

Supporting Information

Photoresponsive Amphiphiles Based on Azobenzene-Dendritic Glycerol Conjugates Show Switchable Transport Behavior

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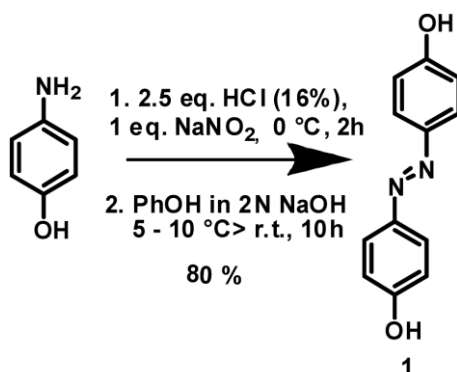
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Experimental Section

Reagents and materials. All commercial compounds were used as received without further purification. We have already published the synthesis of the glycerol dendrons [G2] and [G3]-PG-OH.¹ NMR data were recorded on a Bruker AC 400 and a Bruker AV 700. EI-MS was measured at a MAT 711 from Varian MAT. The electron energy was 80 eV. ESI-MS were measured at Agilent 6210 ESI-TOF from Agilent Technologies. The flow rate was 4 μ l/min. Surface tension was measured with an optical contact angle apparatus (OCA20 from Dataphysics). Switching experiments were done with a 100 W mercury arc lamp from LOT Oriel with filters for 350 nm and 450 nm. Dynamic and static light scattering measurements were performed using Zetasizer-Nano[®] from Malvern with a He-Ne laser (4 mW) at 633 nm (angle 173°). The dn/dc increment was determined with a differential refractometer SEC-3010 from WGE Dr. Bures.

Synthesis of (E)-4,4'-(diazene-1,2-diyl)diphenol (1)



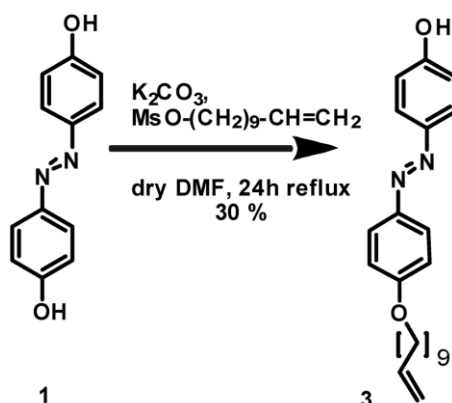
4-Aminophenol (2 g, 18.3 mmol) was added to a 16 % HCl (8.4 ml) solution and stirred at room temperature for 45 min and then cooled to 0 °C–5 °C. A 2 M solution of NaNO₂ (9.2 ml) was slowly added. The excess nitrous acid was neutralized with sulfamic acid. Phenol (1.72 g, 18.3 mmol) was dissolved in a 2 M NaOH (18.4 ml) solution and the solution of the diazonium salt was added dropwise to the phenolic solution at a temperature of 5 °C. The mixture was kept basic with addition of Na₂CO₃ during the formation of diazenes. After addition, the reaction mixture was stirred for 10 h at room temperature. The resulting dark red precipitate was filtered off and washed with cold water. Recrystallization in EtOH/H₂O (1:5) gave the desired azobenzene (80 %) as a dark red solid.

¹H NMR (400 MHz; MeOH-d₄): δ (ppm) = 7.76 – 7.73 (4H, m), 6.91 – 6.88 (4H, m). ¹³C-NMR (100 MHz; MeOH-d₄): δ (ppm) = 161.2; 147.5; 125.4; 116.6. MS (EI): m/z = 214.0750 [M]⁺ (calc: 214.0742) Melting Point: 211 – 212 °C [lit. 216-218 °C]¹

1 W. R. Brode; I. L. Seldin ; P. I. Spoerri ; G.M. Wyman *J. Am. Chem. Soc.* **1955**, *77*, 2762-2765.

Synthesis of undec-10-enyl methanesulfonate (2)

To a solution of 1-undecenol (159 mg, 9.34 mmol, 188 μl) in 100 ml toluene was added triethylamine (1.03 mmol, 104 mg, 145 μl) and the solution was stirred for 30 minutes at room temperature. The mixture was cooled to 0 °C and methansulfonyl chloride (118 mg, 1.03 mmol, 80 μl) was added. The reaction was monitored by TLC (hexane/ethylacetate, 2:1). After complete conversion, the resulting precipitate was filtered off and washed with toluene. The filtrate was dried under reduced pressure to give the crude product as a clear liquid. The crude compound was further used without purification.

