Supplementary Information

Novel photo-switchable polymers based on calix[4]arenes†

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Experimental

Instruments

NMR spectroscopy. The NMR spectra were measured with a 200MHz Varian Gemini 2000 NMR or 500MHz Bruker Avance III (where applicable) spectrometer using $CDCl_3$ or deuterated DMSO as solvent (concentrations around 10mg/ml). Chemical shifts are presented in ppm downfield from internal TMS standard.

Size Exclusion Chromatography (SEC). Analyses were performed using a Waters instrument equipped with Waters Styragel HR6, HR4 and HR2 columns (7.8 x 300 mm each), with Waters 2487 UV and Waters 2410 RI detectors. Tetrahydrofuran with 1% toluene was used as the eluent, with a flow rate of 0.8 mL/min. Conventional calibrations were performed using poly(styrene) standards.

UV-Vis spectra were recorded with Shimadzu 250 1 PC spectrometer. Irradiation of samples was done using a high pressure xenon lamp with monochromator adjusted to 365nm or 450nm (higher concentrations and larger volume samples). Low concentration and volume samples were irradiated using the internal xenon lamp of Fluoromax-4 Spectrofluorometer

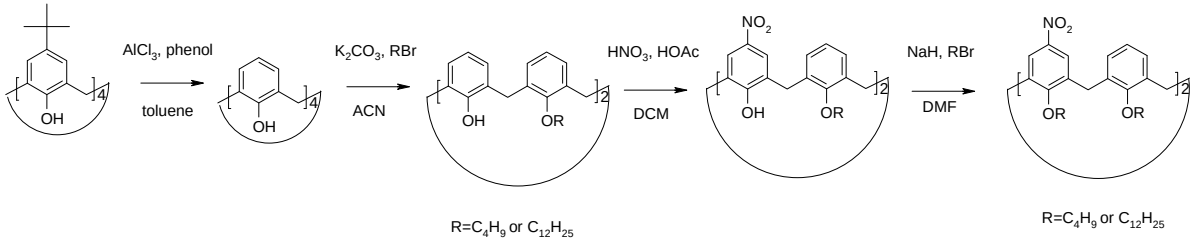
from HoribaJobin Yvon (365nm and 450nm, exit slit: 3nm, detection mode blocked) over a period of 5-145 min. Concentration was set in all samples to 0.025 mg/mL

FTIR measurements were done using a PerkinElmer Spectrum One FTIR Spectrometer in solid state.

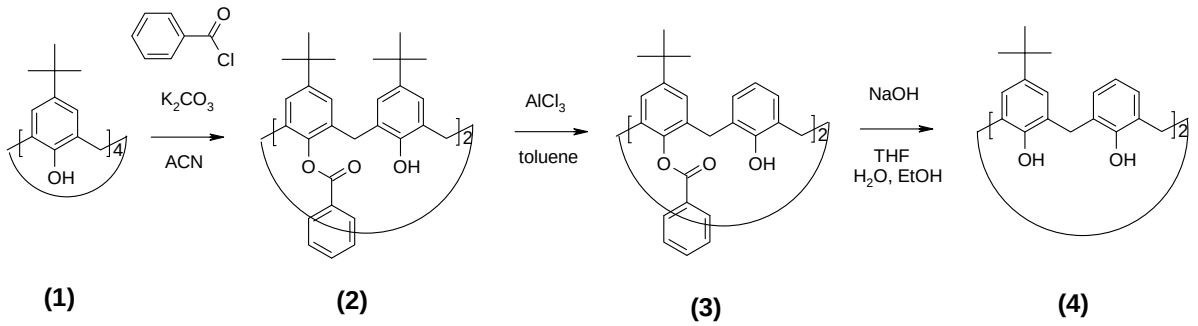
MALDI-ToF mass spectra were obtained on a Bruker microflex which was equipped with 337nm N_2 laser in the reflector mode for determination of molecular weight of all primary compounds **1-8**. Sample preparation : 2,5-dihydroxybenzoic acid (DHB) in THF was used as the matrix (20µL of 40 mg/mL), sodium trifluoroacetate in THF (0.5µL of 10mg/mL) as the cationizing agent and the analyte samples were dissolved in THF (5µL of 10mg/mL).
Molecular modelling was done using Hyperchem Software in *vacuo* conditions.

