Supporting Information

Facile Bisurethane Supramolecular Polymers containing Flexible Alicyclic Receptor Units

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Materials

Reagents were purchased from either Acros Chimica or the Aldrich Chemical Company and were used without further purification. Dry acetonitrile was used as supplied, dichloromethane was distilled from calcium hydride and tetrahydrofuran (THF) was distilled from benzophenone and sodium. 4,4'-Methylene *bis*(phenylisocyanate) (MDI), isophorone diisocyanate (IPDI), hydrogenated 4,4'-methylene *bis*(phenylisocyanate) (HMDI) were supplied by the Aldrich Chemical Company.

Characterisation

Thin-layer chromatography (TLC) was performed on aluminium sheets coated with Merck silicagel 60 F_{254}. Developed TLC plates were stained with potassium permanganate solution or scrutinised under 254nm UV light. Column chromatography was performed using either SI60 Sorbent silica (40-63 μm) supplied from VWR international or Brockmann 1, standard grade, neutral, activated aluminium oxide (*ca.* 150 mesh) supplied from Aldrich Chemical Company. ^{1}H Nuclear magnetic resonance (^{1}H NMR) spectroscopy was performed on either a Bruker DPX250 (MHz), a Bruker AMX400 (400 MHz) spectrometer (using the deuterated solvent as lock) or a Varian INOVA 500 (500MHz) spectrometer. ^{13}C Nuclear magnetic resonance (^{13}C NMR) spectroscopy was performed on Bruker AC250 (62.8 MHz) or Bruker AMX400 (100 MHz) spectrometers. Infrared spectroscopy

was performed using a Perkin Elmer 1720-X Spectrometer with the samples analysed as either neat films or in solution between two potassium bromide or sodium chloride disks. Mass spectrometry was performed on a Bruker MicroToF LCMS with ionisation via electrospray and samples introduced by direct infusion via a syringe pump. Mass spectra obtained via chemical ionisation mode were determined using a Finnigan MAT 95 instrument. Melting points were either determined on an electrothermal digital melting point apparatus and are uncorrected or via DSC on a TA Instruments DSC 2920 differential scanning calorimeter. Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC 2920 differential scanning calorimeter. DSC was performed via two methods, either scanning from -50 °C to 105 °C (at a rate of 3 K/min modulated), or from 75 °C down to -50 °C (at a rate of 2 K/min non-modulated). All of the thermal analysis data were analysed using TA Instruments universal analysis software. DSC analysis involved software controlled smoothing (15°) of the derivative (differential) of complex C_p. Rheological analysis was performed on a TA Instruments AR2000 Rheometer at a constant frequency of 10 Hz.

General Experimental for *Tetra*hydroxy *Bis*urethanes 2-5 and 7

Synthesis of 4,4'-Methylenebis(cyclohexyl-carbamic acid 2-[*bis*-(2-hydroxyethyl)-amino]-ethyl ester) 2. To a solution of triethanolamine (3.09g, 20.7 mmol) in dry THF (25 mL) under an argon atmosphere maintained under reflux was added in a dropwise fashion a solution of methylene*bis*cyclohexyl diisocyanate (2.50 g, 10.2 mmol) in dry THF (75 mL) over a period of approximately 90 minutes. This mixture was then heated and stirred for 1 hour and then allowed to cool to room temperature. The reaction was then poured into *n*-pentane (350 mL) that was cooled down to –78 °C. A precipitate formed which was filtered off under vacuum. This material was reprecipitated from *n*-pentane a further two times and the residual solvent was removed under high vacuum. The desired product **2** was obtained as an off-white solid which upon exposure to air changed its physical form to a transparent light brown viscous oil (4.32 g, 76 %). υ_{max}(thin film)/cm^{-1} 3441, 3019, 2933, 2854, 2400, 1707, 1510, 1450, 1419, 1363, 1320, 1216 and 1068; δ_H(250 MHz; δ_6-DMSO; Me_4Si) 0.84-1.48 (20H, m, cyclohexyl CH_2), 2.54-2.59 (8 H, t, *J* 5.0, 4 × N*C*H_2), 2.68-2.71 (4H, m, 2 × CH_2N), 3.11-3.23 (2H, m, 2 × NC*H*), 3.37-3.34 (8H, m, 4 × CH_2OH), 3.94-4.01 (4 H, m, 2 × OCH_2), 4.29-4.34 (4 H, m, 4 × O*H*) and 6.97-7.00 (2 H, d, *J* 7.5, 2 × N*H*); δ_C(62.5 MHz; δ_6-DMSO) 31.5 (*C*H_2), 31.8 (*C*H_2), 32.5 (*C*H_2), 33.3 (*C*H), 49.8 (*C*H), 53.5 (N*C*H_2), 57.0 (*C*H_2N), 61.7 (*C*H_2O), 67.0 (O*C*H_2) and 155.6 (*C*=O); *m/z* (ESI MS) 561.3860 $(M+H)^+$ $C_{27}H_{52}N_4O_8$ requires 561.3819.

Synthesis of 3-(Carbamic acid 2-[*bis*-(2-hydroxyethyl)-amino]-ethyl esteranato)methyl-3,5,5-trimethyl cyclohexyl carbamic acid 2-[*bis*-(2-hydroxyethyl)-amino]-ethyl ester) 3. This compound was synthesised using the general procedure for *tetra*hydroxy *bis*urethanes using triethanolamine (4.32 g, 29.0 mmol) and isophorone diisocyanate (2.49 g, 16.2 mmol) to furnish the desired product **3** initially as an off-white solid which upon exposure to air changed its physical form to a clear brown viscous oil (7.59 g, 90 %). υ_{max}(thin film)/cm^{-1} 3432, 3018, 2957, 2842, 2435, 2400, 1707, 1520, 1461, 1416 and 1217; δ_H(250 MHz; δ_6-DMSO) 0.79-1.48 (15 H, m, (3 × C*H*$_2$) + (3 × C*H*$_3$)), 2.54-2.59 (8 H, m, 4 × C*H*$_2$), 2.68-2.70 (2 H, m, C*H*$_2$NH), 3.39-3.44 (8 H, m, 4 × C*H*$_2$), 3.56-3.63 (1 H, m, C*H*NH), 3.92-3.99 (4 H, m, 2 × OC*H*$_2$), 4.30-4.35 (4 H, m, 4 × O*H*), 6.95-6.99 (1 H, d, *J* 7.5, N*H*) and 7.08-7.11 (1 H, t, *J* 6.5, N*H*); δ_C(62.5 MHz; δ_6-DMSO) 23.2 (*C*H$_3$), 27.5 (*C*H$_3$), 31.4 (*C*), 35.0 (*C*H$_3$), 36.3 (*C*), 41.3 (*C*H$_2$), 43.9 (*C*H), 45.5 (*C*H$_2$), 46.5 (*C*H$_2$), 53.6 (*C*H$_2$N), 54.2 (*C*H$_2$), 57.0 (N*C*H$_2$), 59.3 (*C*H$_2$OH), 61.8 (O*C*H$_2$), 62.0 (O*C*H$_2$), 155.45 (*C*=O), 156.89 (*C*=O); *m/z* (ESI MS) 521.3558 (M+H)$^+$ $C_{24}H_{48}N_4O_8$ requires 521.3506.

