Electronic Supplementary Information

**Influence of photo-isomerisation on host-guest interaction in poly(azocalix[4]arene)s**

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**Synthesis of 4,4'-bis(n-alkoxy)azobenzene (MC4 and MC12)**

NaH (1.5 eq) was suspended in DMF and stirred under nitrogen atmosphere. To the reaction mixture, p-nitrophenol (1 eq.) was added and stirred for 30 min at room temperature. The mixture was then heated to 80°C and n-butyl or n-dodecyl bromide (1.5 eq) was added to the system and heating was maintained for 5 hours. After cooling to room temperature, water was added cautiously to destroy excess NaH. The solvent was evaporated at high vacuum; the remaining residue was taken up with dichloromethane and washed with 1M HCl and brine (30mL/mmol). The products were recrystallized from 2-propanol. 4-butoxynitrobenzene: Yield 76%; 1H NMR (500MHz, CDCl3): δ=0.98 (t, 3H, OCH2CH2CH2CH3), 1.5 (m, 2H, OCH2CH2CH2CH2CH3), 1.8 (m, 2H, OCH2CH2CH2CH2CH3), 4.05 (t, 2H, OCH2CH2CH2CH2CH3), 6.93 (d, 2H, J=8.8Hz, ArH, m-NO2), 8.18 (d, 2H, J=8.8Hz, ArH, o-NO2); 4-dodecyloxynitrobenzene: Yield 83%; 1H NMR (500MHz, CDCl3): δ=0.88(t, 3H, OCH2CH2CH2(CH2)9CH3), 1.26 (m, 18H, OCH2CH2(CH2)9CH3), 1.81 (m, 2H, OCH2CH2(CH2)9CH3), 4.04(t, 2H, OCH2CH2(CH2)9CH3), 6.93 (d, 2H, J=8.9Hz, ArH, m-NO2), 8.18(d, 2H, J=8.9Hz, ArH, o-NO2).

Red-Al, Vitride — sodium bis(2-methoxyethoxy)aluminumhydride (7 eq) was placed in a round bottom flask under argon and cooled on an ice bath to 0°C. 4-butoxynitrobenzene or 4-dodecyloxynitrobenzene (1 eq.) was dissolved in toluene (1.3mL/mmol). The solution was then cautiously added to the flask containing Red-Al. Once the evolution of gas ceased, the reaction flask was sealed off and the mixture left stirring overnight. Quenching of the reaction occurred by slow addition of methanol (0.5mL/mmol) and upon cooling to room temperature, the solution
was extracted into dichloromethane and washed with water. The organic phase was dried over K$_2$CO$_3$, filtered and the solvents evaporated in vacuo. The products were recrystallized from 2-propanol.

**4,4’-bis(n-butoxy)azobenzene, MC4:** Yield 68%; $^1$H NMR (500MHz, CDCl$_3$): $\delta=0.99$ (t, 3H, OCH$_2$CH$_2$CH$_2$CH$_3$), 1.54 (m, 2H, OCH$_2$CH$_2$CH$_2$CH$_3$), 1.81 (m, 2H, OCH$_2$CH$_2$CH$_2$CH$_3$), 3.93 (m, minimal, OCH$_2$CH$_2$CH$_2$CH$_3$ – cis), 4.04 (t, 2H, OCH$_2$CH$_2$CH$_2$CH$_3$ - trans), 6.76 (m, minimal, ArH, m-azo - cis), 6.88 (m, minimal, ArH, o-azo – cis) 6.98 (d, 2H, J=8.7Hz, ArH, m-azo – trans), 7.85 (d, 2H, J=8.6Hz, ArH, o-azo-trans); $^{13}$C NMR (500MHz, CDCl$_3$): $\delta=161.4$, 143.2, 124.7, 114.9, 68.1, 31.2, 19.34, 13.64.

