

## ELECTRONIC SUPPORTING INFORMATION:

### **Polymer-supported cationic templates for molecular recognition of anionic hosts in water**

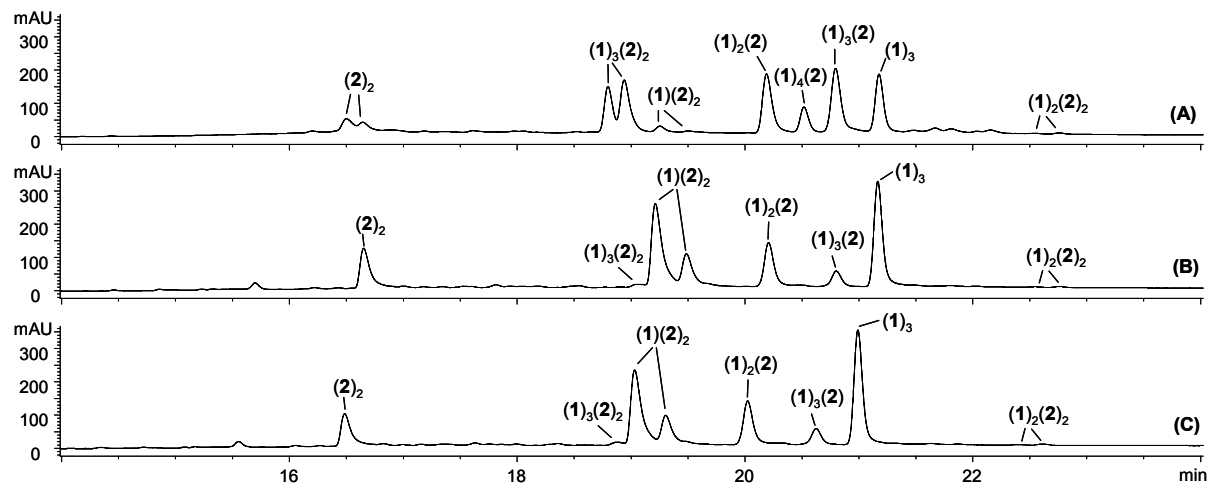
**Pol Besenius,<sup>a</sup> Peter A. G. Cormack,<sup>\*a</sup> R. Frederick Ludlow,<sup>b</sup> Sijbren Otto,<sup>\*b</sup> David C. Sherrington<sup>\*a</sup>**

<sup>a</sup> *WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, UK.*

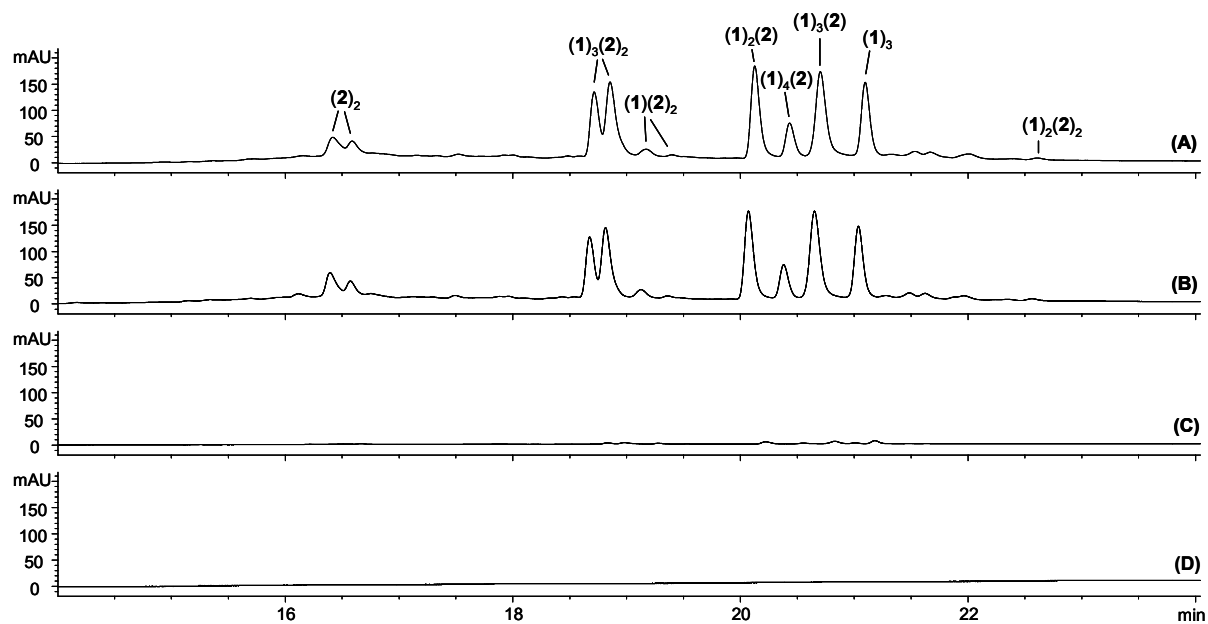
<sup>b</sup> *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK*

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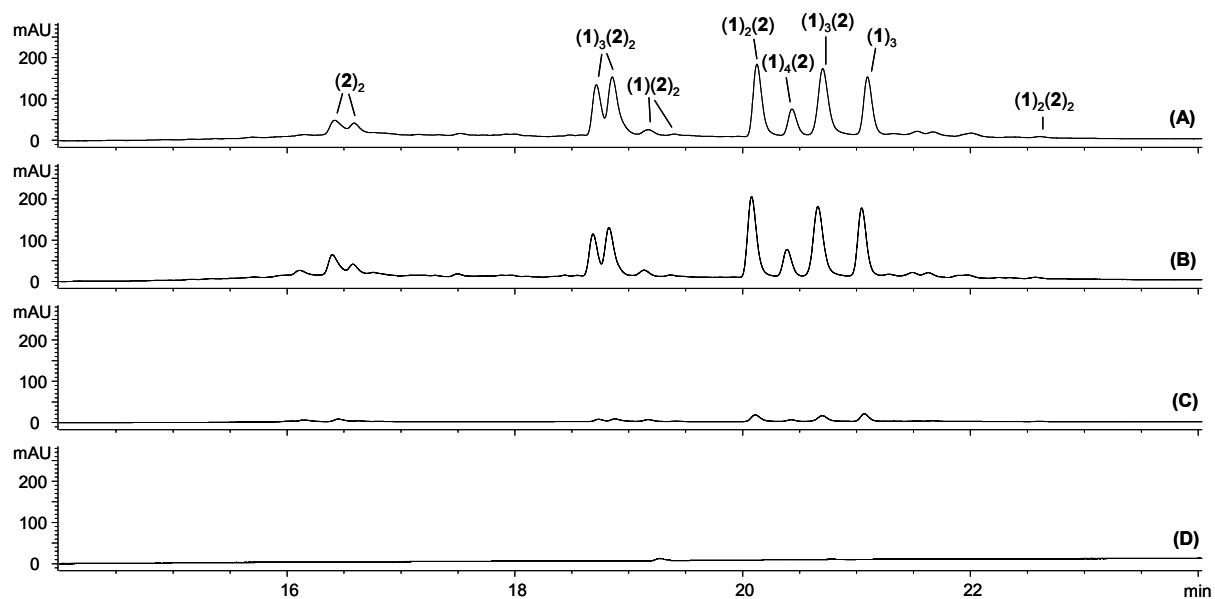
### Additional DCLs and control experiments



