Electronic Supplementary Material (ESI) for Soft Matter.

Substituent interference on supramolecular assembly in urea gelators: synthesis, structure prediction and NMR

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SUPPLEMENTARY INFORMATION

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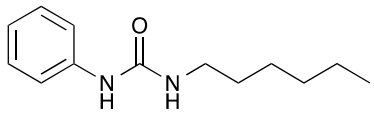
1. General methods

Chemicals were purchased from Sigma-Aldrich or TCI UK Ltd.. All solvents and reagents were used as supplied. Where appropriate, CH_2Cl_2 was distilled from CaH_2 before use.
Air/moisture sensitive reactions were carried out under an inert atmosphere, in oven-dried glassware.
TLC was performed on aluminium-precoated plates coated with silica gel 60 containing F_{254} indicator; visualised under UV light (254 nm) and/or by staining with ninhydrin. Flash column chromatography was performed with Merck Kieselgel 60 silica gel.
Melting points were determined in open capillary tubes on a Gallenkamp Electrothermal apparatus and are uncorrected.
Fourier-transform infrared (FT-IR) spectra are reported in wavenumbers (cm^{-1}) and were collected on solids using a Thermo Scientific Nicolet 380 fitted with an ATR Smart Orbit Goldengate accessory using OMNIC software package.
^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solutions (purchased from either Sigma-Aldrich or Cambridge Isotope Laboratories, Inc.) at 298K using a Bruker DPX400, AVII400, AVIIHD400 (400, 100 and 376 MHz respectively) spectrometers. Chemical shifts values (δ) are reported in parts per million (ppm) relative to residual chloroform (δ 7.27 ppm for ^{1}H, δ 77.00 ppm for ^{13}C) or dimethyl sulfoxide (δ 2.50 ppm for ^{1}H, δ 39.51 ppm for ^{13}C). All spectra were reprocessed using ACD/Labs 12.1. Coupling constants (J) were recorded in Hz. The following abbreviations were used for the multiplicity of the peaks: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad).
Low-resolution mass spectra (LRMS) were recorded on a Waters (Manchester, UK) TQD mass spectrometer equipped with a triple quadrupole analyser. Samples were introduced to the mass spectrometer *via* an Acquity H-Class quaternary solvent manager (with TUV detector at 254 nm, sample and column manager). Ultra-performance liquid chromatography was undertaken via a Waters BEH C18 column (50 mm x 2.1 mm, 1.7 μm). Low-resolution mass spectra were recorded using positive ion electrospray ionisation (ES^+) with gradient 20% acetonitrile (0.2% formic acid) to 100% acetonitrile (0.2% formic acid) in five minutes at a flow rate of 0.6 mL min^{-1}.
High-resolution mass spectra (HRMS) were recorded using positive ion electrospray ionization (ES^+). Samples were analysed using either a MaXis (Bruker Daltonics, Bremen, Germany) mass spectrometer equipped with a Time of Flight (TOF) analyser or a SolariX (Bruker Daltonics, Bremen, Germany) mass spectrometer equipped with a 4.7 T magnet and FT-ICR cell. To the first spectrometer, samples were introduced *via* a Dionex Ultimate 3000 autosampler and uHPLC pump. Ultra performance liquid chromatography was undertaken *via* a Waters UPLC BEH C18 (50 mm x 2.1 mm, 1.7 μm) column. It was used a gradient 20% acetonitrile (0.2% formic acid) to 100% acetonitrile (0.2% formic acid) in five minutes at a flow rate of 0.6 mL min^{-1}. To the second spectrometer, samples were introduced *via* infusion at a flow rate of 5 μL min^{-1}.

2. Procedures and characterisation data

Gelator 1 - 1-Hexyl-3-phenylurea



$C_{13}H_{20}N_2O$
Molecular Weight: 220,32

Hexyl isocyanate (1.50 g, 1.70 mL, 0.01 mol) and phenylamine (0.90 g, 0.90 mL, 0.01 mol) were stirred overnight at room temperature in 20 mL dichloromethane. Hexane was added to the solution until a white precipitate had formed, which was collected after filtration and subsequently dried under high vacuum (2.02 g, 9.19 mmol, 92%).

M.p. 73–75 ºC.

FT-IR (neat) ν_{max} 3332 (N–H), 1632 (amide-I), 1552 (amide-II) cm^{-1}.

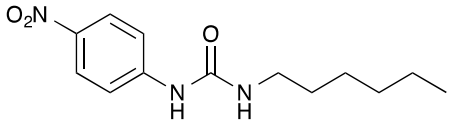
^{1}H NMR (400 MHz, DMSO-d_6) δ 0.86 (3H, t, J = 6.7 Hz, C**H**$_3$), 1.27 (6H, br, CH_3-C**H**$_2$-C**H**$_2$-C**H**$_2$-CH_2-CH_2-NH), 1.37-1.42 (2H, m, CH_3-CH_2-CH_2-CH_2-C**H**$_2$-CH_2-NH), 3.06 (2H, q, J = 6.6 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-NH), 6.09 (1H, t, J = 5.4 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-N**H**), 6.87 (1H, t, J = 7.3 Hz, Ar**H**$_p$), 7.20 (2H, t, J = 7.9 Hz, Ar**H**$_m$), 7.36 (2H, d, J = 7.7 Hz, Ar**H**$_o$), 8.35 (1H, s, N**H**-Ar) ppm.

^{13}C NMR (100 MHz, DMSO-d_6) δ 14.0 (**C**H_3), 22.1 (**C**H_2), 26.1 (**C**H_2), 29.8 (**C**H_2), 31.1 (**C**H_2), 39.5 (**C**H_2), 117.6 (Ar**C**), 121.0 (Ar**C**), 128.7 (Ar**C**), 140.6 (Ar**C**$_q$), 155.3 (**C**O) ppm.

LRMS (ES$^+$) *m/z* 221 $[M+H]^+$, 243 $[M+Na]^+$.

HRMS (ES$^+$) for $C_{13}H_{21}N_2O^+$ $[M+H]^+$, calculated 221.1648 found 221.1651.

Gelator 2 - 1-Hexyl-3-(4-nitrophenyl)urea



$C_{13}H_{19}N_3O_3$
Molecular Weight: 265,31

A solution of 4-nitrophenyl isocyanate (3.00 g, 0.02 mol) and hexylamine (2.00 g, 2.60 mL, 0.02 mol) in 20 mL dichloromethane was shaken in a sealed vial and white solid had formed immediately, which was collected after filtration and dried under high vacuum (3.50 g, 0.01 mol, 50%).

M.p. 112–113 ºC.

FT-IR (neat) ν_{max} 3374 (N–H), 1611 (amide-I), 1546 (amide-II) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6) δ 0.86 (3H, t, J = 6.7 Hz, C**H**$_3$), 1.26 (6H, br, CH_3-C**H**$_2$-C**H**$_2$-C**H**$_2$-CH_2-CH_2-NH), 1.39-1.44 (2H, m, CH_3-CH_2-CH_2-CH_2-C**H**$_2$-CH_2-NH), 3.09 (2H, td, J = 6.7, 5.6 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-NH), 6.48 (1H, t, J = 5.6 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-

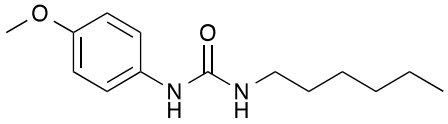
CH_2-N**H**), 7.61 (2H, d, *J* = 8.4 Hz, NH-Ar$\mathbf{H}_{o}$), 8.12 (2H, d, *J* = 8.3 Hz, NH-Ar$\mathbf{H}_{m}$), 9.28 (1H, s, N**H**-Ar) ppm.

^{13}C NMR (100 MHz, DMSO-d_6) δ 14.0 (**C**H_3), 22.1 (**C**H_2), 26.1 (**C**H_2), 29.5 (**C**H_2), 31.0 (**C**H_2), 39.6 (**C**H_2), 116.8 (Ar**C**), 125.2 (Ar**C**), 140.3 (Ar$\mathbf{C}_q$-NH), 147.3 (Ar$\mathbf{C}_q$-NO_2), 154.5 (**C**O) ppm.

LRMS (ES$^+$) *m/z* 266 $[M+H]^+$.

HRMS (ES$^+$) for $C_{13}H_{20}N_3O_3^+$ $[M+H]^+$, calculated 266.1499 found 266.1504.

Gelator 3 - 1-Ethyl-3-(4-methoxyphenyl)urea



$C_{14}H_{22}N_2O_2$
Molecular Weight: 250,34

Hexyl isocyanate (1.50 g, 1.70 mL, 0.01 mol) and *p*-anisidine (1.23 g, 0.01 mol) were stirred overnight at room temperature in 20 mL dichloromethane. Hexane was added to the solution until a purple precipitate had formed, which was collected after filtration and subsequently dried under high vacuum (2.39 g, 9.50 mmol, 95%).

M.p. 97–98 ºC.

FT-IR (neat) ν_{max} 3376 (N–H), 1626 (amide-I), 1548 (amide-II) cm^{-1}.

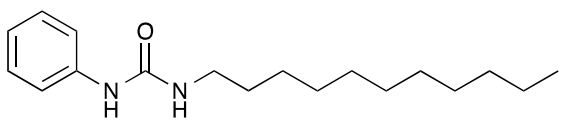
^{1}H NMR (400 MHz, DMSO-d_6) δ 0.86 (3H, t, *J* = 6.9 Hz, C**H**$_3$), 1.26 (6H, br, CH_3-C**H**$_2$-C**H**$_2$-C**H**$_2$-CH_2-CH_2-NH), 1.37-1.40 (2H, m, CH_3-CH_2-CH_2-CH_2-C**H**$_2$-CH_2-NH), 3.04 (2H, td, *J* = 6.7, 5.9 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-NH), 3.68 (3H, s, OCH_3), 5.97 (1H, t, *J* = 5.6 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-N**H**), 6.79 (2H, d, *J* = 8.1 Hz, NH-Ar$\mathbf{H}_{m}$), 7.26 (2H, d, *J* = 8.1 Hz, NH-Ar$\mathbf{H}_{o}$), 8.15 (1H, s, N**H**-Ar) ppm.

^{13}C NMR (100 MHz, DMSO-d_6) δ 14.0 (**C**H_3), 22.1 (**C**H_2), 26.1 (**C**H_2), 29.8 (**C**H_2), 31.1 (**C**H_2), 39.0 (**C**H_2), 55.2 (**C**H_3), 113.9 (Ar**C**), 119.4 (Ar**C**), 133.8 (Ar$\mathbf{C}_q$-OCH_3), 153.9 (Ar$\mathbf{C}_q$-NH), 155.5 (**C**O) ppm.

LRMS (ES$^+$) *m/z* 251 $[M+H]^+$, 273 $[M+Na]^+$, 501 $[2M+H]^+$, 523 $[2M+Na]^+$.

HRMS (ES$^+$) for $C_{14}H_{23}N_2O_2^+$ $[M+H]^+$, calculated 251.1754 found 251.1758.

Gelator 4 - 1-Phenyl-3-undecylurea



$C_{18}H_{30}N_2O$
Molecular Weight: 290,45

A solution of phenyl isocyanate (0.35 g, 0.32 mL, 2.92 mmol) and undecylamine (0.50 g, 0.60 mL, 2.92 mmol) in 20 mL dichloromethane was shaken in a sealed vial and white solid had formed immediately, which was collected after filtration and dried under high vacuum (0.59 g, 2.02 mmol, 69%).

M.p. 86–89 ºC.

FT-IR (neat) ν_{max} 3328 (N–H), 1625 (amide-I), 1557 (amide-II) cm^{-1}.

