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Synthesis and Aggregation Properties of Dansylated Glycerol-Based Amphiphilic Polyether Dendrons

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Glycerol-based amphiphilic polyether mono azide third-generation dendrons were synthesized through a divergent strategy. A repetitive synthetic sequence of *O*-alkylation and isopropylidene deprotection reaction was adopted for the synthesis, pentamethylene was used as spacer. Dansyl chloride was attached to the focal point as a fluorophore. The photophysical property in aqueous solution of the protected dendrons showed self-association behaviour from second generation onwards even at a very low concentration (1×10^{-8} M). A hypsochromic shift of around 60 nm in the emission maximum, significant increase in fluorescence intensity, almost ten-fold increase in the fluorescence anisotropy and a four-fold increase in average fluorescence lifetime of dansyl moiety were observed on going from first generation dendron to higher generation dendrons in aqueous medium. The absence of such behavior in the corresponding unprotected, relatively hydrophilic dendritic units clearly indicated that the aggregation is due to the presence of hydrophobic isopropylidene end groups. Quenching studies of the dendrimers in aqueous solution using a hydrophilic quencher Ag^+ revealed that the dansyl moiety in protected higher generations dendritic units is significantly shielded from the surroundings, which further rendered support to the fact that higher order dendrons undergo aggregation in aqueous medium.

Introduction

Dendrimers and their unique properties have attracted much attention over the past two decades.[1] In particular, amphiphilic dendrimers that can self-assemble into various supramolecular structures are of great interest[2] and have been employed to create functional materials with nanoscale supramolecular structures.[3] Aggregation of the primary units of dendrimers and dendrons into larger and more complex forms leads to a wide range of potential applications in the field of drug delivery,[4] biomedical[5] and nanotechnology.[6] Newkome et al. investigated the first class of amphiphilic dendrimers with an aliphatic core and charged carboxylate groups at the periphery, which can form unimolecular micelles in solution.[7] Self-association of protected Newkome-type second-generation dendrimers at nanomolar concentrations in aqueous solutions was reported by Mohanty et al.[8] Hirsch and co-workers reported that dendro-calixarene amphiphiles that self assembled into completely uniform and structurally persistent micelles in aqueous solution.[9] Over the past few years polyethers, hyperbranched polyglycerols[10,6b] and polyglycerol dendrimers[11,4b,5c] have been shown to be important due to their excellent water solubility and biocompatibility.[12,10b] Polyglycerol dendrimers have shown good transport capacities for poorly water soluble drugs[13,4b] e.g. Paclitaxel (anticancer drug) has been solubilized in water by using polyglycerol dendrimers.[14] Poly(glycerol-succinic acid) anionic dendrimers have been used as antibacterial agents against Gram-positive bacteria.[15] A family of myristylated poly(glycerol-succinic acid) dendritic amphiphiles has shown a wide range of aqueous aggregation behaviour forming supramolecular structures.[16] All this and the fact that glycerol is a biocompatible molecule which is a potentially important bio refinery feedstock, available in surplus as a by-product in the production of biodiesel by transesterification of vegetable oils or animal fats[17] lead us to investigate the synthesis of novel amphiphilic dendrimers using glycerol. In this paper, we report the divergent synthesis of glycerol-based polyether dendrons having pentamethylene spacer, isopropylidene or hydroxy as terminal groups and a dansyl

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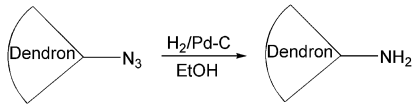
group attached at the focal point. The self-association behaviour of these dendrons was investigated by fluorescence techniques.

Results and Discussion

Synthesis of dendrons: This study describes synthesis of amphiphilic polyglycerol dendrons (Gn)-PGL, where Gn specifies the generation number of the dendron and azide functional group as focal point. Up to third generation dendrons were synthesized through a divergent methodology. These dendrons were attached to 5-(dimethylamino)naphthalene-1-sulfonyl chloride (fluorophore) through covalent linkage. Branching unit 4-(5-bromopentyloxy) methyl-2,2-dimethyl-1,3-dioxalane (**1**) and core molecule 4-(azidomethyl)-2,2-dimethyl-1,3-dioxolane (**2**) were synthesized from glycerol.[18,19] The spacer (pentamethylene group) was used previously in poly alkyl aryl ether dendrimers synthesis.[20] Compounds **1** and **2** were coupled in the presence of sodium hydroxide (NaOH) and tetrabutylammonium bromide (TBAB) in H_2O, tetrahydrofuran (THF) (3:2), at 60 °C to afford the protected dendron (G1)-AZPGL-ipd (**3**), which was easily separated from the branching unit by column chromatography. In the case of the first generation, branching unit 1.5 equiv. were used for 1 mmol, for each hydroxy group, but second generation onwards, 3 equiv. were used for each hydroxy group as the longer reaction times (>12 h), resulted in elimination of the branching unit. The isopropylidene group of (G1)-AZPGL-ipd (**3**) was subsequently deprotected using Dowex resin to yield (G1)-AZPGL-OH (**4**) quantitatively. Similarly, (G2)-AZPGL-ipd (**5**) and (G3)-AZPGL-ipd (**7**) dendrons were synthesized from (G1)-AZPGL-OH (**4**) and (G2)-AZPGL-OH (**6**), respectively (Scheme 1). The etherification reactions were monitored by FTIR spectroscopy. The absence of free hydroxy group signals, i.e. strong O–H stretching at ca. 3400 cm^{-1} confirmed that all OH groups were completely alkylated. The deprotection of isopropylidene groups was monitored by ^1H NMR spectroscopy. The absence of methyl signals around δ = 1.33 and 1.39 ppm confirmed that all isopropylidenes were completely deprotected. All these dendrons (azide as focal point) (G1)-AZPGL-ipd (**3**), (G2)-AZPGL-ipd (**5**) and (G3)-AZPGL-ipd (**7**) were converted into corresponding amine dendrons (G1)-AEPGL-ipd (**9**), (G2)-AEPGL-ipd (**10**) and (G3)-AEPGL-ipd (**11**) in the presence of Pd-C under hydrogen atmosphere (Scheme 2). (2,2-Dimethyl-1,3-dioxolan-4-yl)methanamine (G0)-AEPGL-ipd (**8**) was synthesized from glycerol.[21]

