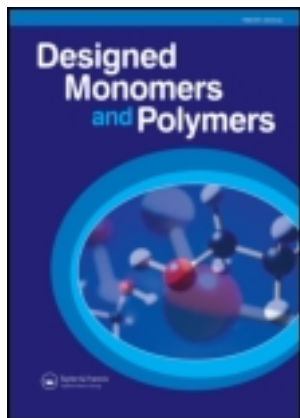


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### Fréchet-type dendrons bearing azobenzene units and flexible oligo(ethylene glycol) spacers: synthesis, characterization, thermal and optical properties

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## Fréchet-type dendrons bearing azobenzene units and flexible oligo(ethylene glycol) spacers: synthesis, characterization, thermal and optical properties

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In this study, we report the synthesis and characterization of a novel series of first- and second-generation Fréchet-type dendrons bearing amino-nitro, amino-methoxy and amino-butyl substituted azobenzene units and tetra(ethylene glycol) spacers. These compounds were fully characterized by FTIR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies, and their molecular weights were determined by MALDITOF. The thermal properties of the obtained dendrons were studied by thermogravimetric analysis and differential scanning calorimetry and their optical properties by absorption spectroscopy in solution. Molecular calculations were performed in order to determine the dipole moment of these molecules. Some of the dendrons showed a liquid crystalline behaviour, which was studied by light polarized microscopy as a function of the temperature in order to determine the transition temperatures and the structure of the mesophase.

**Keywords:** dendron; azobenzene; optical properties; liquid crystals

### Introduction

Recently, dendrimers and dendrons have been considered as one of the most attractive research fields in polymer chemistry, due to their well-defined structures and potential applications.[1–4] These molecules can be modified by introducing functional groups and specific units at different levels of their structure: core, branches or periphery,[5] giving rise to well-structured and highly functionalized molecules. Depending on the type of functional groups present in dendrimers, different properties have been already studied such as response to light. Some reviews include the first examples of photo-responsive dendrimers [6–9] including many examples of azo-dendrimers. The most recent review covering the most important aspects of azobenzene containing dendrons and dendrimers has been published by Deloncle and Caminade.[10]

At the beginning, azobenzenes had been exclusively used as terminal groups of dendrimers and dendrons; the first examples were described by Vögtle and co-workers. [11] The first reported structures were prepared from poly(propyleneimine) dendrimers built from either ethylenediamine [12] or 1,4-diaminobutane [1–14] as core. In most of the cases, all the terminal groups were generally azobenzenes.[15–18]

The most popular types of dendrimers/poly(amido-amine) dendrimers [19] and poly(arylether) dendrimers

[20] have been rarely used as support of azobenzene moieties. The first example of Fréchet type azo-dendrimers was synthesized by grafting through their core poly(arylether) dendrons bearing a single azobenzene group on the surface, leading to original dendrimers,[21–23] having azobenzene units as terminal groups.

On the other hand, dendrons have been infrequently functionalized with azobenzene units on their surface. The first example was synthesized to be used as building block for dendrimers.[21,22] Besides, more sophisticated systems such as polyether dendrons linked to a fullerene as core have been prepared.[24]

Rau classified azobenzenes into three main groups based on their photochemical behaviour.[25] Unsubstituted photochromic azobenzene makes up the first group, known as ‘azobenzenes’. The thermally stable *trans* isomer exhibits a strong  $\pi\text{-}\pi^*$  transition at 350 nm and a weak  $n\text{-}\pi^*$  transition at 440 nm, whereas the *cis* isomer undergoes similar transitions but with a more intense  $n\text{-}\pi^*$  band. In addition, ‘azobenzenes’ have a relatively poor  $\pi\text{-}\pi^*$  and  $n\text{-}\pi^*$  overlap. The second group, known as ‘aminoazobenzenes’ typically includes azobenzenes that are substituted by an electron-donor group and are characterized by the overlapping of the  $\pi\text{-}\pi^*$  and  $n\text{-}\pi^*$  bands. Finally, azobenzenes bearing both electron-donor and electron-acceptor groups belong to the third category, ‘pseudostilbenes’, where the  $\pi\text{-}\pi^*$  and  $n\text{-}\pi^*$  bands

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are practically superimposed and inverted on the energy scale with respect to the 'azobenzenes' bands.[25]

When donor–acceptor substituted azobenzenes are incorporated into a polymer backbone or side-chain, they provide very versatile materials from the applications point of view. In particular, 'pseudostilbene' azobenzenes undergo rapid *trans-cis-trans* photoisomerization when they are irradiated with linear polarized light. The use of polarized light allows the selective activation of 'pseudostilbenes' with polarization axis parallel to the absorbing radiation.[26–32]

Azobenzene molecules can also undergo chromic changes through aggregation in various media including solution, spin-cast films and Langmuir–Blodgett layers. Both H-type and J-type aggregates have been observed.[33] Although many azo-polymers bearing different architectures have been reported in the literature,[34–39] very recently azobenzene and poly(ethylene glycol) have been employed in the synthesis of amphiphilic azo-dyes, copolymers,[40,41] nanomaterials,[42,43] cellulose derivatives [44,45] and cyclodextrin polymers,[46,47] sometimes forming supramolecular complexes with interesting properties.[48] Poly(ethylene glycol) segments provide flexibility and water solubility to the systems to which they are incorporated.[49,50]

Previously, we published the synthesis and characterization of four novel azo-dyes bearing terminal hydroxyl groups (**RED-PEG** series), the preparation of grafted azo-polymer films containing oligo(ethylene glycol) segments (**AC-g-PE-RED-PEG** series),[51] and the synthesis and characterization of a new series of azo-polymers bearing **RED-PEG** units in their structure (**pnPEGMAN** series).[52] Very recently, we reported the synthesis and characterization of a series of liquid crystalline dyes bearing two amino-nitro substituted azobenzene units linked by well-defined oligo(ethylene glycol) spacers (**DIRED-PEG** series).[53]

In the last ten years, our research group has worked on the synthesis and characterization of amphiphilic azo-dyes and azo-polymers bearing oligo(ethylene glycol) segments with different architectures. Herein, we report the incorporation of high and middle dipole moment azo-dyes into Fréchet type dendrons in order to get new liquid crystalline materials bearing azobenzene units. The thermal and optical properties of these dendrons were studied in detail. Some of them exhibited a liquid crystalline behaviour, which was studied by Differential Scanning Calorimetry (DSC) and Light Polarized Microscopy as a function of the temperature.

## Experimental part

### General conditions

All reagents used in the synthesis of the dendrons were purchased from Aldrich and used as received, without

further purification. Acetone and dichloromethane were dried by distillation over calcium hydride. Precursor dye **RED-PEG-4** was synthesized according to the method previously reported by us and the poly(aryl ether) dendrons were prepared as described in the literature.[54]

<sup>1</sup>H and <sup>13</sup>C NMR spectra of these compounds in CDCl<sub>3</sub> solution were recorded at room temperature on a Bruker Avance 400 MHz spectrometer operating at 400 and 100 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively. Thermal properties of the obtained azo-dendrons were studied by determining *T*<sub>10</sub> (10% weight loss temperature) and *T*<sub>m</sub> (melting point). Thermogravimetric analysis (TGA) was conducted on a Hi-Res TGA 2950 Instrument (from 30 to 650 °C) under inert atmosphere and DSC was carried out in a DSC 2910 Instrument (from –50 to 100 °C), in both cases with a heating rate of 10 °C/min.

All dendrons were dissolved in spectral quality solvents purchased from Aldrich, and their absorption spectra were recorded on a Varian Cary 1 Bio UV-vis (model 8452A) spectrophotometer at room temperature, using 1-cm quartz cuvettes.

### Molecular modelling

Molecular modelling was performed on the obtained compounds using HyperChem™ 6.03 for Windows, using the semi-empirical method PM3, employing the Polak Ribière algorithm with a maximum of 1100 cycles and RMS gradient of 0.05 kcal/Åmol.

### Synthesis of the precursors azo-dyes

Precursor azo-dye **RED-PEG-4** (**5**) was prepared according to the method previously reported by us in the literature.[51]

### Synthesis of the 2-{{4-(4-methoxy-phenylazo)-phenyl}-methyl-amino}-ethanol (**6**)

The intermediate 2-(2-{2-[2-(Methyl-phenyl-amino)-ethoxy]-ethoxy}-ethoxy)-ethanol (**4**) have been synthesized according to the method previously reported by us for the synthesis of the **RED-PEG** series. However, the diazonium salts were prepared *in situ*, since they are not commercially available. Then, p-anisidine (4.7 g, 3.74 mmol) and NaNO<sub>2</sub> (2.43 g, 3.74 mmol) were dissolved in a HCl solution 30% (50 mL) at 0 °C with vigorous stirring. Then, the intermediate (**4**) (4.14 g, 1.16 mmol) was added dropwise, and the reaction mixture was stirred for 4 h. Afterwards, it was neutralized with a NaOH solution (10%). The crude product was extracted with CHCl<sub>3</sub> and the organic phase was dried with anhydrous MgSO<sub>4</sub>, filtered and concentrated at reduced pressure. The resulting product was purified by column chromatography in silica gel using mixtures

ethyl acetate/hexane (6:4 and 7:3) as eluent to yield the precursor dye (**6**). Yield: 68%.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) (Scheme 1(a)):  $\delta$  = 7.76 (d,  $J$  = 9.01 Hz, 2 H,  $\text{H}^3$ ), 7.75 (d,  $J$  = 9.29 Hz, 2 H,  $\text{H}^2$ ), 6.91 (d,  $J$  = 9.02, 2 H,  $\text{H}^4$ ), 6.70 (d,  $J$  = 9.23, 2 H,  $\text{H}^1$ ), 3.79 (s, 3H,  $\text{OCH}_3$ ), 3.65–3.51 (m, 16 H,  $\text{NCH}_2$  and  $\text{OCH}_2$ ), 3.02 (s, 3 H,  $\text{NCH}_3$ ) ppm.

