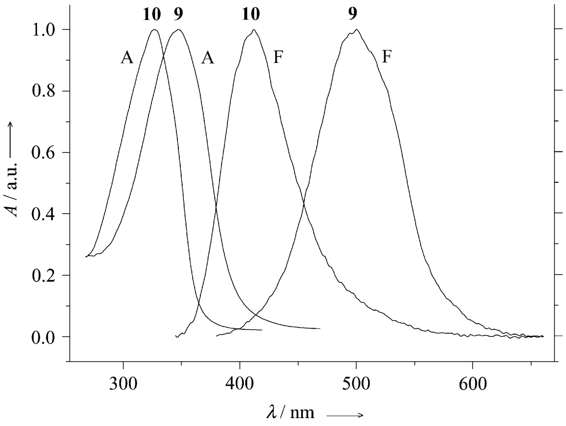


**Figure 1**. Absorption *A* and fluorescence *F* of **9** and **10** ($CHCl_3$).

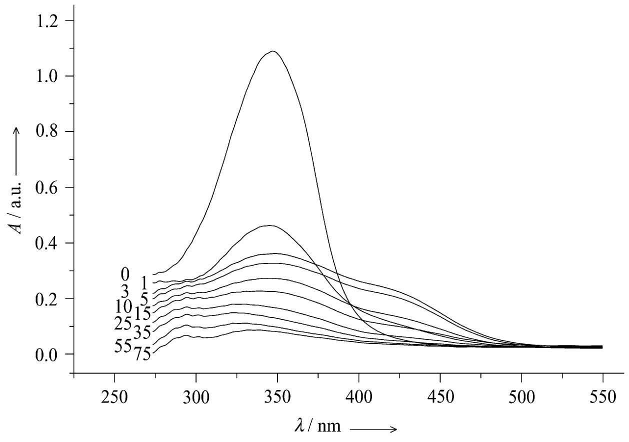


**Figure 2**. Irradiation of **9** ($10^{-5}$ M, absorption in $CHCl_3$). The numbers on the left side of the curves indicate the irradiation time in min using the radiation of a Xenon high-pressure lamp and quartz cuvettes.

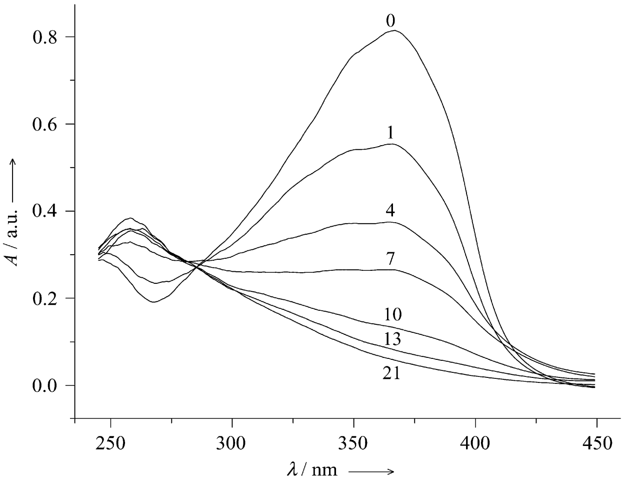


**Figure 3**. Irradiation of **11** ($10^{-5}$ M, absorption in $CHCl_3$). The numbers indicate the irradiation time in min using a Xenon high-pressure lamp and quartz cuvettes.

not uniform. The reaction spectra do not exhibit isosbestic points. In order to conceive a structural concept for the photoreactions, we studied the corresponding $^1$H NMR reaction spectra in $CD_2Cl_2$. The primary photoprocess of **9** and **10** is the $E \rightarrow Z$ isomerization visible by the generation of new olefinic signals at $\delta$=6.6±0.3 ppm. All four stilbene units are finally involved in this complex process, which soon after the beginning of the irradiation is accompanied by an oligomerization. The appearance of saturated CH groups ($\delta$=4.3±0.2 ppm) and the broadening of all $^1$H NMR signals are typical for this route, in which not only the olefinic centers but also some benzene rings are involved. The new absorption in the visble region at 425 nm do we assign, as in earlier OPV studies, to intermediate quinoid systems.[11k,21] Balzani et al. found in their investigation of a related dendrimer the secondary formation of phenanthrenes.[2d] We can definitely rule that out here. The proton in the bay region neighboring to the oxygen atom of a propoxy group would lead to a singlet signal at $\delta$=9.8±0.2 ppm.[22,23] We do not find signals with $\delta \geq 7.5$ ppm. The detection limit is in the range of 3%. ESI and FD mass spectra showed various peaks with *m*/*z* values, which are higher than the *m*/*z* values of the monomers, but no exact oligomer values.

