

Acridizinium-Substituted Dendrimers As a New Potential Rewritable Optical Data Storage Material for Blu-ray

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A second-generation (acridizinium)₁₂-dendrimer based on a poly(2,2-bis(hydroxymethylpropionic acid)) [bis-MPA] scaffold which can undergo photoinduced (4π + 4π) cycloaddition reactions on exposure to blue-violet light at 405 nm, and be reversed upon irradiation at 257 nm, has been synthesized. This provides an alternative chromophore for rewritable optical data storage media to the existing dye materials such as azo, cyanine, and phthalocyanine dyes for Blu-ray recording. The compound was initially tested in ethanol, showing good reversible properties and photoinduced degree of dimerization. The (acridizinium)₁₂-bis-MPA dendrimer was cast on a quartz plate, using poly(vinylpyrrolidone) as a matrix, in order to simulate conditions found in DVD discs for existing dyes. The film showed good transmission, stability, and mechanical properties. Through gray scale recording it may be possible to store more than 75 GB on a single-layer disk of a conventional-sized 5.25 in. disk, using existing Blu-ray disc technology.

Introduction

The Blu-ray disc (BD), is a third generation optical disk format offering more than 5 times the storage capacity of traditional DVDs with storage capacities reaching 25 GB on a single-layer disk.

Whereas the majority of current optical disk technologies (e.g., DVD, DVD ± R, DVD ± RW, and DVD-RAM) rely on a red laser to read and write data, the BD format uses a blue-violet laser instead. Despite the different types of lasers used, Blu-ray products can easily be made backward compatible with CDs and DVDs through the use of a BD/DVD/CD compatible optical pickup unit. By using a blue-violet laser (405 nm) with a shorter wavelength than a red laser (650 nm) and high numerical aperture optics, it is possible to focus the laser spot to a smaller spot size, allowing data to be packed more densely. The key component in a recordable optical storage medium is the recording dye. The dye is responsible for forming the data marks during recording, for media performance, and for the longevity of the information once stored.

Azo, cyanine, and phthalocyanine dyes have so far been the main structures of focus,¹ and significant effort has been

put into finding new types of materials for optical data storage, in order to achieve higher data storage capacity.² In our previous work we showed that digital optical data storage would be feasible through a photodimerization process, by synthesizing and testing possible materials for a fourth generation of optical data storage media, in novel materials such as 1,1'-(α,ω-alkanediyl)bis[pyrimidine] and 1-(ω-bromoalkyl)uracil species,³ di- and oligopeptides,⁴ and dendrimers.⁵ In these fourth-generation materials, storage could be achieved through photoinduced (2π + 2π) cycloaddition reactions on exposure to UV light at 254 nm. The compounds with good degree of dimerization were made as

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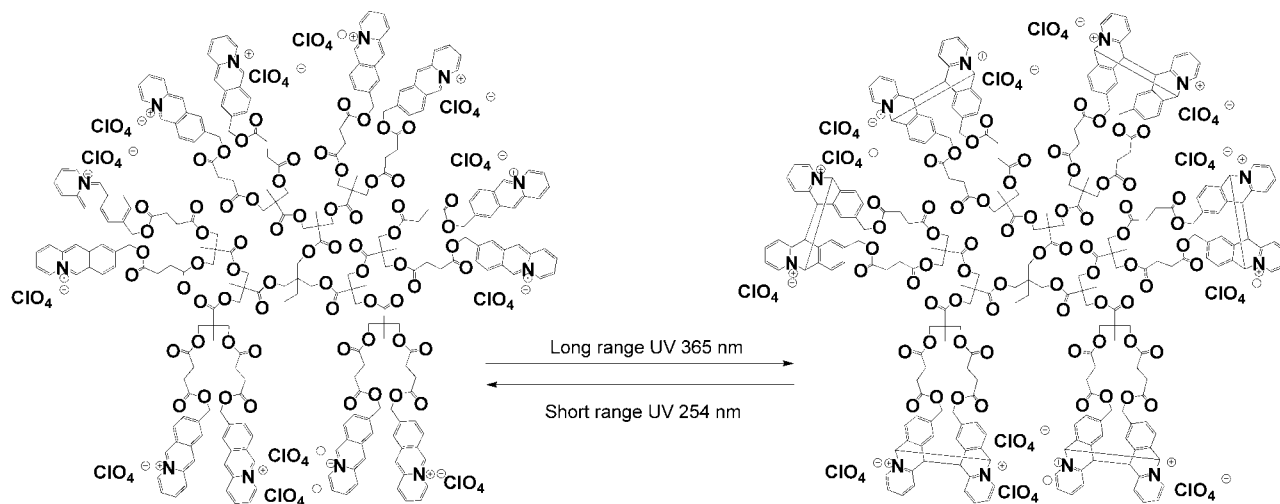


