

SUPPORTING INFORMATION

FROM

**Light Induced Molecular Release from Vesicles Based on Amphiphilic Linear-Dendritic
Block Copolymers**

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Experimental details and characterization data for the synthesis of 6-[4-(4'-isobutyloxyphenylazo)phenyloxy]hexanoic acid (5a) and 11-[4-(4'-isobutyloxyphenylazo)phenyloxy]undecanoic acid (5b)

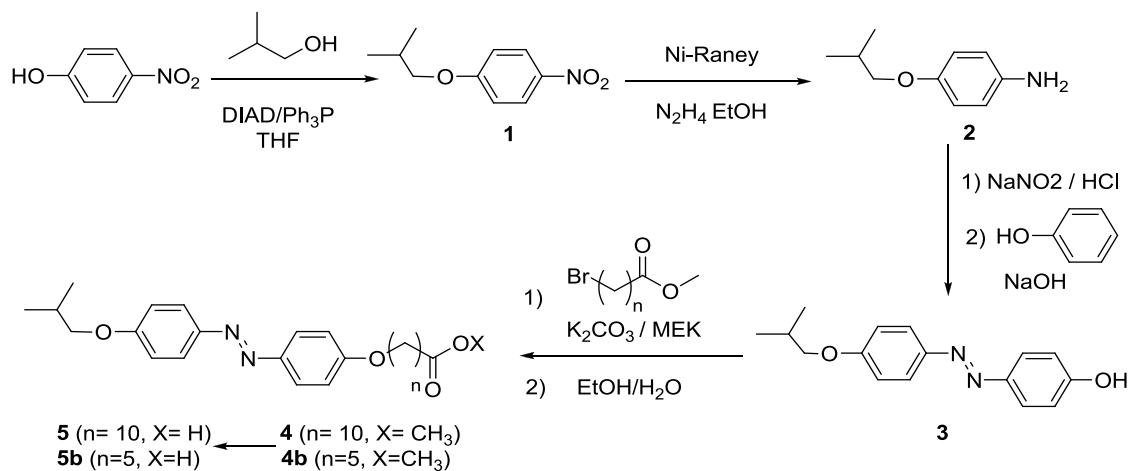


Figure S1. Synthesis of the 4-isobutyloxyazobenzene units

4-Isobutyloxynitrobenzene (1). 2-Methyl-1-propanol (5.33 g, 71.90 mmol), *p*-nitrophenol (10.05 g, 71.90 mmol), and diisopropylazodicarboxylate (14.53 g, 71.90 mmol) were dissolved in dry THF (50 mL) under Ar atmosphere and cooled into an ice-water bath. Then, a solution of triphenylphosphine 18.85 g, 71.90 mmol) in 25 mL of dry THF was added dropwise with stirring. The mixture was stirred at room temperature overnight, the solvent was evaporated and the residue dissolved in dichloromethane. The solution was washed twice with a saturated Na₂CO₃ solution, twice with water, and then with brine. The organic phase was dried, concentrated, and purified by flash column chromatography on silica gel using hexane/ethyl acetate (8:2) as eluent. Yield: 80%. IR (KBr), ν (cm⁻¹): 1592, 1519, 1501, 1344, 1268, 1112, 845. ¹H-NMR (CDCl₃, 400MHz) δ (ppm): 8.21-8.18 (m, 2H), 6.96-6.93 (m, 2H), 3.81 (d, 2H, J=6,5 Hz), 2.11-2.08 (m, 1H), 1.05 (d, 6H, J= 6,7 Hz). ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 164.3, 140.8, 125.9, 114.4, 75.1, 28.1, 19.1.

4-Isobutylloxylaniline (2). Hydrazine monohydrate (98%, 3.5 mL, 71.71 mmol) was added dropwise to a solution of the nitrobenzene derivative (1) (7.00 g, 35.85 mmol) in ethanol (70

mL). After the solution was heated to 40 °C, activated Raney nickel was added and the mixture stirred until no further reaction was observed. The resulting mixture was filtered off of the Raney nickel, and the ethanol was removed under reduced pressure. The crude was dissolved in diethyl ether (60 mL), washed with water and brine, and dried with anhydrous magnesium sulphate. The solvent was distilled off giving the aniline as a yellow oil that was used without further purification. Yield: 90%. IR (KBr), ν (cm⁻¹): 3433, 3358, 1592, 1236, 1036, 823. ¹H-NMR (CDCl₃, 400MHz) δ (ppm): 6.75-6.73 (m, 2H), 6.65-6.62 (m, 2H), 3.64 (d, 2H, J=6,5 Hz), 3,40 (s broad, 2H), 2.09-2.05 (m, 1H), 1.00 (d, 6H, J= 6,7 Hz). ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 152.5, 139.8, 116.5, 115.6, 75.2, 28.3, 19.3.

