Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Controlled Self-Sorting in the Assembly of Multi-Gelator Gels

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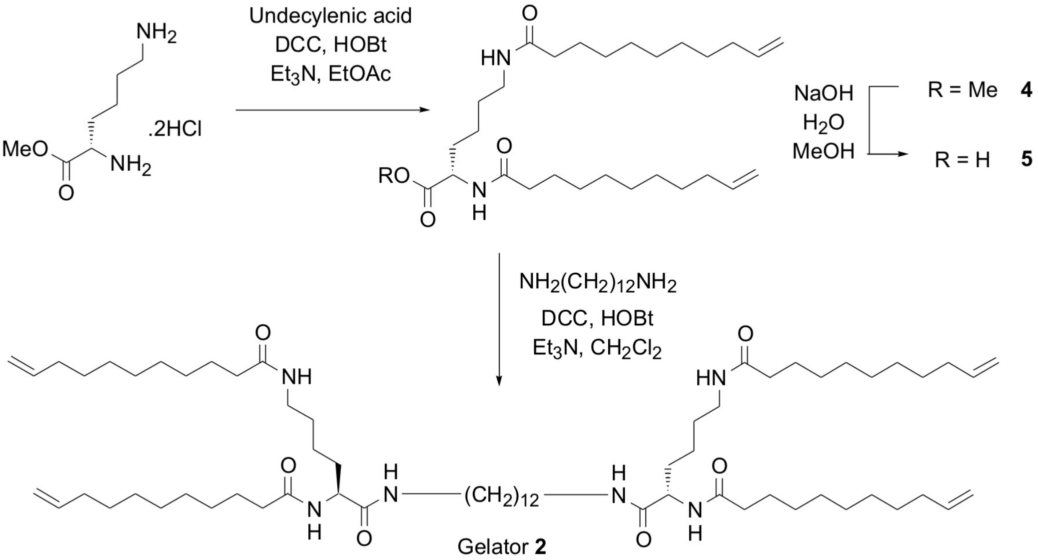
Synthesis and Characterisation of Gelators

General Experimental Methods. L-Lysine methyl ester dihydrochloride was synthesized according to well established literature methodology.[1] The synthesis of compound **1** was carried out according to our published methods.[2] The synthesis of compound **3** was recently reported by us in the literature.[3] Gelator **2** was synthesized according to a three-step reaction procedure (see Scheme 1). All other compounds required in the synthesis were purchased from standard commercial suppliers.



Scheme 1. Synthesis of gelator **2**.

Silica column chromatography was carried out using silica gel provided by Fluorochem Ltd. (35-70µ). Thin layer chromatography was performed on commercially available Merck aluminium backed silica plates. Proton and carbon

NMR spectra were recorded on a Jeol 400 spectrometer (^{1}H 400 MHz, ^{13}C 100 MHz). Samples were recorded as solutions in deuterated NMR solvents as stated and chemical shifts (δ) are quoted in parts per million, referenced to residual solvent. Coupling constant values (J) are given in Hz. The level of assignment of ^{1}H NMR spectra was achieved using model compounds, literature data and standard knowledge of ^{1}H NMR. DEPT experiments were used to assist in the assignment of ^{13}C NMR spectra. Melting points were measured on an Electrothermal IA 9100 digital melting point apparatus and are uncorrected. Positive and negative ion electrospray mass spectra were recorded on a Finnigan LCQ mass spectrometer.

Compound 4

L-Lysine methyl ester dihydrochloride (7.03 g, 30.0 mmol) was suspended in EtOAc (40 mL). Et_3N (8.86 mL, 63 mmol) was added, followed by undecylenic acid (12.75 mL, 63 mmol). The mixture was stirred under a nitrogen atmosphere for 5 min. The mixture was then cooled to 0°C and HOBt (8.53 g, 63 mmol) and DCC (13.02 g, 63 mmol) were added simultaneously as a mixture of solids. The reaction was allowed to return to room temperature and stirred for 24 h. The precipitate was removed by filtration and discarded. The filtrate was then washed with aqueous $NaHSO_4$ (8 g in 50 mL), satd. aq. $NaHCO_3$ (50 mL) and H_2O (50 mL). The solution was dried ovber $MgSO_4$, filtered and rotary evaporated to produce a white solid. The crude product was purified by column chromatography (silica, EtOAc:DCM, 75:25) to give the product in a yield of 73% (10.7 g). R_f 0.38 (EtOAc:hexane, 7:3, CeMo stain); m.p. 71-72°C; α_D^{293} + 4.8 (c = 1.0, $CHCl_3$), - 8.1(c = 1.0, MeOH); δ_H (270 MHz, $CDCl_3$)

