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Dendrimers with peripheral stilbene chromophores

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Abstract—Two types of dendritic nanoparticles were prepared, which contain (*E*)-stilbene chromophores in the terminal positions of the dendrons. The compounds showed a highly efficient photoreactivity in the course of which statistical CC bond formations led to a crosslinking of the particles. Finally, all stilbene chromophores reacted and the typical (*E*)-stilbene absorption and fluorescence disappeared completely.
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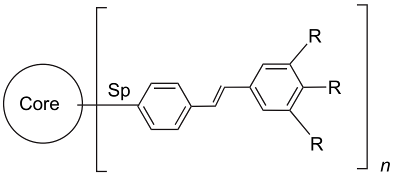
1. Introduction

The stilbene chromophore is a very useful building block for many applications in photochemistry since *E*/*Z* isomerization, [π^6a] cyclization, [π^2s+π^2s] cyclodimerization, and statistical CC bond formations (polymerization, crosslinking) offer various reaction possibilities in synthetic chemistry as well as in materials science.[1] A fast and efficient CC bond formation of stilbenoid compounds can be applied as basic process for imaging and photoresist techniques. A high density of stilbene chromophores on the periphery of dendritic particles is certainly a good precondition for this purpose. Scheme 1 visualizes the fundamental structure of such multi-arm or dendritic compounds in which (*E*)-stilbene chromophores are linked directly or via (saturated and possibly branched) spacers Sp to the core. Anthracene,[2] binaphthyl,[3] porphyrin,[2] and even various stilbenoid systems[4–15] were used as core for such systems.



1 (R = H, alkyl, alkoxy)

Scheme 1. Star-shaped compounds or dendrimers having (*E*)-stilbene chromophores linked by (branched) spacers Sp to the core.

When the absorption of the core chromophore ($S_0 \rightarrow S_1$) overlaps with the emission (deactivation) $S_1' \rightarrow S_0'$ of the (*E*)-stilbene chromophores one has to face an energy transfer (Förster mechanism), which competes with the photochemistry of the stilbene units. The majority of the before-mentioned systems[2–15] shows such processes, which can be avoided, when the absorption of the core lies far in the UV.[16] Amines as core are typical examples for the latter case.[17] We tried now to attach (*E*)-stilbene chromophores in terminal positions to propylene imine or benzene triester cores.

2. Results and discussion

The preparation of a dendrimer with (*E*)-stilbene chromophores fixed on an oligoamine core was based on 3,4,5-tripropoxybenzaldehyde (**2**),[12,18] *N*-(4-iodophenyl)-phthalimide (**3**),[19] and the commercially available amine DAB-Astramol Am-4® (**4**) (Scheme 2). Aldehyde **2** was transformed by a Wittig reaction to 3,4,5-tripropoxystyrene (**5**). A Heck coupling of **5** and iodo compound **3** yielded the stilbene derivative **6**, which was carefully purified by column chromatography. The pure (*E*)-isomer was then subjected to a hydrazinolysis **6**→**7**. The obtained aminostilbene **7** was finally transformed with bis(trichloromethyl)carbonate [triphosgene] to the red isocyanate **8**, which was directly added to amine **4**. A molar ratio **7**:**4** of 4.75:1 was used in order to achieve the complete fourfold coupling of the stilbene chromophore via urea functionalities to the core. The beige solid **9** was obtained in a yield of 93% related to **7**. It showed in the field desorption mass spectrum (FD MS) the expected peak for the [M+H$^+$] molecular ions at m/z=1900 (calculated m/z values for the peak group of [$C_{112}H_{156}N_{10}O_{16}$+H$^+$]: 1898–1903, maximum at 1899). The ^{1}H and ^{13}C NMR spectra of **9** revealed a uniform, symmetrical compound. So we are sure that all four NH_2 groups of **4** were transformed to NH–CO–NH tethers for the stilbene units. The detection limit for a by-product with less than four stilbene units is about 5%. Table 1 summarizes the ^{1}H and ^{13}C NMR data of the central ^{1}H and ^{13}C nuclei of **9**, compared to **4**. The signals listed in Table 1 are sharp for **4**, but, due to a restricted mobility broad for **9**. The signals of the stilbene units in **9** are sharp and well resolved.