4-Isobutyloxy-4'-hydroxyazobenzene (3). A mixture of aniline (**2**) (5.21 g, 31.50 mmol) and HCl 6M (15 mL) was cooled into an ice bath. A 2.5 M NaNO₂ solution (20 mL, 31.50 mmol) was added dropwise to the mixture and it was kept stirring in the ice bath. Then, a solution of phenol (2.96 g, 31.50 mmol) in 2 M NaOH (25 mL) was carefully added. The product was precipitated upon addition of HCl until neutral pH and it was purified by flash column chromatography on silica gel using dichloromethane as an eluent. The product was obtained as a yellow powder. Yield: 65%. IR (KBr), ν (cm⁻¹): 3137, 1599, 1586, 1503, 1261, 1149, 839. ¹H-NMR (CDCl₃, 400MHz) δ (ppm): 7.87-7.85 (m, 4H), 7.84-7.82 (m, 4H), 7.00-6.98 (m, 2H), 6.94-6.92 (m, 2H), 3.81 (d, 2H, J=6,5 Hz), 2.13-2.09 (m, 1H), 1.05 (d, 6H, J= 6,7 Hz). ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 161.4, 157.6, 146.8, 124.6, 124.4, 115.8, 114.7, 74.7, 28.3, 19.3.

Methyl 11-[4-(4'-isobutyloxyphenylazo)phenoxy]undecanoate (4a). A solution of 4-isobutyloxy-4'-hydroxyazobenzene (**3**) (2.05 g, 7.40 mmol), methyl 11-bromoundecanoate (2.48 g, 8.88 mmol) in butanone (40 mL) was prepared. 18-Crown-6 (0.05 g) and potassium carbonate (2.05 g, 14.79 mol) were added. The suspension was stirred and heated under reflux for 24 h. Then, it was filtered and concentrated. The crude product was purified by flash column chromatography on silica gel using dichloromethane as eluent. The product was

obtained as a yellow powder. Yield: 75%. IR (KBr), ν (cm^{-1}): 1739, 1592, 1580, 1465, 1242, 845. ^1H -NMR (CDCl_3 , 400MHz) δ (ppm): 7.87-7.85 (m, 4H), 6.94-6.92 (m, 4H), 4.03 (t, 2H, $J=6.4$ Hz), 3.80 (d, 2H, $J=6.5$ Hz), 3.69 (s, 3H), 2.30 (t, 2H, $J=7.4$ Hz), 2.12-2.07 (m, 1H), 1.88-1.75 (m, 2H), 1.67-1.56 (m, 2H), 1.37-1.21 (m, 12H), 1.05 (d, 6H, $J=6.7$ Hz). ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 174.8, 161.3, 146.9, 124.3, 114.6, 74.6, 68.3, 51.4, 34.1, 29.4, 29.3, 29.2, 29.1, 28.3, 26.0, 24.9, 19.2.

Methyl 6-[4-(4'-isobutyloxyphenylazo)phenoxy]hexanoate (4b). The product was obtained following the procedure described for (4a) using methyl 6-bromohexanoate. Yield: 88%. IR (KBr), ν (cm^{-1}): 1741, 1601, 1580, 1497, 1242, 843. ^1H -NMR (CDCl_3 , 400MHz) δ (ppm): 7.84-7.82 (m, 4H), 7.00-6.98 (m, 4H), 4.04 (t, 2H, $J=6.4$ Hz), 3.81 (d, 2H, $J=6.5$ Hz), 3.69 (s, 3H), 2.37 (t, 2H, $J=7.4$ Hz), 2.13-2.09 (m, 1H), 1.88-1.81 (m, 2H), 1.76-1.69 (m, 2H), 1.57-1.49 (m, 2H), 1.05 (d, 6H, $J=6.7$ Hz). ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 175.0, 161.3, 160.9, 146.9, 124.3, 114.6, 114.6, 74.6, 67.9, 51.53, 33.9, 28.9, 28.3, 25.6, 24.7, 19.3.

11-[4-(4'-isobutyloxyphenylazo)phenoxy]undecanoic acid (5a). An aqueous solution of potassium hydroxide (0.9g, 9mL) was added to a solution of methyl 11-[4-(4'-isobutyloxyphenylazo)phenoxy]undecanoate (4a) (6g, 15.05 mmol) in ethanol (60 mL). The mixture was stirred and heated under reflux for 1 h. Then, the crude product was precipitated by addition of HCl until pH 2 and it was recovered by filtration. The product was recrystallized from ethanol. Yield: 85%. IR (KBr), ν (cm^{-1}): 3300, 1714, 1601, 1579, 1499, 1241, 846. ^1H -NMR (CDCl_3 , 400MHz) δ (ppm): 7.86-7.84 (m, 4H), 7.00-6.98 (m, 4H), 4.02 (t, 2H, $J=6.4$ Hz), 3.79 (d, 2H, $J=6.5$ Hz), 2.33 (t, 2H, $J=7.4$ Hz), 2.11-2.07 (m, 1H), 1.86-1.73 (m, 2H), 1.64-1.59 (m, 2H), 1.48-1.43 (m, 2H), 1.34-1.21 (m, 10H), 1.04 (d, 6H, $J=6.7$ Hz). ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 173.9, 161.6, 147.3, 124.4, 114.5, 74.6, 68.3, 34.1, 29.4, 29.3, 29.2, 28.3, 26.0, 24.8, 19.2.