The dendrimers **11** and **14** exhibit—compared to **9** and **10**—the opposite behavior on irradiation. An $E \rightarrow Z$ photoisomerization is in the (*E*,*E*)-distyrylbenzene chromophore not possible.[6e] The extended conjugation leads in the first excited singlet states $S_1$ to relatively high bond orders of the olefinic double bonds.[24] That prevents the stereoisomerization by rotation. However, as soon as the oligomerization process degradates one olefinic double bond of the chromophore, the isomerization becomes possible. Prolonged irradiation ($\lambda \geq 300$ nm) leads indeed to new $^1$H NMR signals at 6.4±0.2 ppm, which are typical for (*Z*)-stilbene configurations. Monochromatic irradiation at 366 nm does not affect the (*E*,*E*)-distyrylbenzene chromophore. In general, the photooligomerization of stilbenoid compounds is the more efficient, the higher the energy of the UV light is. The Hg emissions at 254 and 313 nm are particularly useful for this purpose. The oligomerization can be used in oligo- and poly(1,4-phenylenevinylene)s[21] and in stilbenoid dendrimers[11f,h] for photoresists. Molecular models reveal that in the stretched (all-*transoid*) conformation the dendrimers discussed here have a maximum length up to 7.3 nm (valid for **14**). However, the flexibility of their structures permits backfolding and coiling. In particular intramolecular [$\pi^2$s+$\pi^2$s] cycloadditions of the stilbene units seem to be possible. Thus, the efficiency of intermolecular C–C bond formations on irradiation is diminished in comparison to rigid stilbenoid dendrimers.[11f,h] Nevertheless, photocrosslinking is still the major process in long-term irradiations.

## 3. Conclusion

Poly(propylene imine) [PPI] dendrimers of first and second generation were prepared by condensation reactions of the parent PPIs and 4-styrylbenzaldehyde **3a** or 4-[4-(styryl)styryl]benzaldehyde **7**. The obtained azomethines can be subsequently or in situ hydrogenated with $LiAlH_4$ to the corresponding secondary amines. Thus, PPI dendrimers with four (*E*)-stilbene (**9**, **10**), four or eight (*E*,*E*)-distyrylbenzene (**11**, **14**) chromophores were obtained. Their long wavelength absorption bands and their fluorescence bands disappear completely on long-term irradiation. Apart form the primary $E \rightarrow Z$ isomerization of **9** and **10**, and the secondary $E \rightarrow Z$ isomerization of **11** and **14**, the predominant photoreaction is a crosslinking by C–C bond formations, which lead to oligomers.

## 4. Experimental

### 4.1. General

Melting points were determined on a Büchi 510 melting point apparatus and are uncorrected. The UV/vis spectra were obtained with a Zeiss MCS 320/340 and the fluorescence spectra with a Perkin–Elmer LS 50B spectrometer. The $^1$H and $^{13}$C NMR spectra were recorded with the Bruker spectrometers AMX 400 and ARX 400. The mass spectra were obtained on a Finnigan MAT 95 (FD and EI techniques) and on a Shimadzu AXIMA-CFR (MALDI-TOF) spectrometer. The FTIR spectra were measured with a Perkin–Elmer GX/200 spectrometer.

**4.1.1. (*E*)-4-(3,4,5-Tripropoxystyryl)benzaldehyde (3a).** A slow Ar stream was purged through a suspension of 3.87 g (34.0 mmol) $KOC(CH_3)_3$ in 75 mL dry THF at 0 °C, before a degassed solution of 5.81 g (14.0 mmol) diethyl 3,4,5-tripropoxybenzylphosphonate (**1**) and 3.19 g (15.0 mmol) 4-(diethoxymethyl)benzaldehyde (**2a**) in 45 mL dry THF was added dropwise. The formation of the ylide was indicated by an orange color. After 12 h stirring under Ar at ambient temperature, the mixture was refluxed for 1 h, poured on crushed ice, and treated with 300 mL $CHCl_3$ and 100 mL diluted HCl. After 3 h stirring at room temperature, the organic layer was separated, washed with $NaHCO_3$ and $H_2O$, dried with $MgSO_4$, and evaporated. Recrystallization from petroleum ether (bp 40–70 °C) furnished 4.48 g **3a**. Compared to a previous procedure,[11k] the yield could be improved from 66 to 84%. The pale yellow solid melted at 62 °C and was identified by comparison with an authentic sample. Anal. Calcd for $C_{24}H_{30}O_4$ (382.5): C 75.36, H 7.91; found: C 75.32, H 7.84.

**4.1.2. Methyl (*E*)-4-(3,4,5-tripropoxystyryl)benzoate (3b).** According to the preparation of **3a**, the reaction of **1** (11.26 g, 28.0 mmol) and methyl 4-formylbenzoate (**2b**) (4.92 g, 30.0 mmol) was performed. After 1 h reflux the crude reaction product was recrystallized from acetone. Yield 5.04 g (43%), yellowish solid, mp 96 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 1.03 (t, 1H, $CH_3$), 1.05 (t, 6H, $CH_3$), 1.76 (m, 2H, $CH_2$), 1.84 (m, 4H, $CH_2$), 3.89 (s, 3H, $CO_2CH_3$), 3.95 (t, 2H, $OCH_2$), 3.98 (t, 4H, $OCH_2$), 6.72 (s, 2H, aromat. H), 6.98/7.09 (AB, 2H, $^3J=16.4$ Hz, olefin. H), 7.52/7.99 (AA′BB′, 4H, aromat. H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 10.6, 10.6 ($CH_3$), 22.8, 23.5 ($CH_2$), 52.0 ($OCH_3$), 70.8, 75.1 ($OCH_2$), 105.5, 126.1, 129.9 (aromat. CH), 126.5, 131.4 (olefin. CH), 131.3, 131.9, 138.8, 141.9, 153.3 (aromat. $C_q$), 166.9 (CO); FD MS: *m*/*z* (%) 412 (100) [$M^{+\bullet}$]. Anal. Calcd for $C_{25}H_{32}O_5$ (412.5): C 72.79, H 7.82; found: C 72.67, H 7.69.