6.19 (1H, d, *J* = 8, CONH), 5.84-5.72 (2H, m, C*H*=CH_2), 5.72-5.70 (1H, m, CON*H*), 5.00-4.90 (4H, m, CH=CH_2), 4.58-4.56 (1H, m, COCHR), 3.73 (3H, s, CO_2CH_3), 3.25-3.21 (2H, m, CH_2CH_2NH), 2.17 (2H, t, *J* = 8, NHCOCH_2), 2.10 (2H, t, *J* = 8, NHCOCH_2), 2.01 (4H, q, *J* = 8, CH_2CH=CH_2), 1.80-1.20, (30H, m, CH_2), δ_C (67.9 MHz, $CDCl_3$) 173.5 (*C*O_2Me), 173.2, 173.1 (CONH), 139.1 (*C*H=CH_2 x 2), 114.1 (CH=*C*H_2 x 2), 52.3 (CO*C*HRNH), 51.6 (CO_2CH_3), 38.7 (CH_2CH_2NH), 36.8, 36.5, 33.7, 32.0, 29.3, 29.0, 28.9, 25.8, 25.6, 22.3 (all *C*H_2); ν_{max} (KBr disc) 3329m (NH), 3079m, 2912m, 2848m (CH_3, CH_2), 1748s (C=O), 1638s (C=O), 1556s (CONH), 1468m, 1172s, 995m, 913m; *m/z* (ES+) $C_{29}H_{52}N_2O_4$ [M] requires 492, found 515 (100%, $[M+Na]^+$).

Compound 5

Compound **4** (8.07 g, 16.30 mmol) was dissolved in MeOH (50 mL). The solution was cooled to 0°C, then aqueous sodium hydroxide solution (48.9 mL, 1 M, 48.9 mmol) was added. The reaction was stirred under N_2 for 24 h. The solvent was removed by rotary evaporation, water added (50 mL), then the mixture was acidified to pH 3 with aqueous $NaHSO_4$. The product was extracted with EtOAc, washed with water and brine, dried over $MgSO_4$, filtered, then rotary evaporated to dryness to yield a white solid (7.63 g, 95 %). R_f 0.10 (EtOAc:hexane, 7:3, CeMo stain); m.p. 90-92°C, α_D^{293} + 6.2 (c = 1.0, $CHCl_3$), - 0.7 (c = 1.0, MeOH); δ_H (270 MHz, $CDCl_3$) 6.80 (1H, d, *J* = 7, CONH), 5.87-5.86 (1H, m, CONH), 5.82-5.78 (2H, m, C*H*=CH_2), 5.01-4.90 (4H, m, CH=CH_2), 4.54-4.50 (1H, m, COCHR), 3.36-3.32 (1H, m, CH_2CH_2NH), 3.24-3.19 (1H, m, CH_2CH_2NH), 2.30-2.22 (4H, m, NHCOCH_2), 2.01 (4H, q, *J* = 5.5, C*H*$_2$CH=CH$_2$), 1.90-1.20, (30H, m, C*H*$_2$); δ_C (67.9 MHz, CDCl$_3$) 174.7 (CO$_2$H), 174.6, 174.3 (CONH), 139.3 (*C*H=CH$_2$ x 2), 114.3 (CH=*C*H$_2$ x 2), 52.3 (CO*C*HRNH), 38.9 (CH$_2$*C*H$_2$NH), 36.8, 36.5, 33.9, 31.3, 29.5, 29.4, 29.2, 29.0, 25.9, 25.8, 22.1 (all *C*H$_2$); ν_{max} (KBr disc) 3310m (NH), 3080m, 2919m, 2849m (CH$_3$, CH$_2$), 1714s (CO$_2$H), 1643s (CONH), 1556s (CONH), 1466m, 996m, 913m; *m/z* (ES+) $C_{28}H_{50}N_2O_4$ [M] requires 478; found 501 (100%, $[M+Na]^+$); (ES-) found 477 (100%, $[M-H]^{-\cdot}$); HR-FABMS $C_{28}H_{51}N_2O_4$ requires 479.3849, found 479.3849.

Gelator 2

1,12-Diaminododecane (0.5 g, 2.5 mmol) was suspended in DCM (25 mL). NEt$_3$ (5.25 mL, 5.25 mmol) was added, followed by compound **5** (3.0 g, 5.8 mmol). The mixture was stirred under nitrogen for 30 min then cooled to 0°C. HOBt (0.70 g, 5.3 mmol) and DCC (1.10 g, 5.3 mmol) were added simultaneously as a mixture of solids. The reaction mixture was allowed to return to room temperature and stirred for 72 h. The precipitate was removed by filtration, washed with EtOAc then discarded. The combined filtrate was then washed, first with satd. aq. NaHCO$_3$ (50 mL), then with aq. NaHSO$_4$ (16 g in 100 mL water), before being washed again with satd. aq. NaHCO$_3$ (50 mL) and finally with water (50 mL). The solution was dried over MgSO$_4$, filtered, then rotary evaporated to produce a white solid, which was washed with MeOH to remove impurities, giving the desired product with a yield of 46% (1.3 g). R_f: 0.47 (CH$_2$Cl$_2$:MeOH 90:10), Melting point: 162-163 °C, α_D^{293}: -8.4 (c = 1.0, CH$_2$Cl$_2$), δ_H (400 MHz, CDCl$_3$) 6.53 (2H, t, J = 5.8, CON*H*R), 6.47 (2H, d, J = 7.6, CON*H*), 5.85-5.80 (2H, m, CON*H*), 5.82-5.75 (4H, m, C*H*=CH$_2$), 5.15-4.91 (8H, m, CH=C*H*$_2$), 4.37-4.33 (2H, m, COC*H*R), 3.24-3.16 (8H, m, CH_2CH_2NH), 2.24-2.16 (8H, m, $NHCOCH_2$), 2.14-2.08 (8H, m, $CH_2CH=CH_2$), 1.95-1.10 (84H, m, CH_2), δ_C (400 MHz, $CDCl_3$) 174.2 (*C*ONH x 2), 173.7 (*C*ONH x 2), 172.7 (*C*ONH x 2), 139.3 ($CH=CH_2$ x 4), 114.3 ($CH=CH_2$ x 4), 52.7, 39.9, 38.6, 38.1, 36.8, 36.6, 33.9, 32.0, 29.5, 29.2, 29.0, 26.2, 25.9 (all CH_2), ν_{max} (solid) 3288m (NH), 3080m ($CH=CH_2$), 2920m, 2851m (CH_3, CH_2), 1636s (CONH), 1541s (CONH), 991m, 912m; *m/z* (ES-) $C_{68}H_{124}N_6O_6$ requires 1121; found 1120.1 (100%, $[M-H]^-$).

