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Synthesis and characterization of chiral azobenzene dye functionalized Janus dendrimers

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ABSTRACT

Eight bischromophoric bisMPA based polyester Janus dendrimers emanating from a pentaerythritol core were synthesized and their properties evaluated. 4-((4-(Ethyl(2-(2-(6-methoxynaphthalen-2-yl)propanoyloxy)ethyl)amino)-phenyl)diazenyl)-benzoic acid and 4-((4-(ethyl(2-(2-(6-methoxynaphthalen-2-yl)propanoyloxy)-ethyl)-amino)phenyl)diazenyl)-3-nitrobenzoic acid were attached to the dendritic polyester skeleton to make chiral dendrimers up to the second generation. The structures and the purity of the molecules were verified with ^{1}H NMR, ^{13}C NMR, ESI TOF mass spectrometry, and elemental analysis. Spectral properties were evaluated with UV–vis and CD spectrometer. The compounds displayed broad absorption maxima in the visible region. The CD spectra confirmed the optical purity of the compounds. The thermal properties were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

1. Introduction

Dendrimers and dendrons are highly branched globular macromolecules with precise structures, prepared through iterative synthesis.[1] Dendrimers consist of three distinct components: at least a bivalent core, layers of branching AB_x monomers (generations), and terminal groups, which are primarily responsible for the properties of dendrimers. Two common synthetic methods, divergent[2] and convergent[3] growth approaches, have been utilized to control the shape, size, and properties of dendrimers. In the divergent approach dendrimers are constructed from the core to the periphery generation by generation. Conversely, in the convergent method, dendrimers are built from periphery to the core, initially preparing dendrons, which are then attached to the core to obtain dendrimers with appropriate size. Due to the structural features providing the versatile properties of the dendritic molecules, they have been widely applied in applications such as light-harvesting systems,[4] drug delivery,[5] and catalysis.[6]

High synthetic control over the structures of dendrimers is a crucial factor that allows one to synthesize dendrimers with diverse (multi)functionalities. Two-faced Janus-type dendrimers, characterized by the differences in the opposite peripheral groups have recently been synthesized.[7] The preparation of Janus dendrimers has generally been performed either by attaching two differently functionalized dendrons covalently together as first described by Fréchet et al.,[8] or constructing molecules from orthogonally protected building blocks,[9] utilizing convenient dendrimer synthetic methods. By choosing appropriate, functionally different end groups, it is possible to control, for example, the solubility[9] or self-assembly[7a,c] of dendrimers.

Azobenzenes are well known synthetic dyes[10] utilized in several applications due to their interesting properties such as the reversible cis–trans photoisomerization about the azo bond when irradiated.[11] Since the first azobenzene dendrimers,[12] several studies concerning synthesis and properties of azobenzene dendrimers and dendrons have been published.[13,14] Our interest was to build up Janus-type dendrimers having possible non-linear optical (NLO) properties arising from the non-centrosymmetric structure of the chiral azobenzene conjugates.[15]

Herein we report the synthesis of bisfunctionalized Janus-type polyester dendrimers, which consist of a polar hydroxyl functionalized end, and a photoactive end constructed from donor–acceptor azobenzenes and chiral naproxen units.

2. Results and discussion

2.1. Synthesis

The synthetic procedure of the chromophore functionalized Janus-type dendrimers involves several iterative protection–deprotection steps of orthogonally protected building blocks. Branching was achieved by the divergent method through esterification of the anhydride of isopropylidene-2,2-bis(methoxy)-propionic acid (bisMPA),[16] affording aliphatic polyester skeleton

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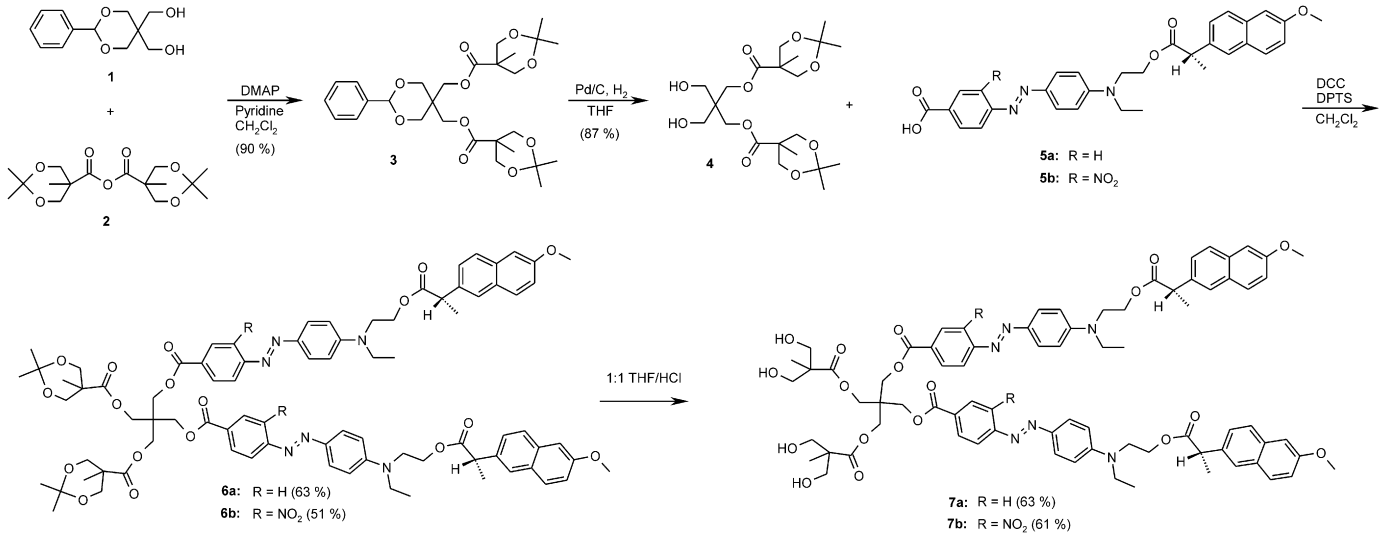
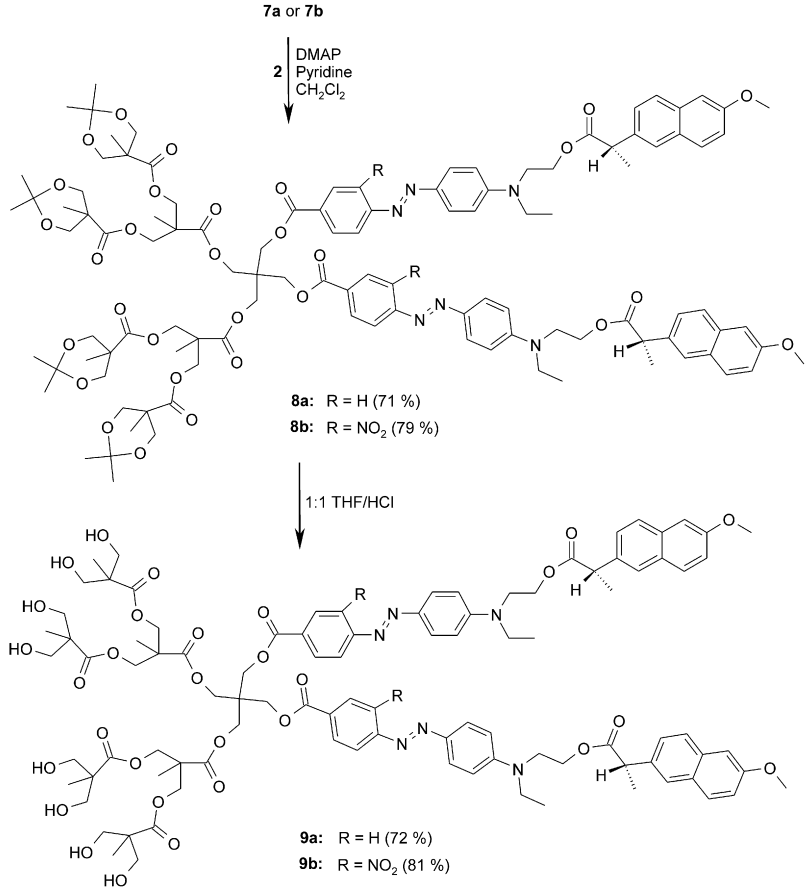


Scheme 1. Synthesis of the first generation dendrimers.

emanating from pentaerythritol core. Azobenzene compounds were chosen as electron donor–acceptor chromophores, since they possess NLO properties.[17] The preparation of chiral azobenzene–naproxen conjugates **5a** and **5b** is reported elsewhere.[15]

The synthesis of the first generation dendrimers is shown in Scheme 1. First, monobenzalpentaerythritol **1** was synthesized by the procedure described by Issidorides and Gulen.[18] Orthogonally protected first generation dendritic core **3** was obtained by the divergent synthesis of **1** with the anhydride **2** in the presence of DMAP and pyridine in dichloromethane. Instead of utilizing *N*,*N*-dicyclohexyl carbodiimide (DCC) coupling of bisMPA,[19] we chose the anhydride of bisMPA as a building block since it affords a simpler working procedure and easier purification over DCC coupling.[16] The purification of the molecule was done by diluting the crude product in DCM followed by extraction with 10% $NaHSO_4$, 10% Na_2CO_3, and brine. Finally, crystallization from hexane–ethyl acetate solution gave **3** in 90% yield with high purity. The activation of the focal point was done by the removal of benzylidene acetal by



Scheme 2. Synthesis of the second generation dendrimers.

catalytic hydrogenolysis described by Ropponen et al.[7b] giving compound **4**.

