

## Supporting Information

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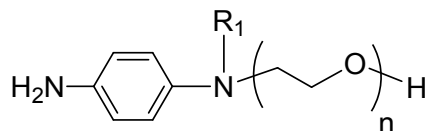
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## 1 Synthesis of the precursor azo-dyes

### 1.1 Synthesis of the (E)-2-(4-(phenyldiazenyl)phenyl)-5,8,11-trioxa-2-azatridecan-13-ol (**3**)

The intermediate 2-(2-{2-[2-(Methyl-phenyl-amino)-ethoxy]-ethoxy}-ethoxy)-ethanol (aminoalcohol **AA**) was synthesized according to the method previously reported by us [Ref. 30].



**AA**

However, the diazonium salts were prepared *in situ*, since these salts are not commercially available. Aniline (1 g, 10.7 mmol) and NaNO<sub>2</sub> (0.74 g, 10.7 mmol) were dissolved in an HCl solution 30% (50 mL) at 0°C with vigorous stirring. Then, **AA** (3.04 g, 10.7 mmol) was added dropwise and the reaction mixture was stirred for 4 h. Afterwards, it was neutralized with a NaOH solution (10%). The crude product was extracted with CHCl<sub>3</sub> and the organic phase was dried with anhydrous MgSO<sub>4</sub>, filtered and concentrated at reduced pressure. The resulting product was purified by column chromatography in silica gel, using mixtures ethyl acetate/hexane 6:4 and 7:3 as eluent, to yield the precursor dye **3**. Yield 80%. FTIR (Film)  $\nu/\text{cm}^{-1}$ : 3440 (OH), 2918, 2869(CH<sub>3</sub>, CH<sub>2</sub>), 1598, 1499 (C=C, Ar), 1452 (N-N), 1347 (CH), 1298, 1248(COC) and 1108 (COC).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (Scheme S1a):  $\delta$  = 7.87 (d,  $J$ = 8.90 Hz, 2 H, H<sup>3</sup>), 7.83 (d,  $J$ = 7.54 Hz, 2 H, H<sup>2</sup>), 7.49-7.35 (m, 3 H, H<sup>4</sup>-H), 6.78 (d,  $J$ = 9.13, 2 H, H<sup>1</sup>), 3.73-3.59 (m, 16 H, NCH<sub>2</sub> and OCH<sub>2</sub>), 3.11 (s, 3 H, NCH<sub>3</sub>) ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (Scheme S1a):  $\delta$  = 160.94 (1 C, C<sup>a</sup>), 152.33 (1 C, C<sup>e</sup>), 146.65 (1 C, C<sup>d</sup>), 130.07 (1 C, C<sup>h</sup>), 128.69 (2 C, C<sup>g</sup>), 124.39 (2 C, C<sup>c</sup>), 122.23 (2 C, C<sup>f</sup>), 113.48 (2

C, C<sup>b</sup>), 72.41 (1 C, HO(CH<sub>2</sub>)<sub>2</sub>), 70.68-70.22 (4 C, OCH<sub>2</sub> of the tetra(ethylene glycol) chain), 68.44 (1 C, N(CH<sub>2</sub>)<sub>2</sub>), 61.62 (1 C, HOCH<sub>2</sub>), 52.06 (1 C, NCH<sub>2</sub>), 39.24 (1 C, NCH<sub>3</sub>) ppm.

[Scheme S1a]

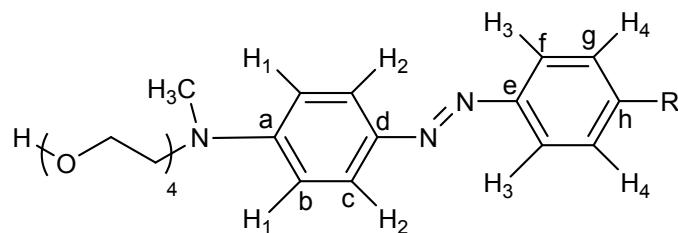
*1.2 Synthesis of the (E)-4-((4-((2-(2-(2 (2hydroxyethoxy)ethoxy)ethoxy)ethyl) (methyl)amino)phenyl)diazanyl)benzonitrile (6)*

