Azobenzene-Functionalized Cascade Molecules: Photoswitchable Supramolecular Systems

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Dedicated to Professor George A. Olah on the occasion of his 70th birthday

Abstract: Cascade molecules bearing up to 32 azobenzene groups in the periphery have been prepared from poly(propylene imine) dendrimers and *N*-hydroxysuccinimide esters. The dendritic azobenzene species show similar isomerization properties as the corresponding azobenzene monomers. The *all-E* azobenzene dendrimer units can be reversibly switched to the *Z* form by light of the appropriate wavelength and can be converted back to the *E* form by either irradiation or by heating. That the photoisomerization quantum yield of each photoactive unit is not dependent on the number of such units present in the species shows there is so far no effective steric constraint towards photoisomerism on increasing dimension (generation) of the dendrimer. The first attempts to use dendrimers for holography materials are described: It is shown that holographic gratings with diffraction efficiencies up to about 20% can be optically recorded in thin films of azobenzene dendrimers.

Keywords: azo compounds • dendrimers • holographic data storage • photochemistry • supramolecular chemistry

Introduction

Cascade molecules/dendrimers are a booming area in supramolecular chemistry.[1] Numerous dendritic architectures have been reported including polyamines,[2] polyphenylethers,[3] polyamidoamines,[4] carbosilanes,[5] phosphorus-containing dendrimers,[6] and polynuclear metal complexes[7] to name just a few. Some systems are already commercially available.[8] The literature and numerous patents indicate that the focus of research on cascade molecules is moving towards future applications in various fields like drug targeting, catalysis, new materials, coolant additives, and conducting polymers.[9]

One of the goals of supramolecular chemists is to construct devices capable of fulfilling tasks on the molecular level. Functional molecular units play a central role as building blocks of molecular machinery.[10] Chemically switchable entities are of particular interest, and molecular arrays have been found that change their properties upon an external input like electricity, redox potential, pH value, and light. The ability to switch between two defined states is a concept also present in nature: Factor EF-Tu, for example, plays a key role in protein biosynthesis.[11] Bacteriorhodopsin is a well known light-driven proton pump that has found artificial application as optical storage and holography material.[12] Light is particularly efficient at manipulating molecular systems because its effect is fast, mild, and often reversible.[10c]

Azobenzene derivatives have been used to construct photoswitchable devices for many years.[13] Azobenzene-type compounds, when they are not strongly sterically hindered, do not show any appreciable fluorescence or phosphorescence, but they can be easily and reversibly photoisomerized. The photoisomerization of azobenzene compounds is indeed one of the cleanest photoreactions known and has been intensively investigated from both an experimental and a theoretical point of view.[13]

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The thermodynamically stable *E* isomer can be photochemically converted to the *Z* isomer, which is converted back to the *E* isomer by excitation with light and thermally in the dark. The two isomers exhibit different absorption spectra. The *E* isomer shows an intense ππ* band in the near-UV region ($\lambda_{max} = 318$ nm, $\varepsilon = 21000\,\text{M}^{-1}\text{cm}^{-1}$) and a weak (symmetry-forbidden) nπ* band in the visible region ($\lambda_{max} = 443$ nm, $\varepsilon = 490\,\text{M}^{-1}\text{cm}^{-1}$) in dichloromethane. In the conversion to the *Z* isomer, the ππ* band shifts to shorter wavelengths, and the intensity of the nπ* band increases noticeably. Consequently, these compounds appear to deepen in color upon *E* → *Z* isomerization.

Isomerization of azobenzene involves a large structural rearrangement. In going from the *E* to the *Z* form, for an unsubstituted azobenzene the distance between the *para*-carbon atoms decreases from 9 to 5.5 Å and the dipole moment increases from zero (since the *E* form is planar and symmetrical) to 3.0 D.[13b]

Azobenzene moieties have been applied in the construction of photoresponsive molecular and supramolecular systems such as molecular tweezers,[14] liquid-crystalline films,[15] concave dyes,[16] photoresponsive polymers,[12c] donor–acceptor complexes,[17] switchable receptor molecules,[18] and surfactants.[19] It has also been shown that azobenzene-functionalized oligopeptides can efficiently be used as holography materials for optical storage (vide infra).[20]

Very recently, Junge and McGrath have reported the synthesis of a two-directional dendrimer with an azobenzene group in the center and have investigated its *E* → *Z* isomerization induced by UV light.[21] The Z → *E* photoisomerization of this type of dendrimers has recently been claimed to occur by excitation with IR radiation.[22] In an even earlier study we reported a dendrimer bearing six peripheral azobenzene groups that showed reversible switching behavior.[23]

We were interested in the effect that the accumulation of a greater number of azobenzene units would have and what effect the spatial proximity of these units in a higher generation dendrimer would have on their photochemical properties. Polyamine dendrimers can be readily functionalized with various functional groups attached as carboxamides by standard peptide chemistry procedures (vide infra). We obtained cascade molecules with up to 32 peripheral azobenzene groups (Figure 1), and we have investigated their photochemical properties and their potential use for holographic data storage. Potential advantages of dendrimers in this field include their good solubility in common organic solvents, their rigidity and their applicability to standard peptide chemistry which permits efficient assembly of a wide range of molecular structures.

Abstract in German: *Kaskadenmoleküle mit bis zu 32 Azobenzoleinheiten in der Peripherie wurden durch Umsetzung von Poly(propylenimin)-Dendrimeren mit N-Hydroxysuccinimidestern erhalten. Die dendritischen Azobenzolverbindungen unterscheiden sich in ihrem Isomerisierungsverhalten nicht von den entsprechenden Monomeren. Mit Licht geeigneter Wellenlänge lassen sich die all-E-Azobenzol-Dendrimere reversibel in die Z-Form und diese durch Bestrahlung oder Wärme zurück zur E-Form isomerisieren. Daß die Quantenausbeute der Photoisomerisierung der einzelnen photoaktiven Gruppe nicht von der Zahl der ans Dendrimer gebundenen Einheiten abhängt, zeigt, daß die Photoisomerisierung auch mit steigender Größe des Kaskadenmoleküls (Generation) noch keiner sterischen Behinderung unterliegt. Die ersten Versuche zum Einsatz von Dendrimeren als Holographie-Materialien werden beschrieben: Holographische Gitter können mit Brechungseffizienzen von bis zu 20% in dünnen Filmen der Azobenzol-Dendrimere optisch aufgezeichnet werden.*

Results and Discussion

Syntheses: The azobenzene dendrimers presented herein were prepared from poly(propylene imine) dendrimers with 4, 8, 16, and 32 primary amino groups in the periphery (generations 1 to 4) and the corresponding *N*-hydroxysuccinimide esters of 3- and 4-(phenylazo)benzoic acid. The carboxylic acids were prepared from aminobenzoic acid and nitrosobenzene and then converted into the acid chlorides with thionyl chloride as described in the literature.[24] "Activated esters", that is *N*-hydroxysuccinimide esters, are well-known in peptide chemistry for their high stability towards hydrolysis and their great selectivity for amide formation. In fact, prior attempts to prepare the azobenzene-substituted cascade molecules by the conversion of the poly(propylene imine) dendrimers with the corresponding carboxylic acid chlorides in the presence of base only led to incomplete conversion, presumably because aside from the desired amides quaternary ammonium chloride salts are formed. The products have to be dried in vacuo for several days since the dendrimers tend to retain solvent molecules tenaciously.

