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Synthesis and Photomodulation of Rigid Polyphenylene Dendrimers with an Azobenzene Core

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ABSTRACT: A series of azobenzene-cored polyphenylene dendrimers have been synthesized. The photoresponsive properties of these dendrimers have been investigated by optical spectroscopy and gel permeation chromatography (GPC). These polyphenylene dendrimers exhibit a photoresponsive behavior upon UV and visible irradiation, resulting in a reversible and appreciable change of the dendrimer structure. Furthermore, the influence of dendrimer generation and degree of branching on the kinetic characteristics of the photoisomerization is discussed. The crystal structures of two precursors and two solvate structures of the first generation are presented.

Introduction

Molecules that are responsive to an external stimulus in a controlled, reproducible, and reversible manner have many applications in diverse areas of research.[1] Azobenzene, due to its efficient and fully reversible photoisomerization and photoinduced anisotropy,[2,3] has widely been investigated as a component in photoresponsive materials. Azobenzene functionalized monolayers[4−8] and thin polymer films[3,9,10] exhibit interesting photoresponsive properties. Dendrimers,[11,12] a type of highly branched and structurally regular macromolecules which are prepared step by step either divergently or convergently, allow a controllable positioning of photoactive moieties in their structures. Dendrimers with azobenzene units in the exterior,[13−15a] interior,[15b−17] or throughout the dendritic structure[18−21] have been prepared and their photoresponsive properties have been investigated. By placing the azobenzene unit in the core of a dendrimer, a small conformational change of the azobenzene moiety should produce a large change in the whole dendritic structure. However, owing to the flexibility of the dendrimer branches such as poly(aryl ether)s and poly(amidoamine)s, obtaining a well-defined and large photoinduced change of the dendrimer structure remains challenging. To this end, rigid dendrimer subunits are a better choice because of their well-defined three-dimensional structure. To our knowledge, the synthesis of only one type of shape-persistent dendrimers (of the phenylacetylene type) with an azobenzene core has been reported.[15e] However, their photoresponsive properties have not been investigated.

It is known that polyphenylene dendrimers have a shape-persistent structure[22,23] and this shape-persistence leads to fascinating properties and applications. For instance, attachment of chromophores to the rim of these rigid dendrimers allows the construction of nanoparticles with a well-defined number of chromophores in a confined volume element and has stimulated the investigation of the photophysical processes of individual multichromophoric dendrimers.[24] The rigid molecular framework of polyphenylene dendrimers ensures a rather narrow variation of the voids in their interior and allows them to be used as ideal sensors for volatile organic solvents with a high degree of reproducibility.[25] We have also recently found that the shape-persistence of polyphenylene dendrimers plays an important role in the formation of self-organized micrometer long nanofibers.[23,26]

In this report, we describe the synthesis, structure, and photochemistry of polyphenylene dendrimers with an azobenzene core. It is our aim to construct, by combining the photoswitchability of the azobenzene unit and the rigid structure of polyphenylene dendrimers, a series of macromolecules in which a light stimulus produces a well-defined and large structural perturbation and to investigate their photoresponsive properties.

Synthesis

A series of azobenzene-cored polyphenylene dendrimers was synthesized by means of the synthetic concept previously presented.[28] The dendrimer synthesis started from 4,4′-bis(4-ethynyl)azobenzene (**3**) (Figure 1), which was prepared in three steps from 4-iodoaniline. In the first step, oxidative coupling gave 4,4′-diiodoazobenzene (**1**).[15e,29] Subsequent aryl−ethynyl coupling after Heck, Cassar, Haghihara, and Sonogashira produced 4,4′-bis(triisoproylsilylethynyl)azobenzene (**2**). The starting compound (**3**) for the dendrimer buildup was then obtained by deprotection with tetrabutylammonium fluoride in tetrahydrofuran.

The divergent synthesis of the dendrimers using Diels−Alder cycloaddition of different cyclopentadienones to alkynes was carried out in refluxing *o*-xylene

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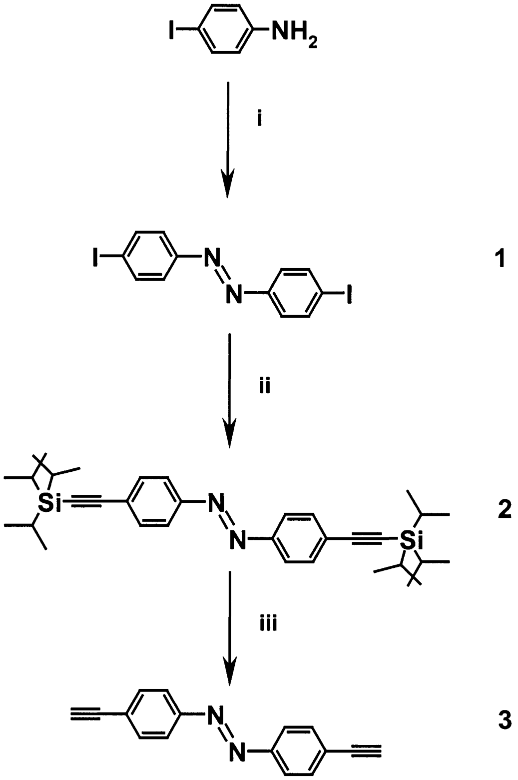


Figure 1. Synthetic route to **3**: (i) $KMnO_4/CuSO_4{\cdot}5H_2O$, CH_2Cl_2, room temperature, 61%; (ii) 4 equiv of triisopropylsilylethyne, $(Pd(PPh_3)_2]Cl_2$, PPh_3, CuI, THF/triethylamine, room temperature, 75%; (iii) 0.4 equiv of nBu$_4$NF, THF, room temperature, 82%.

at 142 °C, except for the AzoG1hex (**11**), which was prepared in diphenyl ether at 210 °C. The structures of all dendrimers are shown in Figures 2−8 together with the abbreviations used in the text.

AzoG1 (**5**) resulted from the Diels−Alder cycloaddition of **3** with tetraphenylcyclopentadienone (**12**). The growth of the higher generations was carried out by repetitive Diels−Alder cycloaddition of the A_2B-branching reagent 3,4-bis(4-triisopropylsilylethynylphenyl)-2,5-diphenylcyclopentadienone (**13**) and quantitative cleavage of the protecting groups with ammonium fluoride as shown in Figures 2 and 3.

The addition/deprotection cycles were carried out one, two, or three times followed by a Diels−Alder addition of **12** to give the unsubstituted dendrimers AzoG2 (**6**), AzoG3 (**7**) (Figure 4), and AzoG4 (**8**) respectively (Figure 5).

To vary the density of the phenyl rings in the second generation an AB- and A_4B-branching reagent were applied.[30] Addition of the AB-building unit 3-(4-triisopropylsilylethynylphenyl)-2,4,5-triphenylcyclopentadienone (**14**) for the AzoG2AB (**9**) (Figure 6) and of the A_4B-building unit 2,3,4,5-tetra(4-triisopropylsilylethynylphenyl)cyclopentadienone (**15**) for the AzoG2A$_4$B (**10**) yielded the protected first generations of the dendrimers, which were thereafter deprotected to yield AzoG1ethin$_2$ and AzoG1ethin$_8$, respectively, which were then capped with **12** (Figure 7).

To produce AzoG1hex (**11**), **1** was reacted with phenylacetylene to give 4,4′-bis(phenylethynyl)azobenzene (**4**), which was then treated in diphenyl ether at 210 °C with tetraphenylcyclopentadienone to give **11** as shown in Figure 8.

Table 1. Unit Cell Parameters of 1, 4, and 5

	1	**4**	**5** (dichloromethane)	**5** (tetrahydrofuran)
a (Å)	6.0067(6)	6.012(3)	11.4007(3)	11.4818(10)
b (Å)	7.3265(6)	9.5956(4)	12.3161(4)	11.4923(10)
c (Å)	28.4091(10)	18.2563(7)	27.1975(8)	12.2369(12)
α (deg)	90	77.783(1)	96.196(1)	103.457(1)
β (deg)	90	85.438(1)	97.992(1)	114.423(1)
γ (deg)	90	75.872(1)	113.470(1)	97.427(1)
V (Å^3)	1250.2	1005.9	2785.1	1382.7
Z	8	2	2	2
D_x (g cm^{-3})	2.306	1.263	1.226	1.306
μ (cm^{-1})	49.520	0.689	1.593	0.718
no. of reflcns	2536	3692	10 470	4257
no. of reflcns (obsd)	1589	2223	7365	1274
R (%)	3.812	7.527	6.789	5.912
R_w (%)	1.993	5.892	6.135	7.490
space group	pnaa (=$Pccn$, no. 56)	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$

The purity and monodispersity of the dendrimers were established by means of NMR spectroscopy, FD, and MALDI−TOF mass spectrometry and elemental analysis (see Experimental Section).

Results and Discussion

Structure. The herein presented azobenzene-cored polyphenylene dendrimers form the first extended series of extensively studied rigid photoswitchable dendrimers, which not only varies in dendrimer size but also in the degree of branching. To elucidate the effect of a rigid dendrimer scaffold on the isomerization of a central azobenzene chromophore in solution, it is important to know the exact structure of the dendrimers.

During various steps of the synthesis we were able to grow crystals to determine the molecular geometry. We here present the structures for **1**, **4**, and **5**. Table 1 summarizes the unit cell parameters.

1 was crystallized from dichloromethane by slow evaporation at room temperature over 3 days. Eight molecules are in an orthorhombic cell with the space group $Pnaa$ (=$Pccn$, No. 56).[31] The molecule is flat and the azo bond is coplanar with the phenyls. Figure 9 shows the projection along the iodine−iodine axis, which reveals the molecules are packed in a herringbone fashion.

The crystallization of *trans*-4,4′-iodoazobenzene (**1**) to form an orthorhombic cell, is in contrast to the behavior of 4,4′-dichloroazobenzene and 4,4′-dibromoazobenzene, which variably display either monoclinic symmetries or are disordered,[32] depending on the crystallization conditions.

