



Incorporation of novel azobenzene dyes bearing oligo(ethylene glycol) spacers into first generation dendrimers



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ABSTRACT

Herein, we report the synthesis and inclusion of a new series of azo-dyes into first generation Fréchet type dendrimers. The incorporated dyes are amino-nitro, amino-methoxy and amino-butyl substituted azobenzenes bearing a well defined oligo(ethylene glycol) side chain. The optical properties of the dendrimers were studied by absorption spectroscopy. Dendrimer bearing amino-nitro substituted azobenzenes ($\lambda = 480$ nm in CHCl_3) behaved as a pseudostilbene type azobenzene whereas the others ($\lambda = 409$ nm in CHCl_3) showed the typical behaviour of aminoazobenzenes. Moreover, the *trans*-*cis* photoisomerization of the dendrimers was studied by UV-vis spectroscopy by irradiating at two different wavelengths (254 and 365 nm). In chloroform, the appearance of an intense red-shifted band revealed the presence of a photoprotonation effect in the azobenzene moiety. This phenomenon was also studied by absorption spectroscopy in function of time. The results were compared to those predicted by molecular modelling using Density Functional Theory calculations.

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1. Introduction

Nowadays, dendrimers and dendrons have been considered one of the most attractive research fields in polymer chemistry due to their well-defined structures, versatility 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 investigated, such as response to light. Some reviews include the first reports of photo-responsive dendrimers [6–9] giving many examples of azo-dendrimers. The most recent review covering the most important aspects of azobenzene containing dendrons and dendrimers, has been published by Caminade and Deloncle [10].

Azobenzenes had been used as terminal groups of dendrimers and dendrons, being the first examples those described by Vögtle and co-workers [11]. The first structures were prepared from poly(propyleneimine) (PPI) dendrimers built from either

ethylenediamine [12] or 1,4-diaminobutane [1–14] as core. In most of the cases, all the terminal groups were azobenzenes [15–18].

The most popular types of dendrimers, poly(amidoamine) [19] and poly(arylether) [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] with azobenzene as terminal groups. Moreover, dendrons have not been frequently functionalized with azobenzenes on their periphery. The first example was used as building block for dendrimers [21,22]. More sophisticated systems, such as polyether dendrons linked to fullerenes, had been also prepared [24].

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

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and electron-acceptor groups belong to the third category, “pseudostilbenes”, where the $\pi-\pi^*$ and $n-\pi^*$ bands 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 constitute versatile materials for several applications. In particular, irradiation with linear polarized light produces rapid *trans*–*cis*–*trans* photoisomerization of “pseudostilbene” azobenzenes. As a consequence, 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-coated films and Langmuir–Blodgett multilayers. In these media, both H-type and J-type aggregates have been observed [33]. On the other hand, azobenzene and poly(ethylene glycol) have been employed in the synthesis of amphiphilic azo-dyes, copolymers [34,35], nanomaterials [36,37], cellulose derivatives [38,39] and cyclodextrin polymers [40,41], sometimes forming supramolecular complexes with interesting properties [42]. In fact, poly(ethylene glycol) segments provide flexibility and water solubility to the systems to which they are incorporated [43,44].

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. We reported the synthesis and characterization of four novel azo-dyes bearing terminal hydroxyl groups, the preparation of grafted azo-polymer films containing oligo(ethylene glycol) segments [45], and the synthesis and characterization of a new series of polymethacrylates bearing amino-nitro azobenzene units and oligo(ethylene glycol) chains their structure [46]. More recently, we published 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 [47].

Many articles about the preparation of new dendritic molecules containing azobenzene have been reported in the literature. Some of these materials exhibited outstanding optical properties, NLO response [48–54] or a liquid crystalline behaviour [55,56]. Last year, we reported the incorporation of amino-nitro substituted azobenzenes containing a tetra(ethylene glycol) side chain and other related dyes into dendritic structures, in order to get new liquid crystalline materials bearing azobenzene units. The thermal and optical properties of such dendrons were studied in detail, and some of them exhibited a liquid crystalline behaviour [57]. Herein, we report the incorporation of novel azo-dyes bearing amino-nitro, amino-methoxy and amino-butyl substituted azobenzenes into first generation Fréchet type dendrimers. The optical properties of these compounds, as well as the *trans*–*cis* photoisomerization and the photoprotonation effect, were studied by absorption spectroscopy. The results were compared to those predicted by molecular modelling using Density Functional Theory calculations. These new azo-dendrimers can be used for optical switching and storage as other azo-polymers previously reported in the literature. In addition, they can act as photochromic sensors since they exhibit noticeable colour changes arising from the photoinduced protonation which occur in CHCl_3 solution when they are irradiated with UV light at 254 nm.