Synthesis of 1,6-*Bis*(carbamic acid 2-[*bis*-(2-hydroxyethyl)-amino]-ethyl esteryl)hexane 4. This compound was synthesised using the general procedure for *tetra*hydroxy *bis*urethanes using triethanolamine (4.70 g, 31.5 mmol) and 1,6-hexane diisocyanate (2.50 mL, 15.5 mmol) to furnish the desired product **4** as a clear brown oil (6.65 g, 92 %); υ_{max}(thin film)/cm^{-1} 3353, 3014, 2938, 2861, 2458, 2401, 1699, 1539, 1462, 1415, 1363, 1256, 1218, 144 and 1039; δ_H(250 MHz; δ_6-DMSO) 1.09-1.22 (4 H, m, 2 × C*H*$_2$), 1.34-1.39 (4 H, m, 2 × C*H*$_2$), 2.54-2.57 (8 H, m, 4 × C*H*$_2$), 2.68-2.70 (4 H, m, 2 × C*H*$_2$), 2.92-2.95 (4 H, m, 2 × C*H*$_2$), 3.35-3.41 (8 H, m, 4 × C*H*$_2$), 3.93-3.98 (4 H, t, *J* 6.5, 2 × OC*H*$_2$), 4.30-4.34 (4 H, m, 4 × O*H*) and 7.03-7.08 (2 H, m, 2 × N*H*); δ_C(62.5 MHz; δ_6-DMSO) 26.3 (*C*H$_2$), 29.7 (*C*H$_2$), 40.5 (*C*H$_2$), 54.0 (*C*H$_2$), 57.5 (*C*H$_2$), 59.7 (*C*H$_2$), 62.2 (O*C*H$_2$) and 156.6 (N*C*O$_2$); *m/z* (ESI MS) 467.3097 (M+H)$^+$ $C_{24}H_{48}N_4O_8$ requires 467.3036.

Synthesis of 3,3'-Methyoxy-4,4'-biphenylene(carbamic acid 2-[*bis*-(2-hydroxyethyl)-amino]-ethyl ester) 5. This compound was synthesised using the general procedure for *tetra*hydroxy *bis*urethanes using triethanolamine (2.57 g, 17.2 mmol) and 3,3'-dimethoxybiphenyl-4,4'-diisocyanate (2.50 g, 8.4 mmol) to furnish the desired product **5** as a clear viscous brown oil (4.21 g, 84 %); υ_{max}(thin film)/cm^{-1} 3392, 2952, 2361, 1718, 1588, 1524, 1401, 1325, 1233, 1177, 1137, 1073 and 1039; δ_H(250 MHz; δ_6-DMSO) 2.54-2.61 (8 H, m, 4 × C*H*$_2$), 2.73-2.77 (4 H, m, 2 × C*H*$_2$), 3.43-3.45 (8 H, m, 4 × C*H*$_2$), 3.89-3.91 (6 H, s, 2 × OC*H*$_3$), 4.12 (4 H, m, 2 × OC*H*$_2$). 4.34-4.38 (4 H, s, 4 × O*H*), 7.21-7.26 (4 H, m, 4 × Ar*H*), 7.71-7.74 (2 H, d, *J* 8.0, 2 × Ar*H*) and 8.43 (2 H, s, 2 × N*H*); δ_C(62.5 MHz; δ_6-DMSO) 25.5 (*C*H$_2$), 53.8 (N*C*H$_2$), 56.2 (O*C*H$_3$), 59.8 (*C*H$_2$OH), 63.1

(O*C*H_2), 109.9 (Ar*C*), 126.7 (Ar*C*), 136.4 (Ar*C*), 150.1 (Ar*C*) and 154.2 (*C*=O); *m/z* (ESI MS) 595.2961 $(M+H)^+$ $C_{28}H_{42}N_4O_{10}$ requires 595.2901.

Synthesis of 4,4'-Methylene*bis*(phenyl-carbamic acid (5-hydroxy-3-(2-hydroxyethyl) pentyl ester) 7. This compound was synthesised via addition of 3-(2-hydroxyethyl)pentane-1,5-diol (2.07 g, 14.0 mmol) to MDI (1.75 g, 7.0 mmol) using the general procedure for *tetra*hydroxy *bis*urethanes and yielded the desired product **7** as a yellow tacky oil (3.42 g, 90 %). υ_{max}(thin film)/cm^{-1} 3344, 2936, 2497, 2247, 2132, 2072, 1705, 1616, 1517, 1445, 1411, 1380, 1249 and 1122; δ_H(250 MHz; CD_3OD) 1.47-1.78 (14 H, m, (6 × C*H*$_2$) + (2 × C*H*)), 3.53-3.58 (8 H, t, *J* 7.0, 4 × C*H*$_2$OH), 3.78 (2 H, s, ArC*H*$_2$Ar), 4.08-4.14 (4 H, t, *J* 7.0, 2 × OC*H*$_2$), 7.00-7.03 (4 H, AA'XX' system, 4 × Ar*H*) and 7.23-7.27 (4 H, AA'XX' system, 4 × Ar*H*); δ_C(62.5 MHz; CD_3OD) 30.0 (*C*H), 34.6 (*C*H_2), 38.1 (*C*H_2), 41.9 (Ar*C*H_2Ar), 61.2 (*C*H_2OH), 64.5 (O*C*H_2), 120.5 (Ar*C*), 130.6 (Ar*C*), 138.0 (Ar*C*), 138.6 (Ar*C*) and 156.6 (*C*=O); *m/z* (ESI MS) 569.2826 $(M+Na)^+$ $C_{29}H_{42}N_2O_8Na$ requires 569.2839.

General Experimental for *Tetra*butyl *Bis*urethanes 9-13

Synthesis of 4,4'-Methylenebis(cyclohexyl-carbamic acid 2-[*bis*-butyl-amino]-ethyl ester) 9. To a solution of methylene*bis*cyclohexyl diisocyanate (2.50 mL, 10.2 mmol) in dry THF (50 mL) under an argon atmosphere maintained under reflux was added a solution of *N*-dibutylaminoethanol (4.50 g, 22.4 mmol) in dry THF. The reaction mixture was stirred and heated for a period of 12 hours and then allowed to cool to room temperature. The solution was concentrated *in vacuo* to yield a light brown viscous oil. The crude product was purified by chromatography (silica; 90:10 dichloromethane:methanol) to afford **9** as a light brown oil (5.02 g, 81 %); υ_{max}(thin film) /cm^{-1} 3017, 2932, 2861, 2400, 1708, 1510, 1458, 1415, 1377, 1319, 1216, 1083 and 1040; δ_H(250 MHz; $CDCl_3$; Me_4Si) 0.84-1.48 (48H, m, (cyclohexyl CH_2) + (4 × CH_3) + (8 × CH_2 butyl), 2.43-2.48 (8 H, m, 4 × NC*H*$_2$), 2.65-2.69 (4 H, m, 2 × C*H*$_2$N), 3.39 (2H, m, 2 × NC*H*), and 4.09-4.14 (4 H, m, 2 × OC*H*$_2$); δ_C(62.5 MHz; $CDCl_3$) 14.5 (*C*H_3), 21.0 (*C*H_2), 28.4 (*C*H_2), 29.6 (*C*H_2), 30.1 (*C*H_2), 32.4 (*C*H_2), 33.8 (*C*H), 50.7 (*C*H), 53.0 (N*C*H_2), 54.9 (*C*H_2N), 63.1 (O*C*H_2) and 156.2 (*C*=O); *m/z* (ESI MS) 609.5302 $(M+H)^+$ $C_{35}H_{68}N_4O_4$ requires 609.5274.

