Preparation and Photochemistry of Dendrimers with Isolated Stilbene Chromophores

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Dedicated to Professor Rolf-Christian Schulz on the occasion of his 85th birthday

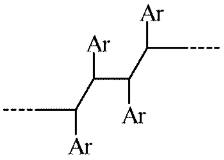
Keywords: Crosslinking / Cyclization / Dendrimers / Isomerization

In addition to the model compounds **4a** and **4b**, the dendrimers **11** and **14** with *trans*-stilbene chromophores in the core and on the periphery of the dendrons were prepared and their photochemistry was studied in solution and in neat films. Due to the flexibility of the arms, *intramolecular* and *intermolecular* CC bonds are formed on irradiation. Thus, the generation of nanoparticles, which represent small oligomers, is much more likely than for the cross-linking of rigid, cross-conjugated stilbenoid dendrimers. The photoreactions in solution were studied by UV and NMR spectroscopy, the transformation of the films was studied by AFM.

Introduction

Cross-conjugated *trans*-stilbene units represent the building blocks for various dendritic systems.[1] Some time ago, we prepared five generations of stilbenoid dendrimers with 9 to 144 alkoxy chains attached to the peripheral benzene rings.[2,3] Two generations of related dendrimers with dibutylamino groups have been obtained as well.[4] Various systems with (*E*,*E*)-1,4-distyrylbenzene or (*E*,*E*,*E*)-1,3,5-tristyrylbenzene units were studied.[5–9] Moreover, one has to mention stilbenoid dendrimers with special cores like N,[10,11] anthracene,[8] binaphthyl[12] or porphyrin.[8] In some fullerodendrimers, C_{60} was attached to the focal position of two-arm stilbenoid dendrimers.[13–15] Recently dendrimers with an oligo(1,4-phenylenevinylene) core and 2, 4 or 8 fullerene groups on the periphery were studied.[16]

Irradiation of (*E*)-stilbene chromophores can lead to four photoreactions, namely *E*/*Z* isomerization, [π^6a] cyclization, [π^2s + π^2s] cyclodimerization and polymerization (statistical CC bond formation, crosslinking).[17] The latter two processes are also relevant for 1,4-distyrylbenzene chromophores.[17] The crosslinking can be applied for imaging processes and negative photoresist techniques, because the soluble compounds become insoluble in organic solvents, as soon as a certain degree of crosslinking is reached. Stilbenoid dendrimers with many (*E*)-stilbene units exhibit a fast and efficient statistical CC bond formation (Scheme 1) on irradiation with energy-rich UV light (λ = 254 nm).[1a,3,18] This leads very soon to insoluble particles of big size.



Scheme 1. Photocrosslinking of stilbenoid materials.

We are trying now to diminish *intermolecular* CC bond formations by competing *intramolecular* processes so that nanoparticles of smaller oligomers of stilbenoid dendrimers are formed by irradiation. The present article deals with the investigation of dendrimers (**11**, **14**), which have still a high density of (*E*)-stilbene chromophores, but contain so flexible dendrons, that intramolecular CC bond formations can occur.

Results and Discussion

Synthesis

In order to study the influence of benzyloxymethyl substituents on the photochemical behaviour of (*E*)-stilbene, we synthesized first the compound **4a** by NBS bromination of 4,4′-dimethylstilbene (**1**) and nucleophilic replacement of the bromine by the reaction with benzyl alcohol (**3a**) (Scheme 2). The solid product had a rather low solubility in

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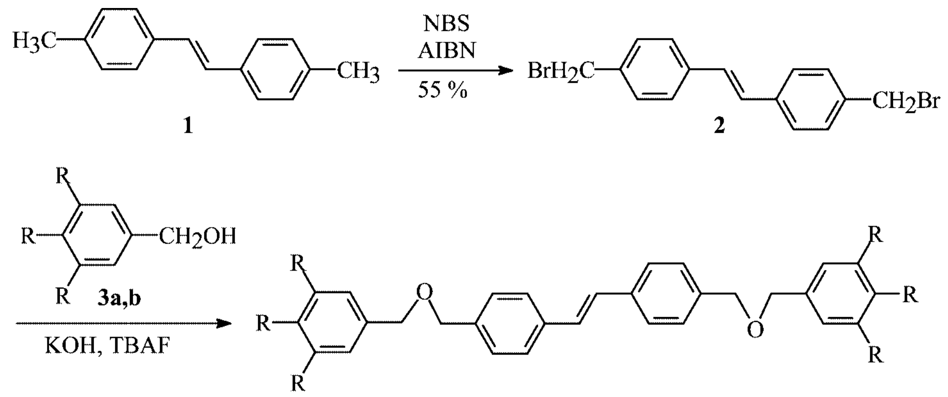
DOI: 10.1002/ejoc.200500185



4	a	b
R	H	OCH3
Yield [%]	40	45

Scheme 2. Preparation of the model compounds **4a**, **b**.

organic solvents. Therefore we took 3,4,5-trimethoxybenzyl alcohol (**3b**) and prepared the well soluble derivative **4b**.

Scheme 3 summarizes the preparation of the dendrimer **11** (first generation). 3,4,5-Trimethoxybenzaldehyde (**5**) was transformed by a Wittig–Horner reaction with phosphonate **6** to yield the stilbene derivative **7**. Wohl–Ziegler bromination furnished monobromide **8** together with some dibromide. Chemoselective alkylation of the phenolic OH groups in **9** by the reaction with **8** in the presence of K_2CO_3 and 18-crown-6 gave the alcohol **10**, which then was coupled to **2** by applying phase transfer conditions.[19] The crystalline dendrimer **11** and its precursors **2**, **7**, **8** and **10** have *trans*-configured double bonds. The limit of detection for the *cis* configuration is lower than 5% in NMR spectroscopy.