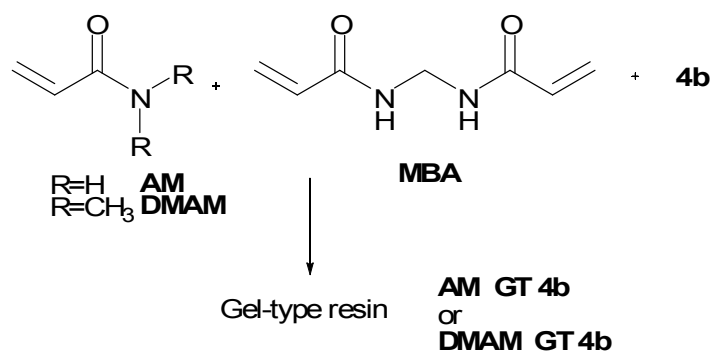
**Figure S 1.** HPLC analyses of a DCL made from building blocks **1** and *rac*-**2** (2 mM in total) (A) in absence of template, (B) after 72h exposure to template **3** (2 mM), and (C) after 72h exposure to template **4a** (2 mM).



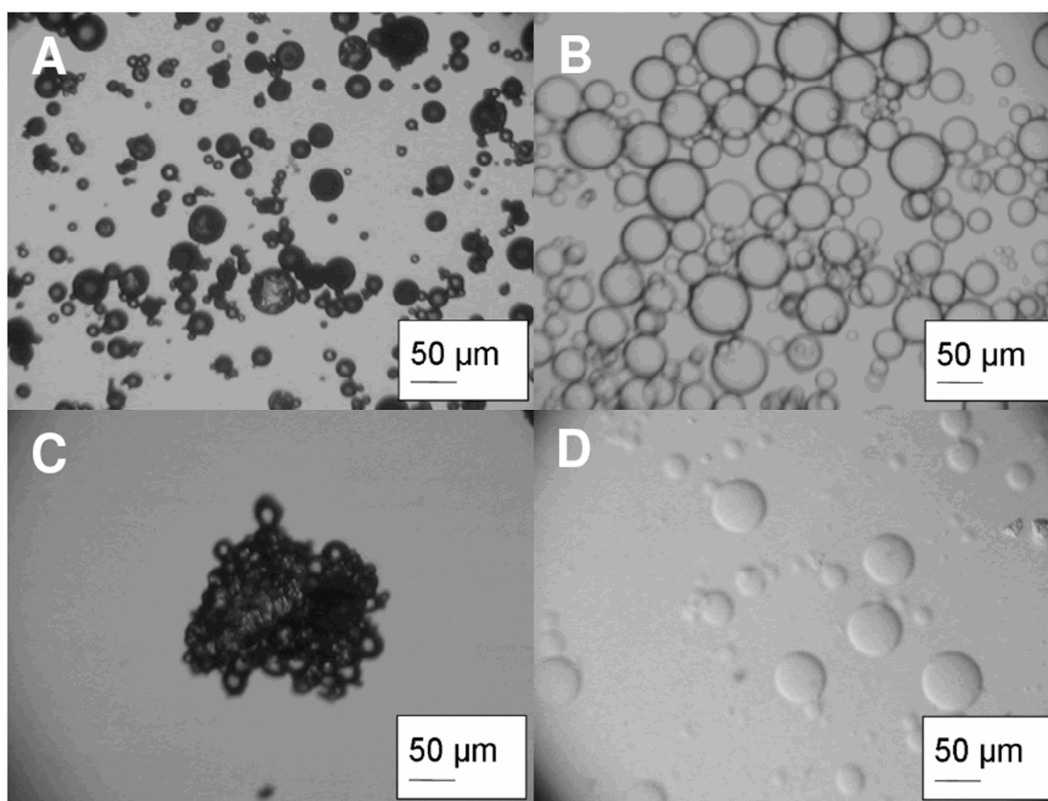
**Figure S 2.** HPLC analyses of a DCL made from building blocks **1** and *rac*-**2** (2 mM in total) (A) in absence of template, and (B) after 72h exposure to **AMGT** (4 mg/ml), (C) borate buffer wash of **AMGT**, and (D) elution with ethanol.



**Figure S 3.** HPLC analyses of a DCL made from building blocks **1** and *rac*-**2** (2 mM in total) (A) in absence of template, and (B) after 72h exposure to **DMAM GT** (4 mg/ml), (C) borate buffer wash of **DMAM GT**, and (D) elution with ethanol.



**Figure S 4.** Synthesis of polymer-supported adamantylamine derivative **AM / DMAM GT 4b** in an inverse-suspension polymerisation using **4b** (20 wt%), **MBA** (4 wt%), **AM** or **DMAM** (76 wt%) to yield a template loading of 0.5 mmol **4b** /g.



**Figure S 5.** Transmission optical microscope photographs at a magnification of x10 showing gel-type beads: (A) dry **AM GT**, (B) H<sub>2</sub>O swollen **AM GT**, (C) dry **DMAM GT**, and (D) H<sub>2</sub>O swollen **DMAM GT**.

### Experimental Section

**Materials.** Building blocks **1** and *rac-2* were provided by collaboration group in Cambridge.<sup>1</sup> Dry tetrahydrofuran and dry dichloromethane were obtained from a solvent purification system (SPS 400, Innovative Technologies) using alumina as drying agent. Ammonium peroxydisulfate (APS) was recrystallised from ethanol/water. All other reagents and solvents were used as received from the supplier.

**Instrumentation and Measurements.** <sup>1</sup>H and <sup>13</sup>C spectra were recorded on a Bruker 400 DPX, 400 AV or 500 AV spectrometer at 300 K. In all spectra the residual solvent signal was used as a reference.

Gel-phase NMR spectra were recorded on a Bruker DRX 400 spectrometer. The samples were analysed by <sup>1</sup>H HR-MAS NMR, by packing them into a 4 mm zirconium HR-MAS rotor. The spectra were acquired under MAS at 4 kHz.

ATR-FTIR spectra were obtained on a Perkin-Elmer 1600 Series FTIR spectrometer, using a diamond compression cell, recording transmission spectra with a resolution of  $4\text{ cm}^{-1}$  and a series of 16 scans.

Mass spectrometry data was obtained from the EPSRC National Mass Spectrometry Service Centre at the University of Wales Swansea. Accurate mass measurements were recorded on a Finnigan MAT 900 XLT high resolution double focussing spectrometer with tandem Ion Trap. Some analyses were also carried out by the Mass Spectrometry Service Centre at the University of Cambridge.

Elemental microanalysis data were obtained from the microanalysis laboratory at Strathclyde University. *C, H, N – analysis:* C, H, N are simultaneously determined in a Perkin Elmer 2400 analyser. The sample, wrapped in tin foil is combusted at  $1800\text{ }^{\circ}\text{C}$  in pure oxygen. The combustion products are catalysed and interferences removed before being swept into the detector zone where each element is separated and eluted as  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{NO}_2$ . The signals are converted to a percentage of the elements. *Halogens (except F) – analysis:* the sample was combusted in an  $\text{O}_2$  flask containing  $\text{H}_2\text{O}_2$  and KOH as absorbent. After 30 minutes the flask was washed down with distilled water. The flask was cooled to room temperature. Absolute alcohol was then added, the solution acidified to bromophenol blue and titrated with a mercuric nitrate solution using diphenylcarbazone as indicator.