**4,4’-bis(n-dodecyloxy)azobenzene, MC12:** Yield 72%; $^1$H NMR (500MHz, CDCl$_3$): $\delta=0.88$(t, 3H, OCH$_2$CH$_2$(CH$_2$)$_9$CH$_3$), 1.27 (m, 18H, OCH$_2$CH$_2$(CH$_2$)$_9$CH$_3$), 1.81 (m, 2H, OCH$_2$CH$_2$(CH$_2$)$_9$CH$_3$), 3.92 (t, minimal, OCH$_2$CH$_2$(CH$_2$)$_9$CH$_3$ - cis) 4.03 (t, 2H, OCH$_2$CH$_2$(CH$_2$)$_9$CH$_3$ - trans), 6.77 (m, minimal, ArH, m-azo - cis), 6.88 (m, minimal, ArH, o-azo – cis), 6.98 (d, 2H, J=8.9Hz, ArH, m-azo – trans), 7.85 (d, 2H, J=8.9Hz, ArH, o-azo-trans); $^{13}$C NMR (500MHz, CDCl$_3$): $\delta=161.6$, 144.3, 124.1, 114.6, 68.4, 31.8, 30.0, 29.5, 28.6, 22.5, 13.64.

![Structure of the model compounds MC4 and MC12 for photoisomerisation studies.](image)

**Fig. S1.** Structure of the model compounds MC4 and MC12 for photoisomerisation studies.

![Scheme S1. Synthesis of cone 5,17-dinitrocalix[4]arenes with aliphatic chains](image)
**Fig. S2.** a: Fractions collected from crude reaction mixture. Monomer, DNCalixC4 (---), Crude reaction, AZ1C4 (---), Fraction 1 (---), 2 (---), 3 (---); b: Fractions collected from reprecipitation of Fraction 1. Monomer, DNCalixC4 (---), Fraction 1 (---), Precipitate 1 (---), 2 (---), 3 (---) from Fraction 1.

**Normalization - UV irradiation studies:** In some cases, when the absorbance of the solutions exceeded the measuring capabilities of the UV-Vis spectrometer (A>2,500) samples needed to be diluted after the irradiation. In order to decrease the experimental error, the absorbance of the solution before the irradiation – A(0) is divided by the absorbance at the isosbestic point (315nm) before the irradiation (Fig. S2). Each measurement of the absorbance after irradiation, which required dilution, is hence similarly calculated with respect to the absorbance at the isosbestic point (IB).

For instance, normalization of the absorbance of a sample irradiated for 30 minutes:

\[ \frac{A_{365}(30 \text{ min})}{A_{IB}(30 \text{ min})} \times \frac{A_{IB}(0)}{A_{365}(0)} \]

In the case, when dilution of the sample is not necessary, the value of \(A_{IB}(30 \text{ min}) = A_{IB}(0)\); and the ratio is simplified to:

\[ \frac{A_{365}(30 \text{ min})}{A_{365}(0 \text{ min})} \]
Fig. S3. Explanation of normalization of the UV-Vis spectra for irradiation of samples at higher concentration range (>0.5 g/L).

Irradiation studies on model compounds, MC4 and MC12 in THF

UV-Vis absorbance measurements (Fig. S3) in THF show a distinct absorption maximum at 360 nm (\(\pi-\pi^*\) transition) and a less intense maximum at 450 nm (\(n-\pi^*\) transition). Upon irradiation of the samples with 360 nm wavelength, the intensity of the 360 nm maximum decreases, while a slight increase in intensity at 450 nm can be observed.

The reduction in the \(\pi-\pi^*\) transition intensity with simultaneous slight increase for \(n-\pi^*\) transition suggests a change in the structure of the azobenzene from \textit{trans} to \textit{cis}. The preferred predominantly \textit{trans} form of the model compounds changes to reach a photostationary state (PSS), which constitutes a predominantly \textit{cis} form after a certain irradiation time (dependent on concentration, volume of irradiated sample, intensity of the light source).

