



Synthesis, characterization and optical properties of novel star azo-oligomers containing well-defined oligo(ethylene glycol) segments

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ABSTRACT

In this work, the synthesis and characterization of a series of star azo-oligomers bearing amino, amino-methoxy, amino-nitro and amino-cyano substituted azobenzene units and oligo(ethylene glycol) segments is reported. The full characterization of the obtained compounds was achieved by FTIR, ^1H and ^{13}C NMR spectroscopies, and their molecular weights were determined by MALDI-TOF mass spectrometry. The optical properties of these compounds were studied by absorption spectroscopy in solution. Finally, light polarized microscopy experiments as a function of the temperature were performed in order to study the liquid-crystalline behavior of these star azo-oligomers.

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1. Introduction

Well-defined three-dimensional structures such as dendrimers, hyperbranched and star branched polymers are macromolecules presenting a growing interest in the field of polymer chemistry [1–5]. Potential use and applications of such sophisticated macromolecular structures are ranging from material science to medicinal chemistry and catalysis [6]. Moreover, light responsive materials were obtained by introducing azobenzene groups to modify their molecular structure [7,8].

The substitution of azobenzene compounds has an important effect on their photochemical behavior. According to Rau, the azobenzene can be classified in three distinct categories [9]. The first one is known as “azobenzene”. This category includes unsubstituted azobenzenes compounds. The UV–visible spectra of the compounds included in this category are presenting a strong π - π^* transition at 350 nm and a weak n - π^* transition at about 440 nm. Moreover, these two bands are presenting a poor overlap. Both isomers of the azo moiety (cis and trans) are leading to similar UV transitions. However, the relation of the intensities of both bands is changing; the n - π^* transition is more intense for the cis isomer than for the trans isomer. When an electron donor group, such as for

example an amino group, is directly linked to the azobenzene moiety, the resulting compound falls in the second category called “aminoazobenzenes” according to Rau's classification. In this case the π - π^* and n - π^* bands are partially overlapped. Finally, the last category contains azobenzene bearing electron-donor as well as electron-acceptor groups. It is named “pseudo-stilbenes”. The UV spectra of these compounds are presenting a superposition of the π - π^* and n - π^* bands. Moreover the energies of the respective bands are inverted, since the n - π^* band represents the strongest transition [9].

Polymers incorporating a “pseudo-stilbenes” moiety in their structures are finding numerous applications thanks to the fast *trans*-*cis*-*trans* photoisomerization as well as the photoinduced anisotropy of the azo moiety [10–15]. Aggregation of azobenzene compounds in solution, in film cast or in Langmuir-Blodgett layers is another factor contributing to changes in the optical properties. Different types of aggregates such as H-type or J-type aggregates have been reported [16].

Polymers containing units of poly(ethyleneglycol) in their constitution have the advantages to turn more soluble in water as well as to become more flexible.

[17,18]. Therefore poly(ethyleneglycol) units have been incorporated in polymers to obtain nanomaterials, copolymers as well as cellulose and cyclodextrin derivatives with interesting properties [19–27]. In an earlier work, we presented a series of azo dyes

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bearing a hydroxyl functional group and its incorporation into polymer films through grafting procedure [28,29]. We also reported a series of azo-dyes dimers, linked through a well defined oligo(ethylene glycol) spacer, bearing nitro and amino group substituent on the azobenzene moiety, which were presenting liquid crystalline properties [30].

Recently, our research group has developed a series of dendrons and dendrimers bearing azobenzene units and oligo(ethylene glycol) spacers with different architectures [31–33]. A detailed study of the thermal and optical properties of these dendritic compounds as well as its liquid crystalline behavior was presented. Herein, we report the synthesis and characterization of a new series of star-oligomers containing azobenzene units and oligo(ethylene glycol) segments.

2. Experimental section

2.1. General conditions

All reagents involved in the synthesis of the star azo-oligomers were purchased from Aldrich and used as received without any further purification. THF was dried by distillation over sodium with benzophenone. The intermediate azo dyes (5) and (6) were synthesized following a methodology detailed by us previously [27,28]. The ^1H and ^{13}C NMR spectra of the compounds in CDCl_3 solutions were recorded at room temperature on a Bruker Advance 400 MHz spectrometer, operating at 400 and 100 MHz for ^1H and ^{13}C , respectively. All the star azo-oligomers were dissolved in spectral quality solvents purchased from Aldrich, and their absorption spectra were recorded on a Varian Cary I Bio UV–vis (model 8452 A) spectrophotometer at room temperature, using 1 cm quartz cuvettes.

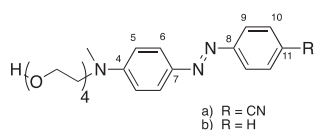
2.2. Synthetic procedures

2.2.1. Synthesis of 4-((4-((2-(2-(2-(2-hydroxyethoxy) ethoxy) ethoxy) ethyl) (methyl) amino) phenyl) diazenyl)benzotrile (7)

From 2-phenyl-5,8,11-trioxa-2-azatridecan-13-ol (4), compound (7) has been prepared according to the method employed for the synthesis of compound (5), where the diazonium salt was commercially available. Nevertheless, for this precursor, the diazonium salt was prepared *in situ* as reported in the literature [31,32].

p-Aminobenzotrile (1.1 g, 4 mmol) was dissolved in an HCl solution 30% (50 mL) at 0 °C with vigorous stirring. NaNO_2 (0.6 g, 9 mmol) was added to the reaction mixture followed by a dropwise addition of the intermediate (4) (1.2 g, 4 mmol). After 4 h, the reaction mixture was neutralized with an aqueous solution of NaOH (5%).² The crude product was extracted with chloroform, dried with anhydrous MgSO_4 , filtered and concentrated at reduced pressure. The crude product was purified by column chromatography in silica gel, using a mixture ethyl acetate/hexanes (8:2) as eluent to give compound (7). Yield: 33% (Scheme 1).