Optical microscopy photographs were all obtained in transmission mode on a Reichert Polyvar 2 MET microscope.

Thin layer chromatography (TLC) was carried out on Silica egl 60  $\text{F}_{254}$  aluminium sheets or on Aluminium oxide (60  $\text{F}_{254}$ ) on TLC foils, using iodine or phosphomolybdic acid as developing agent.

**DCL experiments:** Experimental conditions using polymer-supported conditions were similar to the ones described previously:<sup>2</sup> DCL syntheses took place in 50 mM borate buffer pH 8 in presence of polymer-supported templates, the reaction vials were put on a horizontal shaker. After 3 days the resins were filtered off through syringe filters (0.45  $\mu\text{m}$  cellulose membrane filters), the vials rinsed with a small amount of borate buffer which was then filtered also through the syringe filter, and both filtrates combined. The beads were then washed repeatedly using 2 x 2.0 ml of each of the appropriate solvent (each washing step consisted of shaking the beads for 10 min): borate buffer for the non-disruptive wash which removes unselectively bound oligomers; ethanol for the disruptive wash or elution, which releases selectively amplified and bound receptors by disrupting non-covalent interactions

between host and guest or receptor and template bound on the polymer support. An internal standard was added to each solution: 50  $\mu$ l of a 3,5-dihydroxybenzoic acid solution (20 mM) in borate buffer (50 mM, pH 8).

**LC-MS** was performed using an Agilent LC-MSD-Trap-XCT system. The LC system is an Agilent 1100 series HPLC equipped with an online degasser, binary pump, autosampler, heated column compartment and diode array detector (signal set at 260 nm, reference at 550nm). The following column and conditions were used (the column heater was set at 45°C): Waters symmetry C18 3.5 $\mu$ m, 2.1x150mm: 0-25 min 5/95 to 95/5 MeCN/H<sub>2</sub>O (0.1 vol% TFA) 0.2 ml/min, 25-26 min to 5/95 MeCN/H<sub>2</sub>O (0.1 vol% TFA) 0.2 ml/min. MS was performed using an Agilent XCT ion trap MSD mass spectrometer.

***N*-(1-adamantyl)-*N,N*-dimethylamine (3)** To a stirred solution of 1-adamantylamine (5 g, 33.06 mmol, 151.25 g/mol) in 110 ml methanol was added 35% aqueous formaldehyde (30.9 ml, 385.7 mmol, 30.03 g/mol, 1.07 g/ml) and the solution refluxed for 45 min. After cooling down to room temperature sodium borohydride (4.41 g, 119.04 mmol, 37.03 g/mol) was added carefully and stirred for 1 h. Methanol was removed at reduced pressure and 20 ml of 2 N KOH added to the residue. The resulting mixture was extracted with three 20 ml portions of ether. The combined ether extracts were washed with 20 ml of 0.5 N KOH and then extracted with three 10 ml portions of 1 N HCl. The acid extracts were combined, neutralized with solid KOH and then extracted with three 20 ml portions of ether. The combined ether extracts were dried over K<sub>2</sub>CO<sub>3</sub> and evaporated in vacuo. The colourless liquid was purified by flash chromatography (Al<sub>2</sub>O<sub>3</sub>, ethyl acetate) to remove traces of leftover starting material and side products. Yield: 4.80 g (80%) of a white solid, with a melting point around room temperature. *R*<sub>f</sub> (Al<sub>2</sub>O<sub>3</sub>, ethyl acetate): 0.64. <sup>1</sup>H NMR ( $\delta$  [ppm], CDCl<sub>3</sub>, 400 MHz): 2.23 (s, 6H, 2x N-CH<sub>3</sub>), 2.04 (brs, 3H, 3x -CH), 1.54-1.65 (m, 12H, 6x -CH<sub>2</sub>). <sup>13</sup>C NMR ( $\delta$  [ppm], CDCl<sub>3</sub>, 101 MHz): 38.8 (s, N-C), 37.7 (t, 3x -CH<sub>2</sub>), 36.8 (t, 3x -CH<sub>2</sub>), 36.1 (q, 2x -CH<sub>3</sub>), 30.0 (d, 3x -CH). FT-IR ( $\nu_{\max}$  [cm<sup>-1</sup>]): 3377, 2906, 2777, 1596, 1471, 1451, 1358, 1310, 1258, 1209, 1164, 1082, 1046, 988, 954. HRMS: Found [M+H]<sup>+</sup> 180.1750. C<sub>12</sub>H<sub>22</sub>N requires [M+H]<sup>+</sup>, 180.1752.

**Precursor synthesis: *N*-(1-adamantyl)-*N*-methylamine.** To a stirred solution of 1-adamantylamine (20 g, 132.23 mmol, 151.25 g/mol) in dry 150 ml THF, cooled to -15 °C, *n*-BuLi (52.89 ml, 132.23 mmol, 2.5 M) was added dropwise under N<sub>2</sub>. After 30 min, CH<sub>3</sub>I

(8.25 ml, 132.23 mmol, 141.94 g/mol, 2.275 g/ml) in 70 ml THF was added, and the stirring was continued for about 2 h at -10 to 0 °C and about 5 h at rt. The reaction was quenched with water at 0 °C, evaporated to dryness, dissolved in ether and extracted with saturated sodium hydrogen carbonate. The white solid was purified by flash chromatography (Al<sub>2</sub>O<sub>3</sub>, ethyl acetate) to remove leftover starting material and side products. Yield: 13.10 g (60%) of a white solid. R<sub>f</sub> (Al<sub>2</sub>O<sub>3</sub>, ethyl acetate): 0.46. <sup>1</sup>H NMR (δ [ppm], CDCl<sub>3</sub>, 400 MHz): 2.56 (s, 3H, NH-CH<sub>3</sub>), 2.23 (brs, 3H, 3x -CH), 2.05-2.06 (m, 6H, 3x -CH<sub>2</sub>), 1.70-1.77 (m, 6H, 3x -CH<sub>2</sub>). <sup>13</sup>C NMR (δ [ppm], CDCl<sub>3</sub>, 101 MHz): 55.7 (s, NH-C), 38.5 (t, 3x -CH<sub>2</sub>), 35.6 (t, 3x -CH<sub>2</sub>), 28.9 (d, 3x -CH), 24.8 (q, -CH<sub>3</sub>). FT-IR (ν<sub>max</sub> [cm<sup>-1</sup>]): 3388, 2970, 2750, 1638, 1588, 1455, 1365, 1311, 1209, 1141, 1076, 1045, 1024, 942. HRMS: Found [M+H]<sup>+</sup> 166.1588. C<sub>11</sub>H<sub>20</sub>N requires [M+H]<sup>+</sup>, 166.1590.