Compound **4** (Figure 10) was crystallized from dichloromethane by slow evaporation of the solvent over a week. The triclinic cell contains two crystallographically independent molecules, which are located on two different symmetry centers. As already observed with **1** the molecules are planar within 0.1 Å and pack in a herringbone-like fashion. The phenylacetylene units with torsion angles of the terminal phenyl to the central phenyl units of 6.38 and 4.27 respectively are also rather flat.

5 could be crystallized from either dichloromethane or tetrahydrofuran by slow evaporation at room temperature over a period of 4 weeks. The two different crystals formed under these conditions are displayed in Figure 11. The theoretical point group of the dendrimer is 2/m.

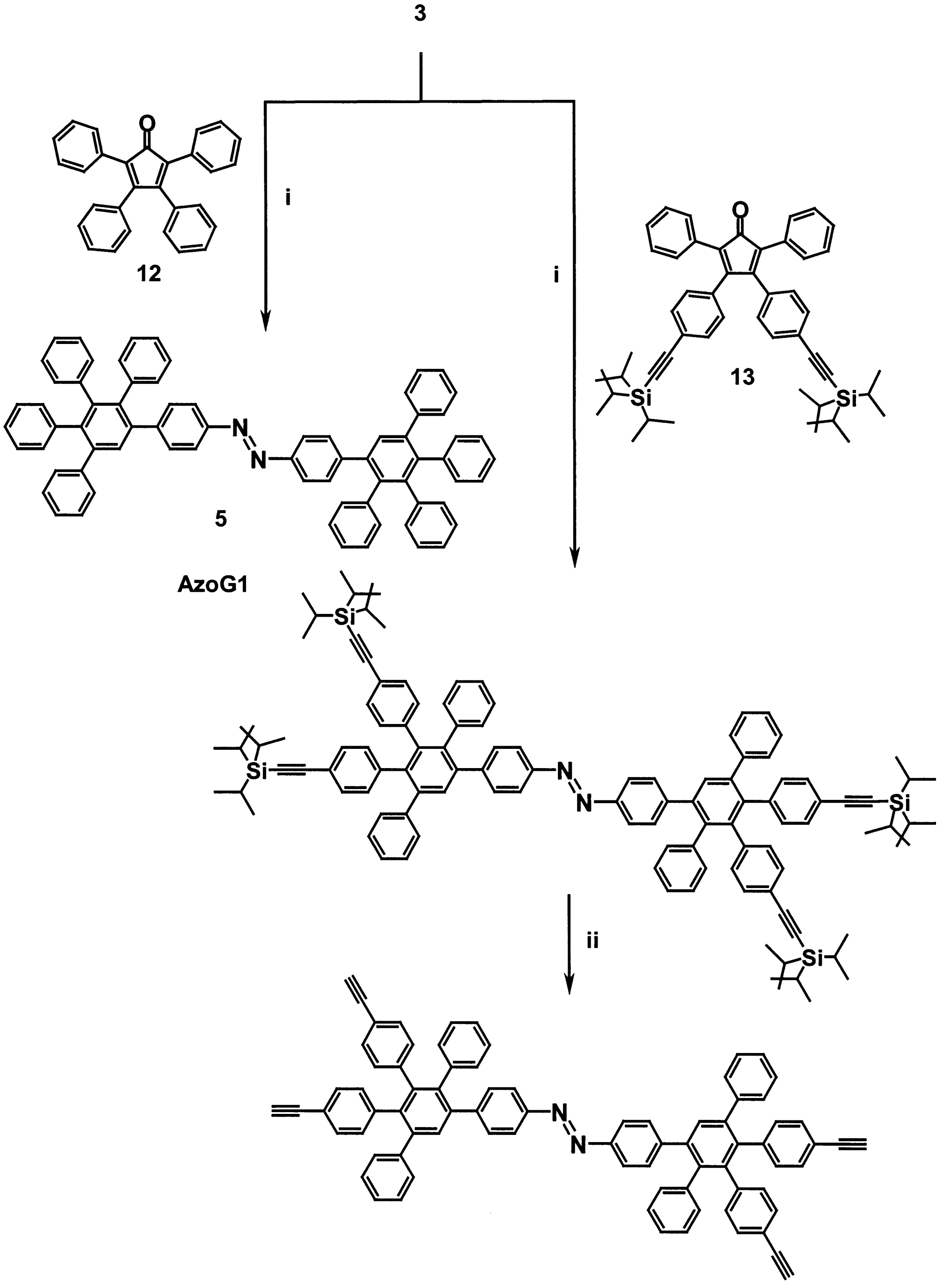


Figure 2. Synthesis of the first generation dendrimers: (i) 3 equiv of **12**/**13**, respectively, *o*-xylene, 142 °C, 92% and 89%, respectively; (ii) 4 equiv of $n\mathrm{Bu}_4\mathrm{NF}$, THF, room temperature.

Both pseudopolymorphs crystallize as solvates in triclinic structures. The dendrimer in the tetrahydrofuran solvate is located on a center of symmetry and contains two solvent molecules per dendrimer. The structure obtained from dichloromethane has the dendrimer located at a common position; i.e., it possesses no special symmetry. The crystal contains two molecules of dichloromethane per dendrimer.

Nevertheless, the conformations of the phenyl groups with respect to each other are quite similar to those observed for other 2,3,4,5-tetraphenylphenyl units reported in the literature.[33] The dihedral angles between the phenyl planes (indicated in Figure 12) are summarized in Table 2. The slightly higher value for plane 3 can be ascribed to the lesser hindrance from the adjacent hydrogen in comparison to the interaction with two neighboring phenyls, which determine the angles of the planes 4, 5, and 6.

These values are also in good agreement with those found in other polyphenylene dendrimers,[34] showing that 2,3,4,5-tetraphenylphenyl moieties can be regarded as groups with fixed conformation.

A common feature in both structures is the observation that the dendrimer molecules are arranged linearly in a preferential orientation (Figure 13). The packing of the dendrimers is always such that the 2,3,4,5-tetraphenylphenyl units are located above the azo bond of the dendrimer in the layer below, so avoiding too much sterical hindrance. Neighboring rows are separated by the trapped solvent molecules.