Keywords: Crosslinking; Dendrimers; Photochemistry.

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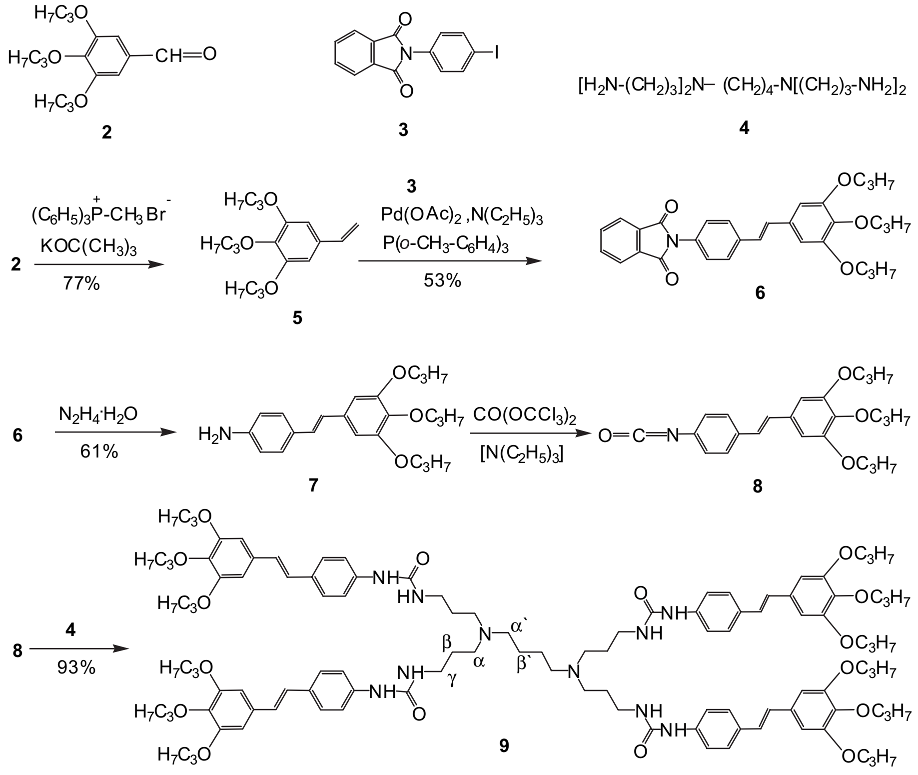


Scheme 2. Preparation of dendrimer **9**.

Scheme 3 shows the preparation of dendrimers of first generation, which have six (*E*)-stilbene chromophores. NBS bromination of the stilbenes **10a**,**b** led to **11a**,**b**,[5,20] which were used for the twofold benzylation of resorcinol **12** in the presence of K_2CO_3 and 18-crown-6.[5] The products **13a**,**b**, which are primary alcohols, reacted then with 1,3,5-benzenetricarboxylic acid trichloride (**14**) in the presence of 4-dimethylaminopyridine (DMAP) and triethylamine. High yields (90–70%) of the corresponding triesters **15a**,**b** were obtained. The mass spectra revealed the correct m/z values. A MALDI-TOF measurement (dithranol, Ag^+) of **15a** gave $m/z=1837$ (calculation for $[C_{120}H_{96}O_{12}+Ag^+]$ leads to a peak group with a maximum at $m/z=1837$). The FD MS spectroscopy of **15b** showed a molecular ion at $m/z=2268$ (calculated peak group maximum: $m/z=2269$). The base peak (100%) in the latter spectrum is owing to the doubly charged molecular ion M^{2+} ($m/z=1134$). The ^1H and ^{13}C NMR spectra of **15a**,**b** are in accordance with D_{3h} symmetry, that means with the attachment of three dendrons to the benzene core. The NMR data reveal constitutionally and configurationally pure dendrimers **15a**,**b**. The detection limit of a by-product with less than six stilbene units or with a (*Z*)-configured double bond is about 5%. Most typical for the threefold ester formation is the change of $^1H/^{13}C$ signals (δ values) of the central benzene ring from 9.02/135.5 for **14** to 8.91/131.3 for **15a** and 8.91/131.2 for **15b**.