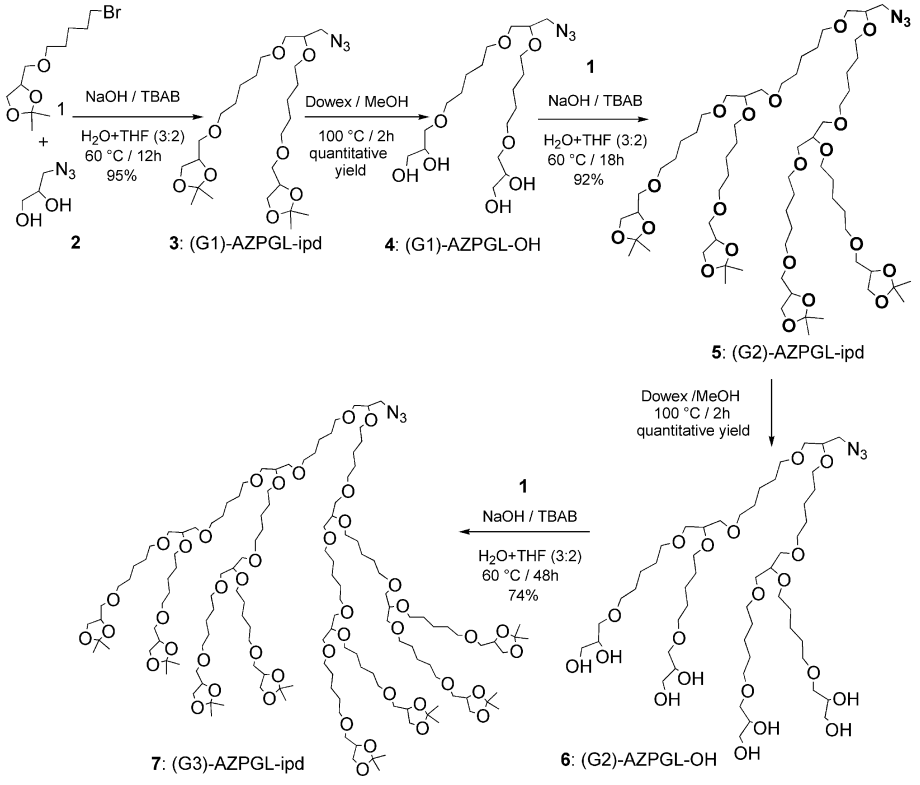


3: (G1)-AZPGL-ipd
5: (G2)-AZPGL-ipd
7: (G3)-AZPGL-ipd

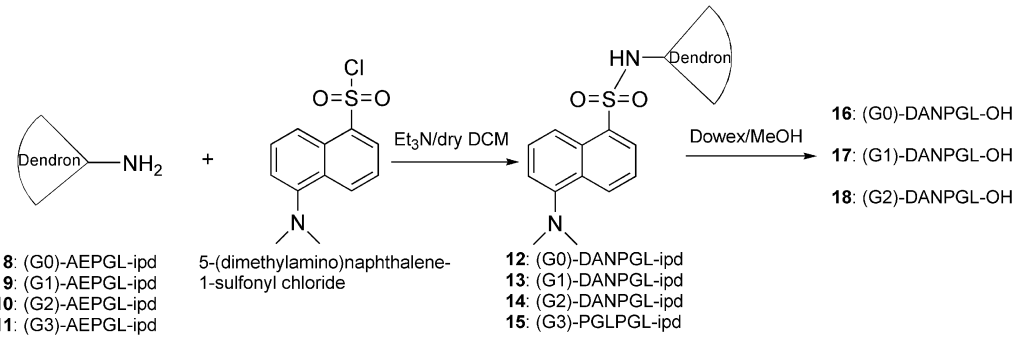
9: (G1)-AEPGL-ipd
10: (G2)-AEPGL-ipd
11: (G3)-AEPGL-ipd

Scheme 2. Synthesis of polyether amine dendrons (G1 to G3).

The dendrons (amine as focal point) (G0)-AEPGL-ipd (**8**), (G1)-AEPGL-ipd (**9**), (G2)-AEPGL-ipd (**10**) and (G3)-AEPGL-ipd (**11**) were coupled to 5-(dimethylamino)-



Scheme 1. Synthesis of polyether dendrons (azide as focal point) G1 to G3.



Scheme 3. Synthesis of isopropylidene protected (G0 to G3) and deprotected (G0 to G2) dansylated polyether dendrons.

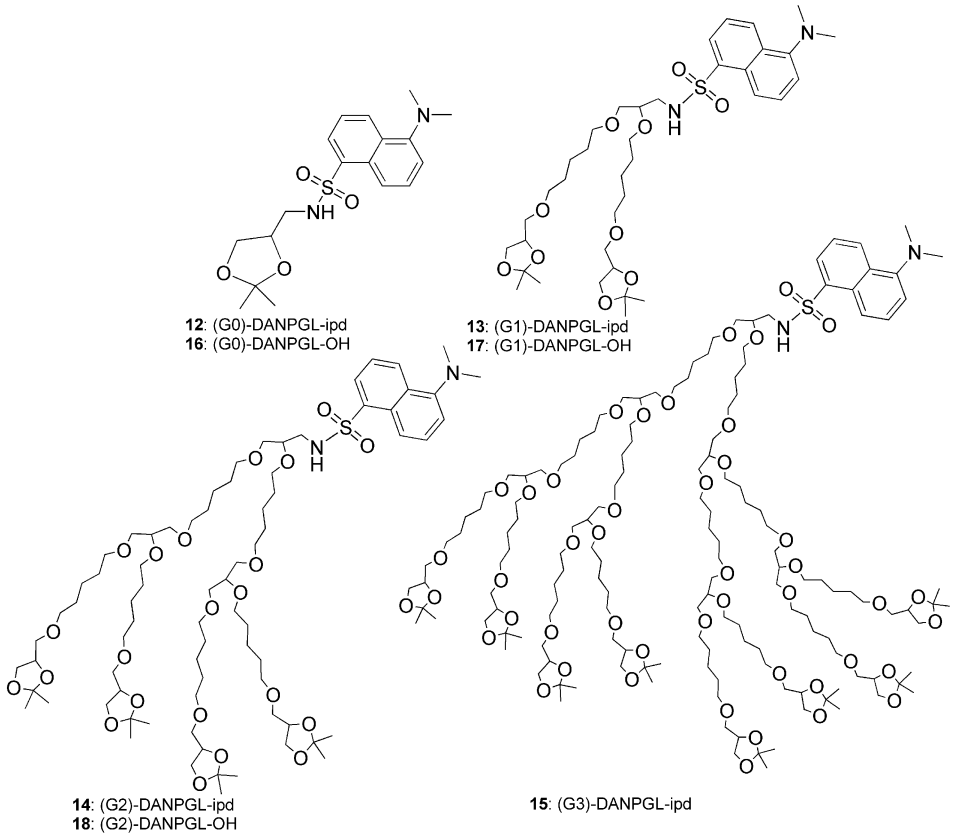


Figure 1. Dansylated polyether-protected (G0 to G3) and deprotected (G0 to G2) dendrons.

naphthalene-1-sulfonyl chloride in the presence of Et_3N and dry DCM to yield the corresponding dansylated dendrons (G0)-DANPGL-ipd (**12**), (G1)-DANPGL-ipd (**13**), (G2)-DANPGL-ipd (**14**), and (G3)-DANPGL-ipd (**15**), respectively. Finally, subsequent deprotection of isopropylidene groups of the dendrons (G0)-DANPGL-ipd (**12**), (G1)-DANPGL-ipd (**13**) and (G2)-DANPGL-ipd (**14**) yielded the corresponding deprotected dendrons (G0)-DANPGL-OH (**16**), (G1)-DANPGL-OH (**17**) and (G2)-DANPGL-OH (**18**) in the presence of Dowex and methanol at 100 °C (Scheme 3, Figure 1).

Molecular weights were determined by ESI/MALDI-TOF and the data agree with the calculated molecular weights (Table 1).

Aggregation Properties of Dansylated Dendrons Studied by Fluorescence Spectroscopy

Dansyl is a well known polarity sensitive chromophore and shows solvatochromic shift in the emission maximum with solvent polarity. In order to verify the solvent effect on the emission maximum of the dansylated dendrons, fluorescence study was carried out in several solvents of varying polarity. The normalised emission spectra of (G0)-DANPGL-ipd (**12**), (G1)-DANPGL-ipd (**13**), (G2)-DANPGL-ipd (**14**) and (G3)-DANPGL-ipd (**15**) in various solvents are represented in Figure 2 **A**, **B**, **C** and **D**, respectively. The solvatochromic shift in the emission maximum is evident for all three generations of dendrons i.e. the emis-

Table 1. ESI/MALDI-TOF spectroscopic data for dendritic units.

	Dendron	Calcd. MW	ESI/MALDI-TOF
3	(G1)-AZPGL-ipd	517	517
4	(G1)-AZPGL-OH	437	437
5	(G2)-AZPGL-ipd	1238	1238
6	(G2)-AZPGL-OH	1078	1078
7	(G3)-AZPGL-ipd	2679	2678
9	(G1)-AEPGL-ipd	492	492
10	(G2)-AEPGL-ipd	1212	1213
11	(G3)-AEPGL-ipd	2653	2655
12	(G0)-DANPGL-ipd	365	365
13	(G1)-DANPGL-ipd	724	724
14	(G2)-DANPGL-ipd	1444	1444
15	(G3)-DANPGL-ipd	2886	2886
16	(G0)-DANPGL-OH	347	347
17	(G1)-DANPGL-OH	644	644
18	(G2)-DANPGL-OH	1285	1285