**2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl methanesulfonate.** Methanesulfonyl chloride (6.78 g, 59.21 mmol, 114.55 g/mol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added to a mixture of tetraethylene glycol (8.88 ml, 51.49 mmol, 194.23 g/mol, 1.125 g/ml) and Ag<sub>2</sub>O (13.72 g, 59.21 mmol, 231.76 g/mol) in CH<sub>2</sub>Cl<sub>2</sub> (100 ml). The reaction was stopped after 48 h by filtration through Celite. Evaporation followed by flash chromatography (SiO<sub>2</sub>, ethyl acetate/MeOH 9:1) afforded the dimesylate followed by the monomesylate. Yield: 6.77 g (48%) of a colourless oil. R<sub>f</sub> (SiO<sub>2</sub>, ethyl acetate/MeOH 9:1): 0.42. <sup>1</sup>H NMR (δ [ppm], CD<sub>3</sub>OD, 400 MHz): 4.32-4.34 (m, 2H, O-CH<sub>2</sub>), 3.72-3.74 (m, 2H, O-CH<sub>2</sub>), 3.58-3.65 (m, 10H, 5x O-CH<sub>2</sub>), 3.51-3.53 (m, 2H, O-CH<sub>2</sub>), 3.08 (s, 3H, -SO<sub>3</sub>-CH<sub>3</sub>). <sup>13</sup>C NMR (δ [ppm], CD<sub>3</sub>OD, 101 MHz): 72.7 (t, O-CH<sub>2</sub>), 70.6 (t, 3x O-CH<sub>2</sub>), 70.4 (t, O-CH<sub>2</sub>), 70.0 (t, O-CH<sub>2</sub>), 69.1 (t, O-CH<sub>2</sub>), 61.3 (t, O-CH<sub>2</sub>), 36.6 (q, -SO<sub>3</sub>-CH<sub>3</sub>). FT-IR (ν<sub>max</sub> [cm<sup>-1</sup>]): 3445, 2936, 1876, 1721, 1643, 1456, 1351, 1249, 1130, 1017, 976, 922. HRMS: Found [M+H]<sup>+</sup> 273.1004. C<sub>9</sub>H<sub>21</sub>O<sub>7</sub>S requires [M+H]<sup>+</sup>, 273.1008.

**2-{2-[2-(2-azidoethoxy)ethoxy]ethoxy}ethanol.** Sodium azide (2.42 g, 37.18 mmol, 65.01 g/mol) was added to a solution of 2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl methanesulfonate (6.75 g, 24.79 mmol, 272.32 g/mol) in dry DMF (27 ml). The mixture was heated at 110 °C for 4 h under N<sub>2</sub>. After cooling down to room temperature the mixture was coevaporated with toluene at 50 °C and purified by flash chromatography (SiO<sub>2</sub>, ethyl acetate/MeOH 9:1). Yield: 5.18 g (95%) of a colourless oil. R<sub>f</sub> (SiO<sub>2</sub>, ethyl acetate/MeOH 9:1): 0.47. <sup>1</sup>H NMR (δ [ppm], CDCl<sub>3</sub>, 400 MHz): 3.65 (t, J=4.6 Hz, 2H, O-CH<sub>2</sub>), 3.58-3.62 (m, 10H, 5x O-CH<sub>2</sub>), 3.52-3.54 (m, 2H, O-CH<sub>2</sub>), 3.22 (t, J=5.1 Hz, 2H, N<sub>3</sub>-CH<sub>2</sub>). <sup>13</sup>C NMR (δ

[ppm], CDCl<sub>3</sub>, 101 MHz): 72.5 (t, O-CH<sub>2</sub>), 70.6 (t, 2x O-CH<sub>2</sub>), 70.5 (t, O-CH<sub>2</sub>), 70.2 (t, O-CH<sub>2</sub>), 70.0 (t, O-CH<sub>2</sub>), 61.6 (t, HO-CH<sub>2</sub>), 50.6 (t, N<sub>3</sub>-CH<sub>2</sub>). FT-IR ( $\nu_{\max}$  [cm<sup>-1</sup>]): 3437, 2874, 2114, 1668, 1453, 1349, 1301, 1100, 938. HRMS: Found [M+NH<sub>4</sub>]<sup>+</sup> 237.1554. C<sub>7</sub>H<sub>13</sub>NO<sub>5</sub>F<sub>3</sub>S requires [M+NH<sub>4</sub>]<sup>+</sup>, 237.1557.

**2-{2-[2-(2-aminoethoxy)ethoxy]ethoxy}ethanol.** A solution of 2-{2-[2-(2-azidoethoxy)ethoxy]ethoxy}ethanol (5.07 g, 23.125 mmol, 219.24 g/mol) in dry THF (65 ml) was cooled to 0 °C. Triphenyl phosphine (6.67 g, 25.44 mmol, 262.29 g/mol) was added after which the mixture was allowed to attain room temperature. The reaction was monitored by TLC (i-PrOH/aqueous NH<sub>3</sub> (5%)/H<sub>2</sub>O 6:3:1), and at completion (12h) water was added (0.75 ml, 41.88 mmol, ) to hydrolyse the adduct (12h). The reaction mixture was diluted with water (25 ml), washed extensively with toluene and the aqueous layer evaporated to dryness. Yield: 3.93 g (88%) of a pale yellow oil. R<sub>f</sub> (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH/Et<sub>3</sub>N 3:3:1): 0.53. <sup>1</sup>H NMR ( $\delta$  [ppm], CDCl<sub>3</sub>, 400 MHz): 3.67 (t, J=4.4 Hz, 2H, O-CH<sub>2</sub>), 3.61-3.63 (m, 8H, 4x O-CH<sub>2</sub>), 3.56 (t, J=4.5 Hz, 2H, O-CH<sub>2</sub>), 3.49 (t, J=5.1 Hz, 2H, O-CH<sub>2</sub>), 2.82 (t, J=4.9 Hz, 2H, N-CH<sub>2</sub>) 2.63 (brs, 2H, NH<sub>2</sub>). <sup>13</sup>C NMR ( $\delta$  [ppm], CDCl<sub>3</sub>, 101 MHz): 72.1 (t, O-CH<sub>2</sub>), 71.7 (t, O-CH<sub>2</sub>), 69.6 (t, 2x O-CH<sub>2</sub>), 69.4 (t, O-CH<sub>2</sub>), 69.3 (t, O-CH<sub>2</sub>), 60.3 (t, HO-CH<sub>2</sub>), 39.8 (t, NH<sub>2</sub>-CH<sub>2</sub>). FT-IR ( $\nu_{\max}$  [cm<sup>-1</sup>]): 3368, 2874, 1643, 1575, 1476, 1351, 1309, 1249, 1099, 938. HRMS: Found [M+H]<sup>+</sup> 194.1395. C<sub>8</sub>H<sub>20</sub>NO<sub>4</sub> requires [M+H]<sup>+</sup>, 194.1392.

