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## ARTICLE

# Multi-stimuli responsive poly(azodibenzo-18-crown-6-ether)s

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New main chain azopolymers comprising of dibenzo-18-crown-6-ether units joined by azo-bridges have been prepared and fractionated. UV-Vis studies show that the polymers are solvatochromic and pH-sensitive. Upon irradiation with specific wavelengths they undergo reversible *trans*-to-*cis* photo-isomerisation. Owing to the nature of the crown ether moiety, the polymers can furthermore interact with low molar mass pyridinium guests and Ba<sup>2+</sup> metal ions, resulting in complex-induced phase separation in solvents of lower polarity. In alcohols, the upper critical solution temperature (UCST) type transitions are observed, which are strongly dependent on the polymer concentration and the degree of polymerization. Irradiation of the polymers leads to reversible photo-tuning of the demixing temperature, which decreases proportionally to the decrease in the *trans* content of the sample. The UCST-type transitions in alcohols are also influenced by water content in the mixtures and addition of barium ions results in an increase of the demixing temperature. Irradiation of the polymer-barium complexes induces the photo-isomerisation but does not change the demixing temperature.

## Introduction

Ever since their discovery by Pedersen in 1967<sup>1</sup> crown ethers and their unique properties have been extensively studied<sup>2</sup> and thus they have greatly contributed to understanding of host-guest interactions. Over the years they have found numerous applications, which include extraction of metal and non-metal ions, as well as neutral molecules<sup>3</sup>, chromatography<sup>4</sup>, catalysis<sup>5</sup>, probing of biological processes<sup>6</sup>, supramolecular<sup>7</sup> systems etc. Several strategies for the preparation of crown-ether containing polymers have been employed, the most popular of which includes immobilization on polymer supports<sup>8</sup>, main and side chain polymer formation<sup>9</sup>.

The preparation of photo-responsive systems<sup>10</sup> has been a recurring trend in chemistry. One of the most well studied molecular switches is azobenzene<sup>11</sup>. The reversible *trans*-to-*cis* photo-isomerisation, which a molecule containing such azo-linkages undergoes, offers a unique structural transition with potential for using in the design of various photo-sensitive polymers<sup>12</sup>. Typically the strategies employed for their preparation include attachment of the prefabricated azo-moieties as side chain or end groups in a polymer.<sup>13</sup> Azo-crown ether<sup>14</sup> pendant groups<sup>15</sup> have been incorporated onto polymeric frameworks and have been shown to influence the polymer conformation upon *trans*-to-*cis* photo-isomerisation. However, main chain azocrown ether polymers have been more challenging to produce. By combining the photo-switchable

character of an azo-polymer with other stimuli-responsive properties (thermo-, pH, host-guest interactions), multi-stimuli responsive polymers may be prepared. These systems may be divided into those exhibiting a parallel, serial or causal interplay<sup>16</sup> of the multiple stimuli-derived effects.

Our group has recently been developing a series of photo-switchable polymers based on calix[4]arenes, the poly(azocalix[4]arene)s.<sup>17</sup> These polymers consisting of calix[4]arene units which have been locked in the cone conformation *via* lower rim substitution and joined by azo-bridges, undergo reversible *trans*-to-*cis* photo-isomerisation. This influences the degree of host-guest interaction with low molar mass guests, dependent on the photostationary state of the polymer<sup>18</sup>. Furthermore, by modifying the polymers with tetraethylene glycol monomethyl ether chains (TEGOME) as lower rim substituents we could induce thermal responsiveness onto the system. The polymers undergo LCST-type transitions in water and UCST-type transitions in alcohols. The latter can be influenced by irradiation resulting in a completely reversible photo-tunable UCST behaviour.<sup>19</sup>

In this study we report on the preparation of poly(azodibenzo-18-crown-6-ether)s in which dibenzo-18-crown-6-ether<sup>20</sup> moieties are joined by azo-bridges (Fig. 1). These polymers are shown to be solvatochromic, pH-sensitive and undergo reversible *trans*-to-*cis* photo-isomerisation. Additionally, interaction with low molar mass pyridinium guests and Ba<sup>2+</sup> ions leads to complex-induced phase separation

in solvents of lower polarity. Furthermore, the polymers are thermo-responsive in alcohols exhibiting the upper critical solution temperature (UCST) type transitions, which are strongly dependent on the polymer concentration and the degree of polymerization. Changing the photo-stationary state (PSS, i.e. isomer equilibrium at given irradiation wavelength and time) of the polymers by means of irradiation leads to a change in the UCST value observed in the measurement. The thermo-responsiveness is also influenced by the presence of water and barium ions in the system.

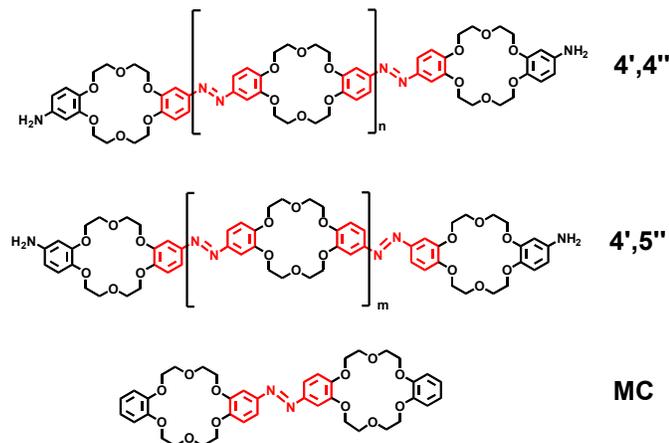


Fig.1. Structure of poly(azodibenzo-18-crown-6-ether)s and the model compound, MC.