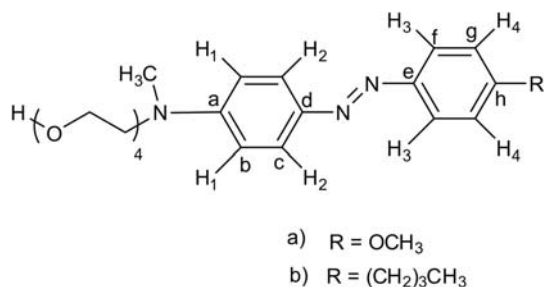
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) (Scheme 1(a)):  $\delta$  = 160.86 (1C,  $\text{C}^b$ ), 151.05 (1C,  $\text{C}^a$ ), 147.36 (1C,  $\text{C}^c$ ), 143.65 (1C,  $\text{C}^d$ ), 124.68 (2C,  $\text{C}^e$ ), 123.81 (2C,  $\text{C}^f$ ), 114.12 (2C,  $\text{C}^g$ ), 111.59 (2C,  $\text{C}^b$ ), 72.72, 70.63, 70.50, 70.18, 66.82, 61.35 (7C,  $\text{OCH}_2$ ), 56.33 ( $\text{CH}_2\text{N}$ ), 55.60 ( $\text{OCH}_3$ ), 39.16 (1C,  $\text{CH}_3\text{N}$ ) ppm.

#### Synthesis of the 2- $\{[4-(4\text{-Butyl-phenylazo})\text{-phenyl}]\text{-methyl-amino}\}$ -ethanol (**7**)

4-butyl-phenylamine (7.89 g, 5.3 mmol) and  $\text{NaNO}_2$  (3.65 g, 5.2 mmol) were dissolved in a HCl solution 30% (80 mL) at  $0^\circ\text{C}$  with vigorous stirring. Then, intermediate (**4**) (10 g, 3.5 mmol) was added dropwise, and the reaction mixture was stirred for 4 h. Afterwards, it was neutralized with a NaOH solution 10%. The crude product was extracted with  $\text{CHCl}_3$ , and the organic solution was dried with anhydrous  $\text{MgSO}_4$ , filtered and concentrated under vacuum. The resulting product was purified by column chromatography in silica gel using mixtures ethyl acetate/hexane (6:4 and 7:3) as eluent, to yield precursor dye (**7**). Yield: 59%.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) (Scheme 1(b)):  $\delta$  = 7.83 (d,  $J$  = 9.1 Hz, 2 H,  $\text{H}^3$ ), 7.73 (d,  $J$  = 8.7 Hz, 2 H,  $\text{H}^2$ ), 7.26 (d,  $J$  = 8.2 Hz, 2 H,  $\text{H}^4$ ), 6.76 (d,  $J$  = 9.1 Hz, 2 H,  $\text{H}^1$ ), 3.72–3.57 (m, 16 H,  $\text{OCH}_2$  and  $\text{NCH}_3$ ), 3.09 (s, 3 H,  $\text{NCH}_3$ ), 2.57 (t, 2 H,  $\text{PhCH}_2\text{CH}_2$ ), 1.54 (m, 2 H,  $\text{PhCH}_2$ ), 1.29 (m, 2H,  $\text{Ph}(\text{CH}_2)_2\text{CH}_2$ ), 0.851 (t, 3H,  $\text{Ph}(\text{CH}_2)_3\text{CH}_3$ ) ppm.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) (Scheme 1(b)):  $\delta$  = 152.67 (1C,  $\text{C}^a$ ), 149.68 (1C,  $\text{C}^c$ ), 148.01 (1C,  $\text{C}^b$ ), 145.02 (1C,  $\text{C}^d$ ), 129.98 (2C,  $\text{C}^g$ ), 127.17 (2C,  $\text{C}^f$ ), 126.53 (2C,  $\text{C}^e$ ), 111.56 (2C,  $\text{C}^b$ ), 72.72, 70.63, 70.50, 70.18, 66.82, 61.35 (7C,  $\text{OCH}_2$ ), 56.33 (1C,  $\text{CH}_2\text{N}$ ), 39.16 1C, ( $\text{CH}_3\text{N}$ ), 34.68 (1C,  $\text{PhCH}_2$ ), 33.50 (1C,



Scheme 1. Assignments for compounds (a) **6** and (b) **7**.

$\text{PhCH}_2\text{CH}_2$ ), 21.84 (1C,  $\text{Ph}(\text{CH}_2)_2\text{CH}_2$ ), 13.77 (1C,  $\text{Ph}(\text{CH}_2)_3\text{CH}_3$ ) ppm.

#### Synthesis of the dendrons

**Synthesis of the 3-Dodecyloxy-5-hydroxybenzyl alcohol (12).** A mixture of 1-bromododecane (1.12 g, 8.02 mmol), 3,5-dihydroxy benzyl alcohol (**11**) (1 g, 4.01 mmol),  $\text{K}_2\text{CO}_3$  (4.43 g, 32 mmol) and 18-crown-6 in 500 mL of acetone was heated to reflux with vigorous stirring for 48 h. The reaction mixture was filtrated and concentrated at reduced pressure. The resulting product was purified by column chromatography in silica gel using mixtures ethyl acetate/hexane (6:4 and 7:3) as eluent, to yield (**12**). Yield: 68%.

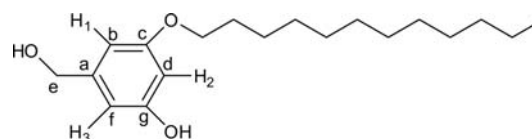
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) (Scheme 2):  $\delta$  = 6.35 (s, 2 H,  $\text{H}^1\text{--H}^3$ ), 6.28 (s, 1 H,  $\text{H}^2$ ), 4.46 (s, 2 H,  $\text{PhCH}_2\text{OH}$ ), 3.80 (t, 2 H,  $\text{PhOCH}_2$ ), 1.69 (m, 2 H,  $\text{PhOCH}_2\text{CH}_2$ ), 1.26 (m, 18 H, all  $\text{CH}_2$  of the aliphatic chain), 0.88 (t, 3 H,  $\text{CH}_3$ ) ppm.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) (Scheme 2):  $\delta$  = 160.41 (1C,  $\text{C}^g$ ), 157.13 (1C,  $\text{C}^c$ ), 142.67 (1C,  $\text{C}^a$ ), 106.32 (1C,  $\text{C}^f$ ), 105.49 (1C,  $\text{C}^b$ ), 101.28 (1C,  $\text{C}^d$ ), 68.13 (1C,  $\text{C}^e$ ), 64.91 (1C,  $\text{PhOCH}_2$ ), 31.88 (1C,  $\text{PhOCH}_2\text{CH}_2$ ), 29.61, 29.41, 29.32, 29.18, 25.98, 22.64 (9C, all  $\text{CH}_2$  of the aliphatic chain), 14.05 (1C,  $\text{CH}_3$ ) ppm.

#### Synthesis of (2- $\{2-[2-(2\text{-Iodo-ethoxy})\text{-ethoxy}]\text{-ethoxy}\}$ -ethyl)-methyl- $\{4-(4\text{-nitro-phenylazo})\text{-phenyl}\}$ -amine (**8**).

The intermediate (**5**) (4.37 g, 10.11 mmol) was reacted with imidazole (0.89 g, 13.1 mmol), triphenylphosphine (3.44 g, 13.1 mmol) and iodine (3.34 g, 13.1 mmol) in 50 mL anhydrous dichloromethane at room temperature. The resulting solution was stirred for 6 h, filtered and concentrated at reduced pressure. The crude product was purified by column chromatography in silica gel, using mixtures of ethyl acetate/hexane (4:6, 5:5, and 6:4) as eluent. Since this intermediate is very unstable, it was immediately used in the next reaction without further purification. Relative yield: 80%.

**Synthesis of [3-dodecyloxy-5-(2- $\{2-[2-(2\text{-methyl-}[4-(4\text{-nitro-phenylazo})\text{-phenyl}]\text{-amino}\}\text{-ethoxy})\text{-ethoxy}\}$ -ethoxy)-phenyl]-methanol (**13G<sub>1</sub>OH**).** (**8**) (0.706 g, 229 mmol), (**12**) (1.14 g, 210 mmol),  $\text{K}_2\text{CO}_3$  (1.58 g, 149 mmol) and 18-crown-6 were dissolved in 50 mL of



Scheme 2. Assignments for compound **12**.

anhydrous DMF, and the reaction mixture was heated with stirring at 80 °C for 48 h. Then, it was filtrated and evaporated at reduced pressure. The crude product was purified by column chromatography in silica gel using mixtures ethyl acetate/hexane (5:5, and 6:4) as eluent, to yield the first generation dendron **13G<sub>1</sub>OH**. Yield: 62%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (Scheme 3(a)): δ = 8.24 (d, *J* = 9.02 Hz, 2 H, H<sup>7</sup>), 7.84 (d, *J* = 9.05 Hz, 2 H, H<sup>6</sup>), 7.81 (d, *J* = 9.21 Hz, 2 H, H<sup>5</sup>), 6.70 (d, *J* = 9.23 Hz, 2 H, H<sup>4</sup>), 6.44 (s, 2 H, H<sup>1</sup>-H<sup>3</sup>), 6.31 (s, 1 H, H<sup>2</sup>), 4.53 (s, 2 H, PhCH<sub>2</sub>OH), 4.03 (t, 2 H, PhOCH<sub>2</sub> of the tetra(ethylene glycol) chain), 3.84 (t, 2 H, PhOCH<sub>2</sub> of the aliphatic chain), 3.75 (t, 2 H, CH<sub>2</sub>N), 3.64–3.57 (m, 12 H, OCH<sub>2</sub>), 3.06 (s, 3 H, CH<sub>3</sub>N), 1.68 (q, 2 H, PhOCH<sub>2</sub>CH<sub>2</sub>), 1.35 (q, 2 H, Ph(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 1.30–1.19 (m, 18 H, all CH<sub>2</sub> of the aliphatic chain), 0.81 (t, 3 H, CH<sub>3</sub>) ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (Scheme 3(a)): δ = 160.63 (1C, C<sup>c</sup>), 160.22 (1C, C<sup>e</sup>), 156.89 (1C, C<sup>k</sup>), 152.67 (1C, C<sup>n</sup>), 147.53 (1C, C<sup>g</sup>), 143.92 (1C, C<sup>j</sup>), 143.37 (1C, C<sup>a</sup>), 126.08 (2C, C<sup>i</sup>), 124.62 (2C, C<sup>m</sup>), 122.59 (2C, C<sup>l</sup>), 111.60 (2C, C<sup>h</sup>), 105.60 (1C, C<sup>b</sup>), 105.26 (1C, C<sup>f</sup>), 101.04 (1C, C<sup>d</sup>), 70.88, 70.77, 69.80, 67.63 (6C, OCH<sub>2</sub>), 68.68 (1C, PhOCH<sub>2</sub> aliphatic chain), 68.22 (1C, PhOCH<sub>2</sub> of the tetra(ethylene glycol) chain), 65.35 (1C, C<sup>o</sup>), 52.31 (1C, NCH<sub>2</sub>), 39.26 (1C, NCH<sub>3</sub>), 31.91, 29.65, 29.62, 29.59, 29.39, 29.31, 26.06, 22.65 (10C, all CH<sub>2</sub> of the aliphatic chain), 14.03 (1C, CH<sub>3</sub>) ppm. MALDITOF: C<sub>40</sub>H<sub>58</sub>N<sub>4</sub>O<sub>8</sub> Calcd: 722.91 Found: (*m/z* = 722.47).

