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Synthesis and Photoisomerization of Azocalixarenes with Dendritic Structures

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The synthesis of dendricalixarenes **1** and **2** containing azo groups at the upper rim of a calix[4]- or calix[6]arene and the corresponding model compounds **3**–**5** are described. Because the kinetics of the *trans* to *cis* isomerization were too fast for accurate determination of the rate constant, this parameter was obtained from the reverse *cis* to *trans* process, which was studied in two different solvents by either a photoinduced or a thermal process. On the basis of the UV/Vis absorption measurements, the global rate constants (k) for calixarenes **1b**, **1c**, and **2b**, obtained for the two different mechanisms (photoinduced and thermal processes), are of the same order of magnitude as that for models **3b** and **4b**. Compound **5b** with an expanded cavity recognizes *N*-methylpyridinium guests. The 1:1 stoichiometry for the complex of 4-(4-dimethylaminostyryl)-*N*-methylpyridinium iodide (DASPMI) with **5b** was confirmed by Job plot analysis. Fluorescence spectroscopic titrations gave $K_a = 3.76 \times 10^5\ M^{-1}$. As expected, receptors **1b**, **1c**, and **2b** (with the azo groups in the *trans* configuration) did not lead to complexation of any of the substrates. Similarly, conversion into the respective *cis* isomers caused structural changes that were too large to allow efficient complexation.

Introduction

Dendrimers are macromolecules characterized by both molecular uniformity and the presence of internal voids, which render them ideal *endo* receptors. Due to the flexibility of the constituting dendrons, substrates can be accommodated inside the dendrimer, but permanent, rigid cavities are absent.[1] In order to reduce the conformational flexibility of dendritic systems, different strategies have been employed such as metal coordination in the interior of the dendrimer[2] or introduction of photoisomerizable groups to induce structural and conformational changes in the macromolecule.[3] If these functionalities are part of the dendrimer core, the directionality of the dendrons and hence the overall morphology of the macromolecule are changed.[4] On the other hand, if the functional groups are located at the periphery of the branches, the accessibility of the interior could be controlled by photoisomerization.[5]

Another strategy is based on the use of rigid scaffolds as the central core in order to control the orientation of the dendrons. For this purpose, calix[4]arenes have been used as building blocks.[6] The first example of a calixarene-based dendrimer was described by Lhotak and Shinkai,[7] and several examples have been reported thereafter,[8] in some cases reaching a second-generation dendrimer.[9] However, the super-structures resulting from the connection of calixarene units through flexible spacers are wide open and not rigid enough to control the overall molecular shape.

We recently reported the use of bulky, rigid subunits as dendrons connected by short, rigid spacers, which allows the conformational mobility of the dendrimer to be controlled, thus generating defined voids from the first generation.[10] Herein we describe the preparation of photoisomerizable dendrimers **1** and **2** based on calix[6]arene dendrons connected through azo groups to the upper rim of a calix[4]- or calix[6]arene core. The *trans*/*cis* photoisomeriza-

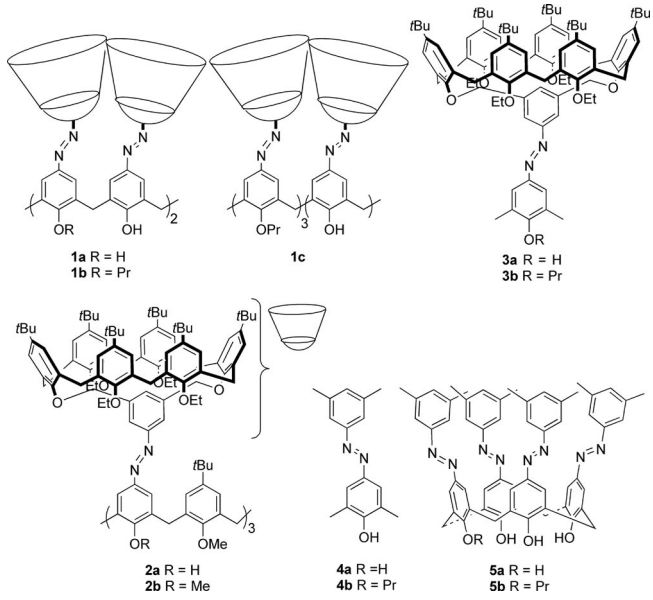

Figure 1. Compounds **1**–**5**.

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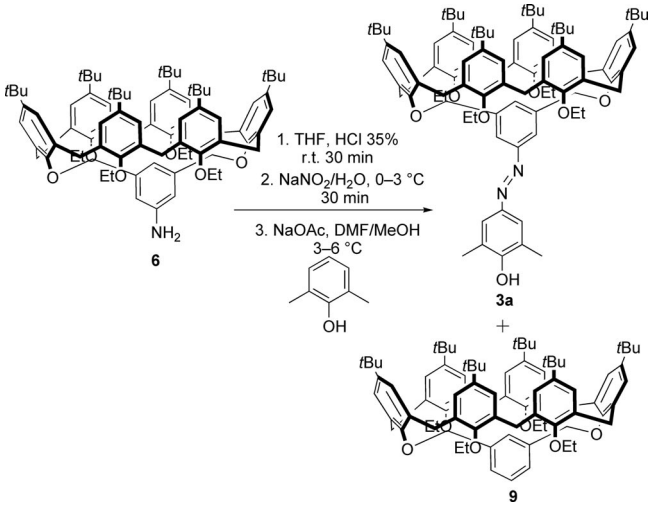
tion of these linkers should control the opening and closure of the surface. Model compounds **3** and **4** carrying a simple azo function were also synthesized to assess the effect of the calix[6]arene dendron on the photoisomerization process. On the other hand, derivatives **5** are proposed as models of the expanded core (Figure 1).

Results and Discussion

Synthesis

The formation of a diazonium salt from a calixarene has only one precedent,[11] and reaction conditions for the azo coupling of lipophilic calixarenes had to be developed. Azo compounds **1a** and **2a** were obtained upon coupling of the diazonium salt of amino compound **6**,[10a] with core calixarenes **7**[12] and **8**.[13] 2,6-Dimethylphenol was selected as a model compound to optimize the reaction conditions.

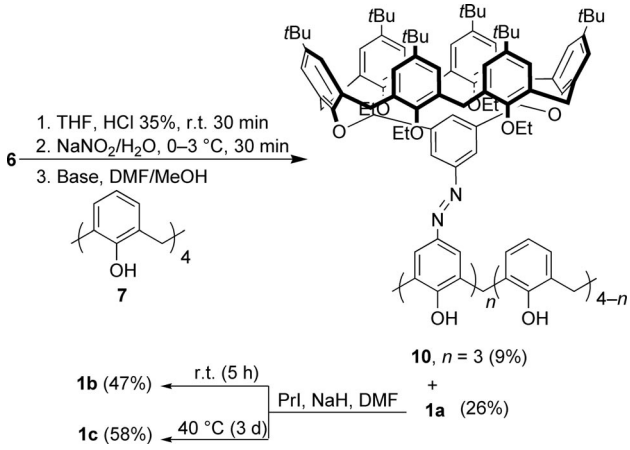
Reaction of **6** with sodium nitrite in a minimum amount of water, followed by coupling with 2,6-dimethylphenol gave **3a** in 80% yield, together with insignificant amounts of **9**[14] (Scheme 1).



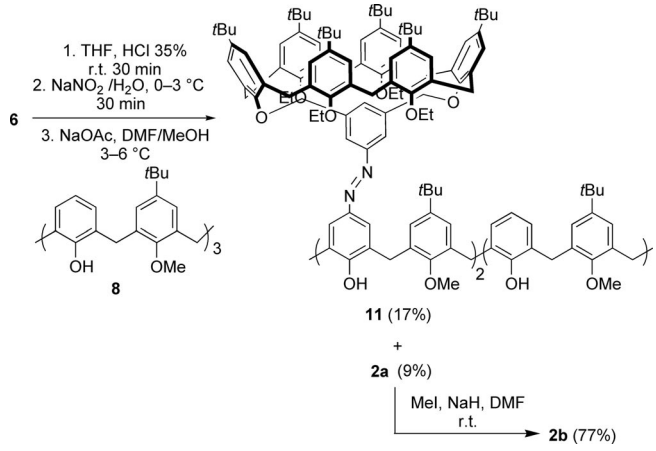
Scheme 1. Synthesis of azocalixarene **3a**.

When calixarene **7**[12] was submitted to similar reaction conditions, compounds **1a** and **10** (containing three azo moieties) were obtained in 3%, and 26% yields, respectively. Optimization of the reaction conditions (time and temperature) produced **1a** in a 26% yield (Scheme 2).