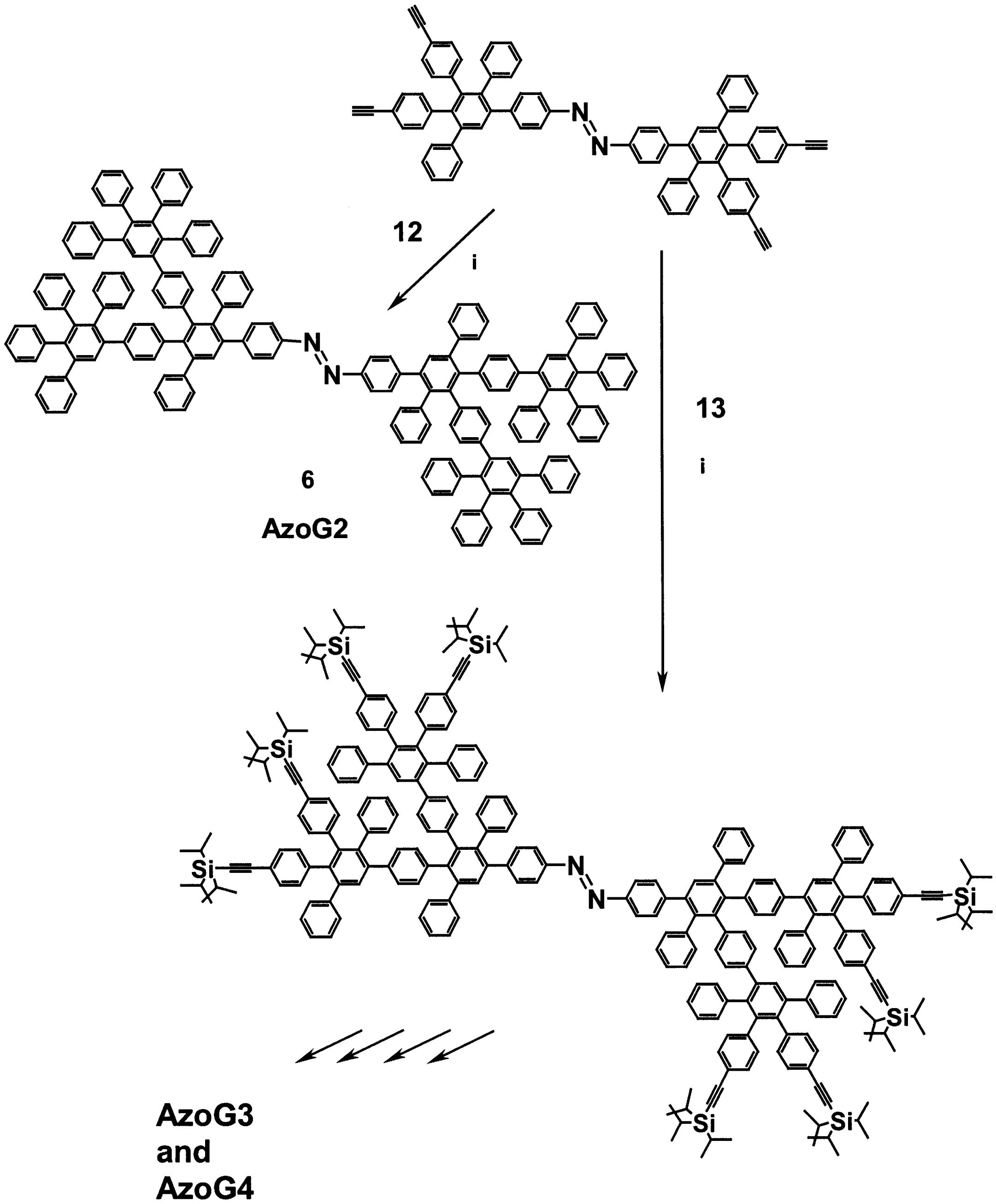


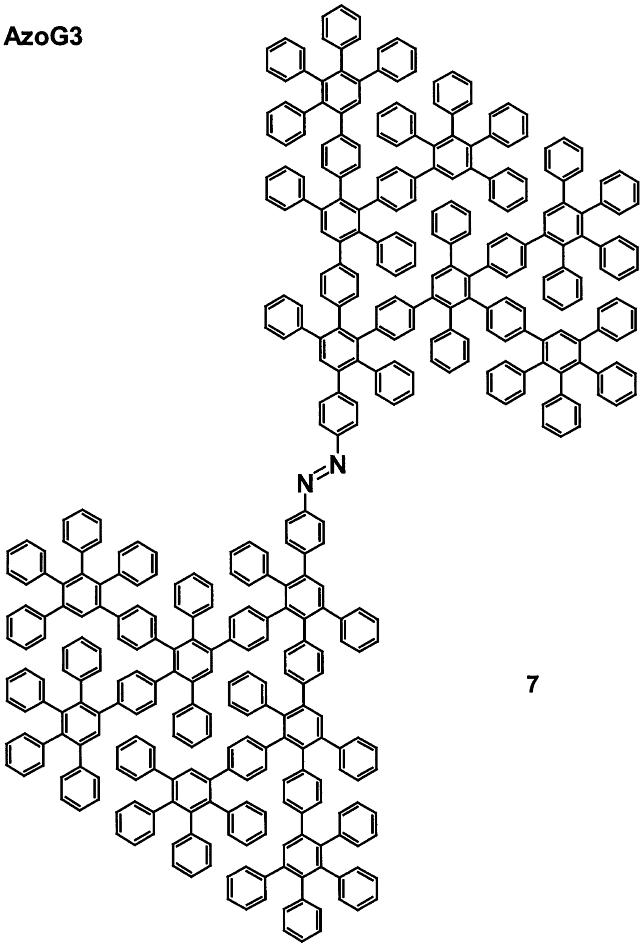
Figure 3. Synthesis of the higher generation dendrimers: (i) 6 equiv of **12**/**13**, respectively, *o*-xylene, 142 °C, 91% and 86% respectively.

The rigidity of the polyphenylene dendrimers has been previously studied in detail. The shape persistence found by PFM−AFM (pulsed force mode−atomic force microscopy) measurements[23] was corroborated by analysis using advanced solid-state NMR spectroscopy techniques,[22] which have demonstrated that only restricted reorientations of single terminal phenyl substituents around fixed axes occur. This can also be assumed to be true for the dendrimers presented here. In contrast to the flexible azobenzene-containing dendrimers studied previously[15−17] the only shape-nonpersistent part of the polyphenylene dendrimers is the azobenzene unit. Because of the rigid dendrons, the change at the center is expressed at the periphery.

Figure 14 shows an energy-minimized structure of AzoG1 (**5**) calculated in vacuo using HyperChem Pro 6.0, MM2 (MM+) force field optimization (the model is a local minimum, not an absolute minimum).

The conformation of the resulting molecule is similar to that of the crystal structure. As a result, we have assumed that the calculated structure for the cis-isomer is as good an approximation as the trans model is. Compared with one another, the trans- and the cis-isomers display dramatic differences in volume, already in the first generation. This change should clearly be detectable by gel permeation chromatography (GPC). GPC measurements of AzoG2, AzoG3, and AzoG4 reveal that azobenzene-cored polyphenylene dendrimers exhibit an increase in elution volume upon 364 nm irradiation to the photostationary state (PSS), as shown in Figure 15, indicating a decrease in hydrodynamic volume of the dendrimer molecules after UV irradiation. The GPC measurements of a dendrimer solution were done in the dark at room temperature immediately after the PSS was reached. Because of the slow rate of the thermal cis−trans isomerization, the trans- and cis-

AzoG3



7

Figure 4. Generation 3 (**7**) prepared in 93% yield.

Table 2. Interplanar Angles (deg) between the Phenyl Rings in Dendrimer 5[a]

	planes					
planes	1	3	4	5	6	7
			(a) Dichloromethane Solvate			
2	53.07	134.37	117.02	114.64	64.23	
8	51.33	118.47	123.83	112.7	67.56	
1						5.4
			(b) Tetrahydrofuran Solvate			
2	51.01	122.56	121.24	111.06	62.61	
1						0

[a] Planes 1 and 7 are the azobenzene's rings. Planes 2 and 8 denote the central planes of the 2,3,4,5-tetraphenylphenyl units. The other planes are arranged in a clockwise manner, with plane 3 having one hydrogen and one phenylene as neighbors. For the assignment of the planes, see also Figure 12.

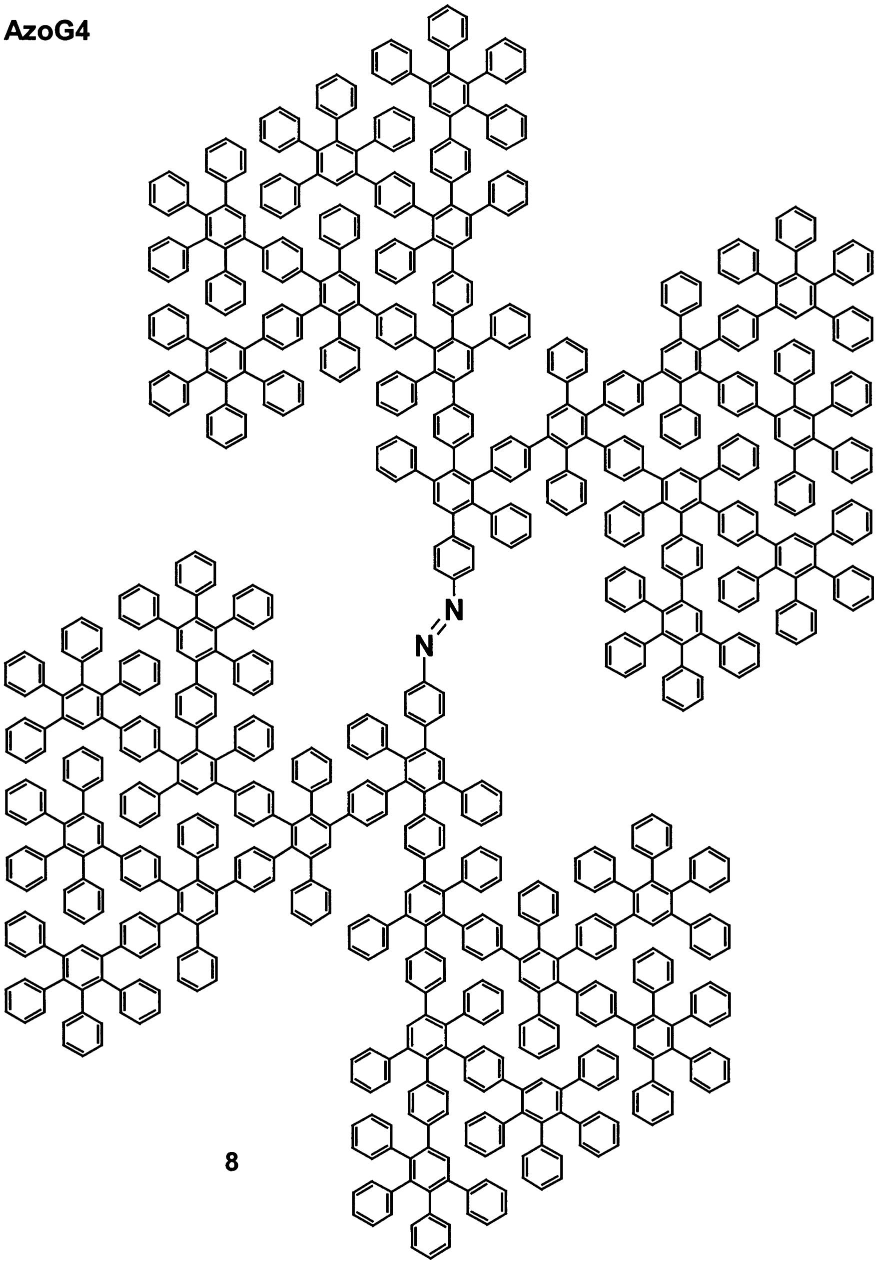
isomer contents of the irradiated dendrimer solution can be considered as invariant during the GPC measurements.