Synthesis of 3-(Carbamic acid 2-[*bis*-butyl-amino]-ethyl esteranato)methyl-3,5,5-trimethyl cyclohexyl carbamic acid 2-[*bis*-butyl-amino]-ethyl ester) 10. To a solution of isophorone diisocyanate (2.50 mL, 16.1 mmol) in dry THF (50 mL) under an argon atmosphere maintained under reflux was added a solution of *N*-dibutylaminoethanol (7.14 mL, 35.5 mmol) in dry THF. The reaction mixture was stirred and heated for a period of 12 hours and then allowed to cool to room

temperature. The solution was concentrated *in vacuo* to yield a brown oil. The crude product was purified by chromatography (silica; 90:10 dichloromethane:methanol) to afford **10** as a light brown oil (6.14 g, 67 %); υ_{max}(thin film)/cm^{-1} 3017, 2958, 2932, 2872, 1708, 1519, 1460, 1378, 1306, 1217, 1137 and 1035; δ_H(250 MHz; δ_6-DMSO) 0.78-1.43 (43 H, m, (7 × C*H*$_3$) + (11 × C*H*$_2$), 2.35-2.41 (8 H, m, 4 × NC*H*$_2$), 2.51-2.55 (4 H, m, 2 × C*H*$_2$N), 2.69-2.72 (2 H, m, NHC*H*$_2$), 3.56-3.59 (2 H, m, C*H*NH) and 3.90-3.97 (4 H, m, 2 × OC*H*$_2$); δ_C(62.5 MHz; δ_6-DMSO) 14.3 (*C*H$_3$), 20.3 (*C*H$_2$), 23.5 (*C*H$_3$), 27.8 (*C*H$_3$), 29.4 (*C*H$_2$), 31.7 (*C*), 35.3 (*C*H$_3$), 36.7 (*C*), 41.7 (*C*H$_2$), 44.2 (*C*H), 45.9 (*C*H$_2$), 47.1 (*C*H$_2$), 52.8 (NCH$_2$), 54.0 (*C*H$_2$N), 62.1 (OCH$_2$), 62.3 (OCH$_2$), 155.8 (*C*=O) and 157.2 (N*C*O$_2$); *m/z* (ESI MS) 569.4997 (M+H)$^+$ $C_{32}H_{64}N_4O_4$ requires 569.4961.

Synthesis of 1,6-*Bis*(carbamic acid 2-[*bis*-butyl-amino]-ethyl esteryl)hexane 11. This compound was synthesised using the general procedure for *tetra*butyl *bis*urethanes using dibutylethanolamine (6.29 mL, 31.2 mmol) and 1,6-hexane diisocyanate (2.50 mL, 15.5 mmol) to furnish the desired product **11** as a clear tan-coloured oil (7.71 g, 96 %); υ_{max}(thin film)/cm^{-1} 2932, 2862, 2807, 1698, 1536, 1465, 1412, 1377, 1256 and 1143; δ_H(250 MHz; δ_6-DMSO) 0.83-0.89 (12 H, t, *J* 7.0, 4 × C*H*$_3$), 1.11-1.36 (24 H, *m*, 12 × C*H*$_2$), 2.35-2.41 (8 H, m, 4 × C*H*$_2$), 2.51-2.57 (4 H, m, 2 × C*H*$_2$), 2.89-2.97 (4 H, m, 2 × C*H*$_2$), 3.91-3.96 (4 H, t, *J* 6.5, 2 × OC*H*$_2$) and 7.01-7.06 (2 H, t, *J* 5.5, 2 × N*H*); δ_C(62.5 MHz; δ_6-DMSO) 14.3 (*C*H$_3$), 20.3 (*C*H$_2$), 26.3 (*C*H$_2$), 29.4 (*C*H$_2$), 29.8 (*C*H$_2$), 40.9 (*C*H$_2$), 52.8 (*C*H$_2$), 54.0 (*C*H$_2$), 62.2 (OCH$_2$) and 156.5 (N*C*O$_2$); *m/z* (ESI MS) 515.4533 (M+H)$^+$ $C_{28}H_{58}N_4O_4$ requires 515.4492.

