

## Supplementary Material

### **Azobenzene-Functionalised Core Cross-Linked Star Polymers and their Host-Guest Interactions**

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## 1. Experimental section

### 1.1 Materials:

$\alpha$ -Cyclodextrin ( $\alpha$ -CD, 98%, Aldrich) was dried *in vacuo* (0.1 mbar, 70 °C) for 12 h immediately prior to use. Copper (II) bromide (Cu(II)Br<sub>2</sub>, 99%, Aldrich), 4-(phenylazo)benzoic acid (98%, Aldrich), *tris*[2-(dimethylamino)ethyl] amine (Me<sub>6</sub>TREN, Aldrich), ethylenediaminetetraacetic acid (EDTA, 99%, Adrich), 4-(dimethylamino)pyridine (DMAP, 99%, Fluka), *N*-(3-(dimethylamino)propyl)-*N*-ethylcarbodiimide hydrochloride (EDCI, 98+%, Acros Organics) were all used as received. The monomers 2-hydroxyethyl acrylate (HEA, 96 %, Aldrich) was purified and distilled according to the literature<sup>1</sup> prior to use and ethylene glycol diacrylate (EGDA, 90 %, Aldrich) was de-inhibited by passing through a column of basic alumina prior to use. 2-Hydroxyethyl 2'-methyl-2'-bromopropionate was synthesised according to the literature.<sup>2,3</sup> SnakeSkin dialysis tubing (MWCO = 7000 and 13000 g.mol<sup>-1</sup>) was obtained from Thermo Scientific. *N,N*-Dimethylformamide (anhyd. DMF, 99.8%, Acros Organics), dimethyl sulfoxide (DMSO), diethyl ether (DEE) and methanol (MeOH) were obtained from Chem-Supply unless otherwise stated and used as received. Deuterated DMSO was obtained from Cambridge Isotope Laboratories and used as received. Copper wire (0.315 mm diameter) was activated by immersion in concentrated sulfuric acid for 10 min. The wire was wash thoroughly with distilled water before it was dried under a stream of Ar. Freshly activated Cu wire was used immediately for every reaction.

### 1.2 Methods:

#### *One-pot macroinitiator P1 and CCS polymer P2 formation*

Synthesis of the macroinitiator **P1** and CCS polymer **P2** in one-pot was adapted from the literature.<sup>4</sup> A solution of HEA (1.98 mL, 17.2 mmol, 60 equiv.), Me<sub>6</sub>TREN (13.8  $\mu$ L, 51.7  $\mu$ mol, 0.18 equiv.) and 2-hydroxyethyl 2'-methyl-2'-bromopropionate (60.6  $\mu$ L, 287  $\mu$ mol, 1 equiv.) was added to a stock solution of Cu(II)Br<sub>2</sub> (0.05 equiv.) in DMSO (7.28 mM, 1.98 mL) and bubbled with N<sub>2</sub> for 30 min. Copper wire (*ca.* 2.2 cm in length) was added and the mixture was stirred at room temperature under N<sub>2</sub> for 2 h. A 100  $\mu$ L aliquot of the macroinitiator **P1** solution was taken for NMR and GPC analysis. To induce star formation, a solution of EGDA (670  $\mu$ L (15 equiv.) cross-linker in 13.85 mL DMSO) that had been bubbled with N<sub>2</sub> beforehand for 30 min was transferred to the

reaction flask containing the macroinitiator **P1** using a syringe and the mixture was stirred at room temperature for a further 16 h. A 100  $\mu\text{L}$  aliquot of the crude star solution was taken for NMR and GPC analysis, and the remainder of the solution was precipitated into DEE (200 mL  $\times$  2). The precipitate was isolated by centrifugation, redissolved in an aqueous solution of ethylenediaminetetraacetic acid (EDTA) (0.04 M, 7 mL) and dialyzed (MWCO = 13000 g.mol<sup>-1</sup>) against EDTA solution (0.04 M), followed by water for 2 days to remove the copper complexes. The solution was then lyophilised to obtain the CCS polymer **P2** as a white solid, 1.81 g (90%). <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO):  $\delta_{\text{H}}$  4.77 (br s, OH), 4.04 (br s, OCH<sub>2</sub>CH<sub>2</sub>), 3.55 (br s, CH<sub>2</sub>CH<sub>2</sub>OH), 2.31-2.19 (m, CH<sub>2</sub>CHCO), 1.86-1.38 (m, CH<sub>2</sub>CH), 1.09 (s, CCH<sub>3</sub>CH<sub>3</sub> end-group), 1.06 (s, CCH<sub>3</sub>CH<sub>3</sub> end-group) ppm. GPC-MALLS (DMF):  $M_{\text{n}}$  = 190 kDa, PDI = 1.07.