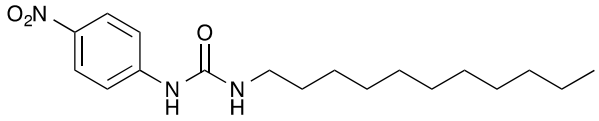
^{1}H NMR (400 MHz, DMSO-d_6) δ 0.85 (3H, t, J = 6.7 Hz, C**H**$_3$), 1.24 (16H, br, CH_3-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-CH_2-CH_2-NH), 1.39-1.42 (2H, m, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-CH_2-NH), 3.05 (2H, td, J = 6.7, 6.0 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-NH), 6.08 (1H, t, J = 5.6 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-N**H**), 6.87 (1H, dd, J = 7.1, 1.1 Hz, NH-Ar**H**$_p$), 7.20 (2H, dd, J = 8.4, 7.5 Hz, NH-Ar**H**$_m$), 7.37 (2H, dd, J = 8.6, 1.0 Hz, NH-Ar**H**$_o$), 8.34 (1H, s, N**H**-Ar) ppm.

^{13}C NMR (100 MHz, DMSO-d_6) δ 14.0 (**C**H_3), 22.1 (**C**H_2), 26.4 (**C**H_2), 28.7 (**C**H_2), 28.8 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.8 (**C**H_2), 31.3 (**C**H_2), 39.3 (**C**H_2), 117.6 (Ar**C**), 121.0 (Ar**C**), 128.7 (Ar**C**), 140.6 (Ar**C**$_q$-NH), 155.3 (**C**O) ppm.

LRMS (ES$^+$) *m/z* 291 $[M+H]^+$, 313 $[M+Na]^+$, 581 $[2M+H]^+$, 603 $[2M+Na]^+$.

HRMS (ES$^+$) for $C_{18}H_{31}N_2O^+$ $[M+H]^+$, calculated 291.2431 found 291.2431.

Gelator 5 - 1-(4-Nitrophenyl)-3-undecylurea



$C_{18}H_{29}N_3O_3$
Molecular Weight: 335,45

A solution of 4-nitrophenyl isocyanate (2.00 g, 0.01 mol) and undecylamine (2.00 g, 2.50 mL, 0.01 mol) in 20 mL dichloromethane was shaken in a sealed vial and yellow solid had formed immediately. This was triturated in ethyl acetate under reflux. The white solid obtained was collected after filtration and dried under high vacuum (2.90 g, 8.60 mmol, 72%).

M.p. 117–119 ºC.

FT-IR (neat) ν_{max} 3331 (N–H), 1633 (amide-I), 1549 (amide-II) cm^{-1}.

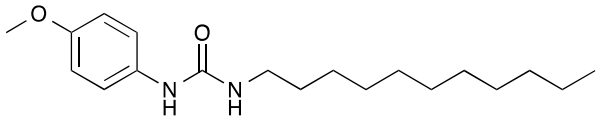
^{1}H NMR (400 MHz, DMSO-d_6) δ 0.84 (3H, t, J = 6.7 Hz, C**H**$_3$), 1.24 (16H, br, CH_3-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-CH_2-CH_2-NH), 1.41-1.45 (2H, m, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-CH_2-NH), 3.09 (2H, td, J = 6.7, 6.0 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-NH), 6.41 (1H, t, J = 5.6 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-N**H**), 7.61 (2H, d, J = 8.2 Hz, NH-Ar**H**$_o$), 8.12 (2H, d, J = 8.2 Hz, NH-**ArH**$_m$), 9.19 (1H, s, N**H**-Ar) ppm.

^{13}C NMR (100 MHz, DMSO-d_6) δ 13.9 (**C**H_3), 22.1 (**C**H_2), 26.3 (**C**H_2), 28.7 (**C**H_2), 28.7 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.5 (**C**H_2), 31.3 (**C**H_2), 39.6 (**C**H_2), 116.7 (Ar**C**), 125.1 (Ar**C**), 140.3 (Ar**C**$_q$-NH), 147.3 (Ar**C**$_q$-NO_2), 154.3 (**C**O) ppm.

LRMS (ES$^+$) *m/z* 336 $[M+H]^+$, 671 $[2M+H]^+$.

HRMS (ES$^+$) for $C_{18}H_{30}N_3O_3^+$ $[M+H]^+$, calculated 336.2282 found 336.2286.

Gelator 6 - 1-(4-Methoxyphenyl)-3-undecylurea



$C_{19}H_{32}N_2O_2$
Molecular Weight: 320,48

A solution of undecyl isocyanate (1.50 g, 1.70 mL, 7.60 mmol) and *p*-anisidine (0.90 g, 7.60 mmol) in 20 mL dichloromethane was shaken in a sealed vial and purple solid had formed immediately, which was collected after filtration and dried under high vacuum (2.08 g, 6.50 mmol, 86%).

M.p. 114–115 ºC.

FT-IR (neat) ν_{max} 3331 (N–H), 1626 (amide-I), 1557 (amide-II) cm^{-1}.

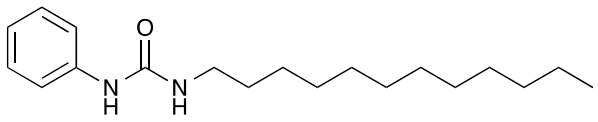
^{1}H NMR (400 MHz, DMSO-d_6) δ 0.85 (3H, t, J = 6.7 Hz, C**H**$_3$), 1.24 (16H, br, CH_3-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-CH_2-CH_2-NH), 1.38-1.41 (2H, m, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-CH_2-NH), 3.04 (2H, td, J = 6.7, 5.9 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-NH), 3.68 (3H, s, OC**H**$_3$), 5.96 (1H, t, J = 5.6 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-N**H**), 6.79 (2H, d, J = 9.2 Hz, NH-Ar**H**$_{m}$), 7.25 (2H, d, J = 9.1 Hz, NH-Ar**H**$_{o}$), 8.14 (1H, s, N**H**-Ar) ppm.

^{13}C NMR (100 MHz, DMSO-d_6) δ 14.0 (**C**H_3), 22.1 (**C**H_2), 26.4 (**C**H_2), 28.7 (**C**H_2), 28.7 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.8 (**C**H_2), 31.3 (**C**H_2), 39.5 (**C**H_2), 55.1 (**C**H_3), 113.8 (Ar**C**), 119.2 (Ar**C**), 133.7 (Ar**C**$_q$-OCH_3), 153.8 (Ar**C**$_q$-NH), 155.4 (**C**O) ppm.

LRMS (ES$^+$) *m/z* 321 $[M+H]^+$, 343 $[M+Na]^+$, 641 $[2M+H]^+$, 663 $[2M+Na]^+$.

HRMS (ES$^+$) for $C_{19}H_{33}N_2O_2^+$ $[M+H]^+$, calculated 321.2537 found 321.2537.

Gelator 7 - 1-Dodecyl-3-phenylurea



$C_{19}H_{32}N_2O$
Molecular Weight: 304,48

A solution of phenyl isocyanate (1.20 g, 1.10 mL, 0.01 mol) and dodecylamine (2.00 g, 2.50 mL, 0.01 mmol) in 20 mL dichloromethane was shaken in a sealed vial and white solid had formed immediately, which was collected after filtration and dried under high vacuum (3.32 g, 0.01 mol, 100%).

M.p. 85–87 ºC.

FT-IR (neat) ν_{max} 3331 (N–H), 1626 (amide-I), 1560 (amide-II) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6) δ 0.85 (3H, t, J = 6.7 Hz, C**H**$_3$), 1.24 (18H, br, CH_3-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-CH_2-CH_2-NH), 1.39-1.42 (2H, m, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-CH_2-NH), 3.05 (2H, q, J = 6.7 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-NH), 6.08 (1H, t, J = 5.6 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-

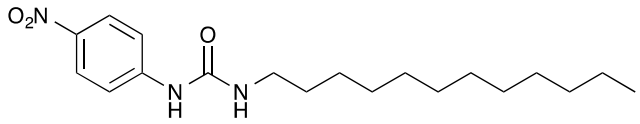
CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-N**H**), 6.87 (1H, t, J = 7.3 Hz, NH-Ar$\mathbf{H}_{p}$), 7.20 (2H, t, J = 7.9 Hz, NH-Ar$\mathbf{H}_{m}$), 7.37 (2H, d, J = 7.9 Hz, NH-Ar$\mathbf{H}_{o}$), 8.34 (1H, s, N**H**-Ar) ppm.

^{13}C NMR (100 MHz, DMSO-d_6) δ 14.0 (**C**H_3), 22.1 (**C**H_2), 26.4 (**C**H_2), 28.8 (**C**H_2), 28.8 (**C**H_2), 29.1 (**C**H_2), 29.1 (**C**H_2), 29.1 (**C**H_2), 29.1 (**C**H_2), 29.8 (**C**H_2), 31.3 (**C**H_2), 39.3 (**C**H_2), 117.6 (Ar**C**), 121.0 (Ar**C**), 128.7 (Ar**C**), 140.6 (Ar$\mathbf{C}_{q}$-NH), 155.3 (**C**O) ppm.

LRMS (ES$^+$) *m/z* 305 $[M+H]^+$, 327 $[M+Na]^+$, 609 $[2M+H]^+$, 631 $[2M+Na]^+$.

HRMS (ES$^+$) for $C_{19}H_{33}N_2O^+$ $[M+H]^+$, calculated 305.2587 found 305.2591.

Gelator 8 - 1-Dodecyl-3-(4-nitrophenyl)urea



$C_{19}H_{31}N_3O_3$
Molecular Weight: 349,48

A solution of 4-nitrophenyl isocyanate (2.10 g, 0.01 mol) and dodecylamine (2.50 g, 3.10 mL, 0.01 mol) in 20 mL dichloromethane was shaken in a sealed vial and yellow solid had formed immediately. This was triturated in ethyl acetate under reflux. The white solid obtained was collected after filtration and dried under high vacuum (2.70 g, 7.70 mmol, 59%).

M.p. 122–124 ºC.

FT-IR (neat) ν_{max} 3377 (N–H), 1613 (amide-I), 1549 (amide-II) cm^{-1}.

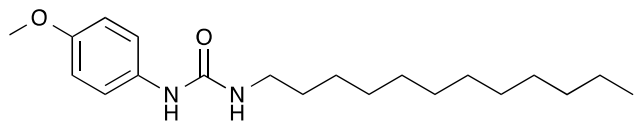
^{1}H NMR (400 MHz, DMSO-d_6) δ 0.84 (3H, t, J = 6.6 Hz, C**H**$_3$), 1.24 (18H, br, CH_3-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-CH_2-CH_2-NH), 1.41-1.44 (2H, m, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-CH_2-NH), 3.09 (2H, td, J = 6.7, 5.9 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-NH), 6.41 (1H, t, J = 5.6 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-N**H**), 7.61 (2H, d, J = 9.4 Hz, NH-Ar$\mathbf{H}_{o}$), 8.12 (2H, d, J = 9.3 Hz, NH-Ar$\mathbf{H}_{m}$), 9.19 (1H, s, N**H**-Ar) ppm.

^{13}C NMR (100 MHz, DMSO-d_6) δ 13.9 (**C**H_3), 22.1 (**C**H_2), 26.3 (**C**H_2), 28.7 (**C**H_2), 28.7 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.5 (**C**H_2), 31.3 (**C**H_2), 39.6 (**C**H_2), 116.7 (Ar**C**), 125.1 (Ar**C**), 140.3 (Ar$\mathbf{C}_{q}$-NH), 147.3 (Ar$\mathbf{C}_{q}$-NO_2), 154.4 (**C**O) ppm.

LRMS (ES$^+$) *m/z* 350 $[M+H]^+$, 699 $[2M+H]^+$.

HRMS (ES$^+$) for $C_{19}H_{32}N_3O_3^+$ $[M+H]^+$, calculated 350.2438 found 350.2439.