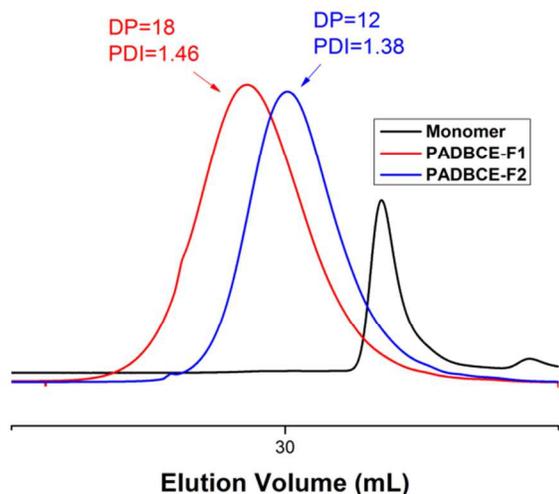


Fig.2. Comparison of SEC eluograms of the selected fractions, PADBCE-F1 (red) and PADBCE-F2 (blue), with the monomer (black).

## Results and discussion

The syntheses of monomers, model compounds and the polymers are detailed in the Electronic Supplementary Information, ESI.

For the purpose of this study we have chosen fractions PADBCE-F1 ( $M_n=8000$  g/mol,  $DP=18$ ,  $PDI=1.46$ ) and PADBCE-F2 ( $M_n=5000$  g/mol,  $DP=12$ ,  $PDI=1.38$ ) for further characterization, both of which correspond to the 4',4''-polymer (Fig. 2). No significant differences in measurements for the 4',5''-poly(azodibenzo-18-crown-6-ether) could be seen.

The polymers were first studied in terms of their response to single external stimulus (solvent, pH, light, temperature, guest presence) and subsequently the interplay between the stimuli-derived effects was evaluated.

### Solvatochromism and pH-sensitivity

The azobenzene moiety in the structure of the polymer acts as a chromophore, which is prone to sensing the changes in the environment and upon complex formation, and is responsible for the photo-isomerisation process. When analysing the UV-Vis spectra of the different fractions of the polymers we see slight changes in the 320 nm absorption (ESI, Fig.S7). The maximum absorption occurs at 360-375 nm and corresponds to the  $\pi-\pi^*$  transitions of the *trans* isomer. The 450 nm maximum of low intensity corresponds to the *cis* isomer and the  $n-\pi^*$  transitions.

When in solution, the polymers are prone to shifts in the absorption maximum, which is affected by the choice of the solvent. This solvatochromism (Fig. 3a) is dependent on the polarity of the solvent and follows the general observations<sup>21</sup>. The more polar the solvent, the longer the wavelength at which the transitions occur: DMSO (373 nm), DMF (369 nm), THF (365 nm) and  $\text{CHCl}_3$  (363 nm).

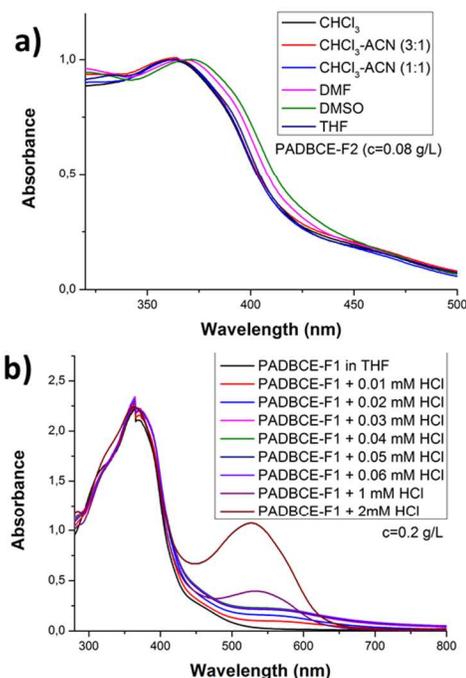


Fig.3. (a) UV-Vis spectra of PADBCE-F2 ( $c=0.08$  g/L) in different solvents; (b) UV-Vis spectra of PADBCE-F1 ( $c=0.2$  g/L) in THF upon addition of HCl.

Furthermore, the polymers are sensitive to changes in the pH of the environment (Fig. 3b). Addition of minute amount (0.01mM) of hydrochloric acid to THF solutions of the polymers results in an increase of absorbance at 530 nm. In the concentration between 0.1mM-1.0mM HCl, the polymer solutions are turbid. Further addition of acid results in a significant increase in the 530 nm absorption and the solubilisation of the polymers. This may be attributed to the protonation of one of the nitrogen atoms of the azo-bridge<sup>22</sup>. It is noteworthy, that upon irradiation, the protonated polymers do not undergo *trans*-to-*cis* photo-isomerisation.

### Photo-isomerisation

The azobenzene derivative present in the structure of the polymers is also responsible for their photo-switchability. This is due to the reversible *trans*-to-*cis* photo-isomerisation of the azo-bridge. Using poly(azocalix[4]arene)s<sup>18-19</sup> we have shown that manipulating the photo-stationary state (PSS) results in induced control of other stimuli-derived effects present in the system (thermo-responsiveness and host-guest interactions). It was thus important to look into the photo-isomerisation process in terms of solvent choice, irradiation wavelengths, PSS and thermal relaxation. A typical UV-Vis spectrum of the polymer upon irradiation in chloroform (0.1 g/L) is presented in Fig. 4a.