The synthesis of the compound **6a** was carried out in dichloromethane utilizing the DCC coupling between intermediate **4** and azobenzene–naproxen derivate **5a** in the presence of 4-(dimethyl amino)pyridinium *p*-toluenesulfonate (DPTS)[20] as catalyst. The protected first generation dendrimer **6a** was obtained after column chromatography in 63% yield. Similarly, the reaction of **4** with **5b** gave compound **6b** in 51% yield after column chromatography. The acetonide protecting groups of the compounds **6a** and **6b** were removed by stirring in 1:1 HCl–THF solutions. After neutralization of the solution, THF was evaporated off and the solid filtered to obtain hydroxyl functionalized G1-dendrimers **7a** and **7b** in 63 and 61% yields, respectively.

The protected second generation dendrimers **8a** and **8b** were synthesized divergently by the anhydride coupling of **2** with the dendrimers **7a** and **7b** in the presence of DMAP and pyridine in DCM (Scheme 2). Dendrimer **8a** was obtained in 43% yield after isolation by column chromatography. However, ^{1}H NMR spectroscopic studies of other fractions from column chromatography revealed incomplete dendrimers with one branch missing. These molecules were further reacted in the anhydride coupling, thus, increasing the total yield of the compound **8a** to 71%, after chromatography. Compound **8b** was obtained in 79% yield after chromatography. The subsequent removal of the acetonide groups of **8a** in 1:1 2 M HCl–THF and **8b** in 1:1 3 M HCl–THF solutions gave the second generation dendrimers **9a** in 72 and **9b** in 81% yields, respectively.

2.2. UV–vis and CD data

The absorption spectra of the molecules were measured in chloroform (Table 1). All compounds showed an intense absorption band in a visible region related to the $\pi \rightarrow \pi^*$ transition of azobenzene moiety. Absorption maxima for compounds **6a**–**9a** were 441–443 nm and 483–484 nm for compounds **6b**–**9b**. Significant bathochromic shift of the compounds **6b**–**9b** over compounds **6a**–**9a** is due to the enhanced delocalization of electrons caused by addition of the strong electron withdrawing nitro group. Monochromophores **5a** and **5b** absorbed at 433 and 474 nm, respectively, thus showing a blue shift of about 10 nm in comparison to dendrimers.

Circular dichroism (CD) spectra of compounds **6a**–**9b** were measured to confirm the chirality of the molecules (Fig. 1). Compounds displayed similar CD absorption spectra to their monochromophore analogues **5a** and **5b**.[15] All compounds showed negative CD signals at the absorption maxima at around 450 and 500 nm.

2.3. TGA and DSC studies

The compounds were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to evaluate their thermal properties. The results from these studies are shown in Figure 2 and Table 2. Ropponen et al. have previously studied the thermal behavior of aliphatic polyester dendrimers[21] as well as bile acid functionalized polyester dendrons.[22]

Table 1
Absorption data of the dendrimers

Compound	λ_{max} (nm)	ε_{max} ($cm^{-1}\,M^{-1}$)	Compound	λ_{max} (nm)	ε_{max} ($cm^{-1}\,M^{-1}$)
6a	442	49,300	**6b**	483	74,800
7a	441	53,300	**7b**	484	69,000
8a	443	52,100	**8b**	483	66,700
9a	443	54,600	**9b**	483	63,700

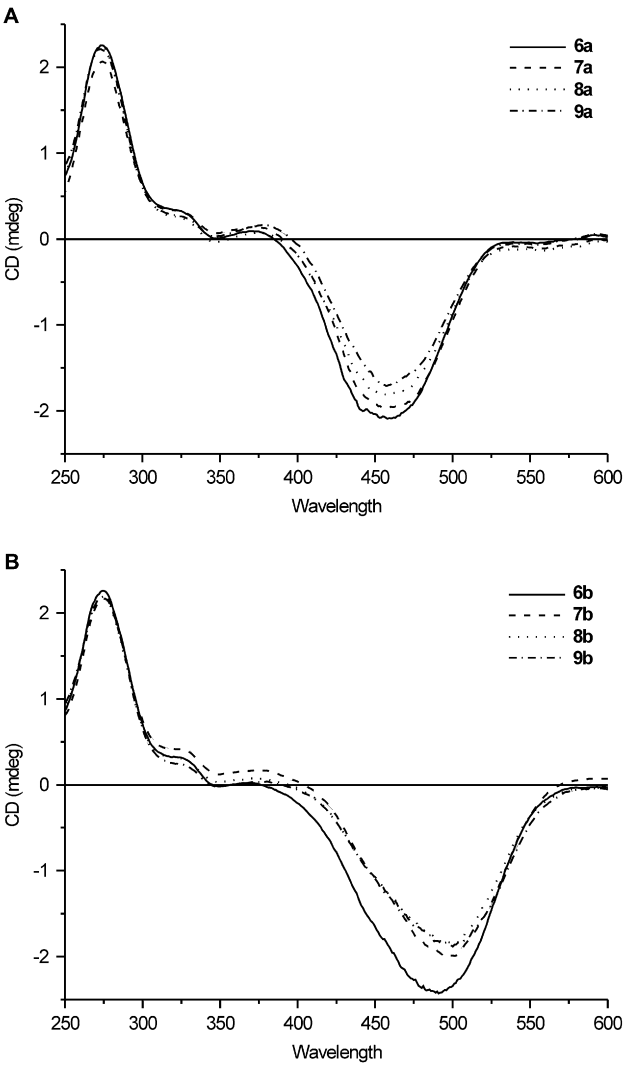


Figure 1. CD spectra of compounds **6a**–**9a** (A), and **6b**–**9b** (B).

TGA was utilized to measure the onset decomposition temperatures (T_d). Increased thermal stability was observed for dendritic structures over the monochromophores. T_d values of compounds **6a**–**9a** were from 71 to 99 °C higher than that of monochromophore **5a** (T_d=222 °C). The highest T_d value (321 °C) was recorded for compound **8a**. Nitro substituted compounds **6b**–**9b** had slightly lower thermal stability displaying onset decomposition temperatures from 49 to 74 °C higher than for **5b** (T_d=213 °C). Unexpectedly, acetonide protected dendrimers showed higher thermal stability over dendrimers containing hydroxyl end groups (Fig. 2A). These results were opposite to the previous results achieved from aliphatic polyester dendrimers, where the bonding interactions of the hydroxyl groups increased T_d values.[21] The decomposition of the compounds occurred in two steps. The compounds were thermally stable up to temperatures around 300 °C, where the first stage of decomposition started. At 350 °C weight loss of about 30–50% had occurred. Slow weight loss continued to around 500 °C where decomposition accelerated until compounds were completely decomposed at around 600 °C. Small weight losses of about 1–4% observed in TG curves at around 100 °C were probably due to removal of water/solvent traces as dendrimers were heated above their glass transition temperatures.

DSC showed only glass transition temperatures (T_g) in consecutive heating–cooling–heating cycles indicating that dendritic compounds were completely amorphous. Glass transition

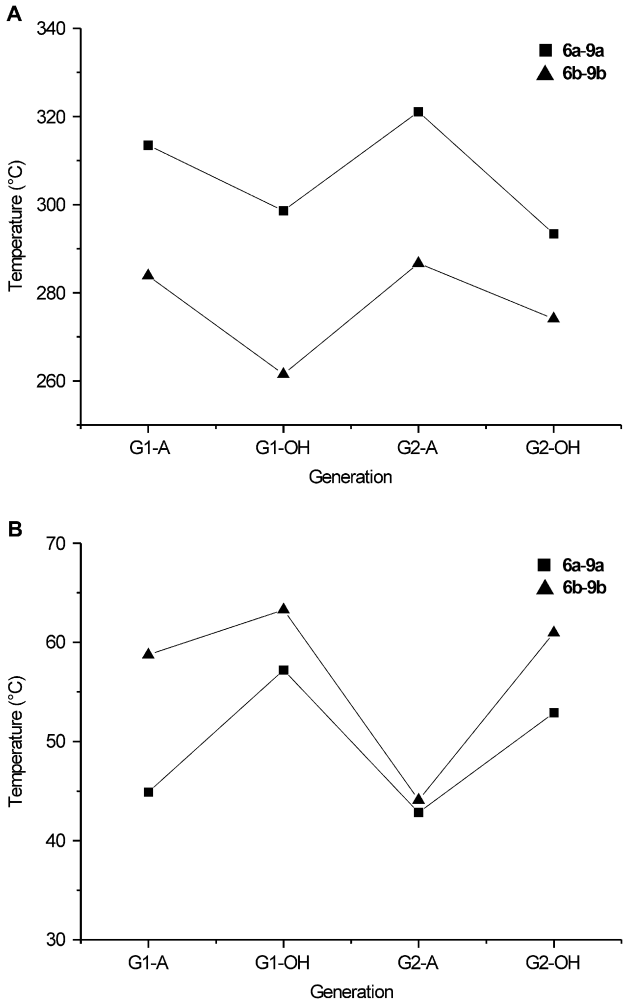


Figure 2. Decomposition temperatures (A) and glass transition temperatures (B) of dendrimers in respect of different generations. Abbreviations on *x*-axis are as follows: G1 and G2 represent the first and second generations, respectively; A=acetonide group, and OH=hydroxyl group.

temperatures were obtained from the second heating scans in order to remove the effects of solvent or water traces. Nitro substituted compounds **6b**–**9b** showed slightly higher T_g values than compounds **6a**–**9a**. Figure 2B shows variations in T_g values of dendritic molecules with respect to different generations and peripheral groups. Hydroxyl functionalized G1 and G2 dendrimers showed higher T_g values than corresponding acetonide functionalized dendrimers of the same generation. This result was expected as it has been reported that increasing polarity of the end groups increases the glass transition temperature.[21,23] An increase of the additional generation decreases slightly T_g values of both acetonide and hydroxyl ended dendrimers. In the case of compound **8b**, T_g was substantially lower than that of corresponding G1 dendrimer **6b**. Decreased T_g values are due to more flexible nature of the G2 dendrimers as polyester chains elongate. The higher T_g values of hydroxyl functionalized dendrimers with respect to protected dendrimers can be explained by the hydrogen bonding interactions of the hydroxyl groups.