Synthesis

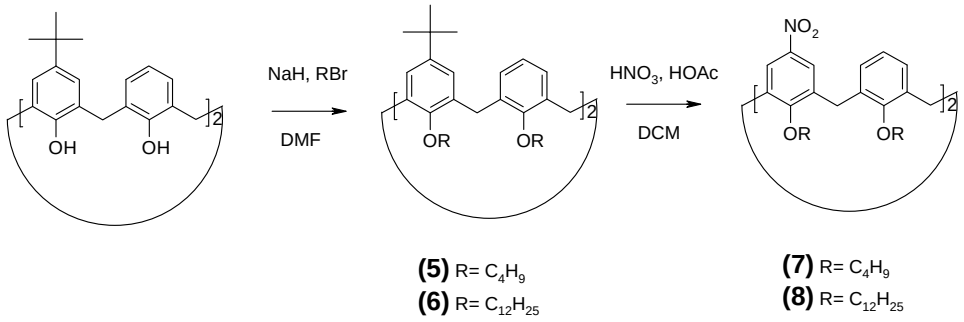
General remarks: All reagents were of reagent grade quality as obtained from commercial suppliers and used without further purification. Solvents were freshly distilled and stored over molecular sieves. Reactions were carried out under nitrogen unless stated otherwise. Compounds 1[1], 2-4[2] were synthesized according to known literature procedures (Scheme S2).



Scheme S1. Preparation of 5,17-dinitrocalix[4]arenes locked in cone conformation *via* step etherification protocol.



Scheme S2. Preparation of 5,17-di(*tert*)butylcalix[4]arene.



(5) R= C_4H_9
(6) R= $C_{12}H_{25}$

(7) R= C_4H_9
(8) R= $C_{12}H_{25}$

Scheme S3. Preparation of substituted 5,17-dinitrocalix[4]arenes – **7** and **8**, in the cone conformation.

General procedure for the preparation of cone 5,17-di(tert)butylcalix[4]arenes, (5) and(6).

5,17-di(*tert)*butylcalix[4]arene, **4**, (1 eq.) was dissolved in DMF (50 mL), sodium hydride (8eq.) was added and the suspension was allowed to stir under argon for 30 min. 1-Dodecylbromide or 1-butylbromide(8 eq.) was then added and the reaction mixture was stirred at 80°C for 20 hours. The mixture was allowed to cool to room temperature and water was added cautiously to destroy any remaining sodium hydride. The solution was then evaporated to dryness. Dichloromethane was added and the solution was washed with 1N HCl (2x) and brine (1x). Solvent was evaporated and the products were recrystallized from isopropanol.

25,26,27,28-tetrabutyloxy-5,17-di(tert)butylcalix[4]arene, 5.

^{1}H NMR (200MHz, $CDCl_3$) : δ=0.93-1.03 (m, 12H; $(CH_2)_3CH_3$), 1.33-1.35 (s, 18H, $(CH_3)C$), 1.50-1.68 (m, 8H, $OCH_2CH_2CH_2$)), 1.77-2.05 (m, 8H, $OCH_2CH_2CH_2$), 3.11 (AB-d, ^{2}J=13.2 Hz, 4H), 3.71 (t, OCH_2CH_2), ^{3}J=6.5 Hz, 4H), 4.00 (t, OCH_2CH_2, ^{3}J=8.2 Hz, 4H), 4.43 (AB-d, ^{2}J=13.2 Hz, 4H), 6.02-6.32 (m, ArH, 6H), 7.04 (s, ArH, 4H).^{13}C NMR (200MHz, $CDCl_3$): δ=155.4, 155.2, 144.2, 135.8, 133.5,127.1, 125.6, 122.0, 74.7, 34.0, 32.5, 32.1, 31.7, 31.2, 19.63, 19.1, 14.2, 14.0. MALDI-TOF MS (*m/z)*: $[M+H]^+$ calcd for $C_{52}H_{73}O_4$: 762.14, found: 762.11, $[M+Na]^+$ calcd for $C_{52}H_{72}NaO_4$: 784.12, found: 785.33.