^1H NMR (400 MHz, CDCl_3 , δ): 7.86 (d, $J = 8.6$ Hz, 2 H, H^9), 7.85 (d, $J = 9.1$ Hz, 2 H, H^6), 7.71 (d, $J = 8.7$ Hz, 2 H, H^{10}), 6.76 (d, $J = 9.3$ Hz, 2 H, H^5), 3.75–3.55 (m, 16 H, OCH_2 and NCH_2), 3.12 (s, 3 H, NCH_3) ppm. ^{13}C NMR (100 MHz, CDCl_3 , δ): 155.5 (1 C, C^8), 152.4 (1 C, C^4),



Scheme 1. Assignment of the signals for compounds (a) 7 and (b) 8.

143.6 (1 C, C^7), 133.1 (2 C, C^{10}), 125.9 (2 C, C^9), 122.7 (2 C, C^6), 119.0 (1 C, C^{11}), 111.8 (1 C, CN), 111.5 (2 C, C^5), 72.5, 70.8, 70.7, 70.6, 70.3, 68.6 (6 C, OCH_2), 61.7 (1 C, CH_2OH), 52.2 (1 C, NCH_2), 39.4 (1 C, NCH_3) ppm. IR (film): $\nu = 3437$ (O–H); 3080 (ν Ar C–H); 2867 (ν CH_3 , CH_2); 2222 (CN); 1593, 1513 (ν Ar C=C); 1443 (N=N); 1378 (δ s CH_3); 1133, 1098 (vas C–O); 822 (δ Ar C–H).

2.2.2. Synthesis of 2-(4-(phenyldiazenyl)phenyl)-5,8,11-trioxa-2-azatridecan-13-ol (8)

Aniline (1.1 g, 4 mmol) was dissolved in HCl 30% (50 mL) at 0 °C with vigorous stirring. NaNO_2 (0.6 g, 9 mmol) was added to the reaction mixture followed by a dropwise addition of the intermediate (4) (1.2 g, 4 mmol). After 4 h, the reaction mixture was neutralized with an aqueous solution of NaOH (5%).² The crude product was extracted with chloroform. The organic phase was dried with anhydrous MgSO_4 , filtered and concentrated at reduced pressure. Then the product was purified by column chromatography in silica gel using a mixture ethyl acetate/hexane (7:3 and 8:2) as eluent to afford compound (8). Yield: 20%.

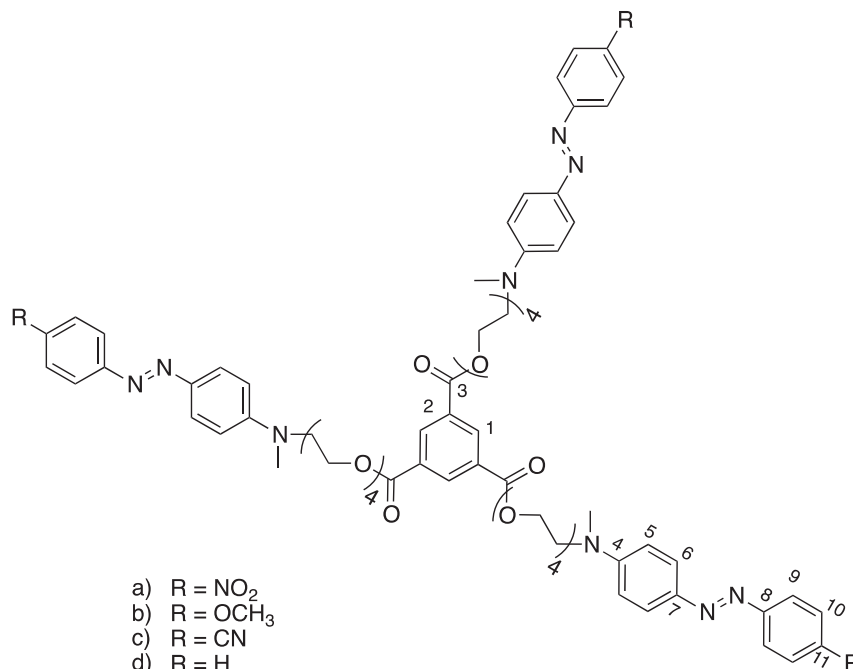
^1H NMR (400 MHz, CDCl_3 , δ): 7.81 (d, $J = 9.0$ Hz, 2 H, H^9), 7.78 (d, $J = 7.6$ Hz, 2 H, H^6), 7.42 (t, $J = 7.8$ Hz, 2 H, H^{10}), 7.32 (t, $J = 7.1$ Hz, 1 H, H^{11}), 6.73 (d, $J = 6.0$ Hz, 2 H, H^5), 3.70–3.50 (m, 16 H, OCH_2), 3.06 (s, 3 H, NCH_3) ppm. ^{13}C NMR (100 MHz, CDCl_3 , δ): 161.3 (1 C, C^4), 152.7 (1 C, C^8), 147.0 (1 C, C^7), 130.5 (1 C, C^{11}), 129.1 (2 C, C^{10}), 124.8 (2 C, C^6), 122.6 (2 C, C^9), 114.9 (2 C, C^5), 72.6, 70.8, 70.6, 70.5, 70.3, 69.6 (6 C, OCH_2), 67.6 (1 C, CH_2OH), 61.6 (1 C, NCH_2), 42.8 (1 C, NCH_3) ppm. IR (film): $\nu = 3389$ (O–H); 3065 (ν Ar C–H); 2920 (vas CH_3 , CH_2); 2859 (vs CH_3 , CH_2); 1594, 1514 (ν Ar C=C); 1457 (N=N); 1373 (δ s CH_3); 1137, 1111 (vas C–O); 1054 (C–OH); 813 (δ Ar C–H).

