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# Synthesis, characterization and optical properties of novel dendronized azo-dyes containing a fullerene C<sub>60</sub> unit and well-defined oligo(ethylene glycol) segments†

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Herein, we report the preparation and characterization of a novel series of dendronized azo-dyes containing a fullerene C<sub>60</sub> unit and well-defined oligo(ethylene glycol) spacers. The azobenzene units present in these dyes were substituted in the 4'-position with different functional groups (-H, -OCH<sub>3</sub>, -C<sub>4</sub>H<sub>9</sub>, -CN and -NO<sub>2</sub>). The optical properties of these compounds were studied by absorption spectroscopy as a function of the dipole moment of the azobenzene moieties. All fullerene C<sub>60</sub>-azobenzene derivatives exhibited *trans*-*cis* photoisomerization and photoprotonation under irradiation with UV-light. The results were compared to those obtained with their precursor azo-dyes without fullerene C<sub>60</sub>. It was found that the presence of the fullerene unit significantly quenches the photoisomerization yield, whereas the photoprotonation was not affected by the presence of this chromophore.

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## 1 Introduction

Fullerene C<sub>60</sub> has been widely studied and employed in the elaboration of many opto-electronic and photovoltaic devices because of its remarkable electronic properties. This chromophore is considered one of the best molecular electron-acceptor groups able to participate in Förster Resonance Energy Transfer (FRET) and Charge Transfer (CT) phenomena either in solution or in the solid state.<sup>1-3</sup> However, the applications of fullerene C<sub>60</sub> itself are very limited because of its poor solubility in organic solvents. The incorporation of alkyl chains and other functional groups into fullerene C<sub>60</sub> has led to the development of novel molecular structures with enormous potential optical applications.<sup>4-8</sup> Very recently, some hybrid systems based on azo-dyes containing fullerene C<sub>60</sub> units have been investigated due to their synergistic effect. Wang *et al.* reported the functionalization of fullerene C<sub>60</sub> *via* the addition of a substituted azobenzene as a carbene active intermediate.<sup>9</sup> Kay *et al.* reported the synthesis and optical properties of a novel azo-dendrimer bearing a fullerene C<sub>60</sub> unit as core.<sup>10</sup> Other related structures combining azobenzene-fullerene, exhibiting interesting optical properties, have been reported in the

literature.<sup>11-13</sup> Some of them led to the development of new materials for molecular photoswitching,<sup>9,10,14</sup> smart optoelectronic devices<sup>15</sup> and organic solar cells.<sup>16,17</sup>

Rau classified azobenzenes into three main categories based on their photochemical behaviour.<sup>18</sup> Unsubstituted photochromic azobenzene belong to the first category, known as "azobenzenes". The thermally stable *trans* isomer exhibits an intense absorption band at 350 nm due to the  $\pi$ - $\pi^*$  transition, as well as a weak intensity band at 440 nm related to the  $n$ - $\pi^*$  transition, whereas the *cis* isomer undergoes similar transitions but with a more intense  $n$ - $\pi^*$  band. Moreover, "azobenzenes" have a relatively poor overlap of the  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  bands. The second category, known as "aminoazobenzenes" usually includes azobenzenes that are substituted by an electron-donor group and are characterized by the significant overlap of the  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  bands. Finally, azobenzenes bearing an electron-donor and an electron-acceptor group belong to the third category, named "pseudostilbenes", where the  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  bands are practically superimposed and inverted on the energy scale.<sup>18</sup>

When donor-acceptor substituted azobenzenes are incorporated into a polymer backbone, they generate very versatile photoactive materials. In particular, the irradiation of these polymers with linear polarized light produces rapid *trans*-*cis* photoisomerization of "pseudostilbene" azobenzenes. In consequence, polarized light allows the selective activation of "pseudostilbenes" bearing a polarization axis parallel to the absorbing radiation, which causes the photoalignment of the azobenzene moieties until they become perpendicular to the light polarization axis.<sup>16-22</sup>

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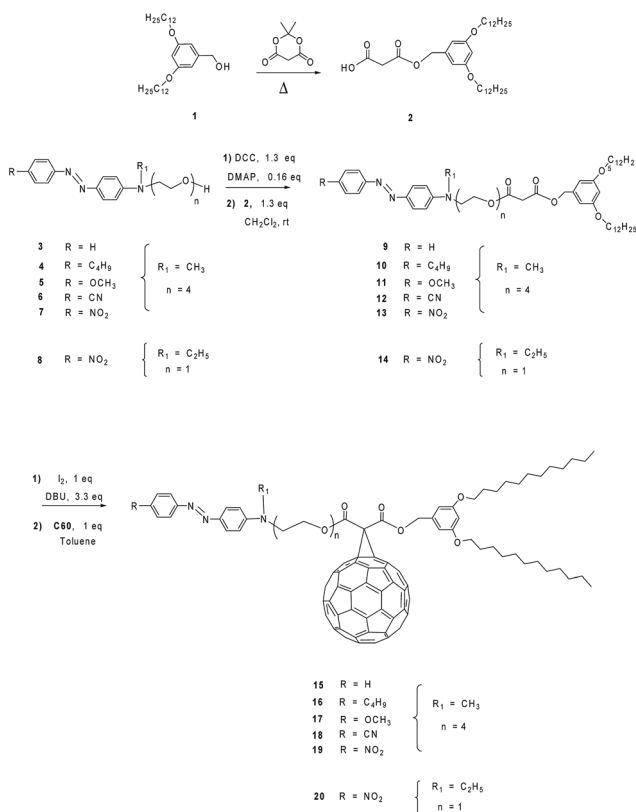


Fig. 1 Synthesis of the fullerene  $C_{60}$ -azobenzene derivatives.

Our research group has developed different series of azo-dyes<sup>23–26</sup> and azo-polymers<sup>27,28</sup> with different structures. Very recently, we reported the preparation and optical properties of some photoactive azo-dendrons and azo-dendrimers bearing a liquid crystalline behaviour, which exhibited a photoprotonation phenomenon.<sup>29</sup> In this work, we describe the synthesis and characterization of a novel series of dendronized azo-dyes containing fullerene  $C_{60}$  units, flexible alkyl and oligo(ethylene glycol) spacers. The amino-azobenzenes reported in this work were substituted in the 4'-position with different functional groups ( $-H$ ,  $-OCH_3$ ,  $-C_4H_9$ ,  $-CN$  and  $-NO_2$ ). The Bingel reaction was used in order to obtain novel fullerene  $C_{60}$ -azobenzene branched systems (Fig. 1 *vide infra*), which exhibit *trans-cis* photoisomerization and photoprotonation under irradiation with UV-light. The optical properties of these compounds were studied in detail by absorption spectroscopy. The aim of this work is to demonstrate the ability of these compounds to modify their optical properties by photoprotonation and their susceptibility to favor the energy transfer phenomenon instead of the *trans-cis* photoisomerization due to the strong acceptor character of the fullerene unit.

## 2 Experimental

### 2.1 General conditions

All reagents used in the synthesis of the fullerene  $C_{60}$ -azobenzene derivatives were purchased from Aldrich and used as received without further purification. Dichloromethane was

dried by distillation over calcium hydride and anhydrous toluene was employed. Precursor azo-dyes were synthesized according to the method previously reported by us,<sup>23,24,30</sup> whereas *N*-ethyl-*N*-(2-hydroxyethyl)-4-(4-nitrophenylazo) aniline (Disperse Red-1, **DR1**) was purchased from Aldrich. The fullerene  $C_{60}$  was incorporated into azobenzene derivatives as described in the literature.<sup>31,32</sup>

$^1H$  and  $^{13}C$  NMR spectra of the intermediates and final compounds involved in the synthesis were recorded in  $CDCl_3$  solution at room temperature on a Bruker Avance 400 MHz spectrometer, operating at 400 MHz and 100 MHz for  $^1H$  and  $^{13}C$ , respectively. All compounds 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 width quartz cuvettes. MALDI-TOF mass spectra were obtained on a Bruker Daltonic Felx Analysis, using dithranol as matrix.

Photoisomerization experiments were carried out in solution and solid state (cast film). For the disubstituted malonic derivatives (**9**, **10**, **11**) and the fullerene  $C_{60}$ -azobenzene derivatives (**15**, **16**, **17**) the photoisomerization experiments were conducted in DMF solution ( $2.5 \times 10^{-4}$  M) at room temperature. Cast films were prepared by depositing a saturated solution of the azo-dye on quartz substrates. Solutions and films were irradiated using a Compact UV lamp model UVGL-25, 254/365 nm (6 W). The samples were irradiated with intervals of 10 s and the spectral changes were monitored by absorption spectroscopy. Meanwhile, photoprotonation experiments with the fullerene  $C_{60}$ -azobenzene derivatives were carried out in  $CHCl_3$  solution. Compounds **15** and **19** were irradiated at 254 nm and monitored by absorption spectroscopy with intervals of 10 and 30 s, respectively.

### 2.2 Synthesis

**2.2.1 Synthesis of the 3-dodecyloxy-5-hydroxybenzyl alcohol (1).** First generation dendron  $G_1OH$  (**1**) was prepared according to the method previously reported by us.<sup>33</sup> The coupling constants were confirmed according a previous work reported by Fréchet *et al.*<sup>34</sup>

$^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 6.49 (t,  $J$  = 2 Hz, 2H,  $H^1$ ), 6.37 (t,  $J$  = 2 Hz, 1H,  $H^2$ ), 4.61 (s, 2H,  $PhCH_2OH$ ), 3.93 (t,  $J$  = 7 Hz, 4H,  $PhOCH_2$ ), 1.79–1.72 (m, 4H,  $PhOCH_2CH_2$ ), 1.47–1.26 (m, 36H, all  $CH_2$  of the aliphatic chain), 0.88 (t,  $J$  = 7 Hz, 6H,  $CH_3$ ) ppm.

$^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 160.52 (2C,  $C^c$ ), 143.16 (1C,  $C^a$ ), 105.02 (2C,  $C^b$ ), 100.52 (1C,  $C^d$ ), 68.03 (2C,  $PhOCH_2$ ), 65.44 (1C,  $PhCH_2OH$ ), 31.90, 29.61–29.18, 26.02, 25.70, 22.87 (20C, all  $CH_2$  of the aliphatic chain), 14.09 (2C,  $CH_3$ ) ppm.

**2.2.2 Synthesis of 3-(3,5-bis(dodecyloxy)benzyloxy)-3-oxopropanoic acid (2).** The synthesis of the monosubstituted malonic ester was achieved according to the method described in the literature.<sup>31</sup>

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  = 6.47 (d,  $J$  = 2 Hz), 6.42 (t,  $J$  = 2 Hz), 5.14, (s, 2H), 3.93 (t,  $J$  = 6 Hz, 4H), 3.50 (s, 2H), 1.77 (m, 4H), 1.26 (m, 36H), 0.88 (t,  $J$  = 6 Hz, 6H) ppm.

$^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 171.38, 166.37, 160.39, 136.88, 106.38, 101.22, 68.01, 67.46, 40.78, 31.87, 29.55–29.16, 25.97, 22.62, 14.05 ppm.



