Supplementary Information

A Tailored Organometallic Gelator with Enhanced Amphiphilic Character and Structural Diversity of Gelation

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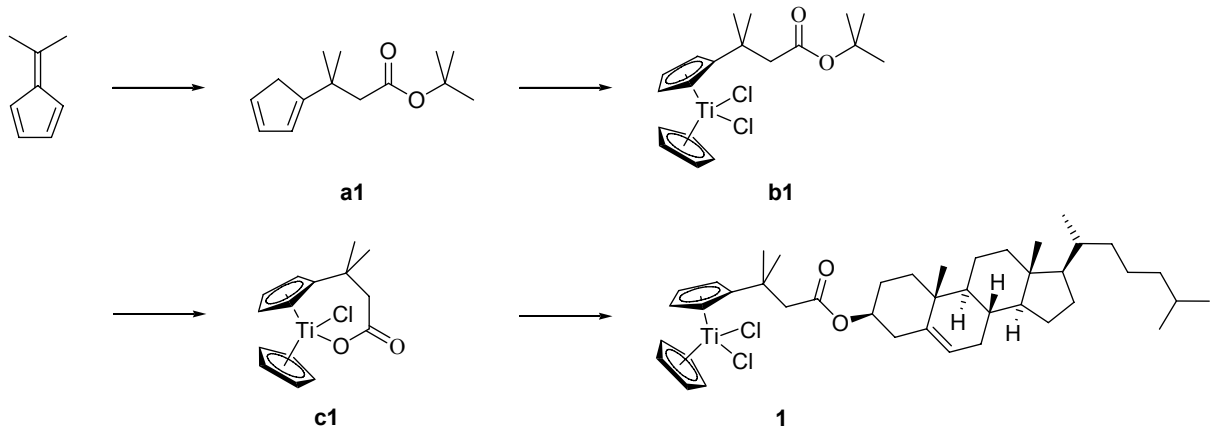
Experimental.

Synthesis of 1 [9]



Cyclopenta-1,3-dienyl-3-methyl-butyric acid tert-butyl ester (a1) (mixture of isomers): *n*-Butyllithium (156 mL of an 1.6 M solution in *n*-hexane, 250 mmol) was added dropwise to a solution of diisopropylamine (30.3 g, 300 mmol) in THF (100 mL) at -60°C. After 1 h *tert*-butylacetate (34.8 g, 300 mmol) was added dropwise. After 1 h at this temperature dimethylfulvene (34.8 g, 300 mmol) was added dropwise and the mixture was stirred for 16 h at -60°C. The mixture was washed with a saturated aqueous solution of NH_4Cl (2 x 100 mL), brine (20 mL) and dried ($MgSO_4$). Distillation (1 mbar, 80-85° C) yielded **a1** (45.0 g, 81 %) as a 54:46 mixture of isomers. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.59 (ddt, ^3J = 5.3 Hz, ^4J = 1.6 Hz, ^3J = 1.6 Hz, 1 H), 6.42 (ddt, ^3J = 5.2 Hz, ^4J = 2.1 Hz, 1.5 Hz, 1 H), *6.40 (ddt, ^3J = 5.3 Hz, ^4J = 1.8 Hz, ^3J = 1.8 Hz, 1 H), *6.29 (ddt, ^3J = 5.3 Hz, ^4J = 1.5 Hz, 1.5 Hz, 1 H), *6.17 (ddt, ^3J = 2.1 Hz, ^4J = 1.2 Hz, 1.2 Hz, 1 H), 6.01 (ddt, ^3J = 1.8 Hz, ^4J = 1.8 Hz, ^3J = 1.8 Hz, 1 H), *2.97 (ddd, ^3J = 1.4 Hz, ^4J = 1.4 Hz, 1.4 Hz, 2 H),

2.94 (ddd, ^3J = 1.5 Hz, 1.5 Hz, ^4J = 1.5 Hz, 2 H), 2.38 (s, 2 H), *2.37 (s, 2 H), 1.36 (s, 9 H), *1.34 (s, 9 H), 1.29 (s, 6 H) *1.29 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.2, *171.1, 156.5, *154.5, 133.4, *132.5, *131.8, 131.0, *125.3, 123.9, 79.9, *79.9, 49.3, *47.8, *40.9, 40.2, *36.0, 34.9, *28.8, 28.0, *28.0, 27.6. IR (neat): ν = 2970, 1725, 1560, 1365, 1245, 1160, 895, 680 cm^{-1}. HRMS: (EI, 70 eV): *m/z* calcd. for $C_{14}H_{22}O_2$: 222.1620, found 222.1617 [*M*]$^+$.

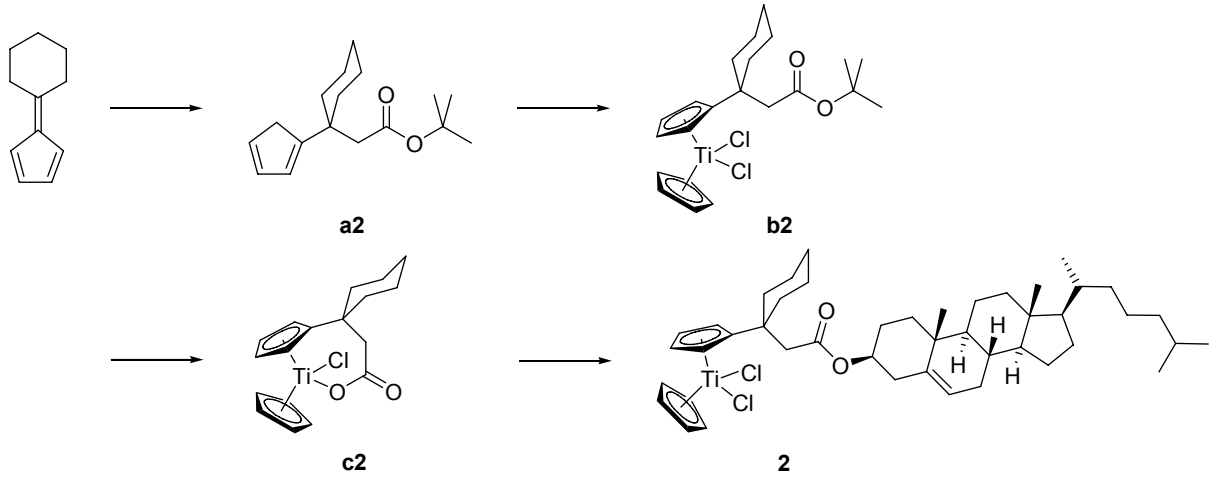
Dichloro-η^5-cyclopentadienyl-η^5-(1-*tert*-butoxy-carbonyl-2,2-dimethylethyl) cyclopentadienyl titanium (b1): *tert*-Butyllithium (70.5 mL of an 1.7M solution in pentane, 120 mmol) was added dropwise to a solution of **a1** in THF (200 mL) at -78°C. After 2 h $CpTiCl_3$ (25.2 g, 115 mmol) in THF (500 mL) was added via a pre-cooled (-40 °C) dropping-funnel in 1.5 h. The mixture was allowed to warm to rt and stirred for 8 h. The solids were filtered off and the precipitate washed with MTBE until the filtrate was colourless (ca. 1 L). The precipitate was dissolved in CH_2Cl_2 (750 mL), filtered and the solvent was removed under reduced pressure yielded **b1** (30.7 g, 66 %) as red solid. m.p.: 219°C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.56 (dd, ^3J = 2.7 Hz, ^4J = 2.7 Hz, 2 H), 6.49 (s, 5 H) 6.40 (dd ^3J = 2.7 Hz, ^4J = 2.7 Hz, 2 H), 2.40 (s, 2 H), 1.41 (s, 6 H), 1.30 (s, 9 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 170.6, 146.8, 120.6, 120.3, 117.4, 80.5, 50.7, 36.9, 28.2, 27.8. IR (pellet): ν = 3105, 2970, 1720, 1445, 1365, 1330, 1245, 1165, 1110, 825 cm^{-1}. HRMS: (ESI, CH_3CN): *m/z* calcd. for $C_{19}H_{26}{}^{35}ClO_2{}^{48}Ti$: 369.1101, found 369.1096 [*M*-Cl]$^+$.

