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# Optical Switching and Antenna Effect of Dendrimers with an Anthracene Core

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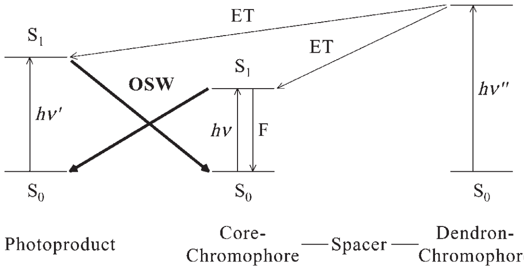
**Abstract:** Dendrimers **6G**$^i$ ($i=1$–4) consisting of an anthracene core and Fréchet dendrons which are attached via a $CH_2OCH_2$ chain in the 9-position undergo quantitative and completely reversible intramolecular [4π+4π] cycloaddition. The process can be monitored by absorption and fluorescence measurements. The Fréchet dendrons act as an energy funnel that collects and focuses the photon energy but does not change the photostationary states, which for both directions are completely on the product side when the separate chromophores are selectively irradiated. The quantum yields of anthracene fluorescence and of singlet energy transfer from the dendrons to the core were studied as a function of dendrimer generation.

**Keywords:** cycloaddition • dendrimers • energy transfer • fluorescence • photochemistry

## Introduction

Molecular switches, which consist of mutually transformable compounds with different absorption and fluorescence, are a highly topical research field.[1–3] The concept presented here concerns optical switching of systems which additionally show light harvesting by means of an antenna effect.[4] The molecular basis is provided by dendrimers whose dendrons have a large cross section for absorption of light and efficiently transfer energy to the photoreactive core chromophore. In the arrangement core-chromophore–saturated spacer–dendron-chromophore (Scheme 1) separate chromophores are present that can be chosen so that selective excitations are possible. When the core chromophore ensures efficient and reversible photoreaction, the optical switch (OSW) (⇄) can be directly operated by irradiation with $\nu$ and $\nu'$ (Scheme 1). In addition, the large cross section of the multidendron chromophores can be exploited, provided that energy transfer (ET) takes place from the excited dendron chromophores to the core (→). Depending on the excitation energy ($\nu'' > \nu'$), singlet energy transfer is also possible on the photoproduct (→). The population of triplet states can be excluded by suitable choice of core and dendron chromophores.

The experimental realization discussed below is based on dendrimers with an anthracene core, a $CH_2OCH_2$ spacer, and poly(benzyl ether) dendrons (Fréchet dendrons).



Scheme 1. Optical switching (OSW) and its amplification by energy transfer (ET) in dendrimer systems with a photoreactive core unit and light-harvesting dendrons. (Representation of the case $\nu < \nu' < \nu''$.)

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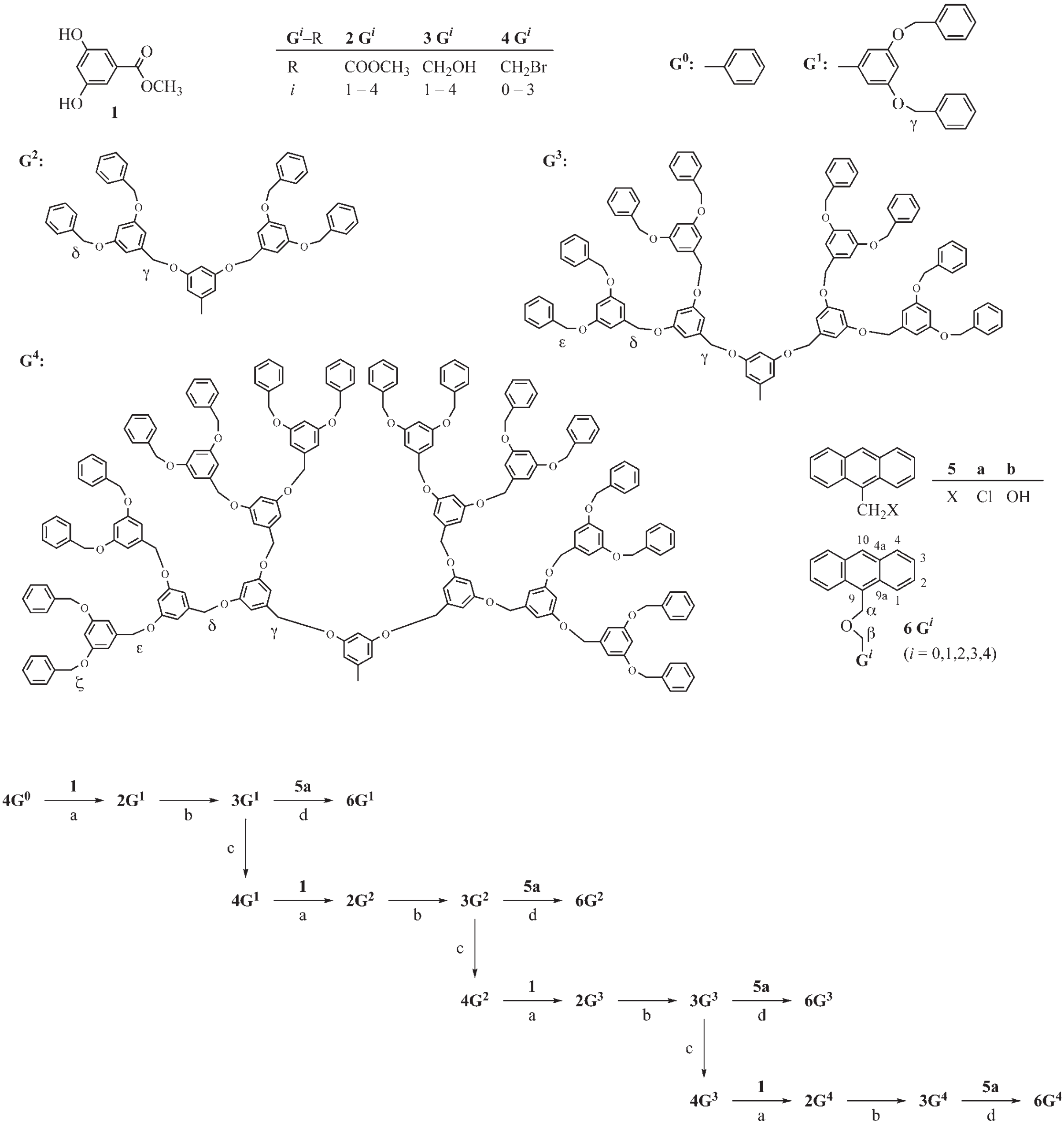
## Results and Discussion