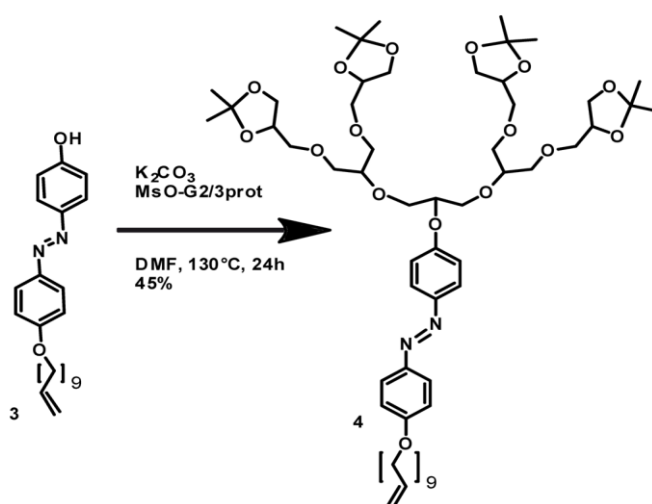


Synthesis of (E)-4-((4-(undec-10-enyloxy)phenyl)diazenyl)phenol (3)

To a solution of **1** (2 g, 9.34 mmol) in dry DMF was added K₂CO₃ (1.29 g, 9.34 mmol) under an argon atmosphere. At a temperature of 100 °C, a 50 mM solution of the freshly prepared mesyl compound (9.3 mmol, from reaction above) in dry DMF was added slowly (over 3 h). The mixture was stirred for 24 h. DMF was removed by cryo distillation. After extraction with CH₂Cl₂ and water, the organic phase was dried with MgSO₄. Subsequent column chromatography over silica gel (hexane/ethyl acetate; 7:1) gave the desired compound (1.11 g, 3 mmol, 33%) as an orange solid.

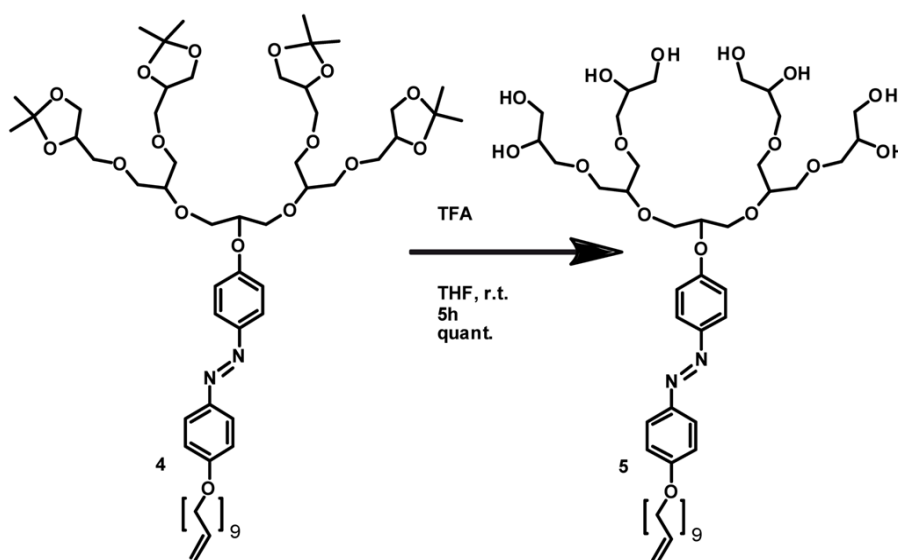
¹H-NMR(400 MHz; Aceton-d₆): δ (ppm) = 8.97 (1H, bs), 7.84–7.82 (2H, m), 7.81–7.78 (2H, m), 7.05–7.03 (2H, m), 6.99–6.97 (2H, m), 5.84–5.73 (1H, m), 4.99–4.94 (1H, m), 4.90–4.87 (1H, m), 4.04 (2H, t, ³J = 6.6 Hz), 2.04–1.99 (2H, m), 1.81–1.74 (2H, m), 1.51–1.41 (2H, m), 1.40–1.25 (10H, m). ¹³C-NMR(100 MHz; Aceton-d₆): δ (ppm)=163.1, 161.8, 148.6, 148.1, 140.8, 126.3, 126.2, 125.9, 125.9, 117.5, 117.5, 116.5, 116.5, 115.6, 69.9, 35.5, 31.2, 31.1, 31.1, 30.9, 30.8, 30.7, 27.7. MS (EI): m/z = 366.2298 [M]⁺ (calc. 366.2307)
Melting Point: 91-92 °C