In the case of 25,27-dihydroxy-26,28-dipropoxycalix[4]arene,[15] the desired azo derivative could only be detected in trace amounts by mass spectrometry. We attribute this to the lower pK_a of **7** with respect to the corresponding *O*-alkyl analogues. After the initial azo coupling, the following nucleophilic substitutions are self-accelerated as described by Shinkai et al. for reactions of calix[4]arenes with diazonium salts.[16] The reaction of calix[6]arene **8**[13] and the diazonium salt of amine **6** gives a complex mixture of products from which only the di- and triazo compounds **11** and **2a** could be isolated in 17 and 9% yield, respectively (Scheme 3).



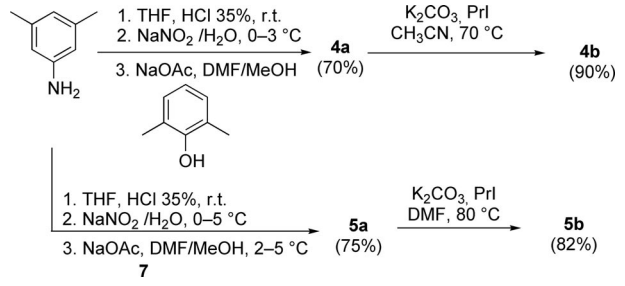
Scheme 2. Synthesis of dendricalixarenes **1a**–**c**.



Scheme 3. Synthesis of azocalixarenes **2a** and **2b**.

Compounds **1a** and **2a** were *O*-alkylated in order to allow photoisomerization of the corresponding dendricalixarenes, a process that does not occur in *O*-unsubstituted free phenols due to tautomerism. Depending on the reaction time, compounds **1b** and **1c** were obtained from **1a**, sodium hydride, and iodopropane in DMF (Scheme 2). Methylation of **2a** in DMF in the presence of NaH gave compound **2b** in 77% yield (Scheme 3).

Model compound **4b** was synthesized in two steps by azo coupling of 3,5-dimethylamine and 2,6-dimethylphenol, followed by propylation, in 61% overall yield. Similarly, **3b** was obtained in 80% yield from **3a** (Scheme 4). The reac-



Scheme 4. Synthesis of model compounds **4** and **5**.

tion of 3,5-dimethylphenyldiazonium chloride with **7**[12] gave 75% of **5a**, which was subsequently converted into **5b** by reaction with iodopropane in the presence of K_2CO_3 (82%, Scheme 4).

Conformational Analysis of the Azocalixarenes

The new azocalixarenes were studied by ^1H and ^{13}C NMR spectroscopy. At room temperature in $CDCl_3$, the ($ArCH_2Ar$) methylene carbon signals of the core calixarene appeared at δ = 31.9 ppm in **1a**, indicative of a *cone* conformation.[17] In variable-temperature NMR experiments (403–183 K) the signal slightly shifted to 32.4 ppm at 263 K, whereas the methylene protons displayed an AX system below 278 K. These results indicate that the *cone* conformation is stable below 263 K and the system is increasingly flexible at higher temperatures (*cone*-*cone* inversion). According to their symmetry, **1b** and **1c** displayed one and two AX systems, respectively. This pattern was maintained over the whole temperature range studied (403–188 K), suggesting a rigid conformation of the core. The chemical shifts for the methylene carbon atoms (**1b**: 32.3 ppm, **1c**: 32.5 ppm) confirm a rigid *pinched cone* conformation. On the other hand, azocalixarenes **2a** and **2b**, based on the calix[6]arene core, displayed the expected *cone*-*cone* inversion.[13] Furthermore, the aromatic proton signals *ortho* to the azo groups were located around 8.00 and 7.40 ppm, typical for the *trans* isomers. However, HPLC analysis of **1b** revealed the presence of two peaks with the same molecular mass as the major components, which could be assigned as two different conformational isomers in a ratio of 1:4.

Photoisomerization of the Azo Derivatives

Comparison of the UV/Vis spectra of **1**–**5** with analogous nitro derivative **12**[10a] revealed that the characteristic azo bands (300–500 nm) do not interfere with the absorptions corresponding to the calixarene cores or dendrons (Figure 2, see Supporting Information).

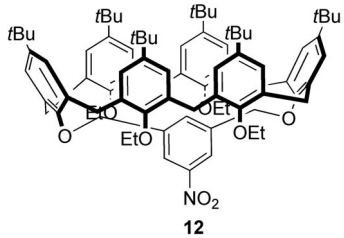


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Figure 2. Compound **12**.

The isomerization experiments were carried out in a photoreactor by using toluene (**1b**, **1c**, **2b**) or a chloroform/toluene mixture (**3b**, **4b**) as solvents for 15 min.[18] Upon irradiation the hypo- and hypsochromic shifts of the π–π* transition, initially at 350 nm, were detected (Figure 3).

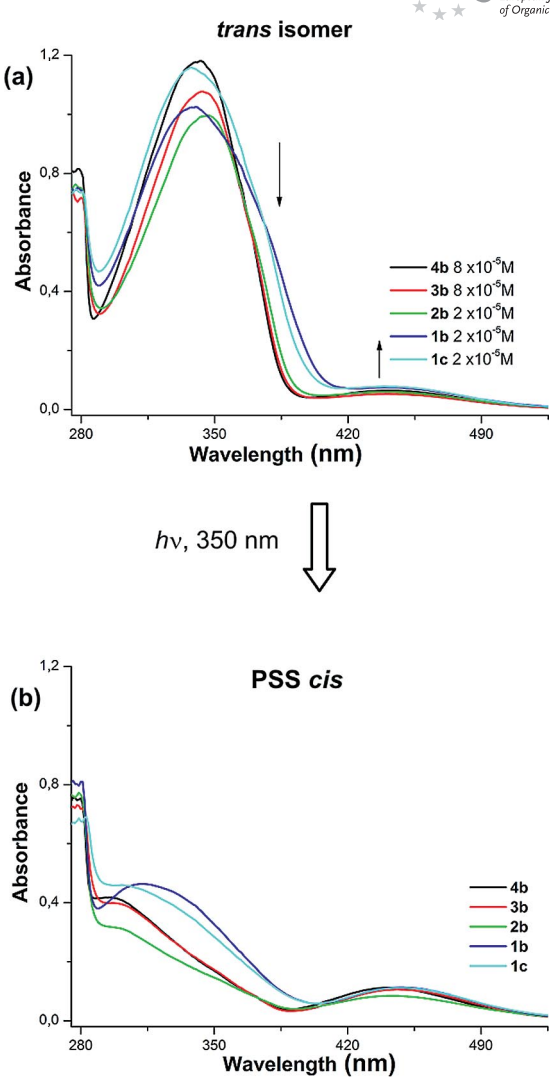

Figure 3. (a) UV/Vis spectra of **1b**, **1c**, **2b**, **4b**, and **3b** in toluene; (b) UV/Vis spectra of **1b**, **1c**, **2b**, **4b**, and **3b** after irradiation at 350 nm.

Simultaneously, a decrease in the intensity of the aromatic protons *ortho* to the azo moiety was observed in the ^1H NMR spectra, accompanied by the appearance of a new set of signals around 6.8 ppm. The maximum percentage of the *cis* isomer could be quantified by NMR spectroscopy. In deuterated benzene, 84% of *cis* isomer of **3b** was obtained, although the initial isomer distribution (90% *trans*,

Table 1. Percentage of *cis* isomer after irradiation at 350 nm. ^1H NMR spectroscopic data.

	Solvent	% *cis*		% *trans* Recovered	
		Before irradiation	After irradiation	Stored in darkness	Stored in daylight
4b	C_6D_6	10	95	40	85
	$CDCl_3$	0	90	53	100
3b	C_6D_6	10	84	69	82
	$CDCl_3$	0–3	82	100	100
2b	C_6D_6	3	92	–	–

Table 2. Values of $k_{v(cis\rightarrow trans)}$ for **4b** and **3b** calculated on the basis of UV/Vis and ^{1}H NMR spectroscopic data.