Table 2
Thermal data of the dendrimers

Compound	T_g[a] (°C) [ΔC_p (J/g°C)]	T_d[b] (°C)	Compound	T_g[a] (°C) [ΔC_p (J/g°C)]	T_d[b] (°C)
6a	44.9 [0.70]	313	**6b**	58.7 [0.36]	284
7a	57.2 [0.41]	299	**7b**	63.3 [0.46]	262
8a	42.8 [0.54]	321	**8b**	44.1 [0.64]	287
9a	52.9 [0.33]	293	**9b**	61.0 [0.49]	274

[a] Glass transition temperatures (T_g) are taken from the second heating run at half ΔC_p.
[b] Decomposition temperatures (T_d) are taken as extrapolated onset temperatures.

2.4. Water solubility

Since it was assumed that increasing the number of hydroxyl groups at the periphery improves the water solubility of the dye, we carried out a simple water solubility test by dissolving 1 mg of hydroxyl functionalized dendrimers (**7a**,**b**, **9a**,**b**) in 1 mL of water in a test tube. The first generation dendrimers **7a** and **7b**, with four hydroxyl groups in the periphery, showed no apparent color change in water solution, indicating that two hydroxyl groups per chromophore were insufficient to give water solubility. The second generation dendrimers **9a** and **9b**, with eight hydroxyl groups were slightly soluble in water, however, observed by apparent colored solution. According to the observations, the second generation dendrimers with four hydroxyl groups per azo conjugate were adequate to enhance water solubility, which was, however, still far less than 1 mg/mL. It is expected that every additional generation, which doubles the number of the peripheral hydroxyl groups will improve the water solubility of the higher generation dendrimers.

3. Conclusions

Eight novel Janus dendrimers were synthesized and characterized. These Janus compounds consist of two different surfaces, aliphatic polyester wedges with peripheral hydroxyl groups, and chiral donor–acceptor azobenzene conjugates, attached by esterification to pentaerythritol core. All compounds showed broad absorption bands at visible region, compounds **6a**–**9a** at around 440 nm, and compounds **6b**–**9b** around 480 nm. Circular dichroism signals verifying the chirality of the compounds were found at absorption wavelengths. All compounds showed negative CD signals relative to the absorption bands of azobenzene moieties, and positive signals at the absorption range of naproxen moiety. Thermal properties were evaluated with TGA and DSC measurements. Compounds exhibited relatively high thermal stability T_d values ranging between 262 and 321 °C. Only glass transition temperatures were obtained from DSC measurements indicating that dendrimers were completely amorphous.

4. Experimental

4.1. Materials and instrumentations

All the starting materials were purchased from major suppliers and used without any further purification. Dichloromethane (DCM) was dried over 4 Å sieves. Isopropylidene-2,2-bis(methoxy)-propionic acid was prepared according to the procedure described by Ihre et al.[19] Compounds **1**,[18] **2**,[16] **4**,[7b] and **5a** and **5b**[15] were synthesized according to published procedures. Column chromatography was performed with Merck 60 F_{254} silica gel, particle size 0.040–0.063 mm. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance DRX 500 NMR (500.13 and 125.76 MHz) or on a Bruker Avance DPX 250 NMR (250.13 and 62.90 MHz) spectrometers in $CDCl_3$ or DMSO-d_6 solution. The solvent signal was used as an internal standard. IR spectra were recorded on Thermo Nicolet Mattson IR300 FTIR spectrometer. Mass spectral data was obtained with Micromass LCT Electronspray ionization time-of-flight (ESI TOF) instrument with positive-ion mode. Absorption spectra were recorded on Varian Cary100 UV–vis Spectrometer with 10 mm quartz cell. Circular dichroism spectra were recorded on a Jasco J-715 CD-spectrometer under following conditions:

temperature 20 °C; cuvette length 1 mm; wavelength area 200–650 mn; scan speed 50 nm/min. Decomposition temperatures were determined with PerkinElmer TGA7 thermogravimetric analyser under following conditions: heating rate 10 °C/min; atmosphere, air at 60 mL/min; sample size 1–2 mg, in a platinum pan. DSC measurements were carried out on PerkinElmer Pyris Diamond DSC with intracooler using 50 μL encapsulated aluminum pans with capillary holes. The temperature calibration was made using onset temperatures of *n*-decane (T_m=−29.6 °C) and indium (T_m=156.6 °C). The heat- flow was calibrated by using the heat of fusion of an indium (28.45 J/g). The DSC runs were made by cycles of heating–cooling–heating scans under nitrogen atmosphere (flow rate 50 mL/min). Heating rate of 20 °C/min and cooling rate of 10 °C/min were used. The sample weights of 1–2 mg were used in the measurements.

4.2. Synthesis

*4.2.1. (2-Phenyl-1,3-dioxane-5,5-diyl)dimethanol (**1**)*

White solid (9.0 g, 61%). ^{1}H NMR (DMSO-d_6): δ_{ppm}=3.25 (d, 2H, CH_2OH, J=5.3 Hz), 3.68 (d, 2H, CH_2OH, J=5.3 Hz), 3.79 (d, 2H, CH_2, J=11.4 Hz), 3.91 (d, 2H, CH_2, J=11.4 Hz), 4.54 (t, 1H, O*H*, J=5.3 Hz), 4.63 (t, 1H, O*H*, J=5.3 Hz), 5.40 (s, 1H, Ar-C*H*), 7.34–7.44 (m, 5H, Ar*H*). ^{13}C NMR (DMSO-d_6): δ_{ppm}=59.5 (*C*-PE), 61.0 (*C*H$_2$OH), 69.1 (OCH$_2$C), 100.7 (*C*H), 126.1 (ArCH), 128.0 (ArCH), 128.6 (ArCH), 138.8 (Ar*C*). ESI TOF MS: m/z calcd for $C_{12}H_{16}O_4$ 247.09 [M+Na]$^+$, found 247.09 [M+Na]$^+$.

*4.2.2. Isopropylene-2,2-bis(methoxy)propionic anhydride (**2**)*

White solid (30.3 g, 85%). ^{1}H NMR (CDCl$_3$): δ_{ppm}=1.21 (s, 6H, CH_3), 1.37 (s, 6H, acetonide-CH_3), 1.41 (s, 6H, acetonide-CH_3), 3.67 (d, 2H, CH_2O, J=12.0 Hz), 4.18 (d, 2H, CH_2O, J=12.0 Hz). ^{13}C NMR (CDCl$_3$): δ_{ppm}=17.59 (*C*H$_3$), 21.51 (acetonide-*C*H$_3$), 25.48 (acetonide-*C*H$_3$), 43.59 (*C*-PE), 65.60 (*C*H$_2$), 98.31 (*C*), 169.43 (*C*O). ESI TOF MS: m/z calcd for $C_{16}H_{26}O_7$ 353.16 [M+Na]$^+$, found 353.11 [M+Na]$^+$.

*4.2.3. Monobenzalpentaerythritol-[G1]-acetonide (**3**) and a general esterification procedure through anhydride coupling*

Compound **1** (4.5 g, 20.07 mmol) and DMAP (0.74 g, 6.02 mmol) were dissolved in pyridine (16 mL), and a solution of **2** (17.24 g, 52.17 mmol) in DCM (40 mL) was added to the reaction vessel. The mixture was stirred at room temperature until completion. The excess of anhydride was quenched by stirring vigorously with 2 mL of water for 2 h. The mixture was diluted to 500 mL of DCM and extracted with 10% $NaHSO_4$ (3×50 mL), 10% Na_2CO_3 (3×50 mL), and once with brine 50 mL. Organic phase was dried over $MgSO_4$, filtered, and filtrate evaporated to give 9.7 g (90%) of white solid. ^{1}H NMR (CDCl$_3$, 250 MHz): δ_{ppm}=1.14 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 1.36 (s, 3H, acetonide-CH_3), 1.39 (s, 3H, acetonide-CH_3), 1.42 (s, 3H, acetonide-CH_3), 1.44 (s, 3H, acetonide-CH_3), 3.65 (d, 2H, CH_2–bisMPA, J=11.9 Hz), 3.67 (d, 2H, CH_2–bisMPA, J=11.9 Hz), 3.92 (d, 2H, CH_2–O, J=11.9 Hz), 4.07 (s, 2H, COOCH_2), 4.17 (d, 2H, CH_2–O, 11.9 Hz), 4.20 (d, 2H, CH_2–bisMPA, J=11.9 Hz), 4.21 (d, 2H, CH_2–bisMPA, J=11.9 Hz), 4.62 (s, 2H, COOCH_2), 5.45 (s, 1H, ArC*H*), 7.34–7.42 (m, 3H, Ar*H*), 7.46–7.50 (m, 2H, Ar*H*). ^{13}C NMR (CDCl$_3$, 63 MHz): δ_{ppm}=18.34 (1C, *C*H$_3$), 18.53 (1C, *C*H$_3$), 21.08 (1C, *C*H$_3$), 21.93 (1C, *C*H$_3$), 25.32 (1C, *C*H$_3$), 26.22 (1C, *C*H$_3$), 38.00 (1C, *C*-PE), 42.17 (1C, OCO*C*), 42.34 (1C, OCO*C*), 62.55 (1C, *C*H$_2$), 63.00 (1C, *C*H$_2$), 66.13 (4C, *C*H$_2$), 69.45 (2C, *C*H$_2$), 98.12 (1C, *C*), 98.19 (1C, *C*), 102.09 (1C, *C*H), 126.09 (2C, Ar*C*), 128.34 (2C, Ar*C*), 129.16 (1C, Ar*C*), 137.62 (1C, Ar*C*), 173.75 (1C, *C*O), 173.78 (1C, *C*O). ESI TOF MS: m/z calcd for $C_{28}H_{40}O_{19}$ 559.25 [M]$^+$, found 559.22 [M+H]$^+$.