**4.1.3. (*E*)-4-(3,4,5-Tripropoxystyryl)benzyl alcohol (4).** Ester **3b** (5.01 g, 12.1 mmol), dissolved in 25 mL dry THF, was treated with $LiAlH_4$ (413 mg, 10.9 mmol) at 0 °C. After refluxing for 3 h, the reaction was stopped with 10 mL $H_2O$ and the mixture neutralized with HCl (10%). The organic layer was washed with 25 mL $H_2O$ and the water phase was extracted with 25 mL diethyl ether. The unified organic layers were dried with $MgSO_4$ and evaporated. Column filtration (8×20 cm $SiO_2$, $CH_2Cl_2$) yielded 3.87 g (83%) of a beige solid, which melted at 90 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 1.02 (t, 1H, $CH_3$), 1.05 (t, 6H, $CH_3$), 1.76 (m, 2H, $CH_2$), 1.83 (m, 4H, $CH_2$), 3.94 (t, 2H, $OCH_2$), 3.97 (t, 4H, $OCH_2$), 4.67 (s, 2H, $CH_2OH$), 6.70 (s, 2H, aromat. H), 6.95/6.98 (AB, 2H, $^3J=16.4$ Hz, olefin. H), 7.32/7.46 (AA′BB′, 4H, aromat. H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 10.6, 10.6 ($CH_3$), 22.7, 23.5 ($CH_2$), 65.1 ($CH_2OH$), 70.8, 75.1 ($OCH_2$), 105.3, 126.5, 127.4 (aromat. CH), 127.3, 128.9 (olefin. CH), 132.5, 136.8, 138.3, 140.1, 153.3 (aromat. $C_q$); EI MS: *m*/*z* (%) 384 (100) [$M^{+\bullet}$], 342 (71), 209 (62), 181 (44), 165 (42), 152 (60). Anal. Calcd for $C_{24}H_{32}O_4$ (384.5): C 74.97, H 8.39; found: C 74.81, H 8.38.

**4.1.4. (*E*)-4′-Bromomethyl-3,4,5-tripropoxystilbene (5).** To a solution of **4** (3.78 g, 9.8 mmol) in 60 mL toluene, $PBr_3$ (1.50 g, 5.6 mmol) was added dropwise at 0 °C. After 30 min at 0 °C and 2 h stirring at 25 °C, 15 mL $H_2O$ was added. The organic layer was washed with $NaHCO_3$ and $H_2O$, dried with $MgSO_4$, and evaporated. Crystallization from toluene yielded 3.82 g (87%) of a pale yellow solid, which melted at 81 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 1.03 (t, 1H, $CH_3$), 1.06 (t, 6H, $CH_3$), 1.76 (m, 2H, $CH_2$), 1.85 (m, 4H, $CH_2$), 3.96 (t, 2H, $OCH_2$), 3.99 (t, 4H, $OCH_2$), 4.50 (s, 2H, $CH_2Br$), 6.71 (s, 2H, aromat. H), 6.95/7.01 (AB, 2H, $^3J=16.3$ Hz, olefin. H), 7.36/7.45 (AA′BB′, 4H, aromat. H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 10.6, 10.6 ($CH_3$), 22.8, 23.5 ($CH_2$), 33.6 ($CH_2Br$), 70.8, 75.1 ($OCH_2$), 105.4, 126.7, 129.4 (aromat. CH), 126.9, 129.7 (olefin. CH), 132.3, 136.8, 137.7, 138.6, 153.3 (aromat. $C_q$); FD MS: *m*/*z* (%) 447/449 (100) [$M^{+\bullet}$, Br isotope pattern]. Anal. Calcd for $C_{24}H_{31}BrO_3$ (447.4): C 64.43, H 6.98; found: C 64.45, H 7.02.