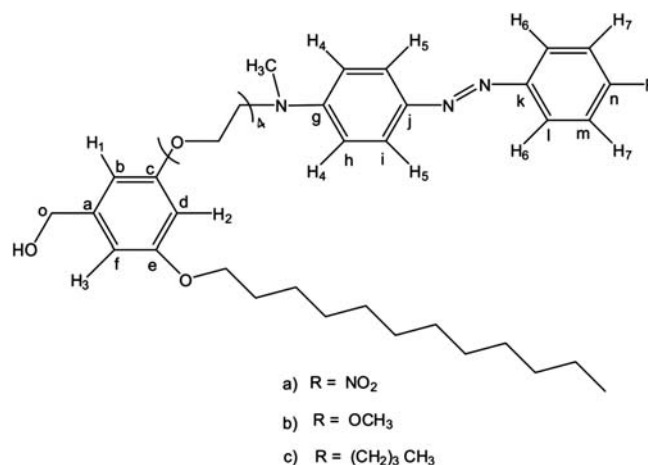
*Synthesis of the (2-{2-[2-(2-Iodo-ethoxy)-ethoxy]-ethoxy}-ethyl)-[4-(4-methoxy-phenylazo)-phenyl]-methyl-amine (9).* (6) (3.77 g, 9.0 mmol), imidazole (0.79 g, 11.7 mmol), triphenylphosphine (3.07 g, 11.7 mmol) and iodine (2.98 g, 11.7 mmol) were dissolved in 50 mL anhydrous dichloromethane at room temperature. The

resulting solution was stirred for 6 h, filtered and concentrated at reduced pressure. The crude product was purified by column chromatography in silica gel using mixtures of ethyl acetate/hexane (7:3) as eluent. Since this intermediate is very instable, it was immediately used in the next step without further purification. Relative yield: 85%.

*Synthesis of the [3-Dodecyloxy-5-(2-{2-[2-(2-{4-(4-methoxy-phenylazo)-phenyl]-methyl-amino}-ethoxy)-ethoxy]-ethoxy)-phenyl]-methanol (14G<sub>1</sub>OH).* A mixture of (12) (2.02 g, 6.89 mmol), (9) (3.02 g, 5.73 mmol), K<sub>2</sub>CO<sub>3</sub> (4.5 g, 32 mmol) and 18-crown-6 dissolved in 50 mL of anhydrous DMF was heated with stirring at 80 °C for 48 h. Then, the reaction mixture was filtrated and evaporated at reduced pressure. The crude product was purified by column chromatography in silica gel using mixtures ethyl acetate/hexane (5:5, 6:4 and 7:3) as eluent to yield the first generation dendron **14G<sub>1</sub>OH**. Yield: 64%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (Scheme 3(b)): δ = 7.83 (d, *J* = 9.1 Hz, 2 H, H<sup>6</sup>), 7.73 (d, *J* = 8.7 Hz, 2 H, H<sup>5</sup>), 7.26 (d, *J* = 8.2 Hz, 2 H, H<sup>7</sup>), 6.76 (d, *J* = 9.1 Hz, 2 H, H<sup>4</sup>), 6.50 (s, 2 H, H<sup>1</sup>-H<sup>3</sup>), 6.37 (s, 1 H, H<sup>2</sup>), 4.60 (s, 2 H, PhCH<sub>2</sub>OH), 4.08 (t, 2 H, PhOCH<sub>2</sub> of the tetra(ethylene glycol) chain), 3.90 (t, 2 H, PhOCH<sub>2</sub> of the aliphatic chain), 3.87 (s, 3 H, PhOCH<sub>3</sub>), 3.82 (t, 2 H, CH<sub>2</sub>N), 3.69–3.62 (m, 12 H, OCH<sub>2</sub>), 3.11 (s, 3 H, CH<sub>3</sub>N), 1.74 (m, 2 H, PhOCH<sub>2</sub>CH<sub>2</sub>), 1.42 (m, 2 H, PhO(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 1.34–1.26 (m, 16 H, all CH<sub>2</sub> of the aliphatic chain), 0.884 (t, 3 H, CH<sub>3</sub>) ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (Scheme 3(b)): δ = 160.72 (1C, C<sup>n</sup>), 160.34 (1C, C<sup>c</sup>), 159.96 (1C, C<sup>e</sup>), 150.90 (1C, C<sup>g</sup>), 147.34 (1C, C<sup>k</sup>), 143.51 (1C, C<sup>a</sup>), 143.35 (1C, C<sup>j</sup>), 124.49 (2C, C<sup>i</sup>), 123.71 (2C, C<sup>l</sup>), 113.99 (2C, C<sup>m</sup>), 111.36 (2C, C<sup>h</sup>), 105.30 (1C, C<sup>f</sup>), 104.86 (1C, C<sup>b</sup>), 100.56 (1C, C<sup>d</sup>), 70.67, 70.59, 69.62,



Scheme 3. Assignments for compounds (a) 13G<sub>1</sub>OH, (b) 14G<sub>1</sub>OH and (c) 15G<sub>1</sub>OH.

67.33 (6C, OCH<sub>2</sub>), 68.46 (1C, PhOCH<sub>2</sub> of the aliphatic chain), 67.97 (1C, PhOCH<sub>2</sub> tetra(ethylene glycol) chain), 65.04 (1C, C<sup>o</sup>), 55.39 (1C, NCH<sub>2</sub>), 52.08 (1C, OCH<sub>3</sub>), 39.10 (NCH<sub>3</sub>), 31.83, 29.58, 29.52, 29.32, 29.26, 29.16, 25.96, 22.60 (10C, all CH<sub>2</sub> of the aliphatic chain), 14.05 (1C, CH<sub>3</sub>) ppm.

MALDITOF: C<sub>41</sub>H<sub>61</sub>N<sub>3</sub>O<sub>7</sub> Calcd: 707 Found: (707.41 *m/z*).

*Synthesis of the [4-(4-Butyl-phenylazo)-phenyl]-(2-{2-[2-(2-iodo-ethoxy)-ethoxy]-ethoxy}-ethyl)-methyl-amine (10).* The intermediate (7) (3.90 g, 8.8 mmol) was reacted with imidazole (0.77 g, 11.4 mmol), triphenylphosphine (2.99 g, 11.4 mmol) and iodine (2.90 g, 11.4 mmol) in 50 mL of anhydrous dichloromethane. The resulting solution was stirred at room temperature for 6 h, filtered and concentrated at reduced pressure. The crude product was purified by flash column chromatography in silica gel, using a mixture ethyl acetate/hexane (7:3) as eluent. Since this intermediate is very instable, it has to be immediately used in the next reaction without further purification. Relative yield: 85%.

*Synthesis of the [3-(2-{2-[2-(2-{[4-(4-Butyl-phenylazo)-phenyl]-methyl-amino}-ethoxy)-ethoxy]-ethoxy}-ethoxy)-5-dodecyloxy-phenyl]-methanol (15G<sub>1</sub>OH).* A mixture of (12) (0.922 g, 5.5 mmol), (10) (1.44 g, 2.6 mmol), K<sub>2</sub>CO<sub>3</sub> (2.06 g, 14.9 mmol) and 18-crown-6 dissolved in 50 mL of anhydrous DMF was heated with vigorous stirring at 80 °C for 48 h. Then, the reaction mixture was filtrated and evaporated at reduced pressure. The crude product was purified by column chromatography in silica gel using mixtures ethyl acetate/hexane (5:5, 6:4 and 7.3) as eluent, to yield the first generation dendron 15G<sub>1</sub>OH. Yield: 63%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (Scheme 3(c)): δ = 7.75 (d, *J* = 9.05 Hz, 2 H, H<sup>6</sup>), 7.67 (d, *J* = 8.29 Hz, 2H, H<sup>5</sup>), 7.19 (d, *J* = 8.66 Hz, 2H, H<sup>7</sup>), 6.67 (d, *J* = 9.14 Hz, 2H, H<sup>4</sup>), 6.42(s, 2 H, H<sup>1</sup>-H<sup>3</sup>), 6.31(s, 1 H, H<sup>2</sup>), 4.48(s, 2 H, PhCH<sub>2</sub>OH), 4.08(t, 2H, PhOCH<sub>2</sub> of the tetra(ethylene glycol) chain), 3.91 (t, 2 H, PhOCH<sub>2</sub> of the aliphatic chain), 3.81(t, 2H, CH<sub>2</sub>N), 3.69–3.60 (m, 12 H, OCH<sub>2</sub>), 3.08 (s, 3H, CH<sub>3</sub>N), 2.65 (t, 2H, PhCH<sub>2</sub>CH<sub>2</sub>), 1.74(m, 2H, PhOCH<sub>2</sub>CH<sub>2</sub>), 1.63(m, 2H, PhCH<sub>2</sub>), 1.43–1.26(m, 20 H, Ph(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub> and all CH<sub>2</sub> of the aliphatic chain), 0.93(t, 3H, CH<sub>3</sub>), 0.87(t, 3H, Ph(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>) ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (Scheme 3(c)): δ = 160.45 (1C, C<sup>e</sup>), 160.08 (1C, C<sup>e</sup>), 151.37 (1C, C<sup>g</sup>), 151.17 (1C, C<sup>k</sup>), 144.66 (1C, C<sup>n</sup>), 143.65 (1C, C<sup>l</sup>), 143.29 (1C, C<sup>a</sup>), 128.91 (2C, C<sup>m</sup>), 124.79 (2C, C<sup>l</sup>), 122.09 (2C, C<sup>l</sup>), 111.39 (2C, C<sup>h</sup>), 105.40 (2C, C<sup>f</sup>), 104.98 (1C, C<sup>b</sup>), 100.70 (1C, C<sup>d</sup>), 70.78, 70.69, 69.70, 68.54 (6C, OCH<sub>2</sub>), 68.06 (1C, PhOCH<sub>2</sub> of the aliphatic chain), 67.44 (1C, PhOCH<sub>2</sub> of the tetra(ethylene glycol) chain), 65.27 (1C, C<sup>o</sup>), 52.17 (NCH<sub>2</sub>), 39.21 (NCH<sub>3</sub>),