sion maximum gets shifted towards lower energy as the polarity of the medium is increased. This implies that the dansyl moiety is considerably accessible to the bulk solvent in all generations of dendrons. Water being the most polar among all the solvents studied, the emission in water is expected to be the most red-shifted, which is noticed for (G0)-DANPGL-ipd (**12**) (G1)-DANPGL-ipd (**13**). But in case of (G2)-DANPGL-ipd (**14**) and (G3)-DANPGL-ipd (**15**) an unusual behaviour is observed. The emission maxima for (G2)-DANPGL-ipd (**14**) and (G3)-DANPGL-ipd (**15**) in aqueous medium show a hypso-chromic shift of around 60 nm as compared to that for (G0)-DANPGL-ipd (**12**) and (G1)-DANPGL-ipd (**13**). (G0)-DANPGL-ipd (**12**) and (G1)-DANPGL-ipd (**13**) exhibit weak fluorescence in water, whereas the fluorescence intensity increases remarkably for (G2)-DANPGL-ipd (**18**) and (G3)-DANPGL-ipd (**19**). The normalised emission spectra for all generations of dendrons in water and the plot of emission energy in cm^{-1} with generation number are represented in parts A and B of Figure 3. There is an abrupt change in the emission energy on going from (G1)-DANPGL-ipd (**13**) to (G2)-DANPGL-ipd (**14**) beyond which it remains constant for (G3)-DANPGL-ipd (**15**). This implies that, as the dendron bulk increases from (G1)-DANPGL-ipd (**13**) to (G2)-DANPGL-ipd (**14**) the dansyl moiety experiences a less polar micro-environment at the core in water, which gives an impression that there might be some sort of structural change taking place for higher generation dendrons in aqueous medium.

It is interesting to note that the steady state fluorescence anisotropy shows variation very similar to that of the emission energy with increasing generation number of the dendron (Figure 4). There is almost a ten-fold increase in the fluorescence anisotropy value on going from (G1)-DANPGL-ipd (**13**) to (G2)-DANPGL-ipd (**14**) and (G3)-DANPGL-ipd (**15**). Fluorescence anisotropy provides information about the rotational diffusibility of a fluorophore. The present study signifies that, the dansyl moiety experiences relatively more viscous and rigid microenvironment at the core in higher generation dendrons in aqueous medium. But studies based on polyether and PAMAM dendrimers have reported that the intrinsic viscosity passes through a maximum as the generation number increases.[22] If the microenvironment of dansyl is intrinsically viscous then the fluorescence anisotropy value should be high for

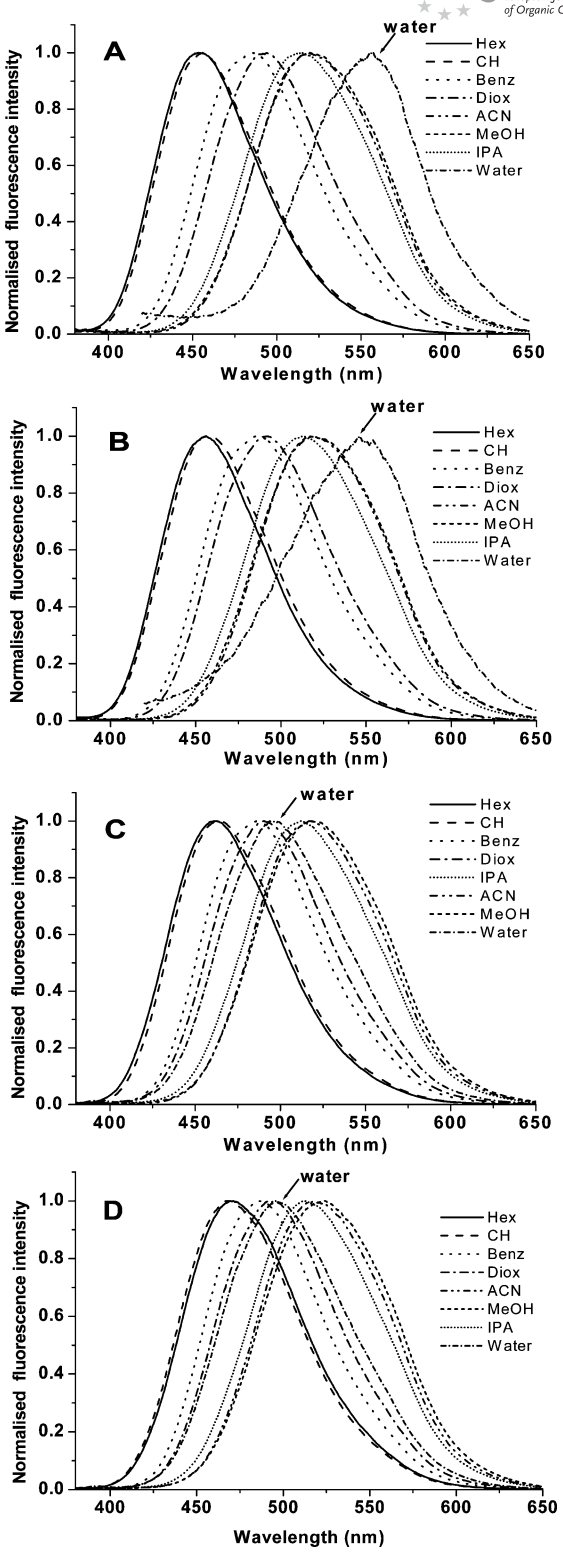


Figure 2. Normalised emission spectra of (A) (G0)-DANPGL-ipd, (B) (G1)-DANPGL-ipd, (C) (G2)-DANPGL-ipd and (D) (G3)-DANPGL-ipd in different solvents (hexane, cyclohexane, benzene, 1,4-dioxane, 2-propanol, acetonitrile, methanol and water).

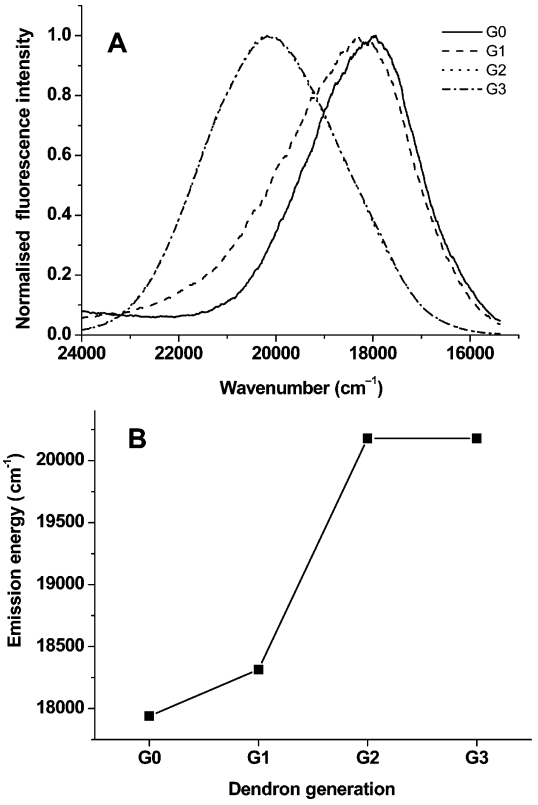


Figure 3. (A) Normalised emission spectra of (G0)-DANPGL-ipd, (G1)-DANPGL-ipd, (G2)-DANPGL-ipd and (G3)-DANPGL-ipd in water. (B) The plot of emission energy in cm^{-1} with generation number.