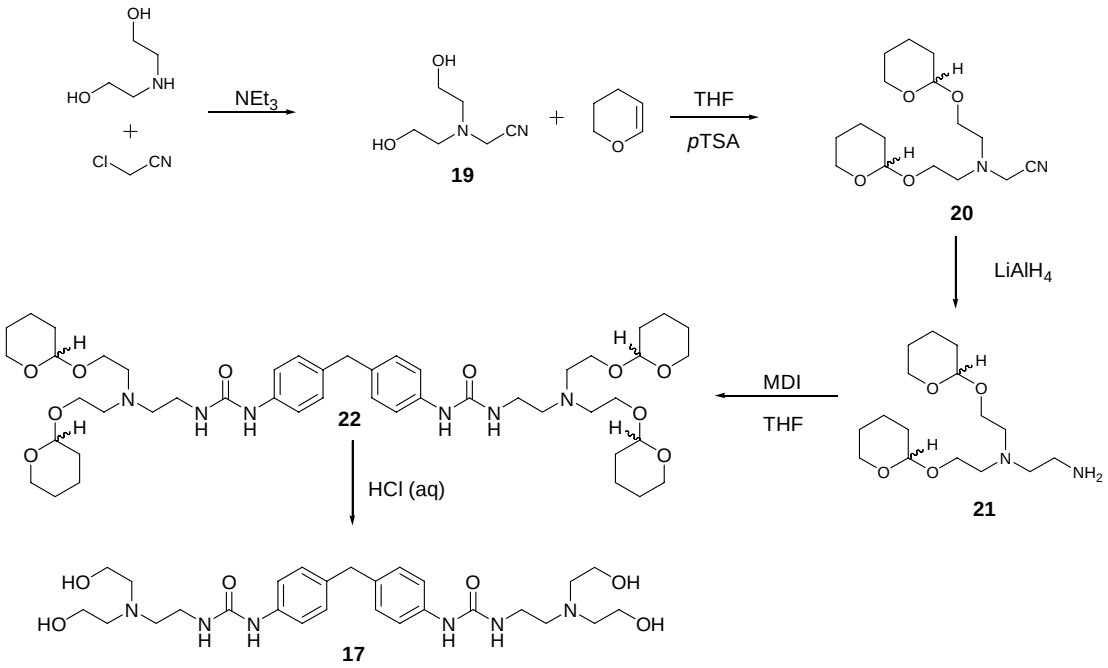
Synthesis of 3,3'-Methyoxy-4,4'-biphenylene(carbamic acid 2-[*bis*-butyl-amino]-ethyl ester) 12. This compound was synthesised using the general procedure for *tetra*butyl *bis*urethanes using dibutylethanolamine (3.74 mL, 18.6 mmol) and 3,3'-dimethoxybiphenyl-4,4'-diisocyanate (2.50 g, 8.4 mmol) to furnish the desired product **12** as a bright orange oil (4.36 g, 81 %); υ_{max}(thin film)/cm^{-1} 3019, 2960, 2934, 2873, 2400, 1728, 1612, 1588, 1520, 1458, 1464, 1327, 1215, 1176 and 1135; δ_H(250 MHz; δ_6-DMSO) 0.84-0.90 (12 H, m, 4 × C*H*$_3$), 1.26-1.39 (16 H, m, 8 × C*H*$_2$), 2.39-2.45 (8 H, m, 4 × C*H*$_2$), 2.62-2.67 (4 H, t, *J* 6.0, 2 × C*H*$_2$), 3.90-3.91 (6 H, m, 2 × OC*H*$_3$), 4.07-4.12 (4 H, m, 2 × OC*H*$_2$), 7.20-7.26 (4 H, m, 4 × Ar*H*), 7.69-7.73 (2 H, d, *J* 8.0, 2 × Ar*H*) and 8.33 (2 H, s, 2 × N*H*); δ_C(62.5 MHz; δ_6-DMSO) 14.3 (*C*H$_3$), 20.3 (*C*H$_2$), 25.5 (*C*H$_2$), 29.4 (*C*H$_2$), 54.1 (NCH$_2$), 56.2 (OCH$_3$), 63.1 (OCH$_2$), 109.8 (Ar*C*), 118.8 (Ar*C*), 126.7 (2 × Ar*C*), 136.5 (Ar*C*), 150.1 (Ar*C*) and 154.1 (*C*=O); *m/z* (ESI MS) 643.4429 (M+H)$^+$ $C_{36}H_{58}N_4O_6$ requires 643.4390.

Synthesis of 1,4-Phenyl *bis*(carbamic acid 2-[*bis*-butyl-amino]-ethyl ester) 13. This compound was synthesised using the general procedure for *tetra*butyl *bis*urethanes using dibutylethanolamine

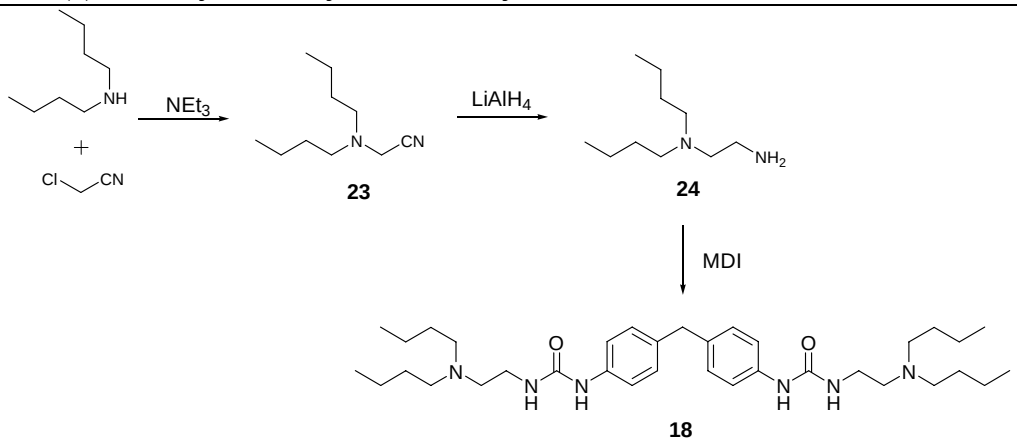
(4.33 g, 25.0 mmol) and 1,4-phenyl diisocyanate (2.00 g, 12.5 mmol) to furnish the desired product **13** as a light yellow crystalline solid (5.21 g, 82 %); m.p. 99.3-101.8 °C; υ_{max}(KBr disc)/cm^{-1} 2925, 2854, 1728, 1535, 1494, 1409, 1310, 1207 and 1069; δ_H(250 MHz; $CDCl_3$; Me_4Si) 0.88-0.93 (12 H, t, *J* 7.0, 4 × C*H*$_3$), 1.22-1.49 (16 H, m, 8 × C*H*$_2$), 2.45-2.51 (8 H, m, 4 × NC*H*$_2$), 2.70-2.75 (4 H, t, *J* 6.0, 2 × C*H*$_2$N), 4.18-4.23 (4 H, t, *J* 6.0, 2 × OC*H*$_2$), 6.65 (2 H, s, 2 × N*H*) and 7.30 (4 H, s, 4 × Ar*H*); δ_C(62.5 MHz; $CDCl_3$) 14.5 (*C*H$_3$), 21.0 (*C*H$_2$), 29.6 (*C*H$_2$), 53.0 (*C*H$_2$N), 54.8 (N*C*H$_2$), 63.7 (O*C*H$_2$), 120.0 (Ar*C*) and 134.0 (Ar*C*); *m/z* (ESI MS) 507.3927 (M+H)$^+$ $C_{28}H_{50}N_4O_4$ requires 507.3866.

Synthesis of *Bis*urea compounds 17 and 18

The *bis*urea compounds **17** and **18** were synthesised by reacting 4,4'-methylene*bis*(phenyl isocyanate) with two different amines (see **Schemes S1** and **S2**). The dihydroxyamine and dibutylamine precursors were synthesised by the initial production of the corresponding nitrile derivatives and then subsequent reduction to form the desired amines.



Scheme S1 Synthesis of the *bis*urea **17** featuring hydroxyl terminal groups



Scheme S2 Synthesis of the *bis*urea **18** featuring *n*-butyl terminal groups

Synthesis of Cyanomethyl-*N,N-bis*(2-hydroxyethyl)amine 19. To a stirred solution of diethanolamine (15.35 g, 146.0 mmol) in THF (50 mL) was added triethylamine (30.0 mL, 146.0 mmol). Chloroacetonitrile (11.09 mL, 175.2 mmol) was then added slowly and the mixture stirred and heated at 40 °C for three hours. The white precipitate formed was filtered under vacuum and the resultant solution was concentrated *in vacuo*. The resultant oil was dissolved in dichloromethane and washed several times with water. The organic layer was separated and dried over magnesium sulfate before filtering and concentration *in vacuo*. The crude product was purified via column chromatography on silica with 30 % ethyl acetate in hexane as the eluent to furnish the product **19** as a clear yellow oil (20.12 g, 96 %); υ_{max}(thin film)/cm^{-1} 3382, 2953, 2888, 2834, 2362, 2235, 1646, 1426, 1363, 1328, 1136, 1044, 975, 935 and 887; δ_H(250 MHz; CD_3OD) 2.70-2.74 (4 H, m, 2 × NC*H*$_2$), 3.64-3.68 (4 H, t, *J* 5.5, 2 × NC*H*$_2$) and 3.82 (2 H, s, C*H*$_2$CN); δ_C(62.5 MHz; $CDCl_3$) 42.3 (*C*H$_2$CN), 56.2 (N*C*H$_2$), 59.3 (*C*H$_2$OH) and 116.0 (*C*N); *m/z* (ESI MS) 167.0796 $(M+Na)^+$ $C_6H_{12}N_2O_2Na$ requires 167.0796. The analytical data obtained was consistent with the data reported for this compound by Song *et al*.[1]