Figure 1. Idealized photodimerization and photocleavage process induced by long- and short-ranged UV light, respectively, for a second-generation (acridizinium)₁₂-bis-MPA dendrimer.

thin films and tested, using a UV laser, for possible storage applications, showing interesting surface properties.⁶ Recording of gray levels has been shown to be possible in thin films leading to the theoretical possibility of a storage capacity of more than 200 GB,^{3,7} on a single-layer disk, using a UV laser. The decrease in the absorbance of the film is taken to be an indicator of the degree of dimerization.

Tomlinson et al.⁸ have investigated reversible photodimerization of acridizinium, by incorporating a acridizinium *p*-toluenesulfonate photodimer into a copolymer of acrylic acid and methyl methacrylate; here dimerization efficiencies of 50% were found. This material was examined for its potential for holographic information storage, as it showed relatively large changes in refractive index on irradiation and was not photochemically degraded. In a holographic setup using 325 nm light from a He–Cd laser, these dimers were broken on irradiation, and a maximum diffraction efficiency of 5% was reported. As the orientation and separation of the chromophores during a dimerization process is crucial, in this case the fabricated dimers were incorporated into a matrix, before they were broken with appropriate irradiation.

The current work is based on using a specific wavelength for optical digital data storage. We propose to use the change in the absorption of the film on irradiation as bit markings. It is then shown that the change in the absorption is large enough to employ a multibit storage in the form of gray levels. The change in the refractive index change estimated from Kramers–Kronig relations may be sufficient for holographic storage; however, it is not large enough for a sensitive gray level storage. The rationale behind the current work is that it is expected that the degree of dimerization will be much larger when the two chromophores are held at a specific distance and orientation from each other through a short molecular tether. Here we use a UV lamp (long-

range UV 365 nm) or a blue laser (blue-violet 405 nm) to photoinduce a $(4\pi + 4\pi)$ cycloaddition and a UV lamp (short-range UV 254 nm) or UV laser (short-range UV 259 nm) to induce photocleavage between acridizinium salt monomers attached to a dendrimer. Here (acridizinium)₁₂-bis-MPA second generation was prepared, and the degree of dimerization, photocleavage, and mechanical properties were studied. The dendrimer scaffold, synthesis, and reason for choosing only one specific dendrimer generation is based on previous work.⁵ Briefly, the first generation was too crystalline to make any functional films, and a clear tendency was observed showing those generations higher than 2 gave rise to lower photoinduced degree of dimerization. The idealized photodimerization process is shown for the synthesized (acridizinium)₁₂-[G#2]-bis-MPA in Figure 1.

Results and Discussion

The synthesized compounds 9-(hydroxymethyl) acridizinium bromide (**1**), 9-(hydroxymethyl) acridizinium perchlorate (**2**), and the acridizinium perchlorate bis-MPA (**3**) all had a concentration of approximately 400 μg in 1 mL of ethanol, in order to reach an absorbance of 1, to make the synthesized products comparable, and to compare results with our previous work.^{3–6} For the photodimerization experiments in solution, a quartz cuvette of the type 110-QS, with the light path of 1 mm, was used. The photodimerization in solution was carried out using a standard UV lamp with 6 W corresponding to 420 $\mu\text{W}/\text{cm}^2$ at wavelengths of 365 and 254 nm. The sample cuvette was placed 5 cm from the irradiating source, in a fixed position, and irradiated for 15, 30, and 60 min, respectively. The sample was measured before irradiation and after each irradiation period in a UV spectrophotometer giving an indication of the degree of dimerization. The decrease in absorbance is an indication of how much of the compound in the solution has dimerized. The degree of dimerization of the compounds **2** to **3** was investigated in this study. The experiments were done on the free chromophores in solution and on the chromophores attached to a carboxylic acid bis-MPA dendrimer. The

