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Synthesis, characterization and optical properties of novel dendronized azo-dyes containing a fullerene C_{60} 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_{60} 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, -OCH₃, -C₄H₉, -CN and -NO₂). 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_{60} -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_{60} . 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 C₆₀ 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.1-3 However, the applications of fullerene C₆₀ itself are very limited because of its poor solubility in organic solvents. The incorporation of alkyl chains and other functional groups into fullerene C₆₀ has led to the development of novel molecular structures with enormous potential optical applications.4-8 Very recently, some hybrid systems based on azo-dyes containing fullerene C₆₀ units have been investigated due to their synergistic effect. Wang et al. reported the functionalization of fullerene C₆₀ via the addition of a substituted azobenzene as a carbene active intermediate.9 Kay et al. reported the synthesis and optical properties of a novel azodendrimer bearing a fullerene C₆₀ unit as core. 10 Other related structures combining azobenzene-fullerene, exhibiting interesting optical properties, have been reported in the

Rau classified azobenzenes into three main categories based on their photochemical behaviour.18 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 π - π * transition, as well as a weak intensity band at 440 nm related to the n- π * 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 π - π * and n- π * 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 π - π * and n- π * bands. Finally, azobenzenes bearing an electrondonor and an electron-acceptor group belong to the third category, named "pseudostilbenes", where the π - π * and n- π * bands are practically superimposed and inverted on the energy scale.18

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 cis–trans* 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. ^{16–22}

literature. $^{11-13}$ Some of them led to the development of new materials for molecular photoswitching, 9,10,14 smart optoelectronic devices 15 and organic solar cells. 16,17

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

Our research group has developed different series of azodyes23-26 and azo-polymers27,28 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.29 In this work, we describe the synthesis and characterization of a novel series of dendronized azo-dyes containing fullerene C₆₀ 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, -OCH₃, -C₄H₉, -CN and -NO₂). The Bingel reaction was used in order to obtain novel fullerene C₆₀azobenzene 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, 23,24,30 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. 31,32

¹H and ¹³C NMR spectra of the intermediates and final compounds involved in the synthesis were recorded in CDCl₃ solution at room temperature on a Bruker Avance 400 MHz spectrometer, operating at 400 MHz and 100 MHz for ¹H and ¹³C, 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 (2.5×10^{-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 CHCl₃ 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.³³ The coupling constants were confirmed according a previous work reported by Fréchet *et al.*³⁴

¹H NMR (400 MHz, CDCl₃): δ = 6.49 (t, J = 2 Hz, 2H, H¹), 6.37 (t, J = 2 Hz, 1H, H²), 4.61 (s, 2H, PhCH₂OH), 3.93 (t, J = 7 Hz, 4H, PhOCH₂), 1.79–1.72 (m, 4H, PhOCH₂CH₂), 1.47–1.26 (m, 36H, all CH₂ of the aliphatic chain), 0.88 (t, J = 7 Hz, 6H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 160.52 (2C, C^c), 143.16 (1C, C^a), 105.02 (2C, C^b), 100.52 (1C, C^d), 68.03 (2C, PhOCH₂), 65.44 (1C, PhCH₂OH), 31.90, 29.61–29.18, 26.02, 25.70, 22.87 (20C, all CH₂ of the aliphatic chain), 14.09 (2C, CH₃) 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.³¹

¹H NMR (400 MHz, CDCl₃) δ = 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.

¹³C NMR (100 MHz, CDCl₃): δ = 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.^{30,33,35}

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-(2-hydroxyethoxy)ethoxy)ethoxy)ethyl)(methyl)amino)phenyl) diazenyl)benzonitrile (6) (see ESI†).

2.4 Synthesis of the disubstituted malonic ester

2.4.1 Synthesis of (*E*)-3,5-bis(dodecyloxy)benzyl-2-(4-(phenyl-diazenyl)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_2Cl_2 . After that, a solution of *N*,*N*-dimethyl-4-aminopyridine (DCC) (0.18 g, 0.87 mmol) in 5 mL of anhydrous CH_2Cl_2 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%.

¹H NMR (400 MHz, CDCl₃): δ = 7.87 (d, J = 9 Hz, 2H, H⁵), 7.84 (d, J = 9 Hz, 2H, H⁴), 7.47–7.37 (m, 3H, H⁶–H), 6.75 (d, J = 9 Hz, 2H, H³), 6.47 (d, J = 2 Hz, 2H, H²), 6.41 (t, J = 2 Hz, 1H, H¹), 5.09 (s, 2H, PhCH₂OOC), 4.29 (t, J = 5 Hz, 2H, OOCCH₂ of the tetra(ethylene glycol) chain), 3.92 (t, J = 6 Hz, 4H, PhOCH₂ of the aliphatic chain), 3.68–3.59 (m, 14H, CH₂N y OCH₂ of the tetra(ethylene glycol) chain), 3.46 (s, 2H, OOCCH₂COO), 3.07 (s, 3H, CH₃N), 1.80–1.71 (m, 4H, PhOCH₂CH₂), 1.46–1.39 (m, 4H, PhO(CH₂)₂CH₂), 1.36–1.27 (m, 32H, all CH₂ of the aliphatic chain), 0.90 (t, J = 6 Hz, 6H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 166.17 (1C, C^g), 166.01 (1C, C^e), 160.28 (2C, C^b), 153.00 (1C, C^h), 151.22 (1C, C^l), 143.45 (1C, C^k), 137.08 (1C, C^d), 129.14 (1C, C^o), 128.70 (2C, Cⁿ), 124.85 (2C, C^j), 122.02 (2C, C^m), 111.21 (2C, Cⁱ), 106.20 (2C, C^c), 100.94 (1C, C^a), 70.58–70.41, 68.37 (6C, OCH₂ of the tetra(ethylene glycol) chain), 68.59 (2C, PhOCH₂ of the aliphatic chain), 67.85 (1C, PhCH₂O), 66.96 (1C, NH₂(CH₂)₂), 64.35 (1C, COOCH₂ of the tetra(ethylene glycol) chain), 51.97 (1C, NCH₂), 41.18 (1C, C^f), 39.00 (1C, NCH₃), 31.75, 29.50–29.07, 25.88, 22.52 (20C, all CH₂ of the aliphatic chain), 13.97 (2C, CH₃) ppm.