Synthesis of Cyanomethyl-*bis*((2-(tetrahydro-2*H*-pyran-2-yloxy)ethyl) amine 20. To a solution of cyanomethyl-*N,N-bis*(2-hydroxyethyl)amine **19** (6.11 g, 42.4 mmol) in THF (100 mL) was added 3,4-dihydropyran (39.00 mL, 423.8 mmol) and *p*-toluene sulfonic acid (8.86 g, 46.6 mmol). The mixture was stirred under reflux for a period of 16 hours. Sodium bicarbonate (7.12 g, 84.4 mmol) was then added to the reaction mixture and the solution was then concentrated *in vacuo*. Dichloromethane (100 mL) was added followed by water (100 mL) and the organic layer was then separated and dried over magnesium sulfate. The mixture was filtered and the filtrate was concentrated *in vacuo* before purification via column chromatography on silica (20 % ethyl acetate in hexane as the eluent) to furnish the desired product **20** as a yellow oil (11.35 g, 86 %); υ_{max}(thin film)/cm^{-1} 2945, 2872, 2232, 1727, 1655, 1455, 1353, 1324, 1261, 1202, 1184, 1122, 1034, 976,

924, 905 and 871; δ_H(250 MHz; $CDCl_3$; Me_4Si) 1.50-1.82 (12 H, m, 6 × C*H*$_2$), 2.82-2.87 (4 H, t, *J* 5.5, 2 × NC*H*$_2$,), 3.49-3.58 (4 H, m, 2 × (C*H*$_a$H$_b$ + C*H*$_a$H$_b$)), 3.82-3.89 (6 H, m, C*H*$_2$CN + 2 × (CH$_a$*H*$_b$ + CH$_a$*H*$_b$)) and 4.60-4.62 (2 H, m, 2 × OC*H*); δ_C(62.5 MHz; $CDCl_3$) 19.3 (*C*H$_2$), 25.3 (*C*H$_2$), 30.5 (*C*H$_2$), 43.6 (*C*H$_2$CN), 54.2 (N*C*H$_2$), 62.2 (O*C*H$_2$), 65.9 (O*C*H$_2$), 98.8 (O*C*H) and 115.8 (*C*N); *m/z* (ESI MS) 335.1946 $(M+Na)^+$ $C_{16}H_{28}N_2O_4Na$ requires 335.1947.

Synthesis of 2-aminoethyl-*bis*(2-(tetrahydro-2*H*-pyran-2-yloxy)ethyl) amine 21. Lithium aluminium hydride (2.19 g, 57.6 mmol) was transferred into a round bottom flask and dry THF (75 mL) was added. A solution of nitrile **20** (6.01 g, 19.2 mmol) in THF (20 mL) was then added dropwise. The reaction was then stirred for approximately 24 hours. The mixture was then quenched carefully by addition of methanol followed by water and a white solid was formed. The solid was filtered off and the solvent removed *in vacuo* to yield a yellow oil. The resultant oil was dissolved in dichloromethane (250 mL) and washed water (250 mL). The dichloromethane was then removed *in vacuo* to yield the desired product **21** as a yellow oil (5.54 g, 91 %); υ_{max}(thin film)/cm^{-1} 2941, 2868, 1654, 1455, 1441, 1352, 1322, 1261, 1201, 1184, 1137, 1121, 1076, 1033, 985, 906 and 870; δ_H(250 MHz; $CDCl_3$; Me_4Si) 1.43-1.76 (12 H, m, 6 × C*H*$_2$), 2.54-2.58 (2 H, m, C*H*$_2$NH$_2$), 2.64-2.73 (6H, m, C*H*$_2$N + (2 × NC*H*$_2$)), 3.37-3.48 (4 H, m, 2 × (C*H*$_a$H$_b$ + C*H*$_a$H$_b$)), 3.70-3.85 (6 H, m, C*H*$_2$CN + 2 × (CH$_a$*H*$_b$ + CH$_a$*H*$_b$)) and 4.52-4.54 (2 H, m, 2 × OC*H*); δ_C(62.5 MHz; $CDCl_3$) 19.8 (*C*H$_2$), 25.7 (*C*H$_2$), 31.0 (*C*H$_2$), 39.9 (*C*H$_2$NH$_2$), 54.6 (N*C*H$_2$), 57.5 (*C*H$_2$N), 62.9 (O*C*H$_2$), 66.2 (O*C*H$_2$) and 99.3 (*C*H); *m/z* (ESI MS) 317.2443 $(M+H)^+$ $C_{16}H_{32}N_2O_4$ requires 317.2396.

Synthesis of 4,4'-methylene*bis*(phenyl 2-(*bis*(2-(tetrahydro-2*H*-pyran-2-yloxy)ethyl) ethyl amino carbonyl amine) 22. To a solution of 4,4'-methylene*bis*(phenylisocyanate) (1.19 g, 4.7 mmol) in dry THF (30 mL) was added a solution of 2-aminoethyl-*bis*((2-(tetrahydro-2*H*-pyran-2-yloxy)ethyl) amine **21** (3.00 g, 9.5 mmol) in dry THF (10 mL) under an argon atmosphere and the mixture was maintained under reflux for a period of 3 hours. This reaction mixture was then allowed to cool to room temperature and concentrated *in vacuo*. The crude product was then purified via chromatography on silica (20 % methanol in ethyl acetate as the eluent) to furnish the desired product **22** as a yellow oil (3.78 g, 90 %); υ_{max}(thin film)/cm^{-1} 2947, 2253, 1684, 1541, 1385, 1121, 1074, 1031 and 909; δ_H(250 MHz; $CDCl_3$; Me_4Si) 1.43-1.88 (24 H, m, 12 × C*H*$_2$), 2.70-2.72 (4 H, m, 2 × C*H*$_2$N), 2.77-2.81 (8 H, m, 4 × NC*H*$_2$), 3.19-3.41 (4 H, br m, 2 × NHC*H*$_2$), 3.46-3.55 (8 H, m, 4 × (C*H*$_a$H$_b$ + C*H*$_a$H$_b$)), 3.72-3.89 (10 H, m, (4 × (CH$_a$*H*$_b$ + CH$_a$*H*$_b$)) + ArC*H*$_2$Ar), 4.60 (4 H, m, 4 × OC*H*), 5.90 (2 H, br s, 2 × N*H*), 6.99-7.07 (4 H, AA'XX' system, 4 ×

Ar*H*) and 7.22-7.27 (6 H, m, (4 × Ar*H*) + (2 × N*H*)); δ_C(62.5 MHz; $CDCl_3$) 20.2 (*C*H_2), 25.8 (*C*H_2), 31.1 (*C*H_2), 39.0 (NH*C*H_2), 41.0 (Ar*C*H_2Ar), 54.7 (*C*H_2N), 55.2 (N*C*H_2), 63.3 (O*C*H_2), 66.6 (O*C*H_2), 99.9 (O*C*H), 119.9 (Ar*C*), 129.7 (Ar*C*), 135.8 (Ar*C*), 138.0 (Ar*C*) and 156.7 (*C*=O); *m/z* (ESI MS) 883.5500 $(M+H)^+$ $C_{47}H_{74}N_6O_{10}$ requires 883.5500.