For dendrimer AzoG2, the peak elution volume increases from 34.17 mL before irradiation to 34.64 mL after, corresponding to an average 38% ± 4% decrease of the hydrodynamic volume.[35] The contractions for AzoG3 and AzoG4 upon UV irradiation are 37% ± 4% and 24% ± 2%, respectively. Such a great photomodulation of molecular size clearly shows that the conformation of azobenzene-cored polyphenylene dendrimers can be substantially altered when stimulated by light. The reduction of the hydrodynamic volume for the polyphenylene dendrimers with one central chromophore is even larger than that achieved by McGrath's dendrimers[15a,c] with a maximal contraction of 29%. This stresses the need for a rigid dendrimer scaffold in order to transfer the structural change of the small central unit to the whole nanosphere and to make use of the whole extent of the trans−cis isomerization. In comparison, in a more flexible dendrimer, the spatial relationship between the functional core and the periphery cannot be absolutely defined, and thus the conformational change cannot be completely expressed at the periphery.[36]

Photochemistry. All the azobenzene-cored polyphenylene dendrimers exhibit an effective photoresponsive behavior. Irradiation of a dendrimer solution at 364 nm results in photoisomerization from the trans- to the cis-isomer, as evidenced in Figure 16, parts A and B, by a decrease in absorbance at about 365 nm and an increase in absorbance at about 450 nm. These correspond to the values for the cis- and trans-isomers reported of other dendronized azobenzenes.[15,17] The presence of isosbestic points in the absorption spectra during photoisomerization is clearly seen in Figure 16, parts A and B. Under the experimental conditions used, a photostationary state (PSS) is reached within 10 min of irradiation. The content of cis-isomer at the PSS was calculated by $(A_0 - A_{\mathrm{PSS(364)}})/A_0$, where A_0 and $A_{\mathrm{PSS(364)}}$ are the absorbances at 365 nm of the unirradiated solution and of the solution at the PSS under 364 nm irradiation, respectively. This calculation is approximate and based on the following assumptions. First, the initial dark-incubated dendrimer solution consists of predominantly trans-isomer.[2,15b,d] This is supported by our crystallographic data in which the crystals contain only trans-isomers. Second, compared to the trans-isomer, the cis-isomer has a negligible absorbance at 365 nm. This has been shown for other azobenzenes and so can also be assumed to be true for our system.[15b,d,27] The absorption spectrum of a polyphenylene dendrimer, whose structure and bulkiness are similar to the polyphenylene arms of dendrimer AzoG4, is shown in Figure 16B as a dotted line, from which it is reasonable to make the third assumption that the polyphenylene branches have a negligible absorbance at 365 nm. The apparent first-order rate constant k_1 for trans−cis photoisomerization is determined from a plot of $\ln(A_t - A_{\mathrm{PSS(364)}}) \sim t$ (Figure 16C), where A_t is the absorbance at 365 nm at irradiation time t. The content of cis-isomer at the PSS and the corresponding apparent first-order rate constants under 364 nm irradiation for various dendrimers are listed in Table 3.

The reverse cis−trans isomerization of azobenzene-cored polyphenylene dendrimers from the PSS obtained upon 364 nm irradiation can be induced thermally or by visible irradiation, for example at 447 nm. Visible irradiation leads to a photostationary state, where the content of the trans-isomer is greatly enhanced (Figure 17A and Table 3), whereas thermal isomerization maximizes the absorbance at about 365 nm which corresponds to the trans-isomer (Figure 17C).[2,15] The same isosbestic points are present during the whole process, indicating a completely reversible and reproducible photoisomerization.

The apparent first-order rate constant for the reverse reaction induced by visible irradiation and the first-order rate constant for thermal isomerization were also determined by a plot of $\ln(A_{\mathrm{PSS(447)}} - A_t) \sim t$



8

Figure 5. Generation 4 (**8**) prepared in 74% yield.

(Figure 17B) and $\ln(A_0 - A_t) \sim t$ (Figure 17D), respectively, where $A_{PSS(447)}$ is the absorbance at 365 nm of the dendrimer solution at the PSS upon irradiation at 447 nm. The cis-isomer content at the PSS, calculated by $(A_0 - A_{PSS(447)})/A_0$, and the (apparent) first-order rate constants for the reverse isomerization are also listed in Table 3. The photoresponsive behavior of polyphenylene dendrimers with an azobenzene core is dependent on their structures, whereas the azobenzene-containing dendrimers with Fréchet type dendritic arms show no such structure dependence.[15a,b] From Table 3, it can be seen that the cis-isomer content at the PSS under 364 nm irradiation decreases with increasing dendrimer generation and degree of branching, the effect of the latter being more profound than the former. This can be explained as a result of the increasing steric effect of the dendrimer branches. In comparison, the cis content at the PSS under 447 nm irradiation depends only slightly on the bulkiness of the dendrimer arms. The steric effect has only a slight influence on the rate of the trans−cis photoisomerization and the reverse photoreaction. The rate constant of the cis−trans thermal isomerization for the first and second dendrimer generations remains almost the same. However, it increases for the third and fourth generations and increases rapidly with an increasing degree of branching (dendrimer AzoG2A$_4$B relative to dendrimer AzoG2AB and AzoG2). It is important to note that the reaction rate of the thermal isomerization is much slower than that of the photoisomerization induced by visible irradiation, as shown in Table 3. In contrast to the structure-dependent photoresponsive behavior of the azobenzene-cored polyphenylene dendrimers studied in this contribution, McGrath and co-workers have reported only a negligible influence of the nature of the attached dendritic fragment[15d] on the cis−trans thermal isomerization of the poly(aryl ether)s which we believe is due to the low generation and the flexibility of the dendrimer fragments used in their study.

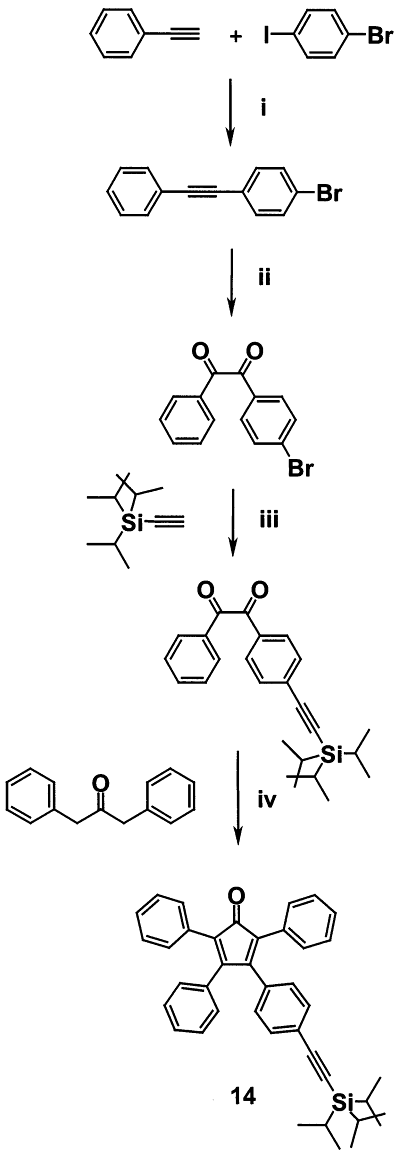


Figure 6. Synthetic route to the AB-branching unit: (i) (Pd(PPh$_3$)$_2$]Cl$_2$, PPh$_3$, CuI, THF/triethylamine, room temperature, 85%; (ii) 0.5 equiv of I$_2$, DMSO, 155 °C, 83%; (iii) (Pd(PPh$_3$)$_2$]Cl$_2$, PPh$_3$, CuI, toluene/triethylamine, 80 °C, 76%; (iv) nBu$_4$NOH, *tert*-butyl alcohol, 80 °C, 75%.

Table 3. Apparent First-Order Rate Constant k_1 for Trans−Cis Photoisomerization under 364 nm Irradiation, Apparent First-Order Rate Constant k_2 for Cis−Trans Photoisomerization under 447 nm Irradiation, First-Order Rate Constant k_3 for Cis−Trans Thermal Isomerization, the Cis-Isomer Content at the PSS under 364 nm Irradiation (C_{364}), and the Cis-Isomer Content at the PSS under 447 nm Irradiation (C_{447})

dendrimer	C_{364}/%	C_{447}/%	k_1/min^{-1}	k_2/min^{-1}	$k_3 \times 10^4$/min^{-1}
AzoG1	88	14	0.85	1.8	2.6
AzoG1hex	89	11	0.51	1.4	1.8
AzoG2AB	81	13	0.88	1.9	2.6
AzoG2	79	13	0.84	1.8	2.7
AzoG2A$_4$B	53	12	0.70	2.0	7.7
AzoG3	77	12	0.84	2.1	2.9
AzoG4	75	11	0.79	2.5	3.3

The trans−cis isomerization of the azobenzene cored polyphenylene dendrimers was followed by UV−vis measurements. The resulting dramatic conformational change of the entire dendrimer structure was apparent in the GPC results as discussed above.

Conclusions

A series of polyphenylene dendrimers with an azobenzene core have been synthesized and characterized. The azobenzene-cored dendrimers exhibit effective, reversible, and reproducible photoresponsive properties upon UV and visible irradiation. The photoresponsive behavior of these dendrimers is highly dependent on their structures. Because of the well-defined and rigid structure of polyphenylene dendrimer arms, the greatest photomodulation of dendrimer molecular size has been observed by switching a single central unit. This can clearly be ascribed to the rigidity of the polyphenylene dendrons and indicates that these dendrimers can be substantially modulated by a light stimulus and express the structural change at the periphery.

Experimental Section

Spectroscopy Measurements. A dark-incubated azobenzene-cored polyphenylene dendrimer solution in toluene in a quartz cuvette of 10 mm path length was irradiated by a 300-W xenon arc light through a band-pass filter (364 ± 7 nm) to induce the trans−cis photoisomerization. A photostationary state will be reached upon a certain time of UV irradiation. The solution was then irradiated with visible light through another band-pass filter (447 ± 17 nm) or kept in the dark to induce the cis-trans reverse isomerization. The absorption spectra of the dendrimer solution were recorded during the whole process on a Perkin-Elmer Lamdba 40 UV/vis spectrometer using toluene as reference. All reactions were carried out at room temperature.

Gel Permeation Chromatography (GPC) Measurements. GPC was performed on a system equipped with a Waters model 610 pump at a flow rate of 1.0 mL/min and a Waters 484 absorbance detector (254 nm). μ-Styragel columns with porosities of 500, 10^3, 10^4, and 10^5 Å were employed. THF was used as mobile phase. Toluene was used as internal standard.

Crystal Structure. The crystal structure determinations were carried out on a Nonius KCCD diffractometer with graphite monochromtated Mo Kα radiation at 120 K. These structures were solved by direct methods (Shelxs97). Refinement was done with anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atoms were refined with fixed isotropic temperature factors in riding mode. Files CCDC 189260, 189261, and 189262 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre. (Address: 12 Union Road, Cambridge CB2 1EZ, U.K. Fax: (+44)-1223-336-033. E-mail: deposit@ccdc.cam.ac.uk.)