25,26,27,28-tetradodecyloxy-5,17-di(tert)butylcalix[4]arene, 6.

^{1}H NMR (200MHz, $CDCl_3$) : δ=0.83-0.92 (m, 12H; $(CH_2)_{10}CH_3$), 1.24-1.32 (s, 64H, $(CH_2)_{10}CH_3$), 1.36-1.42 (s, 18H, $(CH_3)C$)), 1.48-1.64 (m, 8H, $OCH_2CH_2CH_2$), 1.78-2.03 (m, 8H, $OCH_2CH_2CH_2$), 3.09 (AB-d, ^{2}J=13.2 Hz, 4H), 3.69 (m, OCH_2CH_2), 4H), 3.99 (m, OCH_2CH_2, 4H), 4.43 (AB-d, ^{2}J=13.2 Hz, 4H), 6.02-6.28 (m, ArH, 6H), 7.04 (s, ArH, 4H).

^{13}C NMR (200MHz, $CDCl_3$): δ=155.5, 155.2, 144.2, 135.9, 133.5, 127.1, 125.6, 122.0, 74.9, 34.0, 31.9, 31.7, 31.6, 31.3, 30.6, 30.2, 29.9, 29.8, 29.4, 26.9, 26.7, 22.7, 14.1. MALDI-TOF MS (*m/z)*: $[M+Na]^+$ calcd for $C_{84}H_{136}NaO_4$: 1233.01, found: 1234.73.

General procedure for the ipso nitration of cone 5,17-di(tert)butylcalix[4]arenes.

Calix[4]arene – **5** or **6** (1 eq.) was dissolved in dichloromethane (33ml/mmol) and cooled to 0°C on an ice bath. Acetic Acid was added (2mL/mmol), followed by slow addition of 65% nitric acid (3.33mL/mmol). The reaction was stirred at 0°C until a purple coloration persisted, after which it was allowed to thaw to room temperature. Upon disappearance of the purple coloration, the reaction mixture was poured into distilled water and extracted with dichloromethane, washed with water. The organic phase was dried over $MgSO_4$, filtered and the solvent was evaporated to yield the crude product. Recrystallization from isopropanol yielded pure crystals of **7** (Yield: 53%) and **8** (Yield: 59%).

25,26,27,28-tetrabutyloxy-5,17-dinitrocalix[4]arene, 7.

^{1}H NMR (200MHz, $CDCl_3$): δ=0.95-1.06 (m, 12H; $O(CH_2)_3CH_3$), 1.32-1.53 (m, 8H, $OCH_2CH_2CH_2CH_3$)), 1.77-1.98 (m, 8H, $OCH_2CH_2CH_2$), 3.25 (AB-d, ^{2}J=13.5 Hz, 4H), 3.84-4.02 (m, OCH_2CH_2), 8H), 4.47 (AB-d, ^{2}J=13.5 Hz, 4H), 6.73 (s, Ar*H*, 6H), 7.43 (s, NO_2Ar*H*, 4H). ^{1}H NMR (500MHz, $CDCl_3$) : δ=1.027, 1.039 (2t, 12H; $O(CH_2)_3CH_3$), 1.445 (sextet, 4H, $OCH_2CH_2CH_2CH_3$,25,27-O-positions), 1.514 (sextet, 4H,$OCH_2CH_2CH_2CH_3$,26,28-O-positions), 1.886, 1.916 (2 quintet, 8H, $OCH_2CH_2CH_2$), 3.280 (AB-d, ^{2}J=13.67 Hz, 4H), 3.936 (t, 4H, OCH_2CH_2, 25,27-O-positions), 3.988 (t, 4H, OCH_2CH_2, 26,28-O-positions) 4.498 (AB-d, ^{2}J=13.63 Hz, 4H), 6.760 (m, Ar*H*, 6H), 7.453 (s, NO_2Ar*H*, 4H). ^{13}C NMR (200MHz, $CDCl_3$): δ=161.8, 156.2, 142.3, 136.1, 134.0, 128.7, 123.3, 122.9, 75.3, 75.0, 32.1, 30.8, 19.1, 13.8. MALDI-TOF MS (*m/z)*:$[M+Na]^+$ calcd for $C_{44}H_{54}NaN_2O_8$: 762.0, found: 763.5.