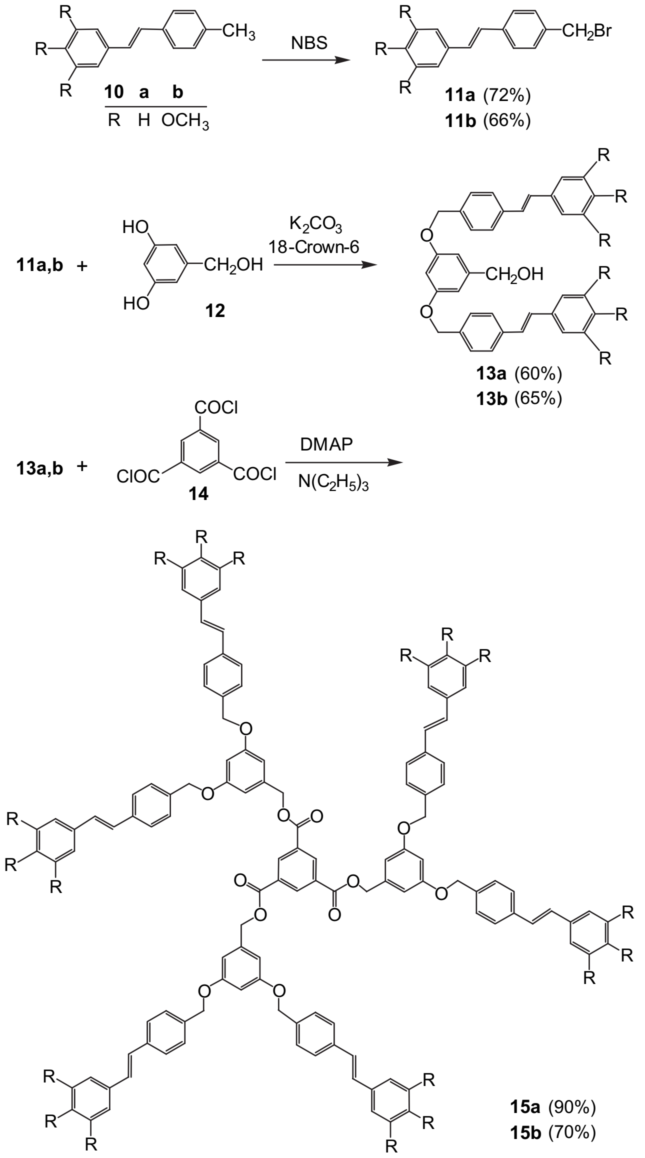
Table 1. ^1H and ^{13}C NMR data of **4** and the core of **9** (δ values in $CDCl_3$, related to TMS as internal standard)

Compound	NMR	α	β	γ	α′	β′
4	^1H	2.40	1.55	2.67	2.36	1.38
	^{13}C	51.1	28.8	39.5	53.4	23.9
9	$^1H^a$	2.8	1.6	3.2	2.7	1.5
	$^{13}C^a$	50.7	24.3	36.6	52.2	21.3

[a] Broad signals.

The long-wavelength absorption of dendrimer **9** shows a maximum at 342 nm ($\varepsilon=11.48\times10^4$ L mol^{-1} cm^{-1}). The fluorescence band of **9** has its maximum at 399 nm and overlaps with the absorption band in the range of the $0\rightarrow0$ transition at 370 nm (measurements in $CHCl_3$). Irradiation of a 1.1×10^{-5} M solution of **9** with the unfiltered light of a Xenon high-pressure lamp leads to a fast alteration of the absorption. Figure 1 shows that the band at 342 nm decreases and changes its shape because of the primary generation of (*Z*)-configured stilbene chromophores with a maximum at around 320 nm. A low-intensity maximum appears at 460 nm. More striking is the formation of a new maximum far in the visible range. We assign these new bands to quinoid species with a short half-life.[21,22] The band at $\lambda_{max}=614$ nm reaches the highest intensity after 15 s and disappears then with a half-life of about 100 s—too fast for an NMR study. Finally, all stilbene chromophores have participated in $[2\pi+2\pi]$photocycloaddition reactions and statistical CC bond formations. The crosslinking of the nanoparticles[23] occurs even much faster in more concentrated solutions.