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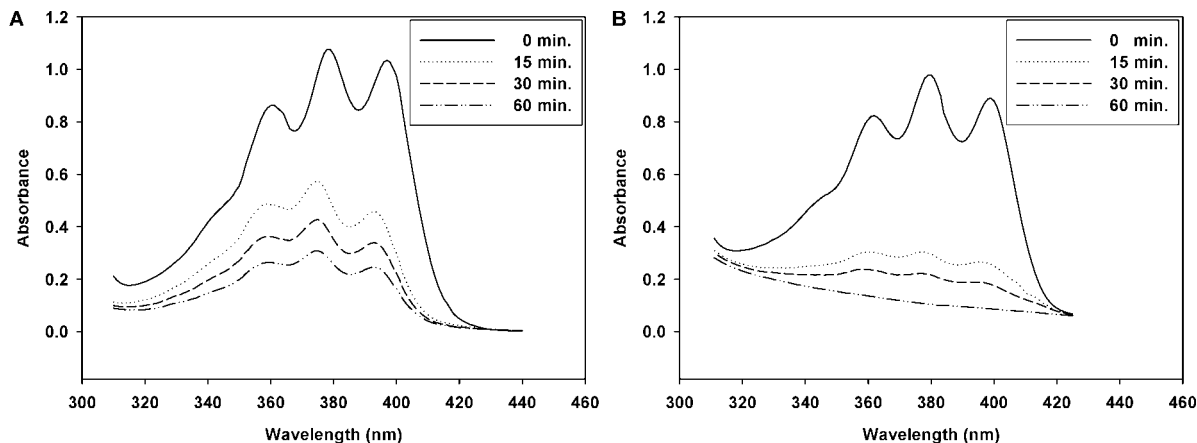


Figure 2. (a) Absorption of **2** in ethanol and (b) absorption of **3** in ethanol, before irradiation and after 15, 30, and 60 min of irradiation at 365 nm in both cases.

absorption spectra of acridizinium shows three strong characteristic peaks at ~ 361 , 378 (λ_{max}), and 397 nm (see Figure 2).

The initial photoinduced degree of dimerization studies were performed on **1** which was only soluble in water, ethanol, and methanol, making it inappropriate for coupling it to the synthesized dendrimer. An exchange of the counterion from bromide to perchlorate gave **2**, which was soluble in dichloromethane permitting the synthesis of **3**, and its photoinduced degree of dimerization could be observed in an ethanol solution and compared with that of **2**. An example of the absorbance spectra of **2** and **3** are shown in Figure 2, parts a and b, respectively.

The absorbance spectra between **1** and **2** do not differ significantly (**1** not shown), but the photoinduced degree of dimerization of **3** is significantly better than that of **1** and **2** as the spectra in Figure 2b shows for **2**, and equally important, the dendrimer prohibited the acridizinium from crystallizing, enabling us to make films for further testing. After 15 min of irradiation **2** had a photoinduced degree of dimerization of 47% while **3** reached 69%. After 60 min **2** and **3** reached a minimum in absorbance, giving a final photoinduced degree of dimerization of 71% and 89%, respectively. The long photodimerization times are due to the low power used in the experiments.

It has been pointed out⁹ that solvent effects can have a negative effect on the photostability of dyes through photooxidation reactions, and in addition, the photostability of dyes is strongly dependent on their chemical structure. To evaluate an appropriate solvent for the later casting of the dye **3** and verify that the material is suitable as an optical recording medium, the photostability of the dye **3** were investigated. Acridizinium salts and their good stability have been studied extensively;¹⁰ however, coupling it to a dendrimer scaffold could influence the photostability and allow photooxidation, which would give rise to a decrease in

absorbance similar to the decrease observed in Figure 2. However, this would give rise to a large shift in λ_{max} and in the NMR spectrum, which we did not observe in any samples; therefore, we concluded that **3** is photostable under the relevant conditions.