The preparation of dendrimer **14** of second generation is summarized in Scheme 4. Williamson ether synthesis of **2** and **9** yielded tetraphenol **12**. Alcohol **10** was subjected to Appel bromination with CBr_4 and PPh_3. The obtained bromide **13** yielded the target compound **14** by fourfold coupling with **12**.

The model compounds **4a**,**b** and the dendrimers **11** and **14** were characterized in detail by ^1H and ^{13}C NMR spectroscopy. For example, Figure 1 shows the exact assignment of the signals of **4b**, which was obtained by the 2D techniques HMQC and HMBC.

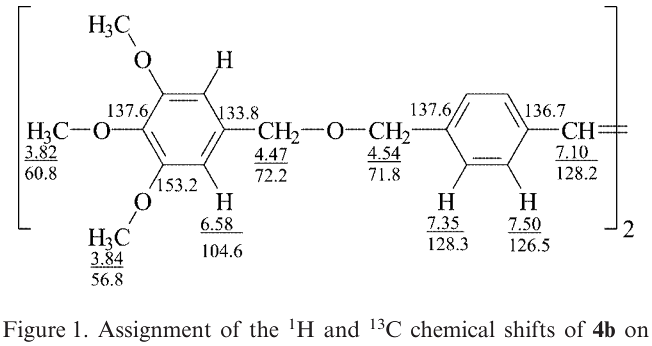


Figure 1. Assignment of the ^1H and ^{13}C chemical shifts of **4b** on the basis of HMQC and HMBC measurements.

Photochemistry

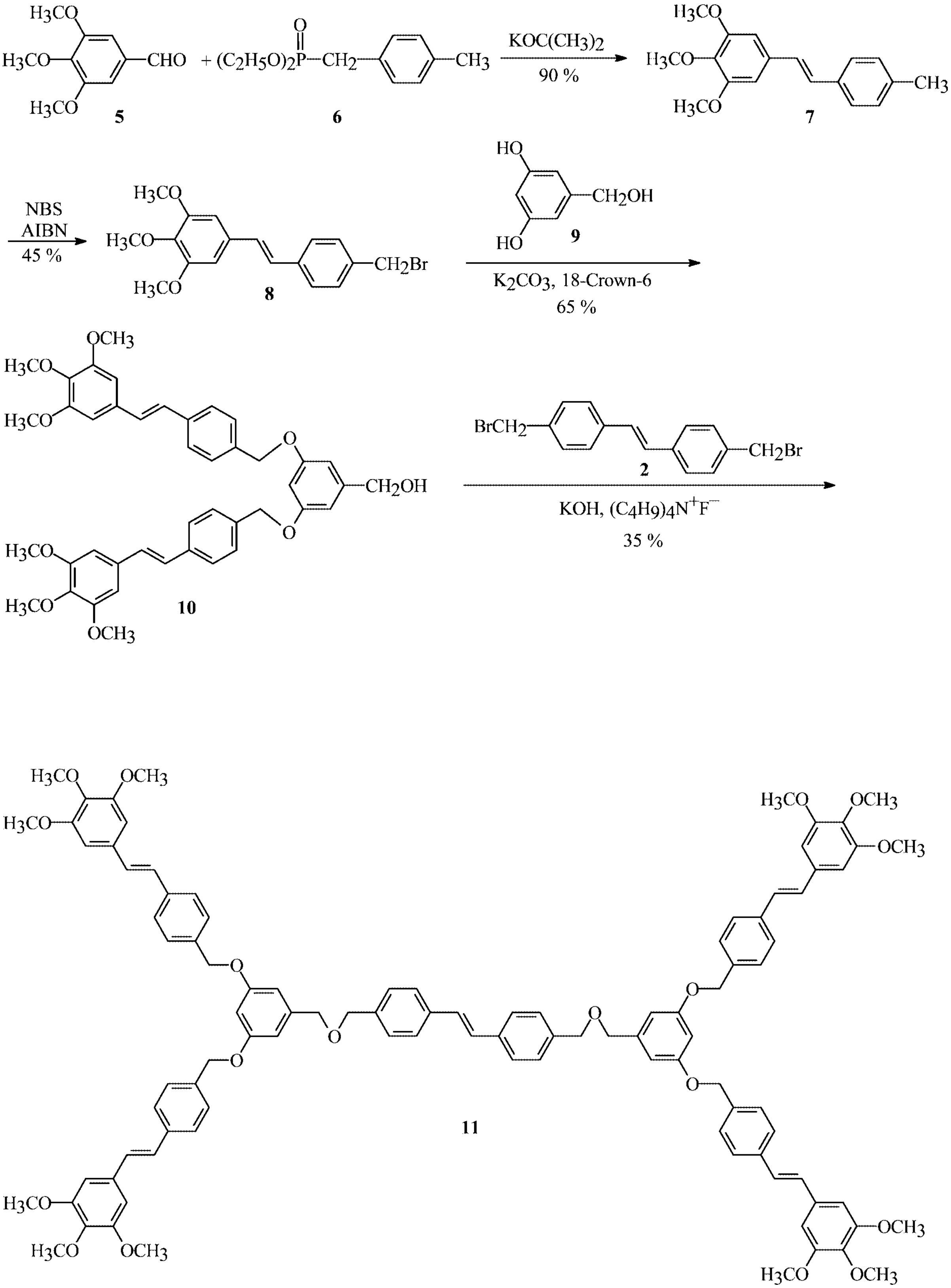
The photochemistry of the model compound **4b** and the dendrimers **11** and **14** were studied in solution as well as in thin films. The absorption bands of spin-coated films are broader and somewhat red-shifted in comparison to solution measurements. A very strong bathochromic shift between solution (λ_{max} = 363 nm) and film (λ_{max} = 512 nm) was observed for the fluorescence of **4b**. We attribute this result to the emission of excimers/aggregates. Dendrimer **11** exhibits this effect to a smaller extent ($\Delta\lambda$ = 74 nm) and dendrimer **14** to an even smaller ($\Delta\lambda$ = 19 nm). The enhanced number of flexible chain segments decreases interactions of the type of *J* aggregates. Table 1 summarizes the observed absorption and emission maxima.