#### *Functionalisation of PHEA CCS polymer **P2** with 4-(phenylazo)benzoic acid to afford **P3-BA***

**P3-BA<sub>5</sub>** and **P3-BA<sub>20</sub>** were synthesised in a similar fashion, as outlined for **P3-BA<sub>5</sub>**: CCS polymer **P2** (250 mg, 2.63  $\mu\text{mol}$ , 1 equiv.) was dissolved in anhyd. DMF (10 mL). EDCI (138 mg, 720  $\mu\text{mol}$ , 274 equiv.), DMAP (6 mg, 49.1  $\mu\text{mol}$ , 19 equiv.) and 4-(phenylazo)benzoic acid (54 mg, 238.7  $\mu\text{mol}$ , 76 equiv.) were then added and the mixture was stirred at 30 °C for 17 h. The reaction mixture was then dialyzed (MWCO = 7000 g.mol<sup>-1</sup>) against MeOH for 2 days, precipitated into DEE and dried *in vacuo* (0.1 mbar, 60 °C) to afford **P3-BA<sub>5</sub>** as an orange solid, 223 mg. <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO):  $\delta_{\text{H}}$  8.17-7.70 (m, 6ArH, 6H), 7.54 (s, 3ArH, 3H), 4.77 (br s, OH), 4.49 (br s, CH<sub>2</sub>O(CO)Ar), 4.04 (br s, OCH<sub>2</sub>CH<sub>2</sub>), 3.55 (br s, CH<sub>2</sub>CH<sub>2</sub>OH), 2.31-2.19 (m, CH<sub>2</sub>CHCO), 1.86-1.38 (m, CCH<sub>2</sub>CH), 1.09 (s, CCH<sub>3</sub>CH<sub>3</sub> end-group), 1.06 (s, CCH<sub>3</sub>CH<sub>3</sub> end-group) ppm. GPC-MALLS (DMF): **P3-BA<sub>20</sub>**  $M_{\text{n}}$  = 214 kDa, PDI = 1.41; **P3-BA<sub>5</sub>**  $M_{\text{n}}$  = 206 kDa, PDI = 1.61.

#### *Inclusion complexation of azobenzene CCS polymers **P3-BA** with $\alpha$ -CD*

Inclusion complexation between the azobenzene groups of **P3-BA** and  $\alpha$ -CD was conducted at equimolar ratios, as outlined for **P3-BA<sub>20</sub>**: **P3-BA<sub>20</sub>** (50 mg, 0.26  $\mu\text{mol}$ , 78  $\mu\text{mol}$  of BA groups) was dissolved in MeOH (1 mL) and added drop-wise to an aqueous solution of  $\alpha$ -CD (76 mg, 78  $\mu\text{mol}$ , 0.16 mM) at 40 °C. The solution was stirred for 5 h, cooled to room temperature and stirred for a further 12 h. The mixture was then

concentrated *in vacuo* (0.1 mbar, 60 °C) to obtain the **P3-BA<sub>20</sub>/α-CD** complex as an orange solid. <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO): δ<sub>H</sub> 8.17-7.70 (m, ArH of **P3**), 7.54 (s, ArH of **P3**), 5.58-5.56 (m, OH of α-CD), 4.94 (br s, CH of α-CD), 4.78 (br s, OH of **P3**), 4.07-3.29 (m, CH & CH<sub>2</sub> of α-CD and OCH<sub>2</sub> of **P3**), 2.25 (m, CH<sub>2</sub>CHCO of **P3**), 1.76-1.34 (m, CCH<sub>2</sub>CH of **P3**).