**2,2,2-trifluoro-N-(2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl)acetamide.** 2-{2-[2-(2-aminoethoxy)ethoxy]ethoxy}ethanol (3.83 g, 19.81 mmol, 193.24 g/mol) was dissolved in 26 ml methanol, and triethylamine (4.13 ml, 29.71 mmol, 101.19 g/mol, 0.728 g/ml) was added, followed by ethyl trifluoroacetate (2.59 ml, 21.79 mmol, 142.08 g/mol, 1.194 g/ml). The reaction was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, the mixture dissolved in 100 ml brine and extracted with 3x 100 ml ethyl acetate, and the solvent evaporated. The crude product was purified by flash chromatography (SiO<sub>2</sub>, ethyl acetate). Yield: 5.13 g (90%) of a colourless oil. R<sub>f</sub> (SiO<sub>2</sub>, ethyl acetate): 0.51. <sup>1</sup>H NMR ( $\delta$  [ppm], CDCl<sub>3</sub>, 400 MHz): 8.82 (brs, 1H, -NH), 3.54-3.73 (m, 16H, 7x O-CH<sub>2</sub> + NH-CH<sub>2</sub>). <sup>13</sup>C NMR ( $\delta$  [ppm], CDCl<sub>3</sub>, 101 MHz): 157.7 (q, J=37.0 Hz, -C=O), 116.1 (q, J=287.5 Hz, -CF<sub>3</sub>), 72.4 (t, O-CH<sub>2</sub>), 70.6 (t, O-CH<sub>2</sub>), 70.3 (t, O-CH<sub>2</sub>), 70.0 (t, O-CH<sub>2</sub>), 69.6 (t, O-CH<sub>2</sub>), 69.4 (t, O-CH<sub>2</sub>), 61.2 (t, HO-CH<sub>2</sub>), 39.8 (t, NH-CH<sub>2</sub>). FT-IR ( $\nu_{\max}$  [cm<sup>-1</sup>]): 3444, 3293, 3090, 2877, 1720, 1561, 1458, 1351, 1212, 1188, 1156, 1102, 941. HRMS: Found [M+H]<sup>+</sup> 290.1216. C<sub>10</sub>H<sub>19</sub>NO<sub>5</sub>F<sub>3</sub> requires [M+H]<sup>+</sup>, 290.1215.



**14,14,14-trifluoro-13-oxo-3,6,9-trioxa-12-azatetradec-1-yl methanesulfonate.**

Methanesulfonylchloride (2.03 ml, 36.20 mmol, 114.55 g/mol, 1.48 g/ml) was added over 20 min to a 0 °C solution of 2,2,2-trifluoro-*N*-(2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethyl)acetamide (5.05 g, 17.47 mmol, 289.25 g/mol) and triethylamine (6.07 ml, 43.67 mmol, 101.19 g/mol, 0.728 g/ml) in dry CH<sub>2</sub>Cl<sub>2</sub> (70 ml). The mixture was stirred under N<sub>2</sub> at room temperature for 4 h and washed successively with 1 N HCl (100 ml) and brine (100 ml). The organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The crude product was purified by flash chromatography (SiO<sub>2</sub>, ethyl acetate). Yield: 6.17 g (96%) of a colourless oil. R<sub>f</sub> (SiO<sub>2</sub>, ethyl acetate): 0.71. <sup>1</sup>H NMR (δ [ppm], CDCl<sub>3</sub>, 400 MHz): 7.28 (brs, 1H, -NH), 4.32-4.34 (m, 2H, O-CH<sub>2</sub>), 3.71-3.74 (m, 2H, O-CH<sub>2</sub>), 3.57-3.66 (m, 10H, 5x O-CH<sub>2</sub>), 3.48-3.54 (m, 2H, NH-CH<sub>2</sub>), 3.03 (s, 3H, -SO<sub>3</sub>-CH<sub>3</sub>). <sup>13</sup>C NMR (δ [ppm], CDCl<sub>3</sub>, 101 MHz): 157.2 (q, J=36.8 Hz, -C=O), 115.9 (q, J=287.6 Hz, -CF<sub>3</sub>), 70.5 (t, O-CH<sub>2</sub>), 70.4 (t, O-CH<sub>2</sub>), 70.3 (t, O-CH<sub>2</sub>), 70.2 (t, O-CH<sub>2</sub>), 69.3 (t, O-CH<sub>2</sub>), 68.9 (t, O-CH<sub>2</sub>), 68.5 (t, SO<sub>3</sub>-CH<sub>2</sub>), 39.7 (q, SO<sub>3</sub>-CH<sub>3</sub>), 37.5 (t, NH-CH<sub>2</sub>). FT-IR (ν<sub>max</sub> [cm<sup>-1</sup>]): 3338, 3096, 3026, 1939, 2879, 1724, 1560, 1456, 1351, 1139, 1017, 977, 924. HRMS: Found [M+H]<sup>+</sup> 368.0995. C<sub>11</sub>H<sub>21</sub>NO<sub>7</sub>F<sub>3</sub>S requires [M+H]<sup>+</sup>, 368.0991.

***N*-[12-(1-adamantyl)-3,6,9-trioxa-12-azatridec-1-yl]-2,2,2-trifluoroacetamide (4a).** To a solution of 14,14,14-trifluoro-13-oxo-3,6,9-trioxa-12-azatetradec-1-yl methanesulfonate (2.63 g, 7.16 mmol, 367.34 g/mol) in dry CH<sub>3</sub>CN (40 ml) were added *N*-(1-adamantyl)-*N*-methylamine (1.30 g, 7.88 mmol, 165.28 g/mol), K<sub>2</sub>CO<sub>3</sub> (2.48 g, 17.91 mmol, 138.21 g/mol) and NaI (1.18 g, 7.88 mmol, 149.89 g/mol). The mixture was heated at reflux under N<sub>2</sub> for 24 h. After cooling to room temperature, the suspension was diluted with CH<sub>3</sub>CN (40 ml) and filtered over celite. CH<sub>3</sub>CN was evaporated under vacuum, the product dissolved in 100 ml CH<sub>2</sub>Cl<sub>2</sub> and washed with 100 ml saturated hydrogen carbonate. The organic phase was then dried using Na<sub>2</sub>SO<sub>4</sub> and evaporated. The orange oil was purified by flash chromatography (SiO<sub>2</sub>, ethyl acetate/MeOH 10:0...8:2 (10% triethylamine)) to remove leftover starting material. Yield: 2.55 g (82%) of a colourless oil. R<sub>f</sub> (SiO<sub>2</sub>, ethyl acetate/MeOH 8:2 (10% triethylamine)): 0.77. <sup>1</sup>H NMR (δ [ppm], CDCl<sub>3</sub>, 400 MHz): 7.54 (brs, 1H, -NH), 3.58-3.65 (m, 10H, 5x O-CH<sub>2</sub>), 3.51-3.55 (m, 2H, NH-CH<sub>2</sub>), 3.48 (t, J=6.8 Hz, 2H, O-CH<sub>2</sub>), 2.61 (t, J=6.8 Hz, 2H, N-CH<sub>2</sub>), 2.24 (s, 3H, N-CH<sub>3</sub>), 2.11 (brs, 3H, 3x -CH), 1.54-1.65 (m, 12H, 6x -CH<sub>2</sub>). <sup>13</sup>C NMR (δ [ppm], CDCl<sub>3</sub>, 101 MHz): 157.3 (q, J=37.0 Hz, -C=O), 115.9 (q, J=288.0 Hz, -CF<sub>3</sub>), 71.3 (t, O-CH<sub>2</sub>), 70.5 (t, 2x O-CH<sub>2</sub>), 70.3 (t, O-CH<sub>2</sub>), 70.2 (t, O-CH<sub>2</sub>), 68.7 (t, O-CH<sub>2</sub>), 54.1 (s, N-C), 48.7 (t, N-CH<sub>2</sub>), 39.7 (t, NH-CH<sub>2</sub>), 38.5 (t, 3x -CH<sub>2</sub>), 36.7 (t,

3x -CH<sub>2</sub>), 34.6 (q, N-CH<sub>3</sub>), 29.4 (d, 3x -CH). FT-IR ( $\nu_{\max}$  [cm<sup>-1</sup>]): 3524, 3271, 2905, 1720, 1562, 1452, 1359, 1310, 1187, 1154, 1001, 940. HRMS: Found [M+H]<sup>+</sup> 437.2606. C<sub>7</sub>H<sub>13</sub>NO<sub>5</sub>F<sub>3</sub>S requires [M+H]<sup>+</sup>, 437.2585.