6-[4-(4'-isobutyloxyphenylazo)phenoxy]hexanoic acid (5b). The product was obtained following the procedure described for (5a) by using methyl 6-[4-(4'-

isobutyloxyphenylazo)phenoxy]hexanoate (**4b**). Yield: 80%. IR (KBr), ν (cm^{-1}): 3300, 1708, 1693, 1601, 1580, 1501, 1240, 843. $^1\text{H-NMR}$ (CDCl_3 , 400MHz) δ (ppm): 7.87-7.85 (m, 4H), 6.94-6.92 (m, 4H), 4.06 (t, 2H, $J=6.4$ Hz), 3.81 (d, 2H, $J=6.5$ Hz), 2.37 (t, 2H, $J=7.4$ Hz), 2.13-2.09 (m, 1H), 1.88-1.81 (m, 2H), 1.76-1.69 (m, 2H), 1.57-1.49 (m, 2H), 1.05 (d, 6H, $J=6.7$ Hz). $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ (ppm): 174.4, 161.0, 146.9, 124.3, 114.7, 74.7, 67.9, 33.6, 28.9, 28.3, 25.6, 24.4, 19.3.

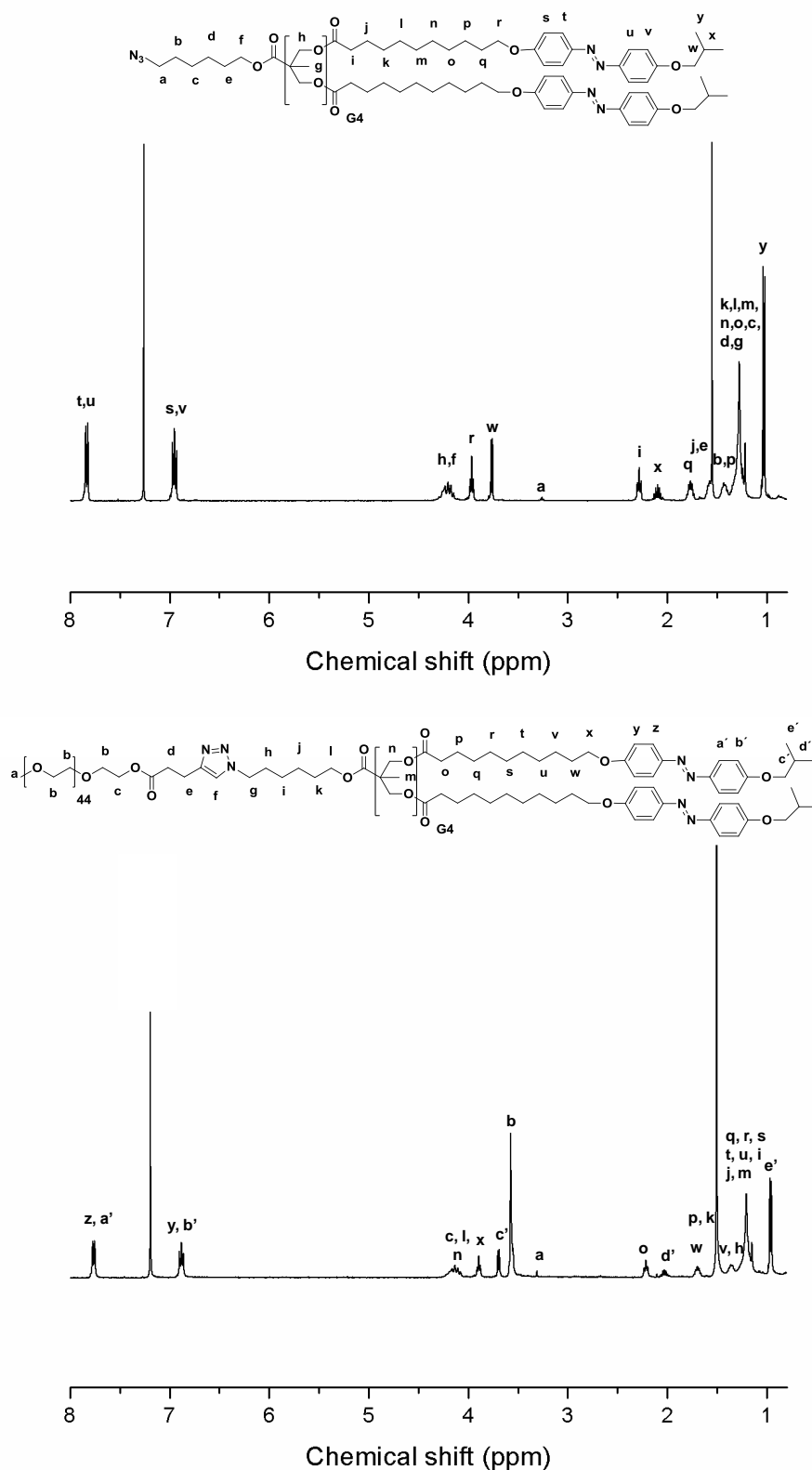


Figure S2. ¹H-NMR of **d16isoAZO** (top) and **PEG-*b*-d16isoAZO** (bottom)