Synthesis of 4,4'-methylene*bis*(phenyl 2-[*bis*-2-hydroxyethyl]-ethyl amino carbonyl amine) 17. To a solution of 4,4'-methylene*bis*(phenyl 2-(*bis*(2-(tetrahydro-2*H*-pyran-2-yloxy)ethyl) ethyl amino carbonyl amine) **22** (2.92 g, 3.3 mmol) in THF (20 mL) and methanol (10 mL) was added hydrochloric acid (2M, 10 mL) and the reaction mixture was stirred and heated to a temperature of 50 °C for 2 hours. Sodium bicarbonate was added until the pH was basic and the reaction mixture was filtered and concentrated *in vacuo*. The crude product was dissolved in the minimum volume of methanol and chloroform then was added to precipitate out the dissolved salts. The mixture was filtered and concentrated *in vacuo* to furnish the desired product **17** as a light yellow crystalline solid (1.42 g, 78 %); m.p. 89.4-90.5 °C; υ_{max}(KBr disc)/cm^{-1} 3343, 2491, 2243, 2216, 2072, 1941, 1656, 1460, 1123 and 977; δ_H(250 MHz; $CDCl_3$/CD_3OD) 2.62-2.66 (12 H, m, (2 × C*H*$_2$N) + (4 × NC*H*$_2$)), 3.24-3.28 (4 H, m, 2 × N*H*CH_2), 3.57-3.61 (8 H, m, 4 × C*H*$_2$OH), 3.83 (2 H, s, ArC*H*$_2$Ar), 7.03-7.07 (4 H, AA'XX' system, 4 × Ar*H*) and 7.22-7.26 (4 H, AA'XX' system, 4 × Ar*H*); δ_C(62.5 MHz; δ_6-DMSO) 37.7 (*C*H_2NH), 41.8 (Ar*C*H_2Ar), 54.9 (C*H*$_2$N), 57.1 (NC*H*$_2$), 59.4 (*C*H_2OH), 118.1 (ArC), 129.1 (ArC), 134.5 (ArC), 138.8 (ArC) and 155.7 (C=O); *m/z* (ESI MS) 547.3242 $(M+H)^+$ $C_{27}H_{42}N_6O_6$ requires 547.3199.

Synthesis of Cyanomethyl-*N*,*N*-*bis*butyl amine 23[2]

This compound was synthesised via the same procedure employed for the synthesis of cyanomethyl amine **19** using *N*,*N*-bisbutyl amine (6.50 mL, 38.7 mmol) and chloroacetonitrile (2.45 mL, 38.7 mmol) to afford the desired product **23** as a yellow oil (5.72 g, 87 %); IR (Thin Film, KBr) ν_{max}/cm^{-1} 2959, 2933, 2823, 1460, 1426, 1379, 1320, 1183, 1151, 1129, 1094, 952, 935, 903, 860, 802; δ_H(250 MHz; $CDCl_3$) 0.89-0.95 (6H, t, *J* 7.0, 2 × CH_3), 1.29-1.47 (8 H, m, 4 × C*H*$_2$), 2.46-2.52 (4 H, t, *J* 7.0, 2 × C*H*$_2$), 3.56 (2H, s, C*H*$_2$); δ_C(62.5 MHz; $CDCl_3$) 14.26 (*C*H_3), 20.67 (*C*H_2), 29.86 (*C*H_2), 42.04 (*C*H_2CN), 54.24 (N*C*H_2), 115.43 (*C*N); ESI LCMS calcd. for $C_{10}H_{20}N_2$ $[M+H]^+$: *m/z* 169.1660, found *m/z* 169.1699 $(M+H)^+$. The analytical data obtained was consistant with the data reported for this compound by Najer *et al.*[2]

Synthesis of 2-Aminoethyl-*N,N-bis*butyl amine 24

This compound was synthesised via the same procedure employed for the synthesis of amine **21** from nitrile **20** using cyanomethyl-*N,N*-bisbutyl amine **23** (6.00 g, 35.7 mmol) to afford the desired product **24** as a yellow oil (5.26 g, 86 %); IR (Thin Film, KBr) ν_{max}/cm^{-1} 3357, 2956, 2870, 2805, 1570, 1467, 1376, 1305; δ_H(250 MHz; $CDCl_3$) 0.88-0.94 (6 H, t, *J* 7.0 × C*H*$_3$), 1.58 (2 H, br s, N*H*$_2$), 1.29-1.47 (8 H, m, 4 × C*H*$_2$), 2.36-2.47 (6H, m, C*H*$_2$N + (2 × NC*H*$_2$)), 2.69-274 (2 H, t, *J* 6.0, C*H*$_2$NH$_2$); δ_C(62.5 MHz; $CDCl_3$) 14.4 (*C*H$_3$), 21.0 (*C*H$_2$), 29.8 (*C*H$_2$), 54.4 (N*C*H$_2$), 57.4 (*C*H$_2$N); ESI LCMS calcd. for $C_{10}H_{24}N_2$ $[M+H]^+$: *m/z* 173.1973, found *m/z* 173.2011 $(M+H)^+$. The analytical data obtained was consistent with the data reported for this compound by Najer *et al*.[2]

Synthesis of 4,4'-Methylene*bis*(phenyl 2-[*bis*-butyl-amino]-ethyl amino carbonyl amine) 18. To a solution of 4,4'-methylenebis(phenylisocyanate) (2.18 g, 8.7 mmol) in dry THF (40 mL) under an argon atmosphere maintained under reflux was added a solution of 2-aminoethyl-*N,N-bis*butyl amine **23** (3.00 g, 17.4 mmol) in dry THF (10 mL). The reaction mixture was stirred and heated under reflux for a period of 12 hours and then allowed to cool to room temperature. The solution was concentrated *in vacuo* to yield the product **17** as a light yellow solid that did not require further purification necessary (4.38 g, 85 %); m.p. 114.9-117.2 °C; υ_{max}(KBr disc)/cm^{-1} 3430, 3338, 2959, 2933, 2864, 2817, 1793, 1662, 1601, 1513, 1469 and 1412; δ_H(62.5 MHz; δ_6-DMSO) 0.83-0.89 (12 H, t, *J* 7.0, 4 × C*H*$_3$), 1.17-1.43 (16 H, m, 8 × C*H*$_2$), 2.38-2.44 (8 H, m, 4 × C*H*$_2$), 2.53-2.57 (4 H, t, *J* 5.5, 2 × C*H*$_2$), 3.24-3.30 (4 H, m, 2 × C*H*$_2$), 5.44 (2 H, br s, 2 × N*H*), 6.98-7.09 (4 H, AA'XX' system, 4 × ArC*H*) and 7.17-7.21 (4 H, AA'XX' system, 4 × ArC*H*); δ_C(62.5 MHz; $CDCl_3$)14.5 (*C*H$_3$), 21.0 (*C*H$_2$), 29.2 (*C*H$_2$), 38.9 (*C*H$_2$NH), 41.0 (Ar*C*H$_2$Ar), 54.4 (C*H*$_2$N + N*C*H$_2$), 121.0 (ArC), 129.7 (ArC), 136.2 (ArC), 137.7 (ArC) and 157.6 (C=O); *m/z* (ESI MS) 595.4686 $(M+H)^+$ $C_{35}H_{58}N_6O_2$ requires 595.4655.