Dendrimers **15a**,**b** behave similar to **9** on irradiation. Figure 2 demonstrates the degradation of the (*E*)-stilbene chromophores of **15a**. The original λ_{max} value of 316 nm decreases and a new maximum, assigned to the (*Z*)-configuration, appears at about 289 nm. Prolonged irradiation causes then the complete degradation of all stilbene chromophores.



Scheme 3. Preparation of dendrimers **15a**,**b**.

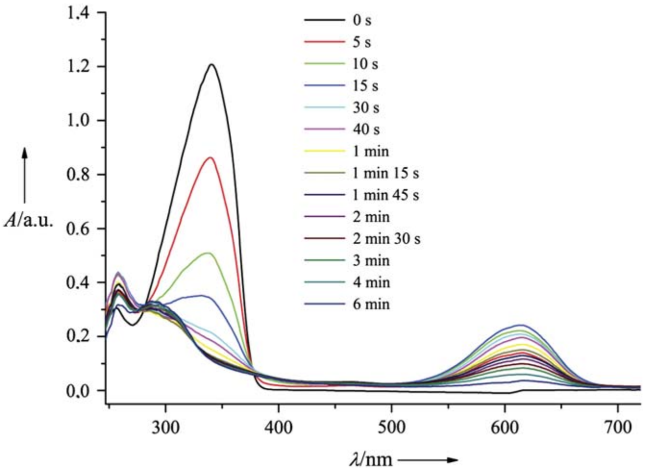


Figure 1. Reaction spectra of the irradiation of a 1.1×10^{-5} M solution of **9** in $CHCl_3$.

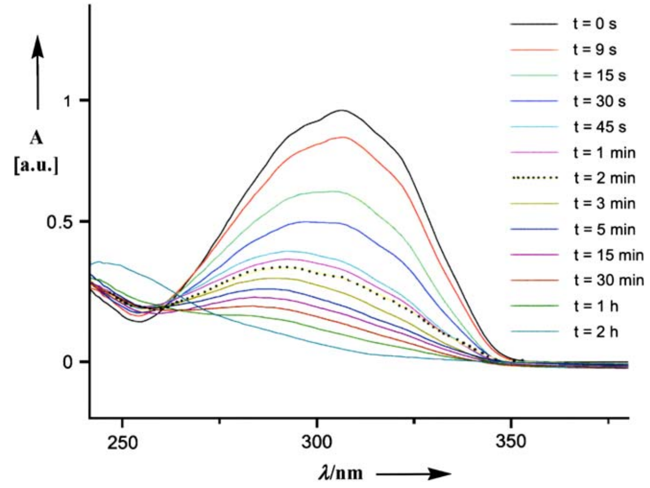
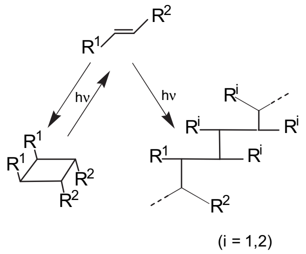


Figure 2. Photodegradation of **15a** in a 3×10^{-6} M solution in CH_2Cl_2 performed by irradiation with monochromatic light (λ=320 nm).

What remains, is the band at about 250 nm, which is typical for benzene systems. An intermediate quinoid structure could not be detected. This difference may be due to the fact that the stilbene chromophores in **9** have on both sides in 4- and 4′-position heteroatoms, whereas they are fixed in **15a**,**b** on a saturated C atom. Simultaneously with the change of the absorption, the fluorescence of **15a** (λ_{max}=359 nm in CH_2Cl_2) disappears. The same behavior is observed for **15b**. The absorption with λ_{max}=310 nm (CH_2Cl_2) and the fluorescence with λ_{max}=404 nm (CH_2Cl_2, excitation at 310 nm) decrease steadily on monochromatic irradiation at 340 nm.[24]