35.48 (1C, PhCH<sub>2</sub>), 33.49 (1C, PhCH<sub>2</sub>CH<sub>2</sub>), 31.89, 29.60, 29.31, 26.02, 22.64 (10C, all CH<sub>2</sub> of the aliphatic chain), 22.31 (1C, Ph(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 14.07 (1C, CH<sub>3</sub>), 13.89 (1C, Ph(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>) ppm.

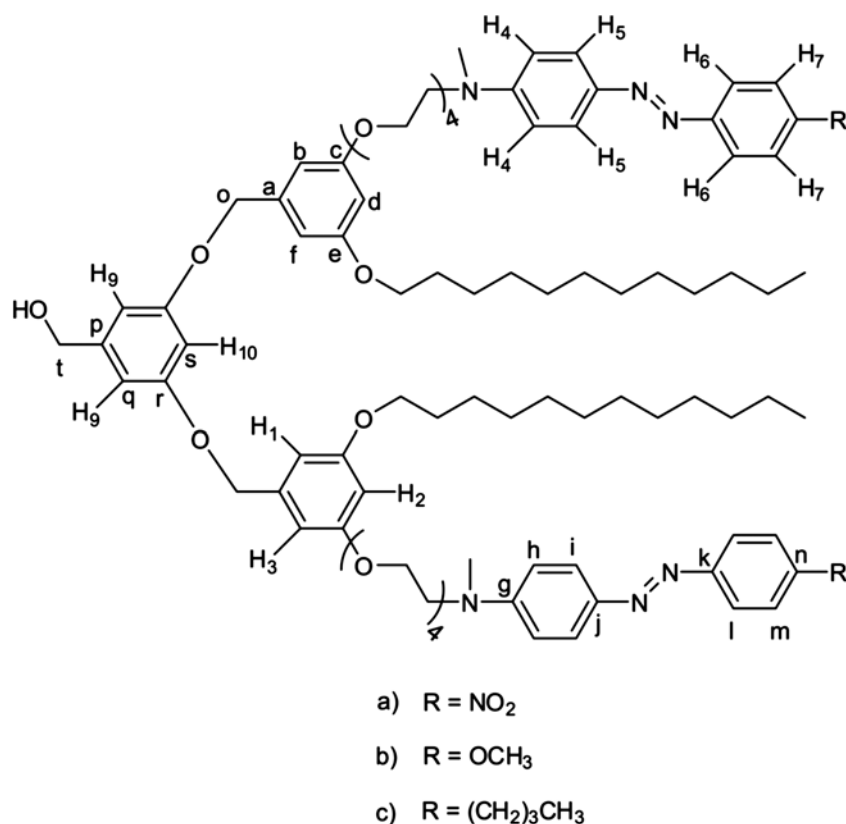
MALDITOF: C<sub>44</sub>H<sub>67</sub>N<sub>3</sub>O<sub>3</sub> Calcd: 733 Found: (*m/z* = 733.54).

*Synthesis of [2-(2-{2-[2-(3-Dodecyloxy-5-iodomethyl-phenoxy)-ethoxy]-ethoxy}-ethoxy)-ethyl]-methyl-[4-(4-nitro-phenylazo)-phenyl]-amine (16G<sub>1</sub>I).* 13G<sub>1</sub>OH (0.22 g, 0.44 mmol) was treated with imidazole (0.055 g, 0.80 mmol), triphenylphosphine (0.21 g, 0.80 mmol) and iodine (0.20 g, 0.80 mmol) in 50 mL anhydrous dichloromethane at room temperature. The resulting solution was stirred for 6 h, filtered and concentrated at reduced pressure. The crude product was purified by column chromatography in silica gel using a mixture ethyl acetate/hexane (5:5 and 6:4) as eluent to give 16G<sub>1</sub>I. Because of its instability, this intermediate was immediately employed in the next step. Relative yield: 65%.

*Synthesis of 3,5-Bis-[3-dodecyloxy-5-(2-{2-[2-(2-{methyl-[4-(4-nitro-phenylazo)-phenyl]-amino}-ethoxy)-ethoxy]-ethoxy}-benzyloxy)-phenyl]-methanol (19G<sub>2</sub>OH).* 3,5-dihydroxy benzylic alcohol (11) (0.043 g, 0.31 mmol) was reacted with 16G<sub>1</sub>I (0.13 g, 0.015 mmol), K<sub>2</sub>CO<sub>3</sub> (0.18 g, 1.2 mmol) and a catalytic amount of 18-crown-6 in 50 mL of dry acetone. The reaction mixture was heated to reflux for 48 h, cooled to room temperature, filtered and concentrated at reduced pressure. The crude product was purified by column chromatography in silica gel using mixtures of ethyl acetate/hexane 8:2, 9:1 and pure ethyl acetate as eluent, to give second-generation dendron 19G<sub>2</sub>OH. Yield: 45%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (Scheme 4(a)): δ = 8.28 (d, *J* = 9.10 Hz, 4 H, H<sup>7</sup>), 7.89 (d, *J* = 9.01 Hz, 4 H, H<sup>6</sup>), 7.87 (d, *J* = 9.30 Hz, 4 H, H<sup>5</sup>), 6.75 (d, *J* = 9.30 Hz, 4H, H<sup>4</sup>), 6.57 (s, 2 H, H<sup>2</sup>), 6.54 (s, 4 H, H<sup>1</sup>-H<sup>3</sup>), 6.49 (s, 1 H, H<sup>10</sup>), 6.39 (s, 2 H, H<sup>9</sup>), 4.92 (s, 4 H, PhCH<sub>2</sub>OPh), 4.59(s, 2 H, PhCH<sub>2</sub>OH), 4.08 (t, 4 H, PhOCH<sub>2</sub> of the tetra(ethylene glycol) chain), 3.89 (t, 4 H, PhOCH<sub>2</sub> of the aliphatic chain), 3.80 (t, 4 H, NCH<sub>2</sub>), 3.70–3.60 (m, 24 H, OCH<sub>2</sub>), 3.11 (s, 6 H, NCH<sub>3</sub>), 1.74 (m, 4 H, PhOCH<sub>2</sub>CH<sub>2</sub>), 1.41 (m, 4H, PhO(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 1.33–1.25 (m, 36 H, all CH<sub>2</sub> of the aliphatic chain), 0.87 (t, 6 H, CH<sub>3</sub>) ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (Scheme 4(a)): δ = 160.51 (1C, C<sup>r</sup>), 160.08 (2C, C<sup>e-c</sup>), 156.09 (2C, C<sup>k</sup>), 152.98 (2C, C<sup>n</sup>), 147.29 (2C, C<sup>g</sup>), 143.74 (2C, C<sup>l</sup>), 143.41 (1C, C<sup>p</sup>), 139.12 (2C, C<sup>a</sup>), 126.50 (4C, C<sup>l</sup>), 124.63 (4C, C<sup>m</sup>), 122.34 (4C, C<sup>l</sup>), 111.85 (4C, C<sup>h</sup>), 106.03 (1C, C<sup>b</sup>), 105.71 (4C, C<sup>q-f</sup>), 101.31 (1C, C<sup>s</sup>), 100.98 (2C, C<sup>d</sup>), 70.71, 70.68, 69.96, 69.66, 67.43 (12c, OCH<sub>2</sub>), 70.81 (2C, C<sup>o</sup>), 68.54 (2C, PhOCH<sub>2</sub> of the aliphatic chain), 68.10 (2C, PhOCH<sub>2</sub> tetra(ethylene glycol)



Scheme 4. Assignments for compounds (a) 19G2OH, (b) 20G2OH and (c) 21G2OH.

chain), 65.17 (1C, C<sup>i</sup>), 55.20 (2C, NCH<sub>2</sub>), 39.33 (2C, NCH<sub>3</sub>), 31.85, 29.67, 29.64, 29.59, 29, 56, 29, 39, 29.32, 29.23, 26.03, 22.66 (20C, CH<sub>2</sub> all of the aliphatic chain), 14.00 (2C, CH<sub>3</sub>) ppm.

MALDITOF: C<sub>87</sub>H<sub>120</sub>N<sub>8</sub>O<sub>17</sub> Calcd: 1549.93 Found: ( $m/z = 1548.19$ ).