2.2.3. Synthesis of tris (2-(4-((4-nitrophenyl) diazenyl) phenyl) –5,8,11-trioxa-2-azatridecan-13-yl) benzene-1,3,5-tricarboxylate (9)

After the synthesis of the precursor azo-dyes, the star azo-oligomers were prepared according to the method previously reported in the literature [33].

Compound (5) (0.45 g, 1.00 mmol) was dissolved in anhydrous dichloromethane under argon atmosphere and triethylamine (0.04 mL, 0.30 mmol) was added and the reaction mixture was stirred for 2 h at room temperature. Then, 1,3,5-benzenetricarbonyl trichloride (0.12 g, 0.43 mmol) was added and the reaction mixture was stirred for five days under the same reaction conditions. The reaction was quenched by pouring into an aqueous solution of HCl (10%). The crude product was extracted with chloroform. The organic phase was dried with anhydrous MgSO_4 , filtered and concentrated under reduced pressure. The crude product was purified by column chromatography in silica gel using mixtures starting with ethyl acetate/hexane 8:2 increasing gradually the polarity until pure ethyl acetate was used to give the desired product (9). Yield: 30% (Scheme 2).

^1H NMR (400 MHz, CDCl_3 , δ): 8.82 (s, 3 H, H^1), 8.30 (d, $J = 9.0$ Hz, 6 H, H^{10}), 7.90 (d, $J = 9.1$ Hz, 6 H, H^9), 7.88 (d, $J = 10$ Hz, 6 H, H^6), 6.69 (d, $J = 9.2$ Hz, 6 H, H^5), 4.49 (t, 6 H, CH_2OCO), 3.81 (t, 6 H, $\text{CH}_2\text{CH}_2\text{OCO}$), 3.69–3.61 (m, 36 H, OCH_2 and NCH_2), 3.12 (s, 9 H, NCH_3) ppm. ^{13}C NMR (100 MHz, CDCl_3 , δ): 164.8 (3 C, C^3), 156.6 (3 C, C^8), 152.6 (3 C, C^4), 147.3 (3 C, C^{11}), 143.7 (3 C, C^7), 134.8 (3 C, C^1), 131.1 (3 C, C^2), 126.2 (6 C, C^6), 124.7 (6 C, C^{10}), 122.5 (6 C, C^9), 111.5 (6 C, C^5), 70.8 (3 C, OCH_2), 70.73 (3 C, OCH_2), 70.66 (6 C, OCH_2), 69.0 (3 C, OCH_2), 68.5 (3 C, OCH_2), 64.7 (3 C, CH_2OCO), 52.2 (3 C, NCH_2), 39.4 (3 C, NCH_3) ppm. IR (film): $\nu = 3091$ (ν Ar C–H); 2917 (vas CH_3 , CH_2); 2845 (vs CH_3 , CH_2); 1729 (ν OC=O); 1601, 1508 (ν Ar C=C); 1445 (N=N); 1376 (δ s CH_3); 1334 (vs Ar– NO_2); 1246 (vs, vas O–CO); 1131, 1101 (vas C–O); 855 (ν R– NO_2); 816, 736 (δ Ar C–H). MALDI-TOF m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{72}\text{H}_{84}\text{N}_{12}\text{O}_{21}$, 1453.58; found, 1453.12.



Scheme 2. Assignments of the signals for compounds (a) **9**, (b) **10**, (c) **11** and (d) **12**.

2.2.4. Synthesis of tris(2-(4-((methoxyphenyl)diazenyl)phenyl)-5,8,11-trioxa-2-azatridecan-13-yl) benzene-1,3,5-tricarboxylate (**10**)

Compound (**6**) (0.45 g, 1.00 mmol) was dissolved in anhydrous dichloromethane (30 mL) under argon atmosphere; then triethylamine (0.04 mL, 0.30 mmol) was added. After 30 min, 1,3,5-benzenetricarbonyl trichloride (0.12 g, 0.43 mmol) was added and the mixture was reacted at room temperature with vigorous stirring for five days. Subsequently, the crude product was treated with an HCl solution (10%) and extracted with chloroform. The organic phase was dried with anhydrous MgSO₄, filtered and concentrated at reduced pressure. The crude product was purified by column chromatography in silica gel using mixtures of ethyl acetate/hexane as eluent starting with 8:2 until pure ethyl acetate was used to give the desired product (**10**). Yield: 20%.