### **Gel-Permeation Chromatography (GPC)**

Polymer molecular weight characterization was carried out via GPC using DMF as the mobile phase. The GPC analysis was conducted on a Shimadzu liquid chromatography system equipped with a PostNova PN3621 MALS detector (λ = 532 nm), Shimadzu RID-10 refractometer (λ = 633 nm) and Shimadzu SPD-20A UV-Vis detector using three Phenomenx columns (500, 104, and 106 Å porosity; 5 μm bead size) in series operating at 50 °C. DMF with 0.05 mol.L<sup>-1</sup> LiBr (> 99%, Aldrich) was employed as the mobile phase at a flow rate of 1 mL.min<sup>-1</sup>. NovaMALS software (PostNova Analytics) was used to determine the molecular weight characteristics using the calculated dn/dc value of 0.076 for HEA<sup>5</sup> or via 100 % mass recovery.

### **Nuclear Magnetic Resonance (NMR) Spectroscopy**

<sup>1</sup>H NMR and 2D Nuclear Overhauser Effect spectroscopy (NOESY) spectroscopy was conducted on a Varian Unity 400 MHz spectrometer operating at 400 MHz, using the deuterated solvent (*d*<sub>6</sub>-DMSO) as reference and a sample concentration of approximately 20 mg.mL<sup>-1</sup>.

Solid-state <sup>13</sup>C cross-polarization/magic-angle spinning (CP-MAS) NMR spectra was acquired using a Varian INOVA 300 MHz NMR spectrometer with a 6 mm CP-MAS probe. Spectra were acquired at 25 °C using a <sup>13</sup>C CP-MAS pulse sequence at 5 kHz spinning.

### **Calculation of CCS average number of arms ( $N_{arms}$ )**

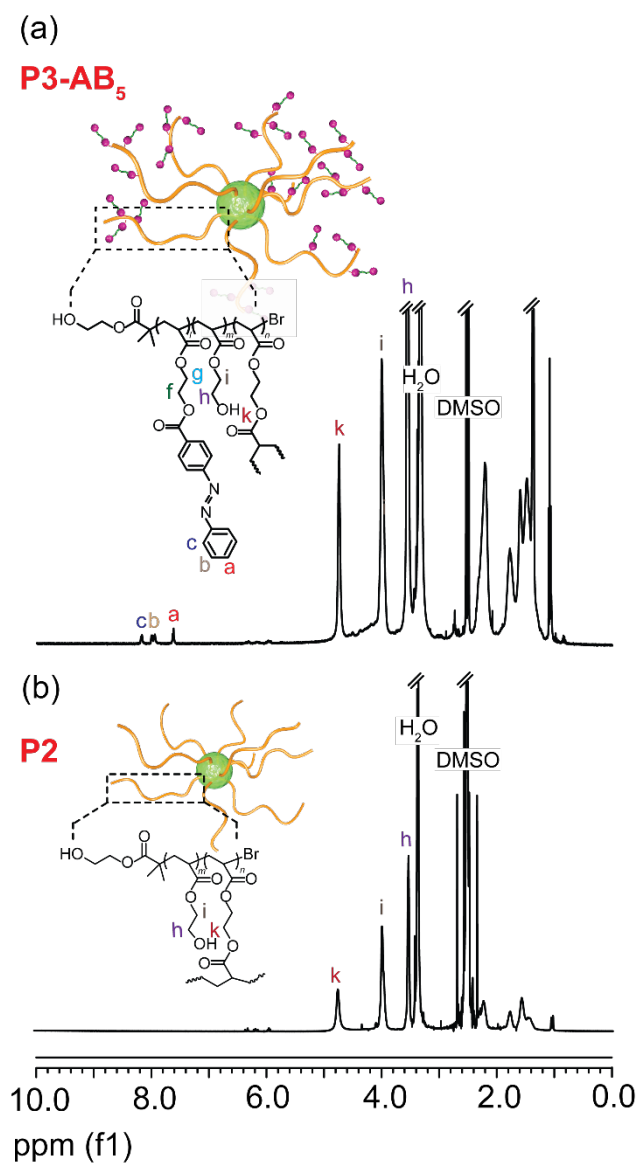
The average number of arms per CCS polymer ( $N_{arms}$ ) was calculated using **Equation S1**:

$$N_{arms} = \frac{WF_{arms} \times M_{W,CCS}}{M_{W,arms}}$$

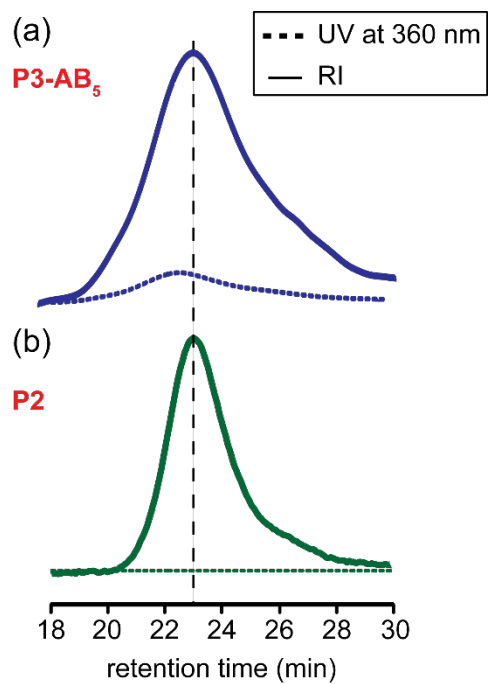
where the CCS molecular weight ( $M_{w,CCS}$ ) and the molecular weight of the linear arms ( $M_{w,arms}$ ) were determined by GPC. The weight fraction of arms ( $WF_{arms}$ ) was determined using **Equation S2**:

$$WF_{arms} = \frac{m(arms)x_a}{m(XL)x_c + m(m)x_m + m(arms)x_a}$$

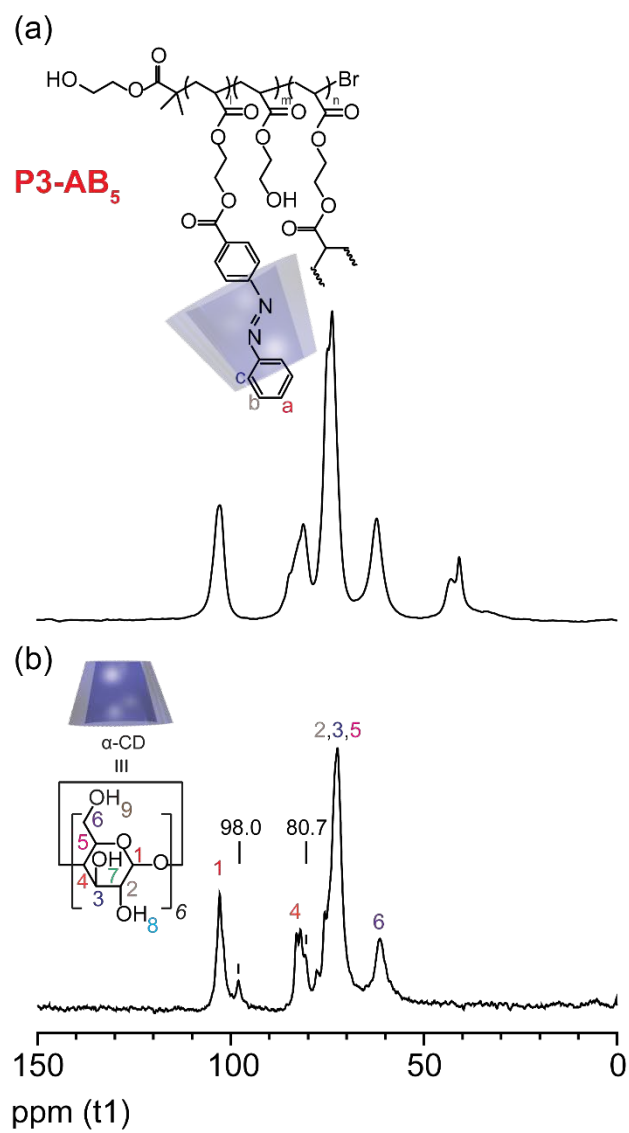
where the conversion of cross-linker ( $x_c$ ) and left-over monomer from the synthesis of the macroinitiator ( $x_m$ ) were determined by NMR and the conversion of arm ( $x_a$ ) was determined by GPC analysis of the DRI chromatogram.  $m(arms)$ ,  $m(m)$  and  $m(XL)$  are the amount (in g) of the macroinitiator, left-over monomer and cross-linker employed in the CCS polymer synthesis, respectively.