Table 1. Absorption and emission of the model compound **4b** and the dendrimers **11** and **14** in CH_2Cl_2 and in neat films.

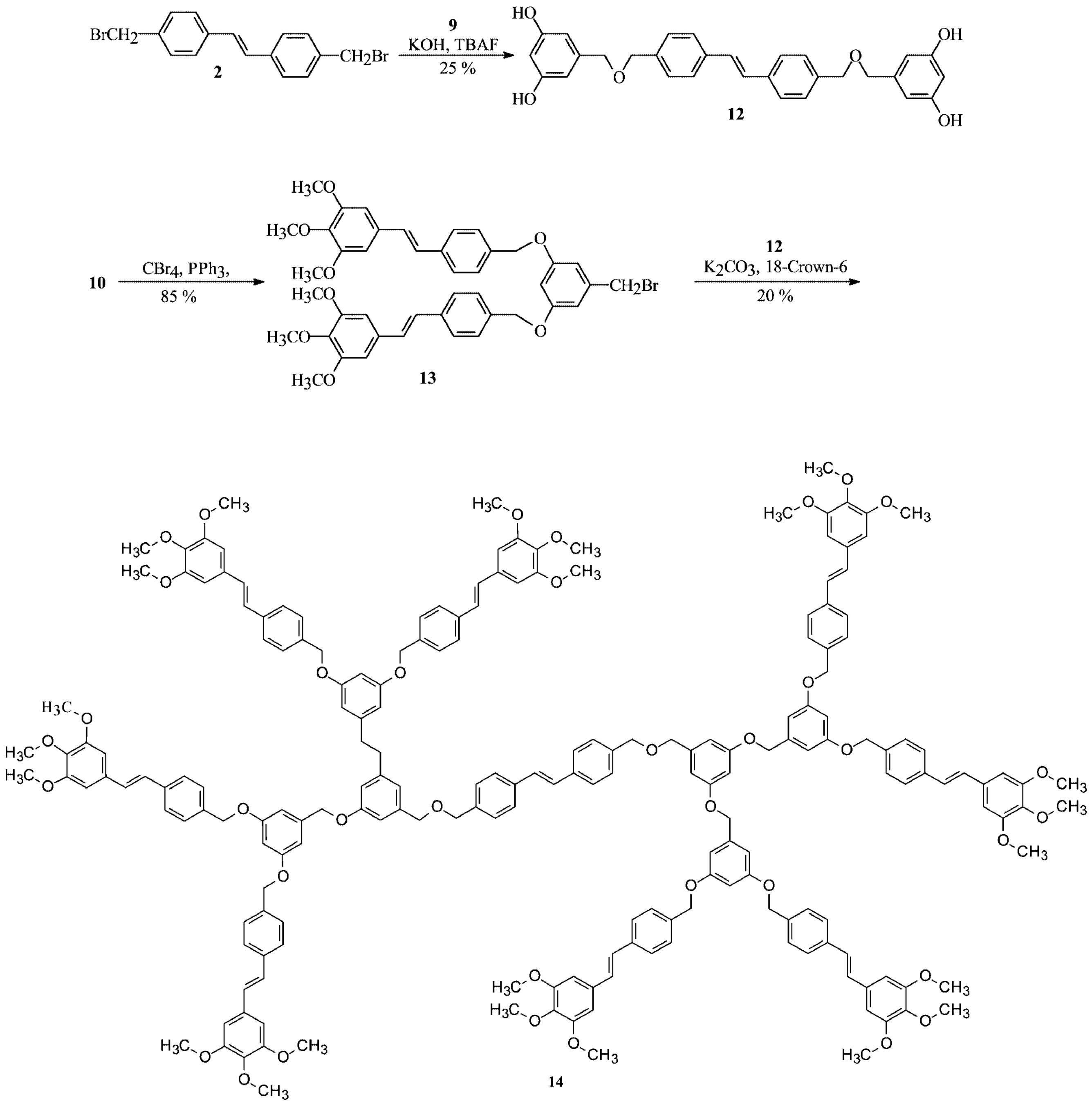
	Absorption (λ_{max} in nm)[a]			Fluorescence[b] (λ_{max} in nm)		
	CH_2Cl_2	film	$\Delta\lambda$	CH_2Cl_2	film	$\Delta\lambda$
4b	312	319	7	363	512	149
11	314	328	14	403	477	74
14	325	341	16	405	424	19

[a] Excitation and absorption spectra differ only slightly (singlet energy transfer). [b] Excitation at the λ_{max} values of the absorption.