25,26,27,28-tetradodecyloxy-5,17-dinitrocalix[4]arene, 8.

^{1}H NMR (200MHz, $CDCl_3$) : δ=0.84-0.95 (m, 12H; $(CH_2)_{10}CH_3$), 1.25-1.45 (m, 72H, $(CH_2)_{10}CH_3$), 1.80-2.01 (m, 8H, $OCH_2CH_2CH_2$), 3.25 (AB-d, ^{2}J=13.5 Hz, 4H), 3.82-4.03 (m, OCH_2CH_2), 8H), 4.47 (AB-d, ^{2}J=13.5 Hz, 4H), 6.72 (s, Ar*H*, 6H), 7.43 (s, NO_2Ar*H*, 4H). ^{1}H NMR (500MHz, $CDCl_3$) : δ=0.91 (t, 12H; $O(CH_2)_3CH_3$), 1.295 (s, 56H, OCH2CH2CH2CH2(CH2)$_7$CH3), 1.383 (m, 12, OCH2CH2CH2CH2(CH2)$_7$CH3 and OCH2CH2CH2CH2(CH2)$_7$CH3 - 25,27-O-positions), 1.454 (m, 4H,

OCH2CH2C*H*2CH2(CH2)$_7$CH3 - 26,28-O-positions), 1.902, 1.917 (2 quintet, 8H, OCH$_2$C*H*$_2$CH$_2$), 3.270 (AB-d, ^{2}J=13.68 Hz, 4H), 3.913 (t, 4H, OC*H*$_2$CH$_2$, 25,27-O-positions), 3.967 (t, 4H, OC*H*$_2$CH$_2$, 26,28-O-positions) 4.486 (AB-d, ^{2}J=13.60 Hz, 4H), 6.755 (m, Ar*H*, 6H), 7.454 (s, NO$_2$Ar*H*, 4H). ^{13}C NMR (200MHz, CDCl$_3$): δ=161.9, 156.3, 142.4, 136.3, 134.1, 128.9, 123.4, 75.4, 31.9, 31.0, 29.8, 26.2, 22.7, 14.1. MALDI-TOF MS (*m/z)*: [M+Na]$^+$ calcd for $C_{76}H_{118}NaN_2O_8$: 1210.7, found: 1211.9.

General procedure for the reductive coupling of 5,17-dinitrocalix[4]arenes.

Lithium aluminium hydride procedure (CAUTION!)

Lithium aluminium hydride (0.1g, 25 eq.) was suspended in diethyl ether (1mL), dimethoxyethane, DME (1mL) or THF (1mL) and stirred at room temperature under nitrogen. Calix[4]arene 7 or 8 (0.14mmol, 1 eq.), was dissolved in THF (7mL/mmol), THF:diethyl ether (1:1 mixture, 7mL/mmol) or DME (7mL/mmol) and added dropwise to the system. The reaction mixtures were stirred for 5 days. Samples were taken out at different intervals (10 min, 1 day, 2 days, 5 days).Quenching of the samples involved slow addition of ethyl acetate (2mL – **caution! exothermic reaction**) followed by water (10mL) and extraction into dichloromethane. Upon evaporation of the solvent, the larger molecular weight fractions were precipitated from isopropanol.

Sodium bis(2-methoxyethoxy)aluminium hydride (Red-Al) procedure (CAUTION!)