Scheme 1

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%.

¹H NMR (400 MHz, CDCl₃): $\delta = 7.83$ (d, J = 9 Hz, 2H, H⁵), 7.74 (d, J = 8 Hz, 2H, H⁴), 7.26 (d, J = 8 Hz, 2H, H⁶), 6.75 (d, J = 9 Hz, 2H, H³), 6.46 (d, J = 2 Hz, 2H, H²), 6.40 (t, J = 2 Hz, 1H, H¹), 5.09 (s, 2H, PhCH₂OOC), 4.29 (t, J = 5 Hz, 2H, OOCCH₂ of the tetra(ethylene glycol) chain), 3.92 (t, J = 7 Hz, 4H, PhOCH₂ of the aliphatic chain), 3.69–3.60 (m, 14H, CH₂N y OCH₂ of the tetra(ethylene glycol) chain), 3.45 (s, 2H, OOCCH₂COO), 3.09 (s, 3H, CH₃N), 2.67 (t, J = 8 Hz, 2H, PhCH₂), 1.79–1.70 (m, 4H, PhOCH₂CH₂), 1.68–1.57 (m, 2H, Ph(CH₂)₂), 1.45–1.26 (m, 38H, Ph(CH₂)₃ and all CH₂ of the aliphatic chain), 0.95 (t, J = 7 Hz, 6H, CH₃), 0.89 (t, J = 6 Hz, 3H, Ph(CH₂)CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 166.37 (1C, C^S), 166.21 (1C, C^S), 160.43 (2C, C^D), 151.38 (1C, C^D), 151.14 (1C, C^D), 144.63 (1C, C^O), 143.68 (1C, C^C), 137.18 (1C, C^D), 128.90 (2C, C^D), 124.77 (2C, C^D), 122.09 (2C, C^D), 111.38 (2C, C^D), 106.39 (2C, C^C), 101.10 (1C, C^D), 70.74–70.57, 68.76 (6C, OCH₂ of the tetra(ethylene glycol) chain), 67.17 (2C, PhOCH₂ of the aliphatic chain), 68.52 (1C, PhCH₂O), 68.05 (1C, N(CH₂)₂) 64.53 (1C, COOCH₂ of the tetra(ethylene glycol) chain), 52.15 (1C, NCH₂), 41.34 (1C, C^D) 39.18 (1C, NCH₃), 35.46 (1C, PhCH₂), 33.48 (1C, PhCH₂CH₂), 31.88, 29.63–29.21, 26.01, 22.65 (20C, all CH₂ of the aliphatic chain), 22.30 (1C, Ph(CH₂)₂CH₂), 14.08 (2C, CH₃), 13.91 (1C, Ph(CH₂)₃CH₃) 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%.

¹H NMR (400 MHz, CDCl₃): $\delta = 7.83$ (d, J = 9 Hz, 2H, H⁵), 7.81 (d, J = 9 Hz, 2H, H⁴), 6.97 (d, J = 9 Hz, 2H, H⁶), 6.76 (d, J = 9 Hz, 2H, H³), 6.46 (d, J = 2 Hz, 2H, H²), 6.40 (t, J = 2 Hz, 1H, H¹), 5.09 (s, 2H, PhCH₂OOC), 4.29 (t, J = 5 Hz, 2H, OOCCH₂ of the tetra(ethylene glycol) chain), 3.92 (t, J = 7 Hz, 4H, PhOCH₂ of the aliphatic chain), 3.86 (s, 3H, PhOCH₃), 3.69–3.61 (m, 14H, CH₂N y OCH₂ of the tetra(ethylene glycol) chain), 3.46 (s, 2H, OOCCH₂COO), 3.08 (s, 3H, CH₃N), 1.78–1.75 (m, 4H, PhOCH₂-CH₂), 1.44–1.26 (m, 36H, all CH₂ of the aliphatic chain), 0.88 (t, J = 7 Hz, 6H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 166.35 (1C, C^g), 166.19 (1C, C^e), 160.78 (1C, C^o), 160.42 (2C, C^b), 150.92 (1C, C^h), 147.43 (1C, C^l), 143.64 (1C, C^k), 137.18 (1C, C^d), 124.53 (2C, C^j), 123.76 (2C, C^m), 114.02 (2C, Cⁿ), 111.41 (2C, Cⁱ), 106.38 (2C, C^c), 101.09 (1C, C^a), 70.73–70.56, 68.75 (6C, OCH₂ of the tetra(ethylene glycol) chain), 68.52 (2C, PhOCH₂ of the aliphatic chain), 68.04 (1C, PhCH₂O), 67.15 (1C, N(CH₂)₂), 64.52 (1C, COOCH₂ of the tetra(ethylene glycol) chain), 55.43 (1C, NCH₂), 52.16 (1C, OCH₃), 41.33 (1C, C^f), 39.15 (1C, NCH₃), 31.87, 29.62–29.20, 26.00, 22.64 (20C, all CH₂ of the aliphatic chain), 14.07 (2C, CH₃) ppm.