The estimation of the optimal sample concentration for the photoisomerisation studies was first established for model compounds. Concentrations of 0.06, 0.6 and 1.2 g/L for MC4 (M=326.4 g/mol) and of 0.1, 1 and 2 g/L for MC12 (550.8 g/mol) in THF were investigated. These series of
concentrations were chosen to ensure that the amount of azobenzene remains the same in the samples with C4 and C12 chains ($M_{MC12}/M_{MC4}=1.66$). By keeping the volume of the samples constant (3mL), we could clearly see that solutions of higher concentrations require longer irradiation times (Fig. S5). No significant differences in photo-isomerisation of the polymers in chloroform and tetrahydrofuran could be observed.

![Absorbance spectra of MC4 (c=0.06g/L) in THF upon irradiation with 360nm and Absorbance spectra of MC12 (c=0.1g/L) in THF upon irradiation with 360nm](image)

**Fig. S4.** (a) Absorbance spectra of MC4 (c=0.06g/L) in THF upon irradiation with 360nm. (b) Absorbance spectra of MC12 (c=0.1g/L) in THF upon irradiation with 360nm

![Comparison of change in absorbance maxima with time for samples of different concentration](image)

**Fig. S5.** Comparison of change in absorbance maxima with time for samples of different concentration; (a): MC4 in THF; (b): MC12 in THF.
Fig. S6. Concentration dependence of the \textit{trans}-to-\textit{cis} photoisomerisation for the A13C4 fraction.

Fig. S7. Concentration dependence of the \textit{trans}-to-\textit{cis} photoisomerisation for the A13C12 fraction.
**Fig. S8.** Concentration dependence of the *trans*-to-*cis* photoisomerisation for the A37C4 fraction.

**Fig. S9.** Concentration dependence of the *trans*-to-*cis* photoisomerisation for the A35C12 fraction.
Fig.S10. Change in the UV-Vis absorption spectra of the model compounds (a) MC4 (d) MC12 and the polymer fractions (b) A13C4 (c) A37C4 (e) A13C12 (f) A35C12 upon irradiation with 360 nm (a and d) or 365 nm (b,c,e,f). Concentration of the samples was set to equimolar azobenzene content.
**Fig.S11.** The UV-Vis absorption spectrum of A13C12 after 90 min of irradiation with 450 nm and 4 days after irradiation.

**Fig.S12.** Comparison of change in absorbance maxima with time for A35C12 sample in THF (●) and chloroform (■).
**Fig.S13.** Comparison of the $^1$H NMR spectra in CDCl$_3$ of A37C4 taken at different time intervals. Before (a), after (b), 0.5h (c), 1h (d), 12h (e), 24h (f), 48h(g) from irradiation with 365 nm wavelength at 20°C.

**Fig.S14.** Comparison of $^1$H NMR spectra in CDCl$_3$ of A13C4 taken at different time intervals. Before (a), after (b), 0.5h (c), 1h (d), 12h (e), 24h (f), 48h(g) from irradiation with 365 nm wavelength at 20°C.
**Fig. S15.** Comparison of $^1$H NMR spectra in CDCl$_3$ of A13C4 taken at different time intervals. Before (a), after (b), 0.5h (c), 1h (d), 12h (e), 24h (f), 48h (g) from irradiation with 365 nm wavelength at 20°C.

**Fig. S16.** Comparison of $^1$H NMR spectra of A35C12 in CDCl$_3$ taken at different time intervals: (a) before the irradiation, (b) immediately after, (c) 0.5 h, (d) 1 h, (e) 12 h, (f) 24 h, and (g) 48 h after irradiation with 365 nm wavelength at 20°C.
Fig.S17. Comparison of the UV-Vis absorption spectrum of fraction A35C12 (black) and calix[4]arene with n-dodecyl chains in the lower rim (red) to show that no spectral overlap at 365nm is present for the azocalix[4]arene moieties.