			Solvent	λ (nm)	Concentration (M)	$k_{v(cis\rightarrow trans)}$ (s^{-1})	R^2
UV/Vis	daylight	**4b**	toluene	343	8.0×10^{-5}	1.29×10^{-3}	0.997
			$CHCl_3$	348	1.0×10^{-4}	1.25×10^{-3}	0.997
		3b	toluene	345	8.0×10^{-5}	1.74×10^{-3}	0.998
			$CHCl_3$	344	1.0×10^{-4}	1.65×10^{-3}	0.992
	darkness	**4b**	toluene	343	8.0×10^{-5}	5.60×10^{-5}	0.996
			$CHCl_3$	348	1.0×10^{-4}	–	–
		3b	toluene	345	8.0×10^{-5}	4.20×10^{-5}	0.992
			$CHCl_3$	344	1.0×10^{-4}	4.97×10^{-5}	0.992
NMR[a]	darkness	**4b**	C_6D_6	$ArCH_3$	1.8×10^{-2}	1.56×10^{-5}	0.999
			$CDCl_3$	$ArCH_3$	1.9×10^{-2}	1.27×10^{-5}	0.999
		3b	C_6D_6	ArH	1.8×10^{-2}	2.10×10^{-5}	0.999
			$CDCl_3$[b]	$ArCH_3$	1.8×10^{-2}	1.20×10^{-4}	0.999

[a] 500 MHz, 298 K. [b] The only case where the equilibrium is completely recovered to the *trans* isomer in the dark.

10% *cis*) was not completely recovered after allowing the sample to relax in the dark, but a final 7:3 ratio (69% *trans*, 31% *cis*) was measured instead (Table 1).

Similar results were obtained for **4b** in deuterated benzene, reaching a maximum of 60% of the *cis* isomer (40% *trans*). Upon exposure of the solutions of **4b** and **3b** to daylight, 85 and 82% of the *trans* isomer were regenerated, respectively, and these values are lower than the initial ratios. Isomerization took place to a minor extent when deuterated chloroform was used as solvent (Table 1).

In the cases of **1b** and **1c**, only partial disappearance of the signals corresponding to the *trans* isomer was detected as a consequence of the presence of the phenol units, which do not isomerize. As a consequence, the resulting spectra were even more complex and did not allow an accurate integration of the signals of the respective isomers. In deuterated benzene, 3% of the *cis* isomer was present for compound **2b** before irradiation, which turned into 92% after irradiation. For all three compounds, the progress of the conformational changes over time was visualized by monitoring the symmetry changes in the core. In none of the cases studied were the initial amounts of the *trans* isomer fully recovered when the relaxation process was determined by a thermal process.

Kinetics of the *trans*/*cis* isomerization were first order. Although the *trans* → *cis* process was too fast for a rate constant to be measured, this parameter can be obtained in the reverse process. This was studied in two different solvents by either a photoinduced (daylight, UV/Vis spectroscopy) or a thermal process (dark, UV/Vis and ^{1}H NMR spectroscopy).[19] In the case of model compounds **4b** and **3b**, similar rate constants *k* were measured in both solvents; the value of *k* was approximately two orders of magnitude lower for the thermal process than for the photoinduced process. The values obtained by ^{1}H NMR spectroscopy (dark, [D_6]benzene,[20] $CDCl_3$) were comparable to those obtained by UV/Vis (Table 2).

The same experiments as those for the model compounds were performed on azodendrimers **1b**, **1c**, and **2b**.[21] Irradiation of **2b** in toluene resulted in hypo- and hypsochromic shifts (48 nm) of the π–π* transition band as for analogue **3b** (45 nm), indicating the isomerization of the three N=N bonds.[22] Minor effects (27 and 36 nm) were found for **1b** and **1c**, owing to the nonisomerizable azo functions in the molecules. A global first-order process could be assumed for the *cis* → *trans* transformation.[3b] On the basis of the UV/Vis absorption measurements, the global rate constants *k* were calculated for the two different mechanisms, which were of the same order of magnitude as the values found for **4b** and **3b** (Table 3).

Table 3. Values of $k_{v(cis\rightarrow trans)}$ for **2b**, **1b**, and **1c** [2×10^{-5} M^{-1}] calculated on the basis of UV/Vis spectroscopic data (298 K, toluene).[23]

		λ (nm)	$k_{v(cis\rightarrow trans)}$ (s^{-1})	R^2
Daylight	**1b**	340	1.25×10^{-3}	0.992
	1c	338	1.50×10^{-3}	0.992
	2b	346	1.35×10^{-3}	0.997
Darkness	**1b**	340	2.60×10^{-5}	0.992
	1c	338	3.28×10^{-5}	0.998
	2b	346	2.60×10^{-5}	0.997

To assess the efficiency of the opening and closing of the cavity of these compounds, the photoisomerization of **2b** and **1b** in chloroform was determined five times consecutively, confirming that in all cases the initial state is reached upon exposure to daylight.

Complexation Studies of 1b, 1c, 2b, and 5b

Complexation studies were evaluated by UV/Vis, fluorescence, and ^{1}H NMR spectroscopy. As substrates, 4-(4-dimethylaminostyryl)-*N*-methylpyridinium iodide (DASPMI), with a rod-like geometry, and some roughly spherical *N*-methylpyridinium halides of different sizes to fill the voids remote from the core were selected. Also, *p*-fluorotoluene was used to determine whether or not a positive charge is necessary in the guest molecule. Additionally, ^{19}F NMR spectroscopy can be employed in this case, avoiding the overlap of signals of the receptor and the substrate (Figure 4).

Using model compound **5b** (UV/Vis and NMR spectroscopy, CD_2Cl_2) proved that the ammonium cation is complexed in the cavity of the calix[4]arene substituted by electron-withdrawing groups. From the blueshift and hypsochromism observed in the absorption spectra we conclude that complexation is occurring, even though the overlap of

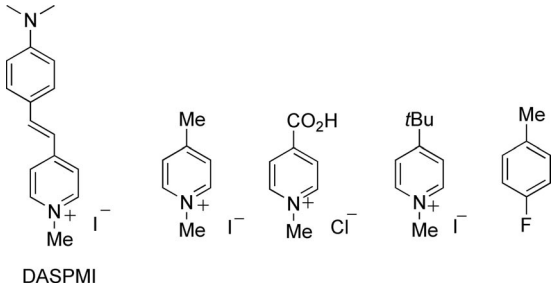

Figure 4. Guests chosen for recognition.

the substrate and receptor (>3 equiv.) bands hampers calculation of a reliable association constant (K_a). From fluorescence spectroscopic measurements, K_a was determined as 3.76×10^5 M^{-1}, and a 1:1 stoichiometry was confirmed by Job plot analysis.

The ^{1}H NMR spectrum of complex **5b**-DASPMI in CD_2Cl_2 clearly shows a high-field shift of the methyl protons of the pyridinium guest ($\Delta\delta$ = 0.10 ppm) as well as the aromatic protons of the calix[4]arene scaffold *ortho* to the azo moiety of **5b**, which confirms the inclusion of the guest (i.e., the pyridinium-CH_3 function) in the calixarene cavity. To evaluate how the photoisomerization of the azo substituents affects the formation of the complex formed, the latter was irradiated and subsequently left at daylight.[24] UV/Vis and ^{1}H NMR spectroscopy revealed the changes expected for the isomerization of the azocalixarene host. Minor changes in the absorption spectrum of the substrate were insignificant, and only a slight upfield shift of the *N*-methyl protons of the pyridinium guest was found in the ^{1}H NMR spectrum, accompanied with general signal broadening. Upon initial irradiation of **5b**, followed by addition of the substrate to the azocalixarene host (*cis* isomer) in the dark, formation of the complex was observed by ^{1}H NMR spectroscopy ($\Delta\delta_{Me}$ = 0.07 ppm), although no band broadening occurred under these conditions.

The same effects were observed by ^{1}H NMR spectroscopy for the rest of the *N*-methylpyridinium substrates. However, no evidence for the complexation of 4-fluorotoluene could be found by ^{19}F NMR spectroscopy, verifying the importance of the positive charge for the substrate to be complexed.

As expected, the use of receptors **1b**, **1c**, and **2b** as hosts (with the azo groups in the *trans* configuration) did not lead to complexation of any of the substrates. Also, complexation was not observed upon conversion into the respective *cis* forms by photoisomerization.

Conclusions

Despite the increased accessibility of the inner spaces of the dendrimers (**1b**, **1c**, and **2b**), the structural changes caused by photoisomerization are too large, which thus prevents efficient complexation, or in any case, makes it difficult. Nevertheless, model compound **5b** gives a stable complex with DASPMI with a large binding constant. On the basis of the results obtained for **5b**, a dendricalixarene receptor with only one photoisomerizable group might be a promising candidate for photocontrolled complexation.