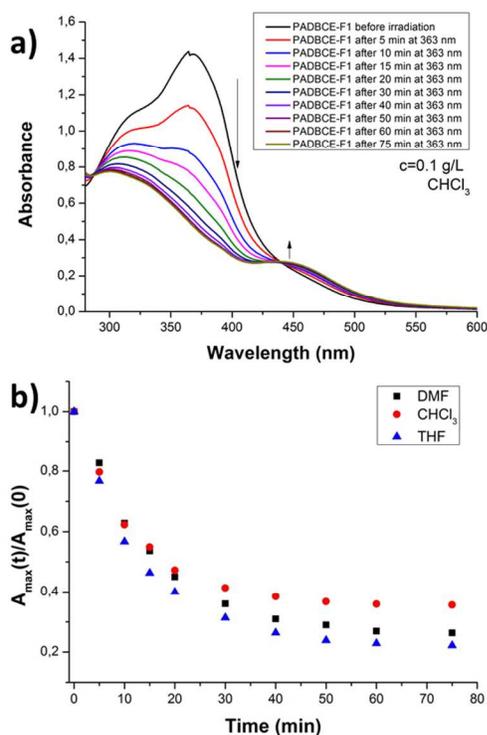


Fig.4. (a) UV-Vis spectrum of PADBCE-F1 in CHCl<sub>3</sub> (0.1 g/L) upon irradiation with 363 nm. (b) Comparison of changes in  $A_{\max}(t)/A_{\max}(0)$  upon *trans*-to-*cis* photo-isomerisation in different solvents with time ( $c=0.1$  g/L).

Under these conditions and light power, the polymers reach their PSS of 37% after 50 min. For DMF the PSS values are lower (28%) and in THF best results could be obtained (22%). (Fig. 4b). In the case of the model compound, MC, the *trans*-to-

*cis* photo-isomerisation is most effective in chloroform, slower in DMF and in THF results in a high PSS (ESI, Fig. S8-S10). The polymers also undergo the reverse *cis*-to-*trans* isomerization (ESI, Fig.S11) which is induced by light (450 nm) or temperature. Both processes are characterized by a plateau region at about 80% *trans* content (ESI, Fig. S12-S13), however given enough time at elevated temperatures, the samples regain their pre-irradiation PSS.

The structural transition which the polymers (Fig. 5) and the model compound (ESI, Fig. S14) undergo is best visualized with <sup>1</sup>H NMR experiments. In the *trans* form of the bridge, the aromatic proton signals of the azo-moiety appear at 7.6, 7.52 and 7.08 ppm. Upon photo-isomerisation to the *cis* state, the signals are shifted to 7.15, 6.7 and 6.4 ppm. Minor peaks corresponding to the remaining *trans* bridges in the system are still present and upon relaxation with time their intensity increases while the *cis* signals disappear. The intensity of the crown ether peaks at 4.2 ppm also changes.

We also wanted to see whether the size of the polymers is influenced by the photo-isomerisation. The polymers were irradiated to *cis*-rich PSS and SEC eluograms (DMF) were recorded with UV-monitoring at 369 nm and referenced to the *trans*-rich sample (ESI, Fig. S15). It is evident that the size of the polymers is not affected significantly upon irradiation.

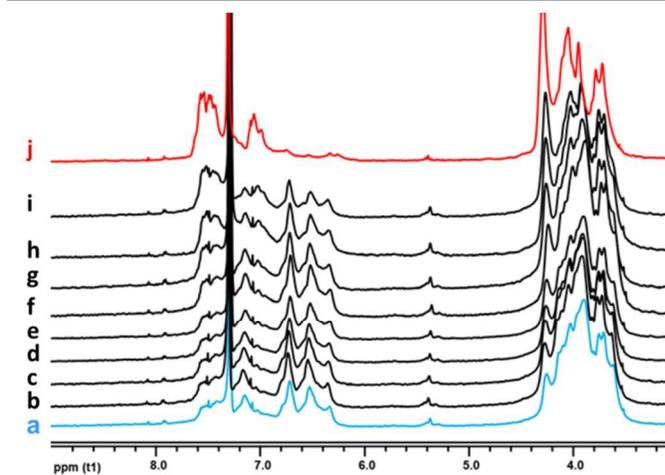


Fig.5. Comparison of <sup>1</sup>H NMR spectra of PADBCE-F1 in CDCl<sub>3</sub> (2.5 g/L at 20°C) upon relaxation from (a) *cis* to (j) *trans* state. (b) 0.5 h; (c) 1 h (d) 1.5 h (e) 2 h (f) 3 h (g) 4 h (h) 6 h (i) 8 h from irradiation.

### Complex Formation

Crown ethers are renowned for their interaction with low molar mass guests and alkali metal ions. In a subsequent series of experiments we wanted to investigate whether the polymers retained this supramolecular activity.

N-methyl pyridinium iodide, NMPI, was used as the guest probe for <sup>1</sup>H NMR host-guest interaction experiments. When in free solution (deuterated chloroform), the shifts of the aromatic signals of the pyridinium moiety appear at 9.32 (H<sub>α</sub>), 8.53 (H<sub>γ</sub>) and 8.15 (H<sub>β</sub>) ppm. The presence of a host molecule influences the shift of these signals to lower ppm values. The extent of this

upfield shift indicates the strength of the host-guest interaction. Due to the short lifetime of this interaction when referenced to the timescale of the NMR experiment, the process may be considered to be a dynamic one, as no distinct populations (bound and free guests) can be observed. In the case of the *trans*-poly(azodibenzo-18-crown-6-ether)s, interaction with NMPI (ESI, Fig. S16) is evidenced by a large upfield shift of  $H_a$  from 9.32 to 8.65 ppm. Under the same conditions, the pyridinium guest in the presence of the model compound (ESI, Fig. S17) experiences a shift from 9.33 to 9.06 ppm (Fig. 6). This difference in model compound:guest and polymer:guest interactions would suggest that the pyridinium species are better trapped within the polymeric framework as a result of a higher local concentration of the crown ether units when referenced to the model compounds. It is noteworthy, that irradiation of the polymers and model compound to the *cis*-rich state, does not yield significant changes in the interaction with the NMPI guest.

We then proceeded to studying the complex formation of the polymers with  $K^+$  and  $Ba^{2+}$ , as dibenzo-18-crown-ether had been shown to interact strongest with these ions<sup>23</sup> in the solvent systems we used for our polymers (DMSO, DMF, THF,  $CHCl_3$  and  $CHCl_3$ -ACN mixtures). UV-Vis spectra were recorded prior to and upon addition of the ions. The samples were then subjected to irradiation studies to determine any influence of the complexation on the kinetics of photo-isomerisation.