Characterization. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX250 spectrometer, a Bruker AC300 spectrometer, and a Bruker AMX500 NMR spectrometer by using residual proton resonance of the solvent or the carbon signal of the deuterated solvent as the internal standard. Chemical shifts are reported in parts per million. For the ^{13}C *j*-modulated spin−echo NMR measurements the abbreviations C$_{quat}$ and C$_{tert}$ represent quaternary C atoms and CH$_2$ as well as CH$_3$ and CH groups, respectively. FD mass spectra were performed with a VG-Instruments ZAB 2-SE-FDP. MALDI−TOF mass spectra were measured with a Bruker Reflex II and dithranol as matrix (molar ratio dithranol/sample 250:1). The elemental analysis was carried out by the Microanalytical Laboratory of the University of Mainz, Mainz, Germany.

4,4′-Diiodoazobenzene (1). 4-Iodoaniline (3 g, 13.7 mmol) was dissolved in 80 mL of degassed dichloromethane under an argon atmosphere. To this was added a finely ground mixture of KMnO$_4$ (5.1 g, 3.13 mmol) and CuSO$_4$·5H$_2$O (5.1 g, 20.26 mmol). The reaction mixture was stirred at room temperature for 3 days and afterward filtered through Celite. The collected fractions were combined and the solvent was evaporated under reduced pressure. The crude product was

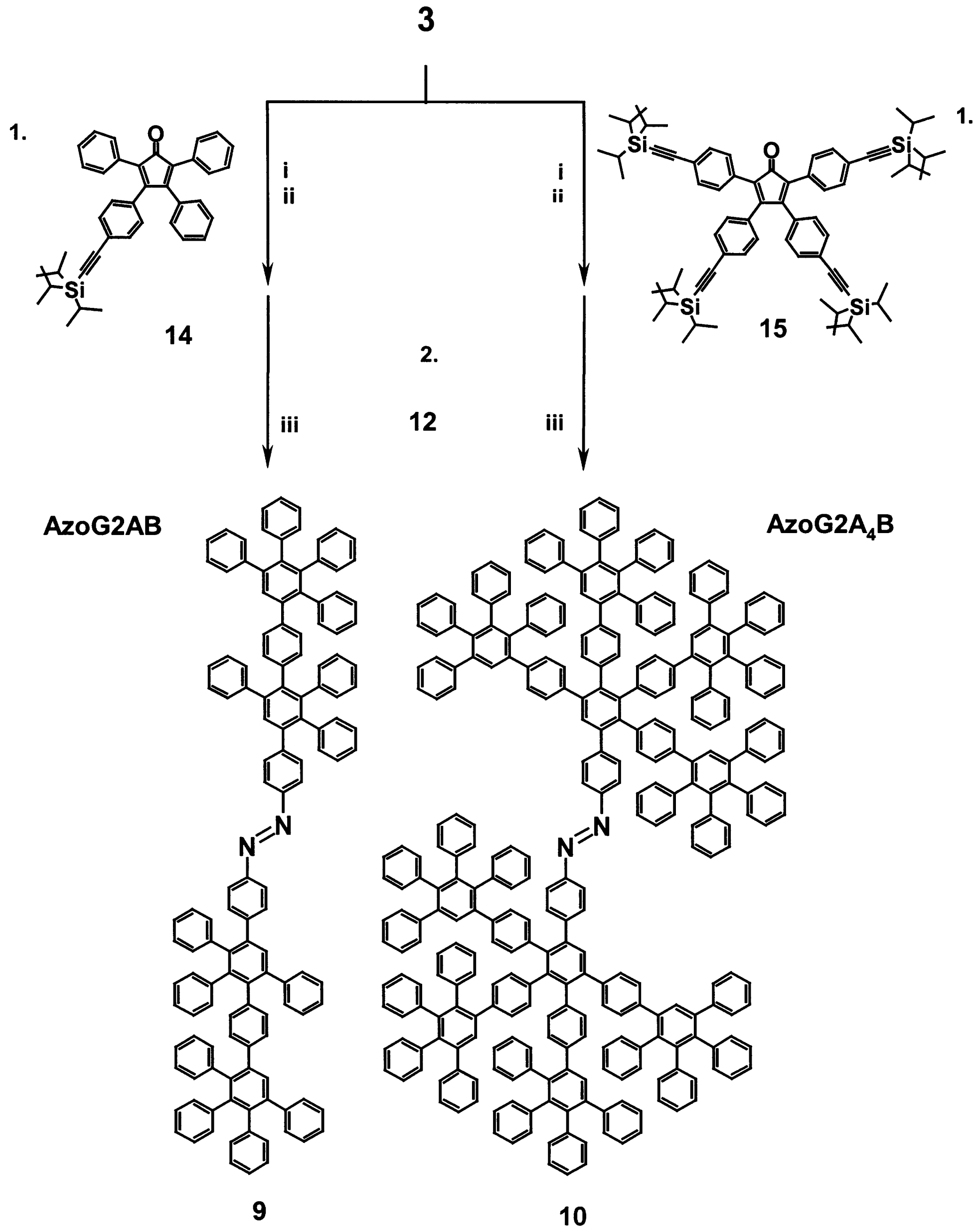


Figure 7. Synthesis of **9** and **10**: (i) 3 equiv **14**/**15**, *o*-xylene, 142 °C; (ii) 2 and 8 equiv of *n*Bu$_4$NF, respectively, THF, room temperature; (iii) 3 and 12 equiv of **12** respectively, *o*-xylene, 142 °C, 96% and 73%, respectively.

purified by column chromatography (silica gel, PE) to give **1** as an orange solid. Yield: 1.81 g (4.17 mmol), 61%.

Mp: 242−244 °C. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 300 K): δ = 7.89 (d, 4H; ^3J = 8.52 Hz); 7.66 (d, 4H; ^3J = 8.8 Hz). ^{13}C NMR (75 MHz, CD$_2$Cl$_2$, 300 K): δ = 151.9, 138.6, 124.5, 98.1. MS (FD 8 kV), *m*/*z*: 434.1 (100%, M$^+$). Anal. Calcd for $C_{12}H_8I_2N_2$ (434.02): C, 33.21; H, 1.86; N, 6.45. Found: C, 33.14; H, 2.06; N, 6.41.

4,4′-Bis(phenylethynyl)azobenzene (4). **1** (300 mg (0.69 mmol) was dissolved in a mixture of 16 mL of triethylamine and 8 mL of tetrahydrofuran. To this were added bis(triphenylphosphine)palladium(II) dichloride (102 mg, 0.14 mmol), copper(I) iodide (53 mg, 0.28 mmol), and triphenylphosphine (73 mg, 0.28 mmol), and then the flask was evacuated and flushed with argon. After the reaction was stirred for 10 min, phenylacetylene (0.2 mL, 186 mg, 1.83 mmol) was injected into the reaction mixture. The reaction mixture was stirred overnight under argon atmosphere and then diluted with dichloromethane and extracted with water. The organic phase was dried over MgSO$_4$, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, PE/CH$_2$Cl$_2$ 1:1) to afford **4** as an orange solid. Yield: 232 mg (0.61 mmol), 88%.

Mp: 254−255 °C. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 300 K): δ = 7.95 (d, 4H; ^{3}J 8.77 Hz); 7.70 (d, 4H; ^{3}J 8.78 Hz); 7.60−7.57 (m, 4H); 7.42−7.39 (m, 6H). ^{13}C *j*-modulated spin echo NMR (125 MHz, CD$_2$Cl$_2$, 303 K): δ = 155.39, 135.9, 135.2, 132.9, 132.2, 132.0, 129.7, 126.5, 126.4, 95.5, 92.5. MS (FD 8 kV), *m*/*z*: 381.8 (100%, M$^+$); 190.9 (10%, M^{2+}). Anal. Calcd for $C_{28}H_{18}N_2$ (382.47): C, 87.93; H, 4.74; N, 7.32. Found: C, 87.78; H, 4.22; N, 6.92.

AzoG1 (5). **3** (120 mg, 0.52 mmol) and **12** (473 mg, 1.23 mmol) were reacted in 10 mL of degassed *o*-xylene at 170 °C for 12 h under an argon atmosphere. The cooled reaction mixture was poured into methanol and the crude product collected by filtration. The filter was washed with pentane until the filtrate became colorless. The crude product was purified by column chromatography (silica gel, PE/CH$_2$Cl$_2$ 2:1) to afford **5** as an yellow amorphous powder. Yield: 451 mg (0.48 mmol), 92%.

Mp: >300 °C. ^{1}H NMR (250 MHz, CD$_2$Cl$_2$, 300 K): δ = 7.67 (d, 4H; ^3J = 8.53 Hz); 7.58 (s, 2H); 7.29 (d, 4H; ^3J = 8.53 Hz);

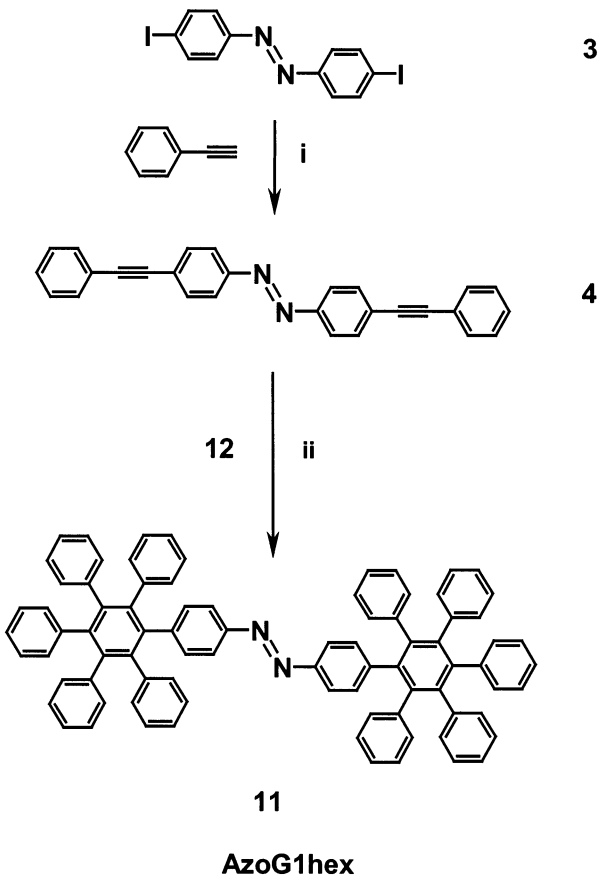


Figure 8. Synthetic route to **11**: (i) 3 equiv of phenylacetylene, (Pd(PPh$_3$)$_2$]Cl$_2$, PPh$_3$, CuI, THF/triethylamine, room temperature, 88%; (ii) diphenyl ether, 195 °C, 62%.