Due to the asymmetrical nature of the acridizinium salt, several isomeric forms of the mesoconnected ion are theoretically possible. Up to six isomeric photodimers are formed,¹¹ but only two of those (plus one mirror image) can form dimer photoproducts in our system, due to the covalent bonding in the ninth position to the dendrimer as shown in Figure 3.

From modeling (not shown) it was found highly unlikely for the remaining three isomeric photodimers to form, due to the characteristics of the dendrimer, steric repulsion, and unfavorable bending. **B** in Figure 3 is also significantly less favorable because the cations are directly above each other including the large perchlorate. From this reasoning we believe that **A** forms in the majority of the three cases shown in Figure 3, and it is believed to be the one giving the spectra in Figure 2. The only way for the last three isomers (not shown) to form was if the photodimerization were to happen intermolecularly (photodimerization between chromophores on different dendrimers) and not only intramolecularly (photodimerization within the same dendrimer between chromophores on neighboring dendrons).

Dynamic light scattering was used in order to confirm that the photodimerization was intramolecular and not intermolecular, since no increase in size or aggregation was observed (results not shown).

After eliminating photooxidation, interfering solvent effects, and intermolecular photodimerization which would essentially cross-link the system, we found **3** to be a suitable candidate as a new novel optical data storage material. By performing photodimerization and photocleavage repeatedly in ethanol, we found that a stable and reversible process was possible. The absorption changes in **3** were observed by irradiating initially at 365 nm (photodimerization) for 10 min and then reirradiation at 254 nm (photocleavage) for 5 min, which is evident from Figure 4.

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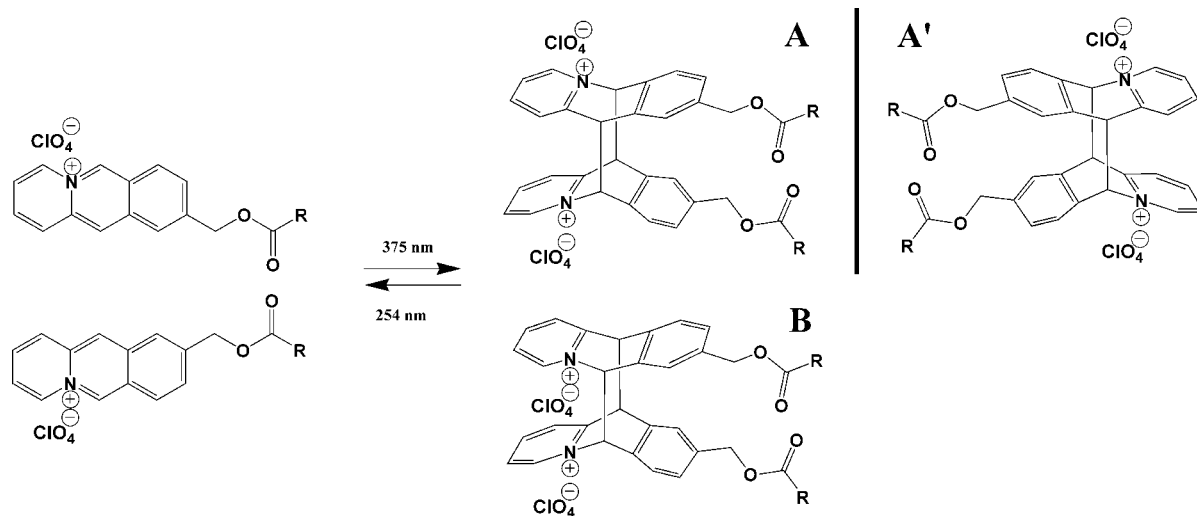


Figure 3. Photodimerization of the acridizinium perchlorate, and the three isomeric photodimers formed in our system (R = dendrimer).

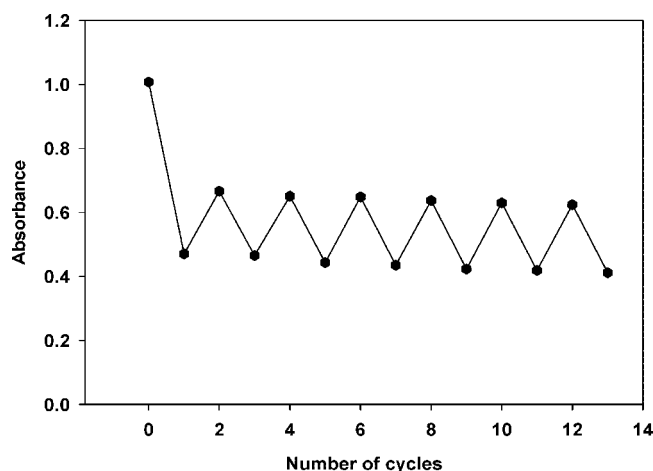


Figure 4. Absorption changes in **3** upon irradiation with 365 nm and reirradiation with 254 nm in ethanol.