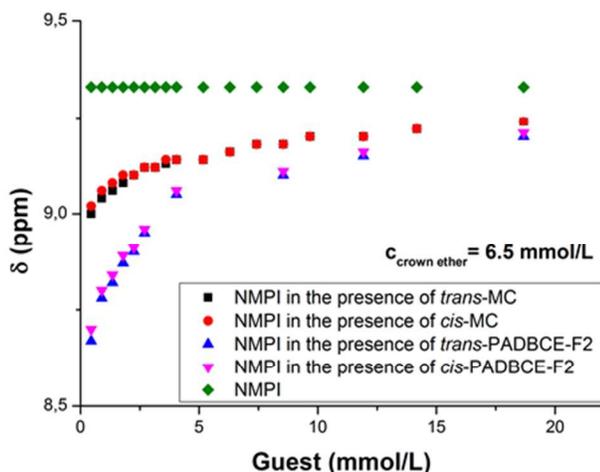


Fig.6. Comparison of the chemical shifts monitored for  $H_a$  of the pyridinium guest in free solution ( $\blacklozenge$ ); in the presence of *trans*-rich ( $\bullet$ ) and *cis*-rich ( $\circ$ ) host model compound, MC, and *trans*-rich ( $\blacktriangle$ ) and *cis*-rich ( $\blacktriangledown$ ) host polymer.  $c=6.5$  mmol/L as calcd per crown ether unit.

In the case of DMSO, no hypsochromic shifts or difference in photo-isomerisation could be observed. In DMF, a slight hypsochromic shift (5 nm) could be observed for  $K^+$ , but no changes in the photo-isomerisation behaviour. When the addition was done to THF solutions, we could observe shifts for  $Ba^{2+}$  ion samples (5 nm) but the  $KClO_4$  salt had limited solubility.

Addition of minimal amount of  $Ba^{2+}$  ions to chloroform solutions of the polymers led to a 12 nm hypsochromic shift and phase separation of the polymers from solution (ESI, Fig. S18). By adjusting the polarity through addition of a co-solvent (acetonitrile) we then studied the effect of the  $Ba^{2+}$  ions on the *trans*-to-*cis* photo-isomerisation. Above 15% ACN in  $CHCl_3$ , the polymers did not phase separate upon addition of minimal amount of  $Ba^{2+}$  ions. Irradiation of the  $Ba^{2+}$ -polymer samples in 25% ACN- $CHCl_3$  induced partial photo-isomerisation (ESI, Fig. S19) and in 50% ACN- $CHCl_3$  the photo-isomerisation behaviour was comparable to that of the free polymers in the same solvent mixture (ESI, Fig. S20). This indicated the importance of the appropriate choice of solvent and its polarity in the preparation of the complexes.

Next, we measured the transmittance of the samples (Fig. 7) upon titration of the polymers with NMPI in chloroform and with barium ions in 50% ACN- $CHCl_3$ . When the titration is done with the model compound, MC, no precipitation occurs upon addition of either NMPI or  $Ba^{2+}$ . However when the NMPI is added to a chloroform solution of the polymers, upon exceeding of a 1:2 (guest:host) molar ratio, the transmittance decreases and each subsequent addition results in further turbidity changes. Titration of the polymers in 50% ACN- $CHCl_3$  with divalent barium ions leads to rapid precipitation upon addition of the salt, which suggests that the barium ions act as a cross-linker for the polymers in this (co)solvent system.

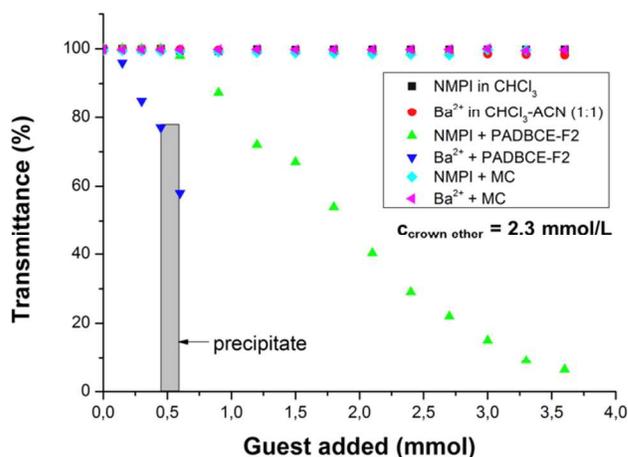


Fig.7. Transmittance measurements (600 nm) as a function of added guest (NMPI in chloroform and  $Ba^{2+}$  in 50% ACN- $CHCl_3$ ). The polymer and model compound concentration was set to 1.0 g/L (2.3 mmol/L as calcd per crown ether unit).

### Thermo-responsive behaviour

We have recently demonstrated that tegylated poly(azocalixarene)s undergo upper critical solution temperature (UCST) type transitions in alcohols.<sup>19</sup> Moreover, this thermo-responsive behaviour is reversibly tuneable by means of irradiation.