Experimental Section

General Procedure for the Synthesis of Azo Derivatives: A solution of amine **6**[10a] or 3,5-dimethylaniline in THF (25.0 mM) and 35% HCl (3 drops for each 0.021 mmol of amine) was stirred for 30 min at room temperature. Next, the mixture was cooled to 2 °C and then it was added to a solution of aqueous sodium nitrite (2.3 equiv., 0.7 M). The mixture was stirred for 30–40 min at 2–5 °C to give the corresponding diazonium salt, which was maintained at 2 °C and used immediately without purification. A suspension of the corresponding phenol or calixarene and NaOAc in DMF/MeOH was stirred for some time at room temperature. The mixture was cooled to 2 °C and a suspension of diazonium salt of amine **6** was added slowly. This mixture was stirred for some time under the same conditions, and finally at room temperature; 25% HCl was added until acidic pH, and then the mixture was heated. The resulting red solid was filtered and purified.

Compound 1a: Prepared by the general procedure described above from calix[4]arene **7**[12] (24.6 mg, 0.058 mmol) and NaOAc (900.0 mg, 11.0 mmol) in DMF/MeOH (3:2, 5.1 mL). The mixture was stirred for 30 min. A first portion of the diazonium salt of amine **6** (150.0 mg) was added, and the mixture was stirred for 2 h; a second portion of the diazonium salt of amine **6** (150.0 mg) recently synthesized was added, and the mixture was stirred for 5.50 h. Finally, the last portion was added, and the mixture was stirred for 14 h until it reached 17 °C, and then it was stirred at room temperature for 30 min. HCl (3 M) was added, and the solution was heated at 60 °C for 1 h. Purification: precipitation in MeOH/H_2O, four consecutive size-exclusion columns (GPC, used Bio-Beads SX-1, toluene), and finally trituration in methanol to give **1a** as an orange solid (78.5 mg, 26%) and byproduct **10** (21.1 mg, 9%). Data for **1a**: M.p. >200 °C (decomp). ^{1}H NMR (500 MHz, CD_2Cl_2, 263 K, ROESY): δ = 10.48 (s, 4 H, ArOH), 7.84 (s, 8 H, ArH_{azo}), 7.69 (s, 8 H, ArH_{azo}), 7.30 (s, 16 H, ArH), 6.81 (s, 16 H, ArH), 6.76 (s, 16 H, ArH), 5.30 (s, 4 H, $ArH_{xylylenyl}$), 4.42 [d, ^2J(H,H) = 14.5 Hz, 4 H, $ArCH_2Ar_{calix[4]arene}$], 4.35 [d, ^2J(H,H) = 15.4 Hz, 16 H, $ArCH_2Ar_{calix[6]arene}$], 4.23–4.12 (m, 24 H, $ArOCH_2$ and $ArCH_2Ar_{calix[6]arene}$), 3.90 [d, ^2J(H,H) = 14.8 Hz, 4 H, $ArCH_2Ar_{calix[4]arene}$], 3.48–3.38 (m, 32 H, OCH_2CH_3), 3.32 [d, ^2J(H,H) = 15.8 Hz, 16 H, $ArCH_2Ar_{calix[6]arene}$], 3.10 [d, ^2J(H,H) = 14.2 Hz, 8 H, $ArCH_2Ar_{calix[6]arene}$], 1.36 [s, 72 H, $C(CH_3)_3$], 0.92–0.80 [m, 192 H, $ArOCH_2CH_3$ and $C(CH_3)_3$] ppm. ^{13}C NMR (125 MHz, CD_2Cl_2, 263 K, DEPT, HSQC): δ = 152.6, 152.5, 152.0, 151.7, 148.2, 146.1, 145.2, 139.6, 133.5, 133.2, 132.9 (Ar), 128.6, 128.4, 125.3, 124.9, 124.3, 117.7 (ArH), 71.5 ($ArOCH_2$), 69.1 ($ArOCH_2CH_3$), 34.5, 34.2 [$C(CH_3)_3$], 32.4 ($ArCH_2Ar_{calix[4]arene}$), 31.8, 31.2 [$C(CH_3)_3$], 30.1, 28.7 ($ArCH_2Ar_{calix[6]arene}$), 15.7 ($ArOCH_2CH_3$) ppm. UV/Vis (ArN=NAr, CH_2Cl_2, 10^{-5} M): λ (ε, mol^{-1} dm^3 cm^{-1}) 340 (62589), 430 (4258) nm. MS (MALDI-TOF, dithranol + NaI): *m*/*z* (%) = 5301.4 (100) [M + Na]$^+$. $C_{356}H_{440}N_8O_{28}\cdot CH_2Cl_2$ (5364.27): calcd. C 79.93, H 8.31, N 2.09; found C 79.63, H 8.37, N 2.23. Data for **10**: M.p. 218 °C (decomp). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 10.46 (br. s, 4 H, ArOH), 7.91 (s, 2 H, ArH_{azo}), 7.87 [d, ^3J(H,H) = 2.0 Hz, 2 H, ArH_{azo}], 7.83 (br. s, 2 H, ArH_{azo}), 7.81 [d, ^3J(H,H) = 1.9 Hz, 2 H, ArH_{azo}], 7.79 (br. s, 4 H, ArH_{azo}), 7.37 (br. s, 13 H, ArH), 7.28 [d, ^3J(H,H) = 7.9 Hz, 2 H, ArH], 6.91–6.76 (m, 24 H, ArH), 5.50 (s, 1 H, $ArH_{xylylenyl}$), 5.46 (s, 2 H, $ArH_{xylylenyl}$), 4.56–4.37 (m, 16 H, Ar-

CH_2Ar), 4.38–4.22 (m, 18 H, $ArOCH_2$, and $ArCH_2Ar_{calix[6]arene}$), 3.91 (br. s, 2 H, $ArCH_2Ar_{calix[4]arene}$), 3.75 (br. s, 2 H, $ArCH_2Ar$), 3.68–3.54 (m, 24 H, $ArOCH_2CH_3$), 3.44 (m, 12 H, $ArCH_2Ar$), 3.28–3.14 (m, 6 H, $ArCH_2Ar$), 1.47 [s, 54 H, $C(CH_3)_3$], 1.04–0.96 [m, 144 H, $ArOCH_2CH_3$ and $C(CH_3)_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K, DEPT): δ = 152.5, 152.3, 151.8, 145.9, 144.9, 139.4, 133.4, 132.9, 132.8 (Ar), 129.6, 128.0, 125.0, 124.1, 117.4 (ArH), 71.3 ($ArOCH_2$), 68.7 ($ArOCH_2CH_3$), 34.3, 34.0 [$C(CH_3)_3$], 31.8, 31.7, 31.28, 31.26 [$C(CH_3)_3$], 30.2, 29.7, 29.4, 28.7 ($ArCH_2Ar$), 15.6 ($ArOCH_2CH_3$) ppm. MS (MADI-TOF, dithranol + NaI): *m/z* (%) = 4088.7 (25) $[M + Na]^+$. HRMS (MALDI): calcd. for $C_{274}H_{336}N_6O_{22}Na$ $[M + Na]^+$ 4088.536; found 4088.536.