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%.

¹H NMR (400 MHz, CDCl₃): $\delta = 7.86$ (d, J = 9 Hz, 2H, H⁵), 7.85 (d, J = 10 Hz, 2H, H⁴), 7.70 (d, J = 9 Hz, 2H, H⁶), 6.75 (d, J = 9 Hz, 2H, H³), 6.45 (d, J = 2 Hz, 2H, H²), 6.40 (t, J = 2 Hz, 1H, H¹), 5.08 (s, 2H, PhCH₂OOC), 4.29 (t, J = 5 Hz, 2H, OOCCH₂ of the tetra(ethylene glycol) chain), 3.91 (t, J = 7 Hz, 4H, PhOCH₂ of the aliphatic chain), 3.68–3.60 (m, 14H, CH₂N y OCH₂ of the tetra(ethylene glycol) chain), 3.45 (s, 2H, OOCCH₂COO), 3.11 (s, 3H, CH₃N), 1.79–1.74 (m, 4H, PhOCH₂CH₂), 1.45–1.25 (m, 36H, all CH₂ of the aliphatic chain), 0.88 (t, J = 7 Hz, 6H, CH₃) ppm.

 $^{13}\text{C NMR}$ (100 MHz, CDCl₃): $\delta = 166.26$ (1C, Cg), 166.09 (1C, Ce), 160.36 (2C, Cb), 155.31 (1C, Cl), 152.24 (1C, Ch), 143.48 (1C, Ck), 137.11 (1C, Cd), 132.90 (2C, Cn), 125.77 (2C, Cm), 122.57 (2C, Cj), 118.84 (1C, Co), 111.70 (1C, PhCN), 111.34 (2C, Ci), 106.31 (2C, Cc), 100.99 (1C, Ca), 70.70–70.50, 68.68 (6C, OCH₂ of the tetra(ethylene glycol) chain), 67.07 (PhOCH₂ of the aliphatic chain), 68.44 (1C, PhCH₂O), 67.97 (1C, N(CH₂)₂), 64.42 (1C, COOCH₂ of the tetra(ethylene glycol) chain), 52.07 (1C, NCH₂), 41.27 (1C, Cf), 39.18 (1C, NCH₃), 31.80, 29.55–29.13, 25.93, 22.56 (20C, all CH₂ of the aliphatic chain), 14.01 (2C, CH₃) 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%.

¹H NMR (400 MHz, CDCl₃): δ = 8.27 (d, J = 9 Hz, 2H, H⁶), 7.88 (d, J = 9 Hz, 2H, H⁵), 7.86 (d, J = 9 Hz, 2H, H⁴), 6.75 (d, J = 9 Hz, 2H, H³), 6.45 (d, J = 2 Hz, 2H, H²), 6.38 (t, J = 2 Hz, 1H, H¹), 5.08 (s, 2H, PhCH₂OCO), 4.29 (t, J = 5 Hz, 2H, PhOCH₂ of the tetra(ethylene glycol) chain), 3.90 (t, J = 7 Hz, 4H, PhOCH₂ of the aliphatic chain), 3.69–3.60 (m, 14H, CH₂N y OCH₂ of the tetra(ethylene glycol) chain), 3.45 (s, 2H, OOCCH₂COO), 3.11 (s, 3H, CH₃N), 1.75–1.70 (m, 4H, PhOCH₂CH₂), 1.45–1.38 (m, 4H, PhO(CH₂)₂CH₂), 1.33–1.24 (m, 32H, all CH₂ of the aliphatic chain), 0.87 (t, J = 7 Hz, 6H, CH₃) ppm.

 $^{13}\text{C NMR}$ (100 MHz, CDCl₃): $\delta = 166.21$ (1C, Ce), 166.06 (1C, Cg), 160.45 (2C, Cb), 156.74 (1C, Cl), 152.54 (1C, Ch), 147.34 (1C, Co), 143.77 (1C, Ck), 137.21 (1C, Cd), 125.99 (2C, Cl), 124.50 (2C, Ch), 122.49 (2C, Cm), 111.46 (2C, Cl), 106.42 (2C, Cl), 101.18 (1C, Cd), 70.77–70.57, 68.74 (6C, OCH₂ of the tetra(ethylene glycol) chain), 67.08 (2C, PhOCH₂ of aliphatic chain), 68.55 (1C, PhCH₂O), 68.06 (1C, N(CH₂)₂), 64.44 (1C, COOCH₂ of the tetra(ethylene glycol) chain), 52.17 (1C, NCH₂), 41.31 (1C, Cl), 39.17 (1C, NCH₃), 31.81, 29.56–29.19, 25.97, 22.57 (20C, all CH₂ of the aliphatic chain), 13.98 (2C, CH₃) 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%.