### 2.3 Synthesis of the precursor azo-dyes

Precursor azo-dyes (4), (5) and RED-PEG-4 (7) were prepared according to the method previously reported by us.<sup>30,33,35</sup>

For the synthesis of azobenzenes (*E*)-2-(4-(phenyldiazenyl)phenyl)-5,8,11-trioxa-2-azatridecan-13-ol (3) and (*E*)-4-((4-((2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)ethyl)(methylamino)phenyl)diazenyl)benzotrile (6) (see ESI†).

### 2.4 Synthesis of the disubstituted malonic ester

**2.4.1 Synthesis of (*E*)-3,5-bis(dodecyloxy)benzyl-2-(4-(phenyldiazenyl)phenyl)-5,8,11-trioxa-2-azatridecan-13-yl-malonate (9).** 3 (0.26 g, 0.67 mmol), *N,N*-dimethyl-4-aminopyridine (DMAP) (0.013 g, 0.1 mmol) and intermediate 2 (0.489 g, 0.87 mmol) were dissolved in 10 mL of anhydrous CH<sub>2</sub>Cl<sub>2</sub>. After that, a solution of *N,N*-dimethyl-4-aminopyridine (DCC) (0.18 g, 0.87 mmol) in 5 mL of anhydrous CH<sub>2</sub>Cl<sub>2</sub> was added dropwise. The reaction mixture was stirred at room temperature for 8 h. Then, the crude product was filtered on Celite many times until the urea was completely removed. The crude product was concentrated at reduced pressure and purified by column chromatography on silica gel using hexanes/ethyl acetate (8 : 2) as eluent to yield compound 9 (Scheme 1a). Yield: 55%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.87 (d, *J* = 9 Hz, 2H, H<sup>5</sup>), 7.84 (d, *J* = 9 Hz, 2H, H<sup>4</sup>), 7.47–7.37 (m, 3H, H<sup>6</sup>–H), 6.75 (d, *J* = 9 Hz, 2H, H<sup>3</sup>), 6.47 (d, *J* = 2 Hz, 2H, H<sup>2</sup>), 6.41 (t, *J* = 2 Hz, 1H, H<sup>1</sup>), 5.09 (s, 2H, PhCH<sub>2</sub>OOC), 4.29 (t, *J* = 5 Hz, 2H, OOCCH<sub>2</sub> of the tetra(ethylene glycol) chain), 3.92 (t, *J* = 6 Hz, 4H, PhOCH<sub>2</sub> of the aliphatic chain), 3.68–3.59 (m, 14H, CH<sub>2</sub>N y OCH<sub>2</sub> of the tetra(ethylene glycol) chain), 3.46 (s, 2H, OOCCH<sub>2</sub>COO), 3.07 (s, 3H, CH<sub>3</sub>N), 1.80–1.71 (m, 4H, PhOCH<sub>2</sub>CH<sub>2</sub>), 1.46–1.39 (m, 4H, PhO(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 1.36–1.27 (m, 32H, all CH<sub>2</sub> of the aliphatic chain), 0.90 (t, *J* = 6 Hz, 6H, CH<sub>3</sub>) ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 166.17 (1C, C<sup>g</sup>), 166.01 (1C, C<sup>e</sup>), 160.28 (2C, C<sup>b</sup>), 153.00 (1C, C<sup>h</sup>), 151.22 (1C, C<sup>l</sup>), 143.45 (1C, C<sup>k</sup>), 137.08 (1C, C<sup>d</sup>), 129.14 (1C, C<sup>o</sup>), 128.70 (2C, C<sup>m</sup>), 124.85 (2C, C<sup>j</sup>), 122.02 (2C, C<sup>m</sup>), 111.21 (2C, C<sup>i</sup>), 106.20 (2C, C<sup>c</sup>), 100.94 (1C, C<sup>a</sup>), 70.58–70.41, 68.37 (6C, OCH<sub>2</sub> of the tetra(ethylene glycol) chain), 68.59 (2C, PhOCH<sub>2</sub> of the aliphatic chain), 67.85 (1C, PhCH<sub>2</sub>O), 66.96 (1C, NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 64.35 (1C, COOCH<sub>2</sub> of the tetra(ethylene glycol) chain), 51.97 (1C, NCH<sub>2</sub>), 41.18 (1C, C<sup>f</sup>), 39.00 (1C, NCH<sub>3</sub>), 31.75, 29.50–29.07, 25.88, 22.52 (20C, all CH<sub>2</sub> of the aliphatic chain), 13.97 (2C, CH<sub>3</sub>) ppm.

**2.4.2 Synthesis of (*E*)-3,5-bis(dodecyloxy)benzyl-2-(4-(4-butylphenyl)diazenyl)phenyl)-5,8,11-trioxa-2-azatridecan-13-yl-malonate (10).** Procedure described for the synthesis of 9, using 4 (0.2 g, 0.5 mmol), DMAP (0.008 g, 0.07 mmol), 2 (0.329 g, 0.6 mmol) and DCC (0.120 g, 0.58 mmol) to give compound 10 (Scheme 1b). Yield: 67%.

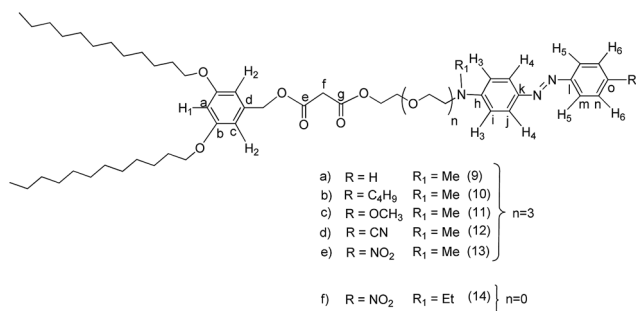
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.83 (d, *J* = 9 Hz, 2H, H<sup>5</sup>), 7.74 (d, *J* = 8 Hz, 2H, H<sup>4</sup>), 7.26 (d, *J* = 8 Hz, 2H, H<sup>6</sup>), 6.75 (d, *J* = 9 Hz, 2H, H<sup>3</sup>), 6.46 (d, *J* = 2 Hz, 2H, H<sup>2</sup>), 6.40 (t, *J* = 2 Hz, 1H, H<sup>1</sup>), 5.09 (s, 2H, PhCH<sub>2</sub>OOC), 4.29 (t, *J* = 5 Hz, 2H, OOCCH<sub>2</sub> of the tetra(ethylene glycol) chain), 3.92 (t, *J* = 7 Hz, 4H, PhOCH<sub>2</sub> of the aliphatic chain), 3.69–3.60 (m, 14H, CH<sub>2</sub>N y OCH<sub>2</sub> of the tetra(ethylene glycol) chain), 3.45 (s, 2H, OOCCH<sub>2</sub>COO), 3.09 (s, 3H, CH<sub>3</sub>N), 2.67 (t, *J* = 8 Hz, 2H, PhCH<sub>2</sub>), 1.79–1.70 (m, 4H, PhOCH<sub>2</sub>CH<sub>2</sub>), 1.68–1.57 (m, 2H, Ph(CH<sub>2</sub>)<sub>2</sub>), 1.45–1.26 (m, 38H, Ph(CH<sub>2</sub>)<sub>3</sub> and all CH<sub>2</sub> of the aliphatic chain), 0.95 (t, *J* = 7 Hz, 6H, CH<sub>3</sub>), 0.89 (t, *J* = 6 Hz, 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>): δ = 166.37 (1C, C<sup>g</sup>), 166.21 (1C, C<sup>e</sup>), 160.43 (2C, C<sup>b</sup>), 151.38 (1C, C<sup>h</sup>), 151.14 (1C, C<sup>l</sup>), 144.63 (1C, C<sup>o</sup>), 143.68 (1C, C<sup>k</sup>), 137.18 (1C, C<sup>d</sup>), 128.90 (2C, C<sup>m</sup>), 124.77 (2C, C<sup>m</sup>), 122.09 (2C, C<sup>j</sup>), 111.38 (2C, C<sup>i</sup>), 106.39 (2C, C<sup>c</sup>), 101.10 (1C, C<sup>a</sup>), 70.74–70.57, 68.76 (6C, OCH<sub>2</sub> of the tetra(ethylene glycol) chain), 67.17 (2C, PhOCH<sub>2</sub> of the aliphatic chain), 68.52 (1C, PhCH<sub>2</sub>O), 68.05 (1C, N(CH<sub>2</sub>)<sub>2</sub>), 64.53 (1C, COOCH<sub>2</sub> of the tetra(ethylene glycol) chain), 52.15 (1C, NCH<sub>2</sub>), 41.34 (1C, C<sup>f</sup>), 39.18 (1C, NCH<sub>3</sub>), 35.46 (1C, PhCH<sub>2</sub>), 33.48 (1C, PhCH<sub>2</sub>CH<sub>2</sub>), 31.88, 29.63–29.21, 26.01, 22.65 (20C, all CH<sub>2</sub> of the aliphatic chain), 22.30 (1C, Ph(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 14.08 (2C, CH<sub>3</sub>), 13.91 (1C, Ph(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>) ppm.

**2.4.3 Synthesis of (*E*)-3,5-bis(dodecyloxy)benzyl-2-(4-(4-methoxyphenyl)diazenyl)phenyl)-5,8,11-trioxa-2-azatridecan-13-yl-malonate (11).** Procedure described for the synthesis of 9, using 5 (0.2 g, 0.5 mmol), DMAP (0.009 g, 0.7 mmol), 2 (0.309 g, 0.6 mmol) and DCC (0.118 g, 0.7 mmol), to give compound 11 (Scheme 1c). Yield: 43%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.83 (d, *J* = 9 Hz, 2H, H<sup>5</sup>), 7.81 (d, *J* = 9 Hz, 2H, H<sup>4</sup>), 6.97 (d, *J* = 9 Hz, 2H, H<sup>6</sup>), 6.76 (d, *J* = 9 Hz, 2H, H<sup>3</sup>), 6.46 (d, *J* = 2 Hz, 2H, H<sup>2</sup>), 6.40 (t, *J* = 2 Hz, 1H, H<sup>1</sup>), 5.09 (s, 2H, PhCH<sub>2</sub>OOC), 4.29 (t, *J* = 5 Hz, 2H, OOCCH<sub>2</sub> of the tetra(ethylene glycol) chain), 3.92 (t, *J* = 7 Hz, 4H, PhOCH<sub>2</sub> of the aliphatic chain), 3.86 (s, 3H, PhOCH<sub>3</sub>), 3.69–3.61 (m, 14H, CH<sub>2</sub>N y OCH<sub>2</sub> of the tetra(ethylene glycol) chain), 3.46 (s, 2H, OOCCH<sub>2</sub>COO), 3.08 (s, 3H, CH<sub>3</sub>N), 1.78–1.75 (m, 4H, PhOCH<sub>2</sub>CH<sub>2</sub>), 1.44–1.26 (m, 36H, all CH<sub>2</sub> of the aliphatic chain), 0.88 (t, *J* = 7 Hz, 6H, CH<sub>3</sub>) ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 166.35 (1C, C<sup>g</sup>), 166.19 (1C, C<sup>e</sup>), 160.78 (1C, C<sup>o</sup>), 160.42 (2C, C<sup>b</sup>), 150.92 (1C, C<sup>h</sup>), 147.43 (1C, C<sup>l</sup>), 143.64 (1C, C<sup>k</sup>), 137.18 (1C, C<sup>d</sup>), 124.53 (2C, C<sup>j</sup>), 123.76 (2C, C<sup>m</sup>), 114.02 (2C, C<sup>n</sup>), 111.41 (2C, C<sup>i</sup>), 106.38 (2C, C<sup>c</sup>), 101.09 (1C, C<sup>a</sup>), 70.73–70.56, 68.75 (6C, OCH<sub>2</sub> of the tetra(ethylene glycol) chain), 68.52 (2C, PhOCH<sub>2</sub> of the aliphatic chain), 68.04 (1C, PhCH<sub>2</sub>O), 67.15 (1C, N(CH<sub>2</sub>)<sub>2</sub>), 64.52 (1C, COOCH<sub>2</sub> of the tetra(ethylene glycol) chain), 55.43 (1C, NCH<sub>2</sub>), 52.16 (1C, OCH<sub>3</sub>), 41.33 (1C, C<sup>f</sup>), 39.15 (1C, NCH<sub>3</sub>), 31.87, 29.62–29.20, 26.00, 22.64 (20C, all CH<sub>2</sub> of the aliphatic chain), 14.07 (2C, CH<sub>3</sub>) ppm.