A decrease after the first reirradiation at 254 nm (cycle 2) compared with the sample before irradiation (cycle 0) is observed. This is due to the fact that, at 254 nm, the monomers absorb slightly, making it impossible to achieve complete reversion. This photostationary equilibrium reached is dependent on two parameters: (a) the quantum yield of the irradiation/reirradiation photoproducts and (b) the absorption coefficients of the monomer and dimer at the respective irradiation wavelengths.

Photodimerization Processes in the Dendrimer Film

In order to prove the efficacy of the dendrimer for purposes of optical storage, it is necessary to fabricate good quality thin films. Good quality films could not be obtained directly using only ethanol and **3** due to crystallization. However, a guest–host system with a polymer matrix consisting of 1 mg of the dendrimer and 10 mg of poly(vinylpyrrolidone) (PVP) in 1 mL of 96% ethanol was found to give good quality films. The films were obtained from casting the solution onto quartz plates through a slow evaporation of the solvent over 24 h, whereafter the films were baked in the oven at 100 °C, to remove any residual

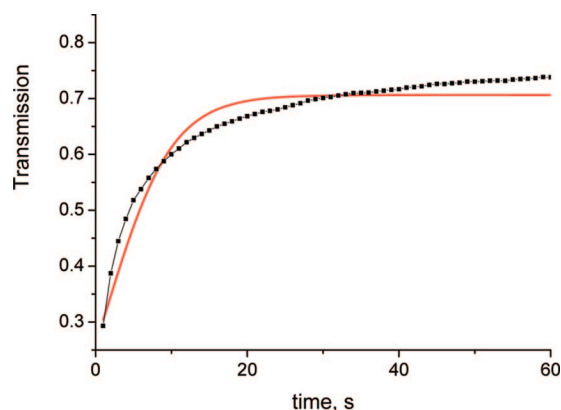


Figure 5. Transmission through a film of **3** from the acridizinium dimerization in a PVP matrix as a function of time. The line joining the squares is the experimental measurement, whereas the solid curve is the simulated transmission.

solvent. Films of fairly uniform thickness of 12 μm were obtained, except at the edges. The variation in the film thickness over a 10 mm diameter was found to be on the order of 1 μm . This thickness ensured an absorbance on the order of 1 at 405 nm, making the results comparable to the ethanol solution. The refractive index change on irradiation at 405 nm was estimated to be 0.017 through Kramers–Kronig relations.

The transmission through the film at 405 nm was then measured as a function of time, using a laser, and the result is shown in Figure 5. Tomlinson¹² has developed a theory for the dynamics of photodimerization in films, and we recently showed how to apply this model on our system in detail.³

Briefly explained, the transmission through the film is given as a function of time, by

$$Tr = \frac{(1 - \alpha)(1 - \exp(-\rho)) + \alpha\rho}{(1 - \alpha)(1 - \exp(-T)) + \alpha T} \Big|_{z=d} \quad (1)$$

where

$$\alpha = \frac{\alpha_s}{\alpha_i} \quad (2)$$

is the ratio of the absorption of the sample in the initial state and the absorption in the final state. ρ is a normalized exposure given by

$$\rho(z, t) = (s_a + s_b) \int_0^t F(z, t') dt' \quad (3)$$

and T is a normalized exposure at the front face of the sample, given by

$$T = (s_a + s_b) F_0 t \quad (4)$$

where F is the flux of photons at time t , at a depth of the film z .

Experimentally, the only value that needs to be determined is α . By matching the experimentally obtained initial slope of the transmission curve as a function of time (line connecting squares) with the simulated transmission (solid line), see Figure 5, a value for the absorption cross section may be obtained. With an initial measured transmission of 30% and a flux of 9×10^{16} photons $\text{cm}^{-2} \text{s}^{-1}$, the best match to the initial slope of the experimental data is obtained when the absorption cross section is estimated to be 1.6×10^{-18} cm^2 .