2. Experimental

2.1. General conditions

All reagents used in the synthesis of the azo-dyes, dendrons and dendrimers were purchased from Aldrich and used as received

without further purification. Acetone and dichloromethane were dried by distillation over calcium hydride. Precursor dyes (E)-2-(4-((4-nitrophenyl)diazanyl)phenyl)-5,8,11-trioxa-2-azatridecan-13-ol (**1**), (E)-2-(4-((4-methoxyphenyl)diazanyl)phenyl)-5,8,11-trioxa-2-azatridecan-13-ol (**2**) and (E)-2-(4-((4-butylphenyl)diazanyl)phenyl)-5,8,11-trioxa-2-azatridecan-13-ol (**3**) were synthesized according to the method previously reported by us [45], and the poly(aryl ether) dendrons were prepared as described in the literature [58]. FTIR spectra of the compounds were carried out on a Spectrum 100 (Perkin Elmer PRECISELY) spectrometer in solid state. ^1H and ^{13}C NMR spectra of these compounds in CDCl_3 solution were recorded at room temperature on a Bruker Avance 400 MHz spectrometer operating at 400 MHz and 100 MHz for ^1H and ^{13}C , respectively.

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.

Photoisomerization and photoprotonation experiments of azo-dendrimers **14G₁** and **15G₁** were carried out in DMF and CHCl_3 solutions (2.5×10^{-5} M) at room temperature. The samples were irradiated with UV light using a Compact UV lamp model UVGL-25, 254/365 nm (6W). Each solution was irradiated at 254 and 365 nm for 5 min. The spectral changes were monitored by absorption spectroscopy with intervals of 5 s.

2.2. Computational and theoretical details

All calculations were carried out by using the Gaussian 09 implementation [59]. Calculations involving atomic geometry and electronic structure were performed by applying the Density Functional Theory (DFT) framework for all the stationary points, using the B3LYP [60] functional and the basis 6-31G [61–65]. In order to verify optimized minima, harmonic analyses were achieved and local minima were identified with zero imaginary frequencies. In order to simulate the UV–visible spectra, time-dependent DFT (TD-DFT) method was employed using the same methodology. The UV–visible spectra were obtained for half singlet and half triplet states, effective for closed-shell systems.

2.3. Synthesis

2.3.1. Synthesis of the precursor azo-dyes

Precursor azo-dyes (E)-2-(4-((4-nitrophenyl)diazanyl)phenyl)-5,8,11-trioxa-2-azatridecan-13-ol (**1**), (E)-2-(4-((4-methoxyphenyl)diazanyl)phenyl)-5,8,11-trioxa-2-azatridecan-13-ol (**2**) and (E)-2-(4-((4-butylphenyl)diazanyl)phenyl)-5,8,11-trioxa-2-azatridecan-13-ol (**3**) were prepared according to the method previously reported by us [45].

2.4. Synthesis of the dendrons

2.4.1. Synthesis of the 3-dodecyloxy-5-hydroxybenzyl alcohol (**8**)

The synthesis and characterization of the dendron (**8**) has been previously reported by us [57]. Yield: 68%.

FTIR (Film) ν/cm^{-1} : 3375 (OH), 2913, 2847 (CH_3 , CH_2), 1595, 1469 ($\text{C}=\text{C}$, Ar), 1378, 1328 (CH_3 , CH_2), 1305 (ArOCH), 1160 (COC) and 1037 (ArOCH).

^1H NMR (400 MHz, CDCl_3): δ = 6.35 (s, J = 2 Hz, 2H, H^1-H^3), 6.28 (s, J = 2 Hz, 1H, H^2), 4.46 (s, 2H, PhCH_2OH), 3.80 (t, J = 6.62 Hz, 2H, PhOCH_2), 1.69 (m, 2H, $\text{PhOCH}_2\text{CH}_2$), 1.26 (m, 18H, all CH_2 of the aliphatic chain), 0.88 (t, J = 6.56 Hz, 3H, CH_3) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ = 160.41 (1C, C^b), 157.13 (1C, C^d), 142.67 (1C, C^f), 106.32 (1C, C^e), 105.49 (1C, C^a), 101.28 (1C, C^c), 68.13 (1C, PhOCH_2C^e), 64.91 (1C, PhCH_2OH), 31.88 (1C, $\text{PhOCH}_2\text{CH}_2$),

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