¹H NMR (400 MHz, CDCl₃): δ = 8.31 (d, J = 9 Hz, 2H, H⁶), 7.91 (d, J = 9 Hz, 2H, H⁵), 7.89 (d, J = 10 Hz, 2H, H⁴), 6.76 (d, J = 9 Hz, 2H, H³), 6.46 (d, J = 2 Hz, 2H, H²), 6.40 (t, J = 2 Hz, 1H, H¹), 5.09 (s, 2H, PhCH₂OCO), 4.36 (t, J = 6 Hz, 2H, NCH₂CH₂OCO), 3.91 (t, J = 7 Hz, 4H, PhOCH₂ of the aliphatic chain), 3.66 (t, J = 6 Hz, 2H, CH₃CH₂NCH₂), 3.51–3.46 (m, 2H, OCOCH₂CH₂NCH₂) 3.45 (s, 2H, OOCCH₂COO), 1.77–1.70 (m, 4H, PhOCH₂CH₂), 1.45–1.38 (m, 4H, PhO(CH₂)₂CH₂), 1.31–1.20 (m, 35H, all CH₂ of the aliphatic chain and NCH₂CH₃), 0.88 (t, J = 7 Hz, 6H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 166.19 (1C, C°), 165.91 (1C, C°), 160.54 (2C, C°), 156.74 (1C, C¹), 151.10 (1C, C°), 147.54 (1C, C°), 144.01 (1C, C^k), 137.16 (1C, C^d), 126.21 (2C, C°), 124.58 (2C, C^j), 122.63 (2C, C°), 111.48 (2C, Cⁱ), 106.61 (2C, C°), 101.21 (1C, C³), 68.15 (2C, PhOCH₂ of the aliphatic chain), 67.26 (1C, PhCH₂O), 62.23 (1C, CH₃CH₂NCH₂CH₂O), 48.57 (1C, CH₃CH₂NCH₂), 45.67 (1C, CH₃CH₂N), 41.43 (1C, C^f), 31.88 (2C, CH₃(CH₂)₂), 29.63–29.25 (14C, all CH₂ of the aliphatic chain), 26.03 (2C, PhO(CH₂)₃), 22.64 (2C, CH₃CH₂), 14.04 (1C, CH₃), 12.27 (1C, NCH₂CH₃) ppm.

2.5 Synthesis of the fullerene C₆₀-azobenzene derivatives

2.5.1 Synthesis of the fullerene C_{60} -amino substituted azobenzene (15). 9 (0.240 g, 0.3 mmol), I_2 (0.065 g, 0.025 mmol) and fullerene 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 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: $C_{115}H_{83}N_3O_9$ calcd: $[M+H]^+$ 1650.90 found (m/z): $[M+H]^+$ 1651.93.

¹H NMR (400 MHz, CDCl₃) (Scheme 2a): δ = 7.85 (d, J = 9 Hz, 2H, H⁵), 7.83 (d, J = 8 Hz, 2H, H⁴), 7.48–7.38 (m, 3H, H⁶–H), 6.75 (d, J = 9 Hz, 2H, H³), 6.58 (d, J = 2 Hz, 2H, H²), 6.40 (t, J = 2 Hz, 1H, H¹), 5.43 (s, 2H, PhCH₂OCO), 4.63 (t, J = 5 Hz, 2H, OOCCH₂ of the tetra(ethylene glycol) chain), 3.89 (t, J = 6.50 Hz, 4H, PhOCH₂ of the aliphatic chain), 3.83 (t, J = 5, 2H, OCH₂), 3.68–3.62 (m, 14H, CH₂N y OCH₂ of the tetra(ethylene glycol) chain), 3.09 (s, 3H, CH₃N), 1.77–1.73 (m, 4H, PhOCH₂CH₂), 1.43–1.25 (m, 36H, all CH₂ of the aliphatic chain), 0.89 (t, J = 7 Hz, 6H, CH₃) ppm.

 $^{13}\mathrm{C}$ NMR (100 MHz, CDCl₃) (Scheme 2a): 163.46 (1C, Cg), 163.29 (1C, Ce), 160.47 (2C, Cb), 153.17 (1C, Ch), 151.34 (1C, Cl), 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, Cd), 129.31 (1C, Co), 128.87 (2C, Cn), 125.02 (2C, Ci), 122.17 (2C, Cm), 111.38 (2C, Ci), 107.15 (2C, Cc), 101.64 (1C, Cd), 71.40 (fullerene carbon), 70.75–70.64, 68.91,

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68.66 (7C, OCH₂ of the chain tetra(ethylene glycol) chain), 68.53 (2C, PhOCH₂ of the aliphatic chain), 68.11 (1C, PhCH₂O), 66.18 (1C, NCH₂), 52.15 (1C, C^f), 39.24 (1C, NCH₃), 31.90, 29.67-29.26, 26.10, 22.67 (20C, CH₂ of the aliphatic chain), 14.12 (2C, CH₃) ppm.

2.5.2 Synthesis of the fullerene C₆₀-amino-butyl substituted azobenzene (16). Procedure employed for the synthesis of 15, using 10 (0.091 g, 0.1 mmol), I_2 (0.023 g, 0.1 mmol), fullerene C_{60} (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: $C_{119}H_{91}N_3O_9$ calcd: $[M + H]^+$ 1707.01 found (m/z): $[M + H]^+$ 1708.59.