This cross section, which is an important parameter in comparing different photochromic processes, compares favorably with the maximum theoretical value of approximately 0.7×10^{-17} cm^2 for acridizinium monomers estimated by Tomlinson et al.⁸ It also fits well with the values for uracil-[G#1]-PAMAM⁵ (1.7×10^{-18}), 1,1'-(1,8-octanediy)bis[uracil]³ (0.85×10^{-18}), uracil-ornithine hexamer^{4b} (9.0×10^{-20}) for the case of the absorption cross sections estimated using different scaffolds, with uracil as the dye and a UV laser as the irradiating source in our previous work.

One of the impediments to an erasable and rewritable process in the PVP films was the presence of an antioxidant, 2,6-di-*tert*-butyl-4-methyl-phenol, in commercial PVP samples. The antioxidant was removed by washing PVP four times in a solution mixture of cyclohexane/acetone (9:1). Repeated photodimerization and photocleavage was possible after this purification procedure using a UV laser (257 nm) and blue laser (405 nm), respectively, as shown in Figure 6.

Conclusion

We have synthesized a new potential optical data storage media, using the well-defined bis-MPA dendrimer as a scaffold, with acridizinium perchlorate as end groups. This material has the potential of becoming an alternative to the existing third-generation technology with a significant increase in storage capacity, based on photodimerization/photocleavage, using a UV laser (257 nm) and a commercially available blue-violet laser (405 nm) for the Blu-ray technology. The synthesized dendrimer in a PVP film did not show any critical side reactions upon irradiation or high temperature (the film was baked at 100 °C), and it proved

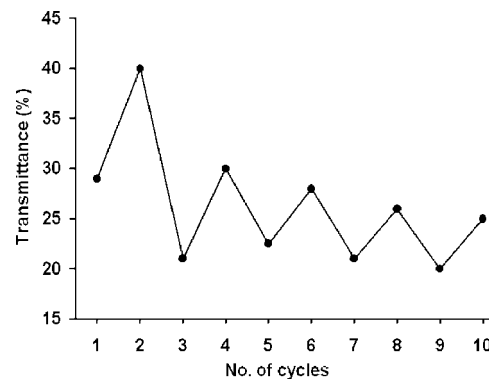


Figure 6. Transmission changes in a 10% v/v of **3** in PVP, upon irradiation with a blue-violet laser at 405 nm and reirradiation with a UV laser at 257 nm, in a film.

to be stable toward photooxidation. The acridizinium-dendrimer/PVP film had an excellent degree of dimerization of 89%, and good quality films could be made. With only 10% v/v of the acridizinium-bis-MPA dendrimer in PVP film we have proved that we can reverse the photodimerization process using a UV laser at 257 nm, making this material suitable for a rewriting technology as well. If a film consisting of a 100% acridizinium dendrimer could be made, e.g., other scaffolds, a significantly larger difference in transmission between irradiation and reirradiation could be made, leaving this material even more potentially interesting, scientifically as well as commercially. Considering the trend of progression toward lower wavelengths going from 780 nm (CD-RW) in 1997, to 650 nm (DVD) in 2000, to 405 nm (BD) in 2003,¹³ the future technology is highly likely to be focused on the use of UV lasers and new materials absorbing in this area, for optical data storage. We have shown here that this novel system and technique based on photodimerization/photocleavage as a comparison to read/erase, respectively, can be considered as an alternative technology for the existing and, through our previous work, for a future technology as well.