Scheme 2 summarizes the structure and the preparation of the dendrimers **6 G**$^i$ (generation $i=1$–4) and the model compound 9-[(benzyloxy)methyl]anthracene (**6 G**$^0$). We used a combination of known reaction steps[5–9] for the preparation of benzyl ether dendrons. 3,5-Dihydroxybenzoic acid methyl ester (**1**) was treated with benzyl bromide (**4 G**$^0$) to give ester **2 G**$^1$, which was reduced with $LiAlH_4$ to alcohol **3 G**$^1$. Reaction with $PBr_3$ yielded the next higher bromo compound **4 G**$^1$ which was then used instead of **4 G**$^0$ for the subsequent analogous reaction sequence. The general sequence is given in Equation (1).

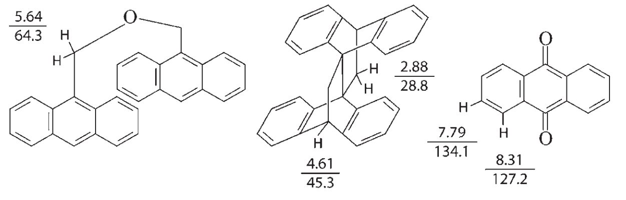
$$\mathbf{1} + \mathbf{4\,G}^i \rightarrow \mathbf{2\,G}^{i+1} \rightarrow \mathbf{3\,G}^{i+1} \rightarrow \mathbf{4\,G}^{i+1} \quad (i = 0-3) \qquad (1)$$

Finally the dendron components, that is, the alcohols **3 G**$^i$, were treated with 9-chloromethylanthracene (**5 a**) to afford target dendrimers **6 G**$^i$. The yields of this step ranged between 21 and 98% when phase-transfer conditions (KOH, $H_2O/(nC_4H_9)_4N^+Br^-$, chlorobenzene) were applied. The low yield of 21% was typically for the fourth-generation **6 G**$^4$, whereby the bulky alcohol **3 G**$^4$ had to attack the 9-chloromethyl group of **5 a**. Model compound **6 G**$^0$ could be prepared from **5 a** and benzyl alcohol (**3 G**$^0$) by using the same type of Williamson synthesis.



Scheme 2. Structures of the target dendrimers **6 G**$^i$ ($i=1$–4), their precursors **1**, **2 G**$^i$, **3 G**$^i$, **4 G**$^i$, **5 a**, and model compounds **6 G**$^0$ and **5 b**. Preparation mode of **6 G**$^i$. a) $K_2CO_3$, $Me_2CO$; b) $LiAlH_4$, THF; c) $PBr_3$, $C_6H_5CH_3$; d) $(nBu)_4N^+Br^-$, $C_6H_5Cl/KOH$, $H_2O$.

In reactions of 9-chloromethyl- or 9-bromomethylanthracene, bis(9-anthrylmethyl) ether (**7**), lepidopterene (**8**), and 9,10-anthraquinone (**9**) were often observed as products or byproducts.[10–14] They can be easily detected by their characteristic intense NMR signals (Scheme 3). We found traces of **7**–**9** in all raw materials **6G**$^i$, particularly in **6G**$^1$.



**7** **8** **9**

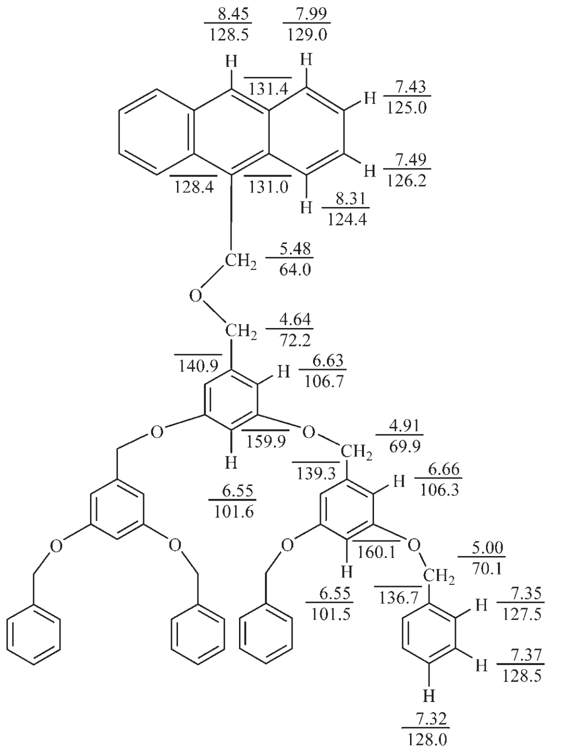
Scheme 3. By-products in the reaction of **5a** and **3G**$^i$ and their most intense $^1H/^{13}C$ NMR signals.

Since even small amounts of **7**–**9** disturb fluorescence measurements and/or photochemical reactions, we purified the dendrimers **6G**$^i$ extremely carefully (see Experimental Section).

The spectroscopic characterization of dendrimers **6G**$^i$ is based on homo- and heteronuclear 2D NMR measurements (COSY, HMQC, HMBC). Scheme 4 shows as an example the complete assignment of all $^1H$ and $^{13}C$ NMR signals of **6G**$^2$ to certain nuclei. Table 1 summarizes the $^1H$ NMR data of **6G**$^i$ ($i=0$–4), which demonstrate the uniformity of the compounds.