**4.1.5. Diethyl (*E*)-4-(3,4,5-tripropoxystyryl)benzyl phosphonate (6).** Triethyl phosphite (20.0 g, 120 mmol) and bromo compound **5** (3.82 g, 8.5 mmol) were heated to 150–155 °C for 2 h. The generated bromoethane was continuously distilled off. At the end of the quantitative reaction 4.28 g viscous yellow oil remained, which was analytically pure. $^1H$ NMR ($CDCl_3$): $\delta$ 1.01 (t, 1H, $CH_3$), 1.04 (t, 6H, $CH_3$), 1.22 (t, 6H, $CH_3$ of ethyl), 1.75 (m, 2H, $CH_2$), 1.82 (m, 4H, $CH_2$), 3.12 (d, 2H, $^2J=21.7$ Hz, $PCH_2$), 3.97 (m, 10H, $OCH_2$ and $P(O)OCH_2$), 6.68 (s, 2H, aromat. H), 6.92/6.95 (AB, 2H, $^3J=16.4$ Hz, olefin. H), 7.26/7.41 (AA′BB′, 4H, aromat. H); $^{13}C$ NMR ($CDCl_3$): $\delta$ 10.5, 10.6 ($CH_3$), 16.3 (d, $^3J$(CP)=6.8 Hz, $CH_3$), 22.7, 23.5 ($CH_2$), 33.6 (d, $^1J$(CP)=137.9 Hz, $PCH_2$), 62.1 (d, $^3J$(CP)=6.8 Hz, $P(O)OCH_2$), 70.7, 75.1 ($OCH_2$), 105.3, 126.5 (d, $^4J$(CP)=3.4 Hz), 130.5 (d, $^3J$(CP)=6.8 Hz) (aromat. CH), 127.2, 128.8 (olefin. CH), 130.7, 132.5, 136.1 (d, $^2J$(CP)=4.5 Hz), 138.3, 153.3 (aromat. $C_q$); FD MS: *m*/*z* (%) 505 (100) [$M^{+\bullet}$]. Anal. Calcd for $C_{28}H_{41}O_6P$ (504.6): C 66.65, H 8.19; found: C 66.71, H 8.17.

**4.1.6. (*E*,*E*)-4-[4-(3,4,5-tripropoxystyryl)styryl]benzaldehyde (7).** According to the procedure described for **3a**, 4.15 g (8.2 mmol) **6**, 1.84 g (8.8 mmol) **2a** and 1.38 g (12.3 mmol) $KOC(CH_3)_3$ furnished an orange solid, which was purified by column filtration (12×7 cm $SiO_2$, toluene/diethyl ether gradient) and recrystallized from cyclohexane. Yield 1.86 g (47%), mp 154 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 1.03 (t, 1H, $CH_3$), 1.05 (t, 6H, $CH_3$), 1.74 (m, 2H, $CH_2$), 1.84 (m, 4H, $CH_2$), 3.95 (m, 2H, $OCH_2$), 3.97 (m, 4H, $OCH_2$), 6.72 (s, 2H, aromat. H), 6.96/7.03 (AB, 2H, $^3J=16.2$ Hz, olefin. H), 7.12/7.23 (AB, 2H, $^3J=16.2$ Hz, olefin. H), 7.49/7.52 (AA′BB′, 4H, aromat. H, central benzene ring), 7.63/7.84 (AA′BB′, 4H, aromat. H), 9.97 (s, 1H, CHO); $^{13}C$ NMR ($CDCl_3$): $\delta$ 10.5, 10.6 ($CH_3$), 22.7, 23.5 ($CH_2$), 70.7, 75.1 ($OCH_2$), 105.3, 126.7, 126.8, 127.3, 130.2 (aromat. CH), 126.9, 127.0, 129.4, 131.7 (olefin. CH), 132.3, 135.2, 135.6, 137.6, 138.5, 143.4, 153.3 (aromat. $C_q$), 191.5 (CHO); FD MS: *m*/*z* (%) 485 (100) [$M^{+\bullet}$]. Anal. Calcd for $C_{32}H_{36}O_4$ (484.6): C 79.31, H 7.49; found: C 79.33, H 7.58.

### 4.2. Preparation of the dendrimers 9, 10, 11, and 14

Astramol DAB-Am-4® (**8**, 0.316 g, 1.0 mmol) or Astramol DAB-Am-8® (**12**, 0.381 g, 0.5 mmol) and the corresponding aldehyde **3a** or **7** in a ratio of 1:6 for **8** and 1:20 for **12** were mixed in 10 mL dry THF. The solvent was evaporated and the mixture heated at 0.1 kP to 70 °C in order to remove completely the generated $H_2O$. After 0.5–1 h the viscous residue, which contained **9**, was recrystallized from ethanol. The hydrogenation **9**→**10** could be performed in situ with the raw product, which was dissolved in 15 mL dry THF, cooled to 0 °C and treated with $LiAlH_4$ (285 mg, 7.5 mmol). After refluxing for 8 h, 16 mL $H_2O$ was added. The Li complex decomposed and the residue was extracted in a Soxhlet apparatus with 250 mL diethyl ether. The volatile parts were removed in the vacuum and the crude **10** purified by column filtration (8×8 cm $SiO_2$, $CH_2Cl_2$ followed by $H_3C{-}CO{-}CH_3$, followed by $CH_3OH/N(C_2H_5)_3$ 10:1). The dendrimers **11** and **14** were obtained by the one-pot procedure. The same procedure applied for **12** and **3a** yielded instead of pure **13** a mixture of dendrimers with incomplete reaction of the eight amino groups. Due to the light sensibility of all resulting dendrimers the entire procedure had to be carried out in the dark for each dendrimer.[25]

**4.2.1. Dendrimer 9: all-(*E*)-4-cascade: 1,4-diaminobutane[4-*N*,*N*,*N*′,*N*′]: (2-azapent-1-enylidene)-1-[5-(1′,4′-phenylenevinylene-1,2,3-tripropoxybenzene)].** Yield 1.15 g (65%) yellowish crystals, which melted at 92 °C. IR (KBr): $\nu$ [cm$^{-1}$] 3024, 2962, 2935, 2873, 1641, 1602, 1581, 1503, 1463, 1433, 1387, 1338, 1230, 1121, 959, 825. FD MS *m*/*z* (%) 1775 (75) [M$^+$], 1353 (25), 915 (100), 861 (44), 761 (23), 550 (45), 491 (75).