Titanocene c1: Dried $ZnCl_2$ (9.30 g, 68.2 mmol) and **b1** (25.1 g, 62.0 mmol) in CH_2Cl_2 were stirred for 16 h at rt. The mixture was washed with 1M HCl containing 1 g of NaCl each 10 mL until all the precipitate was dissolved in the CH_2Cl_2. The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure yielded **c1** (18.6 g, 96%) as red solid. m.p.: 228°C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 6.69 (ddd, ^3J = 2.5 Hz, ^4J = 2.5 Hz, 2.5 Hz, 1 H), 6.54 (s, 5 H), 6.51 (ddd, ^3J = 2.4 Hz, ^4J = 2.4 Hz, 2.4 Hz), 6.15 (ddd, ^3J = 2.4 Hz, 2.4 Hz, ^4J = 2.4 Hz 1 H), 6.08 (ddd, ^3J = 2.6 Hz, 2.8 Hz, ^4J = 2.8 Hz, 1 H), 2.70 (d, ^2J = 14.8 Hz, 1 H), 2.33 (d, ^2J =14.9 Hz, 1 H), 1.29 (s, 3 H), 1.20 (s, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 174.8, 148.1, 122.3, 120.3, 199.6, 114.8, 106.0, 48.0, 29.4, 28.7. IR (pellet): ν = 3095, 2965, 1650, 1315, 1270, 1195, 985, 825 cm^{-1}. HRMS: (EI, 70 eV): *m/z* calcd. for $C_{15}H_{17}{}^{35}ClO_2{}^{46}Ti$: 310.0443, found 310.0438 [*M*]$^+$.

Organometallic ALS-Gelator 1: The titanium carboxylate **c1** (313 mg, 1.00 mmol) was dissolved in $SOCl_2$ (3 mL) and stirred for 1 h at rt. Excess $SOCl_2$ was removed under high-vacuum. The precipitate was dissolved in CH_2Cl_2 (5 mL), added dropwise to a mixture of NaH (120 mg, 5.00 mmol) and the cholesterol (1.00 mmol) in CH_2Cl_2 (5 mL) and stirred for 16 h. After filtration through celite the solvent was removed under reduced pressure, the precipitate dissolved in CH_2Cl_2 (20 mL), and washed with a mixture of (1 N) HCl and NaCl (1.00 g each 10 mL) (3x20 mL). The organic layer was dried ($MgSO_4$) and the solvent removed under reduced pressure. Crystallization (CH_2Cl_2/pentane) yielded

532 mg (74 %) of **1** as a red solid. m.p.: 208°C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 6.59(dd ^{3}J = 2.6 Hz, ^{4}J = 2.6 Hz, 2 H), 6.55 (s, 5 H) 6.47 (dd, ^{3}J = 2.8 Hz, ^{4}J = 2.8 Hz, 2 H) ,5.37 (dd, ^{3}J = 7.7 Hz, ^{3}J = 2.4 Hz, 1 H), 4.47 (dddd, ^{3}J = 10.8 Hz, ^{3}J = 10.7 Hz, ^{3}J = 6.4 Hz, ^{3}J = 4.4 Hz, 1 H), 2.53 (s, 2 H), 2.20-2.26 (m, 2 H), 2.01 (ddd, ^{2}J = 12.5 Hz, ^{3}J = 3.6 Hz, ^{3}J = 3.6 Hz, 1 H), 1.96 (dddd, ^{2}J = 17.4 Hz, ^{3}J = 5.2 Hz, ^{3}J = 5.2 Hz, ^{5}J = 2.1 Hz, 1 H), 1.86 (ddd, ^{2}J = 9.6 Hz, ^{3}J = 9.6 Hz, ^{3}J = 6.0 Hz, 1 H), 1.83 (ddd, ^{3}J = 9.5 Hz, ^{3}J = 9.5 Hz, ^{3}J = 6.0 Hz, 1 H), 1.75 (dddd, ^{2}J = 12.5 Hz, ^{3}J = 9.0 Hz, ^{3}J = 3.7 Hz, ^{3}J = 3.7 Hz, 1 H), 0.98-1.63 (m, 22 H), 1.45 (s, 6 H), 1.00 (s, 3 H), 0.93 (d, ^{3}J = 6.5 Hz, 3 H), 0.88 (d, ^{3}J = 6.4 Hz, 3 H), 0.88 (d, ^{3}J = 6.4 Hz, 3 H) 0.68 (s, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 170.8, 146.9, 140.2, 122.9, 120.0, 120.6, 117.6, 117.6, 74.2, 57.1, 56.5, 50.4, 49.6, 42.7, 40.2, 29.9, 38.5, 37.4, 37.0, 37.0, 36.6, 36.2, 32.3, 32.2, 28.6, 28.4, 28.2, 27.9, 27.9, 24.6, 24.2, 22.9, 22.7, 21.4, 19.5, 18.9, 12.0. IR (pellet): ν = 3110, 2930, 2865, 1730, 1465, 1440, 1365, 1325, 1175, 1110, 1015, 825 cm^{-1}. HRMS: (ESI, CH_3CN/CH_2Cl_2): *m/z* calcd. for $C_{42}H_{62}{}^{35}ClO_2{}^{48}Ti$: 681.3918, found 681.3901 [*M*-Cl]$^{+}$. Anal. Calcd. for $C_{42}H_{62}Cl_2O_2Ti$*1/4 CH_2Cl_2: C, 68.87; H, 8.53. Found: C, 68.65; H, 8.49.