Coupling of the Dendrons



K_2CO_3 (55 mg, 0.4 mmol) was added to a solution of **3** (72 mg, 0.2 mmol) in 100 ml of dry DMF. After 45 min stirring at room temperature, the mesylated G2 dendron (0.6 mmol) was added. The reaction was refluxed for 24 h under argon. Solvent was evaporated and the residue extracted with CH_2Cl_2 and water. The organic phase was dried with $MgSO_4$ and solvent was removed under reduced pressure. Subsequent column chromatography over silica gel (hexane/ethyl acetate, 4:1) gave the desired compound **4** (94 mg, 0.09 mmol, 45 %) as a red-orange solid. The coupling of G3 PG dendron was done following the same procedure with a yield of 28%.

Deprotection of the Dendrons



TFA in a high excess was added to a solution of **4** (100 mg, 0.1 mmol) in methanol. The reaction mixture was stirred for 6 h at room temperature. After removing solvents and reagents under reduced pressure the desired product was obtained quantitatively as an orange oily substance. The deprotection of both PG generations was performed with this

procedure.

G2azoC11: $^1\text{H-NMR}$ (400 MHz; CDCl_3): δ (ppm) = 7.87-7.78 (4H, m), 7.08-6.92 (4H, m), 6.09-5.70 (1H, m), 5.04-4.91 (2H, m), 4.10-3.20 (37H, m), 1.98-1.87 (2H, m), 1.75-1.68 (2H, m), 1.42-1.32 (2H, m), 1.29-1.15 (10H, m). $^{13}\text{C-NMR}$ (100 MHz; CDCl_3): δ (ppm) = 161.31, 159.69, 147.2, 146.7, 139.1, 124.4, 116.1, 114.6, 114.1, 78.5, 72.7, 71.2, 70.8, 68.3, 63.5, 33.8, 32.7, 31.9, 29.7, 29.6, 29.5, 29.3, 26.0,

MS (ESI): m/z = 907.4733 $[\text{M}+\text{Na}]^+$ (calc. 907.4774)

G3azoC11: $^1\text{H-NMR}$ (400 MHz; CDCl_3): δ (ppm) = 7.75-7.69 (4H, m), 7.02-6.96 (2H, m), 6.90-6.85 (2H, m), 5.75-5.65 (1H, m), 4.90-4.78 (2H, m), 4.00-3.20 (74H, m), 1.96-1.88 (2H, m), 1.74-1.66 (2H, m), 1.40-1.31 (2H, m), 1.30-1.14 (10H, m). $^{13}\text{C-NMR}$ (100 MHz; CDCl_3): δ (ppm) = 161.2, 160.0, 147.0, 146.5, 138.9, 124.1, 124.0, 116.0, 114.5, 113.8, 78.2, 72.5, 71.5, 71.0, 70.7, 70.5, 68.2, 63.1, 33.5, 29.2, 29.1, 28.9, 28.8, 28.7, 25.7

MS (ESI): m/z = 1499.7658 $[\text{M}+\text{Na}]^+$ (calc. 1499.7724)

G2azoC16

$^1\text{H-NMR}$ (700 MHz; CDCl_3): δ (ppm) = 7.90-7.70 (4H, m), 7.10-6.85 (4H, m), 4.80-4.40 (8H, bs), 4.00-3.40 (38H, m), 1.78-1.68 (2H, m), 1.43-1.16 (26H, m), 0.87-0.85 (3H, t, $^3J=6.85$ Hz). $^{13}\text{C-NMR}$ (133 MHz; CDCl_3): δ (ppm) = 161.3, 147.3, 146.7, 124.4, 116.2, 114.6, 78.6, 72.7, 70.8, 68.3, 63.5, 31.9, 29.7, 29.6, 29.5, 29.3, 26.0, 22.7, 14.1. MS (ESI): m/z = 979.5672 $[\text{M}+\text{Na}]^+$ (calc. 979.5713)