the higher generation dendrimers irrespective of the solvent. In order to verify this, fluorescence anisotropy was measured in various solvents and it was found that the unusual behaviour of anisotropy is seen only in the aqueous medium. In all other solvents the anisotropy values are very low and no significant difference was observed among the generations. The values in all the solvents are comparable to that observed for (G0)-DANPGL-ipd (**12**) and (G1)-DANPGL-ipd (**13**) in aqueous medium. This implies that the dansyl moiety experiences similar micro-viscosity in (G0)-DANPGL-ipd (**12**) and (G1)-DANPGL-ipd (**13**) irrespective of the solvent medium. The increased micro-viscosity at the core for higher order dendrons is specific to water as a solvent and not a general phenomenon. Thus the relatively higher value of anisotropy for (G2)-DANPGL-ipd (**14**) and (G3)-DANPGL-ipd (**15**) in water as compared to that in other solvents suggests the possible structural changes in higher order dendrons in aqueous medium. Earlier studies on polyether and PAMAM dendrimers have proposed a structural transition from an extended form to a globular form due to back folding as a result of the increased steric constraints in higher order dendrimers.[22] But this transition is known to be accompanied by a lowering of intrinsic viscosity of the dendrimer, hence such a transition is not likely to be happening in the present case. The other possibility is self-association of higher order dendrons. Previous studies on Newkome type dendrimers have shown aggregation of second and higher order dendrimers in aqueous medium even at nanomolar concentrations.[23,8] The polyglycerol dendrons in the present study have isopropylidene end groups, which are considerably hydrophobic and can be the driving force for the aggregation of dendrons in aqueous medium. In order to corroborate the above proposition, three generations of dansylated polyglycerol dendrons with hydroxy end groups were synthesised and the fluorescence studies were carried out. The two types of dendrons are similar in all respect except for the end groups, the later being hydrophilic because of the presence of hydroxy end-groups. The normalised emission spectra of the dendrons with hydroxy end groups (G0)-DANPGL-OH (**16**), (G1)-DANPGL-OH (**17**) and (G2)-DANPGL-OH (**18**) in water are represented in Figure 5. Unlike the dendrons with isopropylidene end groups, the dendrons with hydroxy end groups do not show any change in their emission energy with increased generation number. The emission maximum is found to be the same as that of (G0)-DANPGL-ipd (**12**) and (G1)-DANPGL-ipd (**13**) dendrons with isopropylidene end groups. The fluorescence anisotropy values for all the three generations are low and the values are comparable to that of the (G0)-DANPGL-ipd (**12**) and (G1)-DANPGL-ipd (**13**) of dendrons with isopro-

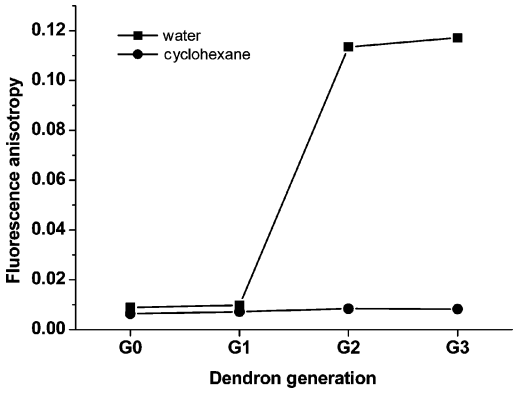


Figure 4. The plot of fluorescence anisotropy of (G0)-DANPGL-ipd, (G1)-DANPGL-ipd, (G2)-DANPGL-ipd and (G3)-DANPGL-ipd in water and cyclohexane with generation number.

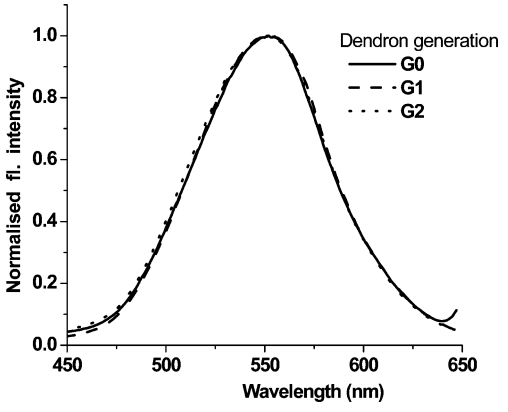


Figure 5. Normalised emission spectra of (G0)-DANPGL-OH, (G1)-DANPGL-OH and (G2)-DANPGL-OH in water.

pylidene end groups. This indicates that the dansyl moiety experiences similar microenvironment both in terms of polarity and micro-viscosity in all three generations of dendrons with hydroxy end groups in aqueous medium. Hence, this finding strongly supports the aggregation of higher generation dendrons with isopropylidene end groups in aqueous medium due to the hydrophobic nature of isopropylidene.

The fluorescence lifetimes were determined for all generations of dendrons in aqueous medium. (G0)-DANPGL-ipd (**12**) and (G1)-DANPGL-ipd (**13**) show monoexponential fluorescence decay, whereas (G2)-DANPGL-ipd (**14**), and (G3)-DANPGL-ipd (**15**) show biexponential decays. Table 2 summarises the fluorescence lifetimes for all generation dendrons in aqueous medium. The plot of average fluorescence lifetime with the generation number of the dendron is shown in Figure 6. There is almost a fourfold increase in the average lifetime from (G0)-DANPGL-ipd (**12**), (G1)-DANPGL-ipd (**13**) to (G2)-DANPGL-ipd (**14**). The biexponential nature of fluorescence decay and appearance of a long lifetime component in (G2)-DANPGL-ipd (**14**), and (G3)-DANPGL-ipd (**15**) is a clear indication of heterogeneity in the microenvironment of the dansyl moiety in these dendrons. The large amplitudes (>90%) associated with the longer lifetime component implies significant aggregation-induced shielding and motional restriction experienced by the fluorophore. This renders strong support towards the occurrence of aggregation of these dendrons in aqueous medium. Fluorescence quenching studies using a hydrophilic quencher can provide valuable information about the solvent accessibility of the fluorophore. In the present case fluorescence quenching studies were carried out using Ag^+ as a hydrophilic quencher for (G0)-DANPGL-ipd (**12**) and (G2)-DANPGL-ipd (**14**) in aqueous medium. The emission spectra of (G0)-DANPGL-ipd (**12**) and (G2)-DANPGL-ipd (**14**) at varying concentrations of Ag^+ (0–0.05 M) are represented in Figure 7 (A and B, respectively). As is evident from the spectra the fluorescence intensity in case of (G0)-DANPGL-ipd (**12**) shows a considerable decrease with increasing concentration of Ag^+ however the change in fluorescence intensity of (G2)-DANPGL-ipd (**14**) is almost insignificant even at the highest concentration of Ag^+ (0.05 M). In order to compare the quenching efficiencies in the above two cases Stern–Volmer plots were constructed by plotting $(F_0/F) - 1$ vs. the concentration of Ag^+ (Figure 8). The Stern–Volmer quenching constants (K_{sv}) were found to be 11.12 M^{-1} and 1.34 M^{-1} for

Table 2. Fluorescence lifetime data for all generations of dendrons in aqueous medium.

Dendron	τ_1 [ns]	a_1 [%]	τ_2 [ns]	a_2 [%]	τ_{avg}
(G0)-DANPGL-ipd	2.8				2.8
(G1)-DANPGL-ipd	4.1				4.1
(G2)-DANPGL-ipd	5.6	8	18.2	92	17.1
(G3)-DANPGL-ipd	5.7	6	19.0	94	18.1

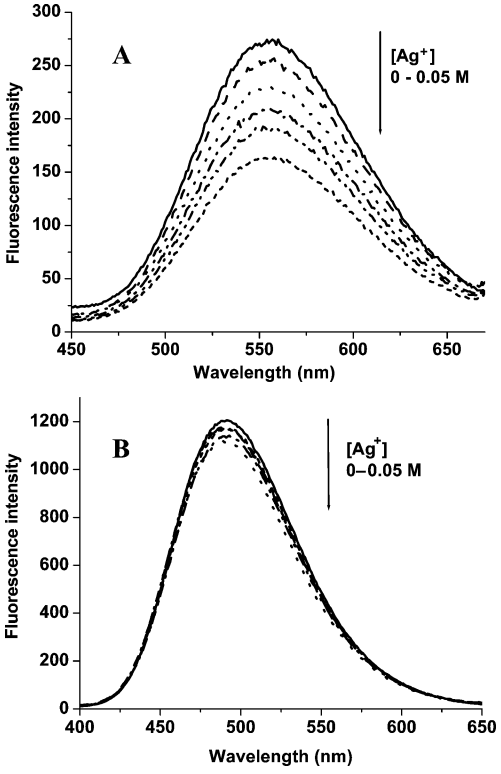


Figure 7. Emission spectra of (A) (G0)-DANPGL-ipd and (B) (G2)-DANPGL-ipd at varying concentrations of Ag^+ (0–0.05 M).

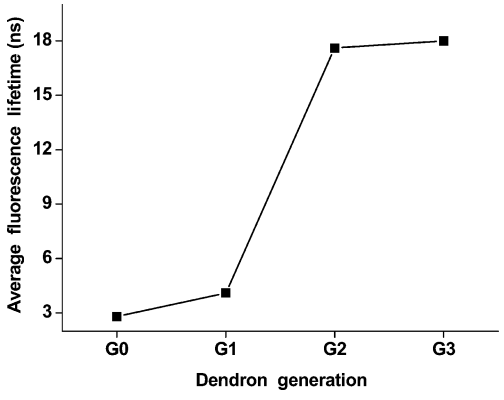


Figure 6. The plot of average fluorescence lifetime with the generation number of the dendron in aqueous medium.