*4.2.4. (OH)$_2$-PE-[G1]-acetonide (**4**)*

White solid (6.9 g, 87%). ^{1}H NMR (CDCl$_3$): δ_{ppm}=1.10 (s, 6H, CH_3), 1.37 (s, 6H, CH_3), 1.44 (s, 6H, CH_3), 2.89 (br s, 2H, O*H*), 3.63 (s, 4H, CH_2OH), 3.67 (d, 4H, bisMPA-CH_2, J=11.9 Hz), 4.20 (d, 4H, bisMPA-CH_2, J=11.9 Hz), 4.27 (s, 4H, CH_2). ^{13}C NMR (CDCl$_3$): δ_{ppm}=18.1 (*C*H$_3$), 20.3 (*C*H$_3$), 26.9 (*C*H$_3$), 42.5 (*C*-bisMPA), 45.5 (*C*-PE), 62.5 (*C*H$_2$OH), 63.7 (*C*H$_2$O-PE), 66.4 (*C*H$_2$O-bisMPA), 98.3 (*C*), 174.8 (*C*O). ESI TOF MS: m/z calcd for $C_{21}H_{36}O_{10}$ 471.22 [M+Na]$^+$, found 471.04 [M+Na]$^+$.

*4.2.5. Bis-[4-[4-(ethyl-{2-[(S)-2-(6-methoxynaphthalen-2-yl)-propionyloxy]-ethyl}-amino)-phenylazo]-benzoic ester]-PE-[G1]-acetonide (**6a**)*

Compound **4** (534 mg, 1.19 mmol), **5a** (1377 mg, 2.62 mmol), and DPTS (351 mg, 1.19 mmol) were dissolved in DCM, and flushed with nitrogen for 30 min. DCC (639 mg, 3.10 mmol) was added in 5 mL of DCM, and the mixture was then stirred at room temperature under nitrogen atmosphere for 46 h. Then, DCC–urea was filtered and solvent evaporated. Crude product was purified by column chromatography (SiO_2) eluting with 3:2 ethyl acetate–hexane to give 1.10 g (63%) of red solid. ^{1}H NMR (CDCl$_3$, 500 MHz): δ_{ppm}=1.04 (t, 6H, NCH$_2$CH_3, J=7.1 Hz), 1.16 (s, 6H, bisMPA-CH_3), 1.35 (s, 6H, acetonide-CH_3), 1.41 (s, 6H, acetonide-CH_3), 1.55 (d, 6H, CHCH_3, J=7.1 Hz), 3.20–3.31 (m, 4H, NCH_2CH$_3$), 3.49–3.58 (m, 4H, NCH_2CH$_2$O), 3.66 (d, 4H, bisMPA-CH_2, J=11.9 Hz), 3.82 (q, 4H, C*H*, J=7.1 Hz), 3.87 (s, 6H, OCH_3), 4.22 (d, 4H, bisMPA-CH_2, J=11.9 Hz), 4.21–4.32 (m, 4H, NCH$_2$CH_2O), 4.50 (s, 4H, PE-CH_2), 4.61 (s, 4H, PE-CH_2), 6.66 (d, 4H, *o*-Ar*H* to NCH$_2$, J=9.2 Hz), 7.08 (d, 2H, Np*H* position 5, J=2.4 Hz), 7.13 (dd, 2H, Np*H* position 7, J=8.9, 2.4 Hz), 7.34 (dd, 2H, Np*H* position 3, J=8.5, 1.8 Hz), 7.61 (d, 2H, Np*H* position 1, J=1.4 Hz), 7.66 (overlapped peaks, 4H, Np*H* positions 4 and 8), 7.81 (d, 4H, *m*-Ar*H* to NCH$_2$, J=9.2 Hz), 7.87 (d, 4H, *m*-Ar*H* to COOH, J=8.7 Hz), 8.14 (d, 4H, *o*-Ar*H* to COOH, J=8.7 Hz). ^{13}C NMR (CDCl3, 126 MHz): δ_{ppm}=11.99 (NCH$_2$CH$_3$), 18.30 (bisMPA-CH$_3$), 18.35 (CHCH$_3$), 21.59 (acetonide-*C*H$_3$), 25.49 (acetonide-*C*H$_3$), 42.25 (*C*-bisMPA), 43.27 (PE-*C*), 45.14 (NCH$_2$CH$_3$), 45.36 (*C*H), 48.54 (HCH$_2$CH$_2$O), 55.19 (O*C*H$_3$), 61.82 (NCH$_2$CH$_2$O), 62.48 (PE-*C*H$_2$), 62.91 (PE-CH$_2$), 66.01 (bisMPA-CH$_2$), 98.13 (acetonide-*C*), 105.57 (Np*C*H position 5), 111.30 (*o*-Ar*C*H to NCH$_2$), 118.97 (Np*C*H position 7), 122.10 (*m*-Ar*C*H to COOCH$_2$), 125.67 (*m*-Ar*C*H to NCH$_2$), 125.92 (Np*C*H position 1), 125.97 (Np*C*H position 3), 127.15 (Np*C*H position 4), 128.84 (Np*C* position 9), 129.15 (Ar*C* next to COOCH$_2$), 129.27 (Np*C*H position 8), 130.56 (*o*-Ar*C*H to COOCH$_2$), 133.67 (Np*C* position 10), 135.24 (Np*C* position 2), 143.72 (*p*-Ar*C* to NCH$_2$), 150.64 (Ar*C* next to NCH$_2$), 156.20 (*p*-Ar*C* to COOCH$_2$), 157.65 (Np*C* position 6), 165.55 (Ar*C*O), 173.65 (bisMPA-*C*O), 174.47 (Np*C*O). IR (KBr): ν_{max}=2969, 1732, 1597, 1514, 1391, 1261, 1133, 826 cm^{-1}. ESI TOF MS: m/z calcd for $C_{83}H_{94}N_6O_{18}$ 1485.62 [M+Na]$^+$, found 1485.80 [M+Na]$^+$. Anal. Calcd for $C_{83}H_{94}N_6O_{18}\cdot 3H_2O$: C 65.68%, H 6.64%, N 5.54%. Found: C 65.40%, H 6.02%, N 5.19%.

*4.2.6. Bis-[4-[4-(ethyl-{2-[(S)-2-(6-methoxynaphthalen-2-yl)-propionyloxy]-ethyl}-amino)-phenylazo]-benzoic ester]-PE-[G1]-(OH)$_4$ (**7a**)*

Compound **6a** (448 mg, 0.31 mmol) was dissolved in 1:1 1 M HCl–THF solution, and the mixture stirred for 1.5 h. The mixture was neutralized with 1 M NaOH, and extracted with DCM. Organic phase was dried over $MgSO_4$, filtered, and evaporated to dryness. Product was purified by column chromatography (SiO_2) eluting with ethyl acetate to give 265 mg (63%) of red solid. ^{1}H NMR (CDCl$_3$, 500 MHz): δ_{ppm}=1.07 (t, 6H, NCH$_2$CH_3, J=7.1 Hz), 1.10 (s, 6H, bisMPA-CH_3), 1.56 (d, 6H, CHCH_3, J=7.1 Hz), 3.12 (s, 4H, O*H*), 3.25–3.34 (m, 4H, NCH_2CH$_3$), 3.52–3.62 (m, 4H, NCH_2CH$_2$O), 3.76 (d, 4H, CH_2OH, J=11.2 Hz), 3.83 (q, 2H, C*H*, J=7.1 Hz), 3.90 (overlapped peaks, 10H, OCH_3 and CH_2OH), 4.24–4.34 (m, NCH$_2$CH_2O), 4.45 (s, 4H, PE-CH_2), 4.60 (s, 4H, PE–CH_2), 6.68 (d, 4H, *o*-Ar*H* to NCH$_2$, J=9.1 Hz), 7.10 (d, 2H, Np*H* position 5, J=2.4 Hz), 7.13 (dd, 2H, Np*H* position 7, J=8.9, 2.4 Hz), 7.35 (dd, 2H, Np*H* position 3, J=8.4, 1.4 Hz), 7.62 (s, 2H, Np*H* position 1), 7.67 (overlapped peaks, 4H, Np*H* position 4 and 8), 7.81 (d, 4H, *m*-Ar*H* to NCH$_2$, J=9.1 Hz), 7.86