*Synthesis of the [2-(2-{2-[2-(3-Dodecyloxy-5-iodomethylphenoxy)-ethoxy]-ethoxy}-ethoxy)-ethyl]-[4-(4-methoxyphenylazo)-phenyl]-methyl-amine (17G<sub>1</sub>I).* **14G<sub>1</sub>OH** (0.45 g, 0.63 mmol), imidazole (0.056 g, 0.82 mmol), triphenylphosphine (0.21 g, 0.82 mmol) and iodine (0.21 g, 0.82 mmol) were dissolved in 50 mL of anhydrous dichloromethane. The resulting solution was stirred at room temperature for 6 h, filtered and concentrated at reduced pressure. The crude product was purified by column chromatography in silica gel using a mixture of ethyl acetate/hexane (8:2) as eluent, to give **17G<sub>1</sub>I**. Because of its instability, this intermediate was immediately used in the next reaction. Relative yield: 61%.

*Synthesis of the {3,5-Bis-[3-dodecyloxy-5-(2-{2-[2-(2-{4-(4-methoxy-phenylazo)-phenyl]-methyl-amino}-ethoxy)-ethoxy]-ethoxy)-benzyloxy]-phenyl}-methanol (20G<sub>2</sub>OH).* 3,5-dihydroxy benzylic alcohol (**11**) (0.017 g, 0.12 mmol), **17G<sub>1</sub>I** (0.20 g, 0.024 mmol), K<sub>2</sub>CO<sub>3</sub>

(0.067 g, 0.48 mmol) and a catalytic amount of 18-crown-6 were dissolved in 50 mL of dry acetone. The reaction mixture was heated to reflux for 48 h, cooled to room temperature, filtered and concentrated at reduced pressure. The crude product was purified by column chromatography in silica gel using mixtures of ethyl acetate/hexane 8:2, 9:1 and pure ethyl acetate as eluent, to give second-generation dendron **20G<sub>2</sub>OH**. Yield: 46%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (Scheme 4(b)):  $\delta = 7.82$  (d,  $J = 6.01$  Hz, 4 H, H<sup>6</sup>), 7.79 (d,  $J = 6.03$  Hz, 4 H, H<sup>5</sup>), 6.96 (d,  $J = 8.88$  Hz, 4 H, H<sup>7</sup>), 6.73 (d,  $J = 8.8$  Hz, 4 H, H<sup>4</sup>), 6.57 (s, 2 H, H<sup>2</sup>), 6.55 (s, 4 H, H<sup>1</sup>-H<sup>3</sup>), 6.5 (s, 1 H, H<sup>10</sup>), 6.4 (s, 2 H, H<sup>9</sup>), 4.92 (s, 4 H, PhOCH<sub>2</sub>Ph), 4.58 (s, 2 H, PhCH<sub>2</sub>OH), 4.08 (t, 4 H, PhOCH<sub>2</sub> of the tetra (ethylene glycol) chain), 3.90 (t, 4 H, PhOCH<sub>2</sub> of the aliphatic chain), 3.85 (s, 6 H, PhOCH<sub>3</sub>), 3.80 (t, 4 H, NCH<sub>2</sub>), 3.63–3.657 (m, 24 H, OCH<sub>2</sub>), 3.05 (s, 6 H, NCH<sub>3</sub>), 1.74 (m, 4 H, PhOCH<sub>2</sub>CH<sub>2</sub>), 1.41 (m, 4 H, Ph (CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 1.25 (m, 36 H, all CH<sub>2</sub> of the aliphatic chain), 0.87 (t, 6H, CH<sub>3</sub>) ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (Scheme 4(b)):  $\delta = 160.77$  (2C, C<sup>n</sup>), 160.45 (2C, C<sup>r</sup>), 160.05 (4C, C<sup>e-c</sup>), 150.95 (2C, C<sup>g</sup>), 147.42 (2C, C<sup>k</sup>), 143.59 (2C, C<sup>j</sup>), 143.50 (1C, C<sup>p</sup>), 139.07 (2C, C<sup>a</sup>), 124.55 (4C, C<sup>i</sup>), 123.77 (4C, C<sup>l</sup>), 114.04 (4C, C<sup>m</sup>), 111.37 (4C, C<sup>h</sup>), 106.03 (2C, C<sup>b</sup>), 105.99 (4C, C<sup>q-f</sup>), 101.30 (1C, C<sup>s</sup>),

100.90 (2C, C<sup>d</sup>), 70.77 (2C, C<sup>o</sup>), 70.74, 70.68, 70.64, 69.95, 69.64, 67.41 (12C, OCH<sub>2</sub>), 68.07 (2C, PhOCH<sub>2</sub> of the aliphatic chain), 68.52 (2C, PhOCH<sub>2</sub> tetra(ethylene glycol) chain), 65.13 (1C, C<sup>i</sup>), 55.46 (2C, NCH<sub>2</sub>), 52.05 (2C, PhOCH<sub>3</sub>), 39.16 (2C, NCH<sub>3</sub>), 31.88, 29.63, 29.60, 29.58, 29.55, 29.38, 29.31, 29.22, 26.02, 22.65 (20C, all CH<sub>2</sub> of the aliphatic chain), 14.11 (2C, CH<sub>3</sub>) ppm.

MALDITOF: C<sub>89</sub>H<sub>126</sub>N<sub>6</sub>O<sub>15</sub> Calcd: 1518 Found: (*m/z* = 1518.14).

*Synthesis of the [4-(4-Butyl-phenylazo)-phenyl]-[2-(2-{2-[2-(3-dodecyloxy-5-iodomethyl-phenoxy)-ethoxy]-ethoxy}-ethoxy)-ethyl]-methyl-amine (18G<sub>1</sub>I). 15G<sub>1</sub>OH (0.5 g, 0.68 mmol), imidazole (0.060 g, 0.88 mmol), triphenylphosphine (0.23 g, 0.88 mmol) and iodine (0.22 g, 0.88 mmol) were dissolved in 50 mL anhydrous dichloromethane. The resulting solution was stirred for 6 h at room temperature, filtered and concentrated at reduced pressure. The crude product was purified by flash column chromatography in silica gel using a mixture of ethyl acetate/hexane (8:2) as eluent to give 18G<sub>1</sub>I. This instable intermediate was immediately employed in the next reaction. Relative yield: 60%.*

*Synthesis of the {3,5-Bis-[3-(2-[2-[2-(2-{[4-(4-butyl-phenylazo)-phenyl]-methyl-amino}-ethoxy)-ethoxy]-ethoxy}-ethoxy)-5-dodecyloxy-benzyloxy]-phenyl}-methanol (21G<sub>2</sub>OH). 3,5-dihydroxy benzylic alcohol (11) (0.018 g, 0.13 mmol) was reacted with 18G<sub>1</sub>I (0.22 g, 0.26 mmol), K<sub>2</sub>CO<sub>3</sub> (0.074 g, 0.53 mmol) and a catalytic amount of 18-crown-6 in dry acetone (50 mL). The reaction mixture was heated to reflux for 48 h, cooled to room temperature, filtered and concentrated at reduced pressure. The crude product was purified by column chromatography in silica gel using mixtures of ethyl acetate/hexane 8:2, 9:1 and pure ethyl acetate as eluent, to give second-generation dendron 21G<sub>2</sub>OH. Yield: 45%.*

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (Scheme 4(c)): δ = 7.75 (d, *J* = 9.01 Hz, 4H, H<sup>6</sup>), 7.66(d, *J* = 8.24 Hz, 4H, H<sup>5</sup>), 7.19(d, *J* = 9.83 Hz, 2H, H<sup>7</sup>), 6.66(d, *J* = 9.09 Hz, 2H, H<sup>4</sup>), 6.51(s, 2H, H<sup>2</sup>), 6.48(s, 4H, H<sup>1</sup>-H<sup>3</sup>), 6.42(s, 1 H, H<sup>10</sup>), 6.33(s, 2H, H<sup>9</sup>), 4.85(s, 4H, PhCH<sub>2</sub>OPh), 4.52(s, 2H, PhCH<sub>2</sub>OH), 4.02(t, 4H, PhOCH<sub>2</sub> of the tetra(ethylene glycol) chain), 3.83(t, 4H, PhOCH<sub>2</sub> of the aliphatic chain), 3.74(t, 4H, NCH<sub>2</sub>), 3.58-3.54(m, 24H, OCH<sub>2</sub>), 2.99(s, 6H, NCH<sub>3</sub>), 2.58(t, 4H, PhCH<sub>2</sub>CH<sub>2</sub>), 1.67(m, 4H, PhOCH<sub>2</sub>CH<sub>2</sub>), 1.55(m, 4H, PhCH<sub>2</sub>), 1.30-1.18(m, 38H Ph(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub> and all CH<sub>2</sub> of the aliphatic chain), 0.86(t, 6H, CH<sub>3</sub>), 0.80(t, 6H, Ph(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>) ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (Scheme 4(c)): δ = 160.44 (2C, C<sup>f</sup>), 160.04 (2C, C<sup>e</sup>), 160.00 (2C, C<sup>c</sup>), 151.37 (2C, C<sup>g</sup>), 151.15 (2C, C<sup>k</sup>), 144.63 (2C, C<sup>n</sup>), 143.63 (2C, C<sup>j</sup>), 139.07 (3C, C<sup>p-a</sup>), 128.89 (4C, C<sup>m</sup>), 124.77 (4C, C<sup>i</sup>), 122.07 (4C, C<sup>l</sup>), 111.36 (4C, C<sup>h</sup>), 106.02 (2C, C<sup>f</sup>), 105.62 (4C, C<sup>q-b</sup>), 101.68 (1C, C<sup>s</sup>), 100.87 (2C,

C<sup>d</sup>), 70.76 (2C, C<sup>o</sup>), 70.73, 70.66, 70.63, 69.63, 67.40 (12C, OCH<sub>2</sub>), 68.50 (2C, PhOCH<sub>2</sub> of the aliphatic chain), 68.06 (2C, PhOCH<sub>2</sub> of the tetra(ethylene glycol) chain), 65.04 (1C, C<sup>i</sup>), 52.13 (2C, NCH<sub>2</sub>), 39.17 (2C, NCH<sub>3</sub>), 35.45 (2C, PhCH<sub>2</sub>), 33.46 (2C, PhCH<sub>2</sub>CH<sub>2</sub>), 31.86, 29.63, 29.62, 29.58, 29.55, 29.37, 29.30, 29.21, 26.00, 22.63 (20C, all CH<sub>2</sub> of the aliphatic chain), 22.28 (2C, Ph(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 14.07 (2C, CH<sub>3</sub>), 13.89 (2C, Ph(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>) ppm.