Compound 2a: Prepared by the general procedure described above from calix[6]arene **8**[13] (22.0 mg, 0.026 mmol) and NaOAc (300 mg, 3.7 mmol) in DMF/MeOH (8:5, 2.6 mL). The mixture was stirred for 30 min. A first portion of the diazonium salt of amine **6** (100.0 mg) was added, and the mixture was stirred for 22 h; a second portion of the diazonium salt of amine **6** (50.0 mg) recently synthesized was added, and the mixture was stirred for 24 h until it reached 17 °C. HCl (3 M) was added, and the mixture was heated at 60 °C for 40 min. Purification: precipitation in $MeOH/H_2O$, 3–4 consecutive size-exclusion columns (GPC, Bio-Beads SX-1, toluene), preparative TLC (silica gel; hexane/THF, 4:1→3:1), and finally trituration in methanol to give **2a** as a yellow solid (10.0 mg, 9%) and **11** (14.6 mg, 17%). Data for **2a**: M.p. >220 °C (decomp.). ^1H NMR (500 MHz, $CDCl_3$, 298 K, ROESY): δ = 7.79 (s, 6 H, $ArH_{azocore}$), 7.77 (s, 6 H, $ArH_{azodendron}$), 7.75 (s, 3 H, ArOH), 7.36 (s, 12 H, $ArH_{dendron}$), 7.10 (s, 6 H, ArH_{core}), 6.89 (s, 12 H, $ArH_{dendron}$), 6.84 (s, 12 H, $ArH_{dendron}$), 5.46 (s, 3 H, $ArH_{xylylenyl}$), 4.50 [d, ^2J(H,H) = 15.4 Hz, 12 H, $ArCH_2Ar$], 4.35 [d, ^2J(H,H) = 13.8 Hz, 6 H, $ArCH_2Ar$], 4.28 (s, 12 H, $ArOCH_2$), 4.02 (br. s, 12 H, $ArCH_2Ar_{core}$), 3.65 (s, 9 H, OCH_3), 3.64–3.57 (m, 24 H, $ArOCH_2CH_3$), 3.45 [d, ^2J(H,H) = 15.5 Hz, 12 H, $ArCH_2Ar$], 3.24 [d, ^2J(H,H) = 14.1 Hz, 6 H, $ArCH_2Ar$], 1.46 [s, 54 H, $C(CH_3)_3$], 1.15 [s, 27 H, $C(CH_3)_{3core}$], 1.04 [t, ^3J(H,H) = 6.9 Hz, 36 H, $ArOCH_2CH_3$], 0.92 [s, 108 H, $C(CH_3)_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K, DEPT, HSQC): δ = 155.5, 152.6, 152.3, 152.0, 147.8, 146.3, 146.0, 145.0, 139.3, 133.5, 132.9, 132.8, 132.0 (Ar), 128.1 (ArH), 127.5 (Ar), 126.0, 125.1, 124.5, 124.3, 124.1, 117.4 (ArH), 71.5 ($ArOCH_2$), 68.8 ($ArOCH_2CH_3$), 61.6 ($ArOCH_3$), 34.4, 34.3, 34.0 [$C(CH_3)_3$], 31.7, 31.4, 31.3 [$C(CH_3)_3$], 31.1 ($ArCH_2Ar_{core}$), 30.2, 28.7 ($ArCH_2Ar$), 15.6 ($ArOCH_2CH_3$) ppm. UV/Vis (ArN=NAr, CH_2Cl_2, 10^{-5} M): λ (ε, $mol^{-1}dm^3cm^{-1}$) = 360 (58539), 445 (3493) nm. MS (MALDI-TOF, dithranol + NaI): *m/z* (%) = 4510.8 (96) $[M + Na]^+$, 4488.9 (15) $[M + H]^+$, 3288.1 (62) $[M - C_{82}H_{105}NO_6+H]^+$, 1225.8 (62) $[C_{82}H_{105}NO_6 + 2H + Na]^+$. $C_{303}H_{378}N_6O_{24}\cdot CHCl_3\cdot$2hexane (4780.00): calcd. C 79.40, H 8.58, N 1.76; found C 79.28, H 8.97, N 1.68. Data for **11**: M.p. >180 °C (decomp.). ^1H NMR (500 MHz, $CDCl_3$, 298 K): δ = 8.93 (s, 1 H, ArOH), 8.13 (s, 2 H, ArOH), 7.88–7.80 (m, 8 H, ArH), 7.44–7.36 (m, 10 H, $ArH_{dendron}$ and ArH_{core}), 7.13–7.00 (m, 7 H, ArH_{core}), 6.94 (s, 8 H, $ArH_{dendron}$), 6.89 (s, 8 H, $ArH_{dendron}$), 5.50 (s, 2 H, $ArH_{xylylenyl}$), 4.55 [d, ^2J(H,H) = 15.4 Hz, 8 H, $ArCH_2Ar_{dendron}$], 4.43–4.27 (m, 12 H, $ArCH_2Ar_{dendron}$ and $ArOCH_2$), 4.08 (br. s, 6 H, $ArCH_2Ar_{core}$), 3.99–3.98 (m, 6 H, $ArCH_2Ar_{core}$), 3.83 (s, 3 H, $ArOCH_3$), 3.72–3.46 (m, 30 H, $ArOCH_3$, $ArCH_2Ar_{dendron}$ and $ArOCH_2CH_3$), 3.29 [d, ^2J(H,H) = 14.2 Hz, 4 H, $ArCH_2Ar_{dendron}$], 1.51 {s, 36 H, $[C(CH_3)_3]$}, 1.20, 1.13 [s, 27 H, $C(CH_3)_3$], 1.09 [t, ^3J(H,H) = 6.9 Hz, 24 H, $ArOCH_2CH_3$], 0.97 [s, 72 H, $C(CH_3)_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K, DEPT): δ = 155.3, 152.6, 152.3, 152.1, 151.9, 148.2, 148.0, 146.4, 146.0, 145.0, 140.4, 139.4, 135.8, 133.4, 132.9, 132.7, 132.3, 131.7, 130.94, 128.3, 128.15, 128.08, 127.4, 127.1 (Ar), 130.90, 128.9, 128.1, 126.9, 126.6, 125.9, 125.8, 125.6, 125.1, 124.8, 124.6, 124.1, 117.4, 117.2 (ArH), 71.4 ($ArOCH_2$), 68.8 ($ArOCH_2CH_3$), 61.9, 61.5 (OCH_3), 34.9, 34.34, 34.26, 34.0 [$C(CH_3)_3$], 31.7, 31.34, 31.27 [$C(CH_3)_3$], 31.9, 31.2, 30.9, 30.6, 30.2, 29.7, 29.4, 28.7 ($ArCH_2Ar$), 15.6, 14.1, 13.8 ($ArOCH_2CH_3$) ppm. MS (MALDI-TOF, dithranol + NaI): *m/z* (%) = 3297.0 (90) $[M + Na]^+$, 3341.9 (50) $[M + 3Na - 2 H]^+$, 3275.0 (20) $[M + H]^+$, 2074.3 (100) $[M - C_{82}H_{105}NO_6]^+$. $C_{221}H_{274}N_4O_{18}\cdot 0.5CHCl_3$ (3334.25): calcd. C 79.79, H 8.30, N 1.68; found C 79.76, H 8.60, N 1.77.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,40,41-tetraethyloxy-39,42-{5-[(4-hydroxy-3,5-dimethyl)phenylazo]-1,3-phenylenbis(methyleneoxy)}calix[6]arene (3a): Prepared by the general procedure described above from 2,6-dimethylphenol (3.0 mg, 0.025 mmol) and NaOAc (404.4 mg, 4.930 mmol) in DMF/MeOH (8:5, 1.3 mL). The mixture was stirred for 10 min. The diazonium salt of amine **6** (25.0 mg, 0.021 mmol) was added. Coupling: 40 min at 0–5 °C and 30 min at room temperature; after HCl (3 M) addition, reflux for 1 h. Purification: recrystallization in $EtOH/CHCl_3$ (22.4 mg, 80%). M.p. >240 °C (decomp.). ^1H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.78 (s, 2 H, ArH_{azo}), 7.65 (s, 2 H, ArH_{azo}), 7.37 (s, 4 H, $ArH_{calix[6]arene}$), 6.89 (s, 4 H, $ArH_{calix[6]arene}$), 6.84 (s, 4 H, $ArH_{calix[6]arene}$), 5.44 (s, 1 H, $ArH_{xylylenyl}$), 4.93 (s, 1 H, ArOH), 4.50 [d, ^2J(H,H) = 15.5 Hz, 4 H, $ArCH_2Ar$], 4.34 [d, ^2J(H,H) = 14.3 Hz, 2 H, $ArCH_2Ar$], 4.28 (s, 4 H, $ArOCH_2$), 3.64–3.57 (m, 8 H, $ArOCH_2$), 3.45 [d, ^2J(H,H) = 15.5 Hz, 4 H, $ArCH_2Ar$], 3.24 [d, ^2J(H,H) = 14.3 Hz, 2 H, $ArCH_2Ar$], 2.35 (s, 6 H, $ArCH_3$), 1.46 [s, 18 H, $C(CH_3)_3$], 1.04 [t, ^3J(H,H) = 6.9 Hz, 12 H, $ArOCH_2CH_3$], 0.92 [s, 36 H, $C(CH_3)_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K, DEPT): δ = 152.3, 145.9, 145.0, 138.2, 133.4, 132.9, 132.8 (Ar), 128.1, 125.0, 124.1, 123.5, 122.4, 117.4 (ArH), 71.7 ($ArOCH_2Ar$), 68.7 ($ArOCH_2CH_3$), 34.3, 34.0 [$C(CH_3)_3$], 31.7, 31.3 [$C(CH_3)_3$], 30.9, 29.7 ($ArCH_2Ar$), 16.0 ($ArCH_3$), 15.5 ($ArOCH_2CH_3$) ppm. UV/Vis (ArN=NAr, CH_2Cl_2, 10^{-5} M): λ (ε, $mol^{-1}dm^3cm^{-1}$) = 353 (17715), 437 (1151) nm. MS (MALDI-TOF, dithranol + NaI): *m/z* (%) = 1358.9 (100) $[M + Na]^+$, 1335.9 (34) $[M + H]^+$. $C_{90}H_{114}N_2O_7\cdot 0.5(EtOH\cdot CHCl_3)$ (1418.85): calcd. C 77.47, H 8.35, N 1.97; found C 77.27, H 8.85, N 1.78.