(d, 4H, *m*-Ar*H* to $COOCH_2$, J=8.5 Hz), 8.13 (d, 4H, *o*-Ar*H* to $COOCH_2$, J=8.5 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz): δ_{ppm}=12.06 (NCH_2CH_3), 17.16 (bisMPA-CH_3), 18.36 ($CHCH_3$), 43.57 (PE-*C*), 45.25 (NCH_2CH_3), 45.44 ($CHCH_3$), 48.62 (NCH_2CH_2O), 49.87 (bisMPA-*C*), 55.28 (OCH_3), 61.87 (PE-CH_2), 61.89 (NCH_2CH_2O), 62.53 (PE-CH_2), 68.30 (CH_2OH), 105.62 (NpCH position 5), 111.36 (*o*-ArCH to NCH_2), 119.05 (NpCH position 7), 122.20 (*m*-ArCH to $COOCH_2$), 125.77 (*m*-ArCH to NCH_2), 125.99 (NpCH position 1), 126.03 (NpCH position 3), 127.22 (NpCH position 4), 128.91 (Np*C* position 9), 129.12 (Ar*C* next to $COOCH_2$), 129.22 (NpCH position 8), 130.67 (*o*-ArCH to $COOCH_2$), 133.73 (Np*C* position 10), 135.30 (Np*C* position 2), 143.78 (*p*-Ar*C* to NCH_2), 150.73 (Ar*C* next to NCH_2), 156.35 (*p*-Ar*C* to $COOCH_2$), 157.71 (Np*C* position 6), 165.84 (Ar*C*O), 174.58 (Np*C*O), 175.19 (bisMPA-*C*O). IR (KBr): ν_{max}=3522, 2968, 1722, 1598, 1514, 1391, 1267, 1134, 823 cm^{-1}. ESI TOF MS: *m*/*z* calcd for $C_{77}H_{86}N_6O_{18}$ 1405.59 $[M+Na]^+$, found 1406.25 $[M+Na]^+$. Anal. Calcd for $C_{77}H_{86}N_6O_{18}\cdot H_2O$: C 65.99%, H 6.33%, N 6.00%. Found: C 66.29%, H 6.02%, N 5.67%.

*4.2.7. Bis-[4-[4-(ethyl-{2-[(S)-2-(6-methoxynaphthalen-2-yl)-propionyloxy]-ethyl}-amino)-phenylazo]-benzoic ester]-PE-[G2]-acetonide (**9a**)*

Compound **7a** (250 mg, 0.82 mmol), **2** (310 mg, 0.94 mmol), and DMAP (13 mg, 0.11 mmol) were reacted according to the general esterification reaction. The mixture was purified by column chromatography (SiO_2) eluting with 3:2 ethyl acetate–hexane to isolate 156 mg (43%) of **8a** as red solid. Residue containing imperfect dendron (revealed by NMR) was allowed to react additional 46 h with **2** (37 mg, 0.11 mmol), DMAP (2 mg, 0.016 mmol), and pyridine (0.05 mL, 0.63 mmol) in DCM (2 mL). The mixture was purified by column chromatography as described above. Additional 103 mg of compound was obtained, giving **8a** in 259 mg (71%) total yield. ^1H NMR ($CDCl_3$, 500 MHz): δ_{ppm}=1.08 (t, 6H, NCH_2CH_3, J=7.1 Hz), 1.10 (s, 12H, G2-CH_3), 1.31 (s, 6H, G1-CH_3), 1.33 (s, 12H, acetonide-CH_3), 1.36 (s, 12H, acetonide-CH_3), 1.56 (d, 6H, $CHCH_3$, J=7.1 Hz), 3.25–3.33 (m, 4H, NCH_2CH_3), 3.52–3.62 (overlapped peaks, 12H, NCH_2CH_2O and G2-CH_2O), 3.83 (q, 2H, C*H*, J=7.1 Hz), 3.90 (s, 6H, OCH_3), 4.24–4.34 (m, NCH_2CH_2O), 4.36 (ABq, 8H, G1-CH_2, J=11.2 Hz), 4.42 (s, 4H, PE-CH_2), 4.56 (s, 4H, PE-CH_2), 6.68 (d, 4H, *o*-Ar*H* to NCH_2, J=9.1 Hz), 7.10 (d, 2H, Np*H* position 5, J=2.4 Hz), 7.13 (dd, 2H, Np*H* position 7, J=8.9, 2.4 Hz), 7.35 (dd, 2H, Np*H* position 3, J=8.5, 1.8 Hz), 7.62 (d, 2H, Np*H* position 1, J=1.5 Hz), 7.67 (overlapped peaks, 4H, Np*H* position 4 and 8), 7.81 (d, 4H, *m*-Ar*H* to NCH_2, J=9.2 Hz), 7.86 (d, 4H, *m*-Ar*H* to $COOCH_2$, J=8.7 Hz), 8.11 (d, 4H, *o*-Ar*H* to $COOCH_2$, J=8.7 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz): δ_{ppm}=12.07 (NCH_2CH_3), 17.64 (G1-CH_3), 18.37 ($CHCH_3$), 18.45 (G2-CH_3), 21.95 (acetonide-CH_3), 25.21 (acetonide-CH_3), 42.01 (*C*-G2), 43.09 (*C*-PE), 45.27 (NCH_2CH_3), 45.44 ($CHCH_3$), 47.14 (*C*-G1), 48.63 (NCH_2CH_2O), 55.28 (OCH_3), 61.87 (NCH_2CH_2O), 62.59 (PE-CH_2), 63.05 (PE-CH_2), 64.95 (G1-CH_2), 65.92 (G2-CH_2O), 65.95 (G2-CH_2O), 98.09 (acetonide-*C*), 105.62 (NpCH position 5), 111.36 (*o*-ArCH to NCH_2), 119.06 (NpCH position 7), 122.21 (*m*-ArCH to $COOCH_2$), 125.76 (*m*-ArCH to NCH_2), 126.00 (NpCH position 1), 126.04 (NpCH position 3), 127.23 (NpCH position 4), 128.92 (Np*C* position 9), 129.22 (Ar*C* next to $COOCH_2$), 129.23 (NpCH position 8), 130.62 (*o*-ArCH to $COOCH_2$), 133.74 (Np*C* position 10), 135.30 (Np*C* position 2), 143.79 (*p*-Ar*C* to NCH_2), 150.72 (Ar*C* next to NCH_2), 156.28 (*p*-Ar*C* to $COOCH_2$), 157.73 (Np*C* position 6), 165.45 (Ar*C*O), 172.05 (G1-*C*O), 173.47 (G2-*C*O), 174.57 (Np*C*O). IR (KBr): ν_{max}=2970, 1733, 1598, 1514, 1392, 1262, 1132, 828 cm^{-1}. ESI TOF MS: *m*/*z* calcd for $C_{109}H_{134}N_6O_{30}$ 2030.91 $[M+Na]^+$, found 2031.20 $[M+Na]^+$. Anal. Calcd for $C_{109}H_{134}N_6O_{30}$: C 65.19%, H 6.73%, N 4.18%. Found: C 65.22%, H 6.51%, N 3.90%.

*4.2.8. Bis-[4-[4-(ethyl-{2-[(S)-2-(6-methoxynaphthalen-2-yl)-propionyloxy]-ethyl}-amino)-phenylazo]-benzoic ester]-PE-[G2]-(OH)8 (**9a**) and a general deprotection procedure of acetonide group*

Compound **8a** (193 mg, 0.096 mmol) was dissolved in 1:1 2 M HCl–THF solution (14 mL), and stirred for 1.5 h. The reaction mixture was neutralized with 1 M NaOH, and THF was evaporated off. Solid residue was filtered, washed with water, and dried to give 135 mg (72%) of red solid. ^1H NMR ($CDCl_3$, 500 MHz): δ_{ppm}=1.04 (s, 12H, G2-CH_3), 1.07 (t, 6H, NCH_2CH_3, J=7.1 Hz), 1.31 (s, 6H, G1-CH_3), 1.56 (d, 6H, $CHCH_3$, J=7.1 Hz), 3.24–3.37 (overlapped peaks, 12H, NCH_2CH_3 and O*H*), 3.52–3.61 (m, 4H, NCH_2CH_2O), 3.67–3.70 (m, 8H, CH_2OH), 3.78–3.85 (overlapped peaks, 10H, CH_2OH and C*H*), 3.83 (q, 2H, C*H*, J=7.1 Hz), 3.89 (s, 6H, OCH_3), 4.23–4.33 (m, NCH_2CH_2O), 4.37 (ABq, 8H, G1-CH_2, J=11.1 Hz), 4.44 (s, 4H, PE-CH_2), 4.58 (s, 4H, PE-CH_2), 6.67 (d, 4H, *o*-Ar*H* to NCH_2, J=9.1 Hz), 7.10 (d, 2H, Np*H* position 5, J=2.4 Hz), 7.13 (dd, 2H, Np*H* position 7, J=8.9, 2.4 Hz), 7.35 (dd, 2H, Np*H* position 3, J=8.6, 1.3 Hz), 7.62 (s, 2H, Np*H* position 1), 7.67 (overlapped peaks, 4H, Np*H* positions 4 and 8), 7.81 (d, 4H, *m*-Ar*H* to NCH_2, J=9.0 Hz), 7.86 (d, 4H, *m*-Ar*H* to $COOCH_2$, J=8.4 Hz), 8.11 (d, 4H, *o*-Ar*H* to $COOCH_2$, J=8.4 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz): δ_{ppm}=12.06 (NCH_2CH_3), 17.10 (G2-CH_3), 17.96 (G1-CH_3), 18.36 ($CHCH_3$), 42.86 (*C*-PE), 45.26 (NCH_2CH_3), 45.43 ($CHCH_3$), 46.90 (*C*-G1), 48.61 (NCH_2CH_2O), 49.81 (*C*-G2), 55.28 (OCH_3), 61.87 (NCH_2CH_2O), 63.04 (PE-CH_2), 63.72 (PE-CH_2), 64.93 (G1-CH_2), 67.36 (G2-CH_2O), 67.48 (G2-CH_2O), 105.62 (NpCH position 5), 111.36 (*o*-ArCH to NCH_2), 119.05 (NpCH position 7), 122.23 (*m*-ArCH to $COOCH_2$), 125.79 (*m*-ArCH to NCH_2), 125.99 (NpCH position 1), 126.03 (NpCH position 3), 127.22 (NpCH position 4), 128.91 (Np*C* position 9), 128.98 (Ar*C* next to $COOCH_2$), 129.22 (NpCH position 8), 130.65 (*o*-ArCH to $COOCH_2$), 133.73 (Np*C* position 10), 135.29 (Np*C* position 2), 143.77 (*p*-Ar*C* to NCH_2), 150.77 (Ar*C* next to NCH_2), 156.42 (p-Ar*C* to $COOCH_2$), 157.71 (Np*C* position 6), 165.79 (Ar*C*O), 172.61 (G1-*C*O), 174.58 (Np*C*O), 175.05 (G2-*C*O). IR (KBr): ν_{max}=2973, 1732, 1597, 1509, 1392, 1262, 1133, 822 cm^{-1}. ESI TOF MS: *m*/*z* calcd for $C_{97}H_{118}N_6O_{30}$ 1870.78 $[M+Na]^+$, found 1871.10 $[M+Na]^+$. Anal. Calcd for $C_{97}H_{118}N_6O_{30}\cdot H_2O$: C 62.44%, H 6.48%, N 4.50%. Found: C 62.35%, H 6.28%, N 4.20%.