Scheme 1



**2.4.4 Synthesis of (*E*)-3,5-bis(dodecyloxy)benzyl-2-(4-((4-cyanophenyl)diazenyl)phenyl)-5,8,11-trioxa-2-azatridecan-13-yl-malonate (12).** Procedure described for the synthesis of **9**, using **6** (0.205 g, 0.5 mmol), DMAP (0.009 g, 0.8 mmol), **2** (0.363 g, 0.6 mmol) and DCC (0.133 g, 0.64 mmol) to give compound **12** (Scheme 1d). Yield: 65%.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.86$  (d,  $J = 9$  Hz, 2H,  $\text{H}^5$ ), 7.85 (d,  $J = 10$  Hz, 2H,  $\text{H}^4$ ), 7.70 (d,  $J = 9$  Hz, 2H,  $\text{H}^6$ ), 6.75 (d,  $J = 9$  Hz, 2H,  $\text{H}^3$ ), 6.45 (d,  $J = 2$  Hz, 2H,  $\text{H}^2$ ), 6.40 (t,  $J = 2$  Hz, 1H,  $\text{H}^1$ ), 5.08 (s, 2H,  $\text{PhCH}_2\text{OOC}$ ), 4.29 (t,  $J = 5$  Hz, 2H,  $\text{OOCCH}_2$  of the tetra(ethylene glycol) chain), 3.91 (t,  $J = 7$  Hz, 4H,  $\text{PhOCH}_2$  of the aliphatic chain), 3.68–3.60 (m, 14H,  $\text{CH}_2\text{N}$  y  $\text{OCH}_2$  of the tetra(ethylene glycol) chain), 3.45 (s, 2H,  $\text{OOCCH}_2\text{COO}$ ), 3.11 (s, 3H,  $\text{CH}_3\text{N}$ ), 1.79–1.74 (m, 4H,  $\text{PhOCH}_2\text{CH}_2$ ), 1.45–1.25 (m, 36H, all  $\text{CH}_2$  of the aliphatic chain), 0.88 (t,  $J = 7$  Hz, 6H,  $\text{CH}_3$ ) ppm.

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 166.26$  (1C,  $\text{C}^{\text{e}}$ ), 166.09 (1C,  $\text{C}^{\text{e}}$ ), 160.36 (2C,  $\text{C}^{\text{b}}$ ), 155.31 (1C,  $\text{C}^{\text{l}}$ ), 152.24 (1C,  $\text{C}^{\text{h}}$ ), 143.48 (1C,  $\text{C}^{\text{k}}$ ), 137.11 (1C,  $\text{C}^{\text{d}}$ ), 132.90 (2C,  $\text{C}^{\text{n}}$ ), 125.77 (2C,  $\text{C}^{\text{m}}$ ), 122.57 (2C,  $\text{C}^{\text{j}}$ ), 118.84 (1C,  $\text{C}^{\text{o}}$ ), 111.70 (1C,  $\text{PhCN}$ ), 111.34 (2C,  $\text{C}^{\text{i}}$ ), 106.31 (2C,  $\text{C}^{\text{c}}$ ), 100.99 (1C,  $\text{C}^{\text{a}}$ ), 70.70–70.50, 68.68 (6C,  $\text{OCH}_2$  of the tetra(ethylene glycol) chain), 67.07 ( $\text{PhOCH}_2$  of the aliphatic chain), 68.44 (1C,  $\text{PhCH}_2\text{O}$ ), 67.97 (1C,  $\text{N}(\text{CH}_2)_2$ ), 64.42 (1C,  $\text{COOCH}_2$  of the tetra(ethylene glycol) chain), 52.07 (1C,  $\text{NCH}_2$ ), 41.27 (1C,  $\text{C}^{\text{f}}$ ), 39.18 (1C,  $\text{NCH}_3$ ), 31.80, 29.55–29.13, 25.93, 22.56 (20C, all  $\text{CH}_2$  of the aliphatic chain), 14.01 (2C,  $\text{CH}_3$ ) ppm.

**2.4.5 Synthesis of (*E*)-3,5-bis(dodecyloxy)benzyl-2-(4-((4-nitrophenyl)diazenyl)phenyl)-5,8,11-trioxa-2-azatridecan-13-yl-malonate (13).** Procedure described for the synthesis of **9**, using **7** (0.208 g, 0.5 mmol), DMAP (0.009 g, 0.8 mmol), **2** (0.352 g, 0.6 mmol) and DCC (0.129 g, 0.62 mmol) to give compound **13** (Scheme 1e). Yield: 77%.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.27$  (d,  $J = 9$  Hz, 2H,  $\text{H}^6$ ), 7.88 (d,  $J = 9$  Hz, 2H,  $\text{H}^5$ ), 7.86 (d,  $J = 9$  Hz, 2H,  $\text{H}^4$ ), 6.75 (d,  $J = 9$  Hz, 2H,  $\text{H}^3$ ), 6.45 (d,  $J = 2$  Hz, 2H,  $\text{H}^2$ ), 6.38 (t,  $J = 2$  Hz, 1H,  $\text{H}^1$ ), 5.08 (s, 2H,  $\text{PhCH}_2\text{OCO}$ ), 4.29 (t,  $J = 5$  Hz, 2H,  $\text{PhOCH}_2$  of the tetra(ethylene glycol) chain), 3.90 (t,  $J = 7$  Hz, 4H,  $\text{PhOCH}_2$  of the aliphatic chain), 3.69–3.60 (m, 14H,  $\text{CH}_2\text{N}$  y  $\text{OCH}_2$  of the tetra(ethylene glycol) chain), 3.45 (s, 2H,  $\text{OOCCH}_2\text{COO}$ ), 3.11 (s, 3H,  $\text{CH}_3\text{N}$ ), 1.75–1.70 (m, 4H,  $\text{PhOCH}_2\text{CH}_2$ ), 1.45–1.38 (m, 4H,  $\text{PhO}(\text{CH}_2)_2\text{CH}_2$ ), 1.33–1.24 (m, 32H, all  $\text{CH}_2$  of the aliphatic chain), 0.87 (t,  $J = 7$  Hz, 6H,  $\text{CH}_3$ ) ppm.

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 166.21$  (1C,  $\text{C}^{\text{e}}$ ), 166.06 (1C,  $\text{C}^{\text{e}}$ ), 160.45 (2C,  $\text{C}^{\text{b}}$ ), 156.74 (1C,  $\text{C}^{\text{l}}$ ), 152.54 (1C,  $\text{C}^{\text{h}}$ ), 147.34 (1C,  $\text{C}^{\text{o}}$ ), 143.77 (1C,  $\text{C}^{\text{k}}$ ), 137.21 (1C,  $\text{C}^{\text{d}}$ ), 125.99 (2C,  $\text{C}^{\text{j}}$ ), 124.50 (2C,  $\text{C}^{\text{n}}$ ), 122.49 (2C,  $\text{C}^{\text{m}}$ ), 111.46 (2C,  $\text{C}^{\text{i}}$ ), 106.42 (2C,  $\text{C}^{\text{c}}$ ), 101.18 (1C,  $\text{C}^{\text{a}}$ ), 70.77–70.57, 68.74 (6C,  $\text{OCH}_2$  of the tetra(ethylene glycol) chain), 67.08 (2C,  $\text{PhOCH}_2$  of aliphatic chain), 68.55 (1C,  $\text{PhCH}_2\text{O}$ ), 68.06 (1C,  $\text{N}(\text{CH}_2)_2$ ), 64.44 (1C,  $\text{COOCH}_2$  of the tetra(ethylene glycol) chain), 52.17 (1C,  $\text{NCH}_2$ ), 41.31 (1C,  $\text{C}^{\text{f}}$ ), 39.17 (1C,  $\text{NCH}_3$ ), 31.81, 29.56–29.19, 25.97, 22.57 (20C, all  $\text{CH}_2$  of the aliphatic chain), 13.98 (2C,  $\text{CH}_3$ ) ppm.

**2.4.6 Synthesis of (*E*)-3,5-bis(dodecyloxy)benzyl-2-(ethyl(4-((4-nitrophenyl)diazenyl)phenyl)amino)ethyl malonate (14).** Procedure described for the synthesis of **9**, using **DR1** (0.1 g, 0.2 mmol), DMAP (0.006 g, 0.02 mmol), **2** (0.184 g, 0.2 mmol) and

DCC (0.078 g, 0.2 mmol) to give compound **14** (Scheme 1f). Yield: 80%.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.31$  (d,  $J = 9$  Hz, 2H,  $\text{H}^6$ ), 7.91 (d,  $J = 9$  Hz, 2H,  $\text{H}^5$ ), 7.89 (d,  $J = 10$  Hz, 2H,  $\text{H}^4$ ), 6.76 (d,  $J = 9$  Hz, 2H,  $\text{H}^3$ ), 6.46 (d,  $J = 2$  Hz, 2H,  $\text{H}^2$ ), 6.40 (t,  $J = 2$  Hz, 1H,  $\text{H}^1$ ), 5.09 (s, 2H,  $\text{PhCH}_2\text{OCO}$ ), 4.36 (t,  $J = 6$  Hz, 2H,  $\text{NCH}_2\text{CH}_2\text{OCO}$ ), 3.91 (t,  $J = 7$  Hz, 4H,  $\text{PhOCH}_2$  of the aliphatic chain), 3.66 (t,  $J = 6$  Hz, 2H,  $\text{CH}_3\text{CH}_2\text{NCH}_2$ ), 3.51–3.46 (m, 2H,  $\text{OCOCH}_2\text{CH}_2\text{NCH}_2$ ) 3.45 (s, 2H,  $\text{OOCCH}_2\text{COO}$ ), 1.77–1.70 (m, 4H,  $\text{PhOCH}_2\text{CH}_2$ ), 1.45–1.38 (m, 4H,  $\text{PhO}(\text{CH}_2)_2\text{CH}_2$ ), 1.31–1.20 (m, 35H, all  $\text{CH}_2$  of the aliphatic chain and  $\text{NCH}_2\text{CH}_3$ ), 0.88 (t,  $J = 7$  Hz, 6H,  $\text{CH}_3$ ) ppm.