The absorption spectra of dendrimers **6G**$^i$ show two distinct and well-separated regions, namely, the anthracene (Chr-1) absorption with the typical vibrational structure between 300 and 410 nm (p band) and the absorption of the benzenoid ππ* transitions below 300 nm (measurement in $CH_2Cl_2$). The range between 250 and 300 nm contains not only the long-wavelength bands of the 1,3,5-trisubstituted benzene rings (Chr-2) and the terminal benzene rings (Chr-3), but also the β and the hidden α band of the anthracene moiety ($S_0 \rightarrow S_2$, $S_3$). Due to the saturated linkers, the three aromatic moieties of the dendrimer molecules can be regarded as independent chromophores. However, the ratio of the three chromophores Chr-1,2,3 present in **6G**$^i$ depends on the generation $i$: anthracene (Chr-1):1,3,5-trisubstituted benzene rings (Chr-2):terminal benzene rings (Chr-3) = 1:-($2^i-1$):$2^i$ ($i=0$–4). Figure 1 shows the absorption spectrum of **6G**$^2$ and its fluorescence.

Irradiation ($\lambda \geq 300$ nm) of **6G**$^0$ leads to the well-known [4π+4π] cyclodimerization.[15] In this case we found a highly regioselective head-to-tail process.[16,17] A monomolecular photoreaction could not be found, even at high dilution. The dendrimers **6G**$^i$ ($i=1$–3) behave completely differently.[18] Highly purified samples in dilute solution in benzene undergo intramolecular [4π+4π] cycloaddition of the central benzene ring of the anthracene unit and the inner benzene ring of the dendron (Scheme 5). This quantitative process leads to complete disappearance of the anthracene absorption. Anthracene fluorescence, which competes with the photoreaction, disappears simultaneously. The difference between the photoreactivity of **6G**$^0$ and **6G**$^i$ ($i \geq 1$) is due to the electron density of the inner benzene ring. Only a high electron density in the 4-position of this ring guarantees a completely selective intramolecular process. We assume either an "intramolecular exciplex" **E**, which is stabilized by charge transfer, or a dipolar, covalently fixed intermediate **I**, obtained as a consequence of a photo-electron-transfer (PET) mechanism. These assumptions are consistent with an al-



Scheme 4. $^1H$ and $^{13}C$ NMR data of **6G**$^2$ (δ values in $CDCl_3$ relative to TMS as internal standard).

Table 1. $^1H$ NMR data of the compounds **6G**$^{0-4}$ (δ values in $CDCl_3$, TMS as internal standard).

| Compound | CH2 | | | | | | Aromat. CH | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | α | β | γ | δ | ε | ζ | 1-H | 2-H, 3-H, $C_6H_5$ | 4-H | 10-H | $C_6H_3$ |
| | s (2H) | s (2H) | s (4H) | s (8H) | s (16H) | s (32H) | m (2H) | m | m (2H) | s (1H) | m |
| **6G**$^0$ | 5.49 | 4.72 | | | | | 8.31 | 7.31–7.54 (9H) | 8.01 | 8.46 | |
| **6G**$^1$ | 5.49 | 4.65 | 4.98 | | | | 8.33 | 7.28–7.52 (14H) | 8.01 | 8.46 | 6.55–6.67 (3H) |
| **6G**$^2$ | 5.48 | 4.64 | 4.91 | 5.00 | | | 8.31 | 7.30–7.50 (24H) | 7.99 | 8.45 | 6.53–6.65 (9H) |
| **6G**$^3$ | 5.48 | 4.63 | 4.91 | 4.93 | 5.00 | | 8.32 | 7.25–7.50 (44H) | 7.96 | 8.43 | 6.50–6.70 (21H) |
| **6G**$^4$ | 5.48 | 4.56 | 4.92 | 4.94 | 4.97 | 4.99 | 8.36 | 7.20–7.45 (84H) | 8.00 | 8.45 | 6.40–6.70 (45H) |

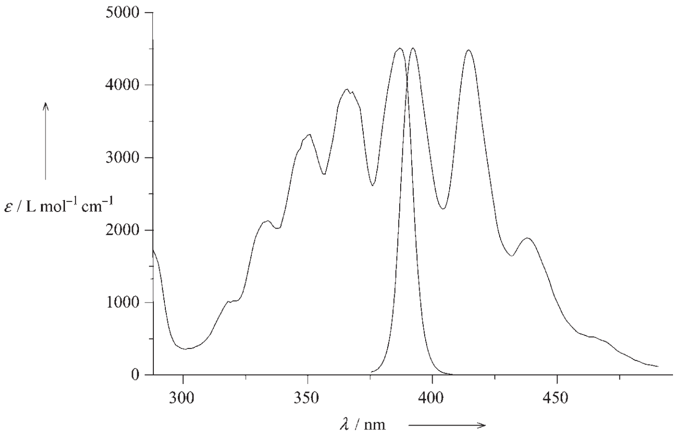
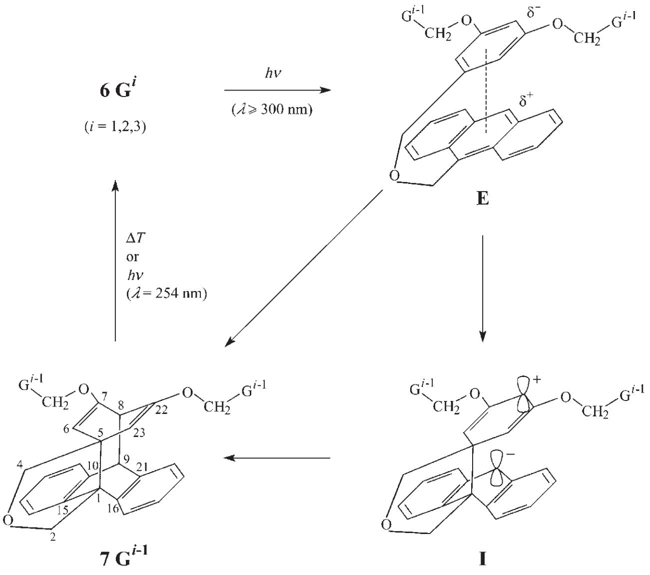


Figure 1. Long-wavelength absorption and normalized fluorescence band ($\lambda_{exc}=260$ nm) of **6G$^2$** in $CH_2Cl_2$.