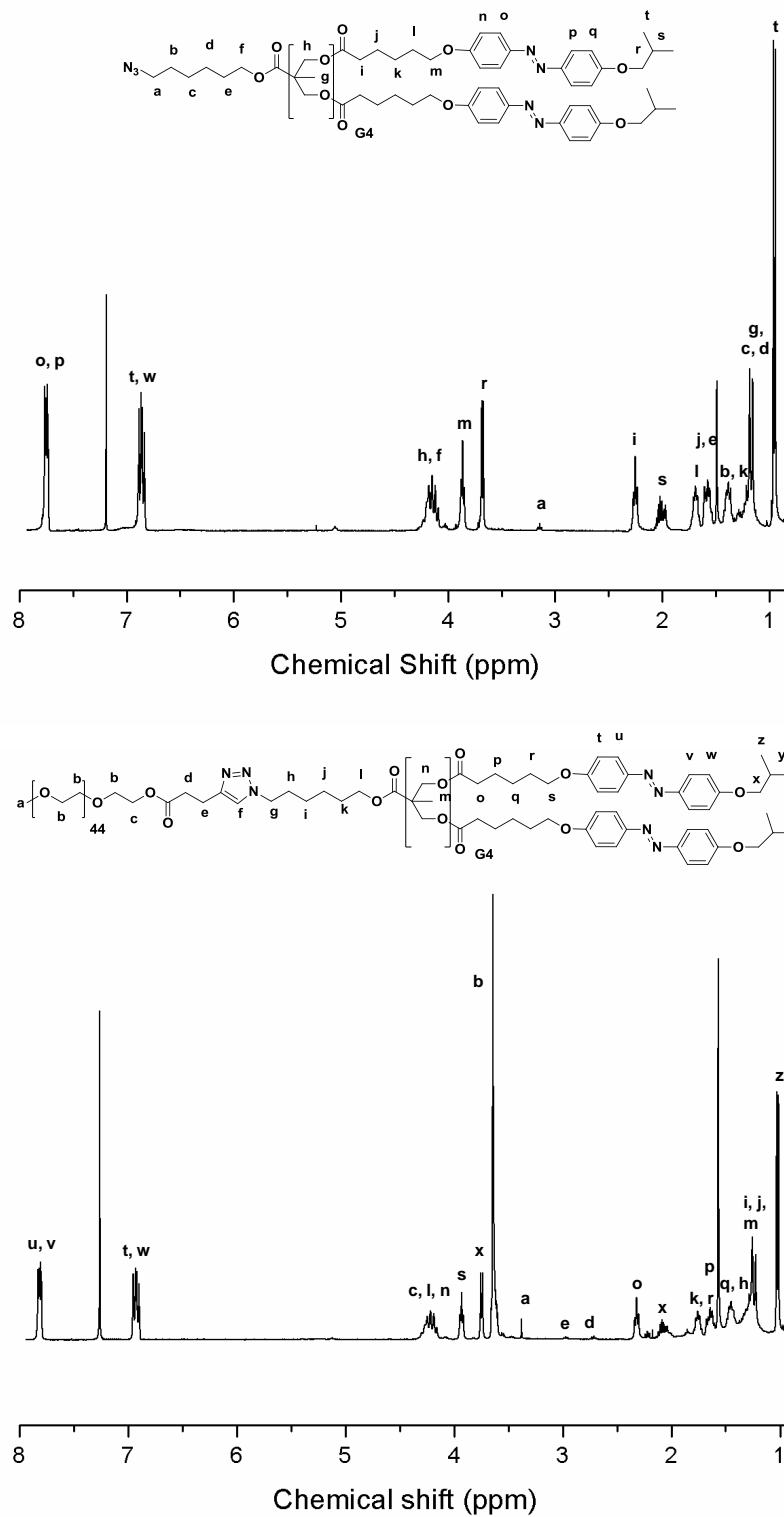


Figure S3. ¹H-NMR of **d16isoAZOb** (top) and **PEG-*b*-d16isoAZOb** (bottom)