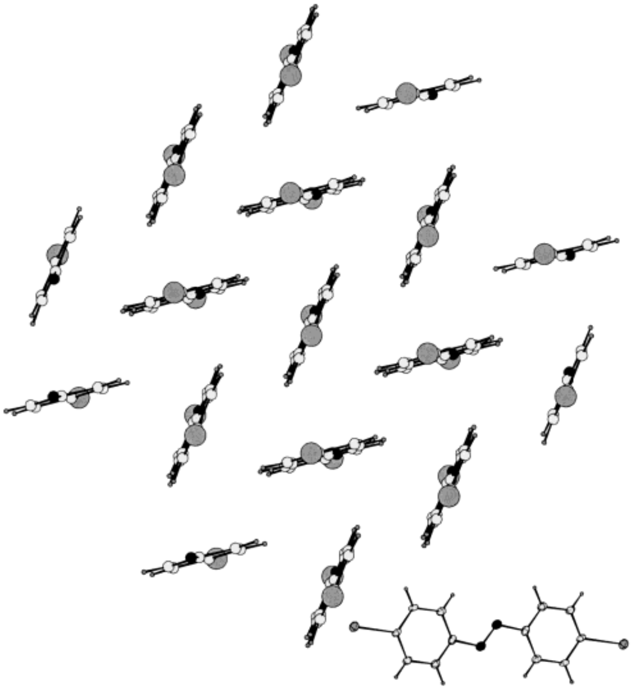


Figure 9. Crystallographic structure of 4,4′-diiodoazobenzene (**1**).

7.15−7.09 (m, 8H); 6.89−6.78 (m, 32H). ^{13}C *j*-modulated spin echo NMR (75 MHz, CD$_2$Cl$_2$, 300 K): δ = 150.9, 144.9, 142.0, 141.8, 141.0, 140.4, 140.1, 140.0, 139.9, 139.4, (C$_{\text{quat}}$); 131.6, 131.5, 131.1, 130.8, 130.0, 127.7, 127.1, 126.9, 126.7, 126.4, 125.8, 125.7, 125.5, 122.1, 120.1 (C$_{\text{tert}}$). MS (FD 8 kV), *m*/*z*: 941.9 [M]$^+$; 470.7 [M]$^{2+}$. Anal. Calcd for $C_{72}H_{50}N_2$ (943.21): C, 91.69; H, 5.34; N, 2.97. Found: C, 90.96; H, 5.40; N, 2.87.

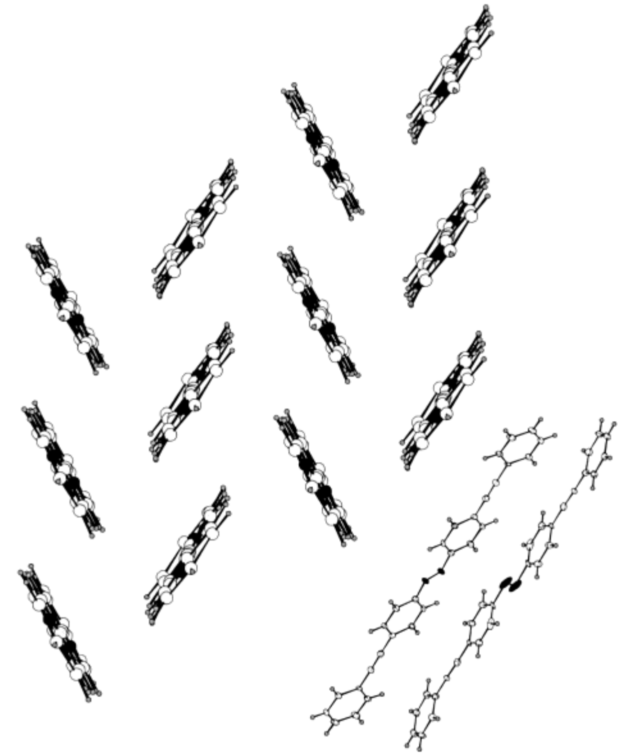


Figure 10. Crystallographic structure of 4,4′-bis(phenylethynyl)azobenzene (**4**).

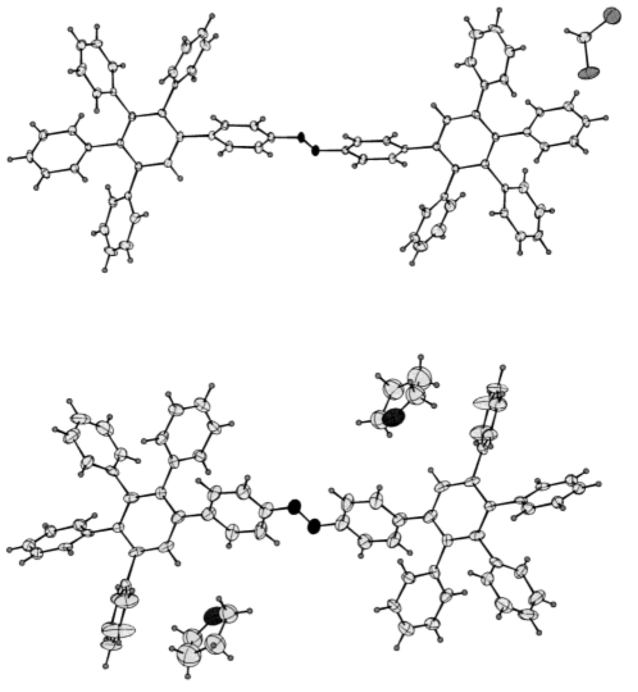


Figure 11. Crystallographic structure of AzoG1 (**5**) crystallized from (a) dichoromethane and (b) tetrahydrofuran.

AzoG1hex (11). 4 (120 mg, 0.31 mmol) and **12** (362 mg, 0.94 mmol) were reacted in 10 mL of degassed diphenyl ether at 210 °C for 5 days under an argon atmosphere. The cooled reaction mixture was poured into methanol and the crude product collected by filtration. The filter was washed with pentane until the filtrate became colorless. The crude product was purified by column chromatography (silica gel, PE/CH$_2$Cl$_2$ 3:1) to afford **11** as an yellow amorphous powder. Yield: 213 mg (0.19 mmol), 62%.

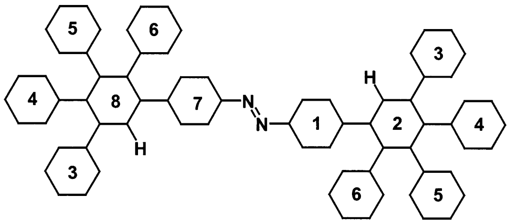


Figure 12. Assignment of the planes for the dihedral angles.

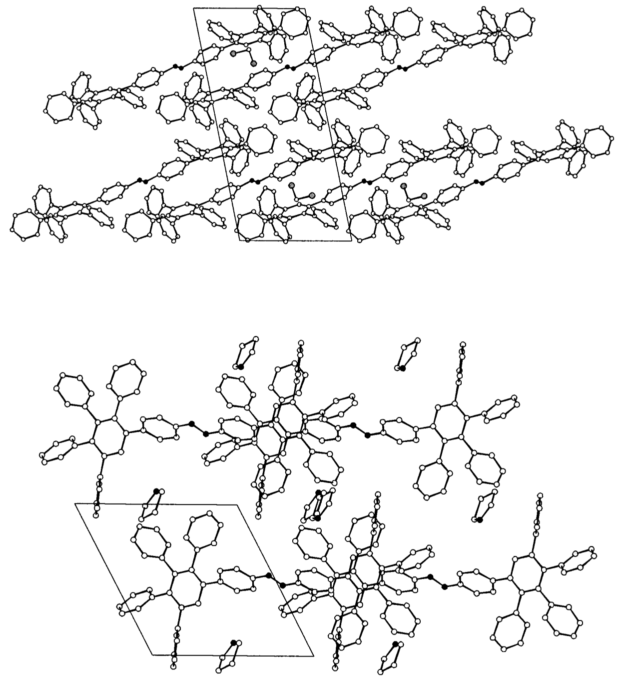


Figure 13. Packing of **5** in the crystals: (a) dichoromethane and (b) tetrahydrofuran.

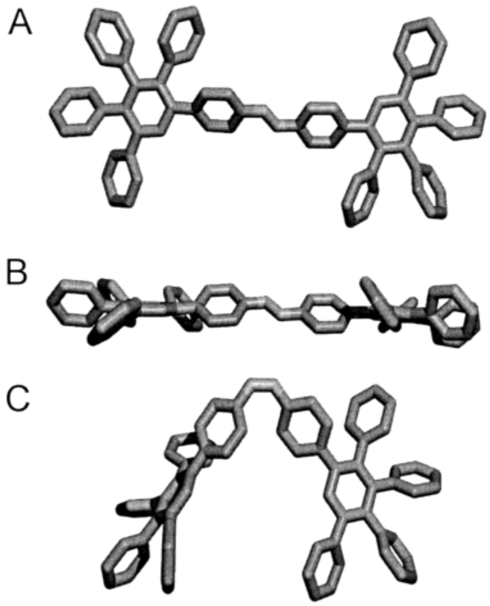


Figure 14. Models of **5** (A) trans-isomer top view, (B) trans-isomer side view, (C) *cis*-isomer side view.