Scheme 5. Intramolecular [4π+4π] cycloaddition and cycloreversion **6G$^i$**$\rightleftarrows$**7G$^{i-1}$**.

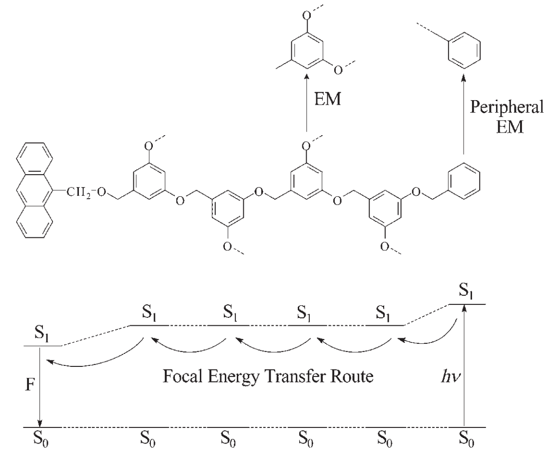
lowed concerted route **6G$^i$**→**E**→**7G$^{i-1}$** and a stepwise process **6G$^i$**→**E**→**I**→**7G$^{i-1}$**.

Irradiation of the cyclomer **7G$^{i-1}$** at 254 nm or heating above 60 °C leads back to **6G$^i$**. Simultaneously, the anthracene fluorescence returns. Thus, the molecular switch can be monitored by absorption and fluorescence.

Irradiation of **7G$^{i-1}$** at 254 nm provokes excitation $S_0 \rightarrow S_1$ of the terminal and trisubstituted benzene rings (Chr-3 and Chr-2) and, moreover, excitation of the dialkoxy 1,4-cyclohexadiene chromophore (Chr-4). Like in 1,4-cyclohexadiene or norbornadiene, interaction of the homoconjugated olefinic π bonds can be assumed, which leads to splitting into an higher and lower energy transitions.[19] However, all these electron transitions of **7G$^{i-1}$** are superimposed in the range between 240 and 290 nm. The electronic transition energies $\Delta E$ are very similar [Eq. (2)].

$$\Delta E(\text{Chr-4}) \approx \Delta E(\text{Chr-2}) \leq \Delta E(\text{Chr-3}) \qquad (2)$$

In addition to direct excitation of Chr-4, efficient energy transfer $S_1(\text{Chr-2,3})+S_0(\text{Chr-4}) \rightarrow S_1(\text{Chr-4})+S_0(\text{Chr-2,3})$ seems to be plausible, since the overlap criterion of donor deactivation energy (fluorescence or radiationless decay) and acceptor excitation energy is ideally fulfilled.[20] Direct proof of an energy transfer $S_1(\text{Chr-2,3})+S_0(\text{Chr-1}) \rightarrow S_1(\text{Chr-1})+S_0(\text{Chr-2,3})$ is possible by monitoring the anthracene fluorescence $[S_1(\text{Chr-1}) \rightarrow S_0(\text{Chr-1})]$. Scheme 6 demonstrates the "downhill" process of singlet energy transfer. Apart from step-by-step transfer, direct transfer from the periphery to the core seems to be possible, since the distances are small enough in comparison to the Förster radius of related systems.[20] One must consider the overlap of the long-wavelength transition $S_1 \rightarrow S_0$ of Chr-2,3 (donor) and a higher electron transition $S_0 \rightarrow S_n$ of Chr-1 (acceptor).



Scheme 6. Downhill focal energy-transfer (ET) route in the dendrimers **6G$^i$** and competing peripheral energy migration (EM).

Fluorescence (F) of dendrimers **6G$^i$** ($i=1$–3) was studied in comparison to that of 1:1 mixtures of **5b** and **3G$^i$** ($i=1$–3). Dilute solutions ($3\times10^{-7}$ M in $CH_2Cl_2$) were prepared so that the absorbance of dendrimer and mixture was exactly the same at $\lambda=260$ nm. It turned out that the absorption of the anthracene chromophore and the dendron chromophores are strictly additive. Since intermolecular singlet energy transfer (Förster transfer) can be excluded under the conditions used, the fluorescence of the mixture is only based on the absorption $A$ ($\lambda=260$ nm) of the anthracene chromophore of **5b**: A higher electronically excited state $S_n$ is generated that undergoes internal conversion (IC) to $S_1$, which fluoresces. The fluorescence quantum yields $\Phi_F'=$ 23.5 % of **6G$^1$** and **6G$^2$** are virtually the same within the error limit (Table 2) as that of **5b**, but somewhat lower than the quantum yield of unsubstituted anthracene (27 %). The third-generation dendrimer has a quantum yield $\Phi_F'$ of 17 %, which is again somewhat lower. The side chains in the 9-position of the anthracene moiety enhance the role of radiationless decay, because they increase the number of vibrational modes. Table 2, however, demonstrates that the overall fluorescence intensity $F'$ of all three dendrimers **6G$^i$** ($i=1,2,3$) is higher than the fluorescence intensity $F$ of model compound **5b** on irradiation at $\lambda_{exc}=260$ nm. This

Table 2. Fluorescence data of dendrimers **6G**$^{i}$ ($i=1$–3) ($\lambda_{exc}=260$ nm, $3\times10^{-7}$ M solution in $CH_2Cl_2$).