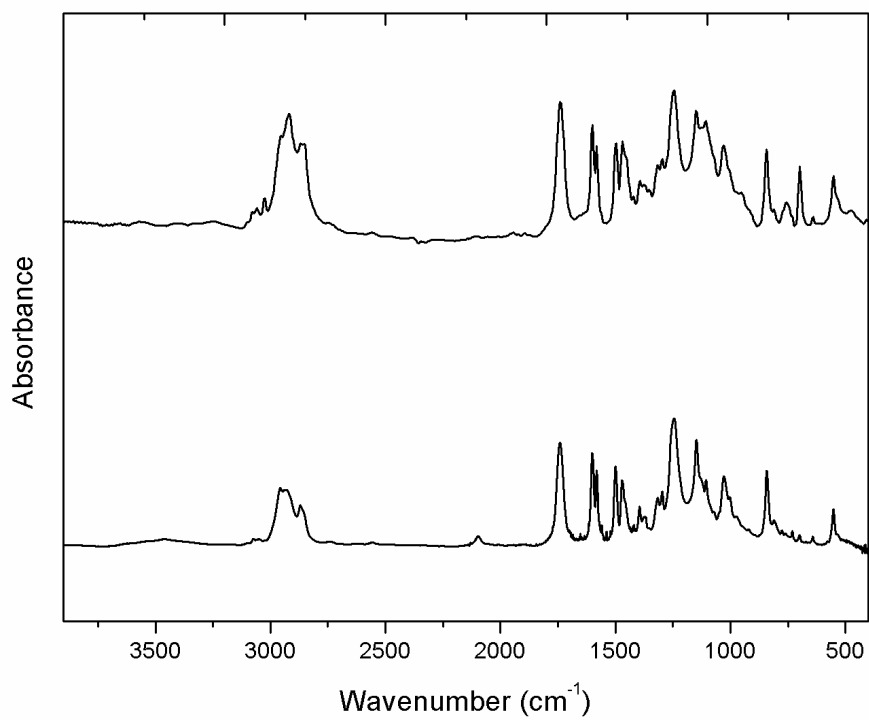


Figure S4. FTIR spectra of the azodendron **PEG-*b*-d16isoAZOb** (top) and **d16isoAZOb** (bottom)

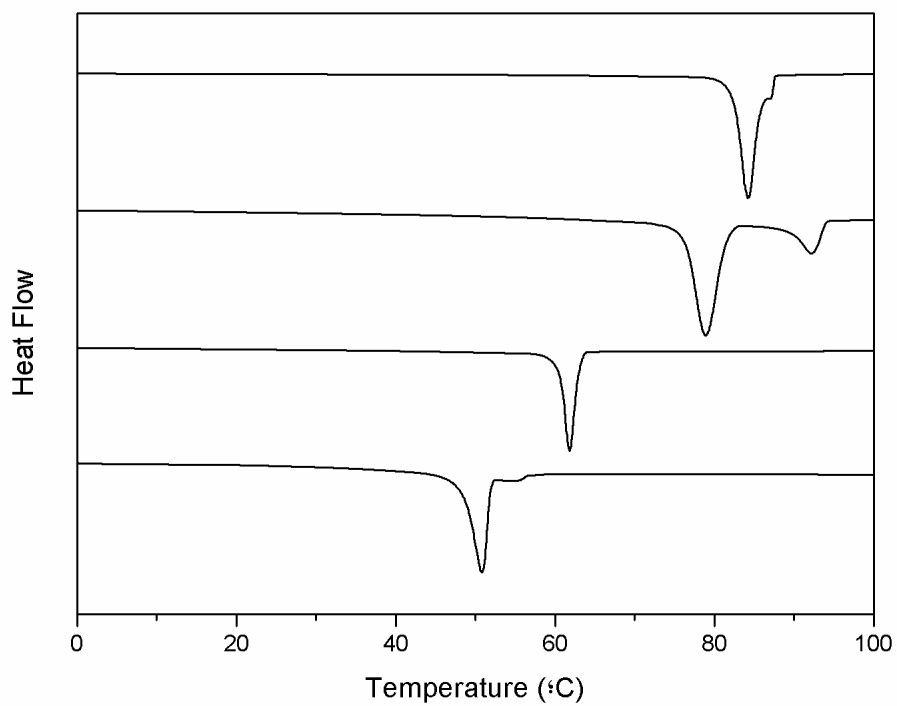


Figure S5. DSC traces (10°C/min) corresponding to the first cooling of **PEG-*b*-d16isoAZO**, **d16isoAZO**, **PEG-*b*-d16isoAZOb**, **d16isoAZOb** (from top to bottom)

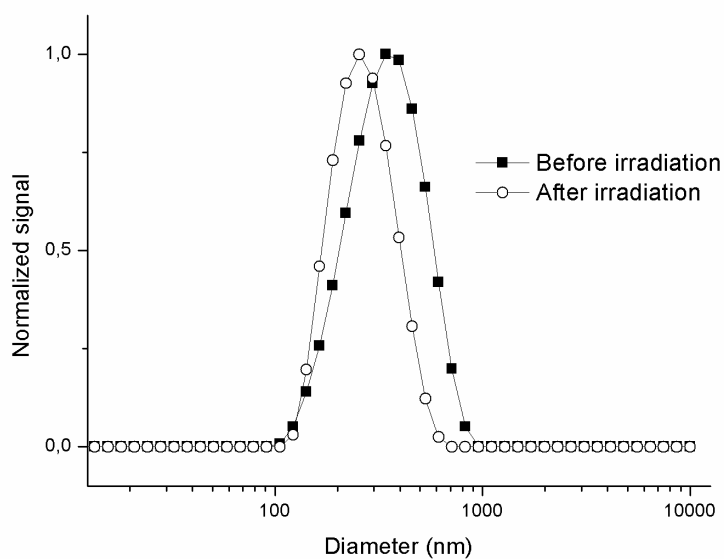


Figure S6. Dynamic light scattering measurements of a water suspension of **PEG-*b*-d16isoAZOb** vesicles before and after UV light irradiation at 365 nm and 2.6 mW/cm²