**4.2.2. Dendrimer 10: all-(*E*)-4-cascade: 1,4-diaminobutane[4-*N*,*N*,*N*′,*N*′]: (2-azapentylidene)-1-[5-(1′,4′-phenylenevinylene-1,2,3-tripropoxybenzene)].** Yield 0.94 g (53%) yellowish oil. IR (KBr): $\nu$ [cm$^{-1}$] 3435, 3020, 2963, 2936, 2875, 2804, 1585, 1506, 1461, 1436, 1382, 1338, 1233, 1118, 961, 829. FD MS *m*/*z* (%) 1785 (100) [M$^+$], 893 (13) [M$^{2+}$].

**4.2.3. Dendrimer 11: all-(*E*)-4-cascade: 1,4-diaminobutane[4-*N*,*N*,*N*′,*N*′]: (2-azapentylidene)-1-[5-(1′,4′-phenylenevinylene-1″,4″-phenylenevinylene-1,2,3-tripropoxybenzene)].** Yield 0.92 g (42%) yellowish waxy solid. FTIR (KBr): $\nu$ [cm$^{-1}$] 3436, 3024, 2963, 2935, 2876, 1576, 1558, 1540, 1507, 1430, 1374, 1121, 1098, 1002, 961, 864, 826, 742, 537. FD MS *m*/*z* (%) 2195 (100) [M$^+$], 1098 (92) [M$^{2+}$].

**4.2.4. Dendrimer 14: all-(*E*)-8-cascade: 1,4-diaminobutane[4-*N*,*N*,*N*′,*N*′]: (1-azabutylidene)[4-*N*″,*N*″,*N*‴,*N*‴]: (2-azapentylidene)-1-[5-(1′,4′-phenylenevinylene-1″,4″-phenylenevinylene-1,2,3-tripropoxybenzene)].** Yield 2.02 g (45%) yellowish waxy solid. FTIR (KBr): $\nu$ [cm$^{-1}$] 3434, 3024, 2962, 2935, 2876, 1636, 1577, 1506, 1431, 1374, 1121, 1003, 961, 866, 748, 538. $^1$H NMR (CDCl$_3$): $\delta$ 1.02 (t, 24H, CH$_3$), 1.03 (t, 48H, CH$_3$), 1.41 (br m, 4H, CH$_2$), 1.60 (br m, 16H, CH$_2$), 1.76 (m, 16H, CH$_2$), 1.83 (m, 32H, CH$_2$), 2.40 (br s, 36H, NCH$_2$), 2.59 (br s, 16H, NCH$_2$), 3.70 (s, 16H, NCH$_2$), 3.93 (t, 16H, OCH$_2$), 3.96 (t, 32H, OCH$_2$), 6.69 (s, 16H, aromat. H terminal benzene rings), 6.93/6.99 (AB, $^3J$=15.8 Hz, 16H, olefin. H), 6.99/7.05 (AB, $^3J$=15.8 Hz, 16H, olefin. H), 7.23–7.50 (m 64H, aromat. H); $^{13}$C NMR (CDCl$_3$): $\delta$ 10.6, CH$_3$/23.4, CH$_2$/75.1, OCH$_2$ (*p*-OC$_3$H$_7$), 10.6, CH$_3$/22.8, CH$_2$/70.7, OCH$_2$ (*m*-OC$_3$H$_7$), 27.5, 29.7, 29.7 (CH$_2$), 48.2, 52.3, 53.9 (NCH$_2$, partly superimposed), 105.3, 126.5, 126.7, 126.8, 128.5 (aromat. CH), 127.2, 127.8, 128.2, 128.7 (olefin. CH), 132.5, 136.0, 136.5, 136.7, 140.1 (aromat C$_q$), 138.4, 153.3 (aromat. C$_q$O).[26]

## 4.3. Irradiation conditions

The irradiation experiments, discussed in Section 2.2, were performed in $10^{-5}$ M degassed solutions in CHCl$_3$ or CH$_2$Cl$_2$. For the $^1$H NMR measurements $10^{-3}$–$10^{-4}$ M solutions in CD$_2$Cl$_2$ were used. A Xe high-pressure lamp (Osram XBO, 1000 W) or a Hg medium-pressure lamp (Hanovia, 450 W) was applied as radiation source. Interference filters (366, 340, 313, 254 nm) or a Pyrex filter ($\lambda \geq 300$ nm) served for the selection of the desired wavelengths. The reaction times, given in the diagrams, are related to unfiltered radiation.