4-Aminobenzonitrile (1 g, 8.47 mmol) and NaNO<sub>2</sub> (0.58 g, 8.47 mmol) were dissolved in an HCl solution 30% (80 mL) at 0°C with vigorous stirring. Then, **AA** (2.39 g, 8.47 mmol) was added dropwise and the reaction mixture was stirred for 4 h. Afterwards, it was neutralized with a NaOH solution 10%. The crude product was extracted with CHCl<sub>3</sub> and the organic solution was dried with anhydrous MgSO<sub>4</sub>, filtered and concentrated under vacuum. The resulting product was purified by column chromatography in silica gel using mixtures ethyl acetate/hexane (6:4 and 7:3) as eluent, to yield precursor dye (**6**). Yield 65% FTIR (Film)  $\nu/\text{cm}^{-1}$ : 3411 (OH), 2919, 2866(CH<sub>3</sub>, CH<sub>2</sub>), 2219 (CN), 1595, 1515 (C=C, Ar), 1443 (N-N), 1373 (CH), 1311, 1249(COC) and 1099 (COC).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) (Scheme S1b):  $\delta$  = 7.87 (d,  $J$ = 8.75 Hz, 2 H, H<sup>3</sup>), 7.86 (d,  $J$ = 9.16 Hz, 2 H, H<sup>2</sup>), 7.72 (d,  $J$ = 8.83 Hz, 2 H, H<sup>4</sup>), 6.77 (d,  $J$ = 9.20 Hz, 2 H, H<sup>1</sup>), 3.70-3.57 (m, 16 H, OCH<sub>2</sub> of the tetra(ethylene glycol) chain and NCH<sub>2</sub>), 3.12 (s, 3 H, NCH<sub>3</sub>) ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) (Scheme S1b):  $\delta$  = 155.37 (1 C, C<sup>e</sup>), 152.30 (1 C, C<sup>a</sup>), 143.51 (1 C, C<sup>d</sup>), 132.97 (1 C, C<sup>g</sup>), 125.82 (2 C, C<sup>f</sup>), 122.61 (2 C, C<sup>c</sup>), 118.92 (2 C, C<sup>h</sup>), 111.71 (1 C, PhCN), 111.41 (2 C, C<sup>b</sup>), 72.41 (1 C, HO(CH<sub>2</sub>)<sub>2</sub>), 70.68-70.22 (4 C, OCH<sub>2</sub>), 68.44 (1 C, N(CH<sub>2</sub>)<sub>2</sub>), 61.62 (1 C, HOCH<sub>2</sub>), 52.06 (1 C, NCH<sub>2</sub>), 39.24 (1 C, NCH<sub>3</sub>) ppm.

[Scheme S1b]



- a) R = H  
b) R = CN

Scheme S1

2.  $^{13}\text{C}$  NMR spectrum of fullerene C<sub>60</sub>-azobenzene derivatives