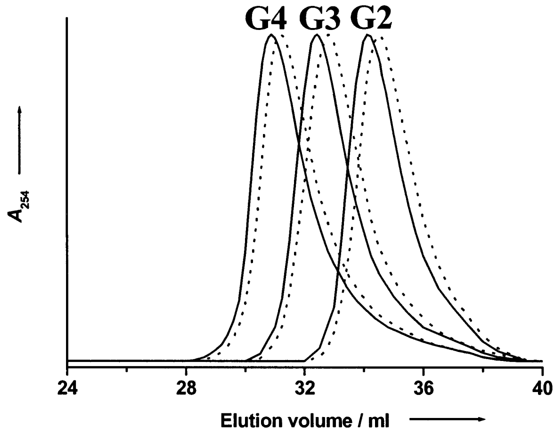


Figure 15. GPC chromatograms for dendrimers **6**, **7**, and **8** before (—) and after (···) irradiation at 364 nm to the photostationary state.

Mp: >300 °C. ^{1}H NMR (250 MHz, CD$_2$Cl$_2$, 300 K): δ_H = 7.29 (d, 4H; ^3J = 8.39 Hz); 6.96 (d, 4H; ^3J = 8.39 Hz); 6.91−6.83 (m, 50H). ^{13}C *j*-modulated spin echo NMR (75 MHz, CD$_2$Cl$_2$, 300 K): δ = 149.9; 144.1, 140.7, 140.7, 140.7, 140.5, 140.4, 140.2, 139.7 (C$_{quat}$); 132.2, 131.4, 126.7, 126.6, 125.5, 125.3, 121.0 (C$_{tert}$). MS (FD 8 kV), *m/z* [ue^{-1}]: 1095.5 (100%, M$^+$); 547.2 (23%, M^{2+}). Anal. Calcd for $C_{84}H_{58}N_2$ (1095.41): C, 92.11; H, 5.34; N, 2.56. Found: C, 91.79; H, 5.13; N, 2.50.

AzoG2AB (9). AzoG1ethin$_2$ (80 mg, 0.081 mmol) and **12** (68 mg, 0.177 mmol) were reacted in 10 mL of degassed *o*-xylene at 170 °C for 12 h under an argon atmosphere. The cooled reaction mixture was poured into methanol and the crude product collected by filtration. The filter was washed with pentane until the filtrate became colorless. The crude product was purified by column chromatography (silica gel, PE/CH$_2$Cl$_2$ 1:1) to afford **9** as an yellow amorphous powder. Yield: 132 mg (0.078 mmol), 96%.

Mp: >300 °C. ^{1}H NMR (250 MHz, CD$_2$Cl$_2$, 300 K): δ_H = 7.66 (d, 4H, ^3J = 8.77 Hz); 7.55 (s, 2H); 7.35, 7.31, (2s, 2H), 7.33 (d, 4H, ^3J = 8.39 Hz); 7.16−7.12 (m, 14H); 7,02−6.58 (m, 64H). ^{13}C *j*-modulated spin echo NMR (75 MHz, CD$_2$Cl$_2$, 300 K): δ = 151.9, 144.9, 144.8, 141.8, 141.7, 141.0, 140.9, 140.8, 140.7, 140.3, 140.3, 140.0, 139.9, 139.5, 139.4, 139.3, 139.3, 139.2, 139.1, 138.7, 138.3, 138.0 (C$_{quat}$); 131.5, 131.2, 131.1, 130.9, 130.8, 130.0. 128.6, 128.3, 127.7, 127.6, 127.6, 127.1, 127.1, 127.0, 126.8, 126.7, 126.5, 126.4, 126.4, 126.3, 126.0, 125.8, 125.6, 125.3, 122.1, 120.1 (C$_{tert}$). MS (FD 8 kV), *m/z* [ue^{-1}]: 1705.0 (100%, M$^+$); 852.2 (36%, M^{2+}); 568.2 (4%, M^{3+}). Anal. Calcd for $C_{132}H_{90}N_2$ (1704.20): C, 93.03; H, 5.32; N, 1.64. Found: C, 92.38; H, 5.65; N, 1.46.

AzoG2 (6). AzoG1ethin$_4$ (115 mg, 0.11 mmol) and **12** (190 mg, 0.49 mmol) were reacted in 10 mL of degassed *o*-xylene at 170 °C for 24 h under an argon atmosphere. The cooled reaction mixture was poured into methanol and the crude product collected by filtration. The filter was washed with pentane until the filtrate became colorless. The crude product was purified by column chromatography (silica gel, PE/CH$_2$Cl$_2$ 1:1) to afford **6** as an yellow amorphous powder. Yield: 248.2 mg (0.1 mmol), 91%.

Mp: >300 °C. ^{1}H NMR (250 MHz, CD$_2$Cl$_2$, 300 K): δ_H = 7.64 (d, 4H, ^3J = 8.53 Hz); 7.53 (s, 2H); 7.42, 7.37 (2s, 4H); 7.25−7.07 (d, 4H; ^3J = 8.53 Hz; m, 32H); 6.98−6.65 (m, 76H); 6.56 (d, 4H, ^3J = 8.53 Hz); 6.50 (d, 4H, ^3J = 8.19 Hz). ^{13}C *j*-modulated spin echo NMR (75 MHz, CD$_2$Cl$_2$, 300 K): δ = 150.8, 144.8, 141.8, 141.7, 140.8, 140.7, 140.6, 140.4, 140.3, 140.2, 140.0, 139.9, 139.3, 139.2, 139.1, 138.9, 138.5, 138.0, 137.8 (C$_{quat}$); 131.6, 131.5, 131.0, 130.9, 130.6, 129.8, 128.6, 128.3, 127.6, 127.4, 127.0, 126.7, 126.7, 126.4, 126.3, 126.1, 125.8, 125.5, 125.2, 121.9 (C$_{tert}$). MS (FD 8 kV), *m/z* [ue^{-1}]: 2466 [M]$^+$. Anal. Calcd for $C_{192}H_{130}N_2$ (2465.19): C, 93.55; H, 5.32; N, 1.14. Found: C, 93.84; H, 5.47; N, 1.09.

AzoG2A$_4$B (10). AzoG1ethin$_8$ (50 mg (0.044 mmol) and **12** (149 mg, 0.38 mmol) were reacted in 10 mL of degassed *o*-xylene at 170 °C for 48 h under an argon atmosphere. The cooled reaction mixture was poured into methanol and the crude product collected by filtration. The filter was washed with pentane until the filtrate became colorless. The crude product was purified by chromatography (silica gel, PE/CH$_2$-

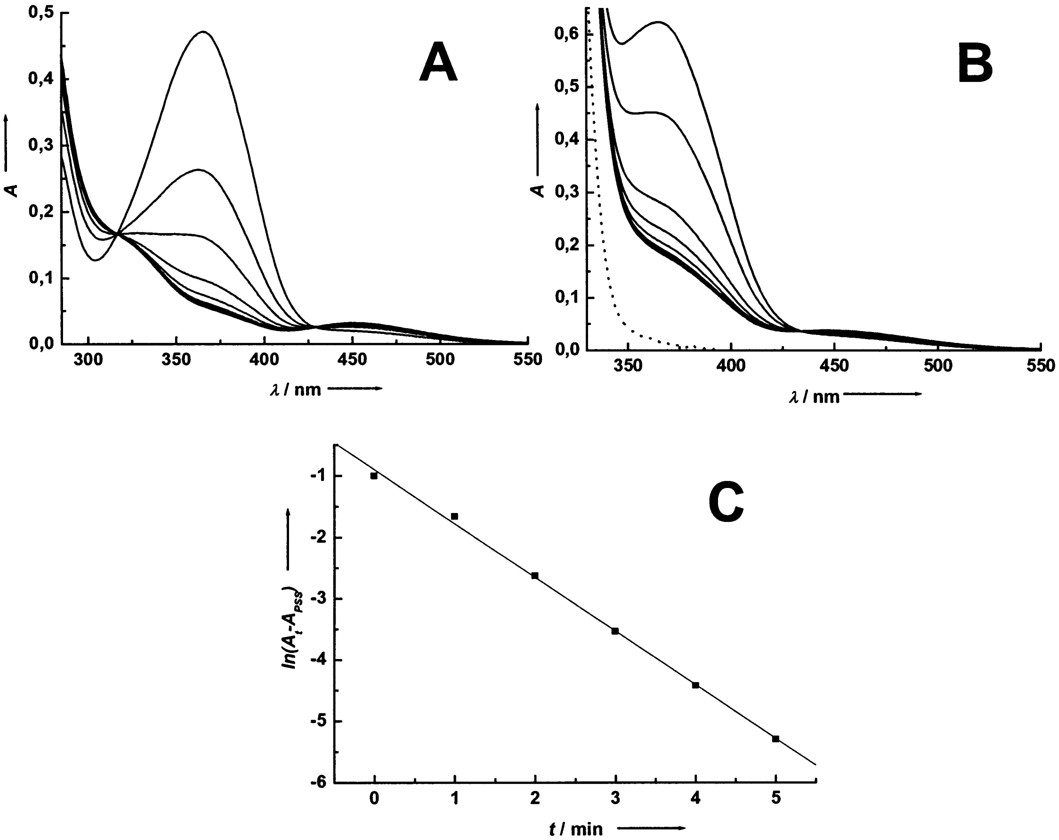


Figure 16. (A) Plots of absorption spectra of ca. 10^{-5} M dendrimer **5** solution in toluene vs time under 364 nm irradiation for 0, 1, 2, 3, 4, 5, 6, 8, and 10 min (from top to bottom at 365 nm), respectively. (B) Plots of absorption spectra of ca. 10^{-5} M dendrimer **8** solution in toluene vs time under 364 nm irradiation for 0, 1, 2, 3, 4, 5, 6, 8, and 10 min (from top to bottom at 365 nm), respectively. The dash line shows the absorption spectrum of a pure polyphenylene dendrimer of the same generation at the same concentration. (C) Determination of the apparent first-order rate constant of dendrimer **5** trans−cis photoisomerization under 364 nm irradiation.