| Generation $i$ | Emission maxima $\lambda$ [nm] | Relative fluorescence intensity $F'$(**6G**$^{i}$)/$F$(**5b**) | Fluorescence quantum yield $\Phi_F'$ [%] | Quantum yield of energy transfer $\Phi_T$ [%] |
|---|---|---|---|---|
| **1** | $393\pm1$<br>$414\pm1$<br>$441\pm1$ | $1.14\pm0.1$ | $23.5\pm2$ | $9\pm1$ |
| **2** | $393\pm1$<br>$415\pm1$<br>$440\pm1$ | $1.41\pm0.1$ | $23.5\pm2$ | $10\pm1$ |
| **3** | $393\pm1$<br>$415\pm1$<br>$441\pm1$ | $1.33\pm0.1$ | $17.0\pm2$ | $12\pm1$ |

effect must be due to singlet energy transfer (ET) from the benzene rings to the anthracene core [Eq. (3)].

$$S_0(\text{Chr-2/Chr-3}) \xrightarrow{A} S_1(\text{Chr-2/Chr-3}) \xrightarrow{ET} S_1(\text{Chr-1}) \xrightarrow{F} S_0(\text{Chr-1}) \qquad (3)$$

Going from the first to the third generation of **6G**$^{i}$, the fluorescence quantum yield $\Phi_F'$ decreases, but the quantum yield for energy transfer $\Phi_T$ increases; 12% of the excited benzene rings in **6G**$^{3}$ undergo singlet energy transfer to the anthracene core (Table 2).

The opposite trends of $\Phi_F'$ and $\Phi_T$ ($i=1$–3) lead to a maximum fluorescence enhancement of 41% for the second-generation **6G**$^{2}$. The amount of absorption $S_0 \rightarrow S_n$ of the anthracene moiety at 260 nm is taken into account in this evaluation (see Experimental Section).

This situation is comparable with the attachment of Fréchet dendrons to porphyrins.[21,22] It is remarkable that energy transfer leads to enhanced fluorescence of the dendrimers **6G**$^{i}$ but not to a visible photoreaction **6G**$^{i}$→**7G**$^{i-1}$. Of course, the photoprocess competes with fluorescence of $S_1$, but the reverse process **7G**$^{i-1}$→**6G**$^{i}$ is obviously more efficient on irradiation at $\lambda=260$ nm. We attribute this to a high quantum yield of the cycloreversion and to additional $S_1(\text{Chr-2/Chr-3}) + S_0(\text{Chr-4}) \rightarrow S_1(\text{Chr-4}) + S_0(\text{Chr-2/Chr-3})$ energy transfer (cf. Scheme 1). The photostationary state for both irradiation wavelengths ($\lambda \geq 300$ nm and $\lambda=254$ or 260 nm) is completely on the product side. Energy transfer does not change that.

## Conclusion

In contrast to 9-[(benzyloxy)methyl]anthracene (**6G**$^{0}$) as model compound, irradiation ($\lambda \geq 300$ nm) of the corresponding dendrimers **6G**$^{i}$ results in intramolecular [4π+4π] cycloaddition to form the cyclomers **7G**$^{i-1}$. The quantitative process is thermally ($T > 60$ °C) and photochemically ($\lambda = 254$ nm) reversible and therefore an ideal example of a molecular switch. For the photochemical process **6G**$^{i}$-($\lambda \geq 300$ nm)→**7G**$^{i-1}$ and its thermal reversion **7G**$^{i-1}$-($T \geq 60$ °C)→**6G**$^{i}$, we did not find any fatigue. The photochemical reversion **7G**$^{i-1}$-($\lambda \geq 254$ nm)→**6G**$^{i}$ also shows high fatigue resistance. However, long-term irradiation at 254 nm leads to decomposition.[23]

The multiple benzenoid chromophores in the dendrons permit singlet energy transfer to the anthracene core with a quantum yield $\Phi_T$ of 9, 10, and 12% for **6G**$^{1}$, **6G**$^{2}$, and **6G**$^{3}$ ($\lambda_{exc}=260$ nm). Accordingly the fluorescence intensity is enhanced (14–41%), but the maximum increase is reached for the second-generation dendrimer **6G**$^{2}$ because the fluorescence quantum yield $\Phi_F'$ for third-generation **6G**$^{3}$ decreases from 23.5% for **6G**$^{1}$ and **6G**$^{2}$ to 17% for **6G**$^{3}$. We ascribe this result to more efficient peripheral energy migration, which the 31 benzenoid chromophores present in **6G**$^{3}$ render more favorable. Moreover, we assume energy transfer from the dendrons to the center of photoproducts **7G**$^{i-1}$, but direct proof of this by fluorescence measurements is not possible. The photostationary states for irradiation at $\lambda_1 \geq 300$ nm are totally on the side of **7G**$^{i-1}$, and those for irradiation at $\lambda_2 = 254$ or 260 nm are totally on the side of **6G**$^{i}$. Singlet energy transfer does not change that. Scheme 7 summarizes the complex photophysical (absorption A ($\lambda_1$) or A ($\lambda_2$), fluorescence F, internal conversion IC, singlet energy transfer ET) and photochemical processes (PhR) of different chromophores (anthracene Chr-1, benzene Chr-2,3, homodiene Chr-4).