¹H NMR (400 MHz, CDCl₃): $\delta = 7.83$ (d, J = 9 Hz, 2H, H⁵), 7.75 (d, J = 8 Hz, 2H, H⁴), 7.27 (d, J = 7 Hz, 2H, H⁶), 6.75 (d, J = 79 Hz, 2H, H^3), 6.58 (d, J = 2 Hz, 2H, H^2), 6.40 (t, J = 2 Hz, 1H, H^1), 5.43 (s, 2H, PhCH₂OOC), 4.62 (t, J = 5 Hz, 2H, OOCCH₂ of the tetra(ethylene glycol) chain), 3.89 (t, J = 6 Hz, 4H, PhOCH₂ of the aliphatic chain), 3.83 (t, J = 5 Hz, OCH₂), 3.69–3.62 (m, 14H, CH₂N y OCH₂ of the tetra(ethylene glycol) chain), 3.09 (s, 3H, CH_3N), 2.67 (t, J = 8 Hz, 2H, $PhCH_2$), 1.77-1.70 (m, 4H, PhOCH₂CH₂), 1.67-1.60 (m, 2H, Ph(CH₂)₂), 1.42-1.25 (m, 38H, $Ph(CH_2)_3$ and all CH_2 of the aliphatic chain), 0.95 (t, J=7 Hz, 6H, CH_3), 0.89 (t, J = 6 Hz, 3H, $Ph(CH_2)CH_3$) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 163.46$ (1C, C^g), 163.31 (1C, C^e), 160.54 (2C, C^b), 151.46 (1C, C^h), 151.18 (1C, C^l), 144.67 (1C, C°), 143.84 (1C, C^k), 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^d), 128.91 (2C, Cⁿ), 124.82 (2C, C^m), 122.16 (2C, C^j), 111.46 (2C, Cⁱ), 107.24 (2C, C^c), 101.77 (1C, C^a), 71.49 (fullerene carbon), 70.76-70.69, 68.94 (6C, OCH₂ of the tetra(ethylene glycol) chain) 68.52 (PhOCH₂ of the aliphatic chain), 68.61 (1C, PhOCH₂), 68.18 (1C, PhCH₂O), 66.22 (1C, NCH₂), 52.23 (1C, C^f), 39.22 (1C, NCH₃), 35.49 (1C, PhCH₂), 33.49 (1C, PhCH₂CH₂), 31.92, 29.69-29.30, 26.13, 22.68 (20C, all CH₂ of the aliphatic chain), 22.33 (1C, Ph(CH₂)₂CH₂), 14.11 (2C, CH_3), 13.93 (1C, $Ph(CH_2)_3CH_3$) ppm.

2.5.3 Synthesis of the fullerene C₆₀-amino-methoxy substituted azobenzene (17). Procedure employed for the synthesis of 15, using 11 (0.149 g, 0.15 mmol), I₂ (0.039 g, 0.15 mmol), fullerene C_{60} (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: $C_{116}H_{85}N_3O_{10}$ calcd: $[M + H]^+$ 1680.93 found (m/z): $[M + H]^+$ 1681.90.

¹H NMR (400 MHz, CDCl₃): $\delta = 7.82$ (d, J = 9 Hz, 2H, H⁵), 7.81 (d, J = 9 Hz, 2H, H⁴), 6.98 (d, J = 8.98 Hz, 2H, H⁶), 6.76 (d, J = 8.98 Hz, 2H, H⁶), 6.78 (d, J = 8.98 $= 9 \text{ Hz}, 2H, H^3$, 6.58 (d, $J = 2 \text{ Hz}, 2H, H^2$), 6.40 (t, J = 2 Hz, 1H, H^{1}), 5.43 (s, 2H, PhCH₂OOC), 4.62 (t, J = 5 Hz, 2H, OOCCH₂ of the tetra(ethylene glycol) chain), 3.89 (t, J = 7 Hz, 4H, PhOCH₂ of the aliphatic chain), 3.82 (t, J = 5 Hz, OCH₂), 3.87 (s, 3H, PhOCH₃), 3.69–3.62 (m, 14H, CH₂N y OCH₂ of the tetra(ethylene glycol) chain), 3.08 (s, 3H, CH₃N), 1.77-1.70 (m, 4H, PhOCH₂-CH₂), 1.45–1.25 (m, 36H, all CH₂ of the aliphatic chain), 0.89 (t, J $= 7 \text{ Hz}, 6H, CH_3) \text{ ppm}.$

¹³C NMR (100 MHz, CDCl₂): $\delta = 163.47$ (1C, C^g), 163.31 (1C, C^e), 160.85 (1C, C^o), 160.54 (2C, C^b), 150.98 (1C, C^h), 147.54 (1C, C^l), 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^d), 124.60 (2C, C^j), 123.83 (2C, C^m), 114.10 (2C, Cⁿ), 111.50 (2C, Cⁱ), 107.26 (2C, Cc), 101.78 (1C, Ca), 71.50 (fullerene carbon), 70.77-70.70, 68.71 (6C, OCH₂ of the tetra(ethylene glycol) chain), 68.96 (PhOCH₂ of the aliphatic chain), 68.63 (1C, PhCH₂O), 68.20 (1C, OOCCH₂ of the tetra(ethylene glycol) chain), 66.23 (1C, NCH₂), 55.50 (1C, OCH₃), 52.26 (1C, C^f), 39.21 (1C, NCH₃), 31.93, 29.70-29.31, 26.13, 22.69 (20C, all CH₂ of the aliphatic chain), 14.11 (2C, CH₃) ppm.

2.5.4 Synthesis of the fullerene C₆₀-amine-cyano substituted azobenzene (18). Procedure employed for the synthesis of 15, using 12 (0.19 g, 0.21 mmol), I_2 (0.052 g, 0.21 mmol), fullerene C_{60} (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: $C_{116}H_{82}N_4O_9$ calcd: $[M + H]^+$ 1675.91 found (m/z): $[M + H]^+$ 1676.83.

¹H NMR (400 MHz, CDCl₃): $\delta = 7.88$ (d, J = 9 Hz, 2H, H⁵), 7.86 (d, J = 9 Hz, 2H, H⁴), 7.73 (d, J = 8 Hz, 2H, H⁶), 6.76 (d, J = 89 Hz, 2H, H^3), 6.58 (d, J = 2 Hz, 2H, H^2), 6.40 (t, J = 2 Hz, 1H, H^{1}), 5.43 (s, 2H, PhCH₂OOC), 4.62 (t, J = 6 Hz, 2H, OOCCH₂ of the tetra(ethylene glycol) chain), 3.90 (t, J = 6 Hz, 4H, PhOCH₂ of the aliphatic chain), 3.83 (t, J = 5 Hz, OCH₂), 3.68–3.62 (m, 14H, CH₂N y OCH₂ of the tetra(ethylene glycol) chain), 3.12 (s, 3H, CH₃N), 1.78-1.68 (m, 4H, PhOCH₂CH₂), 1.45-1.25 (m, 36H, all CH₂ of the aliphatic chain), 0.89 (t, J = 6 Hz, 6H, CH_3) ppm.