The course of the photoreactions can be nicely followed by ^{1}H NMR spectroscopy. Signals, which appear in the range between 6.4 and 6.8 ppm, indicate the primary generation of (*Z*)-stilbene units. Upcoming signals between 4.4 and 4.8 ppm prove then tertiary protons on a saturated carbon atom. In principle, CC bond formation in **9** and **15a**,**b** can occur intra- and intermolecularly. The easily soluble product portions have still the molecular masses of the monomers. The amount of less soluble oligomers increases with the concentration of the solution and the energy of the applied UV light. The latter effect may be due to the fact that the formation of four-membered rings in head-to-head [$\pi^2s+\pi^2s$] cycloadducts is partly reversible (Scheme 4).



Scheme 4. Photoreactivity of the stilbenoid compounds **9** and **15a**,**b**.

The photooligomers give ^{1}H NMR spectra with very broad signals. Molecular masses could not be determined by FD, FAB or ESI mass spectroscopy.[25]

3. Conclusion

The synthetic procedures described in Schemes 2 and 3 afforded dendrimers **9** and **15a**,**b** with (*E*)-stilbene chromophores in peripheral positions of the dendrons. Since an intramolecular energy transfer to the core can be excluded, the excited singlet states S_1 of **9** and **15a**,**b** are deactivated by photophysical processes (fluorescence and radiationless internal conversion) and by photochemical processes (*E*/*Z* isomerization and inter- and intramolecular CC bond formations). The CC bond formation can be realized in head-to-head $[\pi^2s+\pi^2s]$ cycloadditions and statistical crosslinking. The latter photoreaction provokes a fast and complete degradation of all stilbene chromophores indicated by the total loss of the stilbene absorption and fluorescence. In the case of compound **9**, in which the stilbene units are bound by a urea functionality, a short-lived intermediate with an absorption maximum far in the vis region at 614 nm can be detected. It is tentatively assigned to a quinoid species.

4. Experimental

4.1. General remarks

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 technique) or on a Micromass TOF spec E (MALDI-TOF) spectrometer. The elemental analyses were determined in the Microanalytical Laboratory of the Chemistry Department of the University of Mainz.

4.1.1. 3,4,5-Tripropoxybenzaldehyde (2). Preparation according to the literature.[12,18]

4.1.2. *N*-(4-Iodophenyl)phthalimide (3). Preparation according to the literature.[19] ^{1}H NMR ($CDCl_3$): δ=7.21/7.81 (AA′BB′, 4H, phenyl), 7.78/7.93 (AA′BB′, 4H, phthalimide); ^{13}C NMR (CD_3SOCD_3): δ=94.1 (C_qI), 123.6, 129.5, 134.9, 137.8 (aromat. CH), 131.6, 131.8 (aromat. C_q), 166.8 (CO). Anal. Calcd for $C_{14}H_8INO_2$ (349.1): C, 48.46; H, 2.31; N, 4.01. Found: C, 48.26; H, 2.29; N, 3.98.

4.1.3. 3,4,5-Tripropoxystyrene (5). Aldehyde **2** (8.24 g, 29.0 mmol) and methyltriphenyl-phosphonium bromide (15.75 g, 44.0 mmol) were treated in 120 mL THF with $KO(CH_3)_3$ (4.95 g, 44.0 mmol). After 12 h at 25 °C, the mixture was poured on ice and neutralized with HCl. Extraction with CH_2Cl_2 led to the raw product, which was purified by column filtration (13×10 cm SiO_2, CH_2Cl_2). Yield: 6.29 g (77%) oil. ^{1}H NMR ($CDCl_3$): δ=0.99 (t, 3H, CH_3), 1.03 (t, 6H, CH_3), 1.75–1.82 (m, 6H, CH_2), 3.91 (t, 2H, OCH_2), 3.94 (t, 4H, OCH_2), 5.16 (d, ^3J=10.7 Hz, 1H, olefin. H), 5.60 (d, ^3J=17.6 Hz, 1H, olefin. H), 6.59 (dd, ^3J=17.6 Hz, ^3J=10.7 Hz, 1H, olefin. H), 6.60 (s, 2H, aromat. H); ^{13}C NMR ($CDCl_3$): δ=10.6, 10.6 (CH_3), 22.7, 23.5 (CH_2), 70.7, 75.1 (OCH_2), 105.0 (aromat. CH), 112.7 (olefin. CH_2), 132.8, 138.4, 153.2 (aromat. C_q), 138.4 (olefin. CH); FD MS: *m*/*z* (%)=278 (100) [M^+]. Anal. Calcd for $C_{17}H_{26}O_3$ (278.4): C, 73.35; H, 9.41. Found: C, 72.76; H, 10.01.