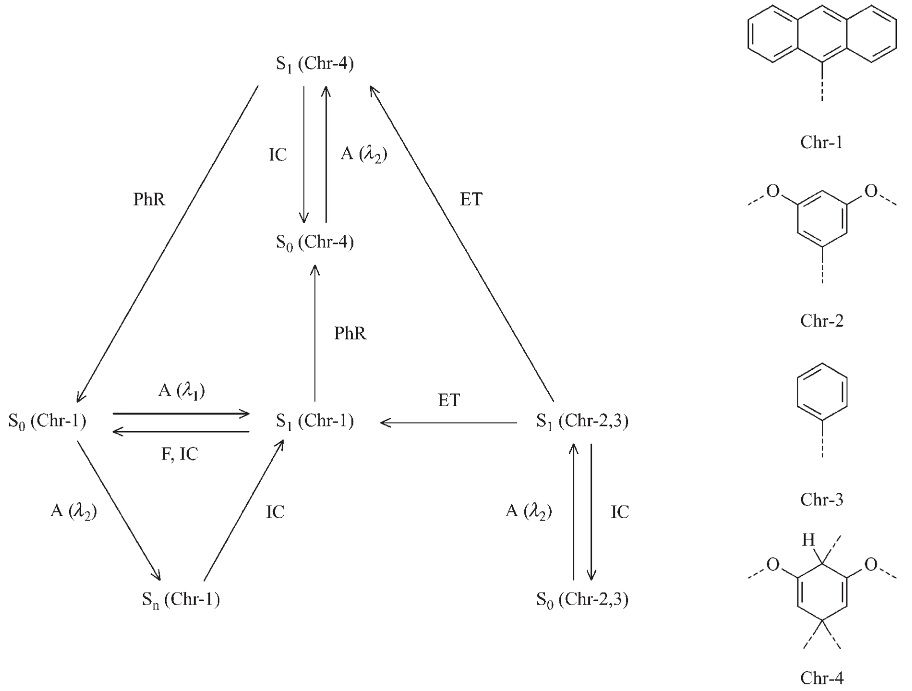
## Experimental Section

**General**: Melting points were determined on a Büchi 510 melting point apparatus and are uncorrected. The UV/Vis spectra were obtained with a Zeiss MCS 320/340, and the fluorescence spectra with a Perkin-Elmer LS 50B spectrometer. The $^{1}H$ and $^{13}C$ NMR spectra were recorded with Bruker AMX 400 and ARX 400 spectrometers. The mass spectra were obtained on a Finnigan MAT 95 (FD and EI) and on a Shimadzu AXIMA-CFR (MALDI-TOF) spectrometer. The elemental analyses were determined in the Microanalytical Laboratory of the Chemistry Department of the University of Mainz.

**Preparation of dendrons and model compounds**: Compounds **1**, **4G**$^{0}$, and **5a,b** are commercially available. Dendrons **2G**$^{i}$ ($i=1$–4), **3G**$^{i}$ ($i=1$–4), and **4G**$^{i}$ ($i=1$–3) were prepared with a combination of known procedures: Step a in Scheme 2 was performed according to references [5,6,10], step b according to references,[6,7,9] and step c in analogy to reference [8]. 9-[(Benzyloxy)methyl]anthracene (**6G**$^{0}$) was obtained as described earlier.[17]

**General procedure for preparation of dendrimers 6G$^{i}$ ($i$=1–4)**: A mixture of 9-chloromethylanthracene (**5a**, 227 mg, 1.0 mmol), alcohol **3G**$^{i}$ (1.05–1.20 mmol), tetrabutylammonium bromide (81–106 mg, 0.25–0.33 mmol) in chlorobenzene (30–50 mL), and KOH (224 mg, 4.0 mmol) in $H_2O$ (1–2 mL) was stirred at 60 °C in an Ar atmosphere. The reaction time was three days for **6G**$^{i}$ ($i=1,2,3$) and six days for **6G**$^{4}$. $CH_2Cl_2$ (100 mL) and $H_2O$ (100 mL) were added at room temperature. The aqueous layer was separated and extracted with $CHCl_3$ ($3\times50$ mL). The unified organic phases were dried with $Na_2SO_4$ and evaporated. The crude product was purified by column chromatography ($SiO_2$ ($50\times3$ cm), cyclohexane/$CH_2Cl_2$/ethyl acetate 1/1/0.03). Intense daylight should be avoided during all operations.

**9-{[3,5-Bis(benzyloxy)benzyloxy]methyl}anthracene (6G$^{1}$)**: Yield 393 mg (77%), m.p. 108 °C, yellowish solid; $^{13}C$ NMR ($CDCl_3$): $\delta=64.0$, 1C (α-$CH_2$), 70.0, 2C (γ-$CH_2$), 72.2, 1C (β-$CH_2$), 101.6, 1CH/106.7, 2CH (trisubst. benzene), 124.4, 2CH/124.9, 2CH/126.1, 2CH/129.0, 2CH (C-1, C-



Scheme 7. Photophysical and photochemical process of the dendrimers $\mathbf{6\,G}^{\boldsymbol{i}}$ ($i=1$–3) with chromophores Chr-1,2,3 and their cyclomers $\mathbf{7\,G}^{\boldsymbol{i-1}}$ with chromophores Chr-2,3,4: A: Absorption, $\lambda_1 \geq 300$ nm, $\lambda_2=254$ or 260 nm; F: Fluorescence; IC: Internal conversion; ET: Singlet energy transfer; PhR: Photoreaction.

2, C-3, C-4), 127.5, 4CH/127.9, 2CH/128.5, 4CH ($C_6H_5$), 128.4, 1CH (C-10), 128.6, 1$C_q$ (C-9), 131.1, 2$C_q$/131.4, 2$C_q$ (C-4a, C-8a), 138.6, 2$C_q$ ($C_6H_5$), 140.9, 1$C_q$/160.0 ppm, 2$C_q$ (trisubst. benzene); FD MS: *m*/*z* (%): 510 (100) [$M^+$]; elemental analysis calcd (%) for $C_{36}H_{30}O_3$ (510.6): C 84.68, H 5.92; found: C 84.61, H 6.04.

**9-({3,5-Bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy}methyl)anthracene ($\mathbf{6\,G^2}$)**: Yield 885 mg (95%), m.p. 132°C, yellowish powder; FD MS: *m*/*z* (%): 936 (100) [$M$+H$^+$]; elemental analysis calcd (%) for $C_{64}H_{54}O_7$ (935.1): C 82.20, H 5.82; found: C 82.44, H 6.06.