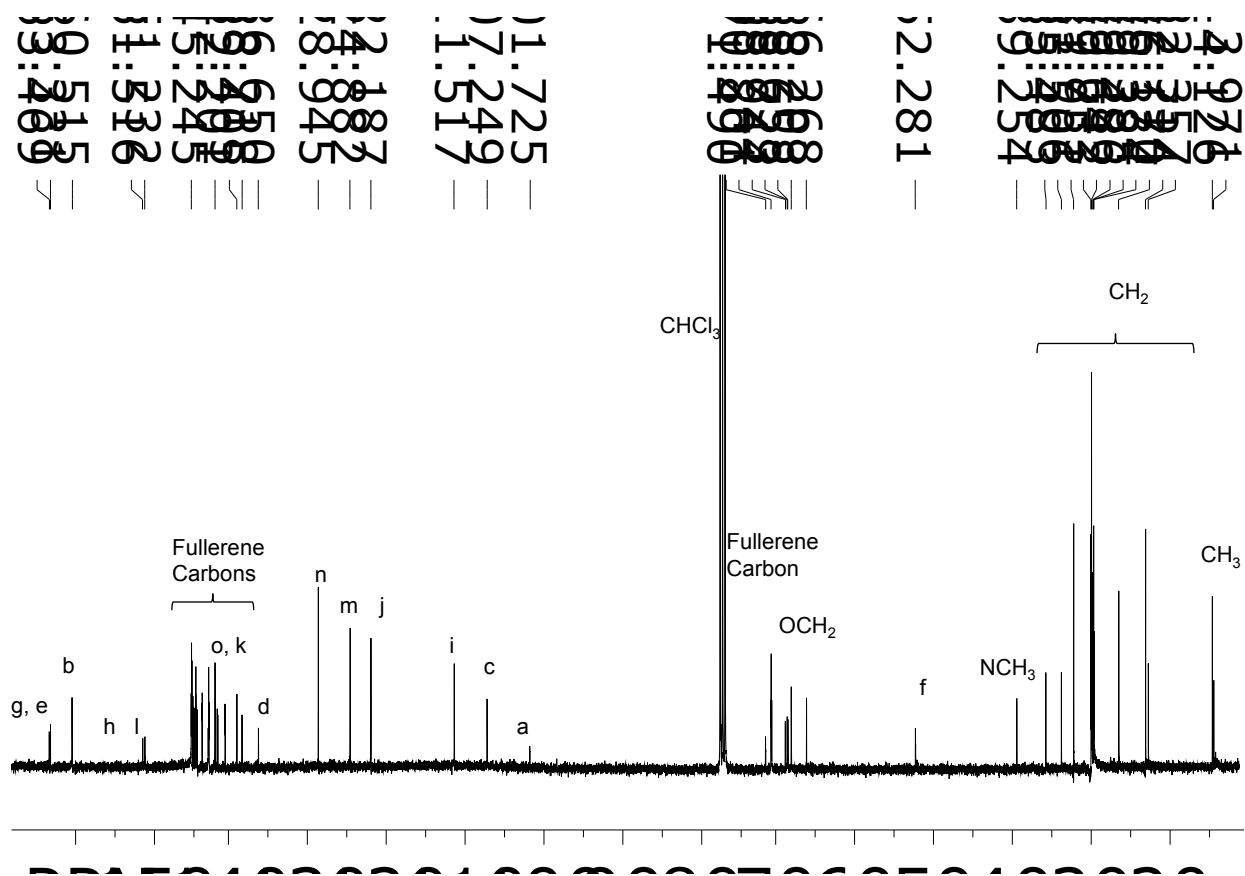


Fig. S1.  $^{13}\text{C}$  NMR spectrum of fullerene C<sub>60</sub>-azobenzene derivative 16