Gelator 9 - 1-Dodecyl-3-(4-methoxyphenyl)urea



$C_{20}H_{34}N_2O_2$
Molecular Weight: 334,50

A solution of dodecyl isocyanate (2.00 g, 2.30 mL, 9.50 mmol) and *p*-anisidine (0.78 g, 6.30 mmol) in 20 mL dichloromethane was shaken in a sealed vial and purple solid had formed

immediately. This was triturated in ethyl acetate under reflux. The white solid obtained was collected after filtration and dried under high vacuum (1.87 g, 5.58 mmol, 89%).

M.p. 114–116 ºC.

FT-IR (neat) ν_{max} 3336 (N–H), 1631 (amide-I), 1558 (amide-II) cm^{-1}.

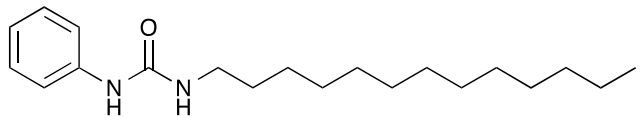
^{1}H NMR (400 MHz, DMSO-d_6) δ 0.85 (3H, t, J = 6.9 Hz, C**H**$_3$), 1.24 (18H, br, CH_3-C**H**$_2$-C**H**$_2$-CH_2-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-CH_2-CH_2-NH), 1.38-1.41 (2H, m, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-CH_2-NH), 3.04 (2H, td, J = 6.7, 6.0 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-NH), 3.68 (3H, s, OC**H**$_3$), 5.96 (1H, t, J = 5.6 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-N**H**), 6.79 (2H, d, J = 8.1 Hz, NH-Ar**H**$_m$), 7.26 (2H, t, J = 8.1 Hz, NH-Ar**H**$_o$), 8.14 (1H, s, N**H**-Ar) ppm.

^{13}C NMR (100 MHz, DMSO-d_6) δ 13.9 (**C**H_3), 22.1 (**C**H_2), 26.4 (**C**H_2), 28.7 (**C**H_2), 28.8 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.8 (**C**H_2), 31.3 (**C**H_2), 39.5 (**C**H_2), 55.1 (**C**H_3), 113.8 (Ar**C**), 119.2 (Ar**C**), 133.7 (Ar**C**$_q$-OCH_3), 153.8 (Ar**C**$_q$-NH), 155.4 (**C**O) ppm.

LRMS (ES$^+$) *m/z* 335 $[M+H]^+$, 357 $[M+Na]^+$, 670 $[2M+H]^+$, 692 $[2M+Na]^+$.

HRMS (ES$^+$) for $C_{20}H_{35}N_2O_2^+$ $[M+H]^+$, calculated 335.2693 found 335.2697.

Gelator 10 - 1-Phenyl-3-tridecylurea



$C_{20}H_{34}N_2O$
Molecular Weight: 318,51

A solution of phenyl isocyanate (1.20 g, 1.10 mL, 0.01 mol) and tridecylamine (2.00 g, 0.01 mol) in 20 mL dichloromethane was shaken in a sealed vial and white solid had formed immediately, which was collected after filtration and dried under high vacuum (4.53 g, 0.01 mol, 100%).

M.p. 93–94 ºC.

FT-IR (neat) ν_{max} 3331 (N–H), 1625 (amide-I), 1560 (amide-II) cm^{-1}.

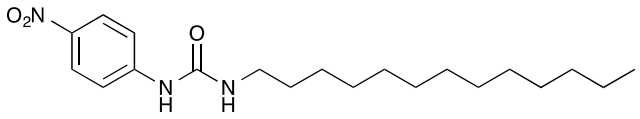
^{1}H NMR (400 MHz, DMSO-d_6) δ 0.85 (3H, t, J = 6.6 Hz, C**H**$_3$), 1.24 (20H, br, CH_3-C**H**$_2$-C**H**$_2$-CH_2-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-CH_2-CH_2-NH), 1.39-1.42 (2H, m, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-CH_2-NH), 3.05 (2H, td, J = 6.7, 5.9 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-NH), 6.07 (1H, t, J = 5.6 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-N**H**), 6.87 (1H, dd, J = 7.1, 1.2 Hz, NH-Ar**H**$_p$), 7.20 (2H, dd, J = 8.4, 7.6 Hz, NH-Ar**H**$_m$), 7.36 (2H, dd, J = 8.6, 1.1 Hz, NH-Ar**H**$_o$), 8.34 (1H, s, N**H**-Ar) ppm.

^{13}C NMR (100 MHz, DMSO-d_6) δ 13.9 (**C**H_3), 22.1 (**C**H_2), 26.4 (**C**H_2), 28.7 (**C**H_2), 28.8 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.7 (**C**H_2), 31.3 (**C**H_2), 39.5 (**C**H_2), 117.5 (Ar**C**), 120.8 (Ar**C**), 128.6 (Ar**C**), 140.6 (Ar**C**$_q$-NH), 155.1 (**C**O) ppm.

LRMS (ES$^+$) *m/z* 319 $[M+H]^+$, 341 $[M+Na]^+$, 638 $[2M+H]^+$, 660 $[2M+Na]^+$.

HRMS (ES$^+$) for $C_{20}H_{35}N_2O^+$ $[M+H]^+$, calculated 319.2744 found 319.2750.

Gelator 11 - 1-(4-Nitrophenyl)-3-tridecylurea



$C_{20}H_{33}N_3O_3$
Molecular Weight: 363,50

A solution of 4-nitrophenyl isocyanate (1.60 g, 0.01 mol) and tridecylamine (2.00 g, 0.01 mol) in 20 mL dichloromethane was shaken in a sealed vial and yellow solid had formed immediately. This was triturated in ethyl acetate under reflux. The white solid obtained was collected after filtration and dried under high vacuum (2.30 g, 6.30 mmol, 63%).

M.p. 124–126 ºC.

FT-IR (neat) ν_{max} 3331 (N–H), 1633 (amide-I), 1550 (amide-II) cm^{-1}.

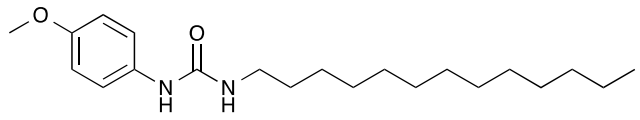
^{1}H NMR (400 MHz, DMSO-d_6) δ 0.85 (3H, t, J = 6.8 Hz, C**H**$_3$), 1.23 (20H, br, CH_3-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-CH_2-CH_2-NH), 1.41-1.45 (2H, m, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-CH_2-NH), 3.09 (2H, td, J = 6.7, 6.0 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-NH), 6.41 (1H, t, J = 5.5 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-N**H**), 7.61 (2H, d, J = 9.3 Hz, NH-Ar**H**$_o$), 8.12 (2H, d, J = 9.3 Hz, NH-Ar**H**$_m$), 9.19 (1H, s, N**H**-Ar) ppm.

^{13}C NMR (100 MHz, DMSO-d_6) δ 13.9 (**C**H_3), 22.1 (**C**H_2), 26.3 (**C**H_2), 28.7 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.5 (**C**H_2), 31.3 (**C**H_2), 39.6 (**C**H_2), 116.7 (Ar**C**), 125.1 (Ar**C**), 140.3 (Ar**C**$_q$-NH), 147.3 (Ar**C**$_q$-NO_2), 154.3 (**C**O) ppm.

LRMS (ES$^+$) *m/z* 364 $[M+H]^+$, 386 $[M+Na]^+$, 728 $[2M+H]^+$.

HRMS (ES$^+$) for $C_{20}H_{34}N_3O_3^+$ $[M+H]^+$, calculated 364.2611 found 364.2609.

Gelator 12 - 1-(4-Methoxyphenyl)-3-tridecylurea



$C_{21}H_{36}N_2O_2$
Molecular Weight: 348,53

A solution of 4-methoxyphenyl isocyanate (1.50 g, 1.30 mL, 0.01 mol) and tridecylamine (2.00 g, 0.01 mol) in 20 mL dichloromethane was shaken in a sealed vial and white solid had formed immediately, which was collected after filtration and dried under high vacuum (3.63 g, 0.01 mol, 100%).

M.p. 118–121 ºC.

FT-IR (neat) ν_{max} 3337 (N–H), 1630 (amide-I), 1559 (amide-II) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6) (gel formation in the NMR tube, broad peaks, correct integrals, multiplicity impossible to determine) δ 0.85 (3H, br, C**H**$_3$), 1.24 (20H, br, CH_3-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-CH_2-CH_2-NH), 1.39 (2H, br, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-CH_2-NH), 3.04 (2H, br, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-NH), 3.68 (3H, br, OC**H**$_3$), 5.97 (1H, br, CH_3-CH_2-CH_2-CH_2-

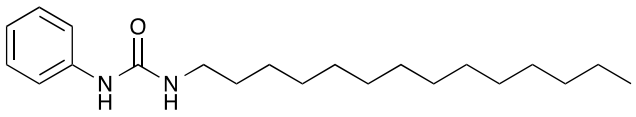
CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-N**H**), 6.80 (2H, br, NH-Ar$\mathbf{H}_{m}$), 7.26 (2H, br, NH-Ar$\mathbf{H}_{o}$), 8.14 (1H, br, N**H**-Ar) ppm.

^{13}C NMR (100 MHz, DMSO-d_6) (gel formation in the NMR tube, Ar$\mathbf{C}_{q}$-NH and **C**O missing) δ 14.0 (**C**H_3), 22.1 (**C**H_2), 26.4 (**C**H_2), 28.7 (**C**H_2), 28.8 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.8 (**C**H_2), 31.3 (**C**H_2), 39.5 (**C**H_2), 55.1 (**C**H_3), 113.8 (Ar**C**), 119.3 (Ar**C**), 133.7 (Ar$\mathbf{C}_{q}$-OCH_3) ppm.

LRMS (ES^+) *m/z* 349 $[M+H]^+$, 371 $[M+Na]^+$, 698 $[2M+H]^+$, 720 $[2M+Na]^+$.

HRMS (ES^+) for $C_{21}H_{37}N_2O_2^+$ $[M+H]^+$, calculated 349.2850 found 349.2848.

Gelator 13 - 1-Phenyl-3-tetradecylurea



$C_{21}H_{36}N_2O$
Molecular Weight: 332,53

A solution of phenyl isocyanate (1.12 g, 1.00 mL, 9.40 mmol) and tetradecylamine (2.00 g, 9.40 mmol) in 20 mL dichloromethane was shaken in a sealed vial and white solid had formed immediately, which was collected after filtration and dried under high vacuum (3.07 g, 9.20 mmol, 98%).

M.p. 93–95 ºC.

FT-IR (neat) ν_{max} 3331 (N–H), 1626 (amide-I), 1557 (amide-II) cm^{-1}.

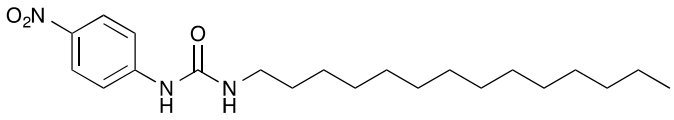
^{1}H NMR (400 MHz, DMSO-d_6) δ 0.85 (3H, t, J = 6.7 Hz, C**H**$_3$), 1.24 (22H, br, CH_3-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-CH_2-CH_2-NH), 1.39-1.42 (2H, m, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-CH_2-NH), 3.05 (2H, td, J = 6.7, 6.0 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-NH), 6.07 (1H, t, J = 5.6 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-N**H**), 6.86 (1H, dd, J = 7.3, 1.1 Hz, NH-Ar$\mathbf{H}_{p}$), 7.20 (2H, t, J = 7.9 Hz, NH-Ar$\mathbf{H}_{m}$), 7.36 (2H, dd, J = 7.9, 1.2 Hz, NH-Ar$\mathbf{H}_{o}$), 8.34 (1H, s, N**H**-Ar) ppm.