4-Hydroxy-3,3′,5,5′-tetramethyl Azobenzene (4a): Prepared by the general procedure described above from 2,6-dimethyphenol (252.0 mg, 2.063 mmol) and NaOAc (700.0 mg, 8.533 mmol) in DMF/MeOH (8:5, 5.1 mL). The mixture was stirred for 10 min. The diazonium salt of 3,5-dimethylaniline (300.0 mg, 2.475 mmol) in DMF (3 mL) was added. Coupling: 5.50 h at 2–5 °C and 30 min at room temperature; after HCl (3 M) addition, reflux for 1 h. Purification: trituration in hexane to give **4a** as an orange solid (342.1 mg, 70%). M.p. 136–139 °C. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.60 (s, 2 H, ArH), 7.49 (s, 2 H, ArH), 7.08 (s, 1 H, ArH), 4.97 (s, 1 H, ArOH), 2.41 (s, 6 H, $ArCH_3$), 2.34 (s, 6 H, $ArCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, DEPT): δ = 154.9, 153.0, 146.4, 138.7 (Ar), 132.0, 123.6 (ArH), 123.5 (Ar), 120.3 (ArH), 21.3, 16.0 (CH_3) ppm. UV/Vis (ArN=NAr, CH_2Cl_2, 10^{-5} M): λ (ε, $mol^{-1}dm^3cm^{-1}$) = 352 (21281), 445 (797) nm. MS (FA+, *m*-NBA): *m/z* (%) = 255.2 (100) $[M + H]^+$. $C_{16}H_{18}N_2O\cdot 0.25H_2O$ (258.83): calcd. C 74.25, H 7.20, N 10.82; found C 74.23, H 7.11, N 10.69.

25,26,27,28-Tetrahydroxy-5,11,17,23-tetra-(3,5-dimethylphenylazo)-calix[4]arene (5a): Prepared by the general procedure described above from calix[4]arene **7**[12] (233.5 mg, 0.550 mmol) and NaOAc (900.0 mg, 11.0 mmol) in DMF/MeOH (8:5, 45.6 mL). The mixture was stirred for 20 min. The diazonium salt of 3,5-dimetylaniline (one portion of 300.0 mg, 2.5 mmol) was added. Coupling: 3.50 h at 2–5 °C and 30 min at room temperature; after HCl addition,

reflux for 1 h. Purification: extraction in CH_2Cl_2, recrystallization in $CHCl_3$ to give **5a** (392 mg, 75%). M.p. >322 °C (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 10.29 (s, 4 H, ArOH), 7.80 (s, 8 H, ArH), 7.47 (s, 8 H, ArH), 7.06 (s, 4 H, ArH), 4.39 (br. s, 4 H, $ArCH_2Ar$), 3.86 (br. s, 4 H, $ArCH_2Ar$), 2.38 (s, 24 H, $ArCH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K, DEPT): δ = 153.0, 151.2, 147.9, 138.7, 128.3 (Ar), 132.3, 124.4, 120.4 (ArH), 31.9 (Ar*C*H$_2$Ar), 21.2 (Ar*C*H$_3$) ppm. MS (MALDI-TOF, dithranol + NaI): *m*/*z* (%) = 975.5 (65) [M + Na]$^+$, 953.5 (100) [M + H]$^+$. $C_{60}H_{56}N_8O_4$·0.5$CHCl_3$ (1012.83): calcd. C 71.74, H 5.62, N 11.06; found C 72.16, H 5.69, N 11.03.

General Procedure for *O*-Alkylation of Compound 1a: A mixture of **1a** (1 equiv.) and NaH (oil mineral suspension 60%, 4 equiv.) in DMF dry was stirred under an argon atmosphere for 10 min. Next, propyl iodide (3–4 equiv.) was added, and the mixture was stirred at room temperature for some time, monitoring the reaction by TLC (hexane/THF, 4:1). H_2O and HCl (1 M) were added, and the mixture was stirred for 30 min. The precipitate was filtered and triturated in methanol. The obtained solid, which contained different proportions of **1b** and **1c** in function of the time and temperature used, was purified by chromatography using a TLC plate (silica gel; hexane/THF, 7:1→7:4).

Compound 1b: Prepared by the general procedure described above from **1a** (20.0 mg, 3.788 μmol), NaH (0.6 mg, 0.015 mmol), and propyl iodide (1.8 μL, 0.018 mmol) in dry DMF (2.5 mL). Time: 5 h (until apparition of **1c** by TLC). After purification by using a TLC plate (silica gel; hexane/THF, 7:1→7:4), the solid was triturated in methanol to give **1b** (9.5 mg, 47%). M.p. >174 °C (decomp.). ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 340 K, COSY, ROESY): δ = 8.85 (s, 2 H, ArOH), 7.87 (s, 2 H, $ArH_{azocalix[4]arene}$), 7.73 (s, 2 H, $ArH_{azocalix[6]arene}$), 7.62 (s, 2 H, $ArH_{azocalix[4]arene}$), 7.60 (s, 2 H, $ArH_{azocalix[6]arene}$), 7.26 (s, 8 H, $ArH_{calix[6]arene}$), 7.19 (s, 8 H, $ArH_{calix[6]arene}$), 6.83 (s, 8 H,$ArH_{calix[6]arene}$), 6.78 (s, 8 H, $ArH_{calix[6]arene}$), 6.74 (s, 8 H, $ArH_{calix[6]arene}$), 6.70 (4s, 8 H, $ArH_{calix[6]arene}$), 5.46 (s, 2 H, $ArH_{xylylenyl}$), 5.42 (s, 2 H, $ArH_{xylylenyl}$), 4.45–4.07 (m, 48 H, $ArCH_2Ar$, $ArOCH_2$ and $ArOCH_2CH_2CH_3$), 3.71 [d, ^2J(H,H) = 13.1 Hz, 4 H, $ArCH_2Ar_{calix[4]arene}$], 3.54–3.44 (m, 32 H, $ArOCH_2CH_3$), 3.43–3.27 (m, 16 H, $ArCH_2Ar_{calix[6]arene}$), 3.23–3.08 (m, 8 H, $ArCH_2Ar_{calix[6]arene}$), 2.11–2.00 (m, 6 H, $ArOCH_2CH_2CH_3$), 1.39 [s, 36 H, $C(CH_3)_3$], 1.33–1.32 (m, 6 H, $ArOCH_2CH_2CH_3$), 1.32 [s, 36 H, $C(CH_3)_3$], 0.99 [t, ^3J(H,H) = 6.9 Hz, 24 H, $ArOCH_2CH_3$], 0.91–0.84 [m, 192 H, $ArOCH_2CH_3$ and $C(CH_3)_3$] ppm. ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 340 K, DEPT, HMQC): δ = 156.6, 154.3, 152.7, 152.5, 152.3, 152.2, 145.9, 145.8, 144.82, 144.78, 139.34, 139.28, 133.7, 133.5, 133.4, 132.7 (Ar), 128.0 (ArH), 127.7 (Ar), 125.0, 124.1, 124.0, 117.4 (ArH), 78.8 ($ArOCH_2CH_2CH_3$), 71.6, 71.3 ($ArOCH_2$), 68.7 ($ArOCH_2CH_3$), 34.1, 33.93, 33.90 [$C(CH_3)_3$], 32.3 ($ArCH_2Ar_{calix[4]arene}$), 31.8, 31.7, 31.33, 31.30 [$C(CH_3)_3$], 30.4, 30.3, 28.9 ($ArCH_2Ar_{calix[6]arene}$), 23.6 ($ArOCH_2CH_2CH_3$), 15.6, 15.5 ($ArOCH_2CH_3$), 11.0 ($ArOCH_2CH_2CH_3$) ppm. UV/Vis (ArN=NAr, CH_2Cl_2, 10^{-5} M): λ (ε, mol^{-1} dm^3 cm^{-1}) = 341 (56718), 438 (5182) nm. MS (MADI-TOF, dithranol + NaI): *m*/*z* (%) = 5386.5 (100) [M + Na]$^+$, 1224.9 (75) [M – $C_{82}H_{105}NO_6$ + 2H + Na]$^+$. HRMS (MALDI): calcd. for $C_{362}H_{452}N_8O_{28}Na$ [M +Na]$^+$ 5385.430; found 5385.426. HPLC: 94.6%.