Experimental Section

Synthesis and Characterization. Preparation of (COOH)₁₂-[G#2]-bis-MPA Dendrimer. Hult's group presented the first dendrimer based on 2,2-bis(hydroxymethyl)propionic acid (bis-MPA).^{14a} This was later refined by the same group using the acetonide-2,2-bis(methoxy)propionic anhydride^{14b} as the building block, and trimethylpropane (TMP) as core moiety.^{14c} The bis-MPA-TMP dendrimer was synthesized according to these methods. The preparation of the final (acridizinium)₁₂-bis-MPA, was prepared by first deprotecting the acetonide derivatives by stirring in the presence of an acidic resin, Dowex 50W-X2.¹⁵ Due to impurities the Dowex resin was purified as described before.⁵

One equivalent of the dendrimer (OH)₁₂-[G#2]-bis-MPA was dissolved in a minimum amount of dichloromethane, 15 equiv of

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succinic anhydride was then added to the dendrimer under stirring, then 10 mL of pyridine, and finally 2.4 equiv of 4-dimethyl aminopyridine. The reaction mixture was then left under stirring at room temperature overnight. The dichloromethane was evaporated off, and the product (COOH)₁₂-[G#2]-bis-MPA was purified by liquid column chromatography, using the TLC system ethyl acetate/methanol/acetic acid (1:1:0.1), then gradually shifting to methanol/acetic acid (9:1). The dendrimer was dried in a vacuum oven overnight to remove the last residues of acetic acid with a yield of 96%.

(COOH)₁₂-[G#2]-bis-MPA-TMP: ¹H NMR (DMSO-*d*₆) δ 0.82 (t, 3H), 1.15 (s, 18H), 1.21 (s, 9H), 1.47 (dd, 2H), 2.38 (dd, 24H), 2.49 (dd, 24H), 4.20 (s, 6H), 4.24 (s, 12H), 4.14 (s, 24H), 9.45 (very broad, 12H, OH); ¹³C NMR (DMSO-*d*₆) δ 8.89, 16.81, 17.03, 28.51, 29.37, 30.18, 40.64, 46.03, 51.64, 64.86, 65.88, 171.69, 173.07, 175.01. *m/z* (MALDI-TOF MS) [found: 2403.10; (C₉₉H₁₃₄O₆₆ + Na⁺)⁺ requires 2403.07]. GPC: PDI = 1.02, MW = 2406.

Preparation of the Acridizinium Salt. Various acridizinium salts were initially synthesized by Bradsher and co-workers,¹⁰ for carcinogenic studies, and later a synthetically more refined method was developed, where the acridizinium salt was used for photocross-linking studies.¹⁶ The synthesis of the 9-(hydroxymethyl) acridizinium bromide was done as described in the literature.¹⁶ The corresponding perchlorate was prepared by refluxing the acridizinium bromide in (70%) perchloric acid (50 mL/g) for 2 h. (**Caution:** explosion danger!) Then ice water was added to the mixture, until precipitation occurred. The mixture was then filtered, washed three times with ice water, and a bright yellow powder was obtained. The powder was then recrystallized in methanol giving thin needle-shaped orange/yellow crystals (overall yield 88%).

¹H NMR (D₂O) δ (ppm) = 10.42 (s, 1H, H-6), 9.30 (d, ³J = 7.0 Hz, 1H, H-4), 9.22 (s, 1H, H-11), 8.60 (d, ³J = 8.9 Hz, 1H, H-7), 8.50 (d, ³J = 8.9 Hz, 1H, H-8), 8.44 (s, 1H, H-10), 8.11 (dd, ³J = 7.9 Hz, 1H, H-2), 8.00 (m, 2H, H-1 and H-3), 5.05 (s, 2H, H-12); ¹³C NMR (D₂O) δ 68.9, 123.01, 125.25, 125.64, 126.68, 127.36, 129.29, 131.89, 132.66, 134.82, 135.64, 140.39, 145.02. *m/z* (MALDI-TOF MS) [found: 210.25; (C₁₄H₁₂ClNO₅ - ClO₄⁻) requires 309.70]. Mp = 158–159 °C. (The perchlorate ion (99.45 g/mol) is detached in the laser irradiation process. Thus, the total weight is 210.25 + 99.45 = 309.70 g/mol.)

Preparation of (Acridizinium)₁₂-bis-MPA Dendrimer. One equivalent of the dendrimer (COOH)₁₂-[G#2]-bis-MPA was dissolved in a minimum amount of dichloromethane, 24 equiv of the 9-(hydroxymethyl) acridizinium perchlorate was then added to the dendrimer under stirring, and finally 24 equiv of dicyclocarbodiimide. The reaction mixture was then left under stirring at room temperature overnight, then filtered. The dichloromethane was evaporated off, and the product (acridizinium perchlorate)₁₂-[G#2]-bis-MPA was purified by diffusion in ethanol (96%), changing the solution twice per day until no 1,3-dicyclocarbodiimide, dicyclohexylurea, or free acridizinium salt was traceable in NMR, by using a molecular porous membrane tubing of the type Spectrum [MWCO: 3500]: flat width, 54 mm; diameter, 34, no. 3 (yield 85%).