¹³C NMR (100 MHz, CDCl₃): $\delta = 163.47$ (1C, C^g), 163.33 (1C, C^e), 160.48 (2C, C^b), 149.98 (1C, C^l), 147.83 (1C, C^h), 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, Cd), 128.90 (2C, Cn), 125.03 (2C, C^m), 122.18 (2C, C^j), 118.01 (1C, C^o), 111.39 (2C, PhCN), 111.34 (1C, Ci), 107.18 (2C, Cc), 101.66 (1C, Ca), 72.87 (fullerene carbon), 70.76-70.66, 68.67 (6C, OCH₂ of the tetra(ethylene glycol) chain) 68.44 (2C, PhOCH₂ of the aliphatic chain), 68.93 (1C, PhCH2O), 68.54 (1C, PhCH2O), 68.12 (1C, OOCCH₂ of the tetra(ethylene glycol) chain), 66.19 (1C, NCH₂), 52.16 (1C, C^f), 39.25 (1C, NCH₃), 31.91, 29.68–29.27, 26.11, 22.68 (20C, all CH₂ of the aliphatic chain), 14.13 (2C, CH₃) ppm.

2.5.5 Synthesis of the fullerene C_{60} -amino-nitro substituted azobenzene (19). Procedure employed for the synthesis of 15, using 13 (0.153 g, 0.15 mmol), I_2 (0.039 g, 0.15 mmol), fullerene C_{60} (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: $C_{115}H_{82}N_4O_{11}$ calcd: $[M+H]^+$ 1695.90 found (m/z): $[M+H]^+$

¹H NMR (400 MHz, CDCl₃): $\delta = 8.32$ (d, J = 9 Hz, 2H, H⁶), 7.91 (d, J = 9 Hz, 2H, H⁵), 7.88 (d, J = 9 Hz, 2H, H⁴), 6.77 (d, J = 9 Hz, 2H, H³), 6.58 (d, J = 2 Hz, 2H, H²), 6.40 (t, J = 2 Hz, 1H, H¹), 5.43 (s, 2H, PhCH₂OCO), 4.63 (t, J = 5 Hz, 2H, PhOCH₂ of the tetra(ethylene glycol) chain), 3.89 (t, J = 7 Hz, 4H, PhOCH₂ of the aliphatic chain), 3.83 (t, J = 5 Hz, OCH₂), 3.69–3.62 (m, 14H, CH₂N and OCH₂ of the tetra(ethylene glycol) chain), 3.13 (s, 3H, CH₃N), 1.76–1.70 (m, 4H, PhOCH₂CH₂), 1.45–1.37 (m, 4H, PhO(CH₂)₂CH₂), 1.35–1.25 (m, 32H, all CH₂ of the aliphatic chain), 0.89 (t, J = 7 Hz, 6H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 163.45 (1C, C^e), 163.30 (1C, C^g), 160.56 (2C, C^b), 156.83 (1C, C^l), 152.55 (1C, C^h), 147.44 (1C, C^o), 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^d), 126.12 (2C, C^j), 124.65 (2C, Cⁿ), 122.60 (2C, C^m), 111.54 (2C, Cⁱ), 107.27 (2C, C^c), 101.75 (1C, C^a), 71.49 (fullerene carbon), 70.85–70.71, 68.72 (6C, OCH₂ of the tetra(ethylene glycol) chain), 68.96 (2C, PhOCH₂ of the aliphatic chain), 68.62 (1C, PhCH₂O), 68.20 (1C, COOCH₂), 66.20 (1C, NCH₂), 52.25 (1C, C^f), 39.35 (1C, NCH₃), 31.92, 29.69–29.30, 26.13, 22.68 (20C, all CH₂ of the aliphatic chain), 14.10 (2C, CH₃) ppm.

2.5.6 Synthesis of the fullerene C_{60} -DR1 (20). Procedure employed for the synthesis of 15, using 14 (0.1094 g, 0.13 mmol), I_2 (0.032 g, 0.13 mmol) and fullerene C_{60} (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: $C_{110}H_{72}N_4O_8$ calcd: $[M + H]^+$ 1577.77 found (m/z): $[M + H]^+$ 1578.47.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.30$ (d, J = 9 Hz, 2H, H⁶), 7.88 (d, J = 7 Hz, 2H, H⁵), 7.87 (d, J = 7 Hz, 2H, H⁴), 6.83 (d, J = 9 Hz, 2H, H³), 6.60 (d, J = 2 Hz, 2H, H²), 6.41 (t, J = 2 Hz, 1H, H¹), 5.41 (s, 2H, PhCH₂OCO), 4.68 (t, J = 6 Hz, 2H, NCH₂CH₂OCO), 3.89 (t, J = 7 Hz, 4H, PhOCH₂ of the aliphatic chain), 3.79 (t, J = 6 Hz, 2H, CH₃CH₂NCH₂), 3.57–3.51 (m, 2H, OCOCH₂CH₂NCH₂), 1.76–1.68 (m, 4H, PhOCH₂CH₂), 1.43–1.36 (m, 4H, PhO(CH₂)₂CH₂), 1.34–1.24 (m, 35H, all CH₂ of the aliphatic chain and NCH₂CH₃), 0.89 (t, J = 6 Hz, 6H, CH₃) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 163.35 (1C, C^e), 163.18 (1C, C^g), 160.53 (2C, C^b), 156.63 (1C, C^l), 151.20 (1C, C^h), 147.40 (1C, C^o), 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^d), 126.47 (2C, Cⁿ), 124.61 (2C, C^j), 122.63 (2C, C^m), 111.56 (2C, Cⁱ), 107.33 (2C, C^c), 101.52 (1C, C^a), 71.18 (fullerene carbon), 68.95 (1C, PhCH₂O), 68.15 (2C, PhOCH₂), 63.96 (1C, NCH₂CH₂O), 51.59 (1C, C^f), 48.23 (1C, CH₃CH₂-NCH₂), 45.34 (1C, NCH₂), 31.91 (2C, CH₃(CH₂)₂), 29.68–29.25