^{13}C NMR (100 MHz, DMSO-d_6) δ 13.9 (**C**H_3), 22.1 (**C**H_2), 26.4 (**C**H_2), 28.7 (**C**H_2), 28.8 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.7 (**C**H_2), 31.3 (**C**H_2), 39.5 (**C**H_2), 117.5 (Ar**C**), 120.8 (Ar**C**), 128.6 (Ar**C**), 140.6 (Ar$\mathbf{C}_{q}$-NH), 155.1 (**C**O) ppm.

LRMS (ES^+) *m/z* 333 $[M+H]^+$, 355 $[M+Na]^+$, 666 $[2M+H]^+$, 688 $[2M+Na]^+$.

HRMS (ES^+) for $C_{21}H_{37}N_2O^+$ $[M+H]^+$, calculated 333.2900 found 333.2900.

Gelator 14 - 1-(4-Nitrophenyl)-3-tetradecylurea



$C_{21}H_{35}N_3O_3$
Molecular Weight: 377,53

A solution of 4-nitrophenyl isocyanate (1.50 g, 9.40 mmol) and tetradecylamine (2.00 g, 9.40 mmol) in 20 mL dichloromethane was shaken in a sealed vial and yellow solid had formed immediately. This was triturated in ethyl acetate under reflux. The white solid obtained was collected after filtration and dried under high vacuum (3.00 g, 8.00 mmol, 85%).

M.p. 125–128 ºC.

FT-IR (neat) ν_{max} 3331 (N–H), 1633 (amide-I), 1549 (amide-II) cm^{-1}.

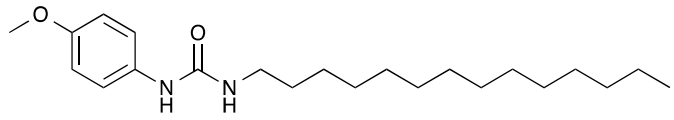
^{1}H NMR (400 MHz, DMSO-d_6) δ 0.85 (3H, t, J = 6.9 Hz, C**H**$_3$), 1.23 (22H, br, CH_3-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-CH_2-CH_2-NH), 1.41-1.45 (2H, m, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-CH_2-NH), 3.09 (2H, q, J = 6.7 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-NH), 6.41 (1H, t, J = 5.6 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-N**H**), 7.61 (2H, d, J = 9.4 Hz, NH-Ar**H**$_o$), 8.13 (2H, d, J = 9.4 Hz, NH-Ar**H**$_m$), 9.19 (1H, s, N**H**-Ar) ppm.

^{13}C NMR (100 MHz, DMSO-d_6) δ 13.9 (**C**H_3), 22.1 (**C**H_2), 26.3 (**C**H_2), 28.7 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.5 (**C**H_2), 31.3 (**C**H_2), 39.6 (**C**H_2), 116.7 (Ar**C**), 125.1 (Ar**C**), 140.3 (Ar**C**$_q$-NH), 147.3 (Ar**C**$_q$-NO_2), 154.3 (**C**O) ppm.

LRMS (ES$^+$) *m/z* 378 $[M+H]^+$, 400 $[M+Na]^+$.

HRMS (ES$^+$) for $C_{21}H_{36}N_3O_3^+$ $[M+H]^+$, calculated 378.2751 found 378.2747.

Gelator 15 - 1-(4-Methoxyphenyl)-3-tetradecylurea



$C_{22}H_{38}N_2O_2$
Molecular Weight: 362,56

A solution of 4-methoxyphenyl isocyanate (1.40 g, 1.20 mL, 9.40 mmol) and tetradecylamine (2.00 g, 9.40 mmol) in 20 mL dichloromethane was shaken in a sealed vial and solid had formed immediately. This was triturated in ethyl acetate under reflux. The white solid obtained was collected after filtration and dried under high vacuum (3.33 g, 9.20 mmol, 98%).

M.p. 118–121 ºC.

FT-IR (neat) ν_{max} 3329 (N–H), 1630 (amide-I), 1558 (amide-II) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6) (gel formation in the NMR tube, broad peaks, correct integrals, multiplicity impossible to determine) δ 0.85 (3H, br, C**H**$_3$), 1.24 (22H, br, CH_3-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-CH_2-CH_2-NH), 1.39 (2H, br, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-CH_2-NH), 3.03 (2H, br, CH_3-CH_2-CH_2-CH_2-

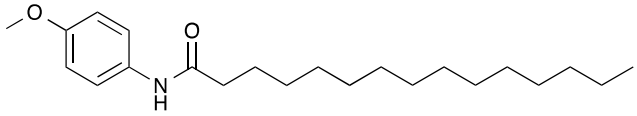
CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-NH), 3.68 (3H, br, OC**H**$_3$), 5.96 (1H, br, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-N**H**), 6.79 (2H, br, NH-Ar**H**$_m$), 7.26 (2H, br, NH-Ar**H**$_o$), 8.14 (1H, br, N**H**-Ar) ppm.

^{13}C NMR (100 MHz, DMSO-d_6) (gel formation in the NMR tube, Ar**C**$_q$-OCH_3, Ar**C**$_q$-NH and **C**O missing) δ 14.0 (**C**H_3), 22.1 (**C**H_2), 26.4 (**C**H_2), 28.7 (**C**H_2), 28.8 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.8 (**C**H_2), 31.3 (**C**H_2), 39.5 (**C**H_2), 55.1 (**C**H_3), 113.8 (Ar**C**), 119.3 (Ar**C**) ppm.

LRMS (ES$^+$) *m/z* 363 $[M+H]^+$, 385 $[M+Na]^+$, 748 $[2M+Na]^+$.

HRMS (ES$^+$) for $C_{22}H_{39}N_2O_2^+$ $[M+H]^+$, calculated 363.3006 found 363.3002.

Gelator 16 - *N*-(4-Methoxyphenyl)pentadecanamide



$C_{22}H_{37}NO_2$
Molecular Weight: 347,54

To a solution of pentadecanoic acid (4.00 g, 0.02 mol) in 50 mL dichloromethane at 0 ºC under N_2 were added oxalyl chloride (2.51 g, 1.70 mL, 0.02 mol) and DMF (3 drops) dropwise. The reaction mixture was stirred for 30 min at 0 ºC then allowed to warm at room temperature and stirred until gas evolution ceased (*ca.* 2 h).
To a solution of *p*-anisidine (2.03 g, 0.02 mol) in 150 mL dichloromethane at 0 ºC under N_2 was added triethylamine (2.00 g, 2.76 mL, 0.02 mol) dropwise over 15 min. The reaction mixture was stirred for 30 min at 0 ºC before the dropwise addition of freshly prepared acid chloride over 30 min. The reaction mixture was stirred for 30 min at 0 ºC then allowed to warm to room temperature and stirred for 3 h. The mixture was poured onto 150 mL sat. aq. NH_4Cl and stirred for 15 min. The phases were separated; the organic phase was washed with 150 mL of sat. aq. brine (2x) while the aqueous phase was washed with 100 mL dichloromethane (2x). The organic phases were collected together, dried with $MgSO_4$ and concentrated under vacuum to yield a brown solid. Purification by recrystallization in ethyl acetate afforded the final product as white solid (4.40 g, 0.01 mol, 77%).

M.p. 108–110 ºC.

FT-IR (neat) ν_{max} 3324 (N–H), 1651 (amide-I), 1563 (amide-II) cm^{-1}.

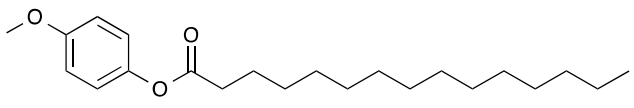
^{1}H NMR (400 MHz, DMSO-d_6) δ 0.85 (3H, t, J = 6.7 Hz, C**H**$_3$), 1.24 (22H, br, CH_3-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-CH_2-CH_2), 1.54-1.58 (2H, m, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$-CH_2), 2.24 (2H, t, J = 7.4 Hz, CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C**H**$_2$), 3.70 (3H, s, OC**H**$_3$), 6.85 (2H, d, J = 9.1 Hz, NH-Ar**H**$_m$), 7.48 (2H, d, J = 9.2 Hz, NH-Ar**H**$_o$), 9.68 (1H, s, N**H**) ppm.

^{13}C NMR (100 MHz, DMSO-d_6) δ 13.9 (**C**H_3), 22.1 (**C**H_2), 25.2 (**C**H_2), 28.6 (**C**H_2), 28.7 (**C**H_2), 28.8 (**C**H_2), 28.9 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 29.0 (**C**H_2), 31.3 (**C**H_2), 36.2 (**C**H_2), 55.1 (**C**H_3), 113.7 (Ar**C**), 120.5 (Ar**C**), 132.5 (Ar**C**$_q$-OCH_3), 154.9 (Ar**C**$_q$-NH), 170.7 (**C**O) ppm.

LRMS (ES$^+$) *m/z* 348 $[M+H]^+$.

HRMS (ES$^+$) for $C_{22}H_{38}NO_2^+$ [M+H]$^+$, calculated 348.2897 found 348.2902.

Gelator 17 - 4-Methoxyphenyl pentadecanoate



$C_{22}H_{36}O_3$
Molecular Weight: 348,53

To a solution of pentadecanoic acid (2.50 g, 0.01 mol) in 25 mL dichloromethane at 0 ºC under N_2 were added oxalyl chloride (1.30 g, 0.90 mL, 0.01 mol) and DMF (3 drops) dropwise. The reaction mixture was stirred for 30 min at 0 ºC then allowed to warm at room temperature and stirred until gas evolution ceased (*ca.* 2 h).
To a solution of 4-methoxyphenol (2.60 g, 0.01 mol) in 75 mL dichloromethane at 0 ºC under N_2 was added triethylamine (1.21 g, 1.70 mL, 0.01 mol) dropwise over 15 min. The reaction mixture was stirred for 30 min at 0 ºC before the dropwise addition of freshly prepared acid chloride over 30 min. The reaction mixture was stirred for 30 min at 0 ºC then allowed to warm to room temperature and stirred for 3 h. The mixture was poured onto 150 mL sat. aq. NH_4Cl and stirred for 15 min. The phases were separated; the organic phase was washed with 150 mL of sat. aq. brine (2x) while the aqueous phase was washed with 100 mL dichloromethane (2x). The organic phases were collected together, dried with $MgSO_4$ and concentrated under vacuum. Purification by column chromatography eluting EtOAC:Hexane (5:95) afforded the final product as white solid (2.50 g, 7.20 mmol, 72%).

M.p. 61–62 ºC.

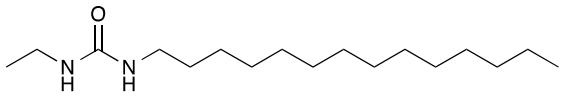
FT-IR (neat) ν_{max} 1746 (C=O stretch) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6) δ 0.85 (3H, t, J = 6.7 Hz, C**H**$_3$), 1.24 (22H, br, CH$_3$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-CH$_2$-CH$_2$), 1.58-1.65 (2H, m, CH$_3$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-C**H**$_2$-CH$_2$), 2.53 (2H, t, J = 7.3 Hz, CH$_3$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-C**H**$_2$), 3.74 (3H, s, OC**H**$_3$), 6.94 (2H, d, J = 9.2 Hz, CO-O-Ar**H**$_m$), 7.01 (2H, d, J = 9.1 Hz, CO-O-Ar**H**$_o$) ppm.