MALDITOF: C<sub>95</sub>H<sub>138</sub>N<sub>6</sub>O<sub>13</sub> Calcd: 1571 Found: (*m/z* = 1571.22).

## Results and discussion

### Synthesis of the dendrons

A convergent synthetic approach was used for the preparation of three different series of first and second generation dendrons bearing azobenzene units in the periphery, using 3,5-dihydroxy benzylic alcohol as built unit. The first series of dendrons was functionalized with amino-nitro substituted azobenzenes, the second one with amino-methoxy-substituted azo-dyes and the third one with amino-butyl substituted ones. The syntheses of the precursor dyes, first-generation (G<sub>1</sub>OH) and second-generation dendrons (G<sub>2</sub>OH) are shown in Figures 1 and 2, respectively.

Precursor dye RED-PEG-4 (5) was prepared according to the method previously reported by us.[51] Precursors (6) and (7) were prepared following the same synthetic methodology used for the synthesis of RED-PEG-4. The intermediate 2-(2-{2-[2-(Methyl-phenyl-amino)-ethoxy]-ethoxy}-ethoxy)-ethanol (4) was synthesized according to the method described by us and the diazonium salts required for the last two series were prepared *in situ*. Then, p-anisidine (1 eq) was reacted with NaNO<sub>2</sub> (1 eq) in a HCl solution (30%) at 0°C. Afterwards, (4) (1 eq) was added dropwise to the reaction mixture in order to obtain (6) with 68% yield. On the other hand, 3,5-dihydroxy benzylic alcohol (11) (1 eq) was reacted with 1-dodecyl bromide (1 eq) using K<sub>2</sub>CO<sub>3</sub> as base and acetone as solvent in the presence of a catalytic amount of 18-crown-6 to give the asymmetric dendron (12). Intermediate (6) was treated in the presence of iodine, imidazole and PPh<sub>3</sub> to give the corresponding alkyl iodide (9). This compound was reacted with (12), using K<sub>2</sub>CO<sub>3</sub> as base and DMF as solvent in the presence of 18-crown-6 to give the first-generation dendron 14G<sub>1</sub>OH. Furthermore, this compound was treated with iodine, imidazole and PPh<sub>3</sub> to give the corresponding alkyl iodide 17G<sub>1</sub>I. Finally, 3,5-dihydroxy benzylic alcohol (11) (1 eq) was reacted with 17G<sub>1</sub>I (2 eq) in the presence of K<sub>2</sub>CO<sub>3</sub> and 18-crown-6 in acetone to give second-generation dendron 17G<sub>2</sub>OH. The other first- and second-generation dendrons were prepared following



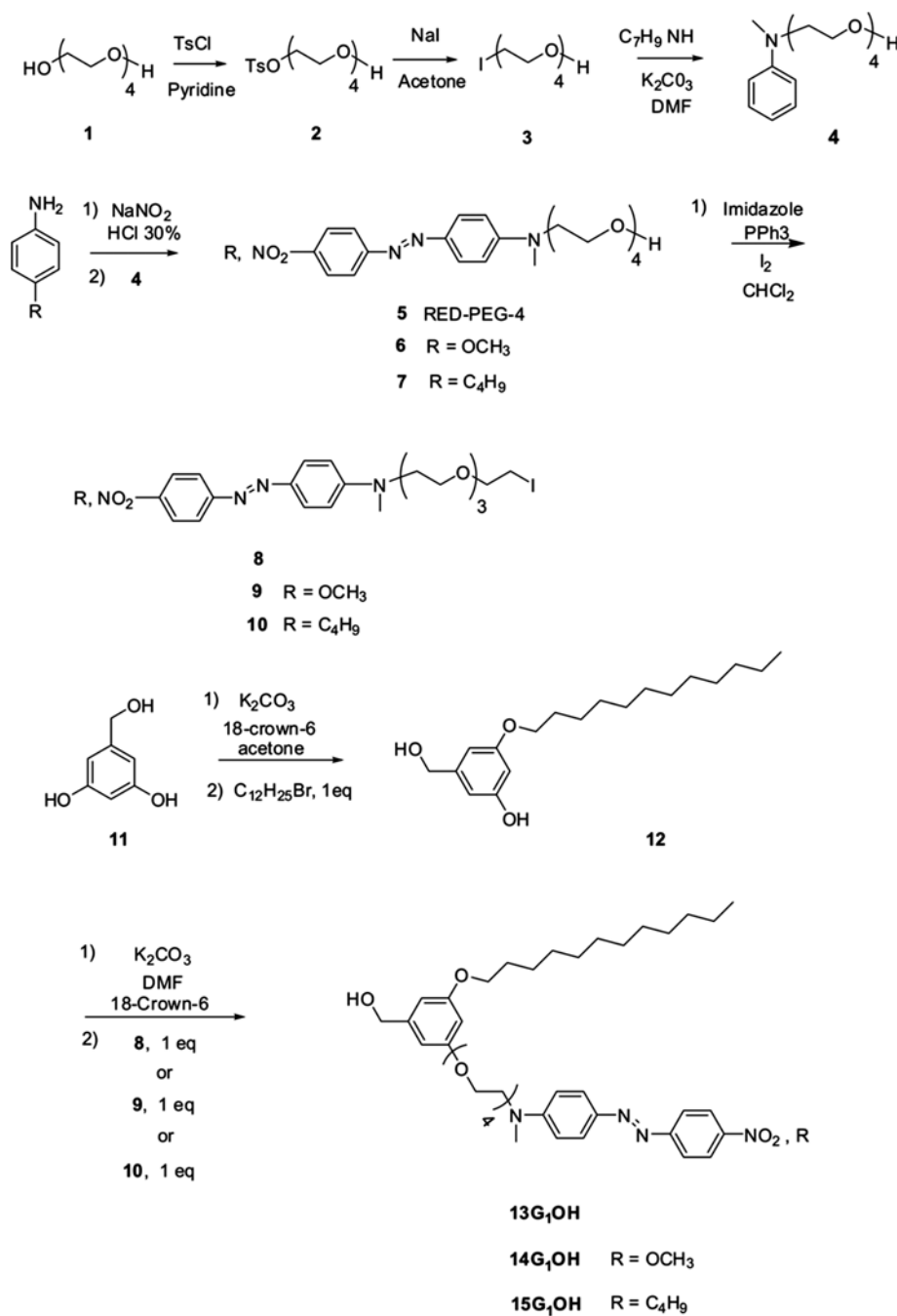


Figure 1. Synthesis of the precursor dyes and the first-generation dendrons.

the same synthetic methodology employed for the obtainment of dendrons **14G<sub>1</sub>OH** and **20G<sub>2</sub>OH**. Their signal assignments are included in the experimental section.

#### Characterization of the dendrons

The structure of all the obtained dendrons were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies, and their

molecular weights and purity were confirmed by MALDITOF mass spectrometry using dithranol as matrix. The <sup>1</sup>H NMR spectrum of **14G<sub>1</sub>OH** in CDCl<sub>3</sub> solution is shown in Figure 3(a). As we can see, there are six signals in aromatic region at 7.83, 7.73, 7.26, 6.76, 6.50 and 6.37 ppm due to the aromatic protons present in the azobenzene unit and the phenyl group H<sup>6</sup>, H<sup>5</sup>, H<sup>7</sup>, H<sup>4</sup>, H<sup>1</sup>-H<sup>3</sup> and H<sup>2</sup>, respectively. In the aliphatic region, we can observe eight signals: a singlet at

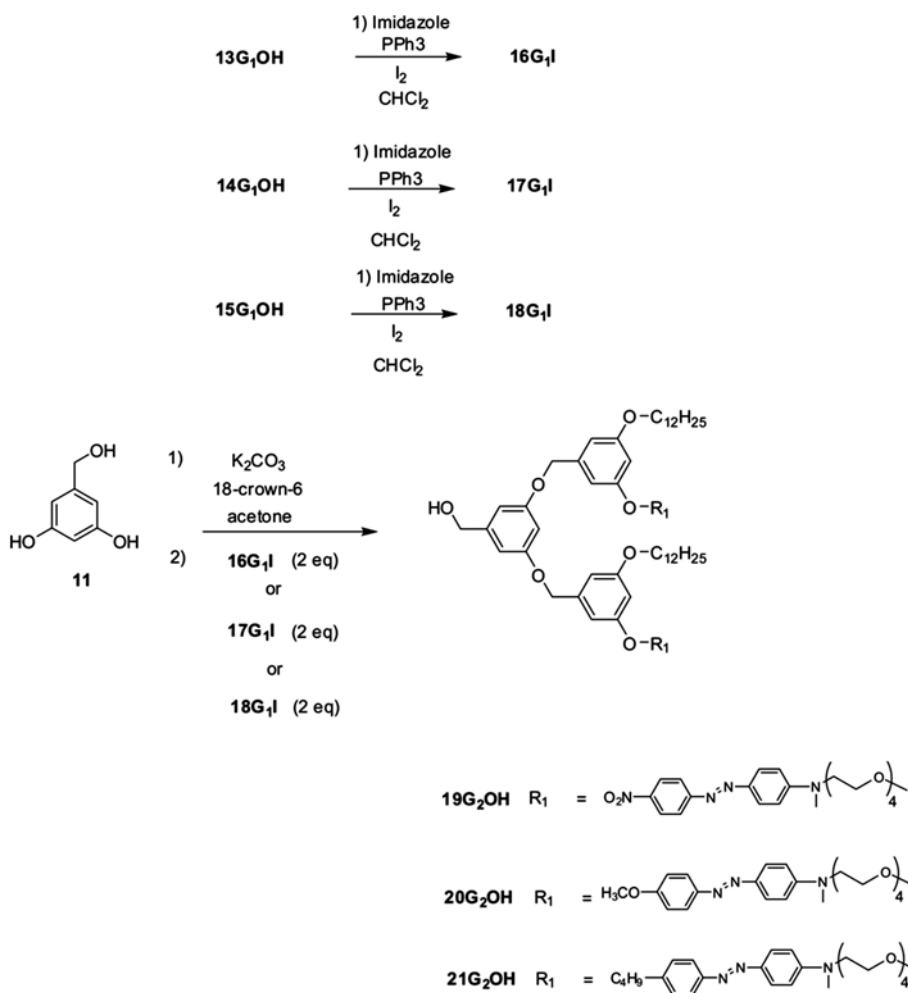


Figure 2. Synthesis of the second-generation dendrons.