(14C, all CH₂ of the aliphatic chain), 26.10 (2C, PhO(CH₂)₃), 22.68 (2C, CH₃CH₂), 14.13 (2C, CH₃), 12.29 (1C, NCH₂CH₃) ppm.

3 Results and discussion

3.1 Synthesis of the fullerene C₆₀-azobenzene derivatives

Generally, the synthesis of the fullerene C_{60} -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, aminonitro, **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_{60} into the precursor malonates by means of a Bingel reaction to give six different fullerene C_{60} -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, ^{30,33} whereas substituted azobenzenes **3** and **6** were synthesized using a similar procedure.²³ 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 NaNO₂ (1 eq.) in an HCl solution (30%) at 0 °C. Afterwards, 2-(2-{2-[2-(methyl-phenyl-amino)-ethoxy]-ethoxy}-ethoxy}-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.³⁰ Similarly, the diazonium salt of 4-cyanoaniline was used to give the corresponding amino-cyano substituted azobenzene (ESI†).

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 C₆₀, iodine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in anhydrous toluene to give the corresponding fullerene C_{60} -azobenzene derivative (15). The other fullerene C₆₀-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 C₆₀-azobenzene derivatives (16), (17), (18), (19) and (20), respectively (Fig. 1).

3.2 Characterization of the fullerene C_{60} -azobenzenes derivatives

The precursor disubstituted malonic azo-dyes and their corresponding fullerene C_{60} -azobenzene derivatives were fully characterized by 1H and ^{13}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 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 H^{5} , H^{4} , H^{6} –H, H^{3} , H^{2} and H^{1} , respectively. In the aliphatic zone, we can see a singlet at 5.09 (PhCH₂OCO), and two triplets at 4.29 (OOCCH₂) and 3.92 ppm (PhOCH₂). In addition, we perceive a multiplet at 3.68–3.59 ppm related to the protons OCH₂ of the oligo(ethylene glycol) segments, as well as two singlets at 3.46 and 3.07 ppm due to the α protons of the malonate (OOCCH₂COO) and the methyl group (NCH₃), respectively. Finally, the protons corresponding to methylenes (CH₂) 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 1H NMR spectrum of fullerene 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 α protons of the malonate (OOCCH₂COO), previously observed at 3.46 ppm, totally disappeared. This is an indication that the Bingel coupling reaction between the fullerene C_{60} and the precursor malonic azo-dye successfully occurred.

On the other hand, in the aromatic region of the ¹³C 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 PhOCH₂ of the aliphatic chain appear at 68.53. Four more signals at 68.11, 66.18, 52.15 and 32.24 ppm,

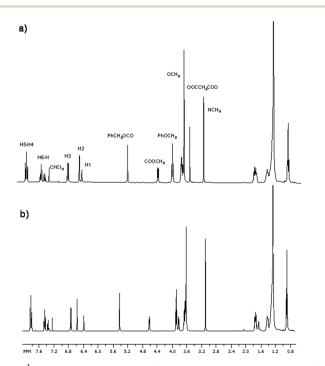


Fig. 2 $\,^{1}$ H NMR spectra in CDCl $_{3}$: (a) precursor malonic azo-dye 9, (b) fullerene C_{60} -azobenzene derivative 15.

corresponding to carbons (PhCH₂O), (NCH₂), (C^f) and (NCH₃), respectively, were also observed. Finally, the signals due to all the CH₂ and CH₃ present in the aliphatic chains appeared at 31.90, 29.67–29.26, 26.10, 22.67, and 14.12 ppm.

In the ¹³C NMR spectrum of fullerene 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 C_{60} sp² 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 C_{60} sp³ carbons and the carbon α to the carbonyl group (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 C_{60} -azobenzene derivatives showed the expected molecular ion peaks, which are in agreement with the calculated molecular weights. The 13 C NMR the fullerene-azobenzene derivatives reported here can be found in the ESI.†

3.3 Optical properties of the fullerene C_{60} -azobenzene derivatives

The optical properties of the fullerene 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 $CHCl_3$, MeOH and DMF solution, whereas those of the fullerene C_{60} -azobenzene derivatives were carried out in $CHCl_3$ 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 CHCl₃ solution, showed a maximum absorption band at λ_{max} = 410 nm followed by red-shifted shoulder at 421 nm due to the π - π * and n- π * transitions, respectively. These compounds have a low dipole moment value and belong to aminoazobenzenes category, according to Rau's classification. ^{18,19} By contrast,

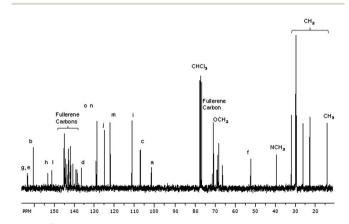


Fig. 3 $\,^{13}\text{C}$ NMR spectra of fullerene $C_{60}\text{-}azobenzene$ derivative 15 in CDCl $_3$