Poly(azodibenzo-18-crown-6-ether)s comprise of ethylene glycol units which are formed into a cyclic structure and joined by photo-switchable azo-bridges. In the next series of

experiments we wanted to evaluate the polymers in terms of their behaviour towards changes in temperature in alcohol solutions. Samples of varying concentrations (0.5, 1.0 and 2.0 g/L) in different alcohols (methanol, ethanol, *i*-propanol) were kept in an oven at 55°C prior to measurements to ensure complete dissolution and the highest photo-stationary state. Transmittance was then measured (cooling rate 1°C/min, unless stated otherwise) as a function of temperature (range dependent on the observed transition, typically 0-70°C). For PADBCE-F2 (DP=12) of 2.0 g/L in methanol the cloud point was observed at 52°C, while in ethanol and *i*-propanol a similar value of 57°C was recorded (ESI, Fig. S21). We could also discern that the UCST is strongly dependent on the polymer concentration (Fig. 8a). Above 2.5 g/L in all alcohols, the polymers were partially soluble. When diluting the samples from 2.0 g/L to 1.0 g/L in *i*-propanol we observe a shift in the demixing temperature from 57°C to 46°C and increase in the broadness of the transition. This is even further shifted at 0.5 g/L ( $T_{cp}$ =35°C). A similar dependence can be observed for samples with varying degree of polymerization (Fig. 8b). In methanol at a concentration of 0.8 g/L, the PADBCE-F1 sample (DP=18) has a cloud point of 49°C, PADBCE-F2 (DP=12) has a lower value of 35°C and the transition for oligomers (DP<5,  $M_n$ <2000 g/mol, PDI=1.2) occurs at 20°C. Thus one can see that by adjusting the concentration, the degree of polymerisation and alcohol we can tune the temperature at which the UCST-type transition occurs.

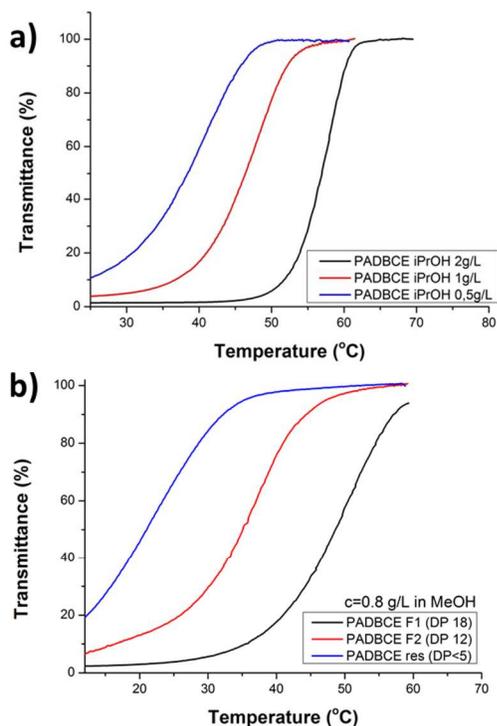


Fig.8. (a) Transmittance vs. Temperature plots for PADBCE-F2 in *i*-propanol at different polymer concentrations. (b) Transmittance vs. Temperature plots for polymers of different DP and the same concentration of 0.8 g/L in methanol.

### Interplay of stimuli responses

The polymers have thus far been shown to respond to single stimuli changes in the environment (i.e. either pH or host-guest interactions or irradiation or temperature) with changes in physicochemical properties.

As was previously reported for poly(azocalix[4]arene)s,<sup>18-19</sup> the manipulation of one stimulus-response in a multi-stimuli responsive polymer may result in unique control of the other stimuli-derived effects present in the system. Solutions of the poly(azodibenzo-18-crown-6-ether)s in alcohols were thus subjected to irradiation with 365 nm, which corresponds to the reversible *trans*-to-*cis* photo-isomerisation. PADBCE-F1 in methanol ( $c$ =0.8 g/L) was kept at 50°C overnight to ensure highest possible *trans* content. Prior to each irradiation and subsequent turbidity measurement, a UV-Vis spectrum was recorded to monitor the photostationary state of the sample. Results showed that the demixing temperatures upon irradiation are significantly decreased and this change is proportional to the *trans/cis* ratio of the sample (Fig. 9). The value shifts from 45°C (*trans* rich state) to 15°C at 35% *trans* content.

Upon thermal relaxation at elevated temperature during 24 h, the demixing temperature value prior to irradiation is regained. This indicates that the *trans*-to-*cis* photo-isomerisation of the polymers results in a reversible tuning of the UCST-type transitions of the polymers in alcohols.

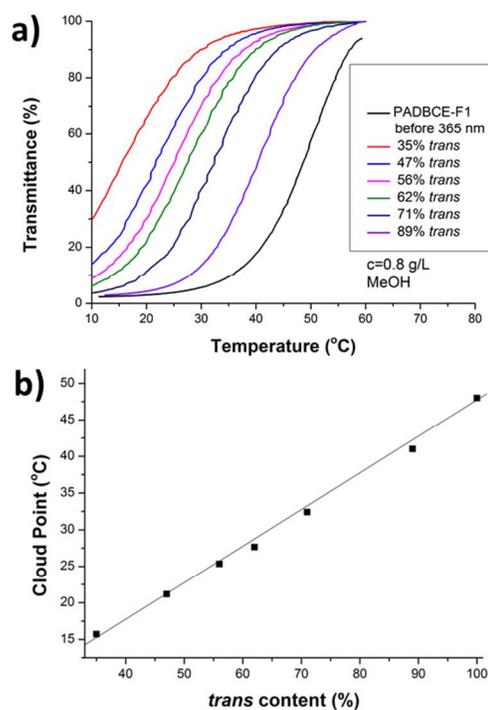


Fig.9. (a) Transmittance vs. Temperature plots for PADBCE-F1 in methanol (0.8 g/L) upon irradiation to different photostationary state (*trans* content) and resulting plot of the cloud point temperature vs. *trans* content (b).

This is an example of serial interplay of stimuli responses. The photo-isomerisation induces a change of the thermo-responsiveness of the polymers in alcohols. The accompanying changes in structure and polarity may be the reason behind this photo-tuning of the UCST.