The dendrimers obtained are well soluble in halogenated organic solvents and insoluble in water. Removal of residual starting materials, *N*-hydroxysuccinimide, and, if formed, only partly functionalized dendrimers is achieved by thoroughly washing the organic reaction solution with water and saturated sodium carbonate solution. A certain polydispersity, particularly of the higher generations originating from imperfections of the polyamine dendrimer skeletons, can, however, not be eliminated with current work-up procedures and has to be accepted.[25]

Analyses: A number of analytical methods have been used to obtain full structural information on the azobenzene dendrimers. ^{1}H and ^{13}C NMR spectroscopy only give qualitative information because spectra become less expressive with increasing generation number, and proton counts increase to several hundred. MALDI-TOF (matrix-assisted laser-desorption ionization time-of-flight) mass spectrometry is an excellent method for the analysis of dendrimers because it allows one to mildly ionize the target molecules and thus to avoid fragmentation. The lower generation dendrimers have also been analyzed by FAB mass spectrometry. Where it was not possible to obtain the molecule peak, characteristic

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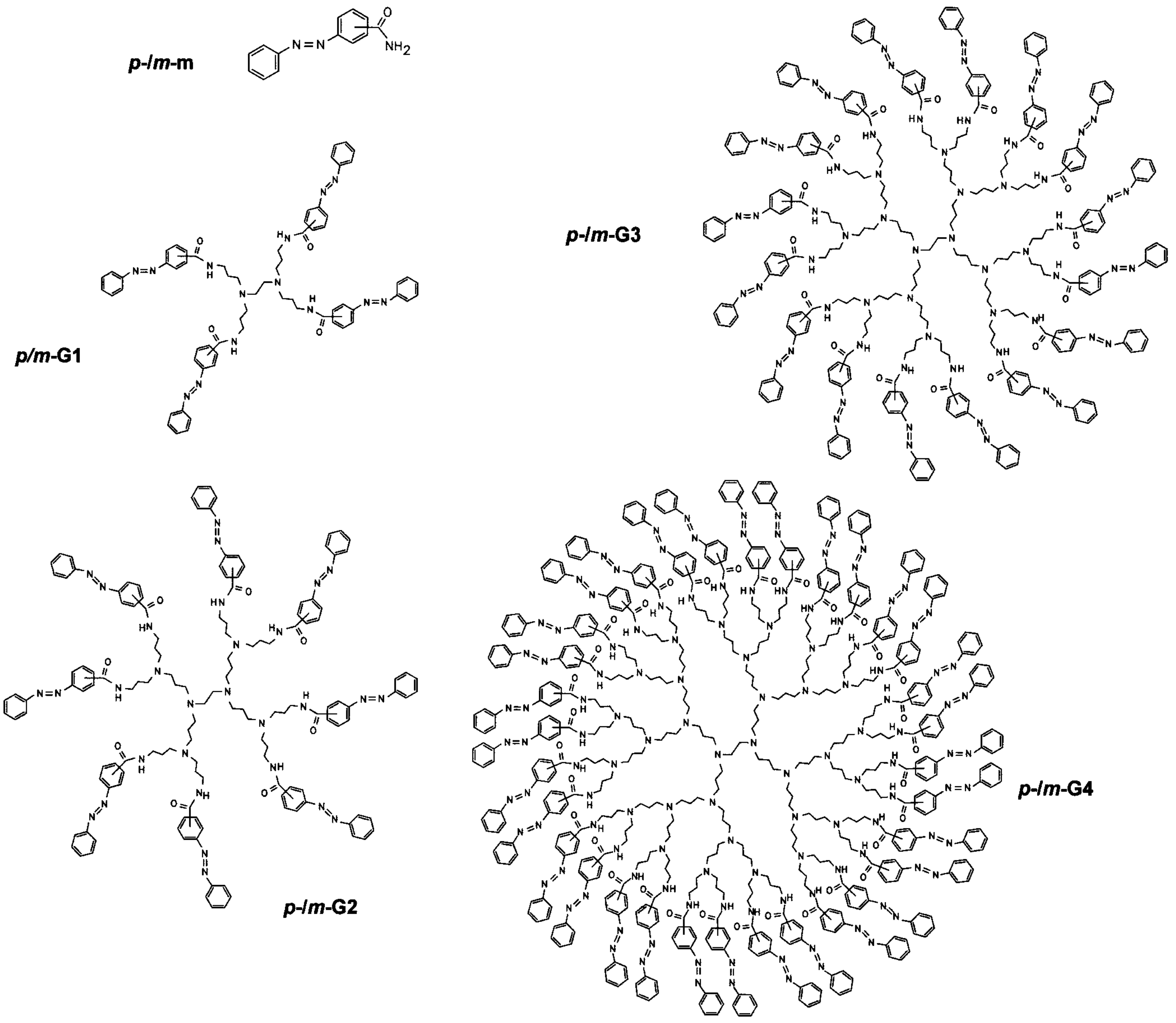

Figure 1. *para*-(***p*-m**) and *meta*-(***m*-m**)carboxamide-substituted azobenzene "monomers" and their dendrimers of generation 1 to 4.

fragmentation gave sufficient information. The strong tendency of the dendrimers investigated to retain solvent molecules makes elemental analyses less informative.[26]

Absorption spectra: The experiments were carried out in CH_2Cl_2 at 298 K. The wavelengths of the maxima of the absorption bands and the values of the molar absorption coefficients are collected in Table 1. Figure 2 shows the absorption spectra of the compounds of the *para* family.

The *para* and *meta* carboxamide-substituted azobenzene model compounds (hereafter called ***p*-m** and ***m*-m**, Figure 1) exhibit $\pi\pi^*$ and $n\pi^*$ absorption bands very similar to those of azobenzene. In the case of the *para* derivative, the $\pi\pi^*$ and $n\pi^*$ absorption bands are slightly red-shifted and the latter is somewhat more intense. In the case of the *meta* derivative, the $\pi\pi^*$ band is less intense.

The ***p*-m** and ***m*-m** azobenzene-type units are the only chromophoric groups in the two families of dendrimers. Therefore, in the absence of intra- or intermolecular interactions, within each family the wavelengths of the absorption maxima should not change, while the molar absorption coefficient should increase linearly with increasing number of azobenzene-type units present in the dendrimer.