Synthesis of 2 [9]



(1-Cyclopenta-1,3-dienyl-cyclohexyl)-acetic acid tert-butyl ester (a2) (mixture of isomers): *n*-Butyllithium (100 mL of an 1.5 M solution in *n*-hexane, 150 mmol) was added dropwise to a solution of diisopropylamine (32.7 g, 225 mmol) in THF (100 mL) at -60°C. After 1 h *tert*-butylacetate (26.1 g, 225 mmol) was added dropwise. After another hour cyclopenta-2,4-dienylidene-cyclohexane (21.9 g, 150 mmol) was added dropwise and the mixture was stirred for 16 h at -60°C. The mixture was washed with a saturated aqueous solutions of NH_4Cl (2 x 100 mL), brine (20 mL) and dried ($MgSO_4$). Distillation (1 mbar, 112° C yielded **a2** (19.7 g, 50 %) as a 53:47 mixture of isomers. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.49 (ddt, ^{3}J = 5.3 Hz, ^{4}J = 1.5 Hz, ^{3}J = 1.5 Hz, 1 H), *6.41 (m, 1 H), *6.36 (ddt, ^{3}J = 3.6 Hz, ^{4}J = 1.8 Hz, ^{3}J = 1.8 Hz, 1 H), *6.23 (ddt, ^{3}J = 5.3 Hz, ^{4}J = 1.5 Hz, 1.5 Hz, 1 H), 6.13 (ddt, ^{3}J = 2.1 Hz, ^{4}J = 1.5 Hz, 1.5 Hz, 1 H), 6.06 (ddt, ^{3}J = 1.7 Hz, ^{4}J = 1.7 Hz, 1.7 Hz, 1 H), 2.89 (ddd, ^{3}J = 1.5 Hz, 1.5 Hz, ^{4}J = 1.5 Hz, 2 H), *2.86 (ddd, ^{3}J = 1.4 Hz, 1.4 Hz, ^{4}J = 1.4 Hz, 2 H), 2.27 (s, 2 H), *2.27 (s, 2 H), 1.77-1.87 (m, 2 H), *1.77-1.87 (m, 2 H), 1.52-1.62 (m,

2 H), *1.52-1.62 (m, 2 H), 1.28-1.51 (m, 6 H), *1.28-1.51 (m, 6 H), 1.23 (s, 9 H), *1.22 (s, 9 H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = *171.3, 171.2, *154.2, 152.0, 133.1, *132.1, *131.3, 133.0, 128.5, *127.7, *80.0, 79.9, *48.4, 47.1, 41.3, *40.2, *40.0, 38.8, *37.0, 36.1, 28.2, *28.1, *26.5, 26.4, *22.6, 22.5. IR (neat): ν = 2925, 2860, 1720, 1455, 1365, 1130, 895, 770, 680 cm^{-1}. Anal. Calcd. for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. Found: C, 77.77; H, 9.85.

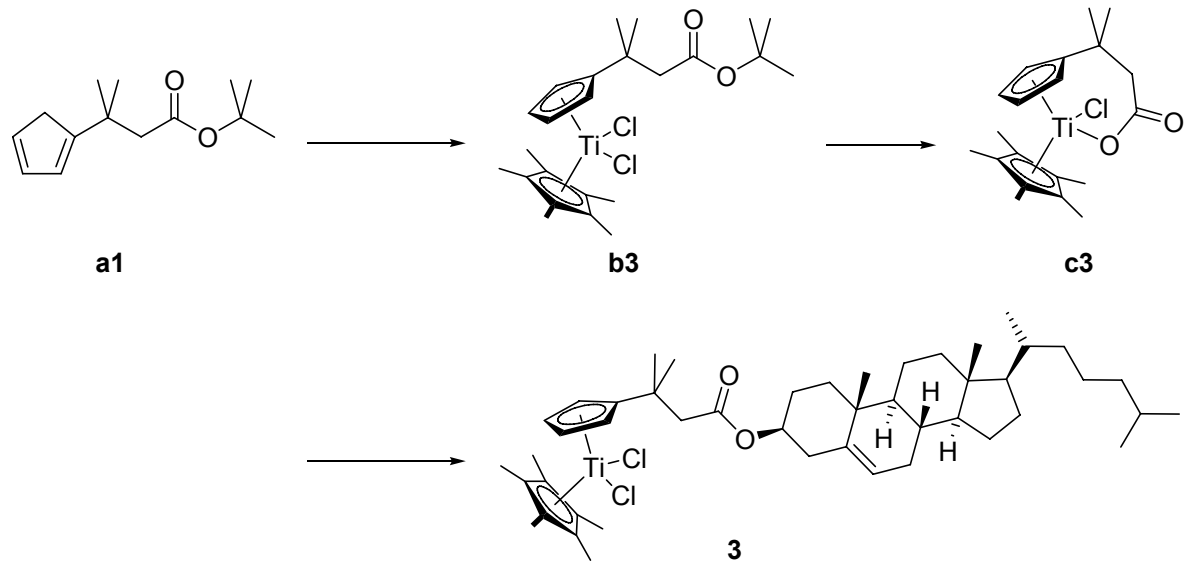
Dichloro-η^5-cyclopentadienyl-η^5-(1-*tert*-butoxy-carbonyl-2-cyclohexyl) cyclopentadienyl titanium (b2): *tert*-Butyllithium (24.5 mL of an 1.7M solution in pentane, 41.7 mmol) was added dropwise to a solution of **a2 (**11.4 g, 43.5 mmol) in THF (70 mL) at -78°C. After 1 h $CpTiCl_3$ (8.77 g, 40.0 mmol) in THF (120 mL) was added within 1.5 h. The mixture was allowed to warm to rt and stirred for 60 h. The mixture was filtered off and the precipitate washed with MTBE (500 mL) until the filtrate was colourless. The precipitate was dissolved in CH_2Cl_2 (500 mL), filtered and the solvent was removed under reduced pressure yielded **b2** (11.0 g, 62 %) as red solid. m.p.: 262°C (decomposition). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.68 (dd, ^3J = 2.6 Hz, ^4J= 2.6 Hz, 2 H), 6.57 (s, 5 H) 6.48 (dd ^3J = 2.8 Hz, ^4J = 2.8 Hz, 2 H), 2.59 (s, 2 H), 1.94-2.06 (m, 4 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 171.1, 147.1, 121.1, 120.3, 117.4, 80.4, 44.0, 39.9, 34.3, 28.1, 25.4, 21.9. IR (pellet): ν = 3110, 2925, 1725, 1445, 1365, 1150, 825, 770 cm^{-1}. Anal. Calcd. for $C_{22}H_{30}Cl_2O_2Ti$: C, 59.35; H, 6.79. Found: C, 59.13; H, 6.65.