The UCST-type transitions are furthermore affected by changes in the water content of the samples (Fig. 10). In 100% ethanol, PADBCE-F2 (DP=12) at 0.5 g/L has a demixing temperature of 26°C. For the same concentration in 98% ethanol, the cloud point is recorded at 18°C. Further changes in ethanol content (87.5%, 75%) result in a lowered cloud point which was undetectable in the instrumental set up. Recently, Theato et al<sup>24</sup>. have suggested that this decrease in UCST values in alcohols for poly[oligo(ethyleneglycol methyl ether) methacrylate], POEGMA upon addition of minimal amount of water may be attributed to the strong hydrogen bonding activity of water which induces better solubilisation of the polymers in alcohols. For the poly(azodibenzo-18-crown-6-ether)s, upon decreasing the alcohol content to 62.5%, the UCST reappears at 11°C. In 50% ethanol:water mixtures, the polymers have a cloud point higher (30°C) than the sample in 100% ethanol. Subsequent changes in the alcohol content to 40% and 30% yield demixing temperatures of 50°C and 62°C respectively. The polymers were not soluble in 100% water. The extent of the photo-tuning of the UCST is also affected by the changes in the alcohol:water content. At 98% ethanol:water, irradiation of the sample shifts the UCST by 20°C, however, when the irradiation is done on the sample in 50% ethanol:water, the cloud point value is only shifted by 10°C. This may suggest that water acts as a stronger precipitant when a certain concentration (approx. 65%) is exceeded.

We also wanted to study the effect of addition of alkali metal ions on the thermo-responsive properties of the polymers in alcohols. The cloud point of the UCST-type transition is increased upon addition of barium ions (ESI, Fig. S22), rendering the system more difficult to solubilize. Furthermore if we compare the photo-tuning of the UCST in the absence and presence of barium ions (Fig. 11), we can observe that the shifting of the cloud point upon irradiation is significantly diminished in the presence of barium. These results would indicate that the barium ions act as strong cross-linkers between the polymers in alcohol solutions.

It is noteworthy, that despite the complexation of barium ions, the polymers still retain their photo-isomerisation behaviour, which proceeds to low photo-stationary states (ESI, Fig. S23). However, this does not translate anymore to photo-tuning of the UCST.

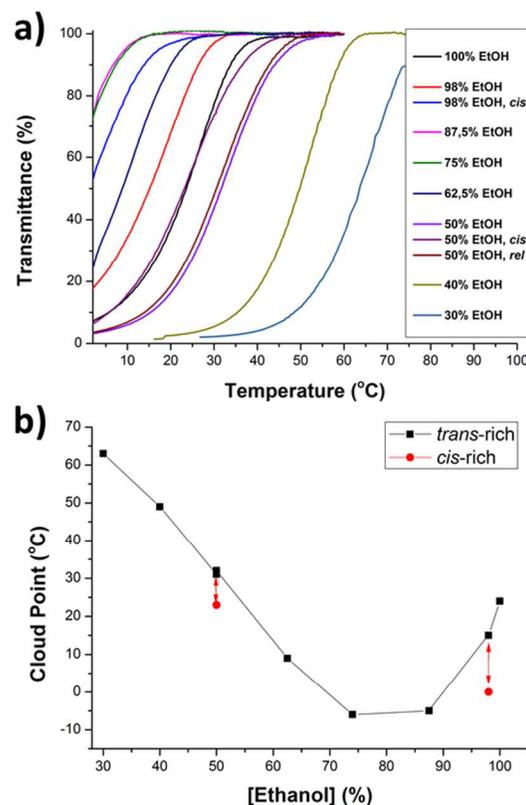


Fig.10 (a). Transmittance vs. Temperature plots for PADBCE-F2 (0.5 g/L) in various ethanol:water mixtures. (b) Cloud point temperature vs. ethanol:water content (values for 87.5% and 75% have been estimated from extrapolation).

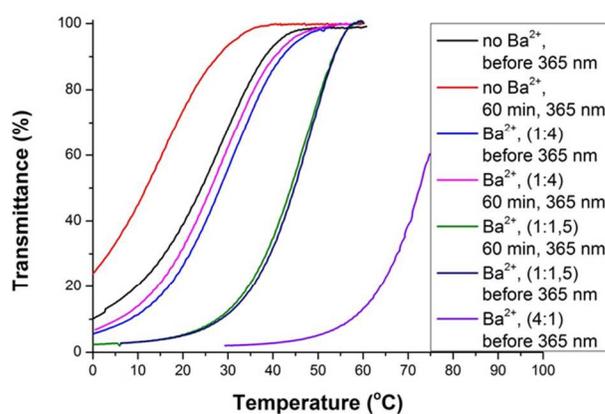


Fig.11. Transmittance vs. Temperature plots for PADBCE-F2 (0.5 g/L) in ethanol upon titration with barium ions ( $\text{Ba}^{2+}$ :polymer = 1:4, 1:1.5 and 4:1) at different PSS.

## Experimental

### Materials and methods

Reagents used in the syntheses were of reagent grade quality as supplied by manufacturers. All solvents were dried prior to experiments with molecular sieves, unless stated otherwise. Synthesis of mono- and dinitrodibenzo-18-crown-6 ethers has been done according to known literature procedures.<sup>25</sup> KClO<sub>4</sub>, BaCl<sub>2</sub>O<sub>8</sub> were purchased from Aldrich and N-methylpyridinium iodide, NMPI was prepared earlier.<sup>19</sup>

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a Bruker Avance III 500MHz spectrometer in deuterated chloroform (CDCl<sub>3</sub>) or dimethyl sulfoxide (DMSO) as solvents. Tetramethylsilane (TMS) was used as the internal standard and chemical shifts are expressed in parts per million (ppm) downfield from the standard.

**Size Exclusion Chromatography** (SEC), was performed in DMF using a Waters instrument which was equipped with Waters Styragel HR6, HR4 and HR2 columns (7.8 x 300 mm each), monitored with Waters 2487 UV (set to 230 nm or 365 nm) and Waters 2410 RI detectors with a flow rate of 0.8 mL/min and referenced against PMMA standards (Polymer Standards Service-USA, Inc.)