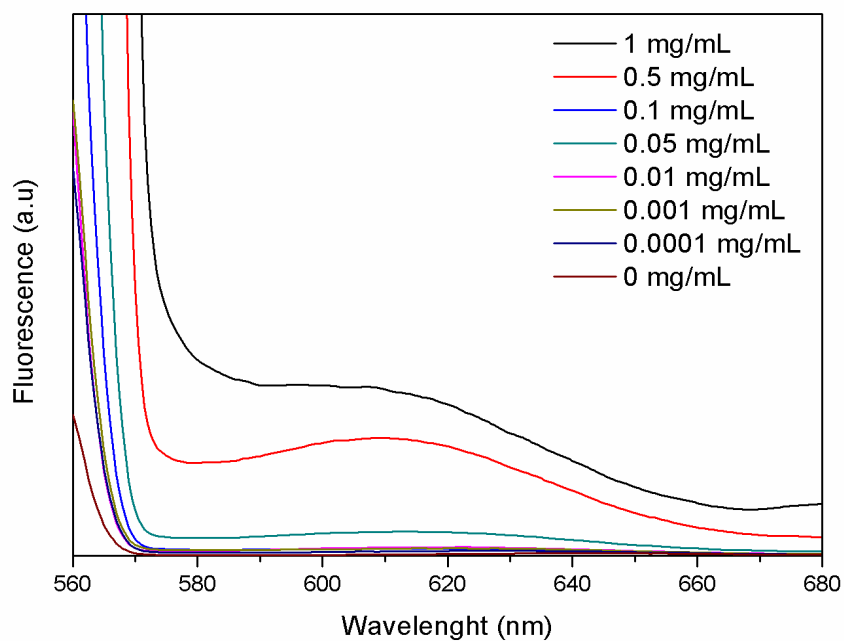


Figure S7. Fluorescence emission spectra of Nile Red in the presence of **PEG-*b*-d16C5AZOisob** vesicles in water

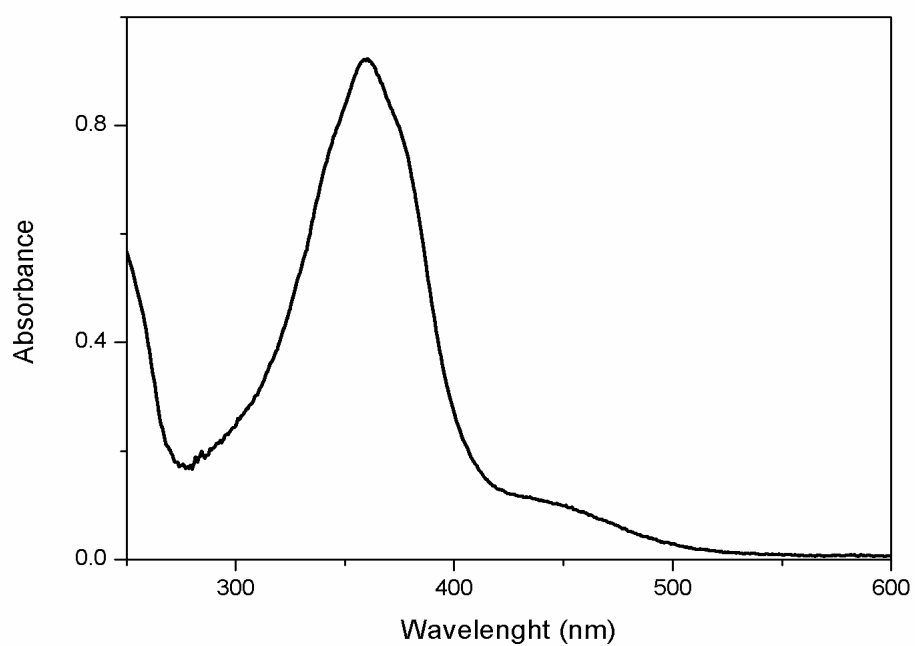


Figure S8. UV-Vis spectra of **PEG-*b*-d16isoAZOb** in a 5×10^{-6} M solution in CHCl_3