G3azoC16

$^1\text{H-NMR}$ (400 MHz; CDCl_3): δ (ppm) = 7.80-7.76 (4H, m), 7.08-7.10 (2H, m), 6.95-6.91 (2H, m), 4.65-4.56 (1H, m), 3.98-3.95 (2H, t, $^3J = 6.55$ Hz), 3.80-3.40 (74H, m), 1.78-1.70 (2H, m), 1.44-1.36 (2H, m), 1.34-1.10 (24H, m), 0.83-0.79 (3H, t, $^3J = 6.89$ Hz). $^{13}\text{C-NMR}$ (100 MHz; CDCl_3): δ (ppm) = 161.3, 146.6, 124.2, 114.6, 78.3, 72.6, 70.6, 68.3, 63.3, 31.8, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 25.9, 22.5, 13.9. MS (ESI): m/z = 1571.8694 $[\text{M}+\text{Na}]^+$ (calc. 1571.8655)

mPEGazoC11

$^1\text{H-NMR}$ (500 MHz; CDCl_3): δ (ppm) = 7.87-7.82 (4H, m), 7.02-6.95 (4H, m), 5.85-5.75 (1H, m), 5.0-4.9 (2H, m), 4.20-4.17 (2H, t, $^3J=4.84$ Hz), 4.02-3.99 (2H, t, $^3J= 6.57$ Hz), 3.89-3.86 (2H, t, $^3J = 4.82$ Hz), 3.74-3.70 (2H, m), 3.68-3.50 (45H, m), 3.36 (3H, s), 2.05-2.00 (2H, m), 1.83-1.75 (2H, m), 1.50-1.20 (12H, m). $^{13}\text{C-NMR}$ (133 MHz; CDCl_3): δ (ppm) = 161.1, 160.6, 147.1, 146.8, 139.1, 124.2, 124.1, 114.7, 114.6, 71.9, 70.8, 70.6, 70.5, 70.4, 69.6, 68.2, 67.6, 58.9, 33.7, 32.1, 29.4, 29.3, 29.1, 29.0, 28.8, 25.9

CMC Measurements

The critical micelle concentration was measured by the concentration dependency of the

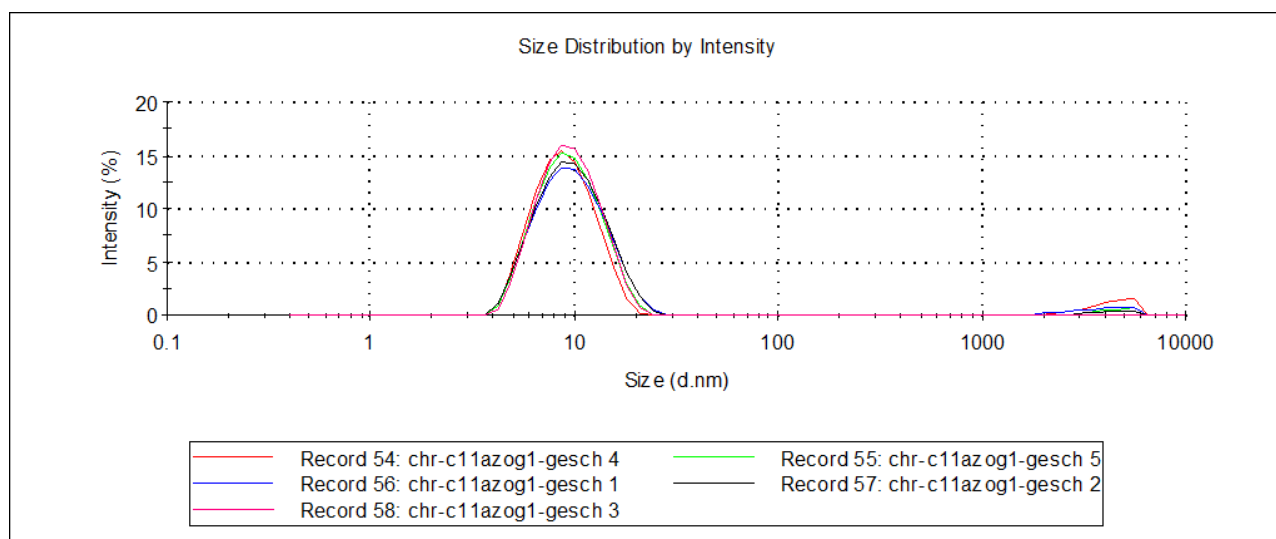
surface tension of a pendant drop. For each amphiphile, the surface tension of nine concentrations ranging from 7.8×10^{-7} M to 1 mM was measured. The samples were left to stand over night at room temperature before measurement. Samples were irradiated (350 nm) over night. The equilibration time before the measurements ranged for the drops from 30 min to 2 hours.