The model compound **4b** is a mono-stilbene which shows on monochromatic irradiation (λ = 340 nm) in CH_2Cl_2 a *trans* → *cis* isomerization. Since the absorbance of the *cis* isomers is negligable at this wavelength, the photostationary state corresponds to an almost pure *cis* configuration, when diluted solutions ($\leq 10^{-4}$ M) in CH_2Cl_2 are irradiated. Apart from the shift of λ_{max} = 312 nm of the (*E*)-configuration to about 274 nm for the (*Z*)-configuration, typical new singlet signals for the olefinic protons appear at δ = 6.60 in the ^1H NMR spectrum. Irradiations in more concentrated solutions ($\geq 10^{-3}$ M) exhibit the disappearance of the absorption of the stilbene chromophore and new ^{1}H NMR signals appear at $\delta = 4.56$ for saturated protons on a tertiary carbon atom (CH). The $[\pi^2 s + \pi^2 s]$cyclodimerization is accompanied by statistical cross-linking processes – particularly when energy-rich UV light (λ = 254 nm) is used.[17,18] The solubility of the material decreases constantly during such an illumination. A mass spectroscopical determination of the oligomers proved to be very difficult. The MALDI-



Scheme 3. Preparation of the stilbenoid dendrimer **11**.



Scheme 4. Preparation of the stilbenoid dendrimer **14**.

TOF technique is not very suitable for the identification of the corresponding oligomers. Only the mass of the dimer could be detected when Ag^+ ions were added (m/z = 1307/1309 for $[C_{72}H_{80}AgO_{16}]^+$ ions).

Monochromatic irradiation (λ = 340 nm) of the dendrimers **11** and **14** in diluted solution (10^{-5} M to 10^{-8} M) in CH_2Cl_2 shows a characteristic decrease of the band which is typical for the inherent (*E*)-stilbene chromophores (Table 1). Figure 2 illustrates the reaction spectra of the irradiation of a $3{\cdot}10^{-8}$ M solution of **14** in CH_2Cl_2. The (*E*)-configured stilbene chromophores are predominantly transformed to their (*Z*)-configuration. According to ^1H NMR measurements a photostationary state is reached which contains less than 10% (*E*)-isomer.

Irradiation ($\lambda \geq 260$ nm) of **11** or **14** in more concentrated solutions ($\geq 10^{-3}$ M) yielded monomers and oligomers with broad ^1H and ^{13}C NMR signals. The odd number of olefinic double bonds in **11** and **14** guarantees that a full degradation of the stilbene chromophores cannot be achieved by exclusively intramolecular processes. Thus,

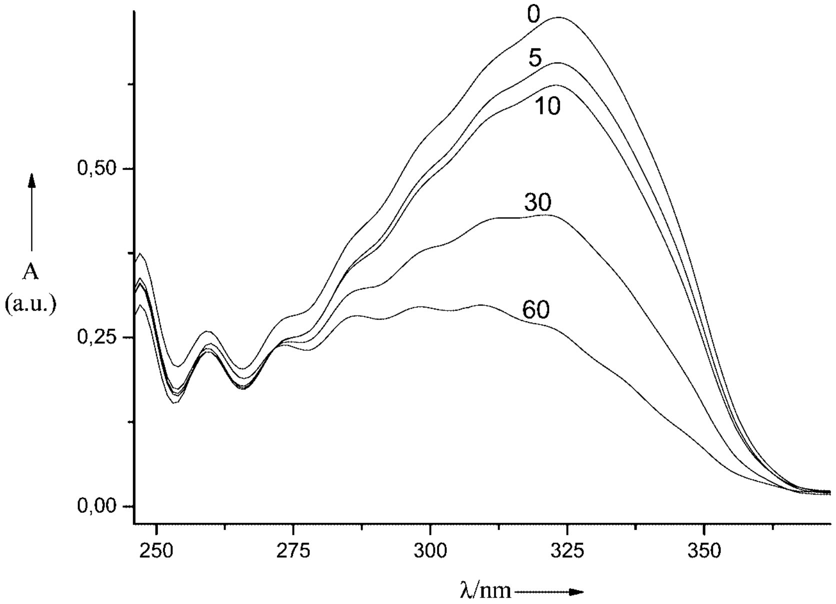


Figure 2. Reaction spectra (0, 5, 10, 30 and 60 s) of the monochromatic irradiation (λ = 340 nm) of a $3 \cdot 10^{-8}$ M solution of **14** in CH_2Cl_2.

the generation of oligomers is taken for granted. Typical ^1H NMR signals for methine protons appeared at $4.1 \leq \delta \leq 4.6$ as broad superimposed multiplets. According to earlier results on stilbene photocrosslinking,[17,18] these signals are owing to concerted [$\pi^2 s + \pi^2 s$] cycloadditions and to statistical CC bond formations.

Intramolecular [2π + 2π] photocycloadditions can occur between all olefinic double bonds of **11** and **14**; however, the highest probability has the formation of a four-membered ring within one dendron. Figure 3 depicts the result of a forcefield calculation MMX of 1,3-bis(4-vinylbenzyloxy)benzene which can serve as a model. The head-to-head *syn* process (upper part) and the head-to-tail *syn* addition (lower part) have the lowest steric energies; the latter one should proceed via a less favourable excimer formation.[17] Nevertheless, we assume that also all other possible generations of four-membered rings as well as statistical crosslinkings are involved.