¹H NMR (400 MHz, CDCl₃, δ): 8.83 (s, 3 H, H¹), 7.82 (d, *J* = 9 Hz, 6 H, H⁹), 7.79 (d, *J* = 9.1 Hz, 6 H, H⁶), 6.96 (d, *J* = 9.1 Hz, 6 H, H¹⁰), 6.72 (d, *J* = 9.8 Hz, 6 H, H⁵), 3.85 (s, 9 H, OCH₃), 3.81 (t, 6 H, CH₂OCO), 3.70–3.50 (m, 42 H, OCH₂ and NCH₂), 3.05 (s, 9 H, NCH₃) ppm. ¹³C NMR (100 MHz, CDCl₃, δ): 157.0 (3 C, C³), 152.5 (3 C, C¹¹), 147.5 (6 C, C^{4,8}), 144.0 (3 C, C⁷), 131.0 (3 C, C¹), 129.0 (3 C, C²), 126.5 (6 C, C⁶), 124.5 (6 C, C⁹), 122.5 (6 C, C¹⁰), 112.0 (6 C, C⁵), 72.5 (6 C, OCH₂), 70.5 (6 C, OCH₂), 70.0 (6 C, OCH₂), 68.0 (3 C, CH₂OCO), 62.0 (3 C, OCH₃), 52.0 (3 C, NCH₂), 39.0 (3 C, NCH₃) ppm. IR (film): ν = 3073 (ν Ar C–H); 2952 (vas CH₃); 2917 (vas CH₂); 2850 (vs CH₃, CH₂); 1737 (ν OC=O); 1597, 1513 (ν Ar C=C); 1452 (N=N); 1373 (δ s CH₃); 1225 (vs, vas O–CO); 1133, 1098 (vas C–O); 1022 (vs Ar–O–CH₃); 844, 813, 712 (δ Ar C–H). MALDI-TOF *m/z*: [M + H]⁺ Calcd for C₇₅H₉₃N₉O₁₈, 1408.65; found, 1408.36.

2.2.5. Synthesis of tris(2-(4-((4-cyanophenyl)diazenyl)phenyl)-5,8,11-trioxa-2-azatridecan-13-yl)benzene 1,3,5-tricarboxylate (**11**)

1,3,5-benzenetricarbonyl trichloride (0.12 g, 0.43 mmol) and triethylamine (0.04 mL, 0.30 mmol) were dissolved in anhydrous dichloromethane under inert atmosphere. The reaction mixture was cooled at –4 °C and (**7**) (0.45 g, 1.00 mmol) was added by means of a cannula. The reaction mixture was stirred for 30 min at

–4 °C, then at room temperature for 4 days. The crude product was treated with an HCl solution (10%) and extracted with chloroform. The organic phase was dried with anhydrous MgSO₄, filtered and concentrated at reduced pressure. The crude product was purified by column chromatography in silica gel, using mixtures of ethyl acetate/hexane as eluent starting with a ratio 8:2, increasing gradually the polarity until pure ethyl acetate was used to give the desired product (**11**). Yield: 30%.

¹H NMR (400 MHz, CDCl₃, δ): 8.83 (s, 3 H, H¹), 7.86 (d, *J* = 8.8 Hz, 6 H, H⁹), 7.84 (d, *J* = 9.2 Hz, 6 H, H⁶), 7.72 (d, *J* = 8.5 Hz, 6 H, H¹⁰), 6.74 (d, *J* = 9.3 Hz, 6 H, H⁵), 4.49 (t, 6 H, CH₂OCO), 3.81 (t, 6 H, CH₂CH₂OCO), 3.70–3.50 (m, 36 H, OCH₂ and NCH₂), 3.10 (s, 9 H, NCH₃) ppm. ¹³C NMR (100 MHz, CDCl₃, δ): 164.8 (3 C, C³), 156.7 (3 C, C⁸), 152.3 (3 C, C⁴), 143.6 (3 C, C⁷), 134.7 (3 C, C¹), 133.0 (6 C, C¹⁰), 131.1 (3 C, C²), 125.8 (6 C, C⁹), 122.6 (6 C, C⁶), 118.9 (3 C, C¹¹), 111.8 (3 C, CN), 111.4 (6 C, C⁵), 70.8 (3 C, OCH₂), 70.7 (3 C, OCH₂), 70.6 (6 C, OCH₂), 68.9 (3 C, OCH₂), 68.5 (3 C, OCH₂), 64.6 (3 C, CH₂OCO), 52.2 (3 C, NCH₂), 39.2 (3 C, NCH₃) ppm. IR (film): ν = 3082 (ν Ar C–H); 2862 (ν CH₃, CH₂); 2222 (CN); 1737 (ν OC=O); 1593, 1512 (ν Ar C=C); 1440 (N=N); 1369 (δ s CH₃); 1220 (vs, vas O–CO); 1135, 1092 (vas C–O); 838, 812, 736 (δ Ar C–H). MALDI-TOF *m/z*: [M + H]⁺ Calcd for C₇₅H₈₄N₁₂O₁₅, 1393.61; found, 1393.49.

2.2.6. Synthesis of tris(2-(4-(phenyldiazenyl)phenyl)-5,8,11-trioxa-2-azatridecan-13-yl)benzene-1,3,5-tricarboxylate (**12**)

A mixture of trimesic acid (0.023 g, 0.11 mmol) and dicyclohexylcarbodiimide (DCC) (0.024 g, 0.12 mmol) were dissolved in anhydrous tetrahydrofuran (THF) (30 mL) under argon atmosphere. The reaction mixture was stirred for 2 h at room temperature. Then, 4-dimethylaminopyridine (DMAP) (0.005 g, 0.04 mmol) was added and the reaction mixture was stirred for 30 min. Afterwards, azodye (**8**) (0.12 g, 0.3 mmol) was added under inert atmosphere and the mixture was stirred for 3 days at room temperature. Then, another portion of DMAP (0.002 g, 0.016 mmol) and DCC (0.003 g, 0.015 mmol) were added and the reaction continued with vigorous stirring for 3 more days. The crude product was filtered, washed with water and dried with anhydrous MgSO₄, and concentrated at

reduced pressure. The crude product was purified by column chromatography in silica gel using mixtures ethyl acetate/hexane as eluent starting with a ratio 6:4, increasing the polarity until pure ethyl acetate was used to give compound 12. Yield: 20%.