568

610

610

12

13

14

CHCl₃ DMF МеОН $\lambda_{\text{max}} (\text{nm})$ Cut off (nm) $\lambda_{max} (nm)$ Cut off (nm) Cut off (nm) Compound $\lambda_{\text{max}} (\text{nm})$ 410 528 418 530 410 42.8 10 410 528 418 530 410 42.8 11 410 528 418 530 410 42.8

574

628

632

462

496

490

Table 1 Optical properties of the precursor malonic azo-dyes

448

478

468

Table 2 Optical properties of the fullerene C_{60} -azobenzene derivatives

562

596

584

Compound	$CHCl_3 \lambda_{max} (nm)$	DMF λ_{max} (nm)	% photoisomerization yield cis isomer $\Delta abs^b/\Delta abs^a$	Film λ_{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

^a Absorbance of the precursor malonic azo-dyes. ^b Absorbance of the fullerene C₆₀-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 π - π * and n- π * bands in other words, only one absorption band can be observed in the UV-vis spectra. 18,19 However, the absorption bands of these compounds in MeOH solution did not show any significant red shift. On the contrary, compound 14 showed a redshift of 10 nm in its absorption band with respect to that observed in CHCl₃ (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 NO2 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 CHCl₃ and DMF solution, respectively (Table 1).

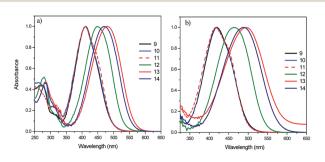


Fig. 4 Normalized absorption spectra of the precursor azo-dyes: (a) in $CHCl_3$, and (b) in DMF solution.

Regarding the optical properties of the fullerene C_{60} -azobenzene derivatives, we noticed that in CHCl₃ 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 π - π * and n- π * 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, azocompounds bearing high dipole moment values (**18**, **19**, **20**) show adsorption bands at 448, 480 and 472 nm, respectively.

450

478

478

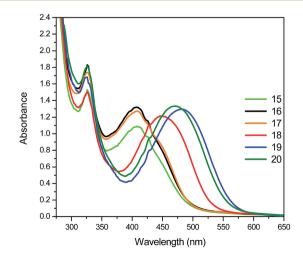


Fig. 5 Absorption spectra of the fullerene C_{60} -azobenzene derivatives in CHCl $_3$ solution.

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

As well, the optical properties of fullerene C_{60} -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 CHCl₃ solution. However, fullerene C_{60} -azobenzene derivatives bearing high dipole moment values (**18**, **19** and **20**) showed maximum absorption bands at $\lambda_{\text{max}} = 462$, 492–494, 488, respectively. They also exhibited a blue-shifted shoulder at 428 nm, which can be due to intramolecular azobenzene–fullerene interactions.³⁶

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.^{29,37} Particularly, we investigated the photoprotonation effect of the fullerene C₆₀-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 C₆₀-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 isosbestic point was situated at 500 nm (Fig. 6b). This fullerene C60-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

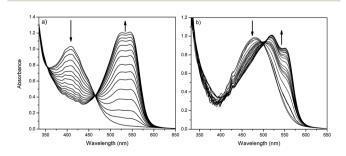


Fig. 6 Photoprotonation effect of [60] fullerene C_{60} -azobenzene derivatives irradiated with UV light at 254 nm: (a) derivative 15, and (b) derivative 19 (Conc. 2.5×10^{-4} M in CHCl $_3$ at room temperature).

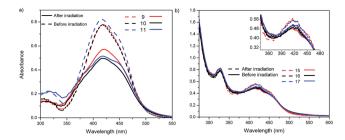


Fig. 7 Absorption spectra upon irradiation with UV light at 365 nm for 10 minutes: (a) precursor azo-dyes 9, 10 and 11, (b) fullerene C_{60} -azobenzene derivatives 15, 16 and 17 (Conc. 2.5×10^{-4} M in DMF at room temperature).

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- π * transition of the cis isomer (Fig. 7a). Meanwhile, in the absorption spectra of the fullerene C60-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 C₆₀-azobenzene derivative 17 exhibited a photoisomerization yield of 13%, which can attributed to the electron-donor effect of the (OCH₃) group. Finally, compounds 15 and 17 bearing low dipole moment values exhibited

Fig. 8 Photoisomerization and photoprotonation of C_{60} -azobenzene derivative 19.

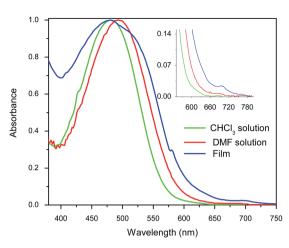


Fig. 9 Absorption spectra of fullerene C_{60} -azobenzene derivatives 19 in CHCl₃, DMF and cast film.

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 CHCl₃, 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 CHCl₃ 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, ²⁸ followed by two discrete shoulders at 580 and 702 nm, respectively (Table 2).³⁸

On the other hand, photoisomerization experiments were carried out in cast film samples. The precursor malonic azodyes 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

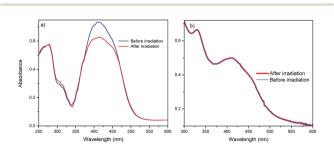


Fig. 10 Absorption spectrum in casted film of: (a) precursor azo-dye 9, (b) fullerene C_{60} -azobenzene derivative 15, after irradiation for 10 minutes.

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 1 H, 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 azodyes 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 π - π * and n- π * transitions, respectively. The presence of a blue-shifted shoulder at 394 nm revealed the presence of Haggregates. 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 Haggregates 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 azodyes 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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