The irradiation ($\lambda \leq 340$ nm) of a spin coated film of **11** was studied by atomic force microscopy (AFM). Figure 4 (part a) shows the film surface before irradiation. The surface is rather smooth. A cross sectional image contains peaks with a height below 1 nm. A short irradiation of 3 s, however, causes unexpected roughness (Figure 4, part b). The cross-section reveals peaks of up to 35 nm height (Figure 4, part d). This corresponds to an oligomer of at least 9 monomer units if we assume a maximum extension by head-to-tail cycloadditions of peripheral double bonds. The real number of involved monomers is certainly much higher, since we have to postulate here a statistical CC bond formation as well. The solubility of the material decreases more and more during the irradiation. After 1 h the film has again a smooth surface (Figure 4c). The cross-sectional im-

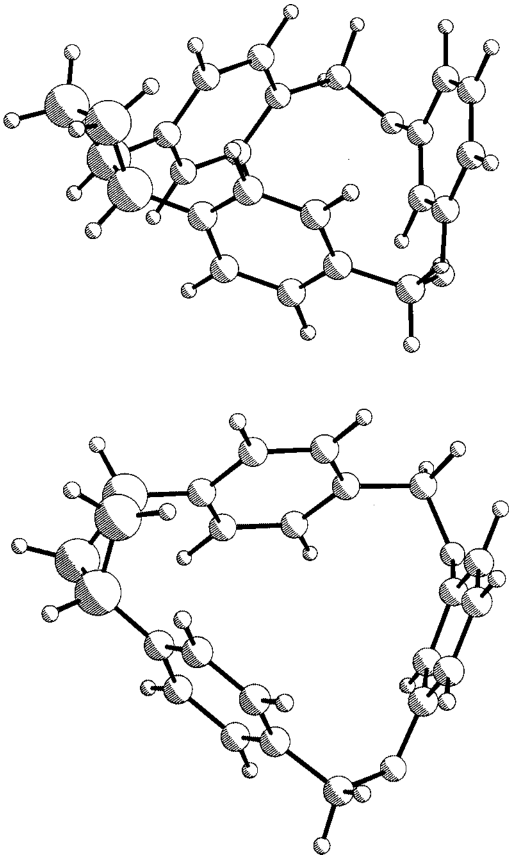


Figure 3. MMX calculation of the intramolecular [2π + 2π] cycloadducts of 1,3-bis(4-vinylbenzyloxy)benzene. Upper part: *syn* head-to-head adduct (ΔH_f = 8.5 kcal · mol^{-1}, strain energy *SE* = 47.0 kcal · mol^{-1}); lower part: *syn* head-to-tail adduct (ΔH_f = 9.9 kcal · mol^{-1}, *SE* = 47.6 kcal · mol^{-1}). Calculation with Serena Software 1998 on the basis of standard bondlengths.

age is similar to that before the irradiation. Some "elevations" remain, but their height is below 10 nm. This status represents the crosslinked material.

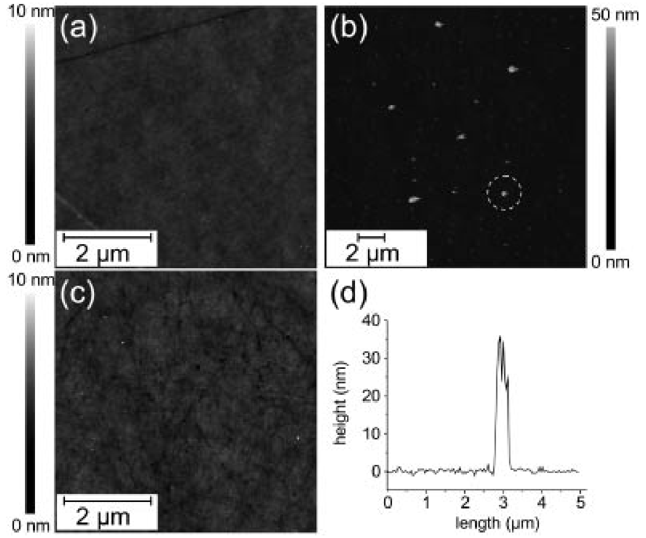


Figure 4. AFM topography picture of the irradiation of a neat film of **11**. (a): Smooth surface before irradiation (root mean square roughness RMS = 0.29 nm); (b): Rough surface (RMS = 1.44 nm) after 3 s irradiation (λ = 340 nm); (c): Surface after 1 h irradiation, which is smoothened by photo-crosslinking (RMS = 0.43 nm). The *z*-scale of each image is shown as well; (d): Line profile along the surface of the elevation (35 nm height) indicated by the dashed white circle in (b).

Conclusions

The newly synthesized dendrimers **11** and **14** contain (*E*)-stilbene chromophores in the core and in the dendrons. The irradiation of **11** and **14** (as well as the irradiation of the model compound **4b**) leads to two typical photoreactions, namely *E*/*Z* isomerizations and intra- and intermolecular CC bond formations. The latter process, which can be used as photocrosslinking, predominates in concentrated solutions ($\geq 10^{-3}$ M) when energy-rich UV light is used.

The irradiation of spin coated films of **11** was studied by AFM measurements. The UV light causes first a strong increase of the roughness of the surface (peaks of up to 35 nm height), before the progressive crosslinking leads again to a relatively smooth surface.