To a solution of Red-Al (65%v/v in toluene, 10 eq.) at 0°C, was added dropwise, under argon, a suspension of calix[4]arene **7** or **8** (1 eq., 0.2mmol) in toluene (2 mL/mmol). The resulting suspension was stirred at room temperature for 5 days. The reaction was quenched by slow dropwise addition (**caution! exothermic reaction**) of methanol until no evolution of gas could be observed. The residue was then taken up with 10% aq. HCl and extracted with dichloromethane. Organic layer was separated, washed with water (2x) and brine (1x) and dried over Na_2SO_4. After filtration of the salt – the solvent was evaporated to give the crude reaction mixture (analyzed with SEC). The larger molecular weight polymers were precipitated from isopropanol.

Cetyltrimethylammonium dichromate (CTADC) procedure.

CTADC was prepared according to literature procedure[3]. Oligomers from reductive coupling procedures (1 eq.) were dissolved in chloroform (10mL/mmol). CTADC (1 eq.) was added to

the reaction mixture and heated at reflux for 5 days. Upon cooling to room temperature, the solvent was evaporated *in vacuo* and further purification was done by column chromatography (THF). Crude reaction mixture samples were analyzed with SEC.

Iron(II)sulphate heptahydrate and potassium permanganate procedure.

A mixture of the oxidant[4] was prepared by grinding equal amounts of $FeSO_4 \cdot 7H_2O$ (1g) and $KMnO_4$(1g). The oxidant mixture was then added to oligomers dissolved in chloroform and heated at reflux for 5 days. Upon cooling to room temperature, the reaction mixture was filtered through a pad of celite. Crude reaction mixture samples were analyzed with SEC.

Polyazocalix[4]arenes with n-butyl chains :

^{1}H NMR (500MHz, $CDCl_3$) : δ= 7.82 (br s, Ar-NO_2, 4H), 6.29 (br s, Ar, 6H), 4.55 (br, Ar-C*H*$_2$-Ar, 4H), 4.24 (br, O-C*H*$_2$, 26,28-positions, 4H), 3.78 (br, O-C*H*$_2$, 25,27-positions, 4H), 3.35 ((br, Ar-C*H*$_2$-Ar, 4H), 2.01-1.90 (br, O-CH_2C*H*$_2$$CH_2CH_3$, 8H), 1.67 (br, O-$CH_2CH_2$C*H*$_2$$CH_3$, 25,27-positions), 1.35 (br, O-CH_2CH_2C*H*$_2$$CH_3$, 26,28-positions), 0.91 (s, O-CH_2(CH_2)C*H*$_3$). ^{13}C NMR (200MHz, $CDCl_3$): δ=160.9, 155.1, 148.8, 147.9, 137.8, 132.6, 127.7, 123.5, 74.9, 32.2, 19.7, 14.0. MALDI-TOF MS: fragmentation observed Δ(m/z) = 761.

Polyazocalix[4]arenes with n-dodecyl chains :

^{1}H NMR (500MHz, $CDCl_3$) : δ= 7.81 (br s, Ar-NO_2, 4H), 6.27 (br s, Ar, 6H), 4.55 (br, Ar-C*H*$_2$-Ar, 4H), 4.22 (br, O-C*H*$_2$, 26,28-positions, 4H), 3.76 (br, O-C*H*$_2$, 25,27-positions, 4H), 3.36 ((br, Ar-C*H*$_2$-Ar, 4H), 2.01-1.90, 1.62, 1.30 (br m, O-CH_2(C*H*$_2$)$_{10}$$CH_3$), 0.91 (s, O-$CH_2$($CH_2$)$_{10}$C*H*$_3$). ^{13}C NMR (200MHz, $CDCl_3$): δ=160.8, 155.2, 147.8, 141.9, 138.3,137.8, 132.6, 128.4, 123.5, 75.5, 31.9, 30.0, 29.8, 26.6, 22.7, 14.1. MALDI-TOF MS: fragmentation observed Δ(m/z) = 1210