^{13}C NMR (100 MHz, DMSO-d_6) δ 13.9 (**C**H$_3$), 22.1 (**C**H$_2$), 24.3 (**C**H$_2$), 28.4 (**C**H$_2$), 28.6 (**C**H$_2$), 28.7 (**C**H$_2$), 28.8 (**C**H$_2$), 28.9 (**C**H$_2$), 29.0 (**C**H$_2$), 29.0 (**C**H$_2$), 29.0 (**C**H$_2$), 29.0 (**C**H$_2$), 31.3 (**C**H$_2$), 33.4 (**C**H$_2$), 55.4 (**C**H$_3$), 114.4 (Ar**C**), 122.5 (Ar**C**), 143.8 (Ar**C$_q$**-OCH$_3$), 156.8 (Ar**C$_q$**-O-CO), 172.1 (**C**O) ppm.

HRMS (ES$^+$) for $C_{22}H_{37}O_3^+$ [M+H]$^+$, calculated 349.2737 found 349.2740.

Gelator 18 - 1-Ethyl-3-tetradecylurea



$C_{17}H_{36}N_2O$
Molecular Weight: 284,49

A solution of ethyl isocyanate (2.30 g, 2.50 mL, 0.03 mol) and tetradecylamine (6.80 g, 0.03 mol) in 20 mL dichloromethane was shaken in a sealed vial and white solid had formed immediately, which was collected after filtration and dried under high vacuum (9.10 g, 0.03 mol, 100%).

M.p. 95–97 ºC.

FT-IR (neat) ν_{max} 3327 (N–H), 1618 (amide-I), 1579 (amide-II) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6) δ 0.85 (3H, t, J = 6.7 Hz, C**H**$_3$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-NH), 0.96 (3H, t, J = 7.2 Hz, C**H**$_3$-CH$_2$-NH), 1.24 (22H, br, CH$_3$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-C**H**$_2$-CH$_2$-CH$_2$-NH), 1.29-1.34 (2H, m, CH$_3$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-C**H**$_2$-CH$_2$-NH), 2.91-3.01 (4H, m, CH$_3$-(CH$_2$)$_{12}$-C**H**$_2$-NH, CH$_3$-C**H**$_2$-NH), 5.66-5.72 (2H, m, CH$_3$-(CH$_2$)$_{12}$-CH$_2$-N**H**, CH$_3$-CH$_2$-N**H**) ppm.

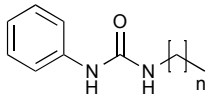
^{13}C NMR (100 MHz, DMSO-d_6) δ 13.9 (**C**H$_3$), 15.7 (**C**H$_3$), 22.1 (**C**H$_2$), 26.4 (**C**H$_2$), 28.7 (**C**H$_2$), 28.8 (**C**H$_2$), 29.0 (**C**H$_2$), 29.0 (**C**H$_2$), 29.0 (**C**H$_2$), 29.0 (**C**H$_2$), 29.0 (**C**H$_2$), 29.0 (**C**H$_2$), 30.0 (**C**H$_2$), 31.3 (**C**H$_2$), 34.0 (**C**H$_2$), 39.7 (**C**H$_2$), 160.0 (**C**O) ppm.

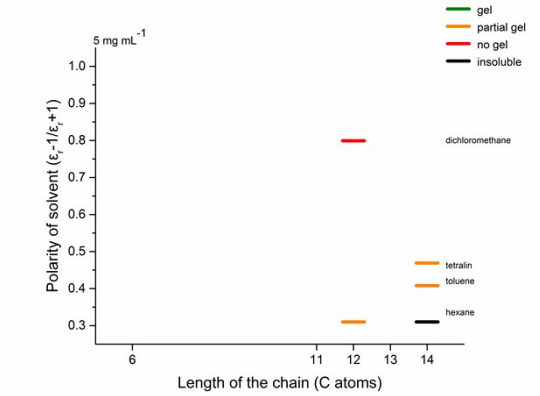
LRMS (ES$^+$) *m/z* 285 [M+H]$^+$, 307 [M+Na]$^+$, 569 [2M+H]$^+$, 591 [2M+Na]$^+$.

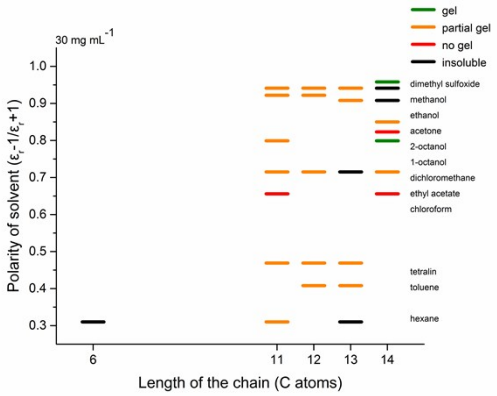
HRMS (ES$^+$) for $C_{17}H_{37}N_2O^+$ [M+H]$^+$, calculated 285.2900 found 285.2900.

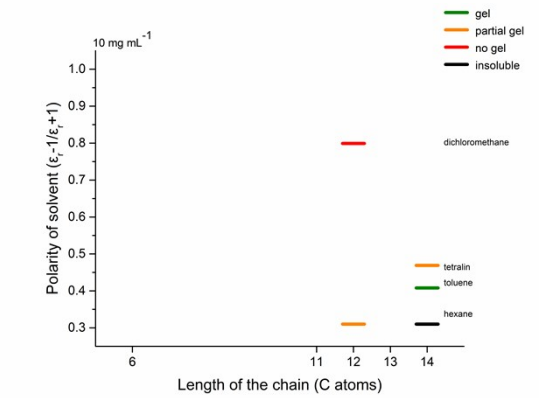
3. Gelation studies

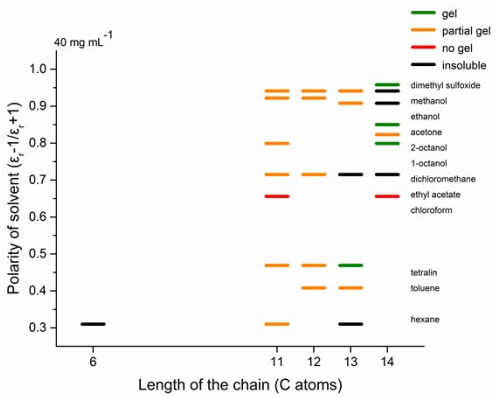
150, 100, 50, 40, 30, 20, 15, 10, 5 mg of gelators **1**–**18** were measured in 3 mL vials. 1 mL of solvents was added. The samples were heated with a heat gun until a homogeneous and clear solution was formed. They were then allowed to stand at room temperature for gelation to occur. Gel formation was confirmed by an inversion test. Note that "insoluble" means the gelator either is insoluble at all temperatures or soluble at high temperature but precipitates upon cooling (instead of gelating). Polarity values are available at www.stenutz.eu/chem. A graph at 20 mg mL^{-1} is always present for all molecules; other concentrations might not be reported as never tested.

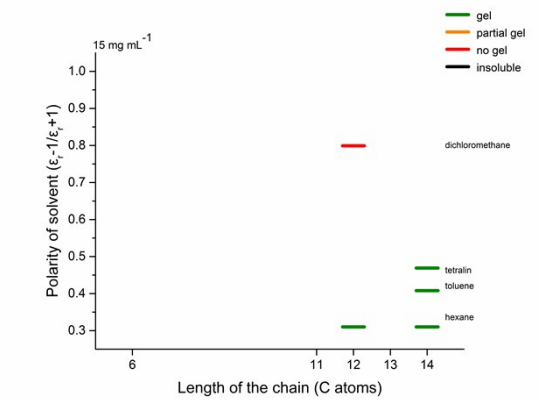

O
N
H
N
H
n

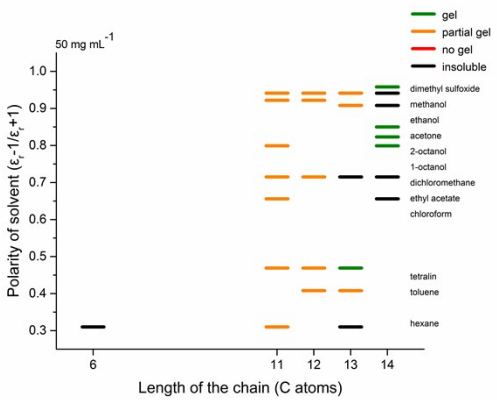

5 mg mL-1
gel
partial gel
no gel
insoluble
dichloromethane
tetralin
toluene
hexane
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)

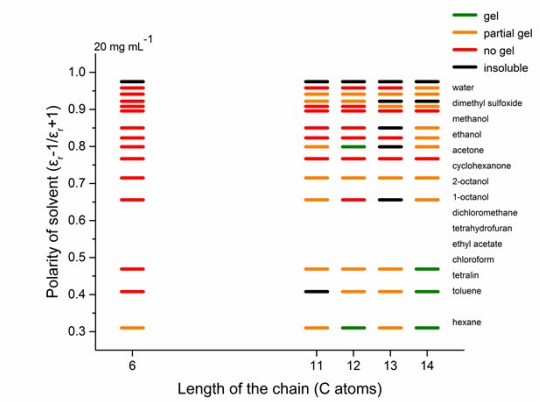

30 mg mL-1
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
methanol
ethanol
acetone
2-octanol
1-octanol
dichloromethane
ethyl acetate
chloroform
tetralin
toluene
hexane
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)

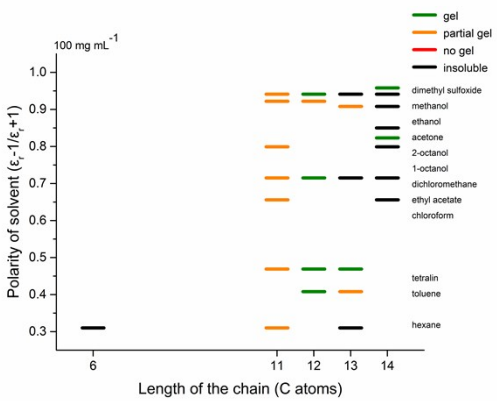

10 mg mL-1
gel
partial gel
no gel
insoluble
dichloromethane
tetralin
toluene
hexane
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)

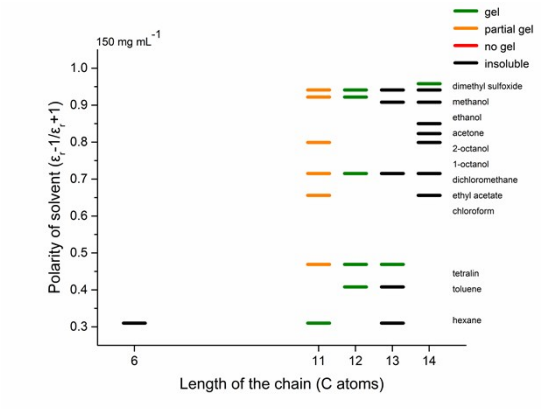

40 mg mL-1
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
methanol
ethanol
acetone
2-octanol
1-octanol
dichloromethane
ethyl acetate
chloroform
tetralin
toluene
hexane
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)

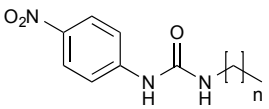

15 mg mL-1
gel
partial gel
no gel
insoluble
dichloromethane
tetralin
toluene
hexane
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)

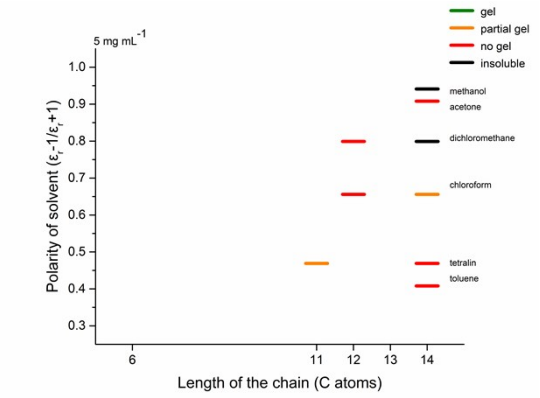

50 mg mL-1
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
methanol
ethanol
acetone
2-octanol
1-octanol
dichloromethane
ethyl acetate
chloroform
tetralin
toluene
hexane
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)