Compound 1c: Prepared by the general procedure described above from **1a** (42.0 mg, 7.956 μmol), NaH (1.3 mg, 0.032 mmol), and propyl iodide (3 μL, 0.0318 μmol) in dry DMF (1.4 mL). Time: 7 d. After the purification by using a TLC plate (silica gel; hexane/THF, 10:1→7:4), the solid was triturated in methanol to give **1c** (25.0 mg, 58%). M.p. 250–255 °C. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 321 K, COSY): δ = 7.85 (s, 2 H, $ArH_{azocalix[4]arene}$), 7.83 (s, 2 H, $ArH_{azocalix[4]arene}$), 7.73 (s, 2 H, $ArH_{azocalix[6]arene}$), 7.71 (s, 2 H, $ArH_{azocalix[6]arene}$), 7.54 (s, 4 H, $ArH_{azocalix[6]arene}$), 7.45 (s, 2 H, $ArH_{azocalix[4]arene}$), 7.41 (s, 2 H, $ArH_{azocalix[4]arene}$), 7.25–7.16 (m, 16 H, $ArH_{calix[6]arene}$), 6.85–6.63 (m, 32 H, $ArH_{calix[6]arene}$), 5.42 (s, 1 H, $ArH_{xylylenyl}$), 5.40 (s, 1 H, $ArH_{xylylenyl}$), 5.36 (s, 2 H, $ArH_{xylylenyl}$), 4.58 [d, ^2J(H,H) = 12.9 Hz, 2 H, $ArCH_2Ar_{calix[4]arene}$], 4.46–4.05 (m, 44 H, $ArCH_2Ar$, $ArOCH_2$ and $ArOCH_2CH_2CH_3$), 3.94–3.78 (m, 4 H, $ArOCH_2CH_2CH_3$), 3.63 [d, ^2J(H,H) = 12.2 Hz, 2 H, $ArCH_2Ar_{calix[4]arene}$], 3.59–2.98 (m, 60 H, $ArOCH_2CH_3$ and $ArCH_2Ar$), 2.30–2.20 (m, 2 H, $ArOCH_2CH_2CH_3$), 2.06–1.88 (m, 4 H, $ArOCH_2CH_2CH_3$), 1.40 [s, 18 H, $C(CH_3)_3$], 1.38 [s, 18 H, $C(CH_3)_3$], 1.32 [s, 18 H, $C(CH_3)_3$], 1.16–0.98 (m, 9 H, $ArOCH_2CH_2CH_3$), 0.94–0.80 [m, 192 H, $ArOCH_2CH_3$ and $C(CH_3)_3$] ppm. ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 298 K, DEPT, 321 K HSQC): δ = 152.3, 152.1, 145.7, 144.8, 144.7, 139.2, 133.4, 132.7 (Ar), 128.0, 125.0, 124.8, 124.3, 124.1, 123.0, 117.3 (ArH), 78.5, 77.5 ($ArOCH_2CH_2CH_3$), 71.2 ($ArOCH_2$), 68.7 ($ArOCH_2CH_3$), 34.2, 34.1, 33.93, 33.89 [$C(CH_3)_3$], 32.0, 32.5 ($ArCH_2Ar_{calix[4]arene}$), 31.8, 31.7, 31.3 [$C(CH_3)_3$], 30.2, 28.7 ($ArCH_2Ar_{calix[6]arene}$), 23.5, 22.8 ($ArOCH_2CH_2CH_3$), 15.66, 15.62, 15.60 ($ArOCH_2CH_3$), 10.8, 9.8 ($ArOCH_2CH_2CH_3$) ppm. UV/Vis (ArN=NAr, CH_2Cl_2, 10^{-5} M): λ (ε, mol^{-1} dm^3 cm^{-1}) = 343 (57348), 436 (4116) nm. MS (MALDI-TOF, dithranol + NaI): *m*/*z* (%) = 5428.5 (100) [M + Na]$^+$, 5406.5 (25) [M + H]$^+$, 4206.7 (25) [M – $C_{82}H_{105}NO_6$ + 2H]$^+$, 1225.7 (40) [$C_{82}H_{105}NO_6$ + 2H + Na]$^+$. $C_{365}H_{458}N_8O_{28}$·2$CHCl_3$ (5644.33): calcd. C 78.09, H 8.21, N 1.99; found C 77.98, H 8.65, N 1.96.

Compound 2b: A suspension of **2a** (20.5 mg, 4.567 μmol) and NaH (oil mineral suspension 60%, 1.2 mg, 0.027 mmol) in DMF dry (2.0 μL) in a sealed tube was stirred for 30 min at room temperature under an argon atmosphere. Next, methyl iodide (1.7 μL, 0.027 mmol) was added, and the mixture was stirred for 24 h at room temperature. H_2O and HCl (1 M) were added, and the precipitate was filtered and purified by trituration in CH_2Cl_2/MeOH to give **2b** as a yellow solid (16.0 mg, 77%). M.p. >242 °C (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, ROESY): δ = 7.80 (s, 6 H, $ArH_{azodendron}$), 7.73 (s, 6 H, $ArH_{azocore}$), 7.36 (s, 12 H, $ArH_{dendron}$), 6.96 (s, 6 H, ArH_{core}), 6.89 (s, 12 H, $ArH_{dendron}$), 6.84 (s, 12 H, $ArH_{dendron}$), 5.48 (s, 3 H, $ArH_{xylylenyl}$), 4.95 [d, ^2J(H,H) = 15.4 Hz, 12 H, $ArCH_2Ar$], 4.33 [d, ^2J(H,H) = 14.5 Hz, 6 H, $ArCH_2Ar$], 4.28 (s, 12 H, $ArOCH_2$), 4.04 (br. s, 12 H, $ArCH_2Ar_{core}$), 3.64–3.56 (m, 24 H, $ArOCH_2CH_3$), 3.46–3.43 (m, 21 H, $ArCH_2Ar$ and $ArOCH_3$), 3.24 [d, ^2J(H,H) = 13.5 Hz, 6 H, $ArCH_2Ar$], 3.01 (br. s, 9 H, $ArOCH_3$), 1.45 [s, 54 H, $C(CH_3)_3$], 1.07 [s, 27 H, $C(CH_3)_{3core}$], 1.04 [t, ^3J(H,H) = 6.9 Hz, 36 H, $ArOCH_2CH_3$], 0.92 [s, 108 H, $C(CH_3)_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K, DEPT, HSQC): δ = 152.6, 152.3, 151.9, 148.6, 146.0, 145.0, 139.4, 135.3, 133.4, 132.9, 132.8 (Ar), 128.1, 125.4, 125.0, 124.1, 117.6 (ArH), 71.4 ($ArOCH_2$), 68.8 ($ArOCH_2CH_3$), 60.3, 60.2 ($ArOCH_3$), 34.3, 34.2, 34.0 [$C(CH_3)_3$], 31.9 ($ArCH_2Ar_{core}$), 31.7, 31.4, 31.3 [$C(CH_3)_3$], 30.8 ($ArCH_2Ar_{core}$), 30.2, 28.7 ($ArCH_2Ar$), 15.6 ($ArOCH_2CH_3$) ppm. UV/Vis (ArN=NAr, CH_2Cl_2, 10^{-5} M): λ (ε, mol^{-1} dm^3 cm^{-1}) = 347 (67932), 436 (3631) nm. MS (MALDI-TOF, dithranol + NaI): *m*/*z* (%) = 4552.9 (100) [M + Na]$^+$, 4529.9 (15) [M + H]$^+$. $C_{306}H_{384}N_6O_{24}$·CH_2Cl_2 (4615.28): calcd. C 79.89, H 8.43, N 1.82; found C 79.90, H 8.83, N 1.70.

General Procedure for *O*-Alkylation of Compounds 3a and 4a: A solution of the corresponding azo derivative and K_2CO_3 in the appropriate solvent was heated at 70 °C for 30 min under an argon atmosphere. Next, propyl iodide was added, and the mixture was heated at 60 °C for 48 h. H_2O and HCl (3 M) were added, and the mixture was stirred at room temperature for 30 min. The aqueous solution was extracted with CH_2Cl_2 (2 × 20 mL), and the organic

phase was washed with H_2O and dried (Na_2SO_4). The solvent was removed under reduced pressure, and the obtained residue was triturated in methanol.