The results obtained show that the λ_{max} of the $\pi\pi^*$ and $n\pi^*$ absorption bands do not change within each family (Table 1). This rules out the presence of strong interchromophoric interactions. The number of azobenzene groups, which is four for the first generation dendrimer, increases in each family according to an arithmetic progression: 4:8:16:32. The molar absorption coefficients should therefore increase with the same progression. For example, since the value of ε for the visible band of the single ***p*-m** unit is $\varepsilon = 600 \pm 60\,\text{M}^{-1}\text{cm}^{-1}$, the ε values for the dendrimers of the *para* family should be the following: ***p*-G1**, $2400 \pm 240\,\text{M}^{-1}\text{cm}^{-1}$; ***p*-G2**, $4800 \pm 480\,\text{M}^{-1}\text{cm}^{-1}$; ***p*-G3**, $9600 \pm 960\,\text{M}^{-1}\text{cm}^{-1}$; ***p*-G4**, $19200 \pm 1920\,\text{M}^{-1}\text{cm}^{-1}$. Comparison of the calculated values with those found for the dendrimers (Table 1) shows that the agreement is satisfactory if one takes into account the experimental

Table 1. Absorption data and photoreaction quantum yields for the *para*- and *meta*-azobenzene dendrimers and some reference compounds in CH_2Cl_2 at 298 K.

	Absorption[a] λ_{max}, nm (ε, M^{-1} cm^{-1}) $\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	Quantum yields ($\times 10^2$)[b] $\Phi_{E\rightarrow Z}$[c]	$\Phi_{E\rightarrow Z}$[d]	$\Phi_{Z\rightarrow E}$[c]	$\Phi_{Z\rightarrow E}$[d]
azobenzene	318 (21000)	443 (490)	14		36	
	para-substituted compounds					
***p*-m**	325 (23700)	451 (600)	10	10	28	28
***p*-G1**	325 (71500)	448 (2000)	3	9	8.2	26
***p*-G2**	325 (180000)	449 (4800)	1.3	10	3.1	25
***p*-G3**	325 (371000)	450 (9200)	0.6	9	2	27
***p*-G4**	326 (644000)	450 (16500)	0.4	11	1	30
	meta-substituted compounds					
***m*-m**	318 (16700)	444 (450)	14	14	38	38
***m*-G2**	319 (130000)	443 (3700)	1.7	13	5	38
***m*-G3**	320 (261000)	442 (7100)	1.1	19	2.2	32
***m*-G4**	319 (449000)	442 (14200)	0.6	19	1.5	40

[a] Estimated error on the molecular absorption coefficient is ±10%. [b] Estimated error, ±15% for the $E \rightarrow Z$ isomerization and ±15% for the $Z \rightarrow E$ photoisomerization; $\lambda_{exc} = 313$ nm for $E \rightarrow Z$ isomerization and 254 nm for $Z \rightarrow E$ isomerization. [c] Overall quantum yield (see text). [d] Quantum yield related to a single chromophoric unit (see text).

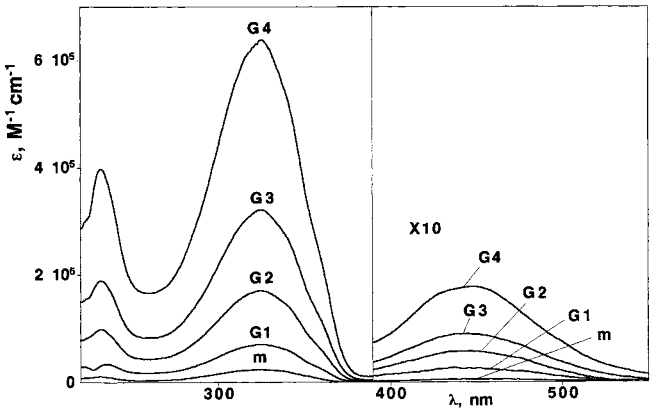

Figure 2. Absorption spectra in CH_2Cl_2 of the compounds of the *para* family. **m** is the carboxamide-substituted azobenzene "monomer", and **G1** to **G4** are the dendrimers of generation 1 to 4.

uncertainty, but the experimental values tend to become lower than the theoretical ones with increasing size of the dendrimer. This is an expected result because imperfectly substituted side products occur at higher generations of dendrimers prepared by a divergent synthetic strategy.[25]

Photochemical reactions: All the azobenzene-type compounds studied in this work have been found to undergo the $E \rightarrow Z$ and $Z \rightarrow E$ photoisomerizations and the $Z \rightarrow E$ thermal isomerization. The experiments were carried out in CH_2Cl_2 at 298 K. The photoreaction quantum yields are collected in Table 1. Figure 3 shows the spectral changes observed for the isomerization of compound ***m*-G4**. Qualitatively similar results have been obtained for all the compounds examined.

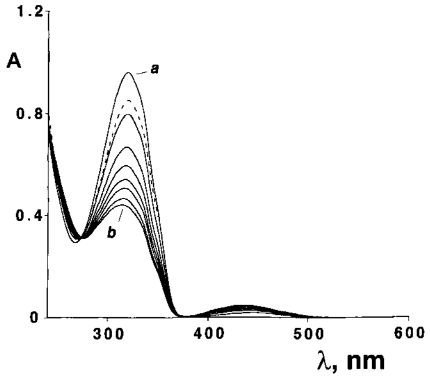

Figure 3. Changes in the absorption spectrum of ***m*-G4** in CH_2Cl_2 upon irradiation at 313 nm. Curve *a* is the initial spectrum and curve *b* is the spectrum of the photostationary state. The dashed curve corresponds to a solution first excited at 313 nm up to the photostationary state and then excited at 254 nm until a new photostationary state is reached. When kept in the dark after 254-nm excitation, the spectrum of the solution returns to that shown by curve *a*.

In each case, excitation of the *E* isomer with 313-nm light (which corresponds to the ππ* absorption band) caused a decrease of absorbance in the near-UV spectral region and an increase in absorbance in the visible region, with maintenance of clear isosbestic points (Figure 3). After a suitable irradiation period, a photostationary state was reached where the *Z* isomer predominates. When the irradiated reaction was left in the dark, a slow thermal $Z \rightarrow E$ isomerization was observed. The $Z \rightarrow E$ back isomerization was much faster upon irradiation with 254-nm light, which corresponds to the ππ* absorption band of the *Z* isomer. The isosbestic points were maintained throughout the back reaction (Figure 3). It should be noted that whereas the back thermal reaction leads to the pure *E* isomer, under 254-nm excitation the back reaction leads to a photostationary state, very rich in the *E* isomer (Figure 3, dashed curve), which reflects the conditions $\varepsilon_Z \phi_{Z\rightarrow E} = \varepsilon_E \phi_{E\rightarrow Z}$. When a solution that had reached the photostationary state under excitation with 254-nm light was placed in the dark, the pure *E* isomer was again obtained.