*4.2.9. Bis-[4-((4-(ethyl(2-((S)-2-(6-methoxynaphthalen-2-yl)propanoyloxy)ethyl)amino)-phenyl)diazenyl)-3-nitrobenzoic ester]-PE-[G1]-acetonide (**6b**)*

The procedure is the same as the synthesis of compound **6a**. Compound **4** (715 mg, 1.59 mmol), **5b** (2183 mg, 3.82 mmol), DPTS (469 mg, 1.59 mmol), and DCC (639 mg, 3.10 mmol) were used. Crude product was purified by column chromatography (SiO_2) eluting 6:5 ethyl acetate–hexane to give 1.26 g (51%) of red solid. ^1H NMR ($CDCl_3$, 500 MHz): δ_{ppm}=1.07 (t, 6H, NCH_2CH_3, J=7.1 Hz), 1.15 (s, 6H, bisMPA-CH_3), 1.33 (s, 6H, acetonide-CH_3), 1.42 (s, 6H, acetonide-CH_3), 1.56 (d, 6H, $CHCH_3$, J=7.1 Hz), 3.23–3.34 (m, 4H, NCH_2CH_3), 3.52–3.63 (m, 4H, NCH_2CH_2O), 3.67 (d, 4H, bisMPA-CH_2, J=11.9 Hz), 3.82 (q, 4H, C*H*, J=7.1 Hz), 3.90 (s, 6H, OCH_3), 4.21 (d, 4H, bisMPA-CH_2, J=11.9 Hz), 4.22–4.35 (m, 4H, NCH_2CH_2O), 4.47 (s, 4H, PE-CH_2), 4.60 (s, 4H, PE-CH_2), 6.64 (d, 4H, *o*-Ar*H* to NCH_2, J=9.4 Hz), 7.10 (d, 2H, Np*H* position 5, J=2.4 Hz), 7.14 (dd, 2H, Np*H* position 7, J=8.9, 2.4 Hz), 7.33 (dd, 2H, Np*H* position 3, J=8.5, 1.8 Hz), 7.60 (d, 2H, Np*H* position 1, J=1.6 Hz), 7.66 (overlapped peaks, 4H, Np*H* positions 4 and 8), 7.77 (d, 2H, *m*-Ar*H* to $COOCH_2$, J=8.5 Hz), 7.78 (d, 4H *m*-Ar*H* to NCH_2, J=9.4 Hz), 8.21 (dd, 2H, *o*-Ar*H* to $COOCH_2$, J=8.5, 1.8 Hz), 8.45 (d, 2H, *o*-Ar*H* to $COOCH_2$ and NO_2, J=1.8 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz): δ_{ppm}=12.00 (NCH_2CH_3), 18.30 ($CHCH_3$),18.31 (bisMPA-CH_3),20.99 (acetonide-CH_3), 26.09 (acetonide-CH_3), 42.36 (*C*-bisMPA), 43.52 (PE-*C*), 45.28 (NCH_2CH_3), 45.37 (*C*H), 48.59 (HCH_2CH_2O), 55.25 (OCH_3), 61.70 (NCH_2CH_2O), 62.11 (PE-CH_2), 63.34 (PE-CH_2), 66.09 (bisMPA-CH_2), 98.20 (acetonide-*C*), 105.60 (NpCH position 5), 111.42 (*o*-ArCH to NCH_2), 118.88 (*m*-ArCH to $COOCH_2$), 119.02 (NpCH position 7), 125.29 (*o*-ArCH to $COOCH_2$ and NO_2), 125.91 (NpCH position 3), 125.97 (NpCH position 1), 126.92 (*m*-ArCH to NCH_2), 127.21 (NpCH position 4), 128.86 (Ar*C* next to COOH), 128.98 (Np*C* position 9), 129.16 (NpCH position 8), 133.25 (*o*-ArCH to $COOCH_2$), 133.70 (Np*C* position 10), 134.19 (Np*C* position

2), 144.11 (*p*-Ar*C* to NCH_2), 147.03 (Ar*C* next to NO_2), 148.62 (*p*-Ar*C* to $COOCH_2$), 151.75 (Ar*C* next to NCH_2), 157.68 (Np*C* position 6), 163.84 (Ar*C*O), 173.61 (bisMPA-*C*O), 174.50 (Np*C*O). IR (KBr): ν_{max}=2975, 1733, 1598, 1537, 1518, 1385, 1235, 1149, 827 cm^{-1}. ESI TOF MS: *m*/*z* calcd for $C_{83}H_{92}N_8O_{22}$ 1575.62 $[M+Na]^+$, found 1575.70 $[M+Na]^+$. Anal. Calcd for $C_{83}H_{92}N_8O_{22}\cdot H_2O$: C 63.43%, H 6.03%, N 7.13%. Found: C 63.34%, H 5.77%, N 7.03%.

4.2.10. Bis-[4-((4-(ethyl(2-((S)-2-(6-methoxynaphthalen-2-yl)propanoyloxy)ethyl)amino)-phenyl)diazenyl)-3-nitrobenzoic ester]-PE-[G1]-OH_4 (**7b**)

Compound **6b** (362 mg, 0.233 mmol) in 14 mL of 1:1 3 M HCl–THF solution was reacted according to general deprotection procedure to give 208 mg (61%) of red solid. ^1H NMR ($CDCl_3$, 500 MHz): δ_{ppm}=1.06 (t, 6H, NCH_2CH_3, *J*=7.1 Hz), 1.10 (s, 6H, bisMPA-CH_3), 1.55 (d, 6H, $CHCH_3$, *J*=7.1 Hz), 3.10 (br s, 4H, O*H*), 3.24–3.32 (m, 4H, NCH_2CH_3), 3.52–3.62 (m, 4H, NCH_2CH_2O), 3.77 (d, 4H, CH_2OH, *J*=11.1 Hz), 3.82 (q, 2H, C*H*, *J*=7.1 Hz), 3.90 (overlapped peaks, 10H, OCH_3 and CH_2OH), 4.22–4.35 (m, 4H, NCH_2CH_2O), 4.46 (s, 4H, PE-CH_2), 4.61 (s, 4H, PE-CH_2), 6.64 (d, 4H, *o*-Ar*H* to NCH_2, *J*=9.3 Hz), 7.10 (d, 2H, Np*H* position 5, *J*=2.4 Hz), 7.13 (dd, 2H, Np*H* position 7, *J*=8.9, 2.4 Hz), 7.33 (dd, 2H, Np*H* position 3, *J*=8.5, 1.8 Hz), 7.60 (d, 2H, Np*H* position 1, *J*=1.4 Hz), 7.65–7.67 (overlapped peaks, 4H, Np*H* positions 4 and 8), 7.75–7.80 (m, 6H, *m*-Ar*H* to $COOCH_2$ and *m*-Ar*H* to NCH_2), 8.21 (dd, 2H, *o*-Ar*H* to $COOCH_2$, *J*=8.5, 1.8 Hz), 8.45 (d, 1H, *o*-Ar*H* to $COOCH_2$ and NO_2, *J*=1.8 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz): δ_{ppm}=12.06 (NCH_2CH_3), 17.16 (bisMPA-CH_3), 18.35 ($CHCH_3$), 43.68 (PE-*C*), 45.35 (NCH_2CH_3), 45.43 ($CHCH_3$), 48.65 (NCH_2CH_2O), 49.83 (bisMPA-*C*), 55.31 (OCH_3), 61.64 (PE-CH_2), 61.75 (NCH_2CH_2O), 63.06 (PE-CH_2),68.48 (CH_2OH), 105.66 (Np*C*H position 5), 111.49 (*o*-Ar*C*H to NCH_2), 118.99 (*m*-Ar*C*H to $COOCH_2$), 119.08 (Np*C*H position 7), 125.33 (*o*-ArCH to $COOCH_2$ and NO_2), 125.97 (Np*C*H position 3), 126.02 (Np*C*H position 1), 127.01 (*m*-Ar*C*H to NCH_2), 127.27 (Np*C*H position 4), 128.87 (Ar*C* next to COOH), 128.92 (Np*C* position 9), 129.21 (Np*C*H position 8), 133.38 (*o*-ArCH to $COOCH_2$), 133.76 (Np*C* position 10), 135.24 (Np*C* position 2), 144.18 (*p*-Ar*C* to NCH_2), 147.04 (Ar*C* next to NO_2), 148.78 (*p*-Ar*C* to $COOCH_2$), 151.86 (Ar*C* next to NCH_2), 157.74 (Np*C* position 6), 164.07 (Ar*C*O), 174.57 (Np*C*O), 175.10 (bisMPA-*C*O). IR (KBr): ν_{max}=3498, 2971, 1730, 1599, 1535, 1519, 1385, 1235, 1149, 823 cm^{-1}. ESI TOF MS: *m*/*z* calcd for $C_{77}H_{84}N_8O_{22}$ 1495.56 $[M+Na]^+$, found 1495.69 $[M+Na]^+$. Anal. Calcd for $C_{77}H_{84}N_8O_{22}\cdot 3H_2O$: C 60.54%, H 5.94%, N 7.34%. Found: C 60.86%, H 5.69%, N 7.29%.