Titanocene c2: Dried $ZnCl_2$ (4.60 g, 33.0 mmol) and **b2** (10.0 g, 22.5 mmol) in CH_2Cl_2 (100 mL) were stirred for 16 h at rt. The mixture was washed with 1M HCl (containing 1 g NaCl per 10 mL) until all the precipitate was dissolved in the CH_2Cl_2. The organic layer was dried ($MgSO_4$). The solvent was removed under reduced pressure yielded **c2** (7.60 g, 98%) as red solid. m.p.: 245°C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 6.70 (ddd, ^3J = 3.1 Hz, ^4J = 3.1 Hz, ^{4} = 2.1 Hz, 1 H, 2'-H), 6.62 (ddd, ^3J = 3.1 Hz, ^3J= 2.2 Hz, ^4J = 2.2 Hz 1 H), 6.52 (s, 5 H), 6.11 (ddd, ^3J = 3.1 Hz, ^4J = 2.1 Hz ^4J = 2.1 Hz, 1 H), 6.09 (ddd, ^3J = 2.3 Hz, ^4J = 3.2 Hz, ^3J = 2.3 Hz, 1 H), 2.73 (d, ^2J = 14.8 Hz, 1 H), 2.37 (d, ^2J = 14.9 Hz, 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 175.3, 147.1, 125.0, 119.5, 118.6, 114.3, 107.7, 47.7, 40.0, 37.5, 37.0, 25.7, 22.0, 22.0. IR (pellet): ν = 3090, 2925, 1645, 1330, 1280, 1160, 1020, 820 cm^{-1}. HRMS: (EI, 70 eV): *m/z* calcd. for $C_{18}H_{21}ClO_2{}^{46}Ti$: 350.0756, found 350.0762 $[M]^+$.

Titanocene 2: The titanocene carboxylate **c2** (353 mg, 1.00 mmol) was dissolved in $SOCl_2$ (3 ml) and the solution was stirred for 1 h. Excess $SOCl_2$ was removed under high-vacuum. The precipitate was dissolved in CH_2Cl_2 (5 ml), the solution added dropwise to a mixture of NaH (120 mg, 5.00 mmol) and cholesterol (387 mg, 1.00 mmol) in CH_2Cl_2 (5 mL) and stirred for 16 h. Purification procedures are in accord with the synthesis of organometallic ALS-gelator **1**. Crystallization (toluene) yielded 682 mg (81 %) of **2** as a red solid. m.p.: 192°C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 6.66-6.70 (m, 2 H), 6.56 (s,

5 H) 6.46-6.49 (m, 3 H), 5.32-5.35 (m, 1 H), 4.47 (dddd, ^3J = 11.9 Hz, ^3J = 11.9 Hz, ^3J = 4.5 Hz, $^3J_{3"\text{-H},2"\text{-H(B)}}$ = 4.4 Hz, 1 H), 2.66 (s, 2 H), 2.17-2.20 (m, 2 H), 1.95-2.07 (m, 6 H), 1.81-1.89 (m, 2 H), 1.70-1.76 (m, 1 H), 1.63-1.70 (m, 3-H), 0.97-1.63 (m, 28 H), 1.56 (s, 6 H), 0.99 (s, 3 H), 0.91 (d, ^3J = 6.5 Hz, 3 H), 0.86 (d, ^3J = 6.4 Hz, 3 H), 0.86 (d, ^3J = 6.4 Hz, 3 H) 0.67 (s, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 171.5, 147.3, 139.9, 123.1, 121.4, 120.6, 117.6, 117.5, 74.2, 57.1, 56.5, 50.4, 43.4, 42.7, 40.2, 40.1, 39.9, 38.5, 37.4, 37.0, 36.6, 36.2, 34.8, 34.7, 32.3, 32.2, 28.6, 28.4, 28.2, 25.7, 24.6, 24.2, 23.2, 23.0, 22.2, 21.4, 19.7, 19.1, 12.3. IR (pellet): ν = 3110, 2935, 2860, 1725, 1460, 1440, 1195, 1160, 1010, 825 cm^{-1}. Anal. Calcd. for $(C_{45}H_{66}Cl_2O_2Ti)_8CH_2Cl_2$: C, 70.53; H, 8.69. Found: C, 70.31; H, 8.94. HRMS: (ESI, CH_3CN/CH_2Cl_2): *m/z* calcd. for $C_{45}H_{66}{}^{35}ClO_2{}^{48}Ti$: 721.4231, found 721.4208 [*M*-Cl]$^+$. Anal. Calcd. for $C_{45}H_{66}Cl_2O_2Ti$*1/8 CH_2Cl_2: C, 70.53; H, 8.69. Found: C, 70.31; H, 8.94.

Synthesis of 3 [9]



Dichloro-η^5-pentamethylcyclopentadienyl-η^5-(1-*tert*-butoxy-carbonyl-2,2-dimethylethyl)-cyclopentadienyl titanium (b3): *tert*-Butyllithium (11.8 mL of a 1.7M solution in pentane, 20 mmol) was added dropwise to a solution of **a1** (4.89 g, 22.0 mmol) in THF (30 mL) at -78°C. After 1 h $Me_5CpTiCl_3$ (4.92 g, 17 mmol) in THF (20 mL) was added. The mixture was allowed to warm to -30 °C and stirred for 16 h. The solvents were removed under reduced pressure and the precipitate was suspended in hexane (20 mL). The mixture was filtered off and the precipitate washed with hexane (20 mL). The precipitate was dissolved in CH_2Cl_2 (100 mL), filtered through celite and the solvent was removed under reduced pressure to yield **b3** (3.78 g, 47 %) as a violet solid. m.p.: 113°C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 6.27 (dd, ^3J = 2.8 Hz, ^4J = 2.8 Hz, 2 H), 5.88 (dd, ^3J = 2.7 Hz, ^4J = 2.7 Hz, 2 H), 2.51 (s, 2 H), 2.03 (s, 15 H), 1.53 (s, 6 H), . ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 171.1, 146.1, 129.6, 122.9, 113.1, 80.0, 50.7, 37.0, 28.2, 27.5, 13.6. IR (pellet): ν = 2975, 2910,

1709, 1370, 1310, 1260, 1160, 1100, 960, 830 cm^{-1}. Anal. Calcd. for $C_{24}H_{36}Cl_2O_2Ti$: C, 60.65; H, 7.63. Found: C, 60.30; H, 7.42.