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## References and notes

1. See for example: (a) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons: Concepts, synthesis, Applications*; Wiley-VCH: Weinheim, 2001; (b) Fréchet, J. M. J.; Tomalia, D. A. *Dendrimers and Other Dendritic Polymers*; Wiley: New York, NY, 2001.
2. (a) Soomro, S. A.; Schulz, A.; Meier, H. *Tetrahedron* **2006**, *62*, 8089; (b) Ong, W.; McCarley, R. L. *Org. Lett.* **2005**, *7*, 1287; (c) Vögtle, F.; Fakhrnabavi, H.; Lukin, O.; Mueller, S.; Friedhofen, J.; Schalley, C. A. *Eur. J. Org. Chem.* **2004**, *22*, 4717; (d) Vicinelli, V.; Ceroni, P.; Maestri, M.; Lazzari, M.; Balzani, V.; Lee, S.-K.; van Heyst, J.; Vögtle, F. *Org. Biomol. Chem.* **2004**, *2*, 2207; (e) Ceroni, P.; Vicinelli, V.; Maestri, M.; Balzani, V.; Gorka, M.; Lee, S.-K.; Dragut, P.; Vögtle, F. *Collect. Czech. Chem. Commun.* **2003**, *68*, 1541; (f) Frerot, E.; Herbal, K.; Herrmann, A. *Eur. J. Org. Chem.* **2003**, *6*, 967; (g) Lee, J. W.; Ko, Y. H.; Park, S.-H.; Yamaguchi, K.; Kim, K. *Angew. Chem.* **2001**, *113*, 769; *Angew. Chem., Int. Ed.* **2001**, *40*, 746; (h) Baars, M. W. P. L.; Kleppinger, R.; Koch, M. H. J.; Yeu, S.-L.; Meijer, E. W. *Angew. Chem.* **2000**, *112*, 1341; *Angew. Chem., Int. Ed.* **2000**, *39*, 1285; (i) Baars, M. W. P. L.; Soentjens, S. H. M.; Fischer, H. M.; Peerlings, H. W. I.; Meijer, E. W. *Chem.—Eur. J.* **1998**, *4*, 2456.
3. (a) Smith, G.; Chen, R.; Mapolie, S. *J. Organomet. Chem.* **2003**, *673*, 111; (b) Volkova, N. N.; Tarasov, E. V.; Kodess, M. I.; Van Meervelt, L.; Dehaen, W.; Bakulev, V. A. *Org. Biomol. Chem.* **2003**, *1*, 4030; (c) Christensen, J. B.; Nielsen, M. F.; van Haare, J. A. E. H.; Baars, M. W. P. L.; Janssen, R. A. J.; Meijer, E. W. *Eur. J. Org. Chem.* **2001**, *11*, 2123; (d) Klein, G.; Robertus, J. M.; Bosman, A. W.; Feiters, M. C.; Meijer, E. W.; Nolte, R. J. M. *Chem.—Eur. J.* **1999**, 65.
4. (a) Heuzé, K.; Méry, D.; Gauss, D.; Blais, J.-C.; Astruc, D. *Chem.—Eur. J.* **2004**, *10*, 3936; (b) Jones, J. W.; Bryant, W. S.; Bosman, A. W.; Janssen, R. A. J.; Meijer, E. W.; Gibson, H. W. *J. Org. Chem.* **2003**, *68*, 2385; (c) Engel, G. D.; Gode, L. H. *Chem.—Eur. J.* **2002**, *8*, 4319; (d) Stephan, H.; Spies, H.; Johannsen, B.; Gloe, K.; Gorka, M.; Vögtle, F. *Eur. J. Inorg. Chem.* **2001**, *11*, 2957.
5. Boas, U.; Karlsson, A.; de Waal, B. F. M.; Meijer, E. W. *J. Org. Chem.* **2001**, *66*, 2136.
6. (a) Saltiel, J.; Sun, Y.-P. *Photochromism, Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 2003; (b) Liu, R. S. H. *Acc. Chem. Res.* **2001**, *34*, 555; (c) Görner, H.; Kuhn, H. J. *Adv. Photochem.* **1995**, *19*, 1; (d) Arai, T.; Tokumaru, K. *Chem. Rev.* **1993**, *93*, 23; (e) Meier, H. *Angew. Chem.* **1992**, *104*, 1425; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1399; (f) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415; (g) Mazzucato, U.; Momicchioli, F. *Chem. Rev.* **1991**, *91*, 1679.
7. Selected newer publications: (a) Onagi, H.; Belke, C. J.; Easton, C. J.; Lincoln, S. F. *Chem.—Eur. J.* **2003**, *9*, 5978; (b) Tokunaga, Y.; Akasaka, K.; Hisada, K.; Shimomura, Y.; Kakuchi, S. *Chem. Commun.* **2003**, 2350; (c) Gracia, H. *Pure Appl. Chem.* **2003**, *75*, 1085; (d) Stanier, C. A.; Alderman, S. J.; Claridge, T. D. W.; Anderson, H. L. *Angew. Chem.* **2002**, *114*, 1847; *Angew. Chem., Int. Ed.* **2002**, *41*, 1769; (e) Jin, S.-H.; Kim, S.-H.; Gal, Y.-S. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 4025; (f) Sànchez, C.; Villacampa, B.; Alcalà, R.; Martinez, C.; Oriol, L.; Piñol, M.; Serrano, J. L. *Chem. Mater.*

**1999**, *11*, 2804; (g) Strashnikova, N.; Papper, V.; Parkhomyuk, P.; Likhtenshtein, G. I.; Ratner, V.; Marks, R. *J. Photochem. Photobiol., A: Chem.* **1999**, *122*, 133; (h) Grabchev, I.; Philipova, T. *Angew. Makromol. Chem.* **1998**, *263*, 1.