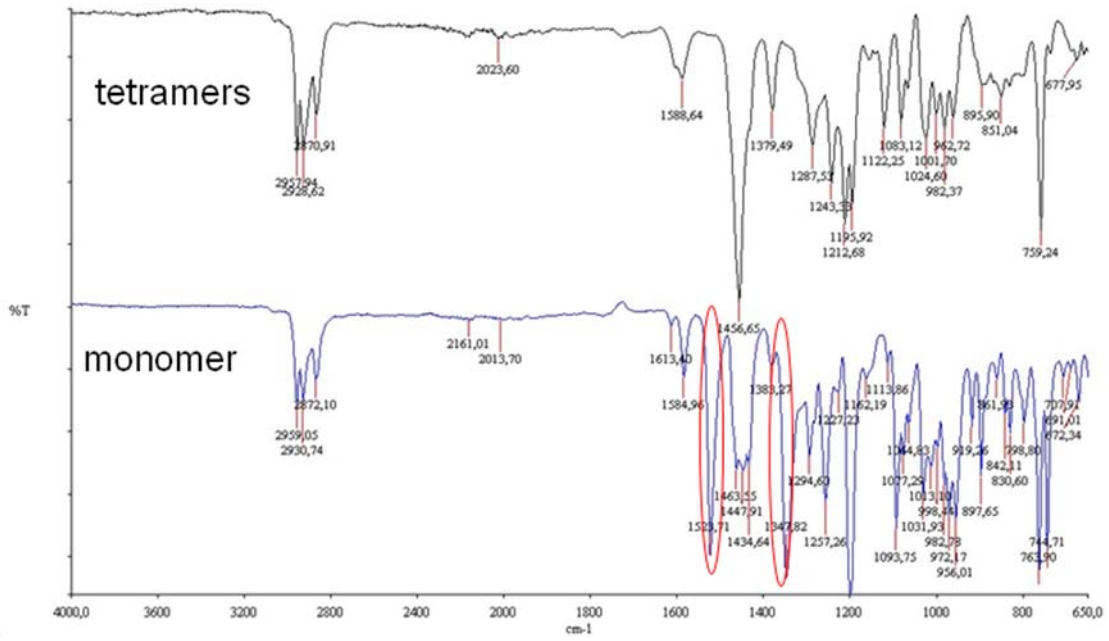


Fig.S1. Comparison of FTIR spectra of monomer **1** (below) and tetramers (above).

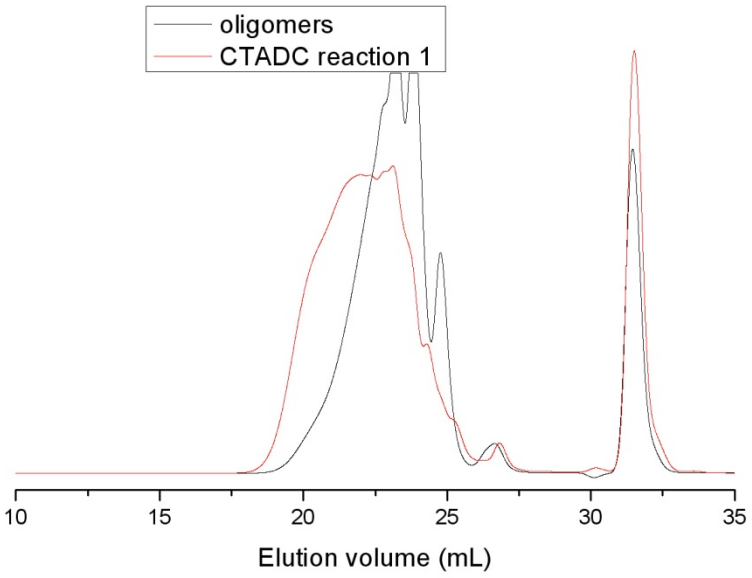


Fig.S2. GPC traces from CTADC-mediated coupling: crude reaction mixture (red line) and oligomers prior to reaction (black line).