(Acridizinium)₁₂-[G#2]-bis-MPA-TMP: ¹H NMR (DMSO-*d*₆) δ 0.82 (t, 3H), 1.15 (s, 18H), 1.21 (s, 9H), 1.47 (dd, 2H), 2.48 (dd, 24H), 2.49 (dd, 24H), 4.20 (s, 6H), 4.24 (s, 12H), 4.14 (s, 24H), 10.42 (s, 12H, H-6), 9.30 (d, ³J = 7.0 Hz, 12H, H-4), 9.22 (s, 12H, H-11), 8.60 (d, ³J = 8.9 Hz, 12H, H-7), 8.50 (d, ³J = 8.9 Hz, 12H, H-8), 8.44 (s, 12H, H-10), 8.11 (dd, ³J = 7.9 Hz, 12H, H-2), 8.00 (m, 24H, H-1 and H-3), 5.34 (s, 24H, H-12); ¹³C NMR (DMSO-*d*₆) δ 8.89, 16.81, 17.03, 28.71, 30.18, 40.64, 46.03, 51.64, 64.86, 65.88, 171.69, 173.07, 72.9, 123.01, 125.25, 125.64, 126.68, 127.36, 129.29, 131.89, 132.66, 134.82, 135.64, 140.39. *m/z* (MALDI-TOF MS) not possible. Elemental analyses: C (54.5); H (4.4); Cl (7.2); N (2.9); O (31.0). GPC: PDI = 1.05, MW = 5880.

Equipment. NMR spectra were recorded on a Bruker 200 MHz apparatus. Irradiation of the compounds in solution was done using a UV lamp, Spectroline model ENF-260C/FE (CM-10), and spectra were recorded on a Shimadzu UV-1700 spectrophotometer. The irradiation of the film was done using a blue-violet laser at 405 nm, and the reirradiation was done using a UV laser at 257 nm. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker Reflex IV, using the following method: Reflectron MALDI-TOF with pulsed ion extraction (PIE), positive ion analysis, where the sample was mixed with the matrix reagent 2,5-dihydroxybenzoic acid (10 mg/mL MeOH). TLC was done in the solvent system ethyl acetate/hexane (3/1 v/v) ratio, using Alugram Sil G/UV₂₅₄ 0.20 mm silica gel 60. DSC analyses were performed on a TA instrument DSC 2920. DSC samples were analyzed over the temperature range of 50–300 °C with a scan rate of 10 °C/min. GPC was performed using a Waters 2690 separation module equipped with Waters 2410 refractive index detector and autosampler. The molecular weight is relative to polystyrene standards. The GPC was equipped with four Ultrastay-gel linear mixed-bed columns (HR 0.5, HR 2, HR 4, and HR 5). DMF with 0.1% LiBr was used as the eluent at constant flow rate of 1.0 mL/min, at 30 °C. The concentrations of all the samples analyzed were 10 mg/mL.

Preparation of Films. A glass plate was cleaned thoroughly (Piranha solution), and 1 mg of **3** the (acridizinium)₁₂-[G#2]-bis-MPA dendrimer was dissolved in a mixture of 1 mg of **3**, 10 mg of PVP, and 1 mL of ethanol 96%. Then the mixture was filtered through a 0.22 μm filter, Millex-GS, and applied directly onto the cleaned glass plate and allowed to dry slowly for 24 h, then inserted into an oven for 1 h at 100 °C.

Laser Experiments. A 25 mW GaN laser at 405 nm was used for the transmission measurements. The beam from the laser was used directly to measure the transmission as a function of time. To measure the absorption spectra, the beam was expanded to a 10 mm spot; broken dimers were obtained by irradiating this area with an expanded beam from a frequency-doubled argon ion laser at 257 nm. An incident power of 5 mW was used, and the beam expanded to 10 mm with quartz optics.

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