4.60 ppm (PhCH<sub>2</sub>OH), two triplets at 4.08 (PhOCH<sub>2</sub> of the tetra(ethylene glycol) chain, 3.90 (PhOCH<sub>2</sub> of the aliphatic chain) followed by a singlet at 3.87 ppm (PhOCH<sub>3</sub>) and a triplet at 3.82 ppm (CH<sub>2</sub>N). In addition, a multiplet at 3.69 ppm due to the protons of the other OCH<sub>2</sub> present in the tetra(ethylene glycol) segments and a singlet related to the methyl group NCH<sub>3</sub> were also seen. Finally, the protons corresponding to methylenes (CH<sub>2</sub>) present in the aliphatic chain appear at 1.74, 1.42, 1.34 and 0.84 ppm.

On the other hand, in the <sup>1</sup>H NMR spectrum of **20G<sub>2</sub>OH** (Figure 3(b)), we can observe almost the same chemical shifts as in the previous case (Figure 3(a)). However, there are two additional peaks in the aromatic region at 6.5 and 6.4 ppm, which are assigned to protons H<sup>9</sup> and H<sup>10</sup>. Moreover, a singlet at 4.58 ppm, due to the methylene protons of the PhCH<sub>2</sub>OH can be also seen.

The <sup>13</sup>C NMR spectrum of **14G<sub>1</sub>OH** is shown in Figure 4(a). As can be seen, there are 14 signals in aromatic region at 160.72, 160.34, 159.96, 150.90, 147.34,

143.51, 143.35, 124.49, 123.71, 113.99, 111.36, 105.30, 104.86, 100.56 ppm due to the 14 types of aromatic carbons present in the structure of the dendron. In the aliphatic region, we can observe various peaks at 70.67, 70.59, 69.62 and 67.33 ppm due to the methylenes present in the tetra(ethylene glycol) segments. The carbons PhOCH<sub>2</sub> of the oligo(ethylene glycol) and the aliphatic chains appear at 68.46 and 67.97 ppm, respectively. Four more signals can be perceived at 65.04, 55.39, 52.08 and 39.10 ppm, corresponding to carbons C<sup>o</sup>, NCH<sub>2</sub>, PhOCH<sub>3</sub> and NCH<sub>3</sub>, respectively. Finally, we can perceive all the CH<sub>2</sub> and CH<sub>3</sub> present in the aliphatic chain at 31.83, 29.58, 29.52, 29.32, 29.26, 29.16, 25.96, 22.60 and 14.05 ppm.

On the other hand, <sup>13</sup>C NMR spectrum of **20G<sub>2</sub>OH** is illustrated in Figure 4(b). In the aromatic region, there are four peaks at 106.45, 143.50, 105.99 and 101.30 ppm due to the carbons of the phenyl group C<sup>r</sup>, C<sup>p</sup>, C<sup>q</sup> and C<sup>s</sup>, respectively. In addition, we can observe an additional peak at 65.16 ppm assigned to the carbon of the methylene (PhCH<sub>2</sub>OH).

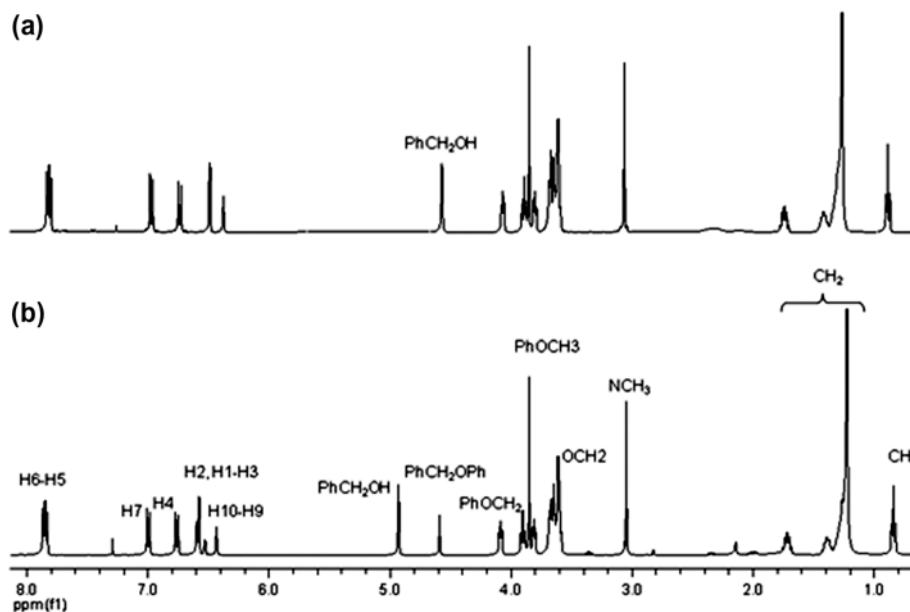


Figure 3.  $^1\text{H}$  NMR spectra of: (a) First-generation dendron **14G<sub>1</sub>OH** and (b) Second-generation dendron **20G<sub>2</sub>OH**.

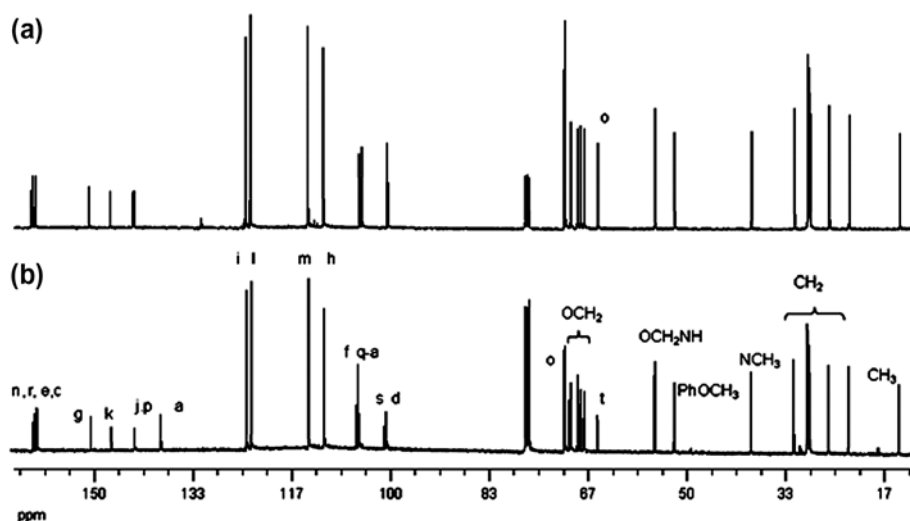


Figure 4.  $^{13}\text{C}$  NMR spectra of: (a) First-generation dendron **14G<sub>1</sub>OH** and (b) Second-generation dendron **20G<sub>2</sub>OH**.

The molecular weights of these compounds were determined by MALDITOF mass spectrometry. All the molecular weight values obtained experimentally match well with those calculated theoretically. Thus, dendrons **14G<sub>1</sub>OH** and **20G<sub>2</sub>OH** showed molecular ion peaks at  $m/z = 701.41$  and  $m/z = 1518.14$ , respectively.

#### Thermal properties of the dendrons

Thermal properties of the dendrons were studied by TGA from 30 to 600 °C. The  $T_{10}$  values (10% weight loss temperature) determined for these compounds are summarized in Table 1. In general, all dendrons exhib-

ited good thermal stability up to 190 °C (Figure 5). As can be seen, the TGA curves of dendrons bearing amino-butyl-substituted azobenzenes **15G<sub>1</sub>OH** and **21G<sub>2</sub>OH** showed  $T_{10}$  values of 219 and 192 °C, respectively. However, dendrons bearing amino-nitro- and amino-methoxy-substituted azobenzenes **13G<sub>1</sub>OH**, **14G<sub>1</sub>OH** and **19G<sub>2</sub>OH**, **20G<sub>2</sub>OH** exhibited  $T_{10}$  values higher than 300 °C. We believe that this increase in thermal stability is due to the polarity of the  $\text{NO}_2$  and  $\text{OCH}_3$  substituents present in the dendrons with respect to those bearing amino-butyl substituted azobenzenes (Table 1). Moreover, dendrons **13G<sub>1</sub>OH** and **19G<sub>2</sub>OH** showed drastic degradation between 252–335 °C. The weakness of the

Table 1. Thermal and optical properties of the dendrons.

Dendrons	$T_{10}$ (°C)	$T_g$ (°C)	$T_m$ (°C)	$\lambda_{max}$ (nm)	Cut off (nm)	Dipole moment $\mu$ (D)*
<b>13G<sub>1</sub>OH</b>	302	–	40	480	628	8.06
<b>14G<sub>1</sub>OH</b>	324	–26.2	–	409	527	1.39
<b>15G<sub>1</sub>OH</b>	219	–33.3	–	409	531	1.11
<b>19G<sub>2</sub>OH</b>	295	–	28	478	615	8.49
<b>20G<sub>2</sub>OH</b>	305	–14.6	–	409	529	2.78
<b>21G<sub>2</sub>OH</b>	192	–31.1	–	409	531	1.55

\*Calculated by the semi-empirical method PM3.