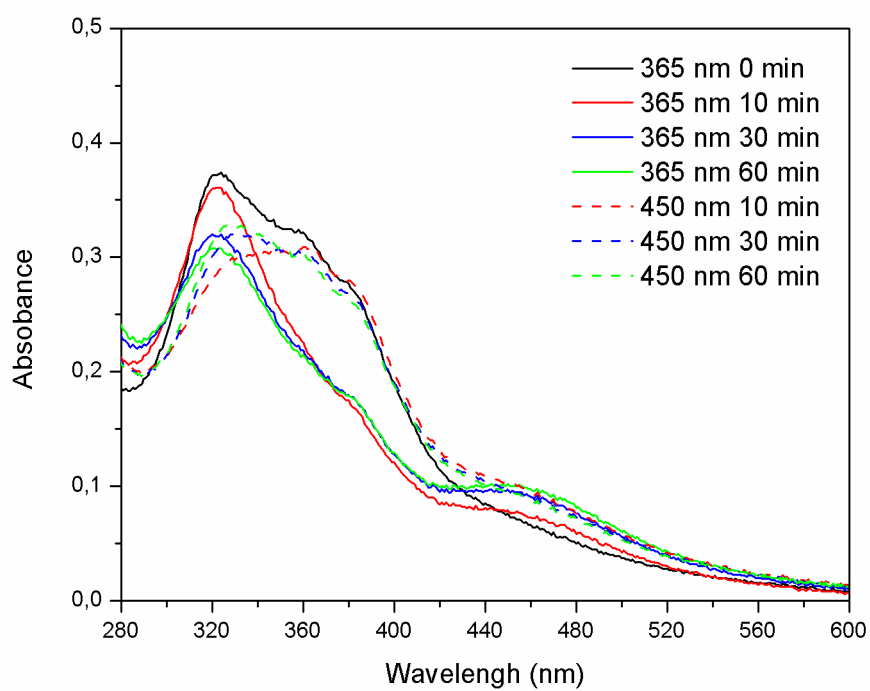


Figure S9. UV-Vis spectra of a water suspension of PEG-b-d16isoAZOb vesicles recorded on irradiating for different time intervals at 365 nm and 450 nm.

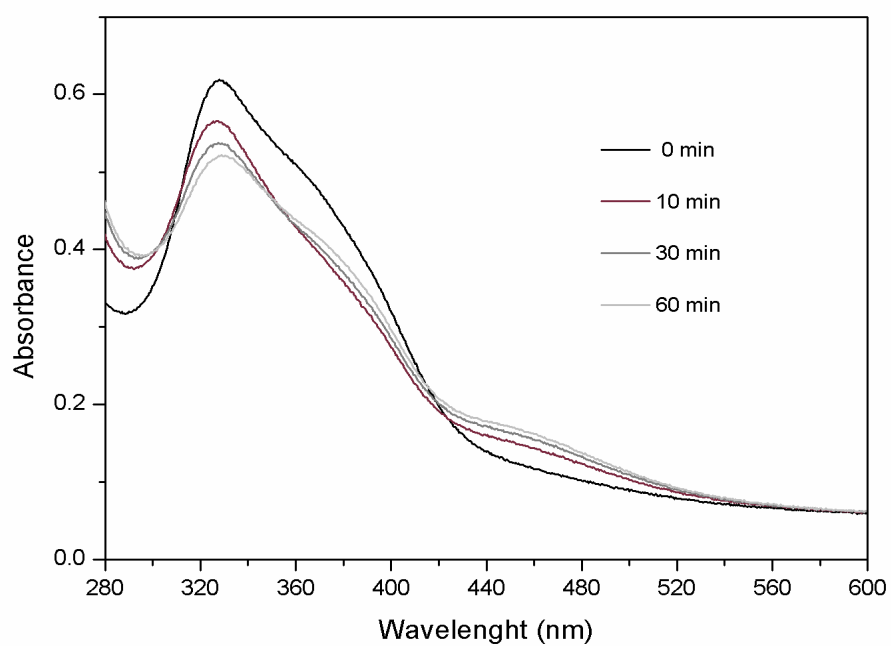


Figure S10. UV-Vis spectra of the irradiated 4-cyanoazobenzene-containing vesicles in water.

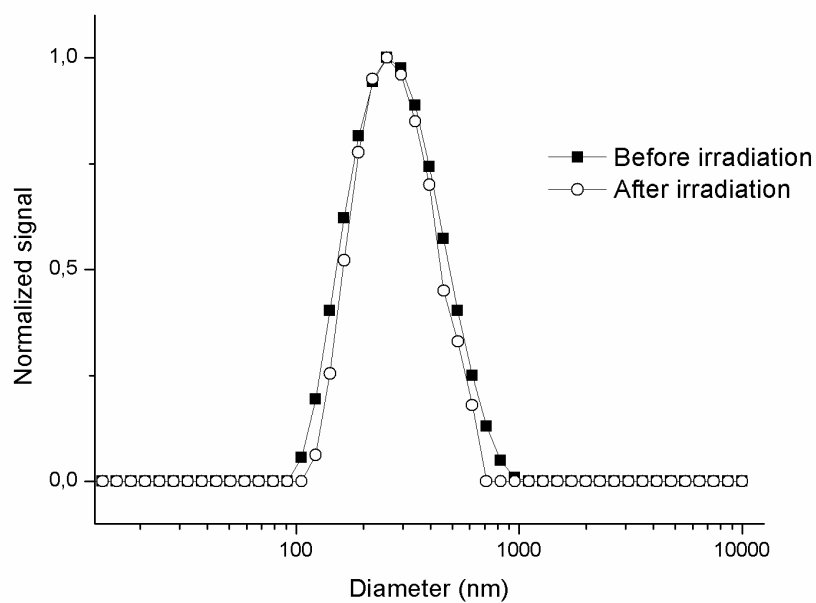


Figure S11. Dynamic light scattering measurements of a water suspension of 4-cyanoazobenzene-containing vesicle before and after UV light irradiation at 365 nm and 2.6 mW/cm²