Experimental Section

General: Melting points were determined with an SMP/3 apparatus from Stuart Scientifique and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded with Bruker AC-300 and AMX-400 spectrometers. $CDCl_3$ was used as solvent and TMS as internal standard. Mass spectra were obtained with a Finnigan MAT-95 instrument with the field desorption techniques (FD). UV/Vis spectra were measured with a Zeiss MCS-320/340 spectrometer.

(*E*)-4,4′-Bis(benzyloxymethyl)stilbene (4a): (*E*)-4,4′-Dimethylstilbene (**1**), obtained by McMurry reaction from 4-methylbenzaldehyde,[20] was brominated by NBS in CCl_4 in the presence of azobis(isobutyronitrile) (AIBN). After refluxing for 6 h (*E*)-4,4′-bis(bromomethyl)stilbene (**2**) was obtained in a yield of 55% (88%[20]) as colorless crystals which melted at 176–178 °C. ^{1}H NMR ($CDCl_3$): δ = 7.48/7.35 (AA′BB′, 8 H, aromat. H), 7.07 (s, 2 H, olefin. H), 4.49 (s, 4 H, CH_2). ^{13}C NMR ($CDCl_3$): δ = 137.3, 137.2 (aromat. C_q), 129.5, 126.9 (aromat. CH), 128.7 (olefin. CH), 33.4 (CH_2Br).

Benzyl alcohol (**3a**) [0.40 g, 3.7 mmol], **2** [0.60 g, 1.8 mmol], KOH [0.23 g, 4.25 mmol] and catalytic amounts of tetrabutylammonium fluoride (TBAF) were refluxed in 25 mL chlorobenzene for 3 h. The mixture was filtered and the solvent evaporated under reduced pressure. The residue was dissolved in 50 mL CH_2Cl_2; 25 mL H_2O and diluted HCl were added until the aqueous phase was slightly acidic. After vigorous shaking, the organic layer was separated, washed with 50 mL H_2O and 50 mL brine, dried with $MgSO_4$ and filtered through SiO_2 (3 × 30 cm). The product **4a** (0.136 g, 40%, light yellow wax) could be eluted with cyclohexane/ethyl acetate 80:20. ^{1}H NMR ($CDCl_3$): δ = 7.51 (AA′ of AA′BB′, 4 H, aromat. H), 7.35 (m, 14 H, aromat. H), 7.10 (s, 2 H, olefin. H), 4.55 ("s", 8 H, CH_2). ^{13}C NMR ($CDCl_3$): δ = 138.2, 137.7, 136.8, (aromat. C_q), 128.4, 128.3, 128.2, 127.8, 127.7, 126.5 (aromat. and olefin. CH), 72.1, 71.8 (CH_2). FD MS: *m*/*z* (%) = 392 (100, $M^{+\cdot}$).

(*E*)-4,4′-Bis(3,4,5-trimethoxybenzyloxymethyl)stilbene (4b): The preparation of **4b** was accomplished according to the procedure described for **4a** – solely the reaction temperature was kept at 60 °C for 24 h. A yellowish glass was obtained in a yield of 45%. ^{1}H NMR ($CDCl_3$): δ = 7.50 (AA′ of AA′BB′, 4 H, aromat. H), 7.35 (BB′, 4 H, aromat. H), 7.10 (s, 2 H, olefin. H), 6.58 (s, 4 H, aromat. H, outer benzene rings), 4.54 (s, 4 H, inner CH_2), 4.47 (s, 4 H, outer CH_2), 3.84 (s, 12 H, OCH_3), 3.82 (s, 6 H, OCH_3). ^{13}C NMR ($CDCl_3$): δ = 153.2, 137.6, 137.6, 136.7, 133.9 (aromat. C_q), 128.3, 128.2, 126.5, 104.6 (aromat. and olefin. CH), 72.2, 72.0 (OCH_2), 60.8, 56.8 (OCH_3). FD MS: *m*/*z* (%) = 601 (100, [M + H^+].

(*E*)-3,4,5-Trimethoxy-4′-methylstilbene (7): The preparation was performed by the reaction of **5** and **6** according to the literature;[21] yield 90% (81%[21]), m.p. 125–127 °C. ^{1}H NMR ($CDCl_3$): δ = 7.42, 7.31 (AA′BB′, 4 H, aromat. H), 7.16, 6.97 (AB, ^{3}J = 16.5 Hz, 2 H, olefin. H), 3.90 (s, 6 H, OCH_3), 3.85 (s, 3 H, OCH_3), 2.34 (s, 3 H, CH_3).

(*E*,*E*)-3,5-Bis{4[2-(3,4,5-trimethoxyphenyl)ethenyl]benzyloxy}benzyl Alcohol (10): Wohl–Ziegler bromination of the methyl group of **7** was achieved according to a method described in the literature.[21] Yield of **8** 45% (66%[21]), m.p. 107 °C. ^{1}H NMR ($CDCl_3$): δ = 7.46, 7.36 (AA′BB′, 4 H, aromat. H), 7.03, 6.97 (AB, ^{3}J = 16.5 Hz, 2 H, olefin. H), 6.72 (s, 2 H, aromat. H), 4.49 (s, 2 H, CH_2Br), 3.90 (s, 6 H, OCH_3), 3.85 (s, 3 H, OCH_3).