**2-(1-adamantyl)-5,8,11-trioxa-2-azatridecan-13-amine.** *N*-[12-(1-adamantyl)-3,6,9-trioxa-12-azatridec-1-yl]-2,2,2-trifluoroacetamide (**4a**) (2.54 g, 5.82 mmol, 436.51 g/mol) and 6 M NaOH (50 ml, 300 mmol) were stirred at room temperature for 12 h. The emulsion was diluted with H<sub>2</sub>O (100 ml) and the product extracted with three portions of CH<sub>2</sub>Cl<sub>2</sub> (100 ml). The organic phase was then dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The oily product was not purified as NMR analysis showed complete removal of the trifluoroacetamide protecting group and absence of any other side products. Yield: 1.92 g (97%) of a colourless oil. <sup>1</sup>H NMR ( $\delta$  [ppm], CDCl<sub>3</sub>, 500 MHz): 3.54-3.60 (m, 8H, 4x O-CH<sub>2</sub>), 3.47-3.52 (m, 4H, 2x O-CH<sub>2</sub>), 2.77-2.79 (m, 2H, NH<sub>2</sub>-CH<sub>2</sub>), 2.57 (t, J=7.0 Hz, 2H, N-CH<sub>2</sub>), 2.20 (s, 3H, N-CH<sub>3</sub>), 2.06 (brs, 3H, 3x -CH), 1.47-1.60 (m, 12H, 6x -CH<sub>2</sub>). <sup>13</sup>C NMR ( $\delta$  [ppm], CDCl<sub>3</sub>, 126 MHz): 73.4 (t, O-CH<sub>2</sub>), 71.4 (t, O-CH<sub>2</sub>), 70.6 (t, 2x O-CH<sub>2</sub>), 70.4 (t, O-CH<sub>2</sub>), 70.3 (t, O-CH<sub>2</sub>), 54.1 (s, N-C), 48.8 (t, N-CH<sub>2</sub>), 41.8 (t, NH<sub>2</sub>-CH<sub>2</sub>), 38.5 (t, 3x -CH<sub>2</sub>), 36.8 (t, 3x -CH<sub>2</sub>), 34.6 (q, N-CH<sub>3</sub>), 28.9 (d, 3x -CH). FT-IR ( $\nu_{\max}$  [cm<sup>-1</sup>]): 3366, 2904, 1655, 1596, 1451, 1358, 1311, 1251, 1218, 1189, 1120, 1080, 990, 957, 936. HRMS: Found [M+H]<sup>+</sup> 341.2793. C<sub>19</sub>H<sub>37</sub>O<sub>3</sub>N<sub>2</sub> requires [M+H]<sup>+</sup>, 341.2799.

***N*-[12-(1-adamantyl)-3,6,9-trioxa-12-azatridec-1-yl]acrylamide (4b).** A suspension of 2-(1-adamantyl)-5,8,11-trioxa-2-azatridecan-13-amine (1.88 g, 5.53 mmol, 340.50 g/mol), K<sub>2</sub>CO<sub>3</sub> (15.29 g, 110.60 mmol, 138.21 g/mol) and DMAP (67.6 mg, 0.55 mmol, 122.17 g/mol) in dry THF (40 ml) was cooled to 0 °C, followed by the gradual addition of acryloyl chloride (2.25 ml, 27.70 mmol, 90.51 g/mol, 1.114 g/ml) by syringe. The mixture was stirred under N<sub>2</sub> for 12 h, after which the suspension was diluted with THF (40 mL) and filtered over celite. THF was evaporated under vacuum, the product dissolved in 50 ml CH<sub>2</sub>Cl<sub>2</sub> and washed with 100 ml saturated hydrogen carbonate. The organic phase was then dried using Na<sub>2</sub>SO<sub>4</sub> and evaporated. The orange oil was purified by flash chromatography (SiO<sub>2</sub>, ethyl acetate/MeOH 10:0...8:2 (10% triethylamine)). Yield: 2.16 g (99%) of a colourless oil. R<sub>f</sub> (SiO<sub>2</sub>, ethyl acetate/MeOH 8:2 (10% triethylamine)): 0.62. <sup>1</sup>H NMR ( $\delta$  [ppm], CDCl<sub>3</sub>, 400 MHz): 6.61 (brs, 1H, -NH), 6.27 (dd, J=17 Hz, 1.8 Hz, 1H, =CH<sub>2</sub>), 6.15 (dd, J=17 Hz, 10.1 Hz, 1H, =CH), 5.59 (dd, J=10.1 Hz, 1.8 Hz, 1H, =CH<sub>2</sub>), 3.49-3.68 (m, 14H, 6x O-CH<sub>2</sub> + NH-CH<sub>2</sub>), 2.63 (t, J=6.8 Hz, 2H, N-CH<sub>2</sub>), 2.26 (s, 3H, N-CH<sub>3</sub>), 2.05 (brs, 3H, 3x -CH), 1.49-1.65 (m, 12H, 6x -CH<sub>2</sub>). <sup>13</sup>C NMR ( $\delta$  [ppm], CDCl<sub>3</sub>, 101 MHz): 165.5 (s,

-C=O), 131.0 (d, =CH), 126.1 (t, =CH<sub>2</sub>), 71.0 (t, O-CH<sub>2</sub>), 70.5 (t, 2x O-CH<sub>2</sub>), 70.3 (t, O-CH<sub>2</sub>), 70.2 (t, O-CH<sub>2</sub>), 69.8 (t, O-CH<sub>2</sub>), 53.4 (s, N-C), 48.7 (t, N-CH<sub>2</sub>), 39.3 (t, NH-CH<sub>2</sub>), 38.5 (t, 3x -CH<sub>2</sub>), 36.7 (t, 3x -CH<sub>2</sub>), 34.7 (q, N-CH<sub>3</sub>), 29.5 (d, 3x -CH). FT-IR ( $\nu_{\max}$  [cm<sup>-1</sup>]): 3299, 3066, 2905, 1663, 1628, 1547, 1451, 1406, 1357, 1311, 1244, 1189, 1123, 989, 956, 806, 733. HRMS: Found [M+H]<sup>+</sup> 395.2904. C<sub>22</sub>H<sub>39</sub>O<sub>4</sub>N<sub>2</sub> requires [M+H]<sup>+</sup>, 395.2904.