4.1.4. *N*-[4-((*E*)-3,4,5-Tripropoxystyryl)-phenyl]phthalimide (6). The Heck reaction was performed with **5** (4.14 g, 14.9 mmol), **3** (4.19 g, 12.0 mmol), $Pd(OAc)_2$ (25 mg, 0.1 mmol), $P(o\text{-}CH_3\text{–}C_6H_4)_3$ (123 mg, 0.4 mmol), and $N(C_2H_5)_3$ (1.7 mL, 12.2 mmol) in 20 mL dry DMF. The reaction mixture was degassed and kept for 12 h at 80 °C. The volatile parts of the filtered solution were evaporated. Repeated column chromatography (8×20 cm SiO_2, CH_2Cl_2) yielded 3.17 g (53%) **6**, which melted at 134 °C. ^{1}H NMR ($CDCl_3$): δ=1.01 (t, 3H, CH_3), 1.05 (t, 6H, CH_3), 1.76–1.84 (m, 6H, CH_2), 3.95 (t, 2H, OCH_2), 3.99 (t, 4H, OCH_2), 6.72 (s, 2H, aromat. H), 6.98 (d, ^3J=16.2 Hz, 1H, olefin. H), 7.02 (d, ^3J=16.2 Hz, 1H, olefin. H), 7.42/7.48 (AA′BB′, 4H, phenylene), 7.78/7.94 (AA′BB′, 4H, phthalimide); ^{13}C NMR ($CDCl_3$): δ=10.6, 10.6 (CH_3), 22.8, 23.5 (CH_2), 70.8, 75.1 (OCH_2), 105.4, 123.7, 126.5, 126.9, 134.4 (aromat. CH), 126.6, 129.9 (olefin. CH), 130.6, 131.8, 132.2, 137.3, 138.5, 159.5 (aromat. C_q), 167.3 (CO); EI MS: *m*/*z* (%)=499 (100) [M^+], 457 (45) [$M^+-C_3H_6$]. Anal. Calcd for $C_{23}H_{17}NO_3$ (499.6): C, 74.53; H, 6.66; N, 2.80. Found: C, 74.57; H, 6.63; N, 2.88.

4.1.5. 4-((*E*)-3,4,5-Tripropoxystyryl)aniline (7). Phthalimide **6** (3.17 g, 6.3 mmol) was treated in 70 mL ethanol under Ar at 50 °C with $N_2H_4\cdot H_2O$ (8.0 mL, 8.24 g, 160 mmol). During refluxing for 1 h, a grey solid precipitated. Crystallization from ethanol yielded 1.42 g (61%) of yellowish product, which melted at 122 °C and turned pink on staying in the air. ^{1}H NMR ($CDCl_3$): δ=1.00 (t, 3H, CH_3), 1.04 (t, 6H, CH_3), 1.75–1.83 (m, 6H, CH_2), 3.93 (t, 2H, OCH_2), 3.97 (t, 4H, OCH_2), 6.66 (s, 2H, aromat. H), 6.82/6.86 (AB, ^3J=16.2 Hz, 2H, olefin. H), 6.73/7.31 (AA′BB′, 4H, aromat. H); ^{13}C NMR ($CDCl_3$): δ=10.6, 10.6 (CH_3), 22.8, 23.5 (CH_2), 70.7, 75.1 (OCH_2), 104.9 (aromat. CH), 115.6, 127.6 (aromat. CH), 125.6, 127.6 (olefin. CH), 128.6, 133.1, 137.8, 145.1, 153.2 (aromat. C_q); FD MS: *m*/*z* (%)=369 (100) [M^+]. Above room temperature, the decomposition of **7** is very fast so that a correct elemental analysis could not be obtained.