The recrystallized compound **8** (m.p. 107 °C from toluene) was directly used for the preparation of **10**. A mixture of 13.96 g (38.4 mmol) **8**, 2.45 g (17.4 mmol) of 3,5-dihydroxybenzyl alcohol[22] **9**, 5.5 g (40.0 mmol) K_2CO_3 and catalytic amounts of 18-crown-6 were refluxed in acetone under nitrogen for 24 h. The filtered mixture was evaporated under reduced pressure, the residue dissolved in CH_2Cl_2, washed with water (3 × 50 mL) and brine (50 mL), dried with $MgSO_4$ and purified by column chromatography on SiO_2 (4 × 40 cm). A mixture of cyclohexane and ethyl acetate with a gradient from 95:5 to 10:90 served for the elution. A yellow glass was obtained (17.6 g, 65%), which was analytically pure **10**. ^{1}H NMR ($CDCl_3$): δ = 7.49, 7.38 (AA′BB′, 4 H, aromat. H), 6.98, (AB, ^{3}J = 16.5 Hz, 4 H, olefin. H), 6.70 (s, 4 H, aromat. H), 6.61 (d, ^{4}J = 2.1 Hz, 2 H, aromat. H), 6.50 (t, ^{4}J = 2.1 Hz, 1 H, aromat. H), 4.99 (s, 4 H, OCH_2), 4.60 (s, 2 H, CH_2O), 3.87 (s, 12 H, OCH_3), 3.83 (s, 6 H, OCH_3). ^{13}C NMR ($CDCl_3$): δ = 160.0, 153.4, 143.9, 138.0, 137.0, 136.2, 133.0 (aromat. C_q), 128.9, 127.9, 127.7, 126.6, 105.6, 103.7, 101.2 (aromat. and olefin. CH), 69.8, 64.9 (OCH_2), 60.9, 56.1 (OCH_3). FD MS: *m/z* (%) = 704 (100, $M^{+\cdot}$). $C_{43}H_{44}O_9$ (704.8): calcd. C 73.28, H 6.29; found C 73.54, H 6.34.

Preparation of the Dendrimer 11 (First Generation) [*all*-(*E*)-4,4′-Bis{3,5-bis[4-(3,4,5-trimethoxystyryl)benzyloxy]benzyloxymethyl}-stilbene (11): A mixture of **10** (300 mg, 0.426 mmol), **2** (60 mg, 0.164 mmol), KOH (230 mg, 4.10 mmol) and catalytic amounts of TBAF in chlorobenzene was heated to 60 °C for 24 h. The filtered solution was evaporated under reduced pressure and the residue dissolved in 100 mL CH_2Cl_2. After washing with 50 mL diluted HCl, the organic phase was washed with 50 mL water and 50 mL brine, dried with $MgSO_4$ and concentrated. The product was purified by colulmn chromatography (4 × 40 cm SiO_2, cyclohexane/ethyl acetate, 80:20). Dendrimer **11** (203 mg, 35%) was obtained as a light yellow wax. ^{1}H NMR ($CDCl_3$): δ = 3.85 (s, 12 H, OCH_3), 3.89 (s, 24 H, OCH_3), 4.49 (s, 4 H, OCH_2), 4.51 (s, 4 H, OCH_2), 5.03 (s, 8 H, OCH_2), 6.55 (t, ^4J = 1.8 Hz, 2 H, aromat. H), 6.67 (d, ^4J = 1.8 Hz, 4 H, aromat. H), 6.72 (s, 8 H, aromat. H), 7.01 (AB, ^3J = 16.1 Hz, 8 H, olefin. H), 7.07 (s, 2 H, olefin. H), 7.29–7.51 (m, 24 H, aromat. H). ^{13}C NMR ($CDCl_3$): δ = 56.1, 60.9 (OCH_3), 69.8, 71.8, 72.0 (OCH_2), 101.5, 103.6, 106.8, 126.5, 126.6, 127.7, 127.9, 128.2, 128.3, 128.9 (aromat. and olefin. CH), 132.9, 136.2, 136.7, 137.0, 137.6, 138.1, 140.8, 153.4, 160.0 (aromat. C_q). FD MS: *m/z* (%) = 1614 (100, $M^{+\cdot}$). $C_{102}H_{100}O_{18}$ (1613.9): calcd. C 75.91, H 6.25, O 17.84; found C 76.10, H 6.35.

Preparation of the Second Generation Dendrimer 14

(*E*)-4,4′-Bis(3,5-dihydroxybenzyloxymethyl)stilbene (12): Dibromide **2** (0.26 g, 0.72 mmol), KOH (0.23 g, 4.25 mmol) and catalytic amounts of TBAF were added to a solution of **9** (0.45 g, 1.45 mmol) in 25 mL chlorobenzene. After 24 h at 60 °C, the mixture was filtered and the solvent evaporated under reduced pressure. The residue was shaked for 6 h in a mixture of 50 mL CH_2Cl_2 and 25 mL diluted HCL. The two layers were separated and the aqueous phase extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with brine (50 mL), dried with $MgSO_4$ and concentrated. The product was purified by column chromatography (3.5 × 40 cm SiO_2, cyclohexane/ethyl acetate, 50:50). A yellowish oil was obtained (0.17 g, 25%). According to the ^{1}H NMR spectrum, it is pure enough for the subsequent reaction step. ^{1}H NMR (CD_3OD): δ = 7.55, 7.36 (AA′BB′, 8 H, aromatic H), 7.15 (s, 2 H, olefinic H), 6.37 ("s", 2 H, aromat. H), 6.27 ("s", 4 H, aromat. H), 4.52 (s, 4 H, OCH_2), 4.43 (s, 4 H, OCH_2).