**Turbidity** measurements (monitoring at 600 nm) were done using a JASCO J-815 CD spectrometer, with cooling rates of 1 and 2 °C/min (where applicable) in the temperature range between 0 - 70°C (depending on the solvent). Cloud point is determined as the temperature at which 50% transmittance of the sample is observed.

All **UV-Vis** spectra were recorded using a Shimadzu 250 1 PC spectrometer in the range between 280-600 nm. Samples were kept at elevated temperatures to induce the highest photo-stationary state (*trans* content). Irradiation of the samples of lower concentration for photo-isomerisation studies (0.1, 0.3 and 0.5 g/L in various solvents) was done using the internal Xenon lamp of a Fluoromax-4 Spectrofluorometer from HoribaJobin Yvon. Samples of higher concentration (0.8, 1.0, 2.0 and 2.5 g/L) were irradiated with a High Power fiber-coupled LED, Black-LED-365, from Prizmatix.

**MALDI ToF** mass spectra were recorded on a Bruker Microflex, equipped with 337 nm N<sub>2</sub> laser in the reflector mode using 2,5-dihydroxybenzoic acid (DHB) in THF as the matrix and sodium trifluoroacetate, NaTFA as the cationizing agent.

### Synthesis of polymers

Dinitrodibenzo-18-crown-6-ether (1 eq.) was suspended in toluene (2 mL/mmol), sonicated and added dropwise, under an argon atmosphere, to a toluene solution (1M, 6eq.) of sodium bis(2-methoxyethoxy)aluminium hydride (Red-Al) maintained at 0°C. The mixture was left to thaw to room temperature and stirred for an additional 3 days. The reaction was then slowly quenched by careful drop-wise addition of methanol (**caution! exothermic reaction**) until no evolution of gas was observed. The residue was taken up with 10% aq. HCl and extracted with chloroform. The organic layer was separated, washed with

water (3x) and dried over MgSO<sub>4</sub>. Upon filtration the residual solvent was evaporated and the crude reaction mixture was analyzed with SEC. For **fractionation** purposes, the polymers were dissolved in THF (25 g/L) and hexane was added dropwise to induce phase separation. A centrifuge operating at 5000 rpm was used to collect the precipitated fractions and the procedure was repeated on the residual solution until no phase separation occurred upon addition of excess hexane.

For the preparation of azobis(dibenzo-18-crown-6-ether) model compound, **MC**, the same synthetic procedure was used and the purification was done by means of column chromatography (10% methanol/chloroform, v/v).

**Azobis(dibenzo-18-crown-6-ether): Yield 63 %;** <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) : δ=3.6-4.25 (m, OCH<sub>2</sub>CH<sub>2</sub>O, 32H), 6.88 (s, ArH, 8H), 7.08 (s, ArH *m*-N=N, 2H), 7.52, 7.6 (s, ArH *o*-N=N, 4H). <sup>13</sup>C NMR (500MHz, CDCl<sub>3</sub>): δ=150.3, 147.1, 144.6, 122.7, 119.4, 114.2, 112.7, 71.5, 70.4. MALDI-TOF MS (m/z): [M+Na]<sup>+</sup> calcd for C<sub>40</sub>H<sub>46</sub>NaN<sub>2</sub>O<sub>12</sub>: 769.8, found: 767.5.

**Poly(azodibenzo-18-crown-6-ether)s** *trans*: <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) : δ=3.6-4.25 (b, OCH<sub>2</sub>CH<sub>2</sub>O, 16H), 7.08 (m, ArH *m*-N=N, 2H), 7.52, 7.6 (m, ArH *o*-N=N, 4H). <sup>13</sup>C NMR (500MHz, CDCl<sub>3</sub>): δ=149.1, 145.2, 120.6, 115.2, 113.6, 71.0, 70.0.

## Conclusions

Poly(azodibenzo-18-crown-6-ether)s have been successfully prepared in a reductive coupling procedure from dinitrodibenzo-18-crown-6-ethers, which indicates the versatility of the previously reported method.

The solutions of fractionated polymers were studied to determine their behaviour under input of external stimuli. Shifts in the UV-Vis spectra for the polymers in solvents of various polarity indicate their solvatochromic nature. Protonation of the polymers results in changes to their absorption spectrum, with the emergence of a strong 530 nm maximum.

The *trans*-to-*cis* photo-isomerisation of the azo-bridges is possible and proceeds with the photo-stationary states depending on the choice of solvent, irradiation wavelength and exposure time. This process is completely reversible either by irradiation with 450 nm wavelength or by means of thermal relaxation. However, changes in the pH of the system result in diminished photo-isomerisation upon protonation.

The interaction with low molar mass pyridinium guests was evidenced by large upfield shifts in the <sup>1</sup>H NMR spectra of the pyridinium signals in the presence of the polymers, as well as phase separation upon titration. Complex formation with barium ions was dependent on solvent choice and supported by shifts of the maximum absorption in the UV-Vis spectra and precipitation of the polymers.

Upper Critical Solution Temperature (UCST) type transitions were observed for the poly(azodibenzo-18-crown-6-ether)s in alcohols, which were shown to be dependent on the concentration, degree of polymerisation and alcohol choice.

The serial interplay between the photo-isomerisation and thermo-responsive properties of the polymers is evidenced by a decrease in the demixing temperatures upon decrease in *trans* content, which may be attributed to changes in polarity. Furthermore the UCST values may be altered by addition of water or barium ions to the alcohol solutions thus allowing for multiple pathways for tuning of the thermo-responsiveness of the polymers.

Studies reported here show the importance of understanding the interdependence of stimuli responses in a multi-stimuli responsive polymer. Also, the versatility of the coupling method used to prepare the main chain azopolymers has been shown. Hence this may contribute to the development of new photo-switchable systems for smart extractions coatings, membranes and sensors.