For the model compounds ***p*-m** and ***m*-m,** the relative amounts of *E* and *Z* isomers at the photostationary state was measured by NMR analysis.[27] From the absorption spectrum of the photostationary mixture it was thus found that the absorbance of the *Z* isomer is negligible at the wavelength of the maximum of the ππ* band of the *E* isomer (ca. 325 nm for the compounds of the *para* family and ca. 320 nm for those of the *meta* family). The quantum yield of the $E \rightarrow Z$ photochemical reaction for the various compounds was then obtained from the changes in absorbance observed at the beginning of the experiment, when the light absorbed by the photoproduct is negligibly small. The quantum yield values given in column 4 of Table 1 were obtained by using the ε values of the compounds (e.g. $\varepsilon = 644\,000\,M^{-1}cm^{-1}$ at 326 nm for ***p*-G4**). Therefore such values refer to "overall" quantum yields, that is quantum yields for the isomerization of *all* the chromophoric units contained in the species under consideration. In order to obtain the quantum yield of a single azobenzene chromophoric unit, the ε value of a single chromophoric unit (i.e., $23\,700\,M^{-1}cm^{-1}$ in the example above) has to be used (Table 1, column 5).

The quantum yields of the back $Z \rightarrow E$ photoisomerization reactions under irradiation with 254-nm light (Table 1, column 6 and 7) were obtained by irradiating solutions previously brought to the photostationary state with 313-nm light. Even in this case the absorbance changes at the maximum of the

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band of the E isomer were monitored at the beginning of the experiment. In these experiments, however, the initial concentration of the "product" was not zero since the solutions contained a mixture of E and Z isomers; thus, the quantum yield values are affected by a larger uncertainty.[13c]

Whereas the qualitative features of the photoisomerization reactions were the same in all cases, the quantum yields were found to depend on the nature of the examined compound. The data collected in Table 1 show that: 1) for the *meta*-carboxamide-substituted azobenzene ***m*-m** both the $E\rightarrow Z$ and $Z\rightarrow E$ photoreactions have quantum yields practically identical to those of azobenzene, whereas the quantum yields are lower for the *para*-carboxamide-substituted azobenzene ***p*-m**; 2) for both families of compounds, the "overall" quantum yields decrease with increasing number of chromophoric groups contained in the molecule, but the quantum yield referred to a single chromophoric unit is practically constant.

The result 1) clearly has its origin in electronic factors related to the different positions of the carboxamide substituent (note that the absorption spectrum of ***m*-m** is very similar to that of azobenzene). The lack of dependence of the quantum yield of a photoactive unit on the number of such units present in the species shows that there is no effective steric constraint towards photoisomerization on increasing dimension (generation) of the dendrimer.

Holography experiments: Thin films of good optical quality could be prepared from dendrimers ***m*-G2**, ***m*-G3**, ***m*-G4**, and ***p*-G1**. For the preparation of a film, the dendrimer in question was dissolved in chloroform, cast onto a glass substrate, and dried at room temperature for 10 min and at 90 °C overnight. Approximate film thicknesses are as follows: ***m*-G2**, 10 µm; ***m*-G3**, 12 µm; ***m*-G4**, 19 µm; ***p*-G1**, 18 µm. Two beam gratings were written in the films using a polarization holographic setup.[28] Two orthogonally circularly polarized beams at 488 nm from an argon ion laser are used for recording the gratings, and a weak, circularly polarized HeNe laser beam is used for the read-out. It has been proposed that repeated $E\rightarrow Z\rightarrow E$ isomerization of the azobenzene orients it statistically perpendicular to the resultant polarization of the incident light beams, resulting in a birefringent grating. During the recording, the argon ion laser beam is switched on after 5 s, and switched off after 60 s. The development of the diffraction was followed for a further 60 s in order to check the temporal stability of the recorded grating. Measurements were made at a laser intensity of 1400 mW cm^{-2}. Figure 4 shows typical recording curves for ***m*-G2** and ***p*-G1**. With both dendrimers, a first-order diffraction efficiency of close to 10 % is reached in less than 1 s. This is followed by a slow increase to 22 % and 18 %, for ***m*-G2** and ***p*-G1**, respectively, in about 55 s. No direct comparison should be made, but it is clear that the profiles of the two curves are quite different. Furthermore, after the argon ion laser is switched off, the diffraction efficiency of ***m*-G2** remains stable, while that of ***p*-G1** decreases. After recording the grating, the effect of increasing the temperature from 25 °C to 75 °C at the rate of 1° per s was examined (Figure 5). In the ***m*-G2** film there is hardly any erasure at all, while the grating completely vanishes in the case of the ***p*-G1** film. Table 2 summarizes the results for the different dendrimers.

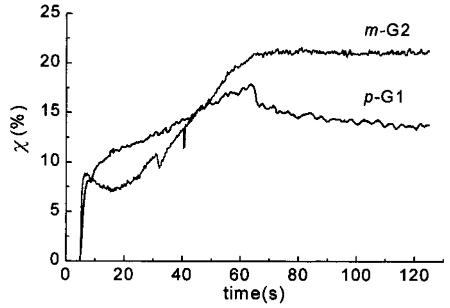

Figure 4. First-order diffraction efficiencies x as a function of time, measured during the grating formation in films of ***m*-G2** and ***p*-G1**. The recording argon ion laser was switched on after 5 s and switched off after 60 s.

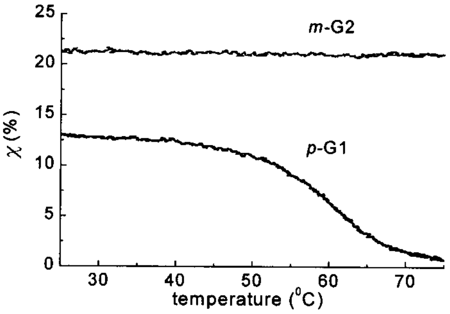

Figure 5. First-order diffraction efficiencies x as a function of temperature, measured after the grating formation in films of ***m*-G2** and ***p*-G1**. The temperature of the films was increased from 25 °C to 75 °C at the rate of 1 degree per second.

Table 2. Holographic storage properties of azobenzene dendrimer films.