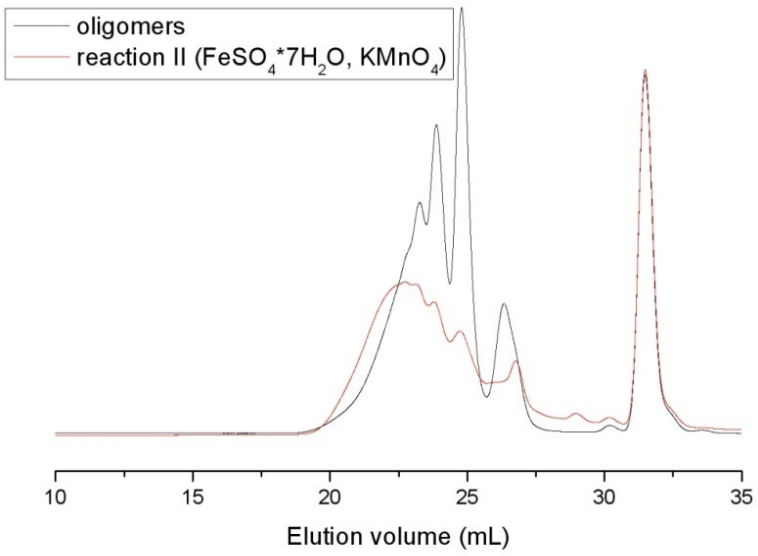


Fig.S3. GPC traces from $KMnO_4$-mediated coupling – crude reaction mixture (red line) and oligomers prior to reaction (black line).

Sample	**monomer**	**Coupling agent**	**T**	**Solvent (v:v)**	**Peak – majority (M_n) [g/mol]**	**DP (n)**	**PDI**	**Isolated Yield***
Reaction A– p	**1**	LAH	25	Ph20:Et2O 1:1	5800	9	1.28	-
Reaction A–p-5d	**1**	LAH	25	Ph20:Et2O 1:1	5200	8	1.29	36
Reaction B –p-1d	**1**	LAH	25	Et2O : THF 4:1	6800	10	1.45	-
Reaction B –p-5d	**1**	LAH	25	Et2O : THF 4:1	14402	21	1.32	32
Reaction C-p	**1**	LAH	80	DME	3100	5	1.30	37
Reaction D-p	**1**	LAH	80	DME	3400	5	1.19	31
Reaction E-p	**1**	LAH	75	THF	5400	8	1.30	29
Reaction F-p	**1**	LAH	25	Et2O : THF 4:1	12200	18	1.33	25
Reaction G-p	**2**	LAH	75	THF	5000	4	1.24	33

Reaction H-p	**2**	LAH	25	Et2O : THF 4:1	14900	13	1.46	
Reaction I-p	**1**	Red-Al	25	toluene	17000	25	1.39	16
Reaction J-p	**2**	Red-Al	25	toluene	16000	15	1.40	15
Reaction K-p	**1**	Red-Al	25	toluene	24000	35	2	13
Reaction L-p	**2**	Red-Al	25	toluene	29000	26	1.63	16
Reaction M-p	**1**	Red-Al	25	toluene	32000	47	1.62	10
Reaction N-p	**1**	Red-Al	25	toluene	34300	50	1.56	12
Reaction O-p	**2**	Red-Al	25	toluene	38000	35	1.57	14

Table S1. Molecular weight characteristics from different coupling conditions obtained from SEC (THF vs. PS standards). P- refers to precipitated fraction. DP – degree of polymerization, PDI – polydispersity index (M_w/M_n). *d* refers to aliquots taken after 1 or 5 days of starting the reaction. Trials involving Red-Al were done under similar conditions to show reproducibility of the reaction. * % of isolated yield of precipitated fraction.