$^1\text{H NMR}$ (400 MHz, CDCl_3 , δ): 8.85 (s, 3 H, H^1), 7.85 (d, $J = 9.1$ Hz, 6 H, H^9), 7.81 (d, $J = 8.2$ Hz, 6 H, H^6), 7.46 (t, $J = 7.6$ Hz, 6 H, H^{10}), 7.36 (t, $J = 7.3$ Hz, 3 H, H^{11}), 6.74 (d, $J = 9.2$ Hz, 6 H, H^5), 4.49 (t, 6 H, CH_2OCO), 3.81 (t, 6 H, $\text{CH}_2\text{CH}_2\text{OCO}$), 3.70–3.50 (m, 36 H, OCH_2 and NCH_2), 3.07 (s, 9 H, NCH_3) ppm. IR (film): $\nu = 3061$ (ν Ar C–H); 2931 (ν CH₃, CH₂); 2850 (ν CH₃, CH₂); 1726 (ν OC=O); 1596, 1504 (ν Ar C=C); 1450 (N=N); 1373 (δ s CH₃); 1235 (ν s, ν O–CO); 1134, 1101 (ν C–O); 813, 733 (δ Ar C–H). MALDI-TOF m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{72}\text{H}_{87}\text{N}_9\text{O}_{15}$, 1318.57; found, 1318.21.

3. Results and discussion

3.1. Synthesis of the star azo-oligomers

The new star-oligomers designed in this study were assembled from four different azo-dye precursors presenting four different functional groups and a tri-substituted benzene core. The synthesis was achieved according to the synthetic sequence illustrated in Fig. 1. Firstly the precursor azo-dyes (**5**, **6**, **7** and **8**) were prepared from the aminoalcohol **4** and the corresponding diazonium salt. Compound **4** was synthesized starting with the tosylation of tetra(ethylene glycol) **1** in the presence of tosyl chloride and pyridine to give the tosylate **2**, which was then treated with NaI using acetone as solvent to yield the corresponding alkyl iodide **3**. This

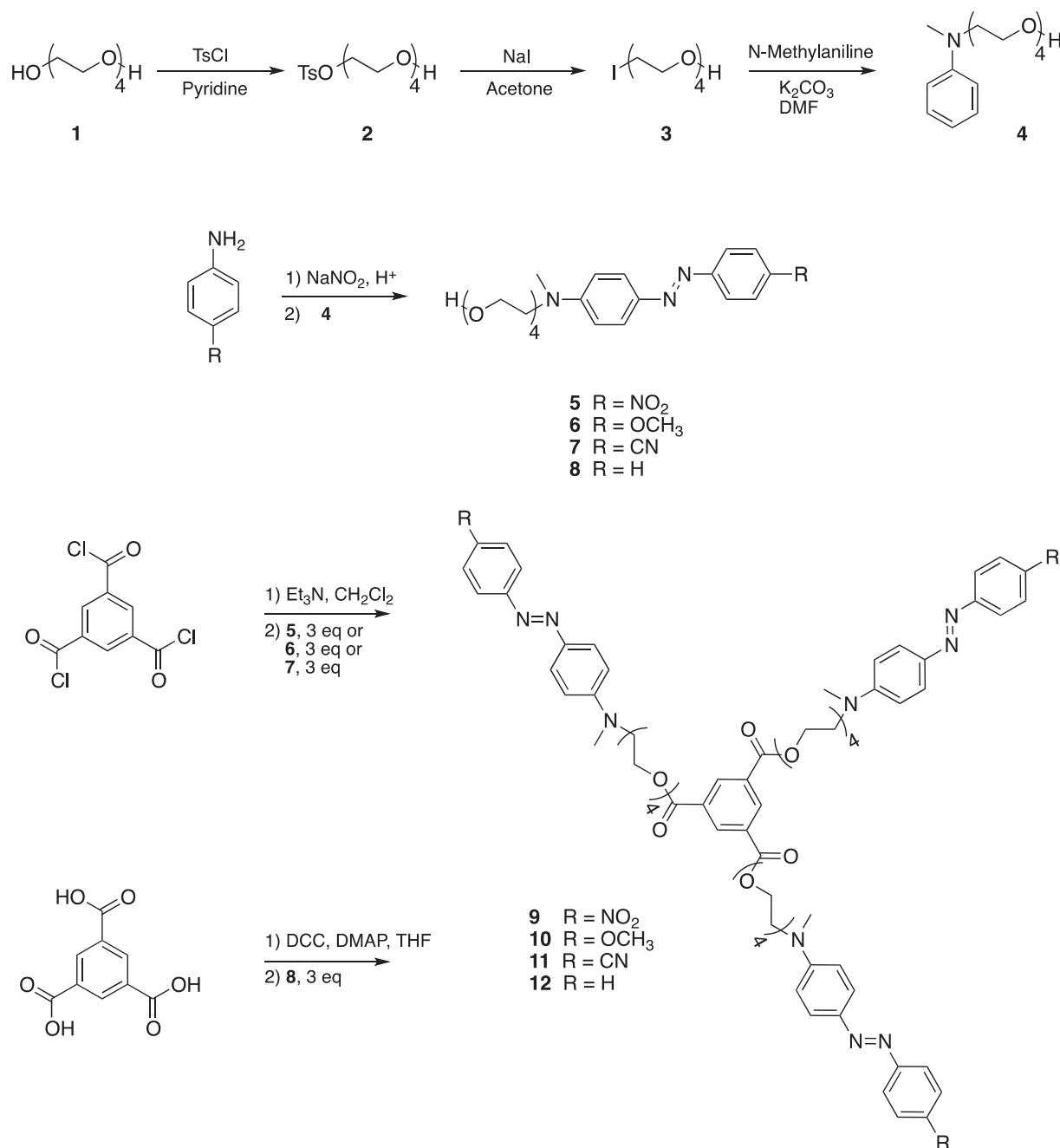


Fig. 1. Synthesis of the precursor azo-dyes and the star azo-compounds.