Static Light Scattering

Before the measurement of the average molecular weight of the micelles, the dn/dc increment was determined with a differential refractometer. A calibration curve with ten different concentrations (1 mg/ml to 10 mg/ml) of KCl in water was taken directly before the sample concentration. The resulting dn/dc value from the sample solutions (0.75 mg/ml to 7 mg/ml) was integrated in the static light scattering of the same solutions. The average molecular weight was calculated out of the Debye Plot. The intercept of the linear curve with the y-axis is designated to the reciprocal of the M_w .

Dynamic Light Scattering (DLS)

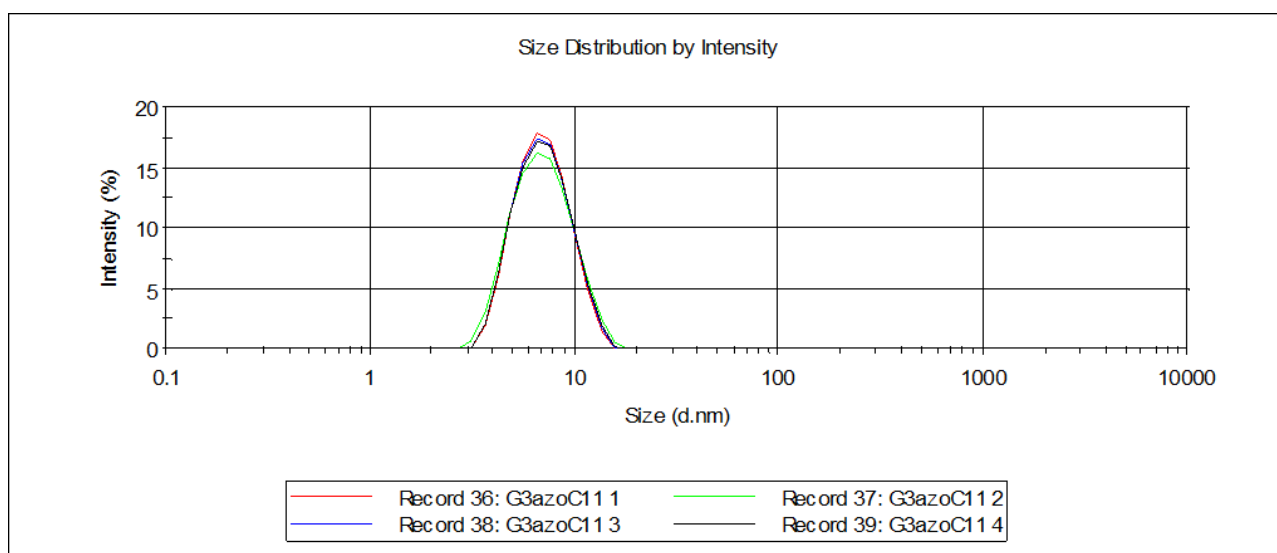
G2azoC11



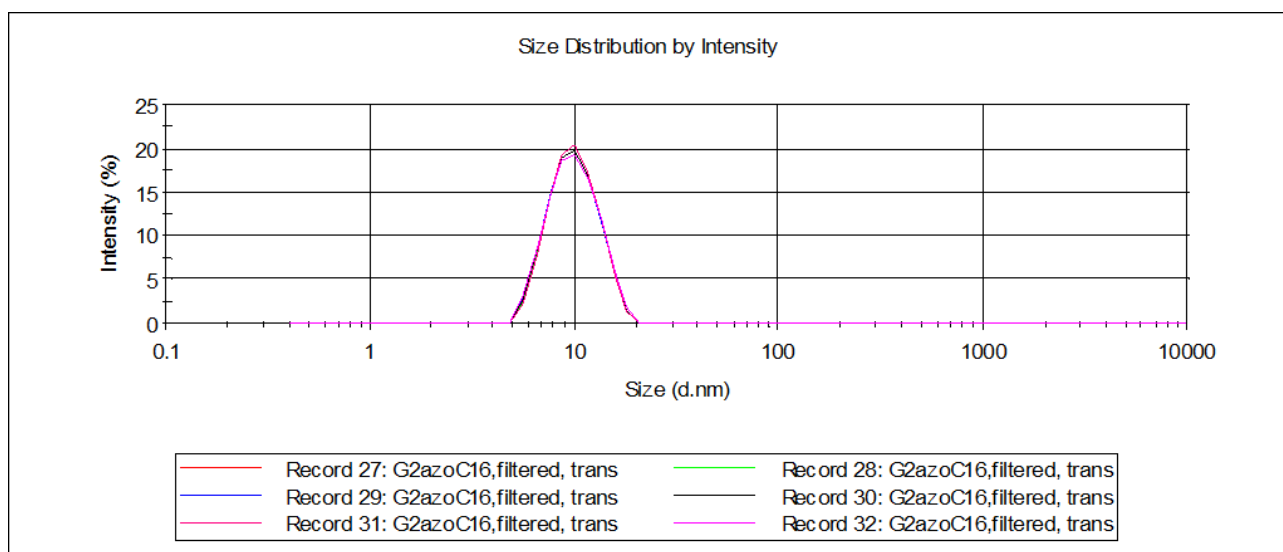
G3azoC11



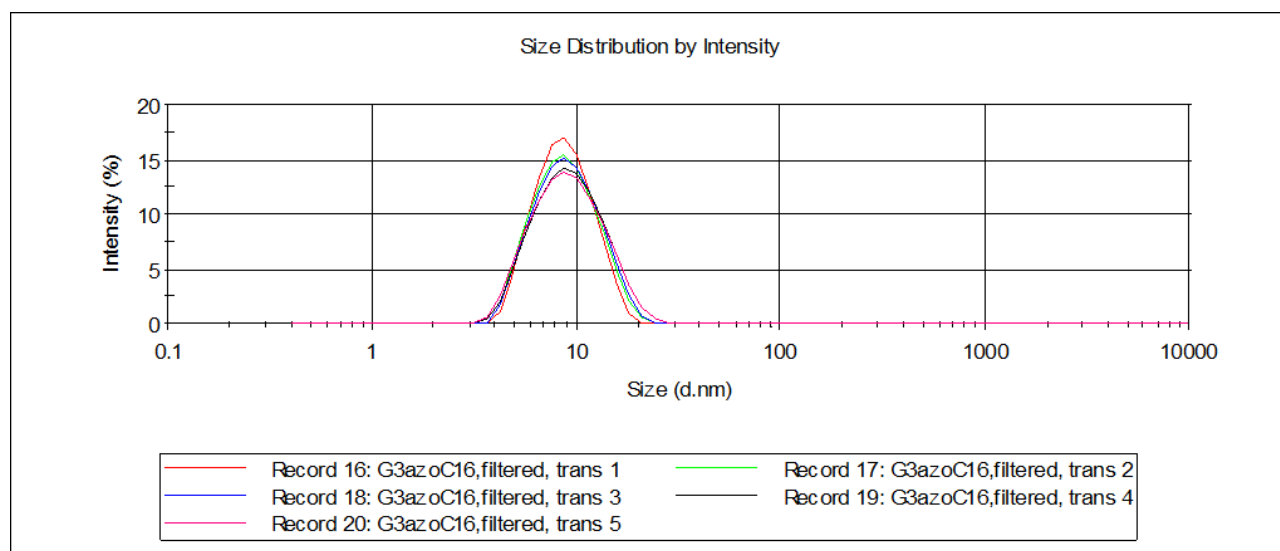
Picture of an azobenzene solution.