**Figure S1.** <sup>1</sup>H NMR (*d*<sub>6</sub>-DMSO, 400 MHz) spectra of the azobenzene functionalised CCS polymers **(a) P3-AB<sub>5</sub>**, and **(b) unfunctionalised PHEA CCS polymer P2**.

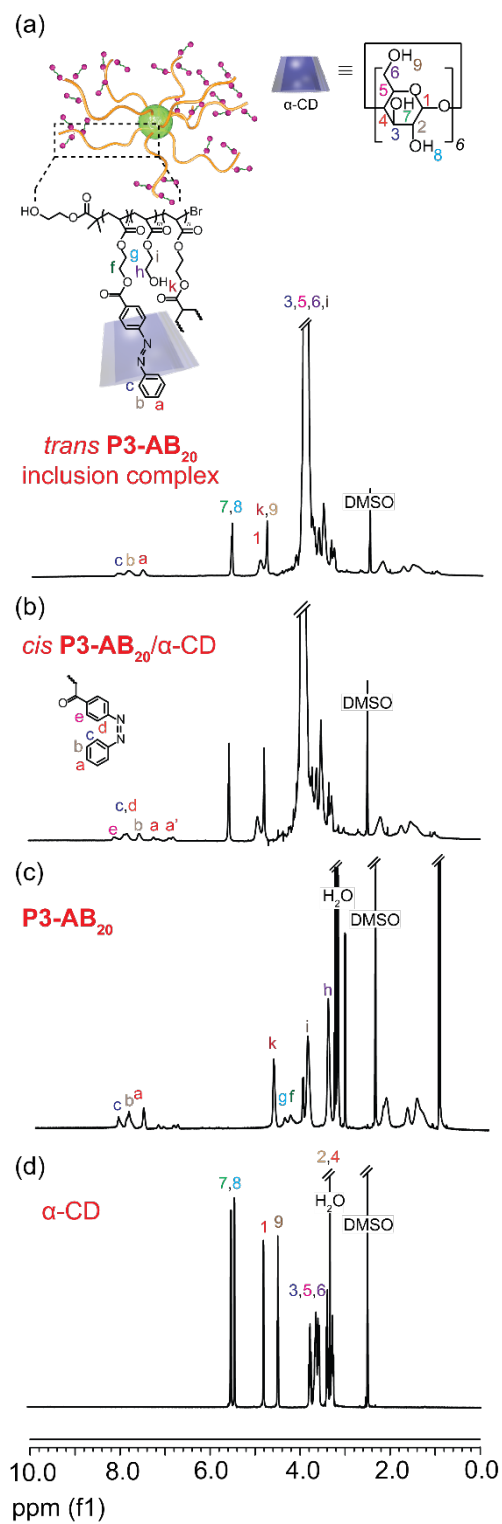


**Figure S2.** GPC DRI (solid lines) and UV ( $\lambda = 360$  nm) (dotted lines) chromatograms of the azobenzene functionalised CCS polymers **(a) P3-AB<sub>5</sub>** and **(b) unfunctionalised CCS polymer P2**.



**Figure S3.**  $^{13}\text{C}$  CP/MAS NMR spectra of **(a)** *trans* **P3-AB<sub>5</sub>**/ $\alpha$ -CD inclusion complex and **(b)** free  $\alpha$ -CD.





**Figure S4.**  $^1\text{H}$  NMR ( $d_6$ -DMSO, 400 MHz) spectra of (a) *trans* P3-AB<sub>20</sub>/α-CD inclusion complex, (b) *cis* P3-AB<sub>20</sub>/α-CD mixture, (c) P3-AB<sub>20</sub>, and (d) free α-CD.

## References

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