intermediate was further reacted with N-methyl aniline to give the corresponding aminoalcohol **4**. The diazonium salts were prepared by reacting the adequate aniline compound with NaNO_2 in acidic medium and were further reacted with compound **4** to form the azo-dyes precursors **5–8**. The star-oligomers **9–11** were obtained from the reaction between the corresponding azo-dyes precursors **5–7** and 1,3,5-benzenetricarbonyl trichloride. In the case of the azo-dye oligomer **8**, different reaction conditions were employed, this compound was reacted with 1,3,5-benzenetricarboxylic acid in the presence of DCC and DMAP using THF as solvent to give the expected star-azo-oligomer **12**.

3.2. Characterization of the star azo-oligomers

The obtained star azo-oligomers were characterized by ^1H and ^{13}C NMR spectroscopies. Since these compounds exhibited very similar features with slight shifts in the signals, we selected the star azo-oligomer containing amino-nitro substituted azobenzene units **9** as example. The ^1H NMR spectrum of **9** is shown in Fig. 2. In the aromatic region, there is a singlet at 8.75 due to the proton H^1 present in the phenyl group acting as core, followed by four doublets at 8.23, 7.83, 7.81 and 6.69 ppm due to the aromatic protons H^5 , H^6 , H^9 and H^{10} , present in the azobenzene unit. In addition, in the aliphatic region we can observe three signals at 4.42, 3.75, 3.70–3.50 ppm related to the methylenes OCH_2 present in the oligo(ethylene glycol) segments followed by a singlet at 3.05 ppm due to the methyl group NCH_3 .

On the other hand, the ^{13}C NMR spectrum of **9** is shown in Fig. 3. Firstly, we can observe a signal at 164.8 ppm due to the carbons of the carbonyl groups present in the star azo-oligomers. Moreover the aromatic carbons of the central phenyl groups are appearing

between 156.6 and 111.5. Finally, in the sp^3 region there are a series of signals due to the methylenes OCH_2 present in the oligo(ethylene glycol) segment, followed by three signals at 64.6, 52.2 and 39.6 ppm related to methylenes CH_2OCO , NCH_2 , and NCH_3 , respectively. The structure of the compounds was confirmed by MALDI-TOF mass spectrometry giving the expected values for all star-compounds. These values are included in the experimental section of this article.

3.3. Optical properties of the star-azo-oligomers

The optical properties of the precursor azo-dyes and the star azo-oligomers were studied by absorption spectroscopy in chloroform solution at room temperature, using concentrations between 5×10^{-5} and 1×10^{-5} M. The absorption spectra are shown in Fig. 4 and the results are summarized in Table 1.

Since the photoactive group is the azobenzene unit the absorption spectra of the precursor azo-dyes and their corresponding star azo-oligomers are very similar without bathochromic or hypsochromic shifts. Although the maximum wavelengths are almost the same the molar extinction coefficients differ. As we can observe, there is a cooperative effect of the three azobenzene units belonging to the star azo-oligomer, since the molar extinction coefficients of the star azo-oligomer is three times higher than the parent azo-dye precursor.

The absorption spectra of the low dipole moment star azo-oligomers bearing $-\text{OCH}_3$ and $-\text{H}$ substituents exhibit an intense absorption band and a shoulder due to the $\pi - \pi^*$ and $n - \pi^*$ transitions, respectively. These characteristics are corresponding to the aminoazobenzene category of compounds described by Rau. The star azo-oligomer containing amino-methoxy substituted