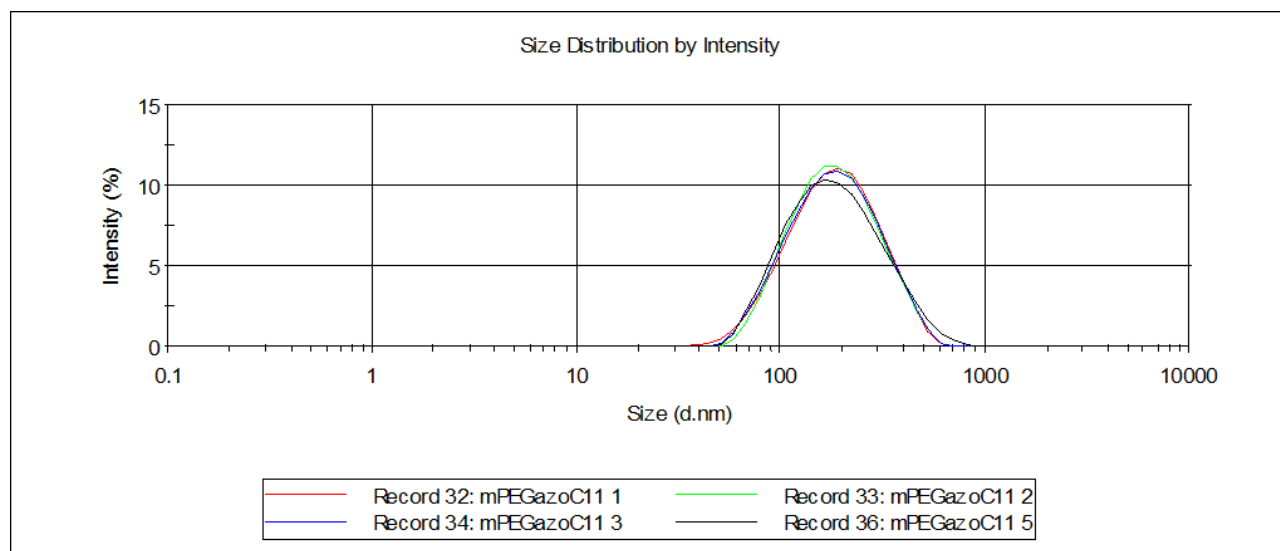
G2azoC16



G3azoC16

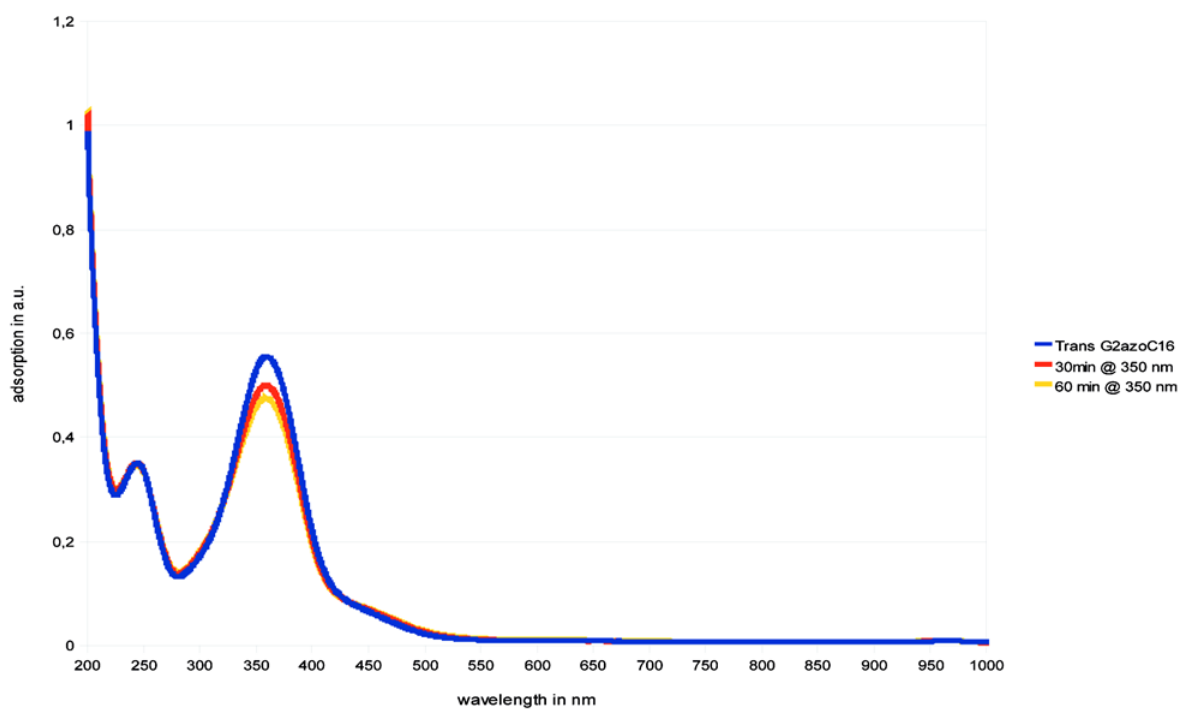
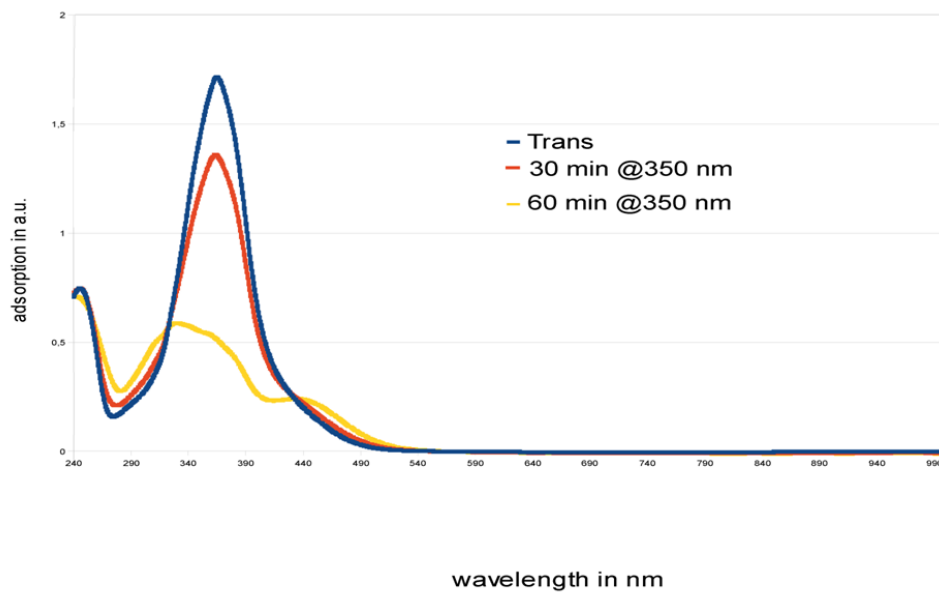