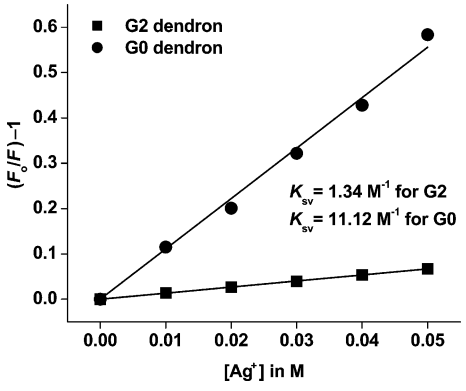


Figure 8. Stern–Volmer plot of $(F_0/F) - 1$ vs. the concentration of Ag^+ for (G0)-DANPGL-ipd and (G2)-DANPGL-ipd.

(G0)-DANPGL-ipd (**12**) and (G2)-DANPGL-ipd (**14**), respectively. This study clearly signifies that the dansyl moiety is easily accessible to the quencher in case of (G0)-DANPGL-ipd (**12**) but in (G2)-DANPGL-ipd (**14**) the dansyl moiety is well-shielded from the bulk water and the quencher. This further supports the fact that there is a hydrophobic aggregation taking place for higher generations of dendrons in aqueous medium.

The concentration of the experimental solution so far was at 1×10^{-5} M. In order to verify whether the aggregation is feasible at lower concentrations, fluorescence studies were carried out for all generations of dendrons at varying concentrations. The concentration was varied between 1×10^{-8} M to 5×10^{-5} M for all generations. The fluorescence emission spectra at varying concentrations for (G2)-DANPGL-ipd 14, and (G3)-DANPGL-ipd (**15**) in aqueous medium are shown in Figure 9 (A and B, respectively). For all generations of dendrons the emission energy remained independent of the concentration. The fluorescence anisotropy and average fluorescence lifetimes also remained almost constant and did not show any concentration dependence. This indicates that the aggregation of higher order dendrons is feasible even at very low concentrations (1×10^{-8} M) in aqueous medium. Similar behaviour has been observed for Newkome-type dendrimers.[23,8]

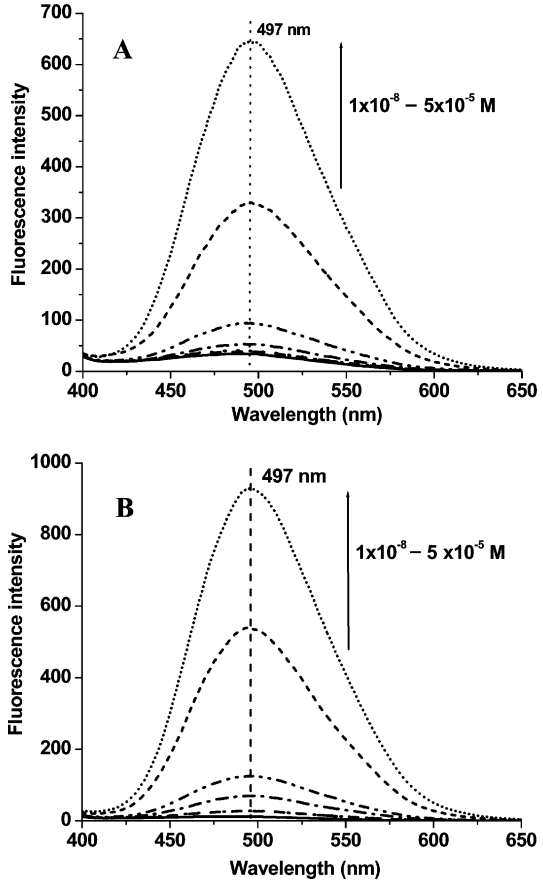


Figure 9. Fluorescence emission spectra at varying concentrations (1×10^{-8}–5×10^{-5} M) for (A) (G2)-DANPGL-ipd and (B) (G3)-DANPGL-ipd in aqueous medium.

Conclusions

In conclusion, we have presented the divergent synthesis of a glycerol-based polyether dendrons up to third generation. Photophysical investigation of the dendrons was carried out by using the fluorescence behavior of the dansyl moiety attached at the focal point of the dendrons. The fluorescence studies revealed the self-association behavior of dendrons from second generation onwards in aqueous medium even at concentrations as low as 1×10^{-8} M. There was a sudden increase in the fluorescence intensity accompanied by almost 60 nm hypsochromic shift in the emission maximum observed on going from the first generation to the second generation. The ten-fold increase in fluorescence anisotropy and fourfold increase in the average fluorescence lifetime clearly indicated the aggregation behavior of higher order dendrons in water. The absence of such behavior in the structurally similar but with hydroxy terminated glycerol-based polyether dendrons implied that the aggregation is due to the hydrophobic nature of the isopropylidene end groups. Quenching studies using a hydrophilic quencher Ag^+ illustrated that the dansyl moiety is significantly shielded from the surrounding in the second generation dendron, which rendered strong support to the proposed phenomenon.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-400 spectrometer operating at 400 and 100.6 MHz, respectively. The spectra were calibrated on the solvent peak ($CDCl_3$: δ = 7.26 ppm for ^{1}H and δ = 77.0 ppm for ^{13}C). Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F254 aluminium sheets (Merck 1.05554). Column chromatography was performed on silica gel (100–200 mesh). FT-IR spectra were recorded on a Nicolet-6700. High-resolution mass spectra were recorded with Q-TOF micromass spectrometer and MALDI-TOF analysis were carried out with Ultraflex Bruker Daltonics spectrometer. UV/Vis spectra were measured on a Perkin–Elmer Lambda 25 spectrophotometer. Fluorescence measurements were recorded on a Hitachi F-4500 spectrofluorimeter. The steady state fluorescence anisotropy (r_{ss}) values were obtained by using the expression

$$r_{ss} = (I_{\parallel} - GI_{\perp})/(I_{\parallel} + 2\,GI_{\perp})$$

where $I_{\parallel}$ and $I_{\perp}$ are fluorescence intensities when the emission polarizer is parallel and perpendicular, respectively to the direction of polarization of the excitation beam and G is the factor that corrects for unequal transmission by the diffraction gratings of the instrument for vertically and horizontally polarized light.

Fluorescence lifetime measurements were carried out using Horiba Jobin Yvon TCSPC lifetime instrument in a time-correlated single-photon counting arrangement. A 340 nm nanoLED was used as the light source. The pulse repetition rate was set to 1 MHz and the instrumental full width half maximum of the 340 nm LED, including the detector response is ca. 800 ps. The instrument response function was collected using a dilute solution of a scatterer (Ludox AS40 colloidal silica). The decay data were analyzed using IBH software. A value of χ^2, $0.99 \leq \chi^2 \leq 1.4$ was considered as a good fit, which was further judged by the symmetrical distribution of the

residuals. The average fluorescence lifetimes were calculated by using the formula

$$\tau_{avg} = (\sum_{i=1}^{n} a_i\tau_i)/(\sum_{i=1}^{n} a_i)$$

where τ_i is the individual lifetime with corresponding amplitude a_i.

The stock solutions (10^{-3} M) of the dendrimers were prepared in cyclohexane. The solutions in other solvents were prepared by evaporating cyclohexane from the desired amount of the stock by gentle purging of nitrogen gas and then sonicating it with the solvent of interest. All the solvents used were of UV-spectroscopic grade and used without further purification. The water used was distilled three times after addition of alkaline permanganate. For the quenching studies appropriate volume of freshly prepared $AgNO_3$ stock solution in water was added to the aqueous solution of dendrimer, the solution was shaken and the spectrum was collected immediately. 1,5-dibromopentane and Dowex® 50WX8-100 were purchased from Aldrich Chemicals and all other chemicals were purchased from Merck (India) Ltd., Mumbai, India.