5,11,17,23,29,35-Hexa-*tert*-butyl-37,38,40,41-tetraethyloxy-39,42-{5-[(3,5-dimethyl-4-propyloxy)phenylazo]-1,3-phenylenbis(methylenoxy)}calix[6]arene (3b): Prepared by the general procedure described above from **3a** (87.5 mg, 0.066 mmol) and K_2CO_3 (18.1 mg, 0.130 mmol) in CH_3CN/DMF (4:2, 6.0 mL). Propyl iodide (9.6 μL, 0.098 mmol) to give **3b** as an orange solid (72 mg, 80%). M.p. 178–181 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.80 (s, 2 H, Ar-H_{azo}), 7.64 (s, 2 H, ArH_{azo}), 7.37 (s, 4 H, ArH), 6.90 (s, 4 H, ArH), 6.85 (s, 4 H, ArH), 5.46 (s, 1 H, Ar$H_{m\text{-xylylenyl}}$), 4.51 [d, ^2J(H,H) = 15.4 Hz, 4 H, ArCH_2Ar], 4.34 [d, ^2J(H,H) = 14.2 Hz, 2 H, Ar-CH_2Ar], 4.29 (s, 4 H, ArOCH_2), 3.80 [t, ^3J(H,H) = 6.6 Hz, 2 H, Ar$OCH_2CH_2CH_3$], 3.66–3.56 (m, 8 H, ArOCH_2CH_3), 3.46 [d, ^2J(H,H) = 15.4 Hz, 4 H, ArCH_2Ar], 3.25 [d, ^2J(H,H) = 14.2 Hz, 2 H, ArCH_2Ar], 2.38 (s, 6 H, ArCH_3), 1.87 [sext., ^3J(H,H) = 7.1 Hz, 2 H, Ar$OCH_2CH_2CH_3$], 1.46 [s, 18 H, C$(CH_3)_3$], 1.12 [t, ^3J(H,H) = 7.4 Hz, 2 H, Ar$OCH_2CH_2CH_3$], 1.04 [t, ^3J(H,H) = 7.0 Hz, 12 H, ArOCH_2CH_3], 0.93 [s, 36 H, C$(CH_3)_3$] ppm. ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K, DEPT): δ = 158.4, 152.6, 152.3, 152.0, 148.8, 146.0, 145.0, 139.5, 133.5, 132.9, 132.8, 131.7 (Ar), 128.1, 125.1, 124.9, 124.1, 123.3, 117.5 (ArH), 74.1 (ArOCH_2), 71.4 (Ar-$OCH_2CH_2CH_3$), 68.8 (ArOCH_2CH_3), 34.3, 34.0 [$C(CH_3)_3$], 31.7, 31.3 [C(CH_3)$_3$], 30.2, 29.7 (ArCH_2Ar), 23.7 (Ar$OCH_2CH_2CH_3$), 16.5 (ArCH_3), 15.5 (ArOCH_2CH_3), 10.7 (Ar$OCH_2CH_2CH_3$) ppm. UV/Vis (ArN=NAr, CH_2Cl_2, 10^{-5} M): λ (ε, $mol^{-1}\,dm^3\,cm^{-1}$) = 342 (23227), 432 (1275) nm. MS (MALDI-TOF, dithranol + NaI): *m*/*z* (%) = 1400.9 (100) [M + Na]$^+$, 1379.0 (70) [M + H]$^+$. $C_{93}H_{120}N_2O_7$·0.5$CHCl_3$ (1435.87): calcd. C 78.11, H 8.45, N 1.95; found C 78.30, H 8.78, N 1.96.

3,3′,5,5′-Tetramethyl-4-propyloxy Azobenzene (4b): Prepared by the general procedure described above from **4a** (100.0 mg, 0.393 mmol) and K_2CO_3 (108.7 mg, 0.786 mmol) in CH_3CN (5.0 mL). Propyl iodide (57 μL, 0.589 mmol) to give **4b** as an orange solid (116.5 mg, 90%). M.p. 63–65 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.60 (s, 2 H, ArH_{azo}), 7.50 (s, 2 H, ArH_{azo}), 7.10 (s, 1 H, ArH), 3.79 [t, ^3J(H,H) = 6.6 Hz, 2 H, Ar$OCH_2CH_2CH_3$], 2.41 (s, 6 H, ArCH_3), 2.37 (s, 6 H, ArCH_3), 1.90–1.83 (m, 2 H, Ar-$OCH_2CH_2CH_3$) 1.10 [t, ^3J(H,H) = 7.4 Hz, 3 H, Ar$OCH_2CH_2CH_3$] ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K, DEPT): δ = 158.6, 153.0, 148.6, 138.7 (Ar), 132.2 (ArH), 131.8 (Ar), 123.3, 120.4 (ArH), 74.0 (Ar$OCH_2CH_2CH_3$), 23.7 (Ar$OCH_2CH_2CH_3$), 21.2, 16.5 (ArCH_3), 10.6 (Ar$OCH_2CH_2CH_3$) ppm. UV/Vis (ArN=NAr, CH_2Cl_2, 10^{-5} M): λ (ε, $mol^{-1}\,dm^3\,cm^{-1}$) = 344 (26829), 435 (1425) nm. MS (70 eV): *m*/*z* (%) = 296.2 (80) [M]$^+$, 163.1 (100) [M – $C_8H_9N_2$]$^+$. $C_{19}H_{24}N_2O$ (296.41): calcd. C 76.99, H 8.16, N 9.45; found C 76.90, H 8.14, N 9.14.

26,27,28-Tetrahydroxy-5,11,17,23-tetra-(3,5-dimethylphenylazo)-25-propyloxycalix[4]arene (5b): To a suspension of **5a** (76.3 mg, 0.080 mmol) and K_2CO_3 (22.1 mg, 0.168 mmol) in dry DMF (3.0 mL) under an argon atmosphere was added propyl iodide (16.3 μL, 0.168 mmol), and the mixture was heated at 80 °C for 6 h. H_2O and HCl (1 M) were added, and the mixture was stirred for 30 min. The precipitate was filtered, and the solid was purified by trituration in MeOH to give **5b** (65.2 mg, 82%) as an orange solid. M.p. >310 °C (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, ROESY): δ = 9.61 (s, 3 H, ArOH), 7.84 [d, ^3J(H,H) = 2.5 Hz, 2 H, ArH_{azo}], 7.81 [d, ^3J(H,H) = 2.2 Hz, 2 H, ArH_{azo}], 7.73 (s, 2 H, ArH_{azo}), 7.72 (s, 2 H, ArH_{azo}), 7.48 (s, 4 H, ArH_{azo}), 7.41 (s, 2 H, ArH_{azo}), 7.40 (s, 2 H, ArH_{azo}), 7.06 (s, 2 H, ArH), 7.04–7.01 (m, 2 H, ArH), 4.48 [d, ^3J(H,H) = 13.1 Hz, 2 H, ArCH_2Ar], 4.38 [d, ^2J(H,H) = 14.0 Hz, 2 H, ArCH_2Ar], 4.23 [t, ^3J(H,H) = 6.7 Hz, 2 H, Ar$OCH_2CH_2CH_3$], 3.77 [d, ^2J(H,H) = 14.0 Hz, 2 H, ArCH_2Ar], 3.75 [d, ^2J(H,H) = 13.0 Hz, 2 H, ArCH_2Ar], 2.39 (s, 12 H, ArCH_3), 2.35 (s, 6 H, ArCH_3), 2.33 (s, 6 H, ArCH_3), 2.26 [sext., ^3J(H,H) = 7.1 Hz, 2 H, Ar$OCH_2CH_2CH_3$], 1.36 [t, ^3J(H,H) = 7.4 Hz, 3 H, Ar$OCH_2CH_2CH_3$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K, DEPT): δ = 154.0, 153.6, 153.1, 153.0, 152.9, 151.4, 150.3, 147.8, 147.0, 138.67, 138.66, 138.60, 134.3 (Ar), 132.6, 132.1, 132.0 (ArH), 128.7, 128.3, 128.1 (Ar), 124.41, 124.38, 124.3, 123.9, 120.5, 120.3 (ArH), 79.5 (O$CH_2CH_2CH_3$), 32.1, 31.8 (ArCH_2Ar), 23.4 ($OCH_2CH_2CH_3$), 21.3, 21.21, 21.18 (ArCH_3), 10.8 ($OCH_2CH_2CH_3$) ppm. UV/Vis (ArN=NAr, CH_2Cl_2, 10^{-5} M): λ (ε, $mol^{-1}\,dm^3\,cm^{-1}$) = 338 (76812), 433 (4314) nm. MS (MALDI-TOF, dithranol + NaI): *m*/*z* (%) = 1017.5 (45) [M + Na]$^+$, 995.5 (100) [M + H]$^+$. $C_{63}H_{62}N_8O_4$·0.5H_2O (1004.23): calcd. C 75.35, H 6.32, N 11.16; found C 75.41, H 6.52, N 10.93.

Supporting Information (see footnote on the first page of this article): Spectral characterization data; VT ^{1}H NMR spectra (403–193 K); photoisomerization, kinetics, and complexation studies.

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[24] The stability of DASPMI to light (dichloromethane, hv = 365 nm, 1 h) was confirmed by UV/Vis and ^{1}H NMR spectroscopy.

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