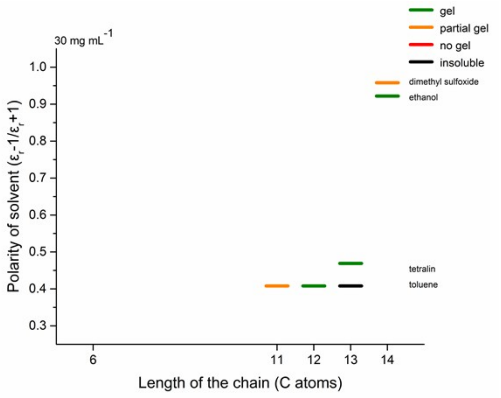

20 mg mL-1
gel
partial gel
no gel
insoluble
water
dimethyl sulfoxide
methanol
ethanol
acetone
cyclohexanone
2-octanol
1-octanol
dichloromethane
tetrahydrofuran
ethyl acetate
chloroform
tetralin
toluene
hexane
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)

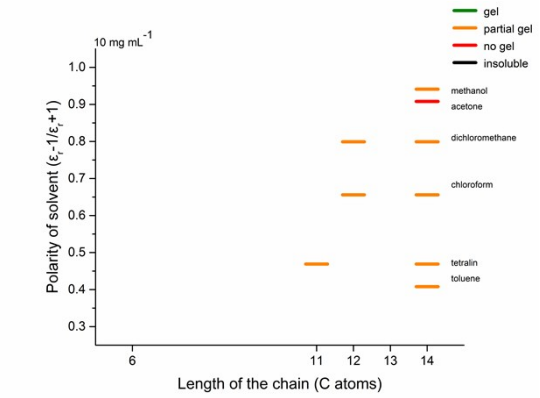

100 mg mL-1
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
methanol
ethanol
acetone
2-octanol
1-octanol
dichloromethane
ethyl acetate
chloroform
tetralin
toluene
hexane
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)

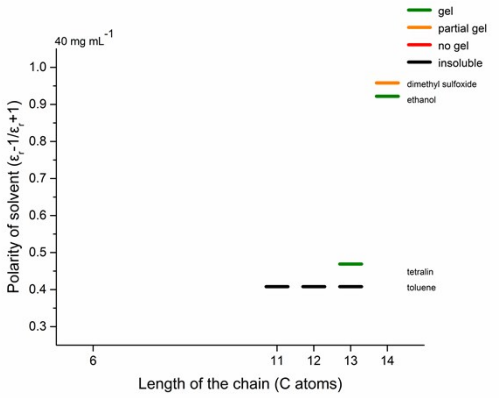

150 mg mL-1
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
methanol
ethanol
acetone
2-octanol
1-octanol
dichloromethane
ethyl acetate
chloroform
tetralin
toluene
hexane
Polarity of solvent (εr-1/εr+1)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
6
11
12
13
14
Length of the chain (C atoms)

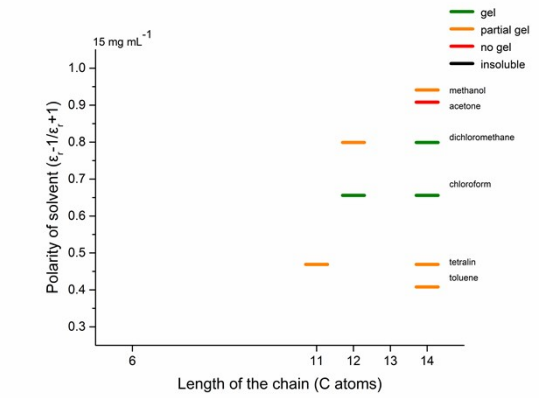

O2N
O
N
H
N
H
n

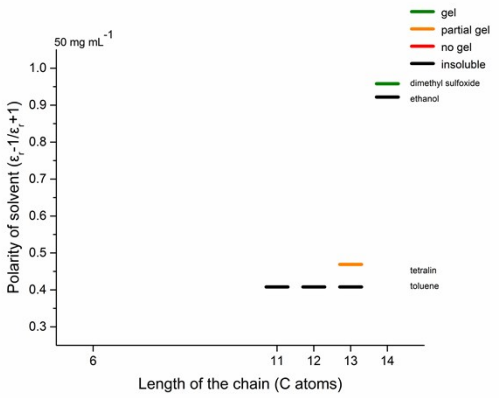

5 mg mL-1
gel
partial gel
no gel
insoluble
methanol
acetone
dichloromethane
chloroform
tetralin
toluene
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)

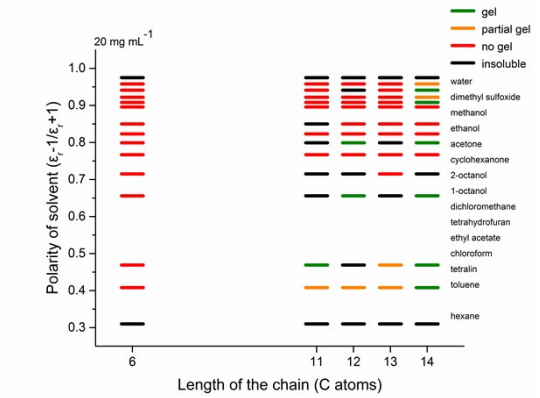

30 mg mL-1
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
ethanol
tetralin
toluene
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)

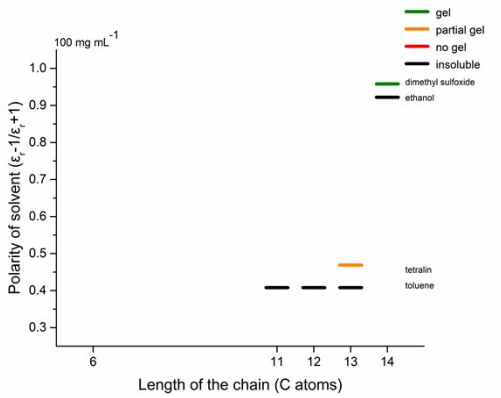

10 mg mL-1
gel
partial gel
no gel
insoluble
methanol
acetone
dichloromethane
chloroform
tetralin
toluene
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)

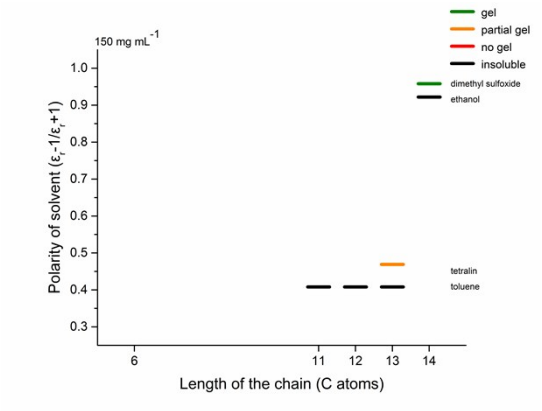

40 mg mL-1
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
ethanol
tetralin
toluene
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)

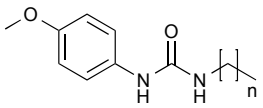

15 mg mL-1
gel
partial gel
no gel
insoluble
methanol
acetone
dichloromethane
chloroform
tetralin
toluene
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)

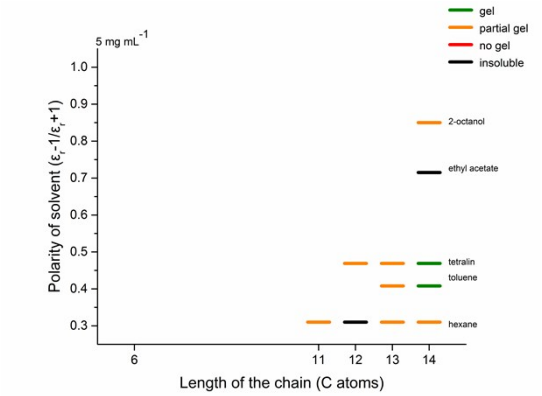

50 mg mL-1
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
ethanol
tetralin
toluene
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)

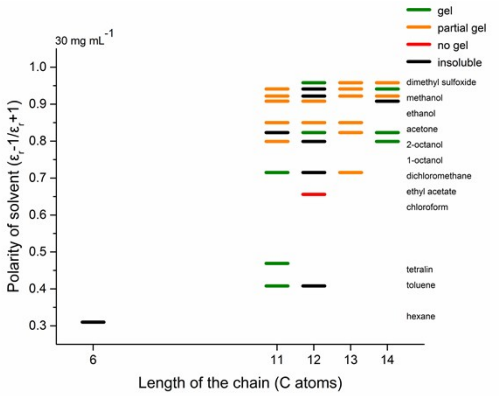

20 mg mL-1
gel
partial gel
no gel
insoluble
water
dimethyl sulfoxide
methanol
ethanol
acetone
cyclohexanone
2-octanol
1-octanol
dichloromethane
tetrahydrofuran
ethyl acetate
chloroform
tetralin
toluene
hexane
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)

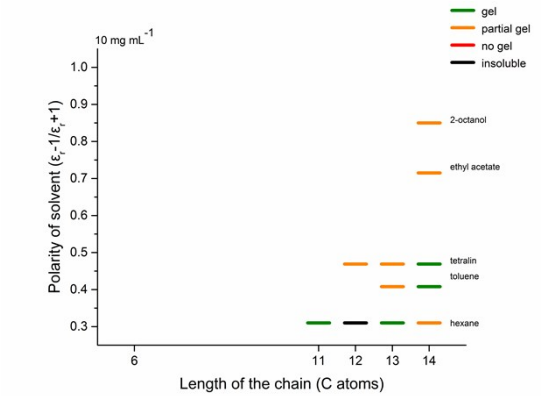

100 mg mL-1
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
ethanol
tetralin
toluene
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)


150 mg mL-1
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
ethanol
tetralin
toluene
Polarity of solvent (εr-1/εr+1)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
6
11
12
13
14
Length of the chain (C atoms)


O
O
N
H
N
H
n


5 mg mL-1
gel
partial gel
no gel
insoluble
2-octanol
ethyl acetate
tetralin
toluene
hexane
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)


30 mg mL-1
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
methanol
ethanol
acetone
2-octanol
1-octanol
dichloromethane
ethyl acetate
chloroform
tetralin
toluene
hexane
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)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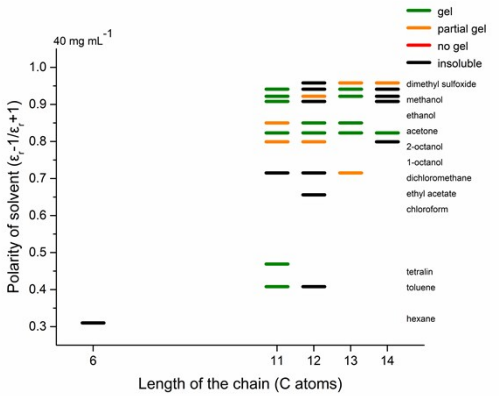
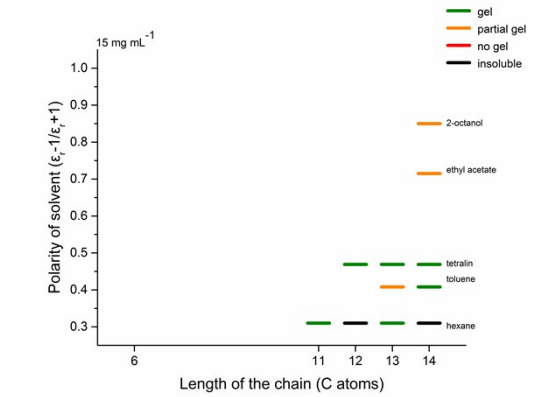
partial gel
no gel
insoluble
2-octanol
ethyl acetate
tetralin
toluene
hexane
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)