General Procedure for the *O*-Alkylation of Hydroxy Groups: 4-[5-(Bromopentyloxy)methyl]-2,2-dimethyl-1,3-dioxalane (**1**) (1.5–3 equiv. per OH group) was added to a solution of the alcohol and TBAB (15–50 mol-%) as phase-transfer catalyst in aqueous NaOH (2 g, per OH group, per 1 mmol). The reaction mixture was stirred at 60 °C for 12–48 h. Progress of the reaction was monitored by TLC. After completion, the crude was washed with EtOAc, water and brine. After drying with anhydrous Na_2SO_4 and removal of solvent under reduced pressure, the crude mixture was purified by column chromatography on silica gel.

(G1)-AZPGL-ipd (3): Reaction conditions and workup were as described above, 3-azidopropane-1,2-diol (**2**) (4.1 g, 35 mmol) and sodium hydroxide (140 g, 3500 mmol) in 105 mL distilled water, 4-[(5-bromopentyloxy)methyl]-2,2-dimethyl-1,3-dioxolane (**1**) (29.4 g, 105 mmol) 70 mL of THF and TBAB (1.69 g, 5.25 mmol, 15 mol-%). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate, 8:2) and (G1)-AZPGL-ipd (**3**) recovered as a colorless oil (17.15 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.23 (m, 2 H), 4.02 (m, 2 H), 3.70 (m, 2 H), 3.50–3.39 (br. m, 17 H), 1.61–1.51 (m, 8 H), 1.39 (s, 6 H, CH_3), 1.38–1.37 (m, 4 H), 1.33 (s, 6 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 109.2, 77.8, 74.7, 71.8, 71.6, 71.5, 70.3, 70.0, 66.8, 51.9, 29.7, 29.3 (2×), 26.7, 25.3, 22.6, 22.5 ppm. IR: $\tilde{\nu}$ = 2985, 2936, 2862, 2097, 1455, 1370, 1255, 1212, 1110, 1052, 975, 845, 792, 699, 557 cm^{-1}. HRMS calcd. for $C_{25}H_{47}N_3O_8$ $[M + Na]^+$ 540.3261; found 540.3261.

(G2)-AZPGL-ipd (5): Reaction conditions and workup were as described above, (G1)-AZPGL-OH (**4**) (1.75 g, 4 mmol) and sodium hydroxide (32 g, 800 mmol) in 24 mL of distilled water, 4-[(5-bromopentyloxy)methyl]-2,2-dimethyl-1,3-dioxolane (**1**) (13.44 g, 48 mmol) 16 mL of THF and TBAB (0.387 g, 1.2 mmol, 30 mol-%). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate, 6:4) and (G2)-AZPGL-ipd (**5**) recovered as a colorless oil (4.55 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.24 (m, 4 H), 4.04 (m, 4 H), 3.71 (m, 4 H), 3.56–3.38 (br. m, 47 H), 1.60–1.53 (m, 24 H), 1.41 (s, 12 H, CH_3), 1.38–1.37 (m, 12 H), 1.35 (s, 12 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 109.5, 77.8, 74.7, 71.8, 71.7, 71.6, 71.4, 70.8, 70.4, 70.3, 69.9, 66.9, 52.1, 29.8, 29.4, 29.3, 26.7, 25.4, 22.6, 22.5 ppm. IR: $\tilde{\nu}$ = 2985, 2935, 2860, 2098, 1456, 1370, 1255, 1213, 1109, 1052, 975, 844, 512 cm^{-1}. (MALDI-TOF): *m*/*z* calcd. for $C_{63}H_{119}N_3O_{20}$ 1237.839; found 1260.821 $[M + Na]^+$.

(G3)-AZPGL-ipd (7): Reaction conditions and workup were as described above, (G2)-AZPGL-OH (**6**) (1.08 g, 1 mmol) and sodium hydroxide (16.0 g, 400 mmol) in 12 mL of distilled water, 4-[(5-bromopentyloxy)methyl]-2,2-dimethyl-1,3-dioxolane (**1**) (6.720 g, 24 mmol) in 8 mL of THF and TBAB (0.161 g, 0.5 mmol, 50 mol-%). Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate, 4:6) and (G3)-AZPGL-ipd (**7**) recovered as a colorless oil (1.98 g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.24 (m, 8 H), 4.04 (m, 8 H), 3.71 (m, 8 H), 3.56–3.38 (br. m, 107 H), 1.60–1.53 (m, 56 H), 1.41 (s, 24 H, CH_3), 1.38–1.37 (m, 28 H), 1.35 (s, 24 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 109.3, 77.9, 76.7, 74.7, 71.8, 71.7, 71.5, 71.4, 70.9, 70.8, 70.4, 70.3, 66.9, 52.2, 29.9, 29.8, 29.5, 29.4, 29.3, 26.7, 25.4, 22.6 (2×) ppm. IR: $\tilde{\nu}$ = 2983, 2937, 2861, 2099, 1458, 1370, 1254, 1213, 1108, 1052, 844, 791, 513 cm^{-1}. (MALDI-TOF): *m*/*z* calcd. for $C_{139}H_{263}N_3O_{44}$ 2678.843; found 2677.587.

General Procedure for the Deprotection of the Isopropylidene Groups: Dowex (30 wt.-%) was added to methanol solution of the protected dendrons and the mixture was stirred at 100 °C for 2 h under open atmosphere. The reaction was monitored by TLC by using MeOH and EtOAc as solvent system (5–20%). The crude product was filtered and the clear methanol solution was concentrated under vacuum.

(G1)-AZPGL-OH (4): Reaction conditions and workup were as described above, (G1)-AZPGL-ipd (**3**) (3.0 g, 5.8 mmol) in 40 mL of methanol, 0.900 g of Dowex (30 wt.-%) resin. (G1)-AZPGL-OH (**4**) obtained as colorless viscous oil in quantitative yield. The product was used for the next reactions without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.84 (m, 2 H), 3.70–3.30 (br. m, 21 H), 1.61–1.53 (m, 8 H), 1.45–1.35 (m, 4 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 78.0, 72.4, 71.5, 70.6, 70.3, 70.2, 64.1, 52.0, 29.7, 29.4, 29.3, 22.8, 22.7 ppm. IR: $\tilde{\nu}$ = 3373, 2936, 2862, 2097, 1456, 1277, 1106, 1041, 930, 735, 553 cm^{-1}. HRMS calcd. for $C_{19}H_{39}N_3O_8$ $[M + Na]^+$ 460.2635; found 460.2643.

(G2)-AZPGL-OH (6): Reaction conditions and workup were as described above, (G2)-AZPGL-ipd (**9**) (2.0 g, 1.62 mmol), 30 mL of methanol, 0.600 g of Dowex-50 resin (30 wt.-%). (G2)-AZPGL-OH (**6**) obtained as colorless viscous oil in quantitative yield. The product was used for the next reactions without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.83 (m, 4 H), 3.68–3.41 (br. m, 55 H), 1.60–1.53 (m, 24 H), 1.43–1.37 (m, 12 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 77.9, 72.2, 71.5 (2×), 71.3, 71.0, 70.7 (2×), 70.4, 70.2, 70.0, 64.0, 51.9, 29.7 (2×), 29.3 (2×), 29.2, 22.7, 22.6 ppm. IR: $\tilde{\nu}$ = 3414, 2933, 2861, 2093, 1457, 1270, 1105, 928, 733, 700, 669 cm^{-1}. HRMS calcd. for $C_{51}H_{103}N_3O_{20}$ $[M + Na]^+$ 1100.7033; found 1100.7034.

General Procedure for the Reduction of the Azide Dendrons: 10% Pd-C was added to ethanol solution of the protected dendrons and the mixture was stirred around room temperature for 2–48 h under hydrogen atmosphere. The reaction was monitored by TLC. After completion, the reaction mixture was filtered through whatman filter paper, washed with ethanol and concentrated under vacuum.