Dendrimer	Max. diffraction efficiency [%]	Erasure with heat (75 °C)
***m*-G2**	22	No
***m*-G3**	19	No
***m*-G4**	16	No
***p*-G1**	18	Yes

Atomic force microscopic (AFM) investigations of the holographic gratings: It was observed visually that a surface roughness was induced in the *meta*-azobenzene films after irradiation with polarized light. It is well known[28-31] that a light-induced surface relief may appear when an azobenzene containing polymer is irradiated with polarized light. Detailed AFM and polarization investigations reveal that the anisotropy and surface relief coexist.[28,31] An atomic force microscope was utilized for examining the films for surface undulation after irradiation with the two polarized beams. A very large surface relief was observed in the *meta*-azobenzene dendrimers. Figure 6a shows the AFM scan in the ***m*-G2** film, in which a remarkable relief height of approximately 1500 nm was observed. In the case of the ***p*-G1** film, no surface relief (only a rough surface; Figure 6b) was observed in the irradiated area. This could explain the different profiles of the recording curves for ***m*-G2** and ***p*-G1**. Also, the surface

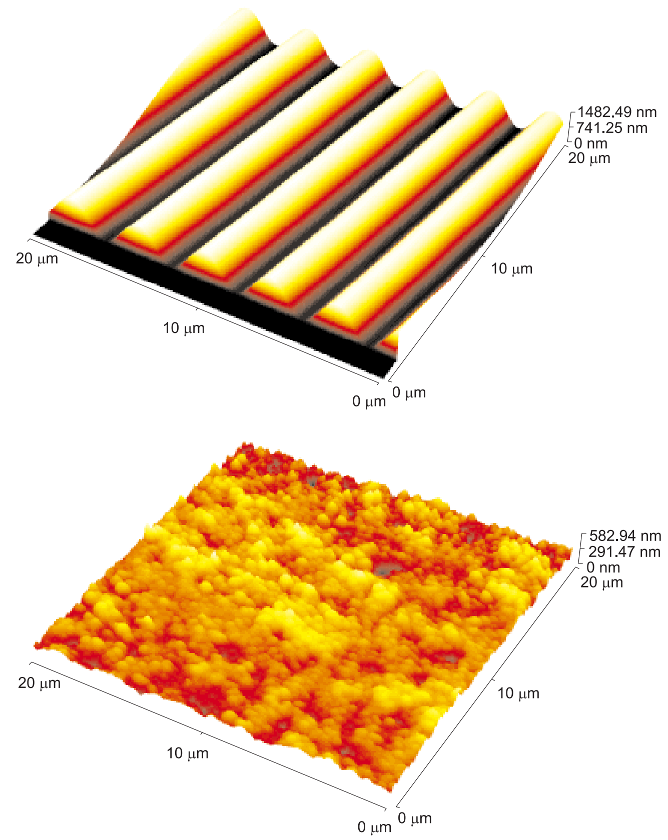

Figure 6. Atomic force microscopic scans of the polarization gratings recorded in (top above) the ***m*-G2** film and (bottom) the ***p*-G1** film. Both films were exposed to a total of 1400 mW cm^{-2} for 55 s.

relief could explain the better thermal stability of holograms recorded in the *meta*-azobenzene dendrimers.

The cause of the light-induced surface relief in azobenzene polymers is still under investigation. A purely thermal origin for the relief can be ruled out, because the total intensity across the film plane is constant in the case of polarization holography. A mean-field theory[34] of photoinduced formation of surface relief in azobenzene liquid-crystalline polyesters due to anisotropic intermolecular interactions using a Maier–Saupe potential[35] has recently been proposed. The hypothesis here is that an attractive potential resulting from chromophores oriented in a side-by-side configuration causes a mass transport. The difference in the packing of the chromophores in the *meta* and *para* configurations may be the reason for the different surface reliefs, and hence also the stability of the diffraction gratings.

Conclusion

The present study shows that functional groups can be accumulated as peripheral substituents of a cascade molecule without losing the original properties of the monomers. The photochemical isomerization experiments reveal that azobenzene dendrimers can be reversibly switched like the corresponding monomeric azobenzene derivatives and that the quantum yield of photoisomerization of a single azobenzene unit is the same in all the examined compounds of each family. This is particularly important for future applications of dendrimers as multipliers of certain functions, for example in diagnostics. Finally, the present work demonstrates that azobenzene dendrimers are potentially useful as materials for holographic data storage.

The dendrimers presented in this study differ from all other known azobenzene-modified systems like polymers, oligopeptides, and others, in their monodispersity, their physical properties (e.g. viscosity), and their molecular architecture (i.e. globular, amphiphilic structure). Dendrimers equipped with azobenzene or other switching units (e. g. thioindigo, spiropyrane) may become building blocks for large supramolecular networks that undergo photoresponsive structural changes or as carriers of smaller molecules that can be locked up and released by means of a light beam.

Experimental Section

Chemicals were purchased from Aldrich and Merck and were used as obtained. Dichloromethane was distilled and dried over molecular sieves (4 Å) prior to use. ^{1}H and ^{13}C NMR: Bruker WM 250 (250 MHz and 62.9 Mhz, respectively) and Bruker AM 400 (400 MHz and 100.6 Mhz, respectively). Mass spectra (EI): MS-30 and MS-50 A.E.I., Manchester, GB. FAB-MS: Concept 1H, Cratos, Manchester, GB, in *m*NBA (*m*-nitrobenzyl alcohol) as the matrix. MALDI-TOF-MS: TofSpec E, Micromass, Manchester, UK, matrix: 3,5-dihydroxybenzoic acid (DBA). Melting points: Kofler microscope heater (Reichert, Vienna); melting points are not corrected. Dendrimer transition temperatures: Shimadzu DSC-50 calorimeter. C,H,N analyses were provided by the Mikroanalytische Abteilung des Kekulé-Institutes für Organische Chemie und Biochemie der Universität Bonn. 3- and 4-azobenzene carboxylic acid and the corresponding acid chlorides were prepared according to literature procedures.[24]

Film thickness measurements: Dektak 3030 profiler. Atomic force microscopy: TopoMetrix Explorer. To increase the temperature of a film containing holographic gratings, it was placed on a Peltier heating-cooling element.

3-(Phenylazo)benzoic acid *N*-hydroxysuccinimide ester: 3-(phenylazo)-benzoic acid chloride (1.75 g, 7.2 mmol) and *N*-hydroxysuccinimide (0.83 g, 7.2 mmol) were dissolved in 1,4-dioxane (40 mL). The stirred solution was cooled in an ice bath to below 10 °C and pyridine (0.65 mL, 8.1 mmol) was added. After the addition, the solution was allowed to warm up to room temperature and was stirred for a further 2 h. The solvent was removed in vacuo, and the residue was redissolved in ethyl acetate. After washing twice with water, the organic phase was evaporated to dryness to give an orange solid (1.54 g, 67 %). M.p.: 150–152 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 2.88$ (s, 4H; succinimide CH_2), 7.50–7.59 (m, 3H; ar. H), 7.67 (dd, ^{3}J = 8.2 Hz, 1H; ar. H), 7.92–7.96 (m, 2H, ar. H), 8.20–8.24 (m, 2H; ar. H), 8.67 (dd, ^{3}J(H,H) = 1,77, 1H; ar. H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 25.82 (succinimide CH$_2$), 123.2, 124.8, 126.38, 129.09, 129.32, 129.89, 131.67, 132.48, 152.41, 152.70 (ar. C), 161.61 (acid COO), 169.30 (succinimide N-CO). MS (EI): m/z (%): 323.2 (93)[M]$^+$, 218 (25) [$M - C_6H_5N_2$]$^+$, 209.1 (98) [$M - C_4H_4NO_3$]$^+$, 105.1 (93) [$C_6H_5N_2$]$^+$, 77.0 (100) [C_6H_5]$^+$; $C_{17}H_{13}N_3O_4$ (323.31).