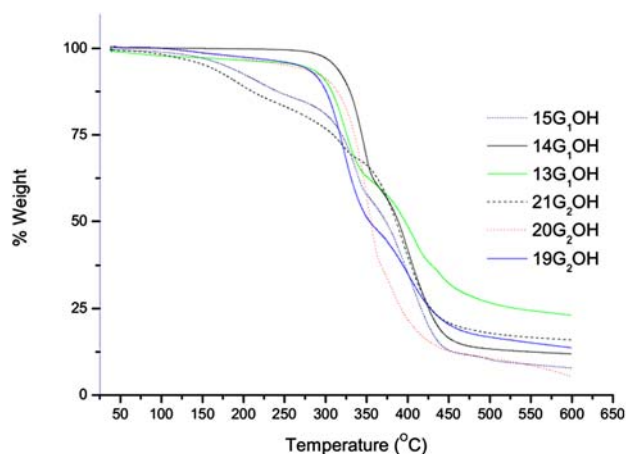


Figure 5. TGA curves of the obtained dendrons.

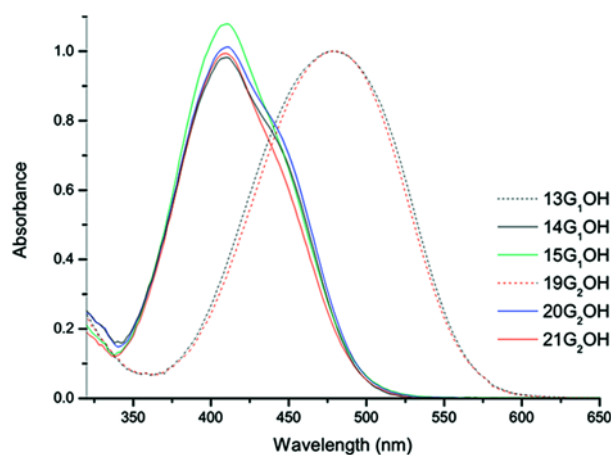
azo group ( $N=N$ ) makes these dendrons more susceptible towards degradation. It is worth to point out that first generation dendrons showed to be thermally more stable than those of second generation, since the structure of the latter is thermodynamically and sterically less stable.

Alternatively,  $T_g$  (glass transition temperature) and  $T_m$  (melting point) of the dendrons were determined by DSC; the results are summarized in the Table 1. DSC curves (not shown) of the dendrons bearing amino-nitro substituted azobenzenes **13G<sub>1</sub>OH** and **19G<sub>2</sub>OH** exhibited only an endothermic peak due to a melting point at 40 and 28 °C, respectively. No glass transition temperature value was found for these azodendrons. On the other hand, dendrons **14G<sub>1</sub>OH**, **20G<sub>2</sub>OH**, **15G<sub>1</sub>OH** and **21G<sub>2</sub>OH** clearly showed glass transitions temperatures at  $T_g = -26.2$ ,  $-14.6$ ,  $-33.3$  and  $-31.1$  °C, respectively. These results are due to the presence of the flexible alkyl and oligo(thylene glycol) chains in the structure of the dendrons as well as to the low dipole moment of their azobenzene units. According to Rau's classification, these compounds belong to the 'aminoazobenzenes' category.

### Optical properties of the dendrons

Optical properties of the dendrons were studied in  $\text{CHCl}_3$  solution by absorption spectroscopy in the UV–vis region,

and the results are summarized in the Table 1. The absorption spectra of high dipole moment dendrons bearing amino-nitro substituted azobenzenes (**13G<sub>1</sub>OH** and **19G<sub>2</sub>OH**) showed a maximum absorption band at  $\lambda_{max} = 480$  nm (Figure 6). High dipole moment azo-dyes usually show the typical photochemical behaviour of azobenzenes belonging to the 'pseudostilbenes' category. According to Rau, these compounds exhibit a total overlap of the  $\pi-\pi^*$  and  $n-\pi^*$  bands, which are inverted in the energy scale so that only one band can be observed in their absorption spectra.[25,32] On the other hand, the absorption spectra of low dipole moment dendrons containing amino-butyl and amino-methoxy substituted azobenzenes **14G<sub>1</sub>OH**, **15G<sub>1</sub>OH**, **20G<sub>2</sub>OH** and **21G<sub>2</sub>OH** are also shown in Figure 6. According to Rau, these low dipole moment azo-dyes belong to the 'aminoazobenzenes' category and behave differently. They showed a maximum absorption band at  $\lambda_{max} = 409$  nm followed by a shoulder at  $\lambda = 423$  nm. In fact, in the absorption spectra of these 'aminoazobenzenes' the  $\pi-\pi^*$  and  $n-\pi^*$  transition bands are blue shifted with respect to those of 'pseudostilbenes' and partially overlap [25,32]. It is worth to point out that there is a significant bathochromic shift in high dipole moment dendrons bearing amino-nitro substituted azobenzenes (**13G<sub>1</sub>OH** and **19G<sub>2</sub>OH**) due to a push-pull effect.

Figure 6. Absorption spectra of the dendrons in  $\text{CHCl}_3$  solution.

### Study of the liquid-crystalline behaviour

The liquid-crystalline (LC) behaviour of the obtained dendrons was studied by DSC and the presence of a mesophase was confirmed by light polarized optical microscopy. The DSC curve (not shown) of the dendrons bearing amino-nitro substituted azobenzene (**13G<sub>1</sub>OH**) showed two endothermic peaks at 21 and 40 °C, corresponding to transition temperatures from Crystal-Liquid-crystal ( $T_{C-LC}$ ) and Liquid-crystal-Isotropic phase ( $T_{LC-I}$ ), respectively. Nevertheless, dendron **19G<sub>2</sub>OH** did not exhibit any liquid crystalline behaviour; instead, it

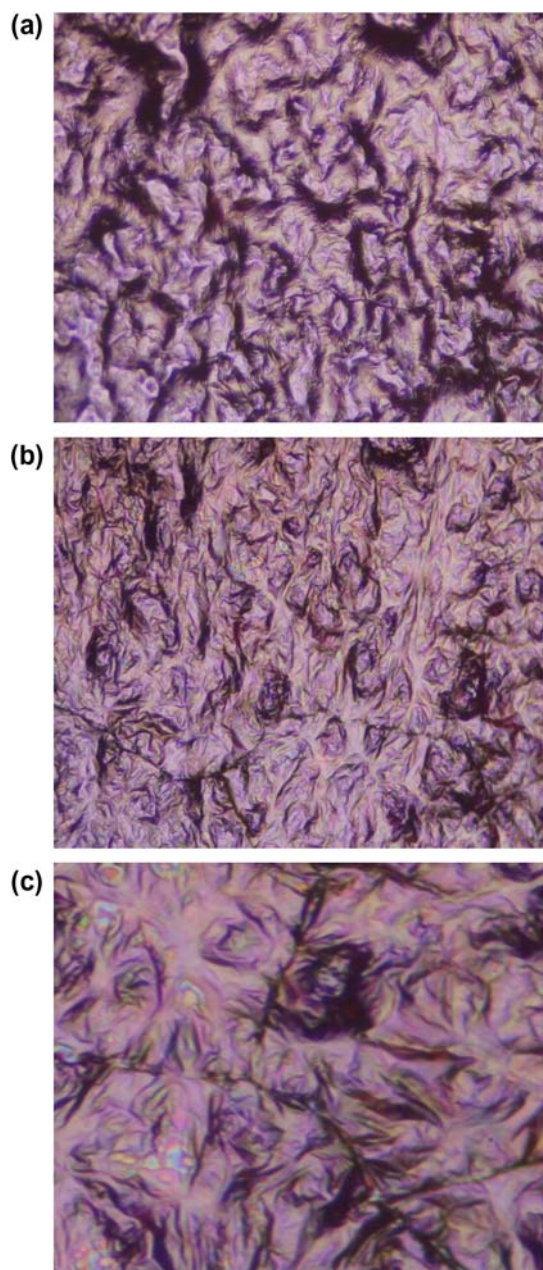


Figure 7. Texture observed upon heating (a) at 27, (b) at 33 and (c) 35 °C, respectively (magnification  $\times 100$ ).

showed an endothermic peak at 28 °C due to a melting point. The optical polarized micrographs of **13G<sub>1</sub>OH** showed the phase transitions upon heating, at 27 °C for the formation of the liquid crystalline phase ( $T_{C-LC}$ ) (Figure 7(a)). When the sample was heated at 33–35 °C, a liquid crystalline-isotropic transition ( $T_{LC-I}$ ) was also observed (Figure 7(b) and (c)). It is clear that the LC phase of **13G<sub>1</sub>OH** exhibits a typical fan texture, which is characteristic of a smectic structure. Further heating above at 40 °C led to disappearance of the LC structure to adopt an isotropic phase. In contrast, the dendrons bearing amino-butyl- and amino-methoxy substituted azobenzenes did not exhibit any liquid crystalline behaviour. Unlike the other dendrons bearing low dipole moment azobenzenes, where  $R = OCH_3$  or Butyl, **13G<sub>1</sub>OH** showed a very good liquid crystallinity. This can be attributed to the high dipole moment of this compound, because the presence of the amino and the nitro groups give rise to intramolecular interactions between neighbouring azobenzene units (mesogens), thereby favouring the orientation of the mesogenic groups in the LC phase.[55]

### Conclusion

Two novel series of first- and second-generation Fréchet type dendrons bearing substituted azobenzene units and tetra(ethylene glycol) spacers were synthesized and characterized. The dendrons exhibited a good thermal stability with  $T_{10}$  values between 192–324 °C, showing drastic degradation between 300 and 500 °C. Dendrons bearing ‘pseudostilbene’ type azobenzene units exhibited a maximum absorption wavelength in the range of  $\lambda = 476$ –480 nm in  $CHCl_3$  solution, whereas low dipole moment dendrons did it at  $\lambda = 409$  nm, which is in agreement with the results obtained by molecular modelling. DSC and Light Polarized Microscopy studies revealed that dendron **13G<sub>1</sub>OH** exhibited a liquid crystalline behaviour with the formation of smectic domains.

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