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### Notes and references

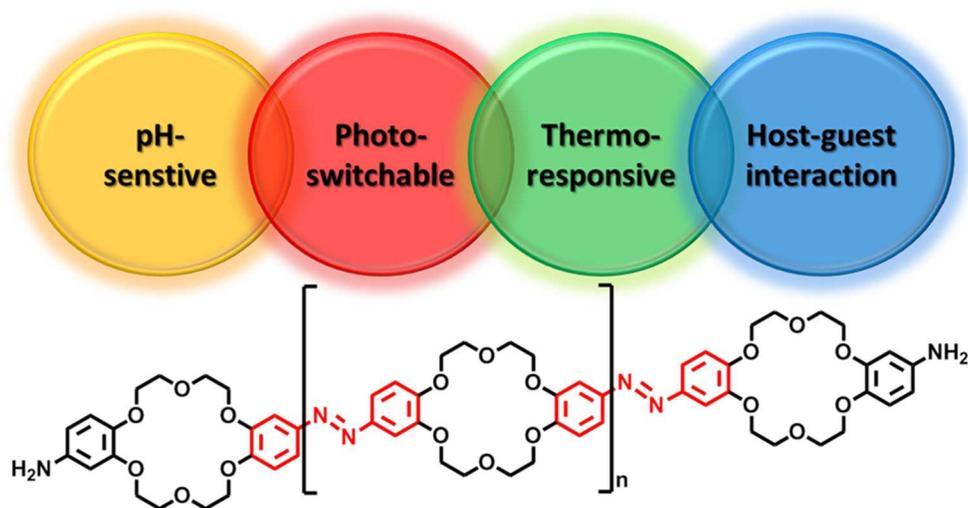
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Electronic Supplementary Information (ESI) available: Synthesis and Fractionation discussion, structure of compounds, SEC of fractions, UV-Vis and photo-isomerisation studies, <sup>1</sup>H NMR titration experiments, turbidity measurements. See DOI: 10.1039/b000000x/

- (a) C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017. (b) C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 2495.
- P. J. Cragg and R. Vahora, in *Supramolecular Chemistry*, John Wiley & Sons, Ltd, 2012.
- G. W. Gokel, W. M. Leevy and M. E. Weber, *Chem. Rev.*, 2004, **104**, 2723.
- (a) R. Mohammadzadeh Kakhki, *J. Incl. Phenom. Macrocycl. Chem.*, 2013, **75**, 11. (b) A. Cavazzini, L. Pasti, A. Massi, N. Marchetti and F. Dondi, *Analytica Chimica Acta*, 2011, **706**, 205.
- (a) T. Ooi and K. Maruoka, *Angew. Chem. Int. Ed.*, 2007, **46**, 4222.
- H. Tsukube, T. Yamada and S. Shinoda, *J. Heterocyclic Chem.*, 2001, **38**, 1401.
- B. Zheng, F. Wang, S. Dong and F. Huang, *Chem. Soc. Rev.*, 2012, **41**, 1621.
- S. D. Alexandratos and C. L. Stine, *React. Funct. Polym.*, 2004, **60**, 3.
- U. Tunca and Y. Yagci, *Prog. Pol. Sci.*, 1994, **19**, 233.
- M.-M. Russew and S. Hecht, *Adv. Mater.*, 2010, **22**, 3348
- H. M. D. Bandara and S. C. Burdette, *Chem. Soc. Rev.*, 2012, **41**, 1809-1825.
- K. G. Yager and C. J. Barrett, in *Smart Light-Responsive Materials*, John Wiley & Sons, Inc., 2008, pp. 1-46.

- A. Natansohn and P. Rochon, *Chem. Rev.*, 2002, **102**, 4139.
- S. Shinkai, in *Molecular Switches*, Wiley-VCH Verlag GmbH, 2001, 281.
- (a) S. Shinkai, H. Kinda, M. Ishihara and O. Manabe, *J. Pol. Sci. Pol. Chem. Ed.*, 1983, **21**, 3525. (b) S. Shinkai, M. Ishihara and O. Manabe, *Polym. J.*, 1985, **17**, 1141. (c) K. Kimura, H. Sakamoto and T. Nakamura, *J. Nanosci. Nanotechnol.*, 2006, **6**, 1741.
- P. Schattling, F. D. Jochum and P. Theato, *Polym. Chem.*, 2014, **5**, 25.
- S. Wiktorowicz, V. Aseyev and H. Tenhu, *Polym. Chem.*, 2012, **3**, 1126
- S. Wiktorowicz, H. Tenhu and V. Aseyev, *Polym. Chem.*, 2013, **4**, 2898
- S. Wiktorowicz, H. Tenhu and V. Aseyev, *Macromolecules*, 2013, **46**, 6209
- (a) C. J. Pedersen, in *Organic Syntheses*, John Wiley & Sons, Inc., 2003. (b) J. F. Stoddart, *Pure & Appl. Chem.*, 1988, **60**, 467.
- E. Rusu, D.-O. Dorohoi and A. Airinei, *J. Mol. Struct.*, 2008, **887**, 216.
- K. Hofmann, S. Brumm, C. Mende, K. Nagel, A. Seifert, I. Roth, D. Schaarschmidt, H. Lang and S. Spange, *New J. Chem.*, 2012, **36**, 1655.
- S. Katsuta, T. Kuwano, Y. Ito and Y. Takeda, *J. Chem. Eng. Data*, 2005, **50**, 1313.
- P. J. Roth, F. D. Jochum and P. Theato, *Soft Matter*, 2011, **7**, 2484.
- (a) M. J. Deetz, M. Shang and B. D. Smith, *J. Am. Chem. Soc.*, 2000, **122**, 6201. (b) W. M. Feigenbaum and R. H. Michel, *J. Pol. Sci. A-1: Polym. Chem.* 1971, **9**, 817.



Multi-stimuli responsive polymers based on dibenzo-18-crown-6-ethers

191x100mm (149 x 149 DPI)