Additional SEM and AFM Images

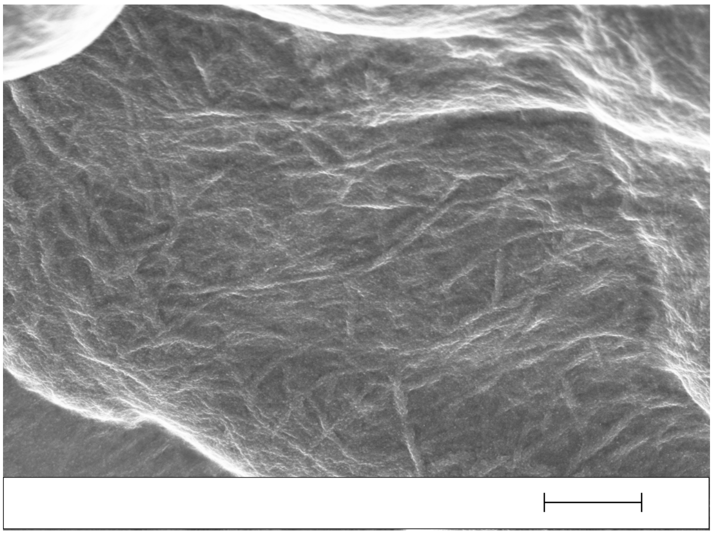


Figure 1. FEG-SEM image of equimolar mixture of **2** and **3** illustrating large fibrillar objects, scale bar: 1 μm.

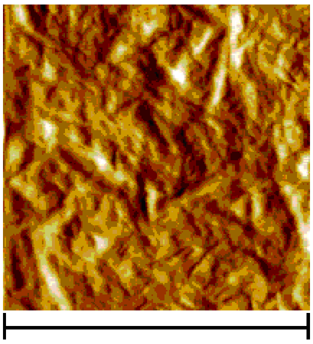


Figure 2. AFM image of dried gel formed by equimolar mixture of **2** and **3**, scale bar: 1 µm. Once again, large fibrous objects are observed.

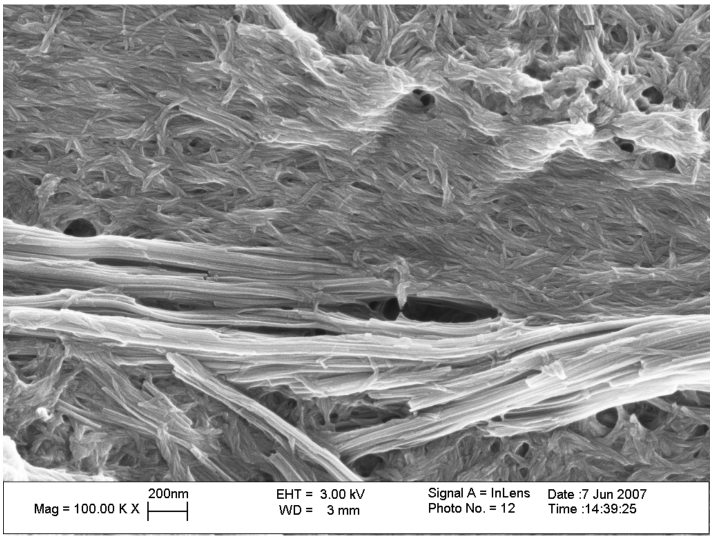


Figure 3. Additional FEG-SEM image of equimolar mixture of gelators **1** and **2** illustrating the self-sorting process.

References

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2. Huang, B.; Hirst, A. R.; Smith, D. K.; Castelletto, V.; Hamley, I. W. *J. Am. Chem. Soc.* 2005, **127**, 7130-7139.
3. Moffat, J. R.; Seeley, G. J.; Carter, J. T.; Burgess, A.; Smith, D. K. *Chem. Commun.* **2008**, DOI 10.1039/b809077g