^{1}H NMR Spectroscopic Determination of Association Constants

Association constants were determined via concentration based ^{1}H NMR spectroscopic titrations with data being analysed with the non-linear least squares regression analysis software BioKin Dynafit. The concentration based ^{1}H NMR spectroscopic data obtained for **16** could only be fitted to a dimerisation model whereas the data obtained for **2** could successfully be fitted to a model encompassing assemblies of multiple molecules arising from association of both hydrogen bonding units on the molecule. An example of the results obtained by this process for model compound **16** in $CDCl_3$ is shown in **Figure S1**.

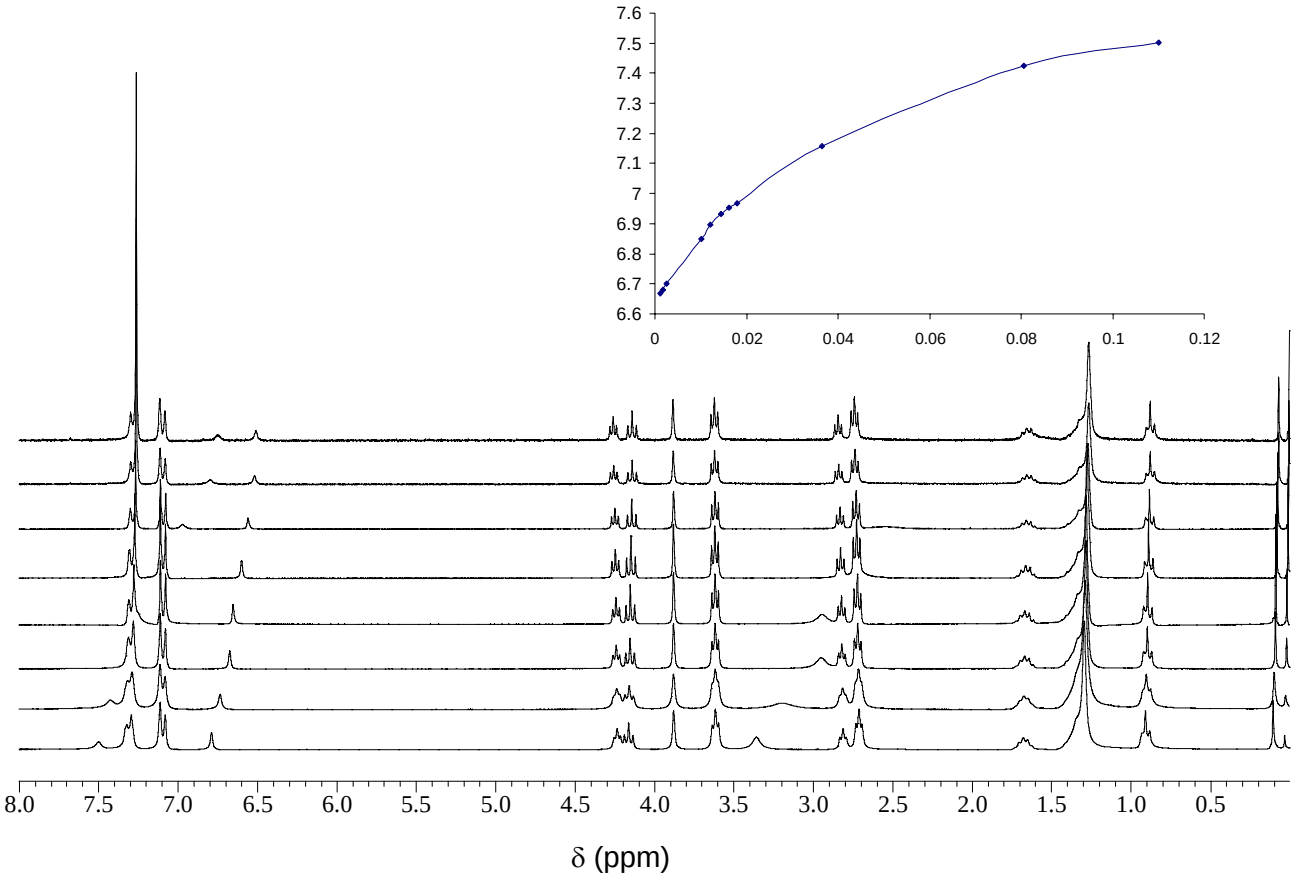


Figure S1 ^{1}H NMR spectroscopic titrations of *bis*urethane **16** with the associated non-linear least squares regression analysis used to determine the dimerisation constant