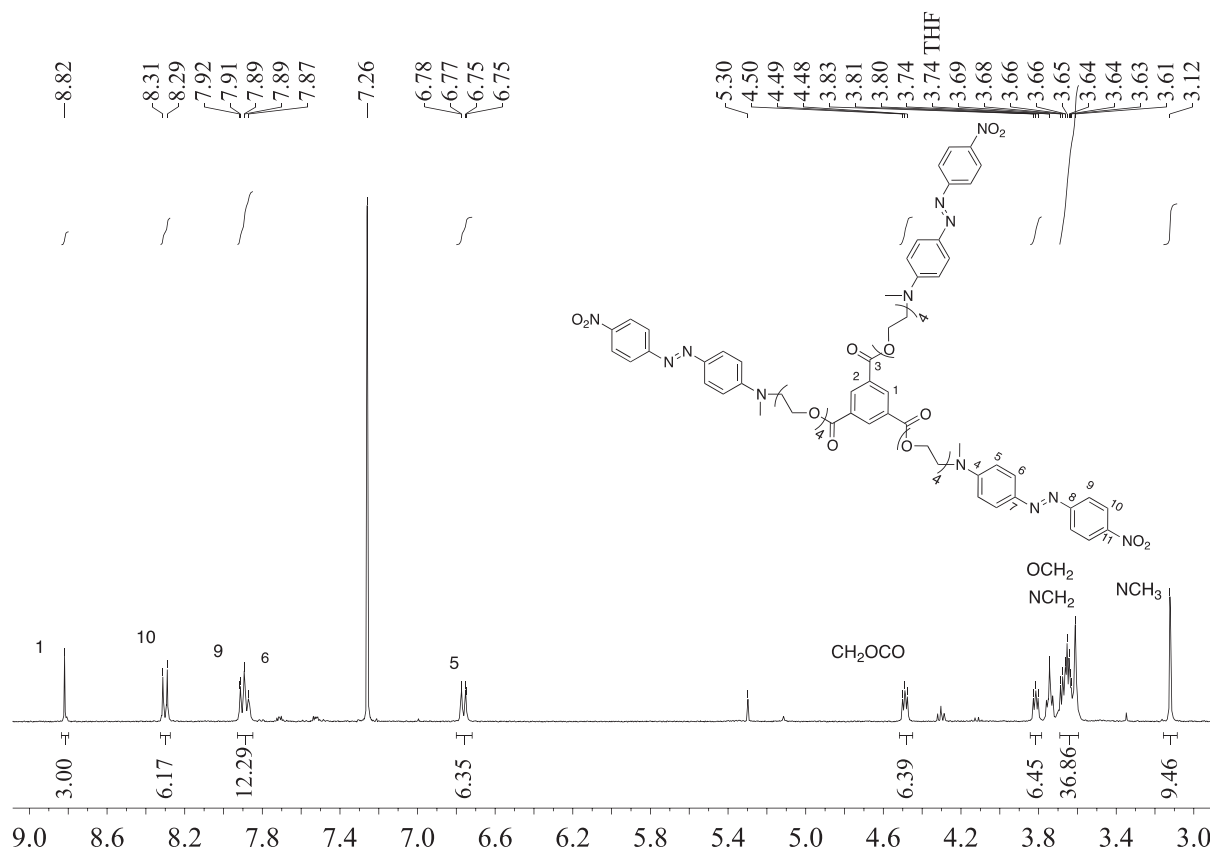


Fig. 2. ^1H NMR spectra of star azo-compound **9**.

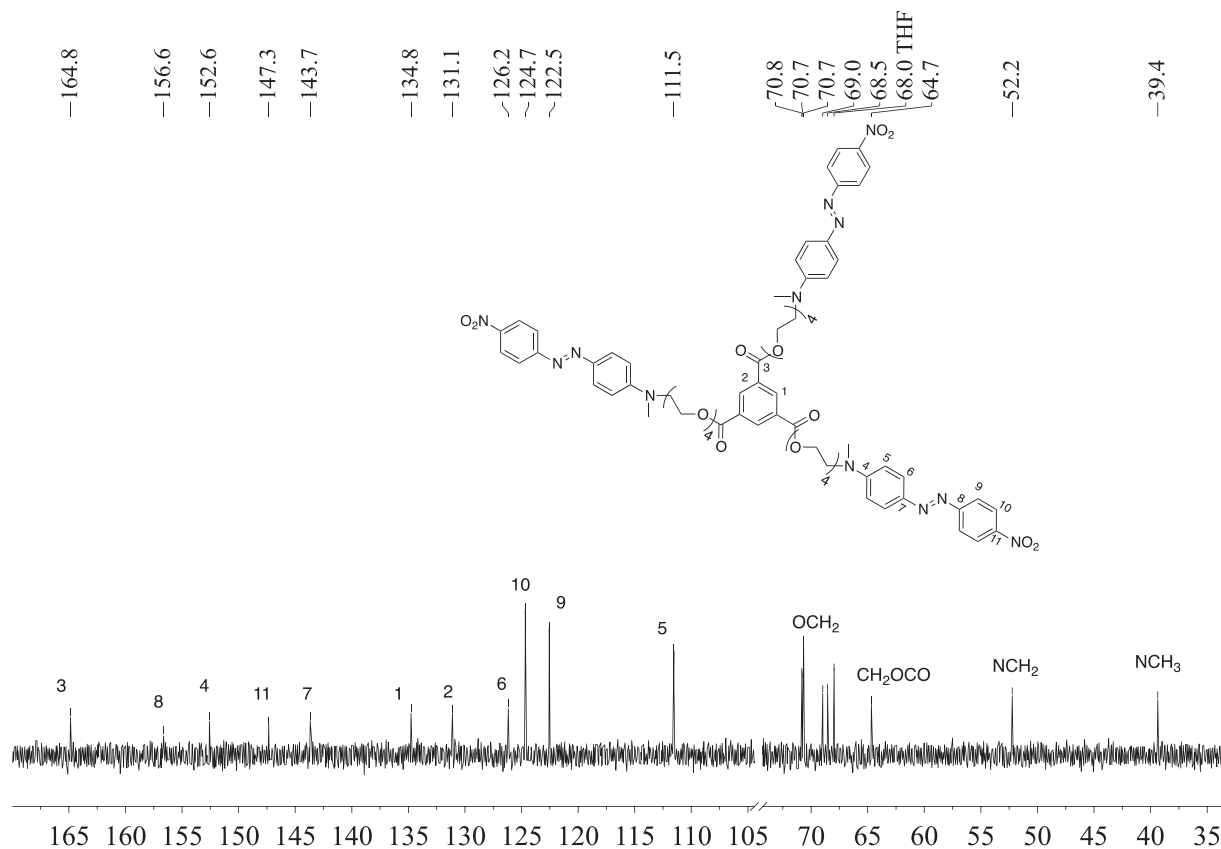


Fig. 3. ^{13}C NMR spectra of star azo-compound **9**.

azobenzenes showed an absorption band at $\lambda_{\text{max}} = 408$ nm with a shoulder at 445 nm. Similarly, star azo-compound bearing amino-azobenzene moieties showed an absorption band at $\lambda_{\text{max}} = 409$ nm followed by a shoulder at 440 nm. For these compounds it was possible distinguish the $\pi - \pi^*$ and $n - \pi^*$ transitions. On the contrary, the star-oligomers with high dipole moment (amino-cyano and amino-nitro group) were presenting absorption spectra with only one band for both transitions. In the case of compound **9**,