4.1.6. Dendrimer 9. To 418 mg (1.4 mmol) bis(trichloromethyl)carbonate (triphosgene) in 7 mL dry CH_2Cl_2, **7** (1.42 g, 3.8 mmol) and $N(C_2H_5)_3$ (0.59 mL, 428 mg, 4.2 mmol) in 24 mL CH_2Cl_2 were added under Ar within 3 h. The temperature was kept at 0 °C and the mixture vigorously stirred. The volatile parts were removed at 1 Torr (133 Pa). Two cooled flasks with propanol were put between vessel and pump in order to remove excess amounts of phosgene. The red residue was then dissolved in 5 mL dry CH_2Cl_2 and treated under Ar with Astramol Am-4® **4** (243 mg, 0.8 mmol) dissolved in 10 mL CH_2Cl_2. After 12 h at ambient temperature, 4 mL CH_3OH were added and the stirring continued for further 12 h. Column chromatography (50×3 cm SiO_2, CH_2Cl_2) afforded a beige solid (1.36 g, 93%), which melted at 137 °C. ^{1}H NMR ($CDCl_3$): δ=0.98 (t, 36H, CH_3), 1.40–1.85 (m, 36H, CH_2), 2.53–3.30 (m, 20H, NCH_2), 3.89 (t, 24H, OCH_2), 6.63 (s, 8H, aromat. H), 6.84 (m, 8H, olefin. H), 7.31/7.42 (AA′BB′, 16H, aromat. H), 8.80 (s, 4H, NH), 9.90 (s, 4H, NH); ^{13}C

NMR ($CDCl_3$): δ=10.5, 10.6 (CH_3), 21.3, 22.7, 23.4, 24.3 (CH_2), 36.7, 50.7, 52.2 (NCH_2), 70.6, 75.0 (OCH_2), 104.9, 118.7, 127.0 (aromat. CH), 127.0, 127.1 (olefin. CH), 131.4, 132.7, 137.9, 139.1, 153.2 (aromat. C_q), 156.5 (CO); FD MS: *m*/*z* (%)=1900 (68) [M^+], 951 (100) [M^{2+}].[27]

4.1.7. (*E*)-4-Bromomethylstilbenes (11a,b). The NBS bromination of the corresponding (*E*)-4-methylstilbenes was performed according to the literature.[5,20]

4.1.8. 3.5-Bis{4-[(*E*)-2-(phenyl)ethenyl]benzyloxy}benzyloxybenzyl alcohol (13a). Compound **13a** was prepared as described for **13b**.[5] Compound **11a** (11.34 g, 41.5 mmol), **12** (2.32 g, 16.6 mmol), K_2CO_3 (5.5 g, 40 mmol), and catalytic amounts of 18-crown-6 yielded 13.06 g (60%) of colorless crystals, which melted (after recrystallization from methanol) at 173–176 °C. ^{1}H NMR ($CDCl_3$): δ=4.62 (s, 2H, CH_2OH), 5.03 (s, 4H, OCH_2), 6.54 (t, ^4J=2.1 Hz, 1H, aromat. H), 6.62 (d, ^4J=2.1 Hz, 2H, aromat. H), 7.08/7.10 (AB, ^3J=16.5 Hz, 4H, olefin. H), 7.26–7.53 (m, 18H, aromat. H); ^{13}C NMR ($CDCl_3$): δ=65.3 (CH_2OH), 69.8 (OCH_2), 101.3, 105.8, 126.5, 126.7, 127.7, 127.9, 128.2, 128.7, 129.0 (aromat. and olefin. CH), 136.1, 137.1, 137.2, 143.4, 160.1 (aromat. C_q); FD MS: *m*/*z* (%)=524 (100, M^+). Anal. Calcd for $C_{37}H_{32}O_3$ (524.7): C, 84.70; H, 6.15. Found: C, 84.80; H, 6.45.