40 mg mL-1
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
methanol
ethanol
acetone
2-octanol
1-octanol
dichloromethane
ethyl acetate
chloroform
tetralin
toluene
hexane
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)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tetralin
toluene
hexane
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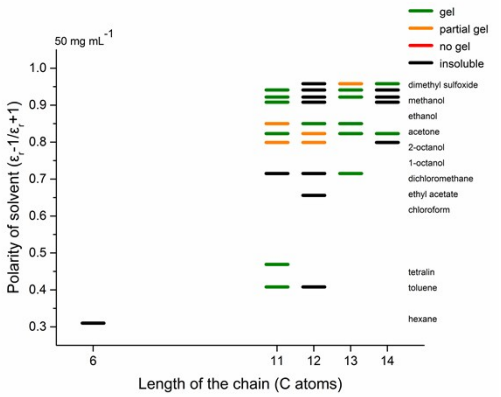
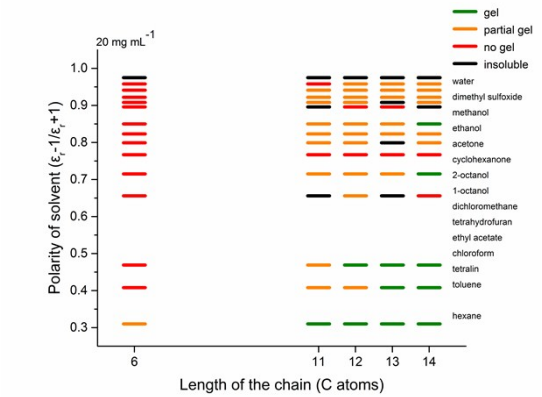
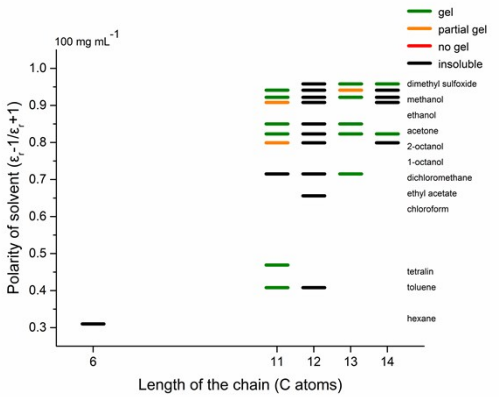
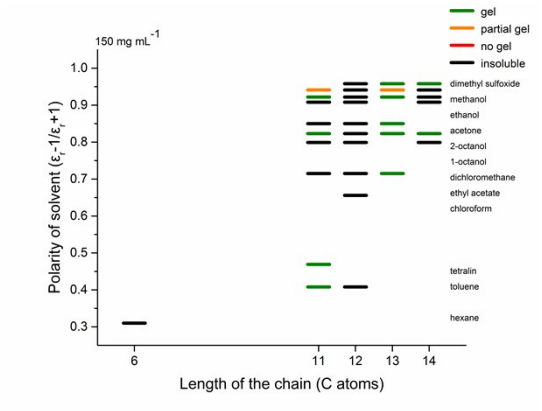
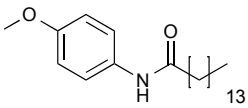
Length of the chain (C atoms)


50 mg mL-1
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
methanol
ethanol
acetone
2-octanol
1-octanol
dichloromethane
ethyl acetate
chloroform
tetralin
toluene
hexane
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)

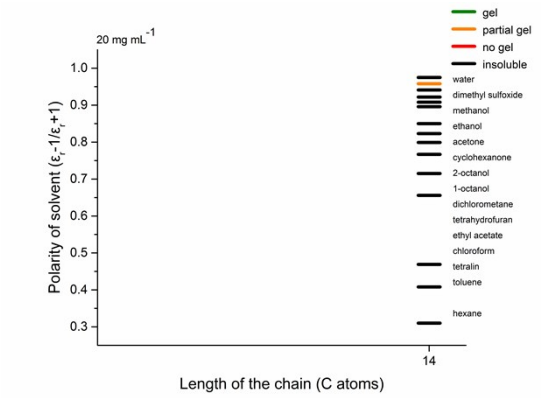

20 mg mL-1
gel
partial gel
no gel
insoluble
water
dimethyl sulfoxide
methanol
ethanol
acetone
cyclohexanone
2-octanol
1-octanol
dichloromethane
tetrahydrofuran
ethyl acetate
chloroform
tetralin
toluene
hexane
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)

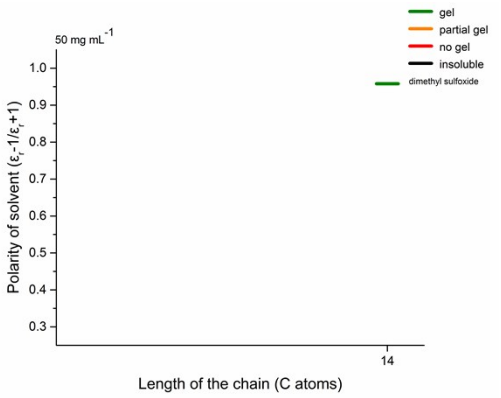

100 mg mL-1
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
methanol
ethanol
acetone
2-octanol
1-octanol
dichloromethane
ethyl acetate
chloroform
tetralin
toluene
hexane
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)


150 mg mL-1
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
methanol
ethanol
acetone
2-octanol
1-octanol
dichloromethane
ethyl acetate
chloroform
tetralin
toluene
hexane
Polarity of solvent (εr-1/εr+1)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
6
11
12
13
14
Length of the chain (C atoms)


O
O
N
H

13


20 mg mL-1
gel
partial gel
no gel
insoluble
water
dimethyl sulfoxide
methanol
ethanol
acetone
cyclohexanone
2-octanol
1-octanol
dichlorometane
tetrahydrofuran
ethyl acetate
chloroform
tetralin
toluene
hexane
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)
14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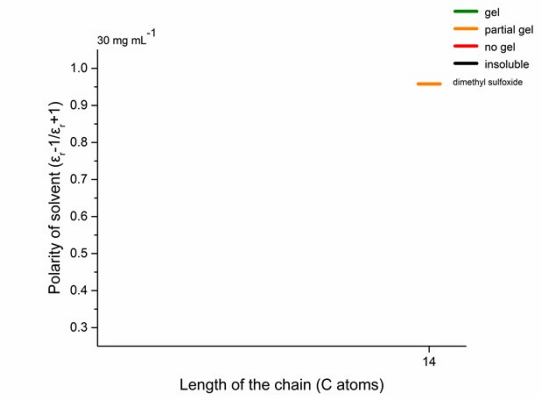
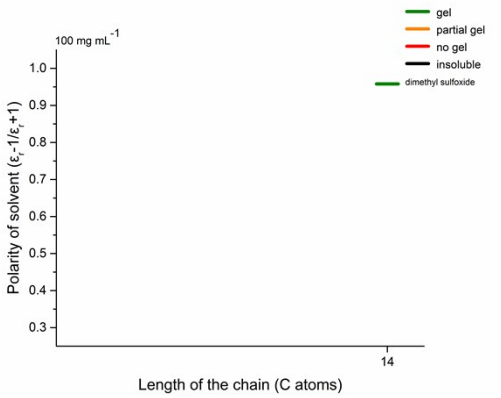
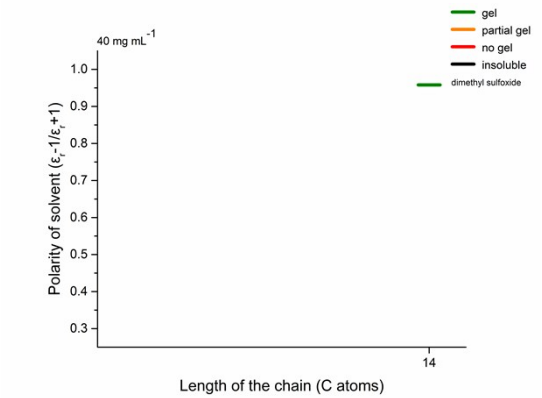
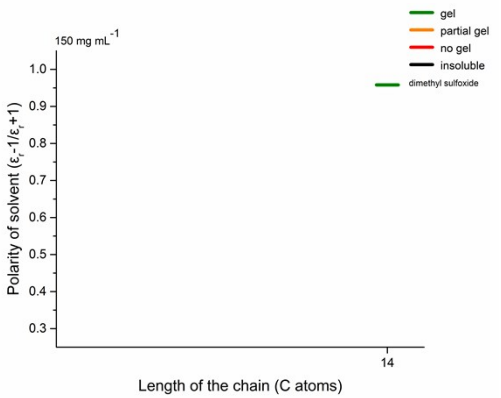
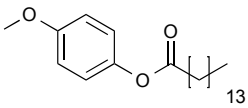
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)
14