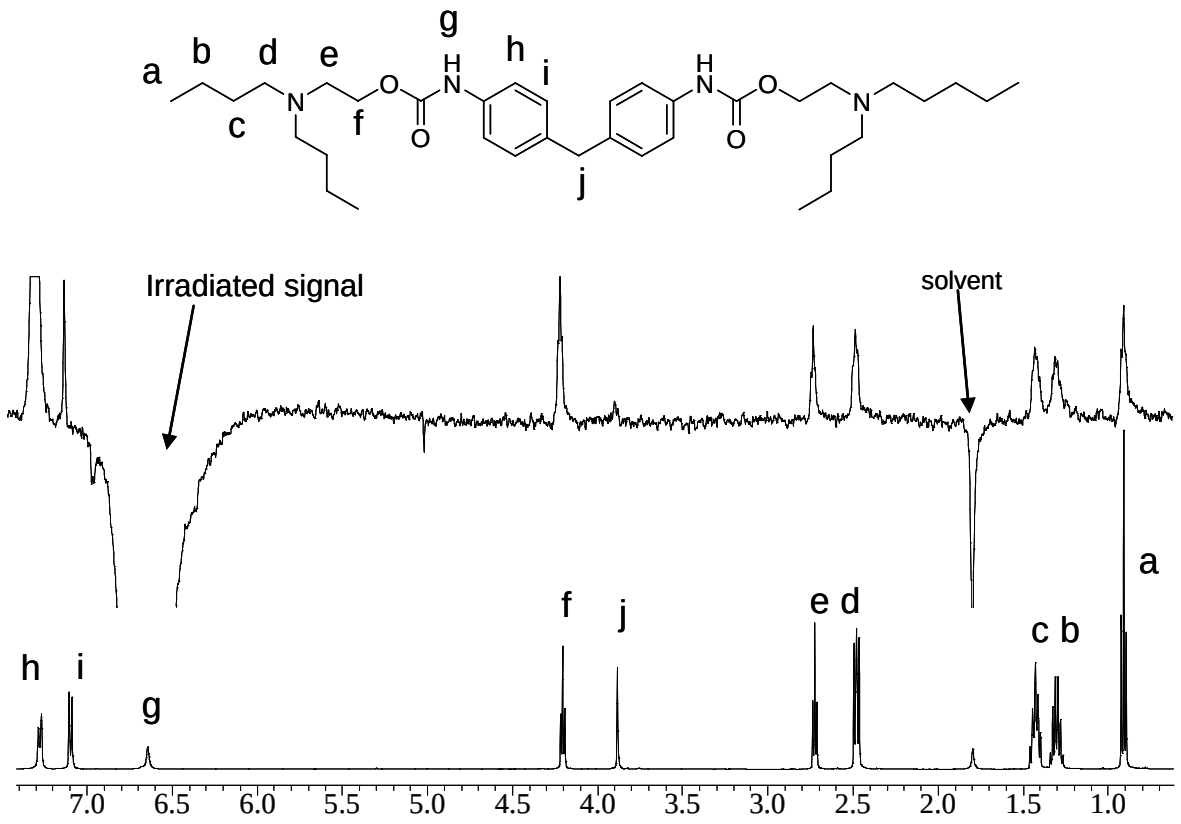


Figure S2. ^{1}H NMR spectrum (bottom) and 1D-NOESY spectrum (top) of **8** in CD_3CN.

Solution Viscometry

Solution based viscometry was carried out in chloroform using the *bis*urethane **2** in order to obtain values of specific viscosity that were dependent on concentration. A plot of the results obtained is shown in **Figure S3**.

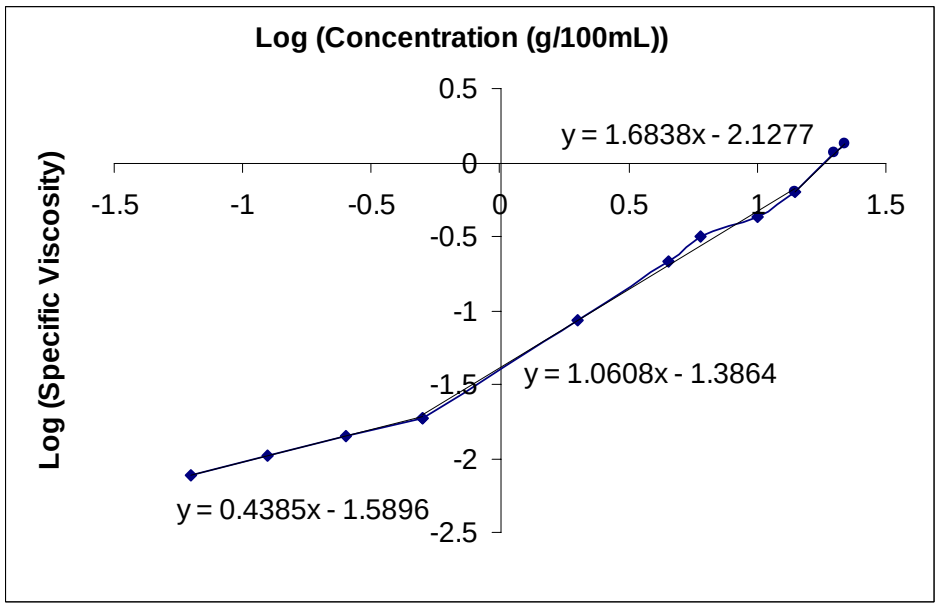
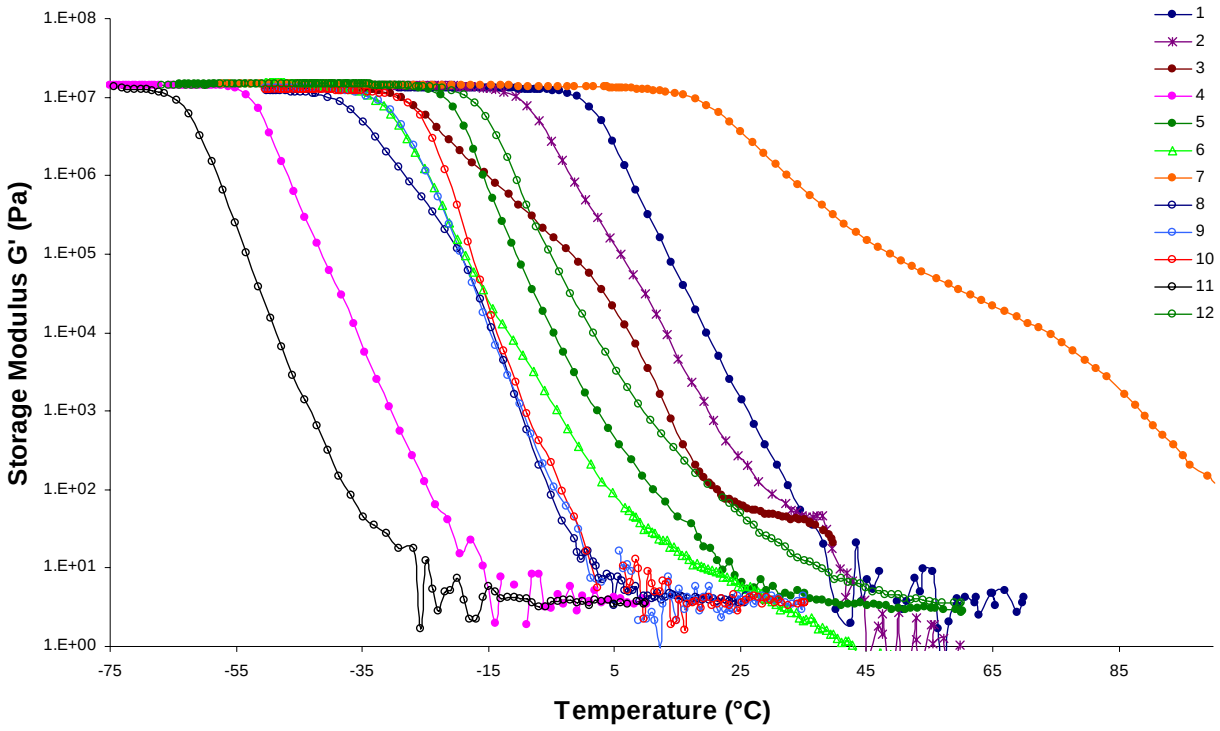


Figure S3 Plot of specific viscosity *versus* concentration for bisurethane **2**

Rheological Analysis

Rheological analysis (storage modulus *versus* temperature) for all of the *bis*urethane compounds **1**-**12** are shown below.



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