(G1)-AEPGL-ipd (9): Reaction conditions and workup were as described above, (G1)-AZPGL-ipd (**3**) (0.589 g, 1.14 mmol) in 12 mL of ethanol, stirred for 2 h. (G1)-AEPGL-ipd (**9**) was recovered as colorless oil (0.550 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.21 (m, 2 H), 4.01 (m, 2 H), 3.68 (m, 2 H), 3.46–3.35 (br. m, 17 H), 2.69 (br. s, 2 H, NH_2), 1.59–1.51 (m, 8 H), 1.38 (s, 6 H, CH_3), 1.35–1.33 (m, 4 H), 1.32 (s, 6 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 109.3, 79.9, 74.7, 71.8, 71.6, 71.4, 71.1, 70.0, 66.8, 43.4, 29.9, 29.4, 29.3, 26.7, 25.3, 22.6 (2×) ppm. IR: $\tilde{\nu}$ = 2985, 2935, 2861, 1456, 1370, 1254, 1212, 1108, 1052, 974, 843, 791, 735, 514 cm^{-1}. HRMS calcd. for $C_{25}H_{50}NO_8$ 492.3536; found 492.3531.

(G2)-AEPGL-ipd (10): Reaction conditions and workup were as described above, (G2)-AZPGL-ipd (**5**) (0.52 g, 0.42 mmol) in 10 mL ethanol, stirred for 12 h. (G2)-AEPGL-ipd (**10**) was recovered as colorless oil (0.5 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.24 (m, 4 H), 4.04 (m, 4 H), 3.71 (m, 4 H), 3.55–3.40 (br. m, 47 H), 2.77 (br. s, 2 H, NH_2), 1.62–1.53 (m, 24 H), 1.41 (s, 12 H, CH_3), 1.38–1.36 (m, 12 H), 1.35 (s, 12 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 109.3, 77.9, 74.7, 71.8, 71.7, 71.6, 71.4, 70.8, 70.3, 43.8, 29.8, 29.4, 29.3, 26.7, 25.4, 22.6, 22.5 ppm. IR: $\tilde{\nu}$ = 2983, 2934, 2860, 1456, 1370, 1255, 1212, 1114, 1054, 846 cm^{-1}. (MALDI-TOF): *m*/*z* calcd. for $C_{63}H_{121}NO_{20}$ 1211.848; found 1241.248 $[M + Na]^+$.

(G3)-AEPGL-ipd (11): Reaction conditions and workup were as described above, (G3)-AZPGL-ipd (**15**) (0.214 g, 0.08 mmol) in 4 mL ethanol, stirred for 48 h. (G3)-AEPGL-ipd (**11**) was recovered as colorless oil (0.201 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.21 (m, 8 H), 4.00 (m, 8 H), 3.50 (m, 8 H), 3.49–3.38 (br. m, 107 H), 2.51 (br. s, 2 H, NH_2), 1.57–1.50 (m, 56 H), 1.38 (s, 24 H, CH_3), 1.36–1.34 (m, 28 H), 1.32 (s, 24 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 109.2, 77.8, 74.7, 71.8, 71.6, 71.4, 71.3, 70.8, 70.3, 66.8, 47.8, 29.8, 29.4, 29.3, 26.7, 25.3, 22.6, 22.5 ppm. IR: $\tilde{\nu}$ = 2984, 2935, 2860, 1456, 1370, 1253, 1212, 1109, 1052, 974, 843 cm^{-1}. (MALDI-TOF): *m*/*z* calcd. for $C_{139}H_{265}NO_{44}$ 2652.853; found 2695.899 $[M + Na]^+ + H_2O$.

General Procedure for the Dansylation of the Amine Dendrons: To a solution of the amine dendrons in dry DCM, added Et_3N (50–400 μL) and 5-(dimethylamino)naphthalene-1-sulfonyl chloride (0.07–1.9 mmol). The reaction mixture was stirred around room temperature for 1–4 h. Progress of the reaction was monitored by TLC. After completion of the reaction, removed excess Et_3N under high vacuum and washed with EtoAc and removal of solvent under reduced pressure, the crude mixture was purified by column chromatography on silica gel.

(G0)-DANPGL-ipd (12): Reaction conditions and workup were as described above, (G0)-AEPGL-ipd (**8**) (0.249 g, 1.9 mmol) in 5 mL dry DCM, (400 μL, 2.87 mmol) Et_3N and 5-(dimethylamino)naphthalene-1-sulfonyl chloride (0.512 g, 1.9 mmol) for 1 h. Purification by column chromatography (*n*-hexane/ethyl acetate, 9.8:0.2), (G0)-DANPGL-ipd (**12**) was recovered as viscous oil in green fluorescent color (0.146 g, 21%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.54 (d, *J* = 8.4 Hz, 1 H), 8.27 (d, *J* = 8.4 Hz, 1 H), 8.24–8.22 (m, 1 H), 7.58–7.51 (m, 2 H), 7.18 (d, *J* = 7.2 Hz, 1 H), 5.11 (br. s, 1 H, NH), 4.10 (m, 1 H), 3.89 (dd, *J* = 6.8, 8.8 Hz, 1 H), 3.57 (dd, *J* = 6, 8.8 Hz, 1 H), 3.10–3.04 (m, 1 H), 2.87 (s, 6 H), 1.21 (s, 6 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 152.0, 134.2, 130.6, 129.8, 129.6, 129.5, 128.5, 123.1, 118.5, 115.2, 109.5, 73.8, 66.4, 45.4 (2×), 26.6, 25.0 ppm. IR: $\tilde{\nu}$ = 3286, 2984, 2938, 2874, 2788, 1588, 1574, 1504, 1478, 1455, 1407, 1371, 1323, 1203, 1144, 1072, 973, 945, 825, 789, 735, 683, 624, 571, 539, 516 cm^{-1}. HRMS calcd. for $C_{18}H_{24}N_2O_4S$ 365.1535; found 365.1545.

(G1)-DANPGL-ipd (13): Reaction conditions and workup were as described above, (G1)-AEPGL-ipd (**9**) (0.453 g, 0.92 mmol) in 4 mL dry DCM, (200 μL, 1.44 mmol) Et_3N and 5-(dimethylamino)-naphthalene-1-sulfonyl chloride (0.270 g, 1 mmol) for 1 h. Purification by column chromatography (*n*-hexane/ethyl acetate, 8:2) (G1)-DANPGL-ipd (**13**) was recovered as viscous oil in green fluorescent color (0.200 g, 30%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.50 (d, *J* = 8.4 Hz, 1 H), 8.24 (d, *J* = 8.8 Hz, 1 H), 8.21 (d, *J* = 7.2 Hz, 1 H), 7.54–7.45 (m, 2 H), 7.14 (d, *J* = 7.2 Hz, 1 H), 5.19 (br. s, 1 H, NH), 4.22 (m, 2 H), 4.01 (m, 2 H), 3.69 (m, 2 H), 3.46–3.20 (br. m, 17 H), 2.84 (s, 3 H), 2.83 (s, 3 H), 1.56–1.40 (m, 8 H), 1.38 (s, 6 H, CH_3), 1.32 (s, 6 H, CH_3), 1.30–1.22 (m, 4 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 152.0, 134.7, 130.3, 129.9, 129.6, 129.5, 128.3, 123.1, 118.7, 115.1, 109.3, 76.1, 74.7, 71.8, 71.6, 71.5, 71.4, 70.5, 69.8, 66.8, 45.4, 44.5, 29.6, 29.2, 26.7, 25.4, 22.5 (2×) ppm. IR: $\tilde{\nu}$ = 2985, 2932, 2859, 1456, 1370, 1254, 1213, 1110, 1052, 975, 843, 791, 735 cm^{-1}. HRMS: calcd. for $C_{37}H_{60}N_2O_{10}S$ $[M + Na]^+$ 747.3866; found 747.3876.