(*E*,*E*)-3,5-Bis{4[2-(3,4,5-trimethoxyphenyl)ethenyl]benzyloxy}benzyl Bromide (13): Alcohol **10** (1.8 g, 2.55 mmol), CBr_4 (1.27 g, 3.80 mmol) and triphenylphosphane (1.0, 3.83 mmol) were stirred at room temperature in 50 mL THF for about 30 min. A colorless precipitate was formed. The process was quenched with 1 mL H_2O and the volatile parts removed in vacuo. The residue was dissolved in CH_2Cl_2, concentrated and poured into 250 mL diethyl ether. The precipitate, which consisted of triphenylphosphane oxide was removed and the organic phase concentrated. The product was purified by column chromatography (4 × 40 cm SiO_2, elution gradient of cyclohexane/ethyl acetate from 80:20 to 20:80). A yellowish solid (1.66 g, 85%) was obtained, which started to decompose above 90 °C. ^{1}H NMR ($CDCl_3$): δ = 7.48, 7.29 (AA′BB′, 8 H, aromatic H), 7.01, 6.99 (AB, ^3J = 16.5 Hz, 4 H, olefin. H), 6.67 (s, 4 H, aromat. H), 6.62 (d, ^4J = 2.1 Hz, 2 H, aromat. H), 6.56 (t, ^4J = 2.1 Hz, 1 H, aromat. H), 4.96 (s, 4 H, OCH_2), 4.47 (s, 2 H, CH_2Br). ^{13}C NMR ($CDCl_3$): δ = 160.1, 153.4, 139.6, 138.1, 137.1, 135.9, 133.0 (aromat. C_q), 129.0, 128.0, 127.6, 126.9, 107.7, 103.7, 102.1 (aromat. and olefin. CH), 69.9 (OCH_2), 60.9, 56.1 (OCH_3), 46.4 (CH_2Br). FD MS: *m/z* (%) = 769/767 (100, [M + H^+], Br isotope pattern). $C_{43}H_{43}BrO_8$ (767.7): calcd. C 67.27, H 5.65; found C 67.60, H 5.70.

Dendrimer 14 (Second Generation): A mixture of tetrahydroxy compound **12** (38 mg, 0.078 mmol), benzyl bromide **13** (240 mg, 0.312 mmol), K_2CO_3 (1100 mg, 8.0 mmol) and catalytic amounts of 18-crown-6 were refluxed in acetone under nitrogen for 24 h. The filtered mixture was evaporated under reduced pressure and the residue dissolved in 1000 mL CH_2Cl_2. The solution was washed with water (3 × 50 mL) and brine (50 mL), dried with $MgSO_4$ and concentrated. The product was purified by column chromatography (SiO_2, 4 × 40 cm, gradient cyclohexane/ethyl acetate, 90:10 to 10:90). The product was obtained as a waxy gum (200 mg, 20%). ^{1}H NMR ($CDCl_3$): δ = 7.52–7.30 (m, 40 H, aromat. H), 7.06 (m, 18 H, olefin. H), 6.72 (m, 16 H, aromat. H), 6.66–6.41 (m, 18 H, aromat. H), 4.98 (s, 16 H, OCH_2), 4.93 (s, 8 H, OCH_2), 4.58 (s, 4 H, inner OCH_2), 4.47 (s, 4 H, OCH_2), 3.89 (s, 48 H, OCH_3), 3.85 (s, 24 H, OCH_3). ^{13}C NMR ($CDCl_3$): δ = 160.1, 160.0, 153.4, 143.6, 139.4, 139.2, 138.0, 137.0, 136.0, 132.9 (aromat. C_q, partly superimposed), 128.9, 128.0, 127.6, 126.6, 126.0 (aromat. and olefin. CH, partly superimposed), 106.3, 105.7, 103.6, 101.6, 101.3 (aromat. CH), 77.3, 69.9, 65.2, 60.9 (OCH_2), 56.1, 54.9 (OCH_3). MS (MALDI-TOF, dithranol matrix, Ag^+): *m/z* (%) = 3339 (100 [M + Ag^+]).[23]

Irradiation Experiments: The UV/Vis measurements were performed with an AMCO LTI Xenon 1000 lamp and an interference filter (λ = 340 nm) in a Zeiss MCS-320/340 spectrometer. The irradiations for the NMR measurements were done with a 450-W Hanovia mercury medium-pressure lamp equipped with a Duran glass filter. A slow stream of Ar purged during the illumination through the solutions of **11** and **14** (about 10^{-2} M) in absolute CH_2Cl_2.

AFM Measurements: All samples have been prepared by using concentrations of 4 mg/L in toluene. In total 3–4 drops have been put on a rectangular quartz plate substrate with edge sizes of 1 cm and 4 cm. The substrate was heated to 200 °C and spin coating was performed at 2000 rpm. All images were recorded under ambient conditions by using a Dimension 3100 Atomic Force Microscope (AFM), which was connected to a NanoScope V controller. The scanner was equipped with a closed loop xy-feedback system. The quartz substrates were attached to the wafer chuck stage by using the vacuum fixture. For recording the topography of samples the AFM was operated in the tapping mode. For the measurements we used Olympus tapping mode cantilevers OMCL-AC160TS-W2 having an Al reflex coating (nominal resonance frequency 300 kHz and spring constant 42 N/m). The tip radius of curvature is typically less than 10 nm.

Acknowledgments

We are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the Center of Materials Science of the University of Mainz for financial support.

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Received: March 10, 2005