8. Meier, H.; Lehmann, M. *Encyclopedia of Nanoscience and Nanotechnology*; Nalwa, H. S., Ed.; American Scientific: Stevenson Ranch, USA, 2004; Vol. 10, p 95.
9. (a) Watanabe, S.; Ikegami, M.; Nagaheta, R.; Arai, T. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 586; (b) Miura, Y.; Momotake, A.; Shinohara, Y.; Wahadoszamen, M.; Nishimura, Y.; Arai, T. *Tetrahedron Lett.* **2007**, *48*, 639; (c) Nishimura, Y.; Kamada, M.; Ikegami, M.; Nagahata, R.; Arai, T. *J. Photochem. Photobiol., A: Chem.* **2006**, *178*, 150; (d) Momotake, A.; Hayakawa, J.; Nagahata, R.; Arai, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1195; (e) Momotake, A.; Arai, T. *J. Photochem. Photobiol., C: Photochem. Rev.* **2004**, *5*, 1; (f) Gutierrez-Nava, M.; Accorsi, G.; Masson, P.; Armaroli, N.; Nierengarten, J.-F. *Chem.—Eur. J.* **2004**, *10*, 5076; (g) Momotake, A.; Uda, M.; Arai, T. *J. Photochem. Photobiol., A: Chem.* **2003**, *158*, 7; (h) Tatewaki, H.; Mizutani, T.; Hayakawa, J.; Arai, T.; Terazima, M. *J. Phys. Chem. A* **2003**, *107*, 6515; (i) Hayakawa, J.; Momotake, A.; Arai, T. *Chem. Commun.* **2003**, 94; (j) Hayakawa, J.; Momotake, A.; Arai, T. *Chem. Lett.* **2003**, *32*, 1008; (k) Uda, M.; Momotake, A.; Arai, T. *Org. Biomol. Chem.* **2003**, *1*, 1635; (l) Uda, M.; Mizutani, T.; Hayakawa, J.; Momotake, A.; Ikegami, M.; Nagahata, R.; Arai, T. *J. Photochem. Photobiol.* **2002**, *76*, 596; (m) Imai, M.; Arai, T. *Tetrahedron Lett.* **2002**, *43*, 5265; (n) Mizutani, T.; Ikegami, M.; Nagahata, R.; Arai, T. *Chem. Lett.* **2001**, 1014.
10. (a) Drobizhev, M.; Karotki, A.; Kruk, M.; Dzenis, Y.; Rebane, H.; Meng, F.; Nickel, E.; Spangler, C. W. *Proc. SPIE-Int. Soc. Opt. Eng.* **2003**, *5211*, 63; (b) Spangler, C. W.; Suo, Z.; Drobizhev, M.; Karotki, A.; Rebane, H. *NATO Science Series, II: Math., Phys., Chem.* **2003**, *100*, 139; (c) Beavington, R.; Frampton, M. J.; Lupton, J. M.; Burn, P. L.; Samuel, I. D. W. *Adv. Funct. Mater.* **2003**, *13*, 211; (d) Pålsson, L.-O.; Beavington, R.; Frampton, M. J.; Lupton, J. M.; Magennis, S. W.; Markham, J. P. J.; Pillow, J. N. G.; Burn, P. L.; Samuel, I. D. W. *Macromolecules* **2002**, *35*, 7891; (e) Guldi, D. M.; Swartz, A.; Luo, C.; Gómez, R.; Segura, J. L.; Martín, N. *J. Am. Chem. Soc.* **2002**, *124*, 10875; (f) Langa, F.; Gómez-Escalonilla, J. M.; Díez-Barra, E.; García-Martínez, J. C.; de la Hoz, A.; Rodriguez-López, J.; González-Cortés, A.; López-Arza, V. *Tetrahedron Lett.* **2001**, *42*, 3435; (g) Segura, J. L.; Gómez, R.; Martín, N.; Luo, C.; Swartz, A.; Guldi, D. M. *Chem. Commun.* **2001**, 707; (h) Burn, P. L.; Beavington, R.; Frampton, M. J.; Pillow, J. N. G.; Halim, M.; Lupton, J. M.; Samuel, I. D. W. *Mater. Sci. Eng., B: Solid-State Mater. Adv. Technol.* **2001**, *85*, 190; (i) Lupton, J. M.; Samuel, I. D. W.; Beavington, R.; Burn, P. L.; Bässler, H. *Synth. Met.* **2001**, *116*, 357; *Adv. Mater.* **2001**, *13*, 258; (j) Díez-Barra, E.; García-Martínez, J. C.; Rodriguez-López, J.; Goméz, R.; Segura, J. L.; Martín, N. *Org. Lett.* **2000**, *2*, 3651; (k) Halim, M.; Pillow, J. N. G.; Samuel, I. D. W.; Burn, P. L. *Adv. Mater.* **1999**, *11*, 371; (l) Pillow, J. N. G.; Halim, M.; Lupton, J. M.; Burn, P. L.; Samuel, I. D. W. *Macromolecules* **1999**, *32*, 5985; (m) Díez-Barra, E.; García-Martínez, J. C.; Rodriguez-López, J. *Tetrahedron Lett.* **1999**, *40*, 8181.