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 166.19$  (1C,  $\text{C}^{\text{e}}$ ), 165.91 (1C,  $\text{C}^{\text{e}}$ ), 160.54 (2C,  $\text{C}^{\text{b}}$ ), 156.74 (1C,  $\text{C}^{\text{l}}$ ), 151.10 (1C,  $\text{C}^{\text{h}}$ ), 147.54 (1C,  $\text{C}^{\text{o}}$ ), 144.01 (1C,  $\text{C}^{\text{k}}$ ), 137.16 (1C,  $\text{C}^{\text{d}}$ ), 126.21 (2C,  $\text{C}^{\text{n}}$ ), 124.58 (2C,  $\text{C}^{\text{j}}$ ), 122.63 (2C,  $\text{C}^{\text{m}}$ ), 111.48 (2C,  $\text{C}^{\text{i}}$ ), 106.61 (2C,  $\text{C}^{\text{c}}$ ), 101.21 (1C,  $\text{C}^{\text{a}}$ ), 68.15 (2C,  $\text{PhOCH}_2$  of the aliphatic chain), 67.26 (1C,  $\text{PhCH}_2\text{O}$ ), 62.23 (1C,  $\text{CH}_3\text{CH}_2\text{NCH}_2\text{CH}_2\text{O}$ ), 48.57 (1C,  $\text{CH}_3\text{CH}_2\text{NCH}_2$ ), 45.67 (1C,  $\text{CH}_3\text{CH}_2\text{N}$ ), 41.43 (1C,  $\text{C}^{\text{f}}$ ), 31.88 (2C,  $\text{CH}_3(\text{CH}_2)_2$ ), 29.63–29.25 (14C, all  $\text{CH}_2$  of the aliphatic chain), 26.03 (2C,  $\text{PhO}(\text{CH}_2)_3$ ), 22.64 (2C,  $\text{CH}_3\text{CH}_2$ ), 14.04 (1C,  $\text{CH}_3$ ), 12.27 (1C,  $\text{NCH}_2\text{CH}_3$ ) ppm.

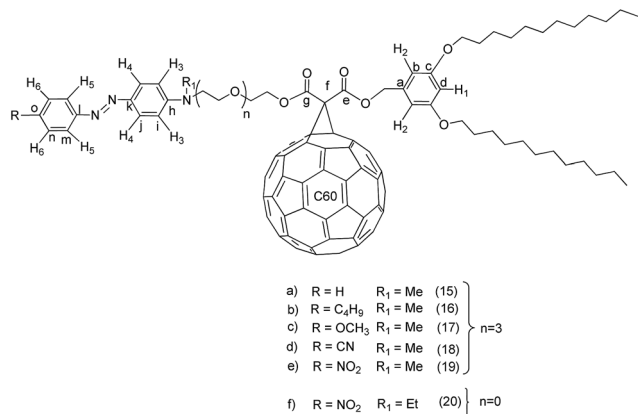
## 2.5 Synthesis of the fullerene $\text{C}_{60}$ -azobenzene derivatives

**2.5.1 Synthesis of the fullerene  $\text{C}_{60}$ -amino substituted azobenzene (15).** **9** (0.240 g, 0.3 mmol),  $\text{I}_2$  (0.065 g, 0.025 mmol) and fullerene  $\text{C}_{60}$  (0.185 g, 0.3 mmol) were dissolved in 180 mL of anhydrous toluene. After some minutes, 1,8-diazabicyclo [5,4,0]undec-7-ene (DBU) (0.185 g, 0.85 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 6 h. Then, the crude product was filtered, concentrated at reduced pressure and purified by column chromatography on silica gel. In the first column, a mixture toluene/hexane (1 : 1) was used as eluent in order to remove unreacted fullerene  $\text{C}_{60}$ . In the second column, a mixture of hexane/ethyl acetate (7 : 3 and 6 : 4) was employed to give the pure desired compound **15** (Scheme 2a). Yield: 31%. MALDI-TOF:  $\text{C}_{115}\text{H}_{83}\text{N}_3\text{O}_9$ , calcd:  $[\text{M} + \text{H}]^+$  1650.90 found ( $m/z$ ):  $[\text{M} + \text{H}]^+$  1651.93.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ) (Scheme 2a):  $\delta = 7.85$  (d,  $J = 9$  Hz, 2H,  $\text{H}^5$ ), 7.83 (d,  $J = 8$  Hz, 2H,  $\text{H}^4$ ), 7.48–7.38 (m, 3H,  $\text{H}^6\text{-H}$ ), 6.75 (d,  $J = 9$  Hz, 2H,  $\text{H}^3$ ), 6.58 (d,  $J = 2$  Hz, 2H,  $\text{H}^2$ ), 6.40 (t,  $J = 2$  Hz, 1H,  $\text{H}^1$ ), 5.43 (s, 2H,  $\text{PhCH}_2\text{OCO}$ ), 4.63 (t,  $J = 5$  Hz, 2H,  $\text{OOCCH}_2$  of the tetra(ethylene glycol) chain), 3.89 (t,  $J = 6.50$  Hz, 4H,  $\text{PhOCH}_2$  of the aliphatic chain), 3.83 (t,  $J = 5$ , 2H,  $\text{OCH}_2$ ), 3.68–3.62 (m, 14H,  $\text{CH}_2\text{N}$  y  $\text{OCH}_2$  of the tetra(ethylene glycol) chain), 3.09 (s, 3H,  $\text{CH}_3\text{N}$ ), 1.77–1.73 (m, 4H,  $\text{PhOCH}_2\text{CH}_2$ ), 1.43–1.25 (m, 36H, all  $\text{CH}_2$  of the aliphatic chain), 0.89 (t,  $J = 7$  Hz, 6H,  $\text{CH}_3$ ) ppm.

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ) (Scheme 2a): 163.46 (1C,  $\text{C}^{\text{e}}$ ), 163.29 (1C,  $\text{C}^{\text{e}}$ ), 160.47 (2C,  $\text{C}^{\text{b}}$ ), 153.17 (1C,  $\text{C}^{\text{h}}$ ), 151.34 (1C,  $\text{C}^{\text{l}}$ ), 145.20, 145.16, 145.11, 144.97, 144.83, 144.63, 144.60, 144.55, 144.48, 144.41, 143.80, 143.78, 143.64, 143.01, 142.96, 142.89, 142.13, 141.85, 141.77, 140.84, 140.82, 139.34, 138.66 (fullerene carbons), 136.55 (1C,  $\text{C}^{\text{d}}$ ), 129.31 (1C,  $\text{C}^{\text{o}}$ ), 128.87 (2C,  $\text{C}^{\text{n}}$ ), 125.02 (2C,  $\text{C}^{\text{j}}$ ), 122.17 (2C,  $\text{C}^{\text{m}}$ ), 111.38 (2C,  $\text{C}^{\text{i}}$ ), 107.15 (2C,  $\text{C}^{\text{c}}$ ), 101.64 (1C,  $\text{C}^{\text{a}}$ ), 71.40 (fullerene carbon), 70.75–70.64, 68.91,





Scheme 2

68.66 (7C, OCH<sub>2</sub> of the chain tetra(ethylene glycol) chain), 68.53 (2C, PhOCH<sub>2</sub> of the aliphatic chain), 68.11 (1C, PhCH<sub>2</sub>O), 66.18 (1C, NCH<sub>2</sub>), 52.15 (1C, C<sup>f</sup>), 39.24 (1C, NCH<sub>3</sub>), 31.90, 29.67–29.26, 26.10, 22.67 (20C, CH<sub>2</sub> of the aliphatic chain), 14.12 (2C, CH<sub>3</sub>) ppm.

**2.5.2 Synthesis of the fullerene C<sub>60</sub>-amino-butyl substituted azobenzene (16).** Procedure employed for the synthesis of **15**, using **10** (0.091 g, 0.1 mmol), I<sub>2</sub> (0.023 g, 0.1 mmol), fullerene C<sub>60</sub> (0.066 g, 0.1 mmol) dissolved in 70 mL of anhydrous toluene, and DBU (0.046 g, 0.3 mmol), to obtain compound **16** (Scheme 2b). Yield: 40%. MALDI-TOF: C<sub>119</sub>H<sub>91</sub>N<sub>3</sub>O<sub>9</sub> calcd: [M + H]<sup>+</sup> 1707.01 found (*m/z*): [M + H]<sup>+</sup> 1708.59.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.83 (d, *J* = 9 Hz, 2H, H<sup>5</sup>), 7.75 (d, *J* = 8 Hz, 2H, H<sup>4</sup>), 7.27 (d, *J* = 7 Hz, 2H, H<sup>6</sup>), 6.75 (d, *J* = 9 Hz, 2H, H<sup>3</sup>), 6.58 (d, *J* = 2 Hz, 2H, H<sup>2</sup>), 6.40 (t, *J* = 2 Hz, 1H, H<sup>1</sup>), 5.43 (s, 2H, PhCH<sub>2</sub>OOC), 4.62 (t, *J* = 5 Hz, 2H, OOCCH<sub>2</sub> of the tetra(ethylene glycol) chain), 3.89 (t, *J* = 6 Hz, 4H, PhOCH<sub>2</sub> of the aliphatic chain), 3.83 (t, *J* = 5 Hz, OCH<sub>2</sub>), 3.69–3.62 (m, 14H, CH<sub>2</sub>N y OCH<sub>2</sub> of the tetra(ethylene glycol) chain), 3.09 (s, 3H, CH<sub>3</sub>N), 2.67 (t, *J* = 8 Hz, 2H, PhCH<sub>2</sub>), 1.77–1.70 (m, 4H, PhOCH<sub>2</sub>CH<sub>2</sub>), 1.67–1.60 (m, 2H, Ph(CH<sub>2</sub>)<sub>2</sub>), 1.42–1.25 (m, 38H, Ph(CH<sub>2</sub>)<sub>3</sub> and all CH<sub>2</sub> of the aliphatic chain), 0.95 (t, *J* = 7 Hz, 6H, CH<sub>3</sub>), 0.89 (t, *J* = 6 Hz, 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>): δ = 163.46 (1C, C<sup>g</sup>), 163.31 (1C, C<sup>e</sup>), 160.54 (2C, C<sup>b</sup>), 151.46 (1C, C<sup>h</sup>), 151.18 (1C, C<sup>l</sup>), 144.67 (1C, C<sup>o</sup>), 143.84 (1C, C<sup>k</sup>), 145.24, 145.20, 145.15, 145.05, 145.02, 144.87, 143.05, 143.00, 142.17, 141.89, 141.82, 140.88, 139.37, 138.71 (fullerene carbons), 136.60 (1C, C<sup>d</sup>), 128.91 (2C, C<sup>n</sup>), 124.82 (2C, C<sup>m</sup>), 122.16 (2C, C<sup>j</sup>), 111.46 (2C, C<sup>i</sup>), 107.24 (2C, C<sup>c</sup>), 101.77 (1C, C<sup>a</sup>), 71.49 (fullerene carbon), 70.76–70.69, 68.94 (6C, OCH<sub>2</sub> of the tetra(ethylene glycol) chain) 68.52 (PhOCH<sub>2</sub> of the aliphatic chain), 68.61 (1C, PhOCH<sub>2</sub>), 68.18 (1C, PhCH<sub>2</sub>O), 66.22 (1C, NCH<sub>2</sub>), 52.23 (1C, C<sup>f</sup>), 39.22 (1C, NCH<sub>3</sub>), 35.49 (1C, PhCH<sub>2</sub>), 33.49 (1C, PhCH<sub>2</sub>CH<sub>2</sub>), 31.92, 29.69–29.30, 26.13, 22.68 (20C, all CH<sub>2</sub> of the aliphatic chain), 22.33 (1C, Ph(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 14.11 (2C, CH<sub>3</sub>), 13.93 (1C, Ph(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>) ppm.