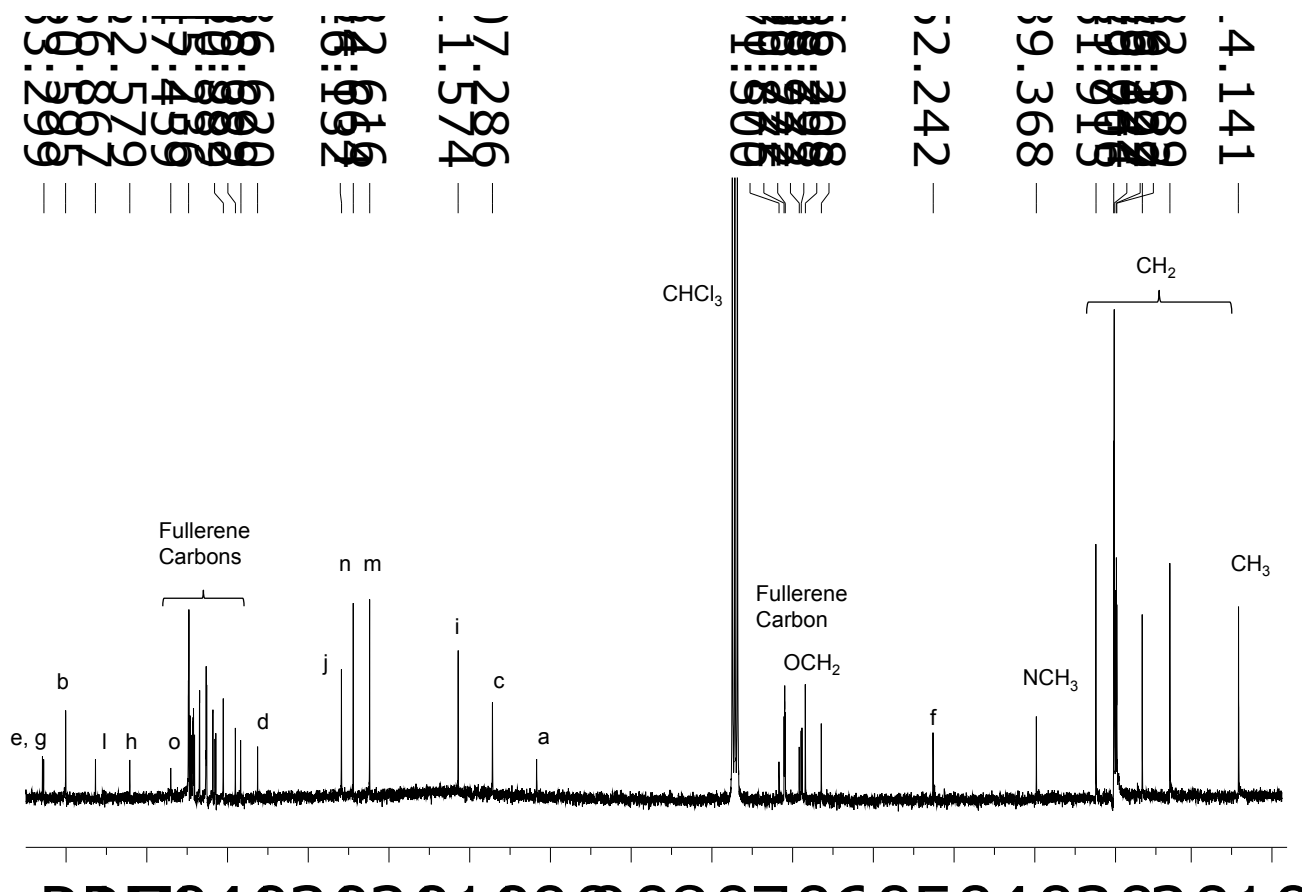


Fig. S4.  $^{13}\text{C}$  NMR spectrum of fullerene  $\text{C}_{60}$ -azobenzene derivative **19**





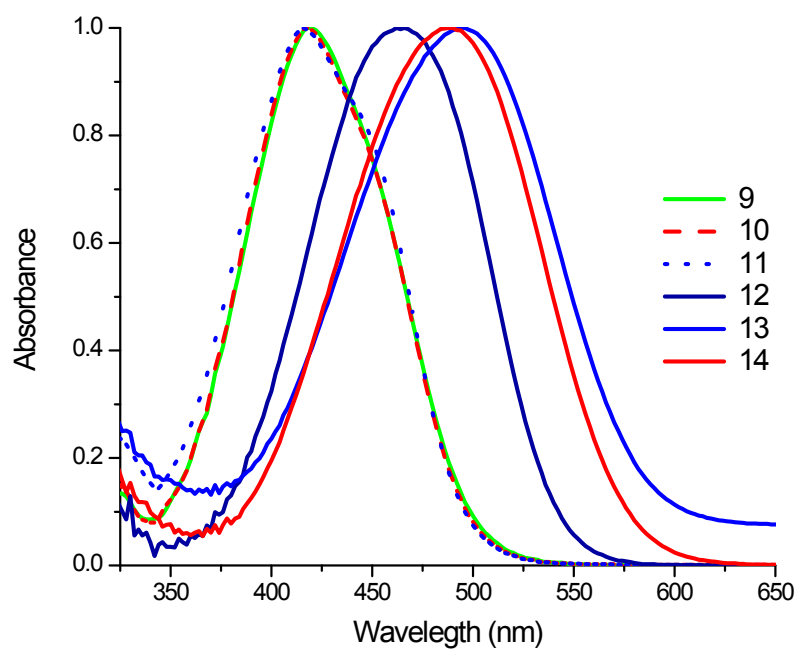


Fig. S6. Optical properties of the precursor malonic azo-dyes in DMF solution