### Polymer synthesis:

**Poly(AM / DMAM-co-MBA) – gel-type resin – AM / DMAM GT.** A typical inverse suspension polymerisation procedure for acrylamide (**AM GT**) or dimethylacrylamide (**DMAM GT**) based resins looks as follows: the discontinuous aqueous phase was prepared by dissolving acrylamide / dimethylacrylamide (96 wt%, 1.440 g), N,N'-methylenebis(acrylamide) (4 wt%, 0.060 g) and ammonium peroxydisulfate (APS) (3 wt%, 0.045 g) in 10 ml 1 M HCl in H<sub>2</sub>O. The organic phase was prepared by dissolving 2 g / 4 g sorbitan monooleate (span 80) in 100ml of a mixture of Petroleum ether 100-120°C and Paraffin Oil (1/1 v/v). The organic and aqueous phases were then added to a 250ml three necked round-bottom flask equipped with a stainless steel paddle stirrer, condenser and nitrogen inlet. The glassware had previously been silanised\* to prevent the hydrophilic comonomer mixture from sticking to the glass wall. The mixture was purged with nitrogen for 30 min, followed by heating up to 80°C under mechanical stirring at 470 rpm. The polymerisation was allowed to proceed for 6 h at 80°C under nitrogen atmosphere. The suspension was cooled down, the beads filtered off using a sintered glass funnel and then washed thoroughly with THF, H<sub>2</sub>O, THF, MeOH, acetone, DCM. They were then Soxhlet extracted twice overnight, once with THF, followed by acetone extraction before being dried at room temperature under high vacuum (0.5 mbar). Yield: **AM GT**: 1.28 g (83%), **DMAM GT**: 1.10 g (73%). Elemental microanalysis: **AM GT**: 45.94%C, 6.79%H, 0.43%Cl, 13.67%N. **DMAM GT**: 47.97%C, 8.40%H, 0.0%Cl, 11.22%N. FT-IR ( $\nu_{\max}$  [cm<sup>-1</sup>]): **AM GT**: .3527, 2935, 2865, 1716, 1649, 1456, 1324, 1194, 1113. **DMAM GT**: .3418, 2926, 2140, 1702, 1622, 1495, 1358, 1255, 1143, 1096, 1056, 909.

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\* To 'silanise' glassware is to coat the inside of said glassware with a hydrophobic layer.

*Silanisation procedure:*

A small quantity of a solution of 2% polydimethylsiloxane in butanone was gently stirred inside the glassware to be silanised, poured out, and then the glassware placed in a hot oven at about 150°C and dried overnight.

**Poly(4b-co-AM / DMAM-co-MBA) – gel-type resin – AM / DMAM GT 4b.** Gel-type polymer-supported adamantyl template derivatives **AM / DMAM GT 4b** were prepared according to the same procedure as described above for **AM GT** or **DMAM GT** depending on the type of polymeric support: poly(acrylamide) or poly(dimethylacrylamide) based resin.

	<b>4b</b>	<b>AM</b>	<b>DMAM</b>	<b>MBA</b>	<b>APS</b>
<b>AM GT 4b</b>	0.296 g	1.144 g	/	0.060 g	0.045 g
<b>DMAM GT 4b</b>	0.296 g	/	1.144 g	0.060 g	0.045 g

Polymer-supported templates were isolated as their hydrochloric acid salts **AM / DMAM GT 4b\*HCl** and characterised analytically. Deprotonation of the tertiary amine functional templates with 0.1 N KOH (25 ml), followed by filtration on a sintered glass funnel and thorough washing steps with THF, H<sub>2</sub>O, THF, MeOH and acetone yielded the free base polymer-supported templates **AM / DMAM GT 4b**. They were again Soxhlet extracted twice overnight, once with THF, followed by acetone extraction before being dried at room temperature under high vacuum (0.5 mbar). Yield: **AM GT 4b\*HCl**: 1.34 g (85%). **DMAM GT 4b\*HCl**: 1.05 g (67%). Elemental microanalysis: **AM GT 4b\*HCl**: 49.10%C, 7.74%H, 0.20%Cl, 11.44%N. **DMAM GT 4b\*HCl**: 50.90%C, 9.06%H, 0.86%Cl, 10.68%N. **AM GT 4b**: 31.55%C, 5.44%H, 0.00%Cl, 7.89%N. **DMAM GT 4b**: 54.70%C, 8.78%H, 0.00%Cl, 11.36%N. FT-IR ( $\nu_{\max}$  [cm<sup>-1</sup>]): **AM GT 4b\*HCl**: 3552, 2923, 2869, 1723, 1611, 1455, 1212, 1116, 1052, 892. **DMAM GT 4b\*HCl**: 3490, 2924, 2864, 1699, 1638, 1456, 1204, 1115, 1048, 889. **AM GT 4b**: 3383, 2934, 2227, 1660, 1539, 1449, 1394, 1353, 1223, 1182, 1115. **DMAM GT 4b**: 3480, 2924, 2128, 1709, 1607, 1506, 1403, 1359, 1258, 1142, 1101, 1060. <sup>1</sup>H HR-MAS-NMR, ( $\delta$  [ppm], D<sub>2</sub>O, 400 MHz): **AM GT 4b**: 3.40-3.80 (m, 14H, 6x O-CH<sub>2</sub> + NH-CH<sub>2</sub>, 4b), 3.10-3.40 (brs, 2H, N-CH<sub>2</sub>, 4b), 2.55-2.75 (m, 3H, N-CH<sub>3</sub>, 4b), 1.9-2.3 (m, 1H, CH-CON, AM), 1.75-1.90 (m, CH<sub>2</sub>, 4b), 1.0-1.75 (m, 2H, CH<sub>2</sub>, AM); **DMAM GT 4b**: 3.40-3.80 (m, 14H, 6x O-CH<sub>2</sub> + NH-CH<sub>2</sub>, 4b), 3.20-3.40 (brs, 2H, N-CH<sub>2</sub>, 4b), 2.65-3.15 (m, 6H, -CON-(CH<sub>3</sub>)<sub>2</sub>, DMAM), 2.20-2.65 (m, 1H, CH-CON, DMAM), 2.0 (brs, 3H, 3x -CH, 4b), 1.10-1.85 (m, 2H, CH<sub>2</sub>, DMAM).

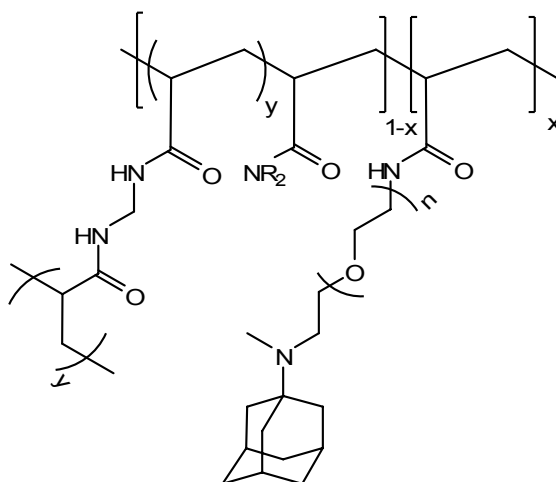
## Polymer characterisation

Table S 1 shows the expected and obtained compositions and template loading for the four different resins. The functional group content can be presented not only by the loading values in  $\text{mmol}\cdot\text{g}^{-1}$ , but also expressed as a segmental or molar ratio  $x$  (Figure S 6 and Table S 2).