Titanocene c3: Dried $ZnCl_2$ (1.02 g, 7.50 mmol) and **b3** (3.09 g, 6.50 mmol) in CH_2Cl_2 (20 mL) were stirred for 3 h at rt. After addition of 1M HCl (50 mL) and CH_2Cl_2 (40 mL) the mixture was extracted until all of the precipitate was dissolved in the CH_2Cl_2. The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure to yield **c3** (2.44 g, 99%) as a red solid. m.p.: 218°C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = δ = 6.46 (ddd, ^3J = 2.6 Hz, ^4J = 2.6 Hz, ^4J = 2.6 Hz, 1 H), 6.31 (ddd, ^3J = 2.7 Hz, ^4J = 2.7 Hz, ^4J = 2.7 Hz, 1 H), 5.59 (ddd, ^3J = 2.9 Hz, ^3J = 2.9 Hz, ^4J = 2.9 Hz 1 H), 5.49 (ddd, ^3J = 2.6 Hz, ^3J = 2.6 Hz, ^4J = 2.6 Hz, 1 H), 2.58 (d, ^2J = 14.3 Hz, 1 H), 2.26 (d, ^2J =14.4 Hz, 1 H), 2.06 (s, 15 H), 1.26 (s, 3 H), 1.14 (s, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 174.8, 145.9, 129.5, 123.3, 117.5, 116.3, 106.9, 47.8, 33.8, 29.2, 28.5, 13.0. IR (pellet): ν = 2960, 2906, 1655, 1380, 1320, 1270, 1115, 985, 920, 845 cm^{-1}. HRMS: (EI, 70 eV): *m/z* calcd. for $C_{20}H_{27}{}^{35}ClO_2{}^{46}Ti$: 380.1226, found 380.1228 $[M]^+$.

Titanocene 3: The titanocene carboxylate **c3** (383 mg, 1.00 mmol) was dissolved in $SOCl_2$ (3 ml) and the solution was stirred for 1 h. Excess $SOCl_2$ was removed under high-vacuum. The precipitate was dissolved in CH_2Cl_2 (5 ml), the solution was added dropwise to a mixture of NaH (120 mg, 5.00 mmol) and cholesterol (387 mg, 1.00 mmol) in CH_2Cl_2 (5 mL) and stirred for 16 h. Purification procedures are in accord with the synthesis of organometallic ALS-gelator **1.** Crystallization (toluene) yielded 682 mg (81 %) of **3** as a red solid. m.p.: 192°C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 6.66-6.70 (m, 2 H), 6.56 (s, 5 H) 6.46-6.49 (m, 3 H), 5.32-5.35 (m, 1 H), 4.47 (dddd, ^3J = 11.9 Hz, ^3J = 11.9 Hz, ^3J = 4.5 Hz, $^3J_{3"\text{-H},2"\text{-H(B)}}$ = 4.4 Hz, 1 H), 2.66 (s, 2 H), 2.17-2.20 (m, 2 H), 1.95-2.07 (m, 6 H), 1.81-1.89 (m, 2 H), 1.70-1.76 (m, 1 H), 1.63-1.70 (m, 3-H), 0.97-1.63 (m, 28 H), 1.56 (s, 6 H), 0.99 (s, 3 H), 0.91 (d, ^3J = 6.5 Hz, 3 H), 0.86 (d, ^3J = 6.4 Hz, 3 H), 0.86 (d, ^3J = 6.4 Hz, 3 H) 0.67 (s, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 171.5, 147.3, 139.9, 123.1, 121.4, 120.6, 117.6, 117.5, 74.2, 57.1, 56.5, 50.4, 43.4, 42.7, 40.2, 40.1, 39.9, 38.5, 37.4, 37.0, 36.6, 36.2, 34.8, 34.7, 32.3, 32.2, 28.6, 28.4, 28.2, 25.7, 24.6, 24.2, 23.2, 23.0, 22.2, 21.4, 19.7, 19.1, 12.3. IR (pellet): ν = 3110, 2935, 2860, 1725, 1460, 1440, 1195, 1160, 1010, 825 cm^{-1}. Anal. Calcd. for $(C_{45}H_{66}Cl_2O_2Ti)_8CH_2Cl_2$: C, 70.53; H, 8.69. Found: C, 70.31; H, 8.94. HRMS: (ESI, CH_3CN/CH_2Cl_2): *m/z* calcd. for $C_{45}H_{66}{}^{35}ClO_2{}^{48}Ti$: 721.4231, found 721.4208 $[M\text{-Cl}]^+$. Anal. Calcd. for $C_{45}H_{66}Cl_2O_2Ti$*1/8 CH_2Cl_2: C, 70.53; H, 8.69. Found: C, 70.31; H, 8.94.

Preparation of gels and determination of T_{gel}

The gels were prepared by dissolving **1** in the relevant solvent and warming with a heat gun or in an oil bath until solution is complete. Upon cooling the gel is formed. For the determination of T_{gel} the "dropping ball method"[10,11] was used: A small glas ball (ø 1.5 mm, weight, 36 mg) was placed on the surface of the gel. The sample was warmed (0.5 °C/min) until the ball dipped into the gel and T_{gel} was determined.

Preparation of NMR samples:

A warmed solution of **1** in C_6D_6 was rapidly transferred into a NMR-tube via a syringe. Upon cooling a homogeneous gel was obtained. The NMR spectra were recorded on a Bruker AMX 500.

Preparation of samples for CD measurements:

The gel was prepared by warming **1** in *t*-butyl methyl ether; then it was rapidly transferred into a 0.2 mm Hellma quartz cuvette via a syringe. To exclude the influence of linear dichroism (LD) and linear birefringence (LB) the measurements were repeated several times after successive rotation of the cuvette without any observable changes in the CD-spectra. Temperature-dependent measurements were performed using a JASCO J-810 spectropolarimeter equipped with a JASCO PTC-423S thermoelectric temperature controller.

Preparation of samples for Transmission Electron Microscopy (TEM):

The samples were prepared on carbon coated copper grids (400-mesh) which were carefully placed on the gel surface. TEM micrographs were obtained from a Zeiss EM 912 OMEGA instrument operating at an acceleration voltage of 120 kV.