**9-[(3,5-Bis{3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy}benzyloxy)methyl]anthracene ($\mathbf{6\,G^3}$)**: Yield 1.74 g (98%), yellowish glassy compound; $^{13}$C NMR ($CDCl_3$): $\delta=64.0$, 1C ($\alpha$-$CH_2$), 70.0, 2C ($\gamma$-$CH_2$), 70.1, 12C ($\delta$-$CH_2$, $\varepsilon$-$CH_2$), 72.2, 1C ($\beta$-$CH_2$), 101.6, 7CH/106.4, 12 CH/106.8, 2CH (trisubst. benzene), 124.4, 2CH/124.9, 2CH/126.1, 2CH/129.0, 2CH (C-1, C-2, C-3, C-4), 127.5, 16CH/128.0, 8CH/128.5, 16CH ($C_6H_5$), 128.4, 1CH (C-10), 128.5, 1$C_q$ (C-9), 131.1, 2$C_q$/131.4, 2$C_q$ (C-4a, C-8a), 136.7, 8$C_q$ ($C_6H_5$), 139.2, 4$C_q$/139.3, 2$C_q$/140.9, 1$C_q$ (trisubst. benzene), 159.9, 2$C_q$/160.0, 4$C_q$/160.1 ppm, 8$C_q$ ($C_qO$, trisubst. benzene); FD MS: *m*/*z* (%): 1785 (100) [$M$+H$^+$]; elemental analysis calcd (%) for $C_{120}H_{102}O_{15}$ (1784.1): C 80.79, H 5.76; found: C 80.64, H 6.01.

**9-{[3,5-Bis(3,5-bis{3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy}benzyloxy)benzyloxy]methyl}anthracene ($\mathbf{6\,G^4}$):** Yield 101 mg (21%) from a preparation which used 0.14 mmol **5**, yellowish glassy compound. $^{13}$C NMR ($CDCl_3$): $\delta=65.2$, 1C ($\alpha$-$CH_2$), 70.0, 6C ($\gamma$-$CH_2$, $\delta$-$CH_2$), 70.1, 24C ($\varepsilon$-$CH_2$, $\zeta$-$CH_2$), 72.6, 1C ($\beta$-$CH_2$), 101.6, 15CH/106.4, 30CH (trisubst. benzene), 125.0, 2CH/127.2, 4CH/129.0, 2CH (C-1, C-2, C-3, C-4), 124.6, 32CH/128.0, 16 CH/128.6, 32CH ($C_6H_5$), 128.7, 1CH (C-10), 133.5, 134.1, 136.8, 139.2, (aromat. $C_q$, partly superimposed), 160.0, 160.1 ppm (aromat. $C_q$, partly superimposed). The MALDI-TOF mass spectrum showed the dendron mass, but not the mass of the dendrimer $\mathbf{6\,G^4}$ (*m*/*z* 3482).

**General procedure for the irradiation of $\mathbf{6\,G}^{\boldsymbol{i}}$ ($\boldsymbol{i}$=1–3)**: A slow Ar stream was passed for 30 min through a solution of 0.1 mmol of $\mathbf{6\,G}^{\boldsymbol{i}}$ in dry benzene (165–170 mL), after which irradiation was started with a 450-W Hanovia medium-pressure lamp equipped with a Duran glass filter ($\lambda \geq$ 300 nm). After about 30 min, TLC ($SiO_2$, toluene) showed total consumption of the starting material. The Ar stream was stopped and the solution evaporated. The obtained residue was pure product $\mathbf{7\,G}^{\boldsymbol{i-1}}$. Heating or traces of acids must be strictly avoided.

**7,22-Bis(benzyloxy)-3-oxahexacyclo[7.6.6.2$^{5,8}$.0$^{1,5}$.0$^{10,15}$.0$^{16,21}$]tricosa-6,10,12,14,16,18,20,22-octaene ($\mathbf{7\,G^0}$)**: Yield: quantitative, m.p. 70°C (decomp); $^1$H NMR ($CDCl_3$): $\delta=3.24$ (m, 1H; 8-H), 3.59/4.25 (AB, $^2J=-10.8$ Hz, 4H; $\gamma$-$CH_2$), 3.90 (s, 2H; $\beta$-$CH_2$), 4.28 (d, $^3J=11.4$ Hz, 1H; 9-H), 4.48 (d, $^4J=2.0$ Hz, 2H; 6-H, 23-H), 4.75 (s, 2H; $\alpha$-$CH_2$), 7.07–7.36 ppm (m, 18H; aromat. H); $^{13}$C NMR ($CDCl_3$): $\delta=50.7$, 1 CH (C-9), 52.8, 1 CH (C-8), 56.6, 1 CH (C-5), 65.4, 1 CH (C-1), 70.2, 2 $CH_2$ ($\gamma$-$CH_2$), 71.1, 1$CH_2$ ($\alpha$-$CH_2$), 80.9, 1$CH_2$ ($\beta$-$CH_2$), 106.4, 2CH (C-6, C-23), 122.5, 2CH/125.4, 2CH/126.0, 2 CH/127.7, 2 CH/128.0, 2 CH/128.1, 4CH/128.4, 4CH (aromat. CH), 136.6, 2$C_q$/144.5, 2$C_q$/146.0, 2$C_q$ (aromat. $C_q$), 162.8 ppm, 2$C_q$ ($C_qO$, C-7, C-22); FD MS: *m*/*z* (%): 511 (15) [$M^+$], 421 (100); elemental analysis calcd (%) for $C_{36}H_{30}O_3$ (510.6): C 84.68, H 5.92; found: C 84.74, H 6.25.