4.2.11. Bis-[4-((4-(ethyl(2-((S)-2-(6-methoxynaphthalen-2-yl)propanoyloxy)ethyl)amino)-phenyl)diazenyl)-3-nitrobenzoic ester]-PE-[G2]-acetonide (**8b**)

Compound **7b** (268 mg, 0.18 mmol), DMAP (20 mg, 0.17 mmol), pyridine (1 mL), and **2** (360 mg, 1.09 mmol) were reacted according to the general esterification reaction. The crude product was purified by column chromatography (SiO_2) eluting with 3:2 ethyl acetate–hexane to give 302 mg (79%) of red solid. ^1H NMR ($CDCl_3$, 500 MHz): δ_{ppm}=1.07 (t, 6H, NCH_2CH_3, *J*=7.1 Hz), 1.11 (s, 12H, G2-CH_3), 1.32 (s, 12H, acetonide-CH_3), 1.33 (s, 6H, G1-CH_3), 1.37 (s, 12H, acetonide-CH_3), 1.56 (d, 6H, $CHCH_3$, *J*=7.1 Hz), 3.26–3.33 (m, 4H, NCH_2CH_3), 3.53–3.63 (overlapped peaks, 12H, NCH_2CH_2O and G2-CH_2O), 3.83 (q, 2H, C*H*, *J*=7.1 Hz), 3.90 (s, 6H, OCH_3), 4.11–4.13 (m, 8H, G2-CH_2O),4.23–4.36 (m, 4H, NCH_2CH_2O), 4.37 (ABq, 8H, G1-CH_2, *J*=11.1 Hz), 4.39 (s, 4H, PE-CH_2), 4.57 (s, 4H, PE-CH_2), 6.65 (d, 4H, *o*-Ar*H* to NCH_2, *J*=9.4 Hz), 7.11 (d, 2H, Np*H* position 5, *J*=2.4 Hz), 7.14 (dd, 2H, Np*H* position 7, *J*=8.9, 2.4 Hz), 7.33 (dd, 2H, Np*H* position 3, *J*=8.5, 1.8, Hz), 7.60 (d, 2H, Np*H* position 1, *J*=1.8 Hz), 7.67 (d, 2H, Np*H* position 4, *J*=8.5 Hz), 7.67 (d, 2H, Np*H* position 8, *J*=8.9 Hz), 7.78 (d, 2H, *m*-Ar*H* to $COOCH_2$, *J*=8.5 Hz), 7.79 (d, 4H *m*-Ar*H* to NCH_2, *J*=9.4 Hz), 8.20 (dd, 2H, *o*-Ar*H* to $COOCH_2$, *J*=8.5, 1.8 Hz), 8.45 (d, 1H, *o*-Ar*H* to $COOCH_2$ and NO_2, *J*=1.8 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz): δ_{ppm}=12.07 (NCH_2CH_3), 17.68 (G1-CH_3), 18.36 ($CHCH_3$), 18.49 (G2-CH_3), 21.80 (acetonide-CH_3), 25.40 (acetonide-CH_3), 42.11 (*C*-G2), 43.26 (*C*-PE), 45.38 (NCH_2CH_3), 45.45 ($CHCH_3$), 47.21 (*C*-G1), 48.68 (NCH_2CH_2O), 55.32 (OCH_3), 61.75 (NCH_2CH_2O), 62.67 (PE-CH_2), 62.98 (PE-CH_2), 64.97 (G1-CH_2), 65.96 (G2-CH_2O), 65.98 (G2-CH_2O), 98.13 (acetonide-*C*), 105.69 (Np*C*H position 5), 111.50 (*o*-Ar*C*H to NCH_2), 119.01 (*m*-Ar*C*H to $COOCH_2$), 119.09 (Np*C*H position 7), 125.30 (*o*-ArCH to $COOCH_2$ and NO_2), 125.91 (Np*C*H position 3), 125.97 (Np*C*H position 1), 127.00 (*m*-Ar*C*H to NCH_2), 127.28 (Np*C*H position 4), 128.94 (Ar*C* next to COOH), 128.96 (Np*C* position 9), 129.22 (Np*C*H position 8), 133.27 (*o*-Ar*C*H to $COOCH_2$), 133.78 (Np*C* position 10), 135.26 (Np*C* position 2), 144.21 (*p*-Ar*C* to NCH_2), 147.09 (Ar*C* next to NO_2), 148.73 (*p*-Ar*C* to $COOCH_2$), 151.84 (Ar*C* next to NCH_2), 157.77 (Np*C* position 6), 163.78 (Ar*C*O), 171.097 (G1-*C*O), 173.52 (G2-*C*O), 174.56 (Np*C*O). IR (KBr): ν_{max}=2967, 1733, 1598, 1538, 1519, 1376, 1235, 1148, 828 cm^{-1}. ESI TOF MS: *m*/*z* calcd for $C_{109}H_{132}N_8O_{34}$ 2120.88 $[M+Na]^+$, found 2120.80 $[M+Na]^+$. Anal. Calcd for $C_{109}H_{132}N_8O_{34}\cdot 2H_2O$: C 61.34%, H 6.42%, N 5.25%. Found: C 61.14%, H 6.23%, N 4.92%.

4.2.12. Bis-[4-((4-(ethyl(2-((S)-2-(6-methoxynaphthalen-2-yl)propanoyloxy)ethyl)amino)-phenyl)diazenyl)-3-nitrobenzoic ester]-PE-[G1]-G2-OH_8 (**9b**)

Compound **8b** (150 mg, 0.072 mmol) in 1:1 3 M HCl–THF solution (14 mL) was reacted according to general deprotection procedure to give 112 mg (81%) of red solid. ^1H NMR ($CDCl_3$, 500 MHz): δ_{ppm}=1.05 (s, 12H, G2-CH_3), 1.07 (t, 6H, NCH_2CH_3, *J*=7.2 Hz), 1.34 (s, 6H, G1-CH_3), 1.55 (d, 6H, $CHCH_3$, *J*=7.1 Hz), 3.23–3.40 (overlapped peaks, 12H, NCH_2CH_3 and O*H*), 3.53–3.63 (m, 4H, NCH_2CH_2O), 3.69 (dd, 8H, CH_2OH, *J*=3.4, 11.3 Hz), 3.78–3.84 (overlapped peaks, 10H, CH_2OH and C*H*), 3.89 (s, 6H, OCH_3), 4.22–4.34 (m, 4H, NCH_2CH_2O), 4.37 (ABq, 8H, G1-CH_2, *J*=11.1 Hz), 4.43 (s, 4H, PE-CH_2), 4.59 (s, 4H, PE-CH_2), 6.64 (d, 4H, *o*-Ar*H* to NCH_2, *J*=9.4 Hz), 7.10 (d, 2H, Np*H* position 5, *J*=2.4 Hz), 7.13 (dd, 2H, Np*H* position 7, *J*=8.9, 2.4 Hz), 7.32 (dd, 2H, Np*H* position 3, *J*=8.5, 1.8 Hz), 7.60 (s, 2H, Np*H* position 1), 7.65 (d, 2H, Np*H* position 4, *J*=8.5 Hz), 7.67 (d, 2H, Np*H* position 8, *J*=8.9 Hz), 7.76–7.78 (d, 6H, *m*-Ar*H* to $COOCH_2$ and *m*-Ar*H* to NCH_2), 8.20 (dd, 2H, *o*-Ar*H* to $COOCH_2$, *J*=8.5, 1.8 Hz), 8.44 (d, 1H, *o*-Ar*H* to $COOCH_2$ and NO_2, *J*=1.8 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz): δ_{ppm}=12.06 (NCH_2CH_3), 17.11 (G2-CH_3), 17.95 (G1-CH_3), 18.34 ($CHCH_3$), 42.97 (*C*-PE), 45.37 (NCH_2CH_3), 45.43 ($CHCH_3$), 46.99 (*C*-G1), 48.68 (NCH_2CH_2O), 49.81 (*C*-G2), 55.30 (OCH_3), 61.74 (NCH_2CH_2O), 63.51 (PE-CH_2), 65.03 (G1-CH_2), 67.50 (G2-CH_2O), 67.61 (G2-CH_2O), 105.67 (Np*C*H position 5), 111.50 (*o*-Ar*C*H to NCH_2), 119.09 (overlapping peaks Np*C*H position 7 and *m*-Ar*C*H to $COOCH_2$), 125.33 (*o*-Ar*C*H to $COOCH_2$ and NO_2), 125.96 (Np*C*H position 3), 126.01 (Np*C*H position 1), 127.03 (*m*-Ar*C*H to NCH_2), 127.27 (Np*C*H position 4), 128.75 (Np*C* position 9), 128.92 (Ar*C* next to COOH), 129.21 (Np*C*H position 8), 133.37 (*o*-Ar*C*H to $COOCH_2$), 133.76 (Np*C* position 10), 135.24 (Np*C* position 2), 144.17 (*p*-Ar*C* to NCH_2), 147.03 (Ar*C* next to NO_2), 148.80 (*p*-Ar*C* to $COOCH_2$), 151.89 (Ar*C* next to NCH_2), 157.74 (Np*C* position 6), 164.04 (Ar*C*O), 172.54 (G1-*C*O), 174.56 (Np*C*O), 175.06 (G2-*C*O). IR (KBr): ν_{max}=3300, 2973, 1731, 1599, 1537, 1519, 1386, 1235, 1149, 823 cm^{-1}. ESI TOF MS: *m*/*z* calcd for $C_{97}H_{116}N_8O_{34}$ 1960.75 $[M+Na]^+$, found 1960.49 $[M+Na]^+$. Anal. Calcd for $C_{97}H_{116}N_8O_{34}\cdot 3H_2O$: C 58.49%, H 6.17%, N 5.62%. Found: C 58.25%, H 5.99%, N 5.56%.