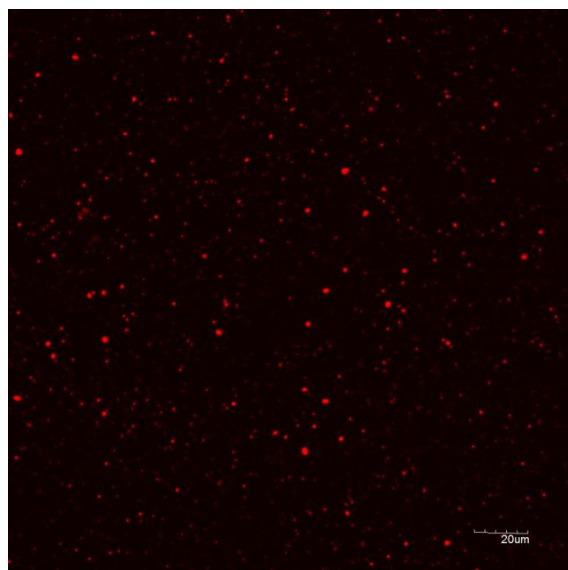


Figure S12. Fluorescence microscopy images of the water suspension of **PEG-*b*-d16isoAZOb** vesicles loaded with Nile Red.

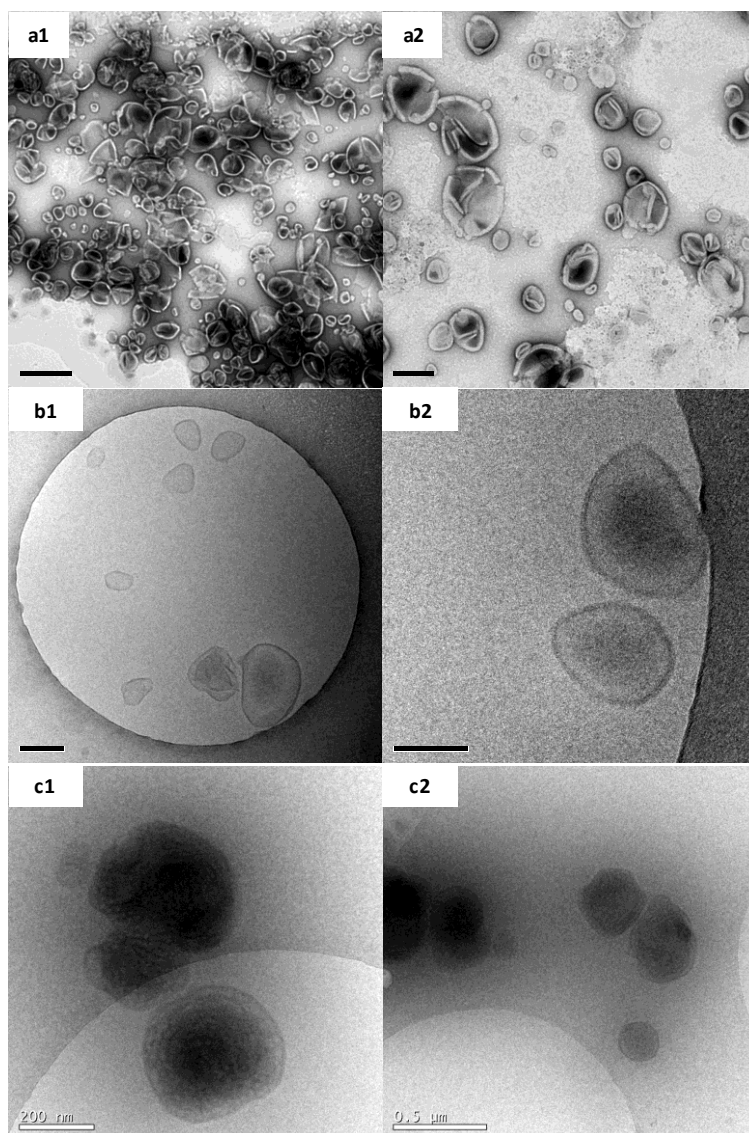


Figure S13. a) TEM image of PEG-b-d16isoAZOb non-irradiated vesicles. Cryo-TEM images of PEG-b-d16isoAZOb vesicles before b) and after c) irradiation for 1 h at 365 nm and 2.6 mW/cm².