Fig.S18. Comparative SEC eluograms of poly(azocalix[4]arene) fractions in THF (a) A37C4 and (b) A12C4 before (black) and after (red) irradiation.
Analysis of the intensity correlation functions, $G_2(t)$, and the corresponding correlation function of the electric field, $g_1(t)$ recorded for A35C12 fraction in THF at 90° scattering angle: (red symbols and lines) sample before irradiation, and (green symbols and lines) sample after irradiation with 365nm light. The dependence of $\ln[g_1(t)]$ vs. the delay time suggests that both corresponding distributions of the apparent hydrodynamic diameter are monomodal and moderately broad, which is visualized in the upper inset. Mean hydrodynamic diameter of both distributions is 20nm. Particles of this size are small in comparison to the wavelength of incident radiation of 637nm. They neither show an angular dependence of scattered intensity nor of the hydrodynamic size. Radius of gyration cannot be determined for the same reason.

Taking into account incomplete all-cis and all-trans conformation transitions, steric hindrance of some repeating units within the polymer chain we do not expect to see changes in particles size due to irradiation.
Synthesis of model compound, MCazo, for complexation experiments.

To a solution of Red-Al (65% v/v in toluene, 10 eq.) maintained at 0°C, was added dropwise, under argon, a mixture of 25,26,27,28-tetrabutyloxy-5,17-dinitrocalix[4]arene (1 eq, 0.3mmol) in toluene (2 mL/mmol) and 4-nitroanisole (4 eq., 1.2mmol). The resulting suspension was stirred at room temperature for 1 day. The reaction was quenched by slow dropwise addition (caution! exothermic reaction) of methanol until no evolution of gas could be observed. The residue was extracted with chloroform, washed with water and brine and dried over Na₂SO₄. After filtration of the salt – the solvent was evaporated and careful column chromatography was done using toluene as the eluent. Yield: 0.04g (20%).

¹H NMR (500MHz, CDCl₃) : δ=1.022, 1.029 (2t, 12H; O(CH₂)₃CH₃), 1.317 (m, 4H, OCH₂CH₂CH₂CH₂CH₃), 1.60 (m, 4H, OCH₂CH₂CH₂CH₂CH₃), 1.91, 1.96 (2 quintet, 8H, OCH₂CH₂CH₂CH₂), 3.32 (AB-d, 2J=13.3 Hz, 4H), 3.81 (t, 4H, OCH₂CH₂, 25,27-O-positions), 3.92 (s, 6H, OMe), 4.16 (t, 4H, OCH₂CH₂, 26,28-O-positions) 4.52 (AB-d, 2J=13.3 Hz, 4H), 6.360 (m, ArH, 6H), 7.00 (m, 4H, o-HArOMe) 7.63 (s, 4H, N=NArH (calix), 7.89 (m, 4H, m-HArOMe). ¹³C NMR(500MHz, CDCl₃): 160, 156.6, 155.4, 147.3, 138.1, 127.8, 124.3, 123.3, 114.1, 75.03, 55.9, 32.5, 31.9, 19.3, 14.02. MALDI-TOF MS (m/z):[M+Na]⁺ calcd for C₅₈H₆₈NaN₄O₆: 940.3, found: 938.6.

Fig.S20. Structure and ¹H NMR spectrum of MCazo.
**Fig.S21.** $^1$H NMR spectra of MCazo in CDCl$_3$ in the *trans* (black) and *cis* (red) form.

**Fig.S22.** Magnification of the $^1$H NMR spectra (5.8-10 ppm) of the pyridinium-based guest, C16Py$^+$ upon titration of the host *trans* A19C4 ($c_{(calix)}=3.6$ mmol/L) in CDCl$_3$: (a) A19C4 before addition, (b to g) subsequent additions, and (h) C16Py$^+$ in the absence of host.
Fig.S23. Magnification of the $^1$H NMR spectra (5.8-10 ppm) of the pyridinium-based guest, C16Py$^+$ upon titration of the host *cis* A19C4 ($c_{(calix)}=3.6$ mmol/L) in CDCl$_3$: (a) A19C4 before addition, (b to f) subsequent additions, and (g) C16Py$^+$ in the absence of host.