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References and notes

1. (a) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons: Concepts, Syntheses and Applications*; Wiley-VCH: Weinheim, 2001; (b) *Dendrimers and Other Dendritic Polymers*; Fréchet, J. M. J., Tomalia, D. A., Eds.; Wiley: Chichester, UK, 2001; (c) Nummelin, S.; Skrifvars, M.; Rissanen, K. *Top. Curr. Chem.* **2000**, *210*, 1–67; (d) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules: Concepts, Syntheses, Perspectives*; VCH: Weinheim, 1996.
2. (a) Buchleier, E.; Wehner, W.; Vögtle, F. *Synthesis* **1978**, 155–158; (b) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roech, J.; Ryder, J.; Smith, P. *Polym. J.* **1985**, *17*, 117–132; (c) Newkome, G. R.; Zao, Z.; Baker, G. R.; Gupta, V. K. *J. Org. Chem.* **1985**, *50*, 2003–2004.
3. (a) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638–7647; (b) Miller, T. M.; Neenan, T. X. *Chem. Mater.* **1990**, *2*, 346–349.
4. (a) Adronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2000**, 1701–1710; (b) Balzani, V.; Ceroni, P.; Maestri, M.; Vicinelli, V. *Curr. Opin. Chem. Biol.* **2003**, *7*, 657–665; (c) Choi, M.-S.; Yamazaki, T.; Yamazaki, I.; Aida, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 150–158; (d) Ceroni, P.; Bergamini, G.; Marchioni, F.; Balzani, V. *Prog. Polym. Sci.* **2005**, *30*, 453–473; (e) Jiang, D.-L.; Aida, T. *Prog. Polym. Sci.* **2005**, *30*, 403–422.
5. (a) Padilla de Jesús, O. L.; Ihre, H. R.; Gagne, L.; Fréchet, J. M. J.; Szoka, F. C., Jr. *Bioconjugate Chem.* **2002**, *13*, 453–461; (b) Ihre, H. R.; Padilla de Jesús, O. L.; Szoka, F. C., Jr.; Fréchet, J. M. J. *Bioconjugate Chem.* **2002**, *13*, 443–452; (c) Boas, U.; Heegaard, P. M. H. *Chem. Soc. Rev.* **2004**, *33*, 43–63; (d) Gillies, E. R.; Dy, E.; Fréchet, J. M. J.; Szoka, F. C. *Mol. Pharm.* **2005**, *2*, 129–138; (e) Gillies, E. R.; Fréchet, J. M. J. *Drug Deliv. Today* **2005**, *10*, 35–43; (f) Guillaudeu, S. J.; Fox, M. E.; Haidar, Y. M.; Dy, E. E.; Szoka, F. C.; Fréchet, J. M. J. *Bioconjugate Chem.* **2008**, *19*, 461–469.
6. (a) van Heerbeek, R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Reek, J. N. H. *Chem. Rev.* **2002**, *102*, 3717–3756; (b) Liang, C.; Fréchet, J. M. J. *Prog. Polym. Sci.* **2005**, *30*, 385–402; (c) Méry, D.; Astruc, D. *Coord. Chem. Rev.* **2006**, *250*, 1965–1979; (d) Hwang, S.-H.; Shreiner, C. D.; Moorefield, C. N.; Newkome, G. R. *New J. Chem.* **2007**, *31*, 1192–1217; (e) Caminade, A.-M.; Servin, P.; Laurent, R.; Majoral, J.-P. *Chem. Soc. Rev.* **2008**, *37*, 56–67.
7. (a) Saez, I. M.; Goodby, J. W. *Chem.—Eur. J* **2003**, *9*, 4869–4877; (b) Ropponen, J.; Nummelin, S.; Rissanen, K. *Org. Lett.* **2004**, *6*, 2495–2497; (c) Percec, V.; Imam, M. R.; Bera, T. K.; Balagurusamy, V. S. K.; Peterca, M.; Heiney, P. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 4739–4745; (d) Wu, P.; Malkoch, M.; Hunt, J. N.; Vestberg, R.; Kaltgrad, E.; Finn, M. G.; Fokin, V. V.; Sharpless, K. B.; Hawker, C. J. *Chem. Commun.* **2005**, 5775–5777; (e) Bury, I.; Heinrich, B.; Bourgogne, C.; Guillon, D.; Donnio, B. *Chem.—Eur. J* **2006**, *12*, 8396–8413; (f) Lukin, O.; Gramlich, V.; Kandre, R.; Zhun, I.; Felder, T.; Schalley, C. A.; Dolgonos, G. *J. Am. Chem. Soc.* **2006**, *128*, 8964–8974.
8. Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1287–1297.
9. Gillies, E. R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2002**, *124*, 14137–14146.
10. Zollinger, H. *Color Chemistry. Synthesis, and Applications of Organic Dyes and Pigments*; Wiley-VCH: Weinheim, 2003.
11. (a) Kumar, G. S.; Neckers, D. C. *Chem. Rev.* **1989**, *89*, 1915–1925; (b) Yagai, S.; Karatsu, T.; Kitamura, A. *Chem.—Eur. J* **2005**, *11*, 4054–4063; (c) Yager, K. G.; Barrett, C. J. *J. Photochem. Photobiol., A: Chem.* **2006**, *182*, 250–261.
12. Mekelburger, H.-B.; Rissanen, K.; Vögtle, F. *Chem. Ber.* **1993**, *126*, 1161–1169.
13. For recent papers, see: (a) Wang, S.; Wang, X.; Li, L.; Advincula, R. C. *J. Org. Chem.* **2004**, *69*, 9073–9084; (b) Liao, L.-X.; Stellacci, F.; McGrath, D. V. *J. Am. Chem. Soc.* **2004**, *126*, 2181–2185; (c) Gabriel, C. J.; Parquette, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 13708–13709; (d) Puntoriero, F.; Ceroni, P.; Balzani, V.; Bergamini, G.; Vögtle, F. *J. Am. Chem. Soc.* **2007**, *129*, 10714–10719; (e) Shen, X.; Liu, H.; Li, Y.; Liu, S. *Macromolecules* **2008**, *41*, 2421–2425.
14. For recent reviews, see: (a) Villavicencio, O.; McGrath, D. V. In *Advances in Dendritic Macro Molecules*; Newkome, G. R., Ed.; Jai Press: Oxford, 2002; vol. 5, pp 1–44; (b) Momotake, A.; Arai, T. *J. Photochem. Photobiol., C: Photochem. Rev.* **2004**, *5*, 1–25.
15. Tuuttila, T.; Lipsonen, J.; Huuskonen, J.; Rissanen, K. *Dyes Pigments*, in press doi: 10/106/j.dyepig.2008.04.007.
16. Malkoch, M.; Malmström, E.; Hult, A. *Macromolecules* **2002**, *35*, 8307–8314.
17. Yokohama, S.; Nakahama, T.; Otomo, A.; Mashiko, S. *J. Am. Chem. Soc.* **2000**, *122*, 3174–3181.
18. Issidorides, C. H.; Gulen, R. In *Organic Syntheses*; Rabjohn, N., Ed.; Wiley: New York, NY, 1963; Coll. Vol. IV, pp 679–680.
19. Ihre, H.; Hult, A.; Fréchet, J. M. J.; Gitsov, I. *Macromolecules* **1998**, *31*, 4061–4068.
20. Moore, J. S.; Stupp, S. I. *Macromolecules* **1990**, *23*, 65–70.
21. Ropponen, J.; Tuuttila, T.; Lahtinen, M.; Nummelin, S.; Rissanen, K. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5574–5586.
22. Ropponen, J.; Tamminen, J.; Lahtinen, M.; Linnanto, J.; Rissanen, K.; Kolehmainen, E. *Eur. J. Org. Chem.* **2005**, 73–84.
23. Wooley, K. L.; Hawker, C. J.; Pochan, J. M.; Fréchet, J. M. J. *Macromolecules* **1993**, *26*, 1514–1519.