4-(Phenylazo)benzoic acid *N*-hydroxysuccinimide ester: Preparation as described above. M.p.: 233 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 2.92$ (s, 4H; succinimide CH_2), 7.53–7.57 (m, 3H; ar. H), 7.94–8.02 (m, 4H; ar. H), 8.29 (dd, ^{3}J(H,H) = 7.03, 2H; ar. H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): δ = 25.76 (succinimide CH$_2$), 120.23, 120.94, 123.1, 126.60, 129.32, 131,80, 152.53, 156.21 (ar. C), 161.48 (acid COO), 169.24 (succinimide N-CO); MS (EI): m/z (%): 323.1 (30) [M]$^+$, 209.1 (100) [$M - C_4H_4NO_3$]$^+$, 105.0 (31) [$C_6H_5N_2$]$^+$, 77.0 (85) [C_6H_5]$^+$; $C_{17}H_{13}N_3O_4$ (323.31).

General procedure for the preparation of azobenzene dendrimers: The appropriate polyamine dendrimer (1 equiv) and triethylamine (1.2 equiv) were dissolved in dry dichloromethane. To this mixture a solution of the 3- or 4-(phenylazo)benzoic acid *N*-hydroxysuccinimide ester (1 equiv) in

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dichloromethane was added dropwise over a period of 1 h. Then the solution was stirred at room temperature for five to seven days. The solution was then washed twice with water, twice with saturated sodium carbonate solution, and again twice with water. After the mixture was dried over sodium sulfate, the solvent was removed in vacuo to give the substituted dendrimer as a red-orange solid. Yields range from 80 to 90%.

8-Cascade:1,2-diaminoethane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidyne)^2:1-carbonyl-3-(phenylazo)benzene (*m*-G2): M.p.: 75.1 °C; ^{1}H NMR (250 MHz, CD_2Cl_2, 25 °C): $\delta = 1.40-1.60$ (br, 8H; CH_2), 1.65–1.90 (br, 16H; CH_2), 2.20–2.60 (br, 36H; -NCH_2), 3.40–3.60 (br, 16H; CH_2NCO), 7.30–7.50 (m, 24H; ar. H), 7.77 (m, 16H; H-6,6′), 7.88 (d, $^3J = 7.74$ Hz, 8H; ar. H) 8.12 (s/br, 8H; amide-H), 8.31 (br, 8H; H-1); ^{13}C NMR (62.9 MHz, CH_2Cl_2, 25 °C): $\delta =$ 24.10, 25.69 (CH_2); 38.88, 51.87, 52.27, 53.48 (CH_2N); 121.50, 122.93, 125.50, 129.10, 129.23, 129.64, 131.34, 135.51, 152.27 (ar. C); 166.98 (amide-C); FAB$^+$: 2410.9 ([M]$^+$); $C_{142}H_{156}N_{30}O_8 \cdot CH_2Cl_2$ (2495.93): calcd C 68.82, H 6.38, N 16.84; found C 68.37, H 6.50, N 16.21.

16-Cascade:1,2-diaminoethane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidyne)^3:1-carbonyl-3-(phenylazo)benzene (*m*-G3): M.p.: 85.0 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 1.3-1.55$ (br, 56H; CH_2), 1.6–2.5 (br, 84H; N-CH_2), 3.48–3.55 (br, 32H; CH_2NCO), 7.30–7.50 (m, 64H; ar. H), 7.76 (br, 32H; ar. H), 7.85 (d, $^3J = 6.89$ Hz, 16H; ar. H), 7.92 (d, $^3J = 7.72$ Hz, 16H; ar. H), 8.25 (d, $^3J = 5.22$ Hz, 16H; amide-H), 8.30 (s, 16H; H1); ^{13}C NMR (62.9 MHz, CH_2Cl_2, 25 °C): $\delta = 25.50$, 27.21 (CH_2); 39.33, 52.35, 52.60 (CH_2N); 120.73, 121.90, 123.21, 131.65, 136.11, 152.65 (ar. C); 167.11 (amide-C); MALDI-TOF-MS: 4989.1 ([M]$^+$); $C_{294}H_{332}N_{62}O_{16} \cdot 3\,CH_2Cl_2$ (5245.08): calcd C 68.01, H 6.50, N 16.56; found C 67.36, H 6.51, N 16.24.

32-Cascade:1,2-diaminoethane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidyne)^4:1-carbonyl-3-(phenylazo)benzene: (*m*-G4): M.p.: 55–56 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 1.35-2.00$ (br, 120H; CH_2), 2.20–2.80 (br, 180H; N-CH_2), 3.20–3.70 (br, 64H; CH_2NCO), 7.20–7.50 (br, 160H; ar. H), 7.60–8.00 (br, 128H; ar. H), 8.31 (s, 32H; H1); ^{13}C NMR (62.9 MHz, CH_2Cl_2, 25 °C): $\delta = 25.39$, 26.52 (CH_2); 38.61, 45.23, 51.42 (CH_2N); 121.95, 122.99, 125.28, 128.86, 129.14, 129.67, 131.38, 135.48, 152.34 (ar. C); 167.11 (amide-C); MALDI-TOF-MS (9-NA/HABA): 10119.21 [M]$^+$, $C_{598}H_{684}N_{126}O_{32}$ (10141.83): calcd C 70.77, H 6.79, N 17.39; found C 67.17, H 6.14, N 15.44.

4-Cascade:1,2-diaminoethane[4-N, N, N′, N′]:(1-azabutylidyne)^1:1-carbonyl-4-(phenylazo)benzene (*p*-G1): M.p.: 107–108 °C; ^{1}H NMR (250 MHz, [D$_6$]DMSO, 25 °C): $\delta = 2.65-2.75$ (m, 8H; CH_2), 2.85–3.00 (br, 12H; NCH_2), 3.35–3.50 (m, 8H; CH_2CON), 7.50–7.70 (m, 12H; ar. H), 7.80–8.05 (m, 8H; ar. H), 8.09 (d, ^3J(H,H) = 8.5 Hz, 8H; ar. H), 8.32 (d, ^3J(H,H) = 8.5 Hz, 8H; ar. H); FAB-MS: 1121.6 ([M]$^+$); $C_{66}H_{68}N_{14}O_4$ (1121.36): calcd C 70.69, H 6.11, N 17.49; found C 65.06, H 6.28, N 15.59.