Preparation of samples for cryo-Scanning Electron Microscopy (cryo-SEM):

A small drop of the gels was placed on a sample holder, quickly frozen in a liquid nitrogen slush and then transferred into the preparation chamber. The samples were warmed to -120°C (toluene 1.5 wt%) and -130°C (acetone 1.5 wt%). The upper parts of the frozen gel drops were divided with a cool knife and the resulting samples were etched with a BALZERS Baf 400 freeze etching system for 5 minutes. Finally, the samples were sputtered *in situ* with 1.5 nm of Au/Pd with a BALZERS sputtering device and transferred into the microscope. The experiments were performed on a JEOL JSM T300 Scanning Microscope (30 kv) equipped for cryo techniques with a HG 001 Plunger injector, BALTEC JFD 030 Propane jet, REICHERT-JUNG CS auto Cryo substitute.

Preparation of samples for Atomic Force Microscopy (AFM):

The copper grids used for the TEM experiments (as described above) were directly investigated by AFM. Images were obtained in Tapping Mode on a Nano-Scope IIIa Microscope (Digital Instruments,

USA) with a 10×10 μm e-scanner and silicon tips (Type NCR-W; tip radius < 10 nm), employing a constant force of 42 N m^{-1} at a resonance frequency of 285 kHz.

Table S1 Gelation abilities of **1**

solvent	property[a]	cgc [wt%][b]	T_{gel} [°C][c] 1.5 wt %	appearance
n-hexane	ns			
di-n-butyl ether	g	1.5	72-76	turbid
t-butyl methyl ether	g	1.0	bp[d]	turbid
toluene	g	0.5	58-62	transparent
benzene	g	0.6	53-56	transparent
diethyl ether	rs			
1,4-dioxane	g	1.0	55-58	turbid
tetrahydrofuran	s			
ethyl acetate	g	0.7	63-68	turbid
chloroform	s			
dichloromethane	g -10°C	4.0	-10°C[d]	transparent
triethylamine	decomp.			
acetone	g	0.8	40-44	turbid
dimethylsulfoxide	g	1.5	53-58	turbid
1-butanol	decomp.			
ethanol	decomp.			

[a] ns: not soluble, g: gelation, rs: rarely soluble, s: soluble, decomp.: decomposition, [b]critical gelation concentration, [c] gel-sol transition temperature[10,11], [d] 4 wt%.

9 A. Gansäuer, D. Franke, T. Lauterbach and M. Nieger, *J. Am. Chem. Soc.* 2005, **127**, 11622.
10 A. Takahashi, M. Sakai and T. Kato, *Polym. J.* 1980, **12**, 335.
11 G. Bühler, C. M. Feiters, J. M. R. Nolte and K. H. Dötz, *Angew. Chem. Int. Ed. Engl.* 2003, **42**, 2494.

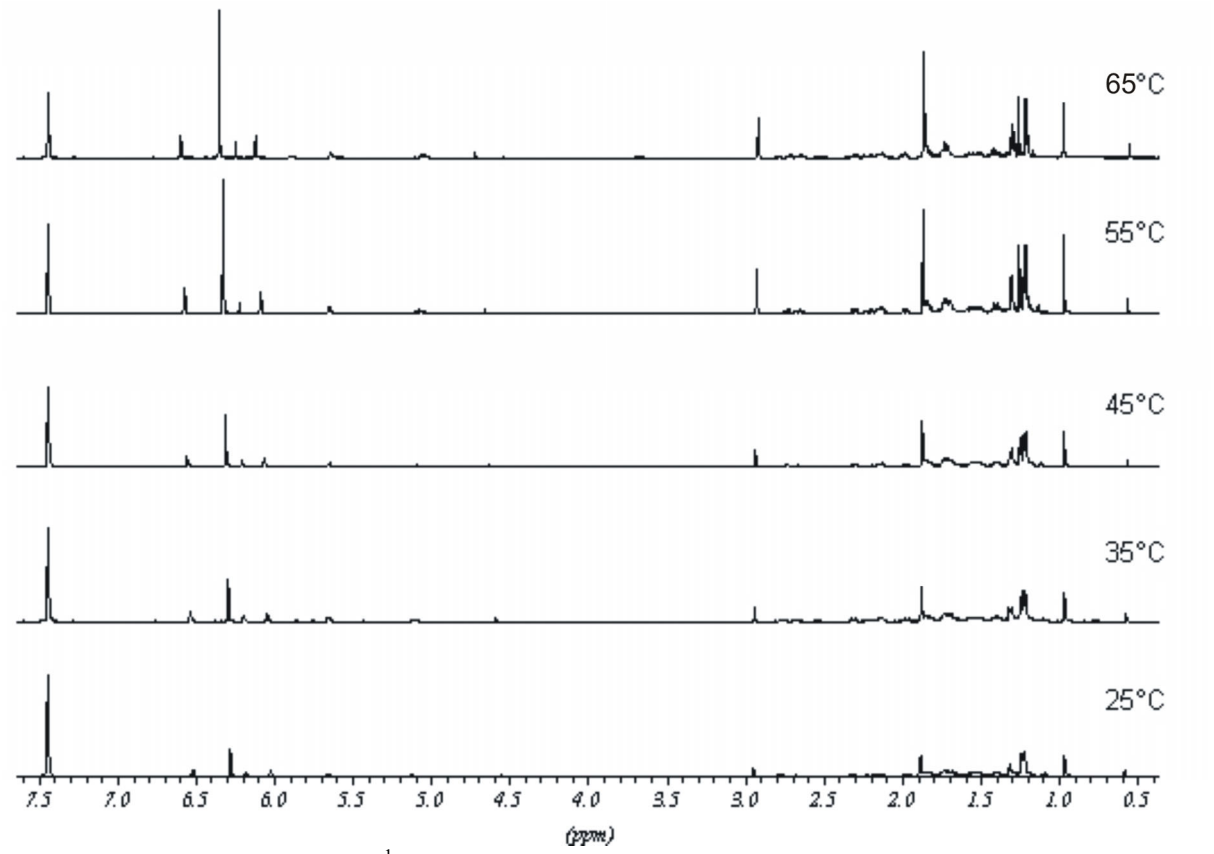


Fig. S1 Temperature-dependent ^{1}H-NMR spectra of **1** in C_6D_6 (1.5 wt%) (500 MHz)