Expected and found elemental microanalytical data do not seem to correlate (Table S 1). One possible explanation is be that the acrylamide based materials are so hygroscopic that after their synthesis, even extensive washing steps and Soxhlet extractions with various organic water miscible solvents are not sufficient in order to remove all the water from the resin. This trend is less pronounced for **DMAM** based resins compared to their **AM** based counterparts, due to the fact that in the latter  $\text{H}_2\text{O}$  can easily be trapped via strong hydrogen bonding interactions. One can estimate the amount of trapped water by comparing ratios of found to expected carbon and nitrogen percentages in elemental analysis results (Table S 1). This is particularly useful when trying to *estimate* the actual template loading values of the prepared materials, assuming that the relative composition of the polymers corresponds to the monomer feed.

Resin	Monomer feed [wt%]		Elemental microanalytical data			Template loading [ $\text{mmol}\cdot\text{g}^{-1}$ ]	
			% C	% H	% N		
<b>AM GT</b>	% AM	96.0	Expected	49.4	7.0	19.4	0
	% MBA	4.0	Found	45.9	6.8	13.7	
<b>AM GT 4b</b>	% AM	76.3	Expected	52.5	7.5	17.0	0.50 <i>0.27 ± 0.03</i>
	% MBA	4.0	Found	31.6	5.4	7.9	
	% <b>4b</b>	19.7					
<b>DMAM GT</b>	% DMAM	96.0	Expected	58.6	8.9	14.2	0
	% MBA	4.0	Found	48.0	8.4	11.2	
<b>DMAM GT 4b</b>	% DMAM	76.3	Expected	59.8	9.0	12.9	0.50 <i>0.45 ± 0.01</i>
	% MBA	4.0	Found	54.7	8.8	11.4	
	% <b>4b</b>	19.7					

**Table S 1.** Monomer feed, expected and found elemental microanalytical data and calculated loadings of the polymers **AM GT x** and **DMAM GT x**.

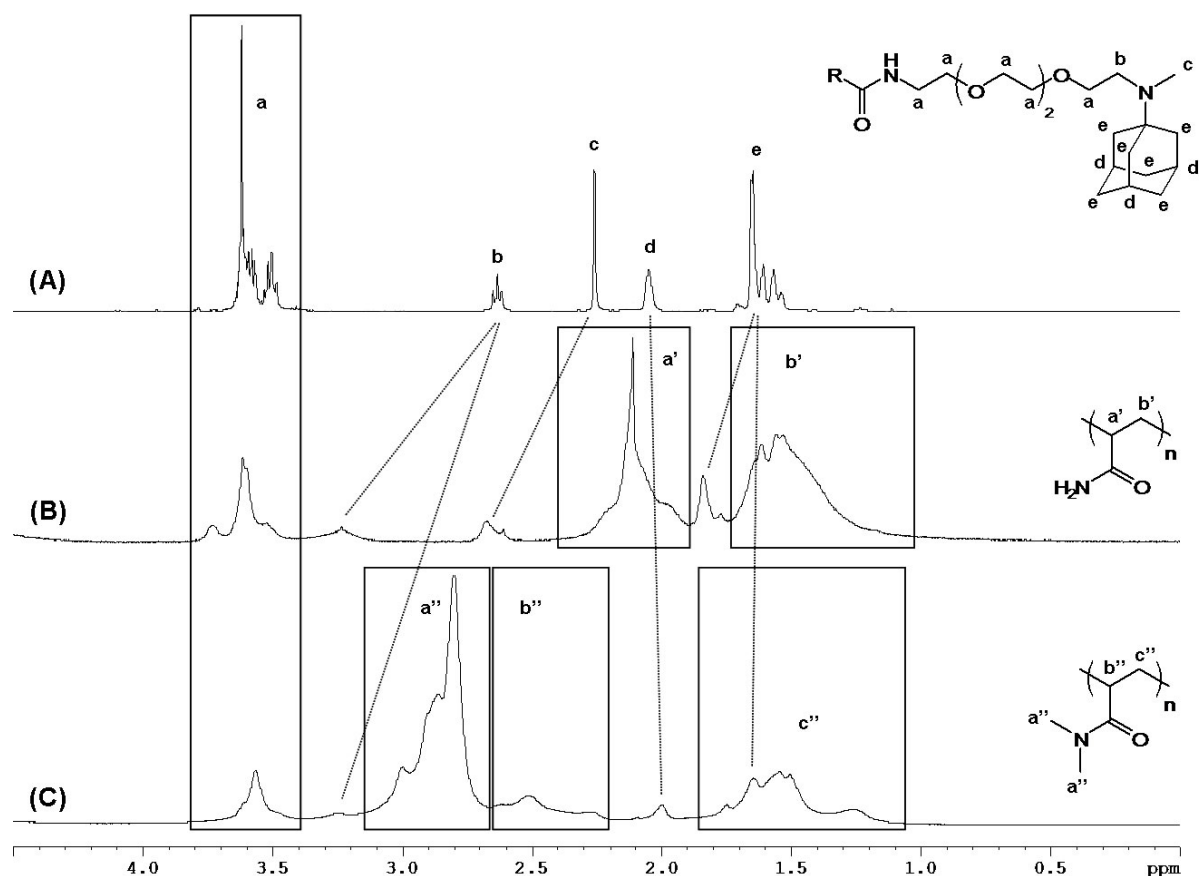


**Figure S 6.** Segmental ratio in **AM** (R=H) or **DMAM** (R=CH<sub>3</sub>) based gel-type polymer-supported templates: n=3, **AM / DMAM GT 4b**.

Incorporation of polymerisable template **4b** into resins **AM GT 4b** and **DMAM GT 4b** was confirmed by gel-phase <sup>1</sup>H HR-MAS NMR spectroscopy (Figure S 7). Segmental ratio values x (Table S 2) were calculated using template specific signals at 2.65 ppm [c, spectrum (B) in Figure S 7] for **AM GT 4b** and signal at 2.0 ppm [d, spectrum (C) in Figure S 7] for **DMAM GT 4b**. Indeed the found and expected values are very close for **DMAM GT 4b**, but about 25% too low for **AM GT 4b**.

<i>Resin</i>	<i>Segmental ratio x</i>	
<b>AM GT 4b</b>	<i>Expected</i>	0.044
	<i>Found</i>	0.032 ±0.002
<b>DMAM GT 4b</b>	<i>Expected</i>	0.059
	<i>Found</i>	0.056 ±0.001

**Table S 2.** Expected and found segmental ratios x, calculated from gel-phase <sup>1</sup>H-HR-MAS NMR spectroscopic data for polymer-supported resins **AM GT 4b** and **DMAM GT 4b**.



**Figure S 7.**  $^1\text{H}$  NMR spectra of (A) polymerisable template **4b** in  $\text{CDCl}_3$ , gel-phase  $^1\text{H}$  HR-MAS NMR spectra of (B) polymer-supported template **AM GT 4b** in  $\text{D}_2\text{O}$  and (C) polymer-supported template **DMAM GT 4b** in  $\text{D}_2\text{O}$ , showing incorporation of template **4b** into the polymer supports [COSY correlation spectra were used to assign proton signals of the products].

## References

1. P. T. Corbett, J. K. M. Sanders and S. Otto, *Chem. Eur. J.*, 2008, **14**, 2153-2166.
2. P. Besenius, P. A. G. Cormack, J. Liu, S. Otto, J. K. M. Sanders and D. C. Sherrington, *Chem. Eur. J.*, 2008, in press.