8-Cascade:1,2-diaminoethane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidyne)^2:1-carbonyl-4-(phenylazo)benzene (*p*-G2): M.p.: 118 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.50-1.90$ (br, 24H; CH_2), 2.25–2.70 (br, 34H; N-CH_2), 3.30–3.60 (br, 16H; CH_2NCO), 7.30–7.60 (br, 24H; ar. H), 7.65–7.90 (br, 32H; ar. H), 7.90–8.05 (br, 16H; ar. H) 8.15 (br, 8H; amide-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 25 °C): $\delta = 25.76$, 26.50 (CH_2); 39.51, 45.51, 51.65 (CH_2N); 123.00, 123.13, 123.40, 128.32, 129.14, 131.78, 136.24, 152.53 (ar. C); 169.23 (amide-C); FT-IR (KBr): $\tilde{\nu}$: 3302 (m), 2927 (m), 2363 (m), 1772 (w), 1741 (m), 1636 (s), 1541 (s), 1484 (w), 1297 (s), 1216 (m), 1072 (m), 860 (w), 776 (m), 687 (m) cm^{-1}; FAB$^+$ (*m*-NBA): 1193.6 [$M/2 - CH_2$]$^+$; $C_{142}H_{156}N_{30}O_8 \cdot 2\,CH_2Cl_2$ (2580.86): calcd C 67.02, H 6.25, N 16.28; found C 67.07 H 6.60, N 15.72.

16-Cascade:1,2-diaminoethane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidyne)^3:1-carbonyl-4-(phenylazo)benzene (*p*-G3): M.p.: 132 °C; yield: 38%; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.50-1.90$ (br, 56H; CH_2), 2.30–2.70 (br, 84H; N-CH_2), 3.30–3.60 (br, 32H; CH_2NCO), 7.30–7.50 (br, 48H; ar. H), 7.70–7.90 (br, 64H; ar. H), 7.90–8.05 (br 32H, ar. H) 8.10–8.30 (br, 16H; amide-H); ^{13}C NMR (62.9 MHz, CH_2Cl_2, 25 °C): $\delta = 25.71$ (CH_2); 45.23, 51.16, 51.25 (CH_2N); 122.79, 122.97, 123.08, 128.34, 129.26, 131.51, 153.38, 154.03 (ar. C); 167.17 (amide-C); MALDI-TOF-MS: 5052.7 [M]$^+$; $C_{294}H_{332}N_{62}O_{16} \cdot 4\,CH_2Cl_2$ (5330.10): calcd C 67.15, H 6.43, N 16.29; found C 66.47, H 6.62, N 15.76.

32-Cascade:1,2-diaminoethane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidyne)^4:1-carbonyl-4-(phenylazo)benzene (*p*-G4): M.p.: 144–146 °C; yield: 81%; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.35-1.90$ (br, 120H; CH_2), 2.10–2.60 (br, 180H; N-CH_2), 3.20–3.70 (br, 64H; CH_2NCO), 7.30–7.55 (br, 96H; ar. H), 7.65–7.90 (br, 128H; ar. H), 7.90–8.10 (br 64H; ar. H) 8.10–8.40 (br, 16H; amide-H); ^{3}C NMR (62.9 MHz, CH_2Cl_2, 25 °C): $\delta = 25.39$, 26.52 (CH_2); 38.61, 45.23, 51.42 (CH_2N); 121.95, 122.99, 125.28, 128.86, 129.14, 129.67, 131.38, 135.48, 152.34 (ar. C); 167.11 (amide-C); MALDI-TOF-MS: $C_{598}H_{684}N_{126}O_{32} \cdot 12\,CH_2Cl_2$ (11168.03): calcd C 65.60, H 6.39, N 15.80; found C 65.58, H 6.30, N 15.86.

3-(Phenylazo)benzoic acid amide (*m*-m):[32] 3-(Phenylazo)benzoic acid chloride (1.0 g, 4.1 mmol) was dissolved in 1,4-dioxane (20 mL). Then an excess of a 25% aqueous ammonia solution (10 mL) was added dropwise. This caused the immediate formation of a light yellow precipitate. After the mixture had been stirred for 15 min, it was poured onto ice/water, neutralized with dilute hydrochloric acid, filtered, and the solid residue was washed with water. Recrystallization from ethanol afforded orange crystals (0.66 g, 72%): M.p.: 205 °C (ref.: 198–199 °C); MS (EI): *m/z* (%): 225.1 (38) [$M + H$]$^+$, 120.1 (24) [$C_6H_4CONH_2$]$^+$, 105.1 (29) [$C_6H_5N_2$]$^+$, 77.0 (100) [C_6H_5]$^+$; $C_{13}H_{10}N_3O$ (224.24).

4-(Phenylazo)benzoic acid amide (*p*-m):[32] Orange crystals (64%). M.p: 230 °C (ref.: 224–225 °C); MS (EI): *m/z* (%): 225.1 (76) [$M + H$]$^+$, 120.0 (40) [$C_6H_4CONH_2$]$^+$, 105.1 (33) [$C_6H_5N_2$]$^+$, 77.0 (100) [C_6H_5]$^+$; $C_{13}H_{10}N_3O$ (224.24).

Photochemical experiments: Absorption spectra were measured in CH_2Cl_2 at room temperature with a Perkin-Elmer Lambda 6 spectrophotometer. Photochemical experiments were carried out at 298 K in air-equilibrated CH_2Cl_2 solutions using medium- or low-pressure Hg lamps. The irradiated solution was contained in a closed spectrophotometric cell (volume, 3 mL; optical path, 1 cm). The excitation wavelengths were selected with Oriel interference filters. The number of incident photons were calculated by using a chemical actinometer.[33] In the photochemical experiments, ^{1}H NMR spectra in $CDCl_3$ were obtained at 298 K by using TMS as reference standard on a Varian Gemini 300 spectrometer. Photostationary composition and conversion percentages for ***p*-m** and ***m*-m** compounds were determined by integration of the signals in the ^{1}H NMR spectra recorded before and after irradiation in $CDCl_3$ (10^{-3} M). The UV/Vis spectrum at the photostationary state was measured after appropriate dilution of the irradiated solution. The spectrum of the *Z* isomer was obtained from the known spectrum of the *E* isomer and the relative amounts of the *Z* and *E* isomers.

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[1] G. R. Newkome, C. Moorefield, F. Vögtle, *Dendritic Molecules: Concepts, Syntheses, Perspectives*, VCH, Weinheim **1996**, and references therein.

[2] a) E. Buhleier, W. Wehner, F. Vögtle, *Synthesis* **1978**, 155–158; b) R. Moors, F. Vögtle, *Chem. Ber.* **1993**, *126*, 2133–2136; c) C. Wörner, R. Mülhaupt, *Angew. Chem.* **1993**, *105*, 1367–1370; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1306–1308; d) E. M. M. de Brabander-van den Berg, E. W. Meijer, *Angew. Chem.* **1993**, *105*, 1370–1372; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1308–1310.

[3] K. L. Wooley, C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1991**, *113*, 4252–4261; C. J. Hawker, J. M. J. Fréchet, *ibid.* **1990**, *112*, 7638–7647.

[4] D. A. Tomalia, H. Baker, J. R. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, P. Smith, *Polym. J.* **1985**, *17*, 117–132; *Macromolecules* **1986**, *19*, 2466–2468.