Cl_2 1:1) to afford **10** as an yellow amorphous powder. Yield: 128 mg (0.032 mmol), 73%.

Mp: >300 °C. ^{1}H NMR (250 MHz, CD_2Cl_2, 300 K): δ_H = 7.73 (d, 4H, ^3J = 8.39 Hz); 7.52, 7.51, 7.50 (3s, 6H), 7. 43(d, 4H, ^3J = 8.40 Hz); 7.21−7.10 (m, 44H); 7.01−7.68 (m, 140H); 6.58 (d, 4H, ^3J = 8.39 Hz); 6.47 (d, 4H, ^3J = 8.01 Hz); 6.45 (d, 4H, ^3J = 8.01 Hz). ^{13}C *j*-modulated spin echo NMR (75 MHz, CD_2Cl_2, 300 K): δ = 150.9, 144.9, 142.0, 141.9, 141.9, 141.8, 141.3, 140.8, 140.8, 140.7, 140.6, 140.5, 140.3, 140.2, 140.1, 139.9, 139.6, 139.4, 139.4, 139.3, 139.2, 139.1, 139.0, 138.8, 138.6, 138.0, 137.9, 137.7 (C_{quat}), 131.6, 131.1, 130.8, 130.0, 129.4, 129.3, 128.8, 138.5, 127.6, 126.9, 126.6, 126.3, 125.6, 125.4, 122.2 (C_{tert}). MALDI−TOF−MS, *m*/*z* [ue^{-1}]: 4091 [M + Ag]$^+$. Anal. Calcd for $C_{312}H_{210}N_2$ (3987.17): C, 93.99; H, 5.31; N, 0.70. Found: C, 93.89; H, 5.41; N, 0.64.

AzoG3 (7). AzoG2ethin$_8$ (125 mg, 0.047 mmol) and **12** (173.6 mg, 0.452 mmol) were reacted in 10 mL of degassed *o*-xylene at 170 °C for 48 h under an argon atmosphere. The cooled reaction mixture was poured into methanol and the crude product collected by filtration. The filter was washed with pentane until the filtrate became colorless. The crude product was purified by chromatography (silica gel, PE/CH_2Cl_2 1:1) to afford **7** as an yellow amorphous powder. Yield: 242.1 mg (0.044 mmol), 93%.

Mp: >300 °C. ^{1}H NMR (250 MHz, CD_2Cl_2, 300 K): δ_H = 7.65 (d, 4H, ^3J = 8.39 Hz); 7.53 (s, 2H); 7.42, 7.41 (2s, 4H); 7.38, 7.37 (2s, 6H); 7.33 (s, 2H); 7.26−7.03 (d, 4H; ^3J = 8.39 Hz; m, 82H); 7.00−6.62 (m, 308H); 6.56−6.43 (m, 24H). ^{13}C *j*-modulated spin echo NMR (75 MHz, CD_2Cl_2, 300 K): δ = 150.9, 144.9, 142.0, 141.8, 141.6, 141.3, 141.0, 140.9, 140.8, 140.7, 140.5, 140.4, 140.3, 140.1, 139.4, 139.3, 139.2, 139.1, 138.9, 138.7, 138.4, 138.1, 137.8 (C_{quat}); 131.6, 131.1, 130.8, 130.0, 128.6, 128.3, 127.6, 126.8, 126.5, 126.3, 125.6, 125.3, 122.1 (C_{tert}). MALDI−TOF−MS, *m*/*z* [ue^{-1}]: 5510 [M]$^+$. Anal. Calcd for $C_{432}H_{290}N_2$ (5509.14): C, 94.19; H, 5.31; N, 0.51. Found: C, 93.90; H, 5.39; N, 0.55.

AzoG4 (8). AzoG3ethin$_{16}$ (70 mg, 0.012 mmol) and **12** (219 mg, 0.57 mmol) were reacted in 10 mL of degassed *o*-xylene at 170 °C for 48 h under an argon atmosphere. The cooled reaction mixture was poured into methanol and the crude product collected by filtration. The filter was washed with pentane until the filtrate became colorless. The crude product was purified by chromatography (silica gel, PE/CH_2Cl_2 1:1) to afford **8** as an yellow amorphous powder. Yield: 102 mg (8.9 × 10^{-3} mmol), 73%.

Mp: >300 °C. ^{1}H NMR (250 MHz, CD_2Cl_2, 300 K): δ_H = 7.65 (d, 4H, ^3J = 8.39 Hz); 7.53 (s, 2H); 7.42, 7.38, 7.37, 7.32 (4s, br, 28H); 7. 24 (d, 4H; ^3J = 8.39 Hz); 7.15−6.41 (m, 572H). ^{13}C *j*-modulated spin echo NMR (75 MHz, CD_2Cl_2, 300 K): δ = 150.9; 144.9, 141.9, 141.8, 141.3, 140.8, 140.7, 140.5, 140.5, 140.3, 140.1, 139.3, 139.2, 139.1, 138.8, 138.7, 138.4, 138.1 (C_{quat}); 131.6, 131.1, 130.0, 128.6, 128.3, 127.6, 126.8, 126.5, 126.3, 125.6, 125.3 (C_{tert}). MALDI−TOF−MS, *m*/*z* [ue^{-1}]: 11597 [M]$^+$. Anal Calcd for $C_{912}H_{610}N_2$ (11597.04): C, 94.46; H, 5.30; N, 0.24. Found: C, 94.02; H, 5.27; N, 0.22.

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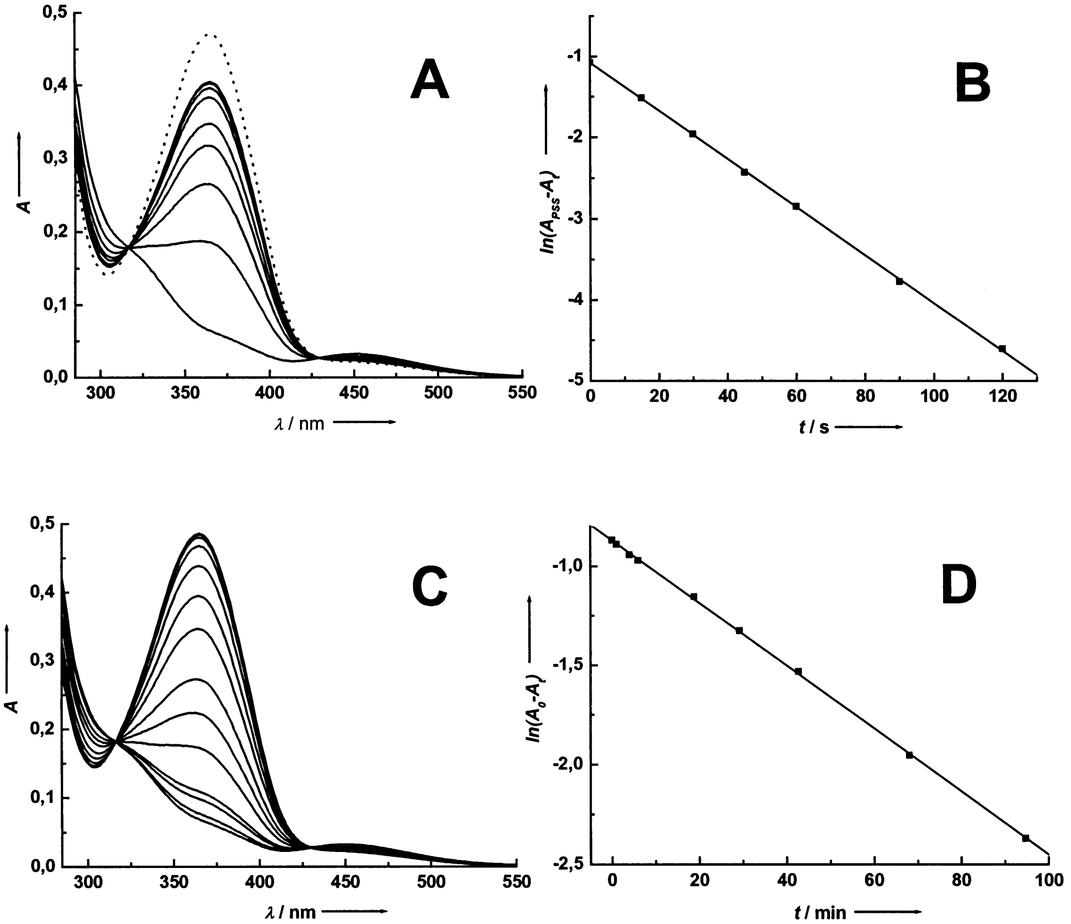

Figure 17. (A) Plots of absorption spectra of ca. 10^{-5} M dendrimer **5** solution in toluene (started from dendrimer solution at the PSS under 364 nm irradiation) vs time under 447 nm irradiation for 0, 15, 30, 45, 60, 90, 120, 180, and 240 s (from bottom to top), respectively. The dash line is the absorption spectrum of the dark-incubated dendrimer **5** solution. (B) Determination of the apparent first-order rate constant of dendrimer **5** cis–trans photoisomerization upon irradiation at 447 nm. (C) Plots of absorption spectra of ca. 10^{-5} M dendrimer **5** solution in toluene (started from dendrimer solution at the PSS under 364 nm irradiation) vs time by thermal isomerization for 0, 1, 4, 6, 19, 29, 43, 68, 95, 144, 218, 311, 384, and 477 h (from bottom to top), respectively. (D) Determination of the first-order rate constant of dendrimer **5** cis–trans thermal isomerization.

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