(G2)-DANPGL-ipd (14): Reaction conditions and workup were as described above, (G2)-AEPGL-ipd **10** (0.412 g, 0.34 mmol) in 8 mL dry DCM, (100 μL, 0.72 mol) Et_3N and 5-(dimethylamino)naphthalene-1-sulfonyl chloride (0.092 g, 0.34 mmol) for 3 h. Purification by column chromatography (*n*-hexane/ethyl acetate, 6:4) (G2)-DANPGL-ipd (**14**) was recovered as viscous oil in fluorescent green color (0.476 g, 97%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.46 (d, *J* = 8.4 Hz, 1 H), 8.23 (d, *J* = 8.4 Hz, 1 H), 8.13 (d, *J* = 7.6 Hz, 1 H), 7.49–7.44 (m, 2 H), 7.11 (d, *J* = 7.6 Hz, 1 H), 4.19 (m, 4 H), 3.99 (m, 4 H), 3.65 (m, 4 H), 3.50–3.33 (br. m, 47 H), 2.82 (s, 3 H), 2.81 (s, 3 H), 1.55–1.50 (m, 24 H), 1.35 (s, 12 H, CH_3), 1.32 (m, 12 H), 1.29 (s, 12 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 151.5, 135.4, 130.0 (2×), 129.9, 129.3, 127.7, 122.9, 119.5, 114.9, 109.0, 77.8, 74.6, 71.7, 71.5, 71.3, 70.7, 70.2, 66.7, 45.2, 43.4, 29.7, 29.2, 26.6, 25.3, 22.5, 22.4 ppm. IR: $\tilde{\nu}$ = 2985, 2935, 2860, 1456, 1370, 1328, 1256, 1212, 1109, 1052, 843, 792, 734, 623 cm^{-1}. (MALDI-TOF): *m*/*z* calcd. for $C_{75}H_{132}N_2O_{22}S$ 1444.899; found 1495.788 $[M + 3Na]^+ - H_2O$.

(G3)-DANPGL-ipd (15): Reaction conditions and workup were as described above, (G3)-AEPGL-ipd (**11**) (0.186 g, 0.07 mmol) in 4 mL dry DCM, (50 μL, 0.36 mmol) Et_3N and 5-(dimethylamino)-naphthalene-1-sulfonyl chloride (0.019 g, 0.07 mmol) for 4 h. Purification by column chromatography (*n*-hexane/ethyl acetate, 4:6), (G3)-DANPGL-ipd (**15**) was recovered as viscous oil in fluorescent green color (0.194 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.51 (d, *J* = 7.2 Hz, 1 H), 8.29 (d, *J* = 8.0 Hz, 1 H), 8.23–8.16 (m, 1 H), 7.54–7.47 (m, 2 H), 7.16 (d, *J* = 6.8 Hz, 1 H), 4.24 (m, 8 H), 4.04 (m, 8 H), 3.71 (m, 8 H), 3.55–3.41 (br. m, 107 H), 1.58–1.55 (m, 56 H), 1.41 (s, 24 H, CH_3), 1.37 (m, 28 H), 1.35 (s, 24 H, CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ = 152.0, 130.3, 130.0, 129.9, 129.6, 129.5, 128.3, 123.1, 118.7, 115.1, 109.3, 77.9, 74.7, 71.8, 71.6, 71.4, 70.8, 70.5, 70.3, 69.9, 66.9, 45.4, 44.5, 29.8, 29.6, 29.4 (2×), 29.3 (2×), 26.7, 25.4, 22.6, 22.5 ppm. IR: $\tilde{\nu}$ = 2985, 2934, 2858, 1456, 1370, 1329, 1255, 1213, 1110, 1052, 975, 843 cm^{-1}. (MALDI-TOF): *m*/*z* calcd. for $C_{151}H_{276}N_2O_{46}S$ 2885.904; found 2936.986 $[M + 3Na]^+ - H_2O$.

General Procedure for the Deprotection of Isopropylidene Groups of the Dansylated Dendrons: Dowex (30 wt.-%) was added to methanol solution of the protected dansylated dendrons and the mixture was stirred at 100 °C for 2 h under open atmosphere. The reaction was monitored by TLC by using MeOH and EtOAc as solvent system (5–20%). The crude product was filtered and the clear methanol solution was concentrated under vacuum.

(G0)-DANPGL-OH (16): Reaction conditions and workup were as described above, (G0)-DANPGL-ipd (**12**) (0.100 g, 0.27 mmol), 2 mL of methanol, 0.030 g of Dowex-50 resin (30 wt.-%). (G0)-DANPGL-OH (**16**) was obtained as viscous oil in green fluorescent color in quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.47 (d, *J* = 8.4 Hz, 1 H), 8.26 (d, *J* = 8.8 Hz, 1 H), 8.15 (d, *J* = 7.2 Hz, 1 H), 7.42 (m, 2 H), 7.08 (d, *J* = 7.6 Hz, 1 H), 6.29 (br. s, 1 H, NH) 3.80 (m, 1 H), 3.58–3.47 (m, 2 H), 2.99–2.85 (m, 2 H), 2.83 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.8, 134.4, 130.5, 129.8, 129.5, 129.3, 128.5, 123.2, 118.8, 115.3, 70.7, 63.9, 45.4 (2×) ppm. IR: $\tilde{\nu}$ = 3280, 1588, 1573, 1473, 1454, 1406, 1354, 1309, 1215, 1202, 1160, 1141, 1102, 1060, 944, 841, 789, 747, 665,

682, 623 cm^{-1}. HRMS $C_{15}H_{20}N_2O_4S$ $[M + Na]^+$ 347.1041; found 347.1040.

(G1)-DANPGL-OH (17): Reaction conditions and workup were as described above, (G1)-DANPGL-ipd (**13**) (0.200 g, 0.28 mmol), 4 mL of methanol, 0.060 g of Dowex-50 resin (30 wt.-%). (G1)-DANPGL-OH (**17**) obtained as viscous oil in green fluorescent color in quantitative yield. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.52 (d, J = 8.4 Hz, 1 H), 8.28 (d, J = 8.4 Hz, 1 H), 8.22 (d, J = 7.2 Hz, 1 H), 7.57–7.49 (m, 2 H), 7.17 (d, J = 7.2 Hz, 1 H), 5.59 (br. s, 1 H, NH), 3.84 (m, 2 H), 3.67–3.08 (br. m, 21 H), 2.87 (s, 6 H), 1.56–1.30 (br. m, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.9, 134.7, 130.3, 129.8, 129.6, 129.4, 128.3, 123.1, 118.8, 115.1, 76.3, 72.3 (3×), 71.4, 71.3, 70.6 (2×), 70.5, 69.7, 64.1, 45.4, 45.3, 44.3, 29.3 (2×), 29.1 (2×), 29.0 (2×), 22.6, 22.5 ppm. IR: $\tilde{\nu}$ = 3373, 2936, 2865, 1736, 1575, 1456, 1395, 1373, 1356, 1323, 1214, 1201, 1093, 1043, 919, 791, 732, 683 cm^{-1}. HRMS calcd. for $C_{31}H_{52}N_2O_{10}S$ $[M + Na]^+$ 667.3240; found 667.3240.

(G2)-DANPGL-OH (18): Reaction conditions and workup were as described above, (G2)-DANPGL-ipd (**14**) (0.160 g, 0.11 mmol), 4 mL of methanol, 0.048 g of Dowex-50 resin (30 wt.-%). (G2)-DANPGL-OH (**18**) obtained as viscous oil in green fluorescent color in quantitative yield. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.48 (d, J = 8.4 Hz, 1 H), 8.23 (d, J = 8.4 Hz, 1 H), 8.14 (d, J = 6.8 Hz, 1 H), 7.54–7.45 (m, 2 H), 7.13 (d, J = 7.6 Hz, 1 H), 3.82–3.61 (m, 4 H), 3.54–3.21 (br. m, 55 H), 2.84 (s, 3 H), 2.83 (s, 3 H), 1.54–1.46 (m, 24 H), 1.427–1.29 (m, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.5, 135.2, 130.1, 130.0, 129.8, 129.4, 127.9, 123.0, 119.5, 115.0, 77.7, 72.0, 71.4, 71.2, 70.9 (2×), 70.6, 70.4, 70.2, 63.8, 45.3, 43.4, 29.6, 29.3, 29.2, 29.1, 22.6, 22.5 ppm. IR: $\tilde{\nu}$ = 3372, 2935, 2865, 1737, 1395, 1372, 1322, 1241, 1201, 1093, 1043, 918, 790, 734 cm^{-1}. (MALDI-TOF): m/z calcd. for $C_{63}H_{116}N_2O_{22}S$ 1284.774; found 1335.696 $[M + 3 Na]^+ - H_2O$.

Supporting Information (see also the footnote on the first page of this article): ^1H, ^{13}C NMR spectra of all the dendrons, HSQC spectra of **3**, DEPT spectra of **3**, **12** and HRMS/MALDI of all the dendrons.

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