**2.5.3 Synthesis of the fullerene C<sub>60</sub>-amino-methoxy substituted azobenzene (17).** Procedure employed for the synthesis of **15**, using **11** (0.149 g, 0.15 mmol), I<sub>2</sub> (0.039 g, 0.15 mmol), fullerene C<sub>60</sub> (0.11 g, 0.15 mmol) dissolved in 110 mL of

anhydrous toluene, and DBU (0.077 g, 0.51 mmol) to obtain compound **17** (Scheme 2c). Yield: 34%. MALDI-TOF: C<sub>116</sub>H<sub>85</sub>N<sub>3</sub>O<sub>10</sub> calcd: [M + H]<sup>+</sup> 1680.93 found (*m/z*): [M + H]<sup>+</sup> 1681.90.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.82 (d, *J* = 9 Hz, 2H, H<sup>5</sup>), 7.81 (d, *J* = 9 Hz, 2H, H<sup>4</sup>), 6.98 (d, *J* = 8.98 Hz, 2H, H<sup>6</sup>), 6.76 (d, *J* = 9 Hz, 2H, H<sup>3</sup>), 6.58 (d, *J* = 2 Hz, 2H, H<sup>2</sup>), 6.40 (t, *J* = 2 Hz, 1H, H<sup>1</sup>), 5.43 (s, 2H, PhCH<sub>2</sub>OOC), 4.62 (t, *J* = 5 Hz, 2H, OOCCH<sub>2</sub> of the tetra(ethylene glycol) chain), 3.89 (t, *J* = 7 Hz, 4H, PhOCH<sub>2</sub> of the aliphatic chain), 3.82 (t, *J* = 5 Hz, OCH<sub>2</sub>), 3.87 (s, 3H, PhOCH<sub>3</sub>), 3.69–3.62 (m, 14H, CH<sub>2</sub>N y OCH<sub>2</sub> of the tetra(ethylene glycol) chain), 3.08 (s, 3H, CH<sub>3</sub>N), 1.77–1.70 (m, 4H, PhOCH<sub>2</sub>-CH<sub>2</sub>), 1.45–1.25 (m, 36H, all CH<sub>2</sub> of the aliphatic chain), 0.89 (t, *J* = 7 Hz, 6H, CH<sub>3</sub>) ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 163.47 (1C, C<sup>g</sup>), 163.31 (1C, C<sup>e</sup>), 160.85 (1C, C<sup>o</sup>), 160.54 (2C, C<sup>b</sup>), 150.98 (1C, C<sup>h</sup>), 147.54 (1C, C<sup>l</sup>), 145.24, 145.21, 145.16, 145.06, 144.88, 144.68, 144.60, 144.54, 144.46, 143.85, 143.06, 143.00, 142.18, 141.90, 141.83, 140.89, 139.38, 138.71 (fullerene carbons), 136.61 (1C, C<sup>d</sup>), 124.60 (2C, C<sup>j</sup>), 123.83 (2C, C<sup>m</sup>), 114.10 (2C, C<sup>n</sup>), 111.50 (2C, C<sup>i</sup>), 107.26 (2C, C<sup>c</sup>), 101.78 (1C, C<sup>a</sup>), 71.50 (fullerene carbon), 70.77–70.70, 68.71 (6C, OCH<sub>2</sub> of the tetra(ethylene glycol) chain), 68.96 (PhOCH<sub>2</sub> of the aliphatic chain), 68.63 (1C, PhCH<sub>2</sub>O), 68.20 (1C, OOCCH<sub>2</sub> of the tetra(ethylene glycol) chain), 66.23 (1C, NCH<sub>2</sub>), 55.50 (1C, OCH<sub>3</sub>), 52.26 (1C, C<sup>f</sup>), 39.21 (1C, NCH<sub>3</sub>), 31.93, 29.70–29.31, 26.13, 22.69 (20C, all CH<sub>2</sub> of the aliphatic chain), 14.11 (2C, CH<sub>3</sub>) ppm.

**2.5.4 Synthesis of the fullerene C<sub>60</sub>-amine-cyano substituted azobenzene (18).** Procedure employed for the synthesis of **15**, using **12** (0.19 g, 0.21 mmol), I<sub>2</sub> (0.052 g, 0.21 mmol), fullerene C<sub>60</sub> (0.148 g, 0.21 mmol) dissolved in 150 mL of anhydrous toluene, and DBU (0.103 g, 0.68 mmol) to yield product **18** (Scheme 2d). Yield: 34%. MALDI-TOF: C<sub>116</sub>H<sub>82</sub>N<sub>4</sub>O<sub>9</sub> calcd: [M + H]<sup>+</sup> 1675.91 found (*m/z*): [M + H]<sup>+</sup> 1676.83.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.88 (d, *J* = 9 Hz, 2H, H<sup>5</sup>), 7.86 (d, *J* = 9 Hz, 2H, H<sup>4</sup>), 7.73 (d, *J* = 8 Hz, 2H, H<sup>6</sup>), 6.76 (d, *J* = 9 Hz, 2H, H<sup>3</sup>), 6.58 (d, *J* = 2 Hz, 2H, H<sup>2</sup>), 6.40 (t, *J* = 2 Hz, 1H, H<sup>1</sup>), 5.43 (s, 2H, PhCH<sub>2</sub>OOC), 4.62 (t, *J* = 6 Hz, 2H, OOCCH<sub>2</sub> of the tetra(ethylene glycol) chain), 3.90 (t, *J* = 6 Hz, 4H, PhOCH<sub>2</sub> of the aliphatic chain), 3.83 (t, *J* = 5 Hz, OCH<sub>2</sub>), 3.68–3.62 (m, 14H, CH<sub>2</sub>N y OCH<sub>2</sub> of the tetra(ethylene glycol) chain), 3.12 (s, 3H, CH<sub>3</sub>N), 1.78–1.68 (m, 4H, PhOCH<sub>2</sub>CH<sub>2</sub>), 1.45–1.25 (m, 36H, all CH<sub>2</sub> of the aliphatic chain), 0.89 (t, *J* = 6 Hz, 6H, CH<sub>3</sub>) ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 163.47 (1C, C<sup>g</sup>), 163.33 (1C, C<sup>e</sup>), 160.48 (2C, C<sup>b</sup>), 149.98 (1C, C<sup>l</sup>), 147.83 (1C, C<sup>h</sup>), 145.21, 145.17, 145.13, 144.99, 144.84, 144.65, 144.58, 144.43, 143.80, 142.97, 142.91, 142.15, 141.86, 141.78, 140.86, 140.83, 139.36, 136.56 (fullerene carbons), 129.33 (1C, C<sup>d</sup>), 128.90 (2C, C<sup>n</sup>), 125.03 (2C, C<sup>m</sup>), 122.18 (2C, C<sup>j</sup>), 118.01 (1C, C<sup>o</sup>), 111.39 (2C, PhCN), 111.34 (1C, C<sup>i</sup>), 107.18 (2C, C<sup>c</sup>), 101.66 (1C, C<sup>a</sup>), 72.87 (fullerene carbon), 70.76–70.66, 68.67 (6C, OCH<sub>2</sub> of the tetra(ethylene glycol) chain) 68.44 (2C, PhOCH<sub>2</sub> of the aliphatic chain), 68.93 (1C, PhCH<sub>2</sub>O), 68.54 (1C, PhCH<sub>2</sub>O), 68.12 (1C, OOCCH<sub>2</sub> of the tetra(ethylene glycol) chain), 66.19 (1C, NCH<sub>2</sub>), 52.16 (1C, C<sup>f</sup>), 39.25 (1C, NCH<sub>3</sub>), 31.91, 29.68–29.27, 26.11, 22.68 (20C, all CH<sub>2</sub> of the aliphatic chain), 14.13 (2C, CH<sub>3</sub>) ppm.



**2.5.5 Synthesis of the fullerene C<sub>60</sub>-amino-nitro substituted azobenzene (19).** Procedure employed for the synthesis of **15**, using **13** (0.153 g, 0.15 mmol), I<sub>2</sub> (0.039 g, 0.15 mmol), fullerene C<sub>60</sub> (0.113 g, 0.15 mmol) dissolved in 120 mL of anhydrous toluene, and DBU (0.078 g, 0.51 mmol) to give the desired compound **19** (Scheme 2e). Yield: 69%. MALDI-TOF: C<sub>115</sub>H<sub>82</sub>N<sub>4</sub>O<sub>11</sub> calcd: [M + H]<sup>+</sup> 1695.90 found (*m/z*): [M + H]<sup>+</sup> 1696.85.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.32 (d, *J* = 9 Hz, 2H, H<sup>6</sup>), 7.91 (d, *J* = 9 Hz, 2H, H<sup>5</sup>), 7.88 (d, *J* = 9 Hz, 2H, H<sup>4</sup>), 6.77 (d, *J* = 9 Hz, 2H, H<sup>3</sup>), 6.58 (d, *J* = 2 Hz, 2H, H<sup>2</sup>), 6.40 (t, *J* = 2 Hz, 1H, H<sup>1</sup>), 5.43 (s, 2H, PhCH<sub>2</sub>OCO), 4.63 (t, *J* = 5 Hz, 2H, PhOCH<sub>2</sub> of the tetra(ethylene glycol) chain), 3.89 (t, *J* = 7 Hz, 4H, PhOCH<sub>2</sub> of the aliphatic chain), 3.83 (t, *J* = 5 Hz, OCH<sub>2</sub>), 3.69–3.62 (m, 14H, CH<sub>2</sub>N and OCH<sub>2</sub> of the tetra(ethylene glycol) chain), 3.13 (s, 3H, CH<sub>3</sub>N), 1.76–1.70 (m, 4H, PhOCH<sub>2</sub>CH<sub>2</sub>), 1.45–1.37 (m, 4H, PhO(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 1.35–1.25 (m, 32H, all CH<sub>2</sub> of the aliphatic chain), 0.89 (t, *J* = 7 Hz, 6H, CH<sub>3</sub>) ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 163.45 (1C, C<sup>e</sup>), 163.30 (1C, C<sup>g</sup>), 160.56 (2C, C<sup>b</sup>), 156.83 (1C, C<sup>h</sup>), 152.55 (1C, C<sup>h</sup>), 147.44 (1C, C<sup>o</sup>), 145.24, 145.23, 145.17, 145.04, 145.01, 144.88, 144.69, 144.64, 144.59, 144.46, 143.84, 143.06, 143.01, 142.95, 142.18, 141.90, 141.81, 140.88, 139.36, 138.71 (fullerene carbons), 136.59 (1C, C<sup>d</sup>), 126.12 (2C, C<sup>j</sup>), 124.65 (2C, C<sup>n</sup>), 122.60 (2C, C<sup>m</sup>), 111.54 (2C, C<sup>i</sup>), 107.27 (2C, C<sup>c</sup>), 101.75 (1C, C<sup>a</sup>), 71.49 (fullerene carbon), 70.85–70.71, 68.72 (6C, OCH<sub>2</sub> of the tetra(ethylene glycol) chain), 68.96 (2C, PhOCH<sub>2</sub> of the aliphatic chain), 68.62 (1C, PhCH<sub>2</sub>O), 68.20 (1C, COOCH<sub>2</sub>), 66.20 (1C, NCH<sub>2</sub>), 52.25 (1C, C<sup>f</sup>), 39.35 (1C, NCH<sub>3</sub>), 31.92, 29.69–29.30, 26.13, 22.68 (20C, all CH<sub>2</sub> of the aliphatic chain), 14.10 (2C, CH<sub>3</sub>) ppm.