mPEGazoC11



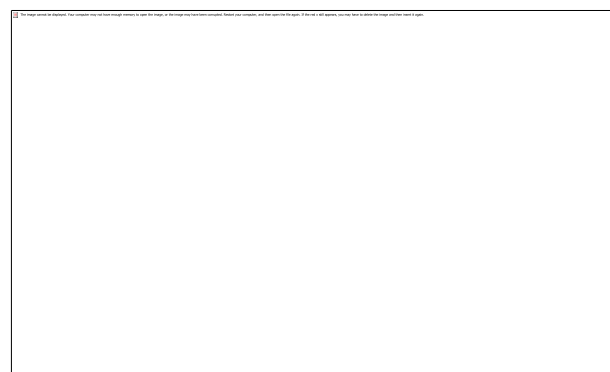
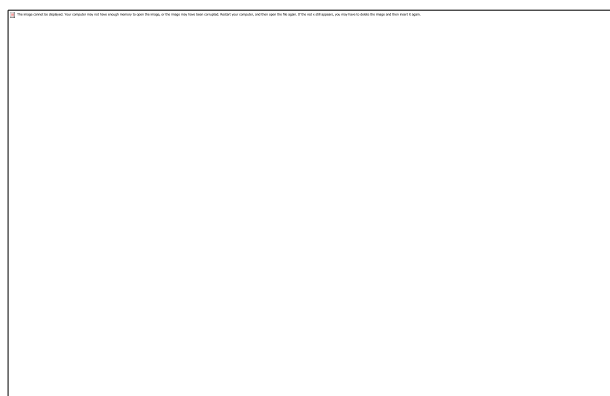
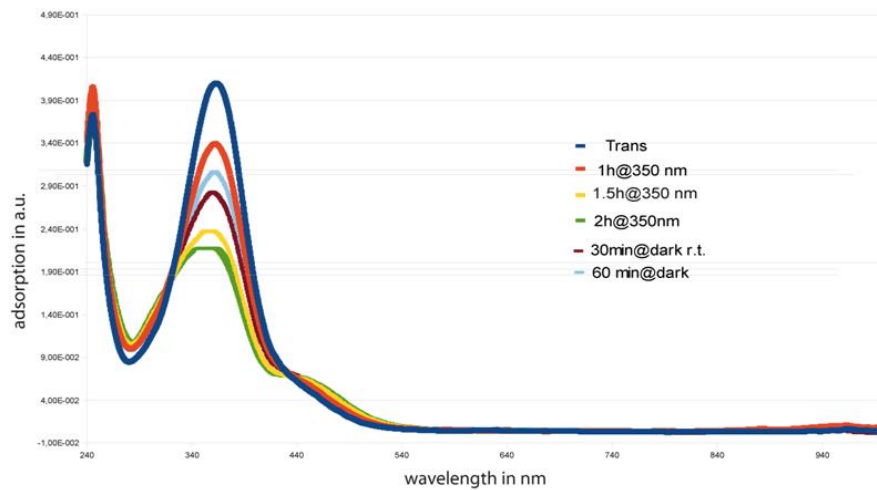
UV/Vis Spectra:

G3azoC11



G2azoC16

G3azoC16



Debye Plots:

Trans-G3azoC11

Cis-G3azoC11

1 Wyszogrodzka, M.; Haag, R. *Chem. Eur. J.* **2008**, *14*, 9202.