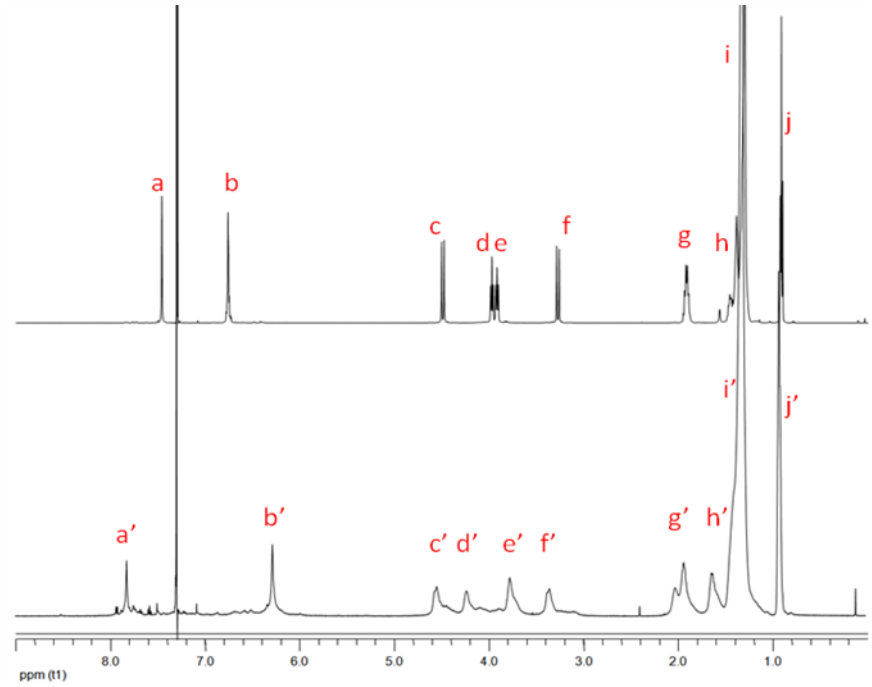


Fig. S4. ^{1}H NMR spectra (500MHz, $CDCl_3$) of monomer **2** (above) and polyazocalix[4]arene with n-dodecyl chains (below).

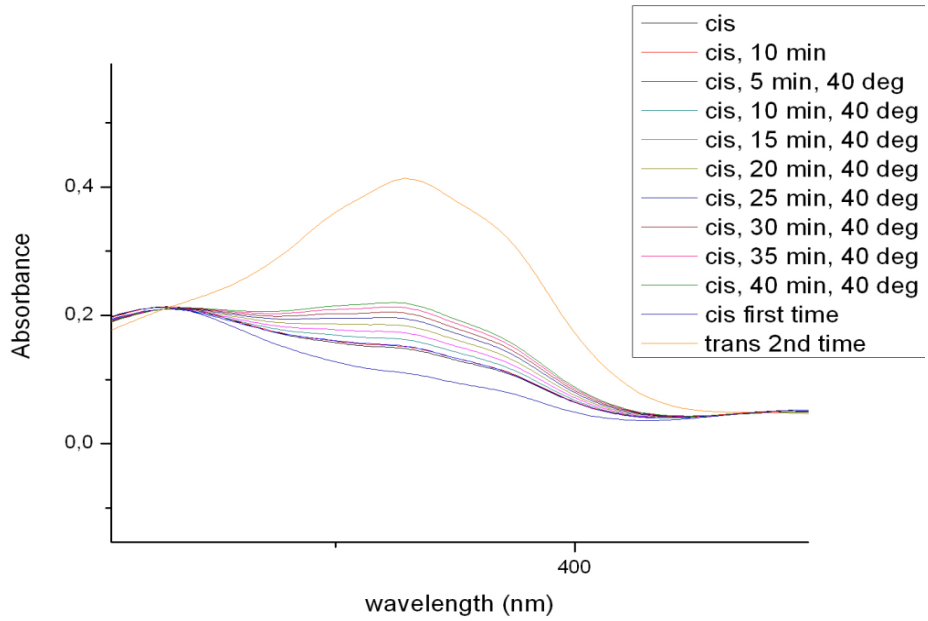


Fig.S5. Magnification of UV-VIS absorbance spectrum (250-450nm) of poly(azocalix[4]arene) (n-butyl chains, DP=12) in THF (c=0.01 mg/mL). The sample was irradiated at 365 nm and heated at 40°C. Thermal isomerisation is observed.

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