**2.5.6 Synthesis of the fullerene C<sub>60</sub>-DR1 (20).** Procedure employed for the synthesis of **15**, using **14** (0.1094 g, 0.13 mmol), I<sub>2</sub> (0.032 g, 0.13 mmol) and fullerene C<sub>60</sub> (0.091 g, 0.13 mmol) were dissolved in 100 mL of anhydrous toluene and DBU (0.006 g, 0.038 mmol) to obtain the desired compound **20** (Scheme 2f). Yield: 70%. MALDI-TOF: C<sub>110</sub>H<sub>72</sub>N<sub>4</sub>O<sub>8</sub> calcd: [M + H]<sup>+</sup> 1577.77 found (*m/z*): [M + H]<sup>+</sup> 1578.47.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.30 (d, *J* = 9 Hz, 2H, H<sup>6</sup>), 7.88 (d, *J* = 7 Hz, 2H, H<sup>5</sup>), 7.87 (d, *J* = 7 Hz, 2H, H<sup>4</sup>), 6.83 (d, *J* = 9 Hz, 2H, H<sup>3</sup>), 6.60 (d, *J* = 2 Hz, 2H, H<sup>2</sup>), 6.41 (t, *J* = 2 Hz, 1H, H<sup>1</sup>), 5.41 (s, 2H, PhCH<sub>2</sub>OCO), 4.68 (t, *J* = 6 Hz, 2H, NCH<sub>2</sub>CH<sub>2</sub>OCO), 3.89 (t, *J* = 7 Hz, 4H, PhOCH<sub>2</sub> of the aliphatic chain), 3.79 (t, *J* = 6 Hz, 2H, CH<sub>3</sub>CH<sub>2</sub>NCH<sub>2</sub>), 3.57–3.51 (m, 2H, OCOCH<sub>2</sub>CH<sub>2</sub>-NCH<sub>2</sub>), 1.76–1.68 (m, 4H, PhOCH<sub>2</sub>CH<sub>2</sub>), 1.43–1.36 (m, 4H, PhO(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 1.34–1.24 (m, 35H, all CH<sub>2</sub> of the aliphatic chain and NCH<sub>2</sub>CH<sub>3</sub>), 0.89 (t, *J* = 6 Hz, 6H, CH<sub>3</sub>) ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 163.35 (1C, C<sup>e</sup>), 163.18 (1C, C<sup>g</sup>), 160.53 (2C, C<sup>b</sup>), 156.63 (1C, C<sup>h</sup>), 151.20 (1C, C<sup>h</sup>), 147.40 (1C, C<sup>o</sup>), 145.21, 145.18, 145.11, 144.89, 144.83, 144.59, 144.56, 144.43, 143.99, 143.79, 143.76, 142.98, 142.86, 142.80, 142.11, 142.08, 141.81, 141.69, 140.78, 140.75, 139.21, 138.60 (fullerene carbons), 136.47 (1C, C<sup>d</sup>), 126.47 (2C, C<sup>n</sup>), 124.61 (2C, C<sup>j</sup>), 122.63 (2C, C<sup>m</sup>), 111.56 (2C, C<sup>i</sup>), 107.33 (2C, C<sup>c</sup>), 101.52 (1C, C<sup>a</sup>), 71.18 (fullerene carbon), 68.95 (1C, PhCH<sub>2</sub>O), 68.15 (2C, PhOCH<sub>2</sub>), 63.96 (1C, NCH<sub>2</sub>CH<sub>2</sub>O), 51.59 (1C, C<sup>f</sup>), 48.23 (1C, CH<sub>3</sub>CH<sub>2</sub>-NCH<sub>2</sub>), 45.34 (1C, NCH<sub>2</sub>), 31.91 (2C, CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>), 29.68–29.25

(14C, all CH<sub>2</sub> of the aliphatic chain), 26.10 (2C, PhO(CH<sub>2</sub>)<sub>3</sub>), 22.68 (2C, CH<sub>3</sub>CH<sub>2</sub>), 14.13 (2C, CH<sub>3</sub>), 12.29 (1C, NCH<sub>2</sub>CH<sub>3</sub>) ppm.

## 3 Results and discussion

### 3.1 Synthesis of the fullerene C<sub>60</sub>-azobenzene derivatives

Generally, the synthesis of the fullerene C<sub>60</sub>-azobenzene derivatives was carried out according to the synthetic sequence illustrated in Fig. 1. Six different substituted azobenzenes (amino, amino-butyl, amino-methoxy, amino-cyano, amino-nitro, **DR1**) (**3**, **4**, **5**, **6**, **7** and **8**) bearing different dipole moment values were prepared and incorporated into a substituted malonate containing a phenyl group with aliphatic chains, to give the corresponding precursor compounds (**9**, **10**, **11**, **12**, **13** and **14**). The last step consisted on the incorporation of fullerene C<sub>60</sub> into the precursor malonates by means of a Bingel reaction to give six different fullerene C<sub>60</sub>-azobenzene derivatives (**15**, **16**, **17**, **18**, **19** and **20**).

Precursor substituted azobenzenes **4**, **5**, and **7** have been prepared according to the method previously reported by us,<sup>30,33</sup> whereas substituted azobenzenes **3** and **6** were synthesized using a similar procedure.<sup>23</sup> Intermediate 2-(2-{2-[2-(methyl-phenyl-amino)-ethoxy]-ethoxy}-ethoxy)-ethanol was prepared according to our method previously reported in the literature and the diazonium salts were prepared *in situ*. Aniline (1 eq.) was reacted with NaNO<sub>2</sub> (1 eq.) in an HCl solution (30%) at 0 °C. Afterwards, 2-(2-{2-[2-(methyl-phenyl-amino)-ethoxy]-ethoxy}-ethoxy)-ethanol (1 eq.) was added dropwise to the reaction mixture in order to obtain the amino substituted azobenzene (**3**) with 68% yield.<sup>30</sup> Similarly, the diazonium salt of 4-cyanoaniline was used to give the corresponding amino-cyano substituted azobenzene (ESI<sup>+</sup>).

Dendron GIOH (**1**) (1 eq.) was treated in the presence of Meldrum's acid (1 eq.) to afford the monosubstituted malonic ester (**2**). This intermediate was further reacted with intermediate (**3**) in the presence of *N,N*-dimethyl-4-aminopyridine (DCC) and *N,N*-dimethyl-4-aminopyridine (DMAP) in dry dichloromethane to give the azobenzene containing disubstituted malonic ester (**9**). Finally, this compound was reacted with fullerene C<sub>60</sub>, iodine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in anhydrous toluene to give the corresponding fullerene C<sub>60</sub>-azobenzene derivative (**15**). The other fullerene C<sub>60</sub>-azobenzene systems were obtained according to the same synthetic method, under the same reaction conditions described above. In the same manner, compounds (**10**), (**11**), (**12**), (**13**) and (**14**) were reacted under the Bingel reaction conditions to give the corresponding fullerenes C<sub>60</sub>-azobenzene derivatives (**16**), (**17**), (**18**), (**19**) and (**20**), respectively (Fig. 1).

### 3.2 Characterization of the fullerene C<sub>60</sub>-azobenzenes derivatives

The precursor disubstituted malonic azo-dyes and their corresponding fullerene C<sub>60</sub>-azobenzene derivatives were fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies. The molecular weights and purity of the final products were confirmed by MALDI-TOF mass spectrometry using dithranol as matrix.



For instance, in the  $^1\text{H}$  NMR spectrum of compound **9** (Fig. 2a), we observe six signals in the aromatic region at 7.87, 7.84, 7.47–7.37, 6.75, 6.47 and 6.41 ppm, due to the aromatic protons present in the azobenzene unit and the phenyl group, corresponding to  $\text{H}^5$ ,  $\text{H}^4$ ,  $\text{H}^6\text{--H}$ ,  $\text{H}^3$ ,  $\text{H}^2$  and  $\text{H}^1$ , respectively. In the aliphatic zone, we can see a singlet at 5.09 ( $\text{PhCH}_2\text{OCO}$ ), and two triplets at 4.29 ( $\text{OOCCH}_2$ ) and 3.92 ppm ( $\text{PhOCH}_2$ ). In addition, we perceive a multiplet at 3.68–3.59 ppm related to the protons  $\text{OCH}_2$  of the oligo(ethylene glycol) segments, as well as two singlets at 3.46 and 3.07 ppm due to the  $\alpha$  protons of the malonate ( $\text{OOCCH}_2\text{COO}$ ) and the methyl group ( $\text{NCH}_3$ ), respectively. Finally, the protons corresponding to methylenes ( $\text{CH}_2$ ) present in the aliphatic chain appear at 1.80–1.71, 1.46–1.39, 1.36–1.27 and 0.90 ppm.

In the  $^1\text{H}$  NMR spectrum of fullerene  $\text{C}_{60}$ -azobenzene derivative **15**, the chemical shifts of the protons are very similar (Fig. 2b). As we can notice, the signal due to the  $\alpha$  protons of the malonate ( $\text{OOCCH}_2\text{COO}$ ), previously observed at 3.46 ppm, totally disappeared. This is an indication that the Bingel coupling reaction between the fullerene  $\text{C}_{60}$  and the precursor malonic azo-dye successfully occurred.

On the other hand, in the aromatic region of the  $^{13}\text{C}$  NMR spectrum of the malonic azo-dye **9**, there are 14 signals at 163.46, 163.29, 160.47, 153.17, 151.34, 143.78, 136.55, 129.31, 128.87, 125.02, 122.17, 111.38, 107.15, 101.64 ppm, assigned to the aromatic carbons of the phenyl groups present in the structure. Moreover, in the aliphatic region, we observe various signals at 70.75–70.64, 68.91, 68.66 ppm due to the methylenes present in the tetra(ethylene glycol) spacers. In addition, the carbons  $\text{PhOCH}_2$  of the aliphatic chain appear at 68.53. Four more signals at 68.11, 66.18, 52.15 and 32.24 ppm,

corresponding to carbons ( $\text{PhCH}_2\text{O}$ ), ( $\text{NCH}_2$ ), ( $\text{C}^f$ ) and ( $\text{NCH}_3$ ), respectively, were also observed. Finally, the signals due to all the  $\text{CH}_2$  and  $\text{CH}_3$  present in the aliphatic chains appeared at 31.90, 29.67–29.26, 26.10, 22.67, and 14.12 ppm.