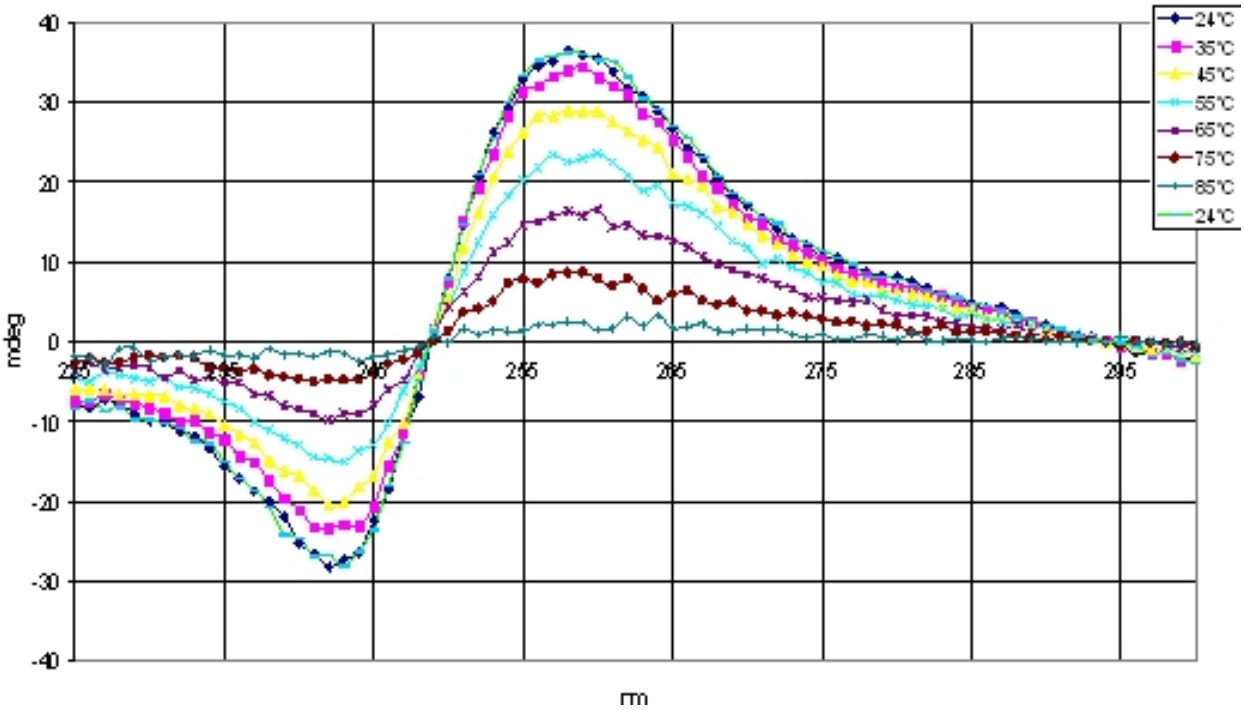


Fig. S2 Temperature-dependent CD-measurements of **1** in *t*-butyl methyl ether (1.5 wt%)

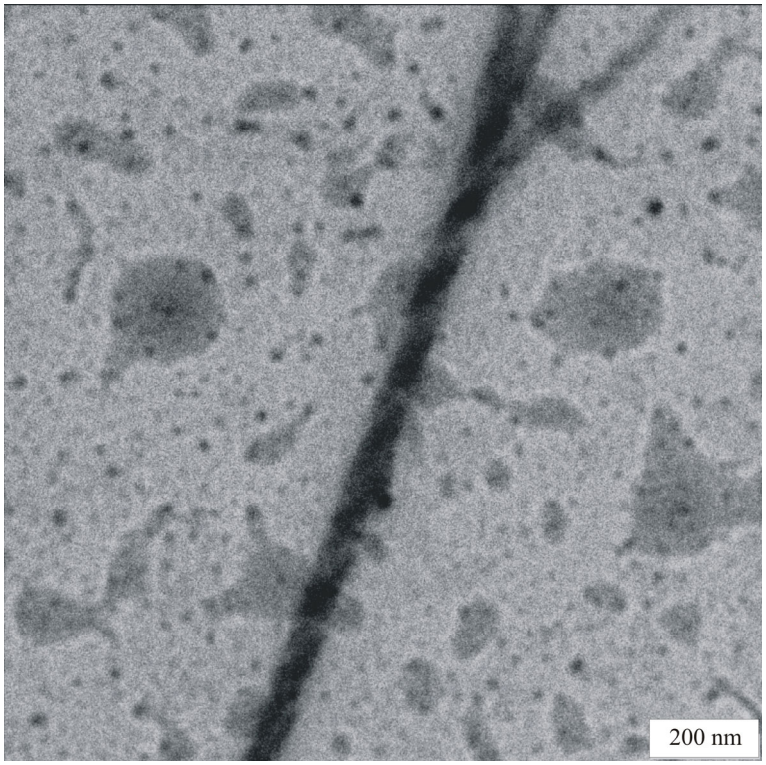


Fig. S3 TEM image of a helical structure formed by **1** in toluene (1.5 wt%)

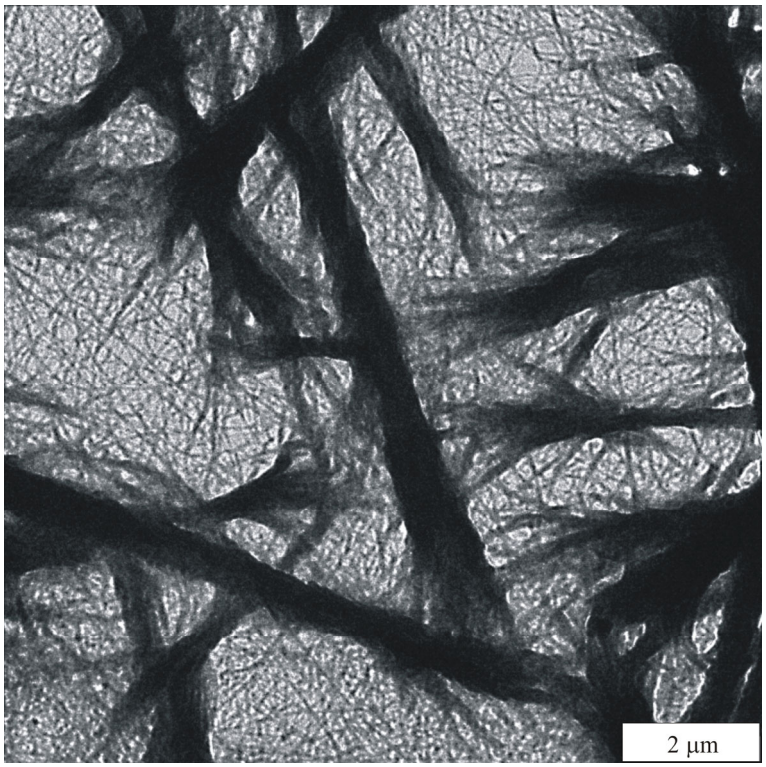


Fig. S4 TEM image of a gel of **1** in acetone (1.5 wt%)