[5] a) C. Kim, K. An, *Bull. Korean Chem. Soc.* **1997**, *18*, 164–170; b) K. Lorenz, R. Mülhaupt, H. Frey, U. Rapp, F. J. Mayer-Posner, *Macromolecules* **1995**, *28*, 6657–6661; c) D. Seyferth, D. Y. Son, A. L.

Rheingold, R. L. Ostrander, *Organometallics* **1994**, *13*, 2682–2690; d) A. W. van der Made, P. W. N. M. van Leeuwen, J. C. de Wilde, R. A. C. Brandes, *Adv. Mater.* **1993**, 5, 466–468; e) A. W. van der Made, P. W. N. M. van Leeuwen, *J. Chem. Soc. Chem. Commun.* **1992**, 1400–1401.

[6] a) N. Launay, A.-M. Caminade, R. Lahana, J.-P. Majoral, *Angew. Chem.* **1994**, *106*, 1682–1684; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1589–1592; b) M.-L. Lartigue, M. Slany, A.-M. Caminade, J.-P. Majoral, *Chem. Eur. J.* **1996**, *2*, 1417–1426.

[7] S. Serroni, A. Juris, M. Venturi, S. Campagna, I. R. Resino, G. Denti, A. Credi, V. Balzani, *J. Mater. Chem.* **1997**, *7*, 1227–1236.

[8] PAMAM dendrimers are available from Aldrich; poly(propylene imine) dendrimers can be obtained from the DSM corporation, Netherlands, and from Aldrich.

[9] J. Issberner, R. Moors, F. Vögtle, *Angew. Chem.* **1994**, *106*, 2507–2514; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2413–2420.

[10] a) For an introduction to nanotechnology see: K. E. Drexler, *Nanosystems*, Wiley-Interscience, New York, **1992**; b) switchable devices in supramolecular chemistry: J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim,**1995**; c) photochemical devices in supramolecular chemistry: V. Balzani, F. Scandola, *Supramolecular Photochemistry*, Horwood, Chichester, **1991**.

[11] H. Vennen, *Hoechst High Chem Magazin* **1994**, *15*, 57–59.

[12] C. Bräuchle, N. Hampp, D. Oesterhelt, *Adv. Mater.* **1991**, *3*, 420–428.

[13] For pertinent reviews see: a) S. Shinkai, O. Manabe, *Topics Curr. Chem.* **1984**, *121*, 67–104; b) G. S. Kumar, D. C. Neckers, *Chem. Rev.* **1989**, *89*, 1915–1925; c) H. Rau in *Photochromism, Molecules and Systems* (Eds.: H. Dürr, H. Bouas-Laurent), Elsevier, Amsterdam **1990**, chapter 4; d) V. Balzani, F. Scandola, *Supramolecular Photochemistry*, Horwood, Chichester **1991**, chapter 7.

[14] F. Würthner, J. Rebek, Jr., *Angew. Chem.* **1995**, *107*, 503–505; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 446–448.

[15] T. Ikeda, O. Tsutsumi, *Science* **1995**, *268*, 1873–1875.

[16] M. Bauer, F. Vögtle, *Chem. Ber.* **1992**, *125*, 1675–1686.

[17] K. T. Ranjit, S. Marx-Tibbon, I. Ben-Dov, I. Willner, *Angew. Chem.* **1997**, *109*, 91–93; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 147–150;

[18] S. Shinkai in: *Comprehensive Supramolecular Chemistry*, (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle), Pergamon, Oxford, **1996**.

[19] S. Shinkai, K. Matsuo, A. Harada, O. Manabe, *J. Chem. Soc. Perkin Trans. 2* **1982**, 1261–1265.

[20] R. H. Berg, S. Hvilsted, P. S. Ramanujam, *Nature* **1996**, *383*, 505–508.

[21] a) D. M. Junge, D. V. McGrath, *Chem. Commun.* **1997**, 857–858; b) M. Freemantle, *Chem. Eng. News* **1997**, *May 26*, 30.

[22] D.–L. Jiang, T. Aida, *Nature* **1997**, *388*, 454–456.

[23] H.-B. Mekelburger, K. Rissanen, F. Vögtle, *Chem. Ber.* **1993**, *126*, 1161–1169.

[24] P. Jacobson, *Liebigs Ann.* **1909**, *367*, 329; H. D. Anspon, *Org. Synth.* **1945**, *25*, 86–87; G. H. Coleman, G. Nichols, C. M. McCloskey, H. D. Anspon, *ibid*. **1945**, *25*, 87–89.

[25] MALDI-TOF mass spectrometry does not show peaks that could be attributed to impurities originating from structural defects of the polyamine precursor or from incomplete conversion with the activated esters up to generation 3. In the case of generation 4 there are additional peaks below the molecule ion peak that originate from imperfect polyamine starting material, that is dendritic polyamines with less than 32 propylene amine arms in the periphery. For the sake of reliability of the photochemical investigations we have thus not extended our study to generation 5 azobenzene dendrimers although these are now commercially available (see ref. [8]). Structural defects in poly(propylene imine) dendrimers have been investigated and categorized recently, cf.: a) P. R. Ashton, S. E. Boyd, C. L. Brown, S. A. Nepogodiev, E. W. Meijer, H. W. I. Peerlings, J. F. Stoddart, *Chem. Eur. J.* **1997**, *3*, 974–984; b) J. C. Hummelen, J. L. J. van Dongen, E. W. Meijer, *Chem. Eur. J.* **1997**, *3*, 1489–1493.

[26] Compare: P. Lange, A. Schier, H. Schmidbaur, *Inorg. Chem.* **1996**, *35*, 637–642.

[27] A. Bencini, M. A. Bernardo, A. Bianchi, M. Ciampolini, V. Fusi, N. Nardi, A.–J. Parola, F. Pina, B. Valtancoli, *J. Chem. Soc. Perkin Trans. 2*, **1998**, 413–418.

[28] P. S. Ramanujam, N. C. R. Holme, S. Hvilsted, *Appl. Phys. Lett.* **1996,** *68*, 1329–1331.

[29] P. Rochon, E. Batalla, A. Natansohn, *Appl. Phys. Lett.* **1995,** *66*, 136–138.

[30] D. Y. Kim, S. K. Tripathy, L. Li, J. Kumar, *Appl. Phys. Lett.* **1995,** *66*, 1166–1168.

[31] N. C. R. Holme, L. Nikolova, P. S. Ramanujam, S. Hvilsted, *ibid.*, **1995,** *70*, 1518–1520.

[32] P. Freundler, *Bull. Soc. Chim. Fr.* **1907**, [4] *1*, 221.

[33] E. Fischer, *EPA Newsletter* **1984**, *21*, 33.

[34] T. G. Pederson, P. M. Johansen, N. C. R. Holme, P. S. Ramanujam, S. Hvilsted, *Phys. Rev. Lett.* **1998**, *80*, 89–92.

[35] W. Maier, A. Saupe, *Z. Naturforsch. A* **1959**, *14*, 882.

0947-6539/98/0404-0706 $ 17.50+.50/0