In the  $^{13}\text{C}$  NMR spectrum of fullerene  $\text{C}_{60}$ -azobenzene derivative **15**, the signals of the aromatic rings did not show any significant chemical shift with respect to its precursor compound **9** (Fig. 3). However, we observe the appearance of the signals arising from the fullerene  $\text{C}_{60}$   $\text{sp}^2$  carbons at 145.20, 145.16, 145.11, 144.97, 144.83, 144.63, 144.60, 144.55, 144.48, 144.41, 143.80, 143.78, 143.64, 143.01, 142.96, 142.89, 142.13, 141.85, 141.77, 140.84, 140.82, 139.34, and 138.66 ppm. Meanwhile, in the aliphatic region, we can notice an additional signal of the fullerene  $\text{C}_{60}$   $\text{sp}^3$  carbons and the carbon  $\alpha$  to the carbonyl group ( $\text{C}^f$ ) at 71.40 and 52.15 ppm, respectively.

The structure and purity of these compounds were confirmed by MALDI-TOF mass spectrometry. All fullerene  $\text{C}_{60}$ -azobenzene derivatives showed the expected molecular ion peaks, which are in agreement with the calculated molecular weights. The  $^{13}\text{C}$  NMR the fullerene-azobenzene derivatives reported here can be found in the ESI.†

### 3.3 Optical properties of the fullerene $\text{C}_{60}$ -azobenzene derivatives

The optical properties of the fullerene  $\text{C}_{60}$ -azobenzene derivatives were studied by absorption spectroscopy in the UV-vis region; the results are summarized in Tables 1 and 2. The absorption spectra of the precursor malonic azo-dyes without fullerene were recorded in  $\text{CHCl}_3$ , MeOH and DMF solution, whereas those of the fullerene  $\text{C}_{60}$ -azobenzene derivatives were carried out in  $\text{CHCl}_3$  and DMF.

The absorption spectra of the precursor malonic azo-dyes without fullerene were normalized for a better comparison. As we can notice, the absorption spectra of compounds **9**, **10** and **11**, in  $\text{CHCl}_3$  solution, showed a maximum absorption band at  $\lambda_{\text{max}} = 410$  nm followed by red-shifted shoulder at 421 nm due to the  $\pi\text{--}\pi^*$  and  $n\text{--}\pi^*$  transitions, respectively. These compounds have a low dipole moment value and belong to aminoazobenzenes category, according to Rau's classification.<sup>18,19</sup> By contrast,

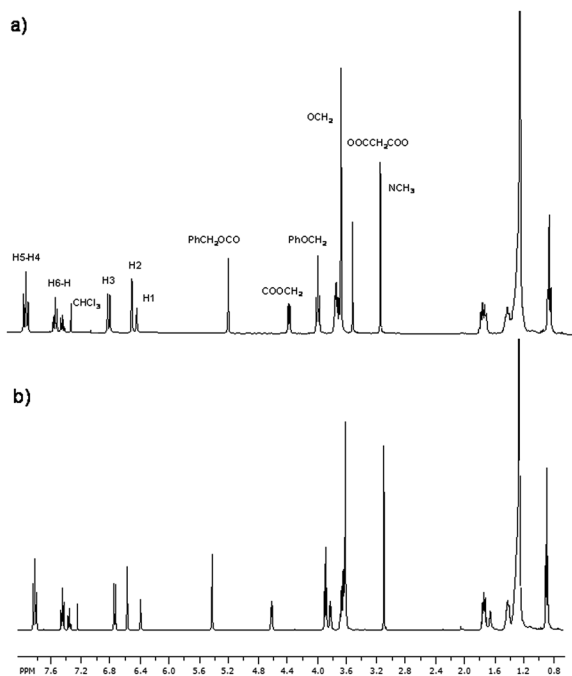


Fig. 2  $^1\text{H}$  NMR spectra in  $\text{CDCl}_3$ : (a) precursor malonic azo-dye **9**, (b) fullerene  $\text{C}_{60}$ -azobenzene derivative **15**.

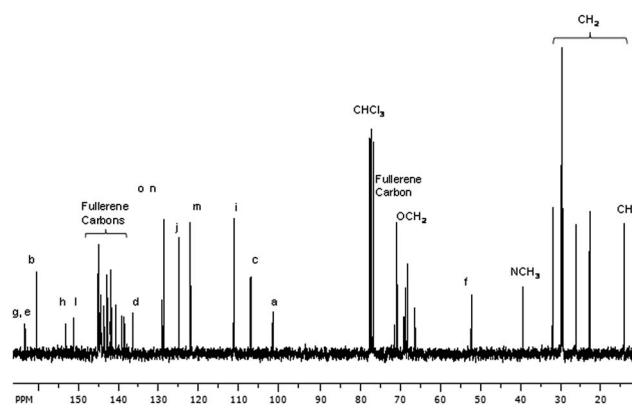


Fig. 3  $^{13}\text{C}$  NMR spectra of fullerene  $\text{C}_{60}$ -azobenzene derivative **15** in  $\text{CDCl}_3$ .



Table 1 Optical properties of the precursor malonic azo-dyes

Compound	CHCl <sub>3</sub>		DMF		MeOH	
	$\lambda_{\max}$ (nm)	Cut off (nm)	$\lambda_{\max}$ (nm)	Cut off (nm)	$\lambda_{\max}$ (nm)	Cut off (nm)
9	410	528	418	530	410	428
10	410	528	418	530	410	428
11	410	528	418	530	410	428
12	448	562	462	574	450	568
13	478	596	496	628	478	610
14	468	584	490	632	478	610

Table 2 Optical properties of the fullerene C<sub>60</sub>-azobenzene derivatives

Compound	CHCl <sub>3</sub> $\lambda_{\max}$ (nm)	DMF $\lambda_{\max}$ (nm)	% photoisomerization yield <i>cis</i> isomer $\Delta\text{abs}^b/\Delta\text{abs}^a$	Film $\lambda_{\max}$ (nm)
15	408	416	6.4	408
16	408	416	3	408
17	408	416	15.5	408
18	446–450	462	—	446
19	480	492–494	—	480
20	470–472	488	—	476

<sup>a</sup> Absorbance of the precursor malonic azo-dyes. <sup>b</sup> Absorbance of the fullerene C<sub>60</sub>-azobenzene system.

compounds **12**, **13** and **14** exhibited well defined absorption bands at 448, 478 and 468 nm, respectively (Fig. 4a). These compounds possess high dipole moment values and belong to the pseudostilbenes category, so that they exhibit a total overlap of the  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  bands in other words, only one absorption band can be observed in the UV-vis spectra.<sup>18,19</sup> However, the absorption bands of these compounds in MeOH solution did not show any significant red shift. On the contrary, compound **14** showed a red-shift of 10 nm in its absorption band with respect to that observed in CHCl<sub>3</sub> (Table 1), and in DMF a significant solvatochromic effect was observed. Compounds having low dipole moments (**9**, **10** and **11**) showed a red-shift of 8 nm in their adsorption bands, whereas compounds bearing high dipole moments (**12**, **13** and **14**) exhibited red-shifts of 14, 18 and 22 nm, respectively (Fig. 4b, Table 1). On the other hand, malonic azo-dyes bearing NO<sub>2</sub> as acceptor group (**13**, **14**) exhibited a maximum absorption band at  $\lambda_{\max}$  = 478 nm in MeOH solution, showing slight shifts of 10 and 6 nm in CHCl<sub>3</sub> and DMF solution, respectively (Table 1).

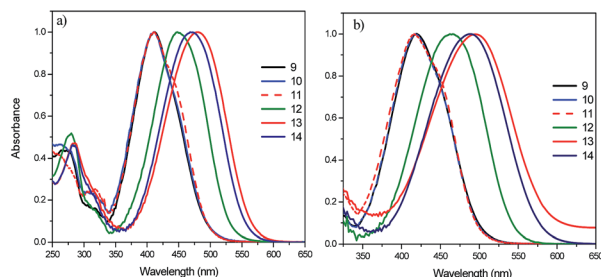


Fig. 4 Normalized absorption spectra of the precursor azo-dyes: (a) in CHCl<sub>3</sub>, and (b) in DMF solution.

Regarding the optical properties of the fullerene C<sub>60</sub>-azobenzene derivatives, we noticed that in CHCl<sub>3</sub> solution the absorption band of compounds **15**, **16** and **17** (low dipole moment) are blue-shifted by 2 nm with respect to their precursor malonic azo-dyes without fullerene (Table 2). These compounds exhibited a maximum absorption band at  $\lambda_{\max}$  = 408 nm with a red-shifted shoulder at 422 nm arising from the  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transitions, respectively. In addition, we note the presence of a blue-shifted shoulder at 394 nm, which reveals the presence of H-aggregates (Fig. 5). Alternatively, azo-compounds bearing high dipole moment values (**18**, **19**, **20**) show adsorption bands at 448, 480 and 472 nm, respectively.

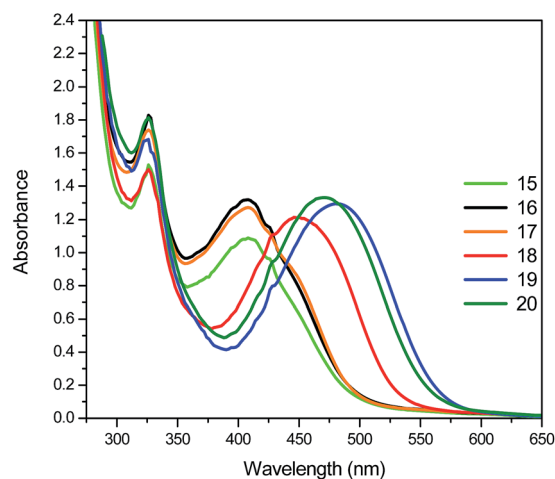


Fig. 5 Absorption spectra of the fullerene C<sub>60</sub>-azobenzene derivatives in CHCl<sub>3</sub> solution.



