Supporting Information

Index

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)

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

2. $^{13}$C NMR spectrum of the fullerene C$_{60}$-azobenzene derivatives

Fig. S1. $^{13}$C NMR spectrum of the fullerene C$_{60}$-azobenzene derivative 16

Fig. S2. $^{13}$C NMR spectrum of the fullerene C$_{60}$-azobenzene derivative 17

Fig. S3. $^{13}$C NMR spectrum of the fullerene C$_{60}$-azobenzene derivative 18

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

Fig. S5. $^{13}$C NMR spectrum of the fullerene C$_{60}$-azobenzene derivative 20

Fig. S6. Optical properties of the fullerene C$_{60}$-azobenzene derivatives in DMF solution
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].

However, the diazonium salts were prepared in situ, since these salts are not commercially available. Aniline (1 g, 10.7 mmol) and NaNO₂ (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 CHCl₃ and the organic phase was dried with anhydrous MgSO₄, 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 (CH₃, CH₂), 1598, 1499 (C= C, Ar), 1452 (N-N), 1347 (CH), 1298, 1248 (COC) and 1108 (COC).

\(^1\)H NMR (400 MHz, CDCl₃) (Scheme S1a): \( \delta = 7.87 \) (d, \( J= 8.90 \) Hz, 2 H, H^3), 7.83 (d, \( J= 7.54 \) Hz, 2 H, H^2), 7.49-7.35 (m, 3 H, H^4-H), 6.78 (d, \( J= 9.13 \) 2 H, H^1), 3.73-3.59 (m, 16 H, NCH₂ and OCH₂), 3.11 (s, 3 H, NCH₃) ppm.

\(^13\)C NMR (100 MHz, CDCl₃) (Scheme S1a): \( \delta = 160.94 \) (1 C, C^a), 152.33 (1 C, C^e), 146.65 (1 C, C^d), 130.07 (1 C, C^b), 128.69 (2 C, C^g), 124.39 (2 C, C^c), 122.23 (2 C, C^f), 113.48 (2
C, C\textsuperscript{b}), 72.41 (1 C, HO(CH\textsubscript{2})\textsubscript{2}), 70.68-70.22 (4 C, OCH\textsubscript{2} of the tetra(ethylene glycol) chain), 68.44 (1 C, N(CH\textsubscript{2})\textsubscript{2}), 61.62 (1 C, HOCH\textsubscript{2}), 52.06 (1 C, NCH\textsubscript{2}), 39.24 (1 C, NCH\textsubscript{3}) ppm.

**Scheme S1a**

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

4-Aminobenzonitrile (1 g, 8.47 mmol) and NaNO\textsubscript{2} (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\textsubscript{3} and the organic solution was dried with anhydrous MgSO\textsubscript{4}, 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) \(\nu/\text{cm}\textsuperscript{-1}\): 3411 (OH), 2919, 2866(CH\textsubscript{3}, CH\textsubscript{2}), 2219 (CN), 1595, 1515 (C\textsuperscript{=}, Ar), 1443 (N-N), 1373 (CH), 1311, 1249(COC) and 1099 (COC).

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

\(^{13}\text{C} \text{NMR} \ (100 \text{ MHz, CDCl\textsubscript{3}}) \ (\text{Scheme S1b}): \delta = 155.37 \ (1 \text{ C, C\textsuperscript{c}}), 152.30 \ (1 \text{ C, C\textsuperscript{a}}), 143.51 \ (1 \text{ C, C\textsuperscript{b}}), 132.97 \ (1 \text{ C, C\textsuperscript{e}}), 125.82 \ (2 \text{ C, C\textsuperscript{f}}), 122.61 \ (2 \text{ C, C\textsuperscript{c}}), 118.92 \ (2 \text{ C, C\textsuperscript{b}}), 111.71 \ (1 \text{ C, PhCN}), 111.41 \ (2 \text{ C, C\textsuperscript{b}}), 72.41 \ (1 \text{ C, HO(CH\textsubscript{2})\textsubscript{2}}), 70.68-70.22 \ (4 \text{ C, OCH\textsubscript{2}}), 68.44 \ (1 \text{ C, N(CH\textsubscript{2})\textsubscript{2}}), 61.62 \ (1 \text{ C, HOCH\textsubscript{2}}), 52.06 \ (1 \text{ C, NCH\textsubscript{2}}), 39.24 \ (1 \text{ C, NCH\textsubscript{3}}) \text{ ppm.}

**Scheme S1b**
2. $^{13}$C NMR spectrum of fullerene C60-azobenzene derivatives

Fig. S1. $^{13}$C NMR spectrum of fullerene C$_{60}$-azobenzene derivative 16
Fig. S2. $^{13}$C NMR spectrum of fullerene C$_{60}$-azobenzene derivative 17
Fig. S3. $^{13}$C NMR spectrum of fullerene C$_{60}$-azobenzene derivative 18
Fig. S4. $^{13}$C NMR spectrum of fullerene $C_{60}$-azobenzene derivative \textit{19}
Fig. S5. $^{13}$C NMR spectrum of fullerene C$_{60}$-azobenzene derivative 20
Fig. S6. Optical properties of the precursor malonic azo-dyes in DMF solution