4.1.9. *all*-(*E*)-Tris(3,5-bis{4-[2-(phenyl)ethenyl]benzyloxy}benzyl)benzene-1,3,5-tri-carboxylate (15a). A solution of **13a** (0.5 g, 0.95 mmol), benzene-1,3,5-tricarboxylic acid trichloride (**14**)[26] (0.079 g, 0.30 mmol), triethylamine (0.67 g, 6.60 mmol), and 4-dimethylaminopyridine (0.03 g, 0.24 mmol) in 25 mL dry THF was refluxed under Ar for 6 h. The filtered mixture was concentrated and purified by column chromatography (50×4 cm SiO_2, petroleum ether bp 40–70 °C/ethyl acetate 1:1). Yield: 1.94 g (90%) of a colorless solid which melted at 168–170 °C. ^{1}H NMR ($CDCl_3$): δ=4.62 (s, 12H, OCH_2), 5.30 (s, 6H, CH_2OCO), 6.50 (t, ^4J=1.8 Hz, 3H, aromat. H), 6.67 (d, ^4J=1.8 Hz, 6H, aromat. H), 7.03–7.07 (AB, ^3J=16.5 Hz, 12H, olefin. H), 7.31–7.47 (m, 54H, aromat. H), 8.91 (s, 3H, aromat. H, central benzene ring); ^{13}C NMR ($CDCl_3$): δ=67.2 (CH_2OCO), 69.9 (OCH_2), 102.2, 107.3, 126.6, 126.7, 127.1, 127.7, 128.2, 128.7, 129.0 (aromat. and olefin. CH), 131.3, 135.0, 136.0, 137.2, 137.2, 137.9 (aromat. C_q and CH of central benzene ring), 160.2 (aromat. C_qO), 164.7 (CO); MALDI-TOF: *m*/*z* (%)=1837 (100) [M+Ag^+]. Anal. Calcd for $C_{120}H_{96}O_{12}$ (1730.1): C, 85.31; H, 5.59. Found: C, 85.45; H, 5.90.

4.1.10. *all*-(*E*)-Tris(3,5-bis{4-[2-(3,4,5-trimethoxyphenyl)-ethenyl]benzyloxy}benzyl)benzene-1,3,5-tricarboxylate (15b). The preparation was performed according to the procedure described for **15a**. Compound **13b** (0.75 g, 1.06 mmol), **14** (0.085 g, 0.32 mmol), Et_3N (0.87 g, 8.7 mmol), and DMAP (0.03 g, 0.24 mmol) afforded 1.68 g (70%) of **15b**, a glassy material. ^{1}H NMR ($CDCl_3$): δ=3.83 (s, 18H, OCH_3), 3.87 (s, 36H, OCH_3), 4.99 (s, 12H, OCH_2), 5.30 (s, 6H, CH_2OCO), 6.50 (t, ^4J=1.8 Hz, 3H, aromat. H), 6.67 (d, ^4J=1.8 Hz, 6H, aromat. H), 6.70 (s, 12H, aromat. H), 6.94/7.00 (AB, ^3J=16.5 Hz, 12H, olefin. H), 7.36/7.46 (AA′BB′, 24H, aromat. H), 8.91 (s, 3H, aromat. H, central benzene ring); ^{13}C NMR ($CDCl_3$): δ=56.1, 60.9 (OCH_3), 67.1 (CH_2OCO), 69.9 (OCH_2), 102.1, 103.7, 107.3, 126.6, 127.6, 127.9, 128.9 (aromat. and olefin. CH), 131.2, 132.9, 134.9, 135.9, 137.0, 137.9, 138.1, 153.4, 160.1 (aromat. C_q and CH of central benzene ring), 164.6 (CO); FD MS: *m*/*z* (%)=2265 (11) [M^+], 1133 (100) [M^{2+}]. Anal. Calcd for $C_{138}H_{132}O_{30}$ (2270.6): C, 73.00; H, 5.86. Found: C, 72.84; H, 5.90.

Irradiations: The irradiations for the UV/vis reaction spectra were performed with a xenon high-pressure lamp (LTI LPS1000X) with or without interference filters. Preparative samples for ^{1}H NMR control were irradiated with a Hanovia 450-W middle-pressure lamp. CH_2Cl_2 or $CHCl_3$ served as solvent in both cases.

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22. See also the behavior of related stilbenoid compounds in Ref. 13.
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