These compounds exhibited also a blue-shifted shoulder at 432 nm, which indicates the presence of H-aggregation (Fig. 5, Table 2).<sup>36</sup>

As well, the optical properties of fullerene C<sub>60</sub>-azobenzene derivatives were studied in DMF solution (ESI, Fig. S6†). These hybrid systems having low dipole moments (15, 16, 17) exhibited a maximum absorption band which is 8 nm red-shifted with respect to the absorption value in CHCl<sub>3</sub> solution. However, fullerene C<sub>60</sub>-azobenzene derivatives bearing high dipole moment values (18, 19 and 20) showed maximum absorption bands at  $\lambda_{\text{max}} = 462, 492\text{--}494, 488$ , respectively. They also exhibited a blue-shifted shoulder at 428 nm, which can be due to intramolecular azobenzene–fullerene interactions.<sup>36</sup>

### 3.4 Protonation effect upon irradiation

We decided to study the photoprotonation effect on the series of azo-dyes containing first generation Fréchet type dendrons. In these compounds, the formation of an azo-hydrazone *via* tautomerism can be induced by irradiating with UV light at 254 nm.<sup>29,37</sup> Particularly, we investigated the photoprotonation effect of the fullerene C<sub>60</sub>-azobenzene derivatives 15 and 19, having the lowest and the highest dipole moment value, respectively. After irradiation with UV light for 140 s, compound 15 reached a photostationary state (PPS). However, over time we noticed that absorption band at 410 nm decreases drastically in intensity and two new absorption bands appear in the visible region at 524 nm and 546 nm, respectively; the isobestic point was located at 430 nm (Fig. 6a). Similarly, fullerene C<sub>60</sub>-azobenzene derivative 19, bearing a high dipole moment value, exhibited the same photochromic effect as its homologue with low dipole moment 15. Upon irradiation the absorption band at 480 nm decreased drastically in intensity and the appearance of two additional bands at 520 and 552 nm was observed; in this case the isobestic point was situated at 500 nm (Fig. 6b). This fullerene C<sub>60</sub>-azobenzene system reached a photostationary state (PPS) after irradiation for 600 s. From these results, we can remark that the photochromic behavior of this azo-dye was not perturbed at all by the incorporation of the fullerene unit (Fig. 8).

### 3.5 *trans*–*cis* photoisomerization

Photoisomerization experiments were performed with the samples in DMF solution, which were irradiated with UV light at

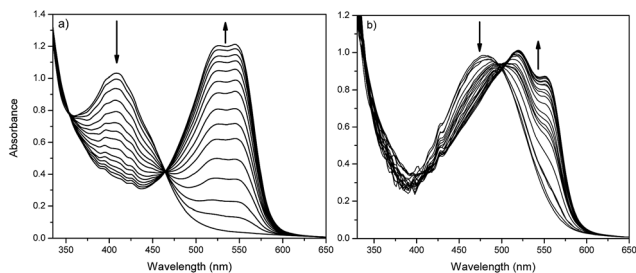


Fig. 6 Photoprotonation effect of [60] fullerene C<sub>60</sub>-azobenzene derivatives irradiated with UV light at 254 nm: (a) derivative 15, and (b) derivative 19 (Conc.  $2.5 \times 10^{-4}$  M in CHCl<sub>3</sub> at room temperature).

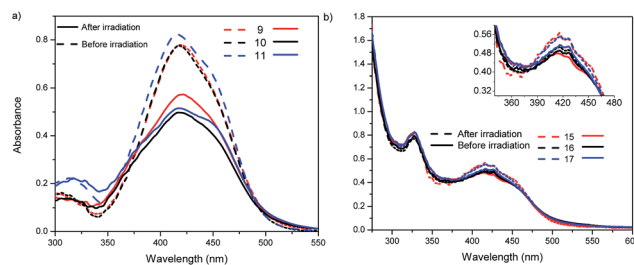


Fig. 7 Absorption spectra upon irradiation with UV light at 365 nm for 10 minutes: (a) precursor azo-dyes 9, 10 and 11, (b) fullerene C<sub>60</sub>-azobenzene derivatives 15, 16 and 17 (Conc.  $2.5 \times 10^{-4}$  M in DMF at room temperature).

365 nm for 10 min. After this time, we noticed that the intensity of the absorption band as well as the extinction molar coefficient of compounds 9, 10 and 11 decreased, due to the photoisomerization from the *trans* (*E*) to the *cis* (*Z*) isomer. Moreover, in the UV region of the absorption spectrum of these compounds there is a shoulder at 450 nm, related to the  $n\text{--}\pi^*$  transition of the *cis* isomer (Fig. 7a). Meanwhile, in the absorption spectra of the fullerene C<sub>60</sub>-azobenzenes derivatives 15, 16 and 17 the intensity of the bands did not vary significantly (Fig. 7b). The photoisomerization yield in these compounds depends in large measure on the donor/acceptor character of the substituents present in the azobenzene units (Table 2). Fullerene C<sub>60</sub>-azobenzene derivative 17 exhibited a photoisomerization yield of 13%, which can be attributed to the electron-donor effect of the (OCH<sub>3</sub>) group. Finally, compounds 15 and 17 bearing low dipole moment values exhibited

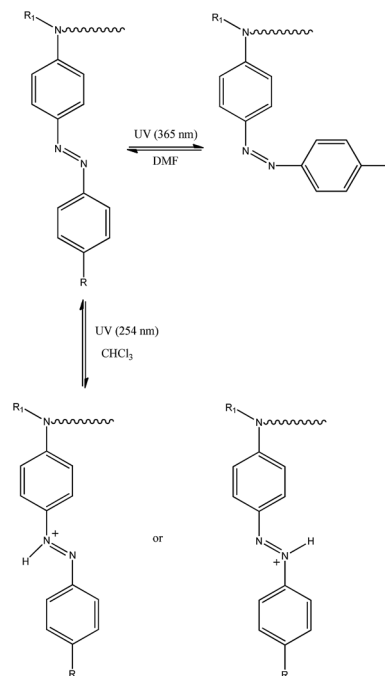


Fig. 8 Photoisomerization and photoprotonation of C<sub>60</sub>-azobenzene derivative 19.



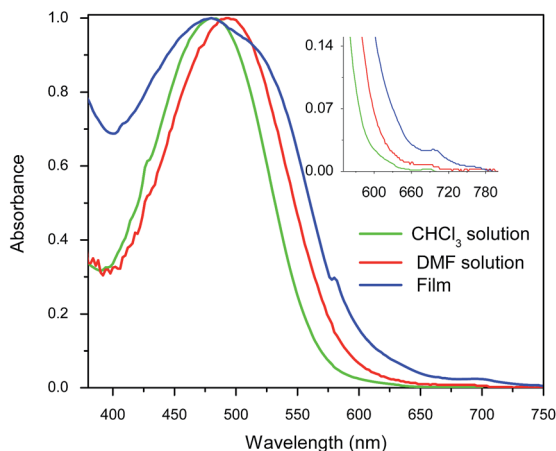


Fig. 9 Absorption spectra of fullerene  $C_{60}$ -azobenzene derivatives **19** in  $CHCl_3$ , DMF and cast film.

photoisomerization yields of 6.4 and 3.0%, respectively (Table 2). These low yields are due to the fact that the fullerene  $C_{60}$  strongly absorb in the UV region, which causes a partial quenching the photoisomerization process (Fig. 8).

### 3.6 Optical properties and *trans-cis* photoisomerization in cast films

The optical properties of the fullerene  $C_{60}$ -azobenzenes derivatives were also studied in cast films, and the results are summarized in Table 2. The normalized absorption spectra of the fullerene  $C_{60}$ -azobenzene derivative **19** in  $CHCl_3$ , DMF and cast film are shown in Fig. 9. As we can see, the absorption band in a cast film did not show any significant shift with respect to the absorption band observed in  $CHCl_3$  solution. However, in DMF this absorption band was red-shifted by 8 nm, and we note a shoulder at 524 nm due to the presence of J-aggregates,<sup>28</sup> followed by two discrete shoulders at 580 and 702 nm, respectively (Table 2).<sup>38</sup>

On the other hand, photoisomerization experiments were carried out in cast film samples. The precursor malonic azo-dyes without fullerene bearing low dipole moments (**9**, **10** and **11**) exhibited *trans-cis* photoisomerization when they were irradiated with UV light at 365 nm for 10 minutes. After this time, we noticed a decrease in intensity of the absorption band

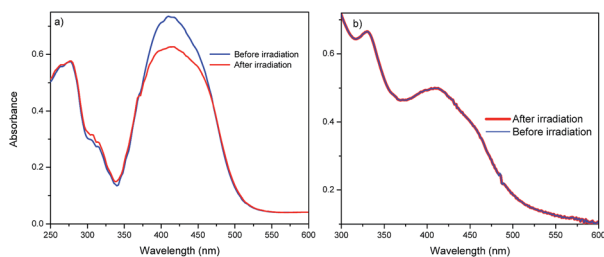


Fig. 10 Absorption spectrum in casted film of: (a) precursor azo-dye **9**, (b) fullerene  $C_{60}$ -azobenzene derivative **15**, after irradiation for 10 minutes.

at 410 nm, jointly with the appearance of a shoulder at 450 nm due to the  $n-\pi^*$  transition of the *cis* isomer (Fig. 10a). On the contrary, when the fullerene  $C_{60}$ -azobenzene derivatives (**15**, **16**, **17**) were irradiated with UV light for 10 minutes, the absorption bands did not change at all (Fig. 10b). This is certainly due to a quenching of the photoisomerization process by the presence of the fullerene unit in these derivatives.

## 4 Conclusions

Six different fullerene  $C_{60}$ -azobenzene derivatives (**15**, **16**, **17**, **18**, **19** and **20**) were successfully synthesized and fully characterized by  $^1H$ ,  $^{13}C$  NMR and MALDI-TOF. The optical properties of the fullerene  $C_{60}$ -azobenzene dyes were studied by UV-vis spectroscopy and compared to those of their precursor malonic azo-dyes without fullerene (**9**, **10**, **11**, **12**, **13** and **14**).

Fullerene  $C_{60}$ -azobenzene derivatives bearing low dipole moment (**15**, **16** and **17**) in  $CHCl_3$  exhibited a maximum absorption band at  $\lambda_{max} = 408$  nm and a shoulder at 422 nm due to  $\pi-\pi^*$  and  $n-\pi^*$  transitions, respectively. The presence of a blue-shifted shoulder at 394 nm revealed the presence of H-aggregates. Fullerene  $C_{60}$ -azobenzene derivatives bearing a high dipole moment (**18**, **19** and **20**) showed maximum absorption bands between 448 and 472 nm; the presence of H-aggregates was also detected.

The photoprotonation effect in the fullerene  $C_{60}$ -azobenzene derivatives **15** and **19**, having the lowest and the highest dipole moment, respectively, was studied by absorption spectroscopy. Compound **15** (lowest dipole moment) reached a photostationary state (PPS). The absorption band at 410 nm decreased drastically in intensity and two absorption bands appeared at 524 and 546 nm. Compound **19** (highest dipole moment) behaved similarly and exhibited the same photochromic effect. It was found that the photoprotonation behavior of these azo-dyes was not perturbed by the incorporation of the fullerene unit.

Photoisomerization experiments were performed with the precursor dyes with low dipole moment (**9**, **10** and **11**) in DMF solution. A typical *trans-cis* photoisomerization behavior was observed. The absorption band at 410 nm decreased in intensity and a shoulder at 450 nm due to the  $n-\pi^*$  transition (*cis* isomer) appeared. On the contrary, in the UV-vis spectra of the fullerene  $C_{60}$ -azobenzenes derivatives (**15**, **16** and **17**) the intensity of the bands did not vary remarkably. It was found that the presence of the fullerene moiety drastically decreases the photoisomerization yield because of a strong quenching effect.

The optical properties of the fullerene  $C_{60}$ -azobenzenes derivatives were also studied in cast films, where the presence of J-aggregates was detected. Malonic azo-dyes without fullerene (**9**, **10** and **11**) exhibited typical *trans-cis* photoisomerization, whereas the fullerene  $C_{60}$ -azobenzene derivatives (**15**, **16**, **17**) did not since the fullerene moiety acts as quencher.

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