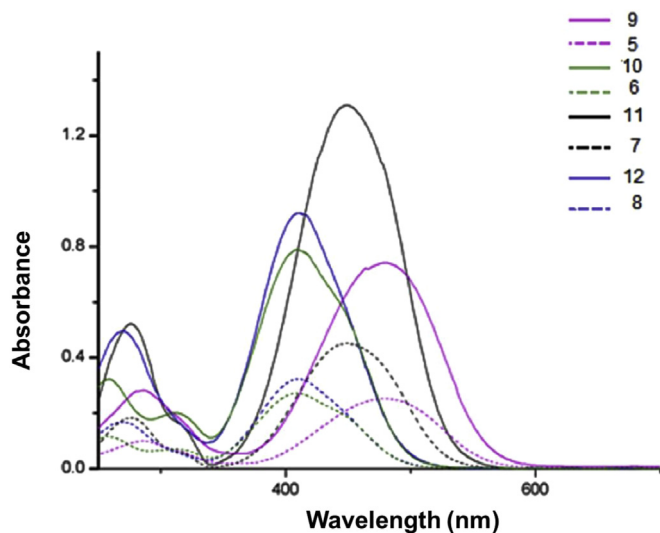


Fig. 4. Absorption spectra of the precursor azo-dyes **5–8** and the star azo-compounds **9–12** in CHCl_3 solution.

Table 1
Optical properties of the precursor dyes and the star azo-oligomers.

| Compound | λ_{max} (nm) | ϵ ($\text{M}^{-1}\text{cm}^{-1}$) |
|-----------|-----------------------------|--|
| 5 | 480 | 27,890 |
| 6 | 408 | 16,300 |
| 7 | 449 | 27,080 |
| 8 | 409 | 19,360 |
| 9 | 480 | 82,220 |
| 10 | 408 | 47,410 |
| 11 | 449 | 78,790 |
| 12 | 409 | 55,540 |

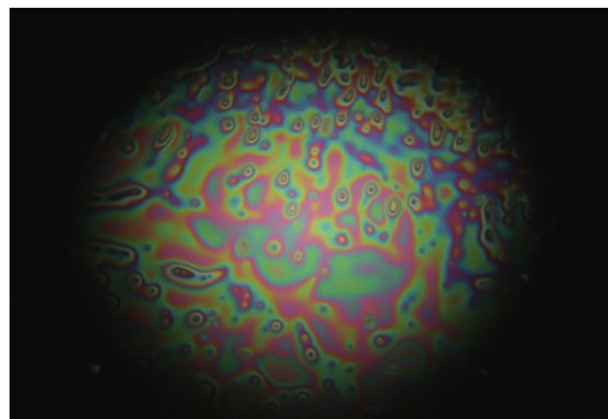


Fig. 5. Image of the mesophase of compound **9** at 75°C .

bearing a nitro substituent, the absorption maximum was recorded at 480 nm and for compound **11** with a cyano group the same absorption band was found with a maximum at 449 nm. These azobenzenes belong to the pseudo-stilbenes category of azobenzene, where only one absorption band is distinguished as a consequence of the fact that the energies of $\pi - \pi^*$ and $n - \pi^*$ bands are inverted [13].

3.4. Liquid crystalline behavior of the star azo-oligomers

The liquid crystalline behavior of the star azo-oligomers was studied by light polarized microscopy as a function of the temperature, from 25 to 100 °C. Only the star azo-oligomer containing amino-nitro substituted azobenzenes (**9**) showed liquid crystalline behavior. This compound exhibited a nematic mesophase in the range between 70 and 82 °C. Fig. 5 shows the image of the compound at 75 °C. We can attribute this behavior to the extended rigidity of the high polar azobenzene unit, which is easier to orient under the influence of light. A similar behavior was also observed in other related compounds containing amino-nitro azobenzene units such as azo-dyes containing two azobenzene units linked by an oligo(ethylene glycol) segment [28], and dendrons containing azobenzene units [29,30].

4. Conclusions

A novel series of star azo-oligomers containing substituted azobenzene units (amino-methoxy, amino, amino-cyano and amino-nitro) were successfully synthesized and characterized by ^1H and ^{13}C NMR spectroscopy and the structure was confirmed by mass spectrometry.

The star azo-oligomer containing amino-methoxy substituted azobenzenes showed an absorption band at $\lambda_{\text{max}} = 408$ nm with a shoulder at 445 nm. Similarly, star compound bearing amino azobenzene moieties showed an absorption band at $\lambda_{\text{max}} = 409$ nm followed by a shoulder at 440 nm. In all cases it is possible distinguish the $\pi - \pi^*$ and $n - \pi^*$ transitions. On the other hand, in the absorption spectra of the star azo-oligomers with high dipole moment bearing amino-cyano and amino-nitro substituted azobenzene units, we can observe only one absorption band in the visible region at 449 and 480 nm, respectively, due to the $\pi - \pi^*$ and $n - \pi^*$ transitions. These azobenzenes belong to the third category of Rau's classification "pseudostilbenes", where the $\pi - \pi^*$ and $n - \pi^*$ bands totally overlap. Only the star azo-oligomer containing amino-nitro substituted azobenzene units exhibited a liquid crystalline behavior, showing a mesophase between 70 and 82 °C due to the higher polarity and rigidity of the amino-nitro substituted azobenzene units, which can be easily oriented with polarized light.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.molstruc.2018.01.082>.

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