11. (a) Rosenfeldt, S.; Karpuk, E.; Lehmann, M.; Meier, H.; Lindner, P.; Harnau, L.; Ballauff, M. *Chem. Phys. Chem.* **2006**, *7*, 2097; (b) Lehmann, M.; Köhn, C.; Meier, H.; Renker, S.; Oelhof, A. *J. Mater. Chem.* **2006**, *16*, 141; (c) Soomro, S. A.; Benmouna, R.; Berger, R.; Meier, H. *Eur. J. Org. Chem.* **2005**, 3586; (d) Uda, M.; Momotake, A.; Arai, T. *Tetrahedron Lett.* **2005**, *46*, 3021; (e) Momotake, A.; Arai, T. *Polymer* **2004**, *45*, 5369; (f) Lehmann, M.; Fischbach, I.; Spiess, H. W.; Meier, H. *J. Am. Chem. Soc.* **2004**, *126*, 772; (g) Segura, J. L.; Goméz, R.; Martín, N.; Guldi, D. M. *Org. Lett.* **2001**, *3*, 2645; (h) Meier, H.; Lehmann, M.; Kolb, U. *Chem.—Eur. J.* **2000**, *6*, 2462; (i) Petermann, R.; Schnorpfeil, C.; Lehmann, M.; Fetten, M.; Meier, H. *J. Inf. Recording* **2000**, *25*, 259; (j) Meier, H.; Lehmann, M.; Schnorpfeil, C.; Fetten, M. *Mol. Cryst. Liq. Cryst.* **2000**, *352*, 85; (k) Lehmann, M.; Schartel, B.; Hennecke, M.; Meier, H. *Tetrahedron* **1999**, *55*, 13377; (l) Meier, H.; Lehmann, M. *Angew. Chem.* **1998**, *110*, 666; *Angew. Chem., Int. Ed.* **1998**, *37*, 643; (m) Deb, S. K.; Maddux, T. M.; Yu, L. *J. Am. Chem. Soc.* **1997**, *119*, 9079.
12. Schenning, A. P. H. J.; Peeters, E.; Meijer, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 4489.
13. Such procedures for the extension of stilbenoid chains have often been successfully used; see for example Refs. 14–16.
14. Armaroli, N.; Accorsi, G.; Clifford, J. N.; Eckert, J.-F.; Nierengarten, J.-F. *Chem. Asian J.* **2006**, *1*, 564.
15. Gutiérrez-Nava, M.; Jaeggy, M.; Nierengarten, H.; Masson, P.; Guillon, D.; Van Dorsselaer, A.; Nierengarten, J.-F. *Tetrahedron Lett.* **2003**, *44*, 3039.
16. The olefinic AB spin patterns of the (*Z*)-configurations can be found in the range of 6.6±0.3 ppm. The (*Z*)-isomer of **3a** has for example the AB pattern at 6.62 and 6.52 ppm with $^3J$=12.1 Hz and a singlet for the protons on the alkoxy-substituted benzene ring at 6.38 ppm. The latter signal is particularly useful for the detection of traces of the (*Z*)-isomer.
17. Meier, H. *Angew. Chem.* **2005**, *117*, 2536; *Angew. Chem., Int. Ed.* **2005**, *44*, 2482.
18. Lewis, F. D.; Wu, T.; Burch, E. L.; Bassani, D. M.; Yang, J.-S.; Schneider, S.; Jäger, W.; Letsinger, R. L. *J. Am. Chem. Soc.* **1995**, *117*, 8785.
19. Song, X.; Geiger, C.; Farahat, M.; Perlstein, J.; Whitten, D. G. *J. Am. Chem. Soc.* **1997**, *119*, 12481.
20. Lewis, F. D. *Acc. Chem. Res.* **1986**, *19*, 401 and references therein.
21. Meier, H.; Kretzschmann, H.; Lang, M. *J. Prakt. Chem.* **1994**, *336*, 297.
22. Mamane, V.; Hannen, P.; Fürstner, A. *Chem.—Eur. J.* **2004**, *10*, 4556.
23. Mervič, M.; Ghera, E. *J. Org. Chem.* **1980**, *45*, 4720.
24. Sandros, K.; Sundahl, M.; Wennerström, O.; Norinder, U. *J. Am. Chem. Soc.* **1990**, *112*, 3082.
25. Careful drying in the vacuum did not lead to complete evaporation of water. Therefore exact elemental analyses could not be obtained for the dendrimers **9**, **10**, **11**, and **14**.
26. A correct mass spectrum, which contains the molecular ion, could not be obtained (FD MS, ESI, MALDI-TOF).