**7,22-Bis[3,5-bis(benzyloxy)benzyloxy-3-oxahexacyclo[7.6.6.2$^{5,8}$.0$^{1,5}$.0$^{10,15}$.0$^{16,21}$]tricosa-6,10,12,14,16,18,20,22-octaene ($\mathbf{7\,G^1}$):** Yield: quantitative, m.p. 74°C (decomp); $^1$H NMR ($CDCl_3$): $\delta=3.22$ (m, 1H; 8-H), 3.48/4.14 (AB, $^2J=-11.0$ Hz, 4H; $\gamma$-$CH_2$), 3.85 (s, 2H; $\beta$-$CH_2$), 4.23 (d, $^3J=10.6$ Hz, 1H; 9-H), 4.41 (d, $^4J=1.9$ Hz, 2H; 6-H, 23-H), 4.71 (s, 2H; $\alpha$-$CH_2$), 5.01 ("s", 8H; $\delta$-$CH_2$), 6.44 (d, $^4J=2.3$ Hz, 4H; trisubst. benzene), 6.53 (t, $^4J=2.3$ Hz, 2H; trisubst. benzene), 6.97–7.35 ppm (m, 28H; aromat. H); $^{13}$C NMR ($CDCl_3$): $\delta=50.7$, 1 CH (C-9), 52.7, 1 CH (C-8), 50.5, 1$C_q$ (C-5), 65.4, 1$C_q$ (C-1), 70.1, 6$CH_2$ ($\gamma$-$CH_2$, $\delta$-$CH_2$), 71.1, 1$CH_2$ ($\alpha$-$CH_2$), 80.8, 1$CH_2$ ($\beta$-$CH_2$), 101.6, 2CH (trisubst. benzene), 106.5, 2CH (C-6, C-23), 107.0, 4CH (trisubst. benzene) 122.4, 2CH/125.4, 2CH/126.0, 2CH/127.5, 8CH/127.6, 2CH/128.0, 4CH/128.6, 8CH (aromat. CH), 136.8, 4$C_q$/138.9, 2$C_q$/144.4, 2$C_q$/145.9, 2$C_q$ (aromat. $C_q$), 159.4, 4$C_q$/162.6 ppm, 2$C_q$ (aromat. $C_qO$); FD MS: *m*/*z* (%): 935 (100) [$M^+$]; elemental analysis calcd (%) for $C_{64}H_{54}O_7$ (935.1): C 82.20, H 5.82; found: C 82.19, H 5.34.

**7,22-Bis{3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy-3-oxahexacyclo[7.6.6.2$^{5,8}$.0$^{1,5}$.0$^{10,15}$.0$^{16,21}$]tricosa-6,10,12,14,16,18,20,22-octaene ($\mathbf{7\,G^2}$)**: Yield: quantitative, m.p. 80°C (decomp); $^1$H NMR ($CDCl_3$): $\delta=3.29$ (m, 1H; 8-H), 3.52/4.19 (AB, $^2J=-11.2$ Hz, 4H; $\gamma$-$CH_2$), 3.91 (s, 2H; $\beta$-$CH_2$), 4.28 (d, $^3J=10.7$ Hz, 1H; 9-H), 4.47 (d, $^4J=1.5$ Hz, 2H; 6-H, 23-H), 4.76 (s, 2H; $\alpha$-$CH_2$), 4.99 ("s", 8H; $\delta$-$CH_2$), 5.03 (s, 16H; $\varepsilon$-$CH_2$), 6.48–6.71 (m, 18H; trisubst. benzene), 6.98–7.50 ppm (m, 40H; aromat. H); FD MS: *m*/*z* (%): 1785 (100) [$M$+H$^+$].

**Reverse reaction**: A short heat shock to neat $\mathbf{7\,G}^{\boldsymbol{i-1}}$ ($i=1$–3) ($T \geq 60$°C) or short irradiation ($t \leq 1$ min) at $\lambda=254$ nm ($10^{-4}$ M solution in $CH_2Cl_2$) in the absence of traces of acids yields quantitatively the dendrimers $\mathbf{6\,G}^{\boldsymbol{i}}$ ($i=1$–3).

**Fluorescence measurements**: $3\times10^{-7}$ M solutions of $\mathbf{6\,G}^{\boldsymbol{i}}$ ($i=1$–3) in $CH_2Cl_2$ were compared with 1:1 mixtures of $\mathbf{3\,G}^{\boldsymbol{i}}$ ($i=1$–3) and **5b** which had the same absorbance. The excitation wavelength was in both cases $\lambda=260$ nm. The fluorescence intensities $F$ and $F'$, respectively, were obtained by integration using the software of the fluorescence spectrometer. The data compiled in Table 2 were obtained according to Equations (4) and (5),

$$\frac{F'}{F} = \frac{\frac{\varepsilon_1}{\varepsilon_1 + \varepsilon_2}\phi_{\rm F}{}' \frac{\varepsilon_1}{\varepsilon_1 + \varepsilon_2}\phi_{\rm T}\phi_{\rm F}{}'}{\frac{\varepsilon_1}{\varepsilon_1 + \varepsilon_2}\phi_{\rm F}} \tag{4}$$

$$\phi_{\rm T} = \frac{\varepsilon_1}{\varepsilon_2}\left(\frac{F'}{F}\cdot\frac{\phi_{\rm F}}{\phi_{\rm F}{}'} - 1\right) \tag{5}$$

where $F'/F$ is the ratio of fluorescence intensities of **6G**$^i$ and the mixture **3G**$^i$/**5b** for excitation of both at $\lambda = 260$ nm (equal absorbance); $\varepsilon_1$ the molar absorption coefficient of the anthracene chromophore (Chr-1) at $\lambda = 260$ nm (measurement on **5b**); $\varepsilon_2$ the molar absorption coefficient of the benzene-ring chromophores (Chr-2, Chr-3) at $\lambda = 260$ nm (measurement on **3G**$^i$); $\phi_{\rm F}{}'$ the quantum yield of the $S_1 \rightarrow S_0$ fluorescence of the dendrimers **6G**$^i$ with ($\lambda_{\rm exc} = 260$ nm); $\phi_{\rm F}$ the quantum yield of the fluorescence of **5b** ($\lambda_{\rm exc} = 260$ nm); and $\phi_{\rm T}$ the quantum yield of singlet energy transfer from the benzene rings to the anthracene core.

The fluorescence quantum yields of **5b** and **6G**$^i$ ($i = 1,2,3$) were obtained by comparison with unsubstituted anthracene as standard ($\Phi_{\rm F} = 27\%$).

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[23] Practical optimization should combine a complete intramolecular photocycloaddition with a partial cycloreversion with the most favorable wavelength between 254 and 400 nm. Thus, the disappearance and appearance of the fluorescence should permit high-performance monitoring of optical switching.

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