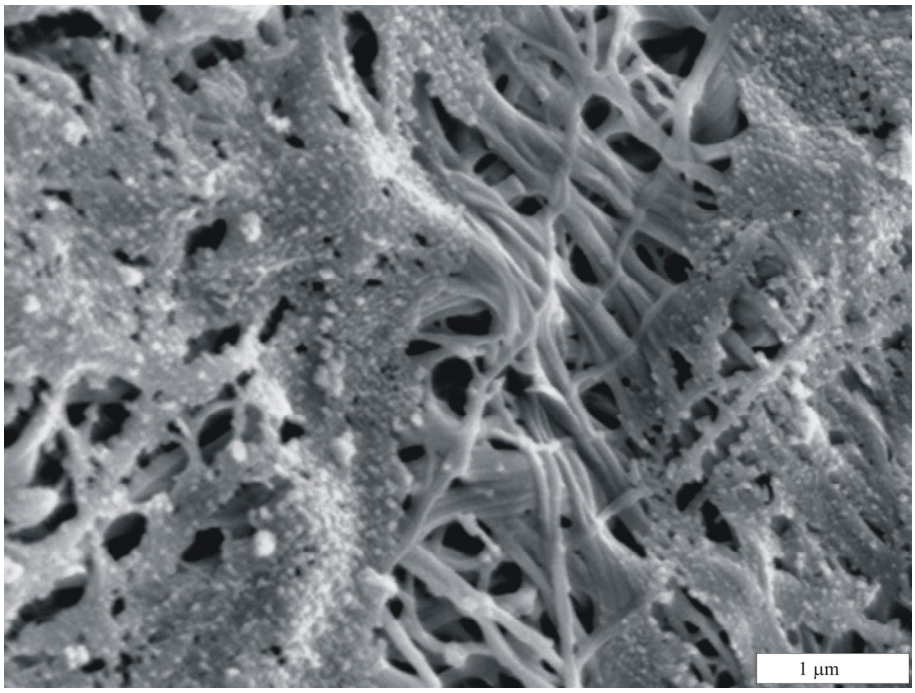


Fig. S5 Cryo-SEM image of the intertwined fibers of a gel network of **1** in toluene (1.5 wt%)

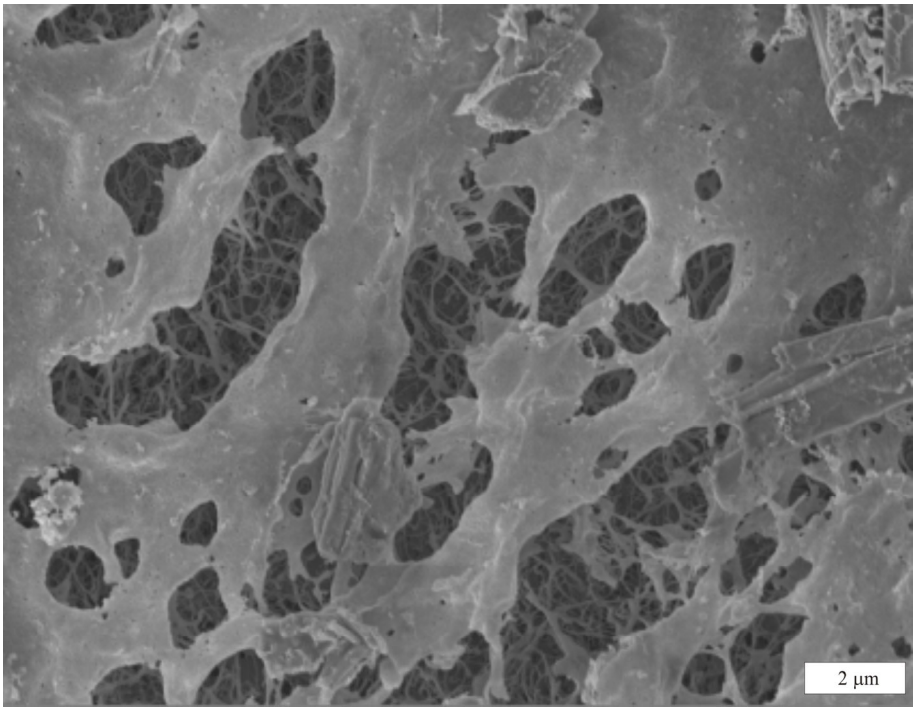


Fig S6 Cryo-SEM image depicting the gel network in ethyl acetate (1.5 wt%)

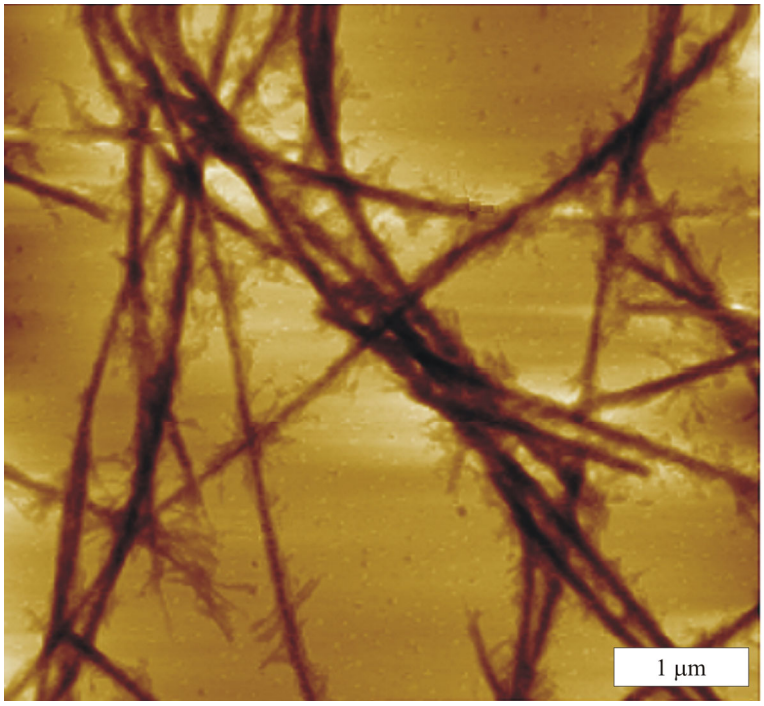


Fig. S7 AFM images of a gel of **1** in toluene (1.5 wt%) with intertwined and fringed structures