30 mg mL-1
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)
14

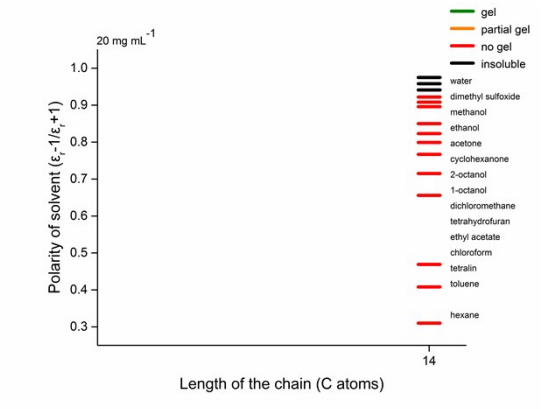

100 mg mL-1
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)
14

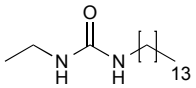

40 mg mL-1
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)
14

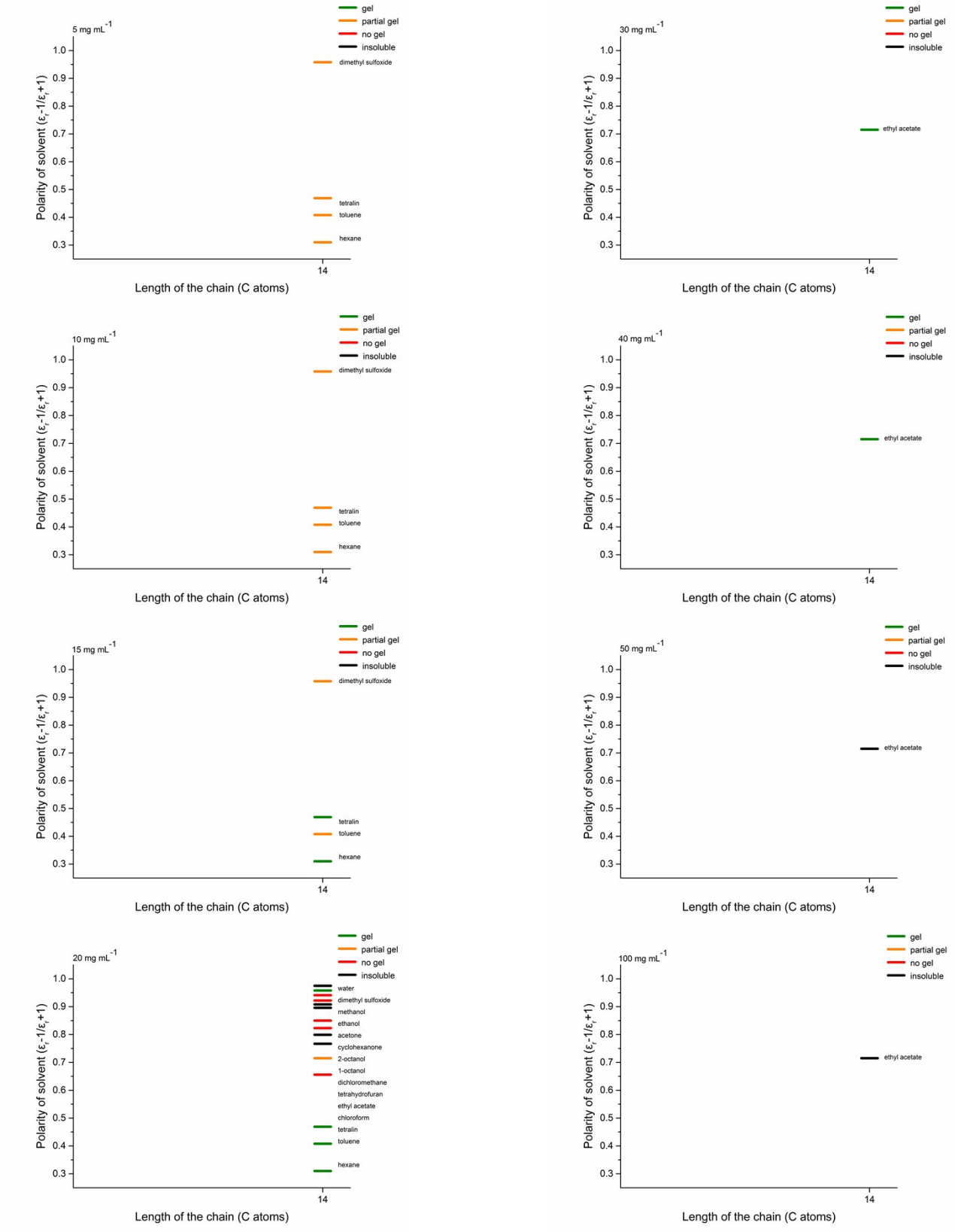

150 mg mL-1
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)
14

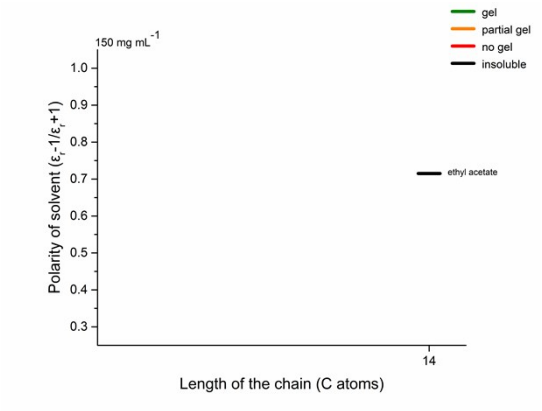

O
O
O

13


20 mg mL-1
Polarity of solvent (εr-1/εr+1)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
gel
partial gel
no gel
insoluble
water
dimethyl sulfoxide
methanol
ethanol
acetone
cyclohexanone
2-octanol
1-octanol
dichloromethane
tetrahydrofuran
ethyl acetate
chloroform
tetralin
toluene
hexane
14
Length of the chain (C atoms)


O
N
H
N
H
13


5 mg mL-1
30 mg mL-1
10 mg mL-1
40 mg mL-1
15 mg mL-1
50 mg mL-1
20 mg mL-1
100 mg mL-1
gel
partial gel
no gel
insoluble
dimethyl sulfoxide
ethyl acetate
tetralin
toluene
hexane
water
methanol
ethanol
acetone
cyclohexanone
2-octanol
1-octanol
dichloromethane
tetrahydrofuran
chloroform
Polarity of solvent (εr-1/εr+1)
Length of the chain (C atoms)
14


gel
partial gel
no gel
insoluble
150 mg mL-1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
Polarity of solvent (εr-1/εr+1)
ethyl acetate
14
Length of the chain (C atoms)

4. Differential Scanning Calorimetry

Measurements were carried out under N_2 atmosphere using a Perkin Elmer DSC7. Around 20 mg of gels **14** and **15** (20 mg mL^{-1}) were tested. All gels were prepared in toluene following the procedure described in Section 3. Note that the exothermic peak in the cooling ramp represents the condensation of toluene.

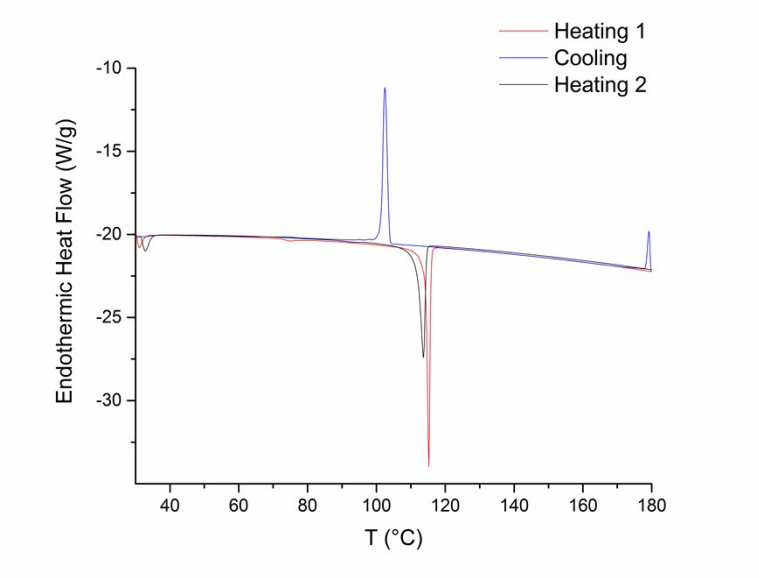


Figure S1: DSC trace of gel **14**.

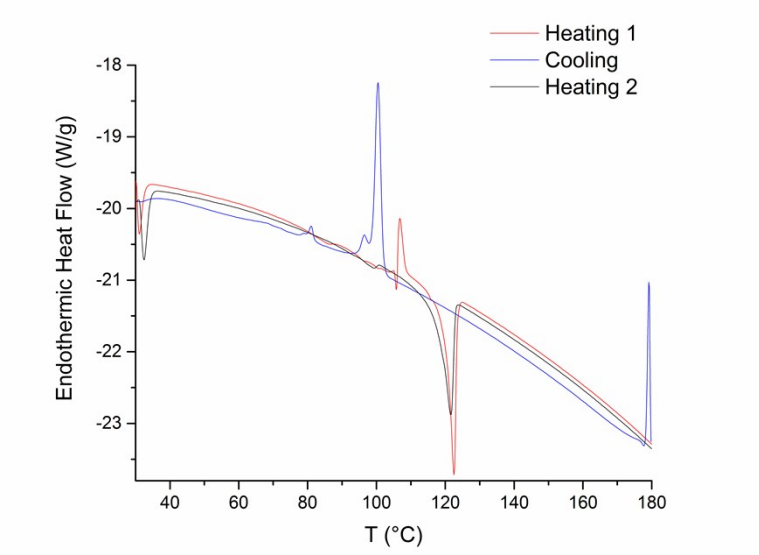


Figure S2: DSC trace of gel **15**.

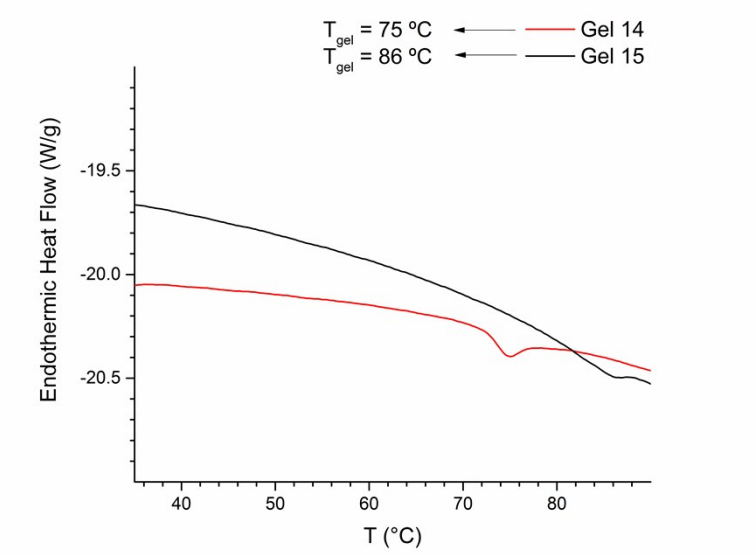


Figure S3: Comparison of the first heating ramp of gels **14** and **15**.

5. Rheology of gels

Rheology experiments were performed using an AR2000EX rheometer. Measurements of the gels were made using 40 mm crosshatched stainless steel plates with a gap of 1000 μm. In the LVER a constant oscillatory shear stress of 0.4 Pa was applied to monitor the dependence on angular frequency ranging between 6.28 and 628.0 rad s^{-1} (1-100 Hz). Rheological experiments were carried out at r.t.. Storage (G') and loss (G'') moduli were also obtained from sweep measurements. Gels **14**, **15** (20 mg mL^{-1}) were investigated. All gels were prepared in toluene following the procedure described in Section 3.

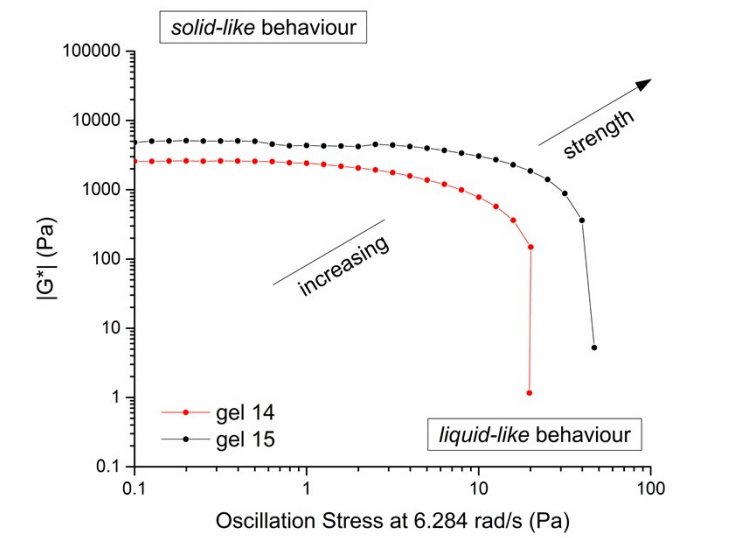


Figure S4: Oscillation stress sweep experiments of gels **14** and **15**.

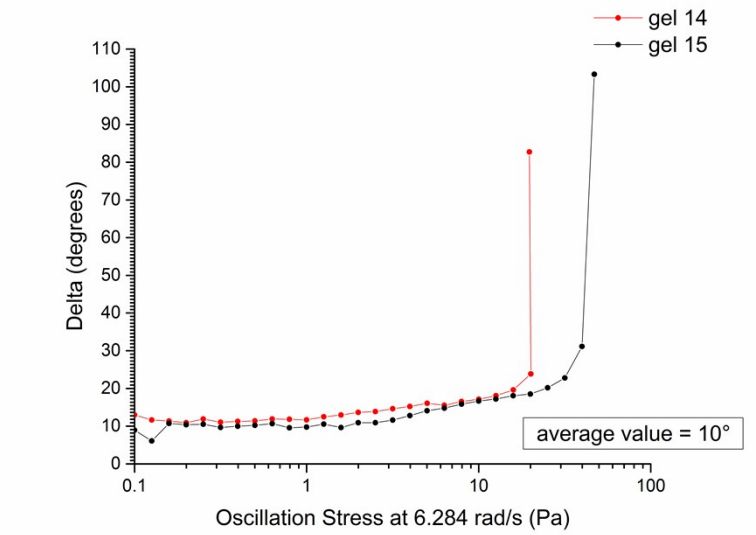


Figure S5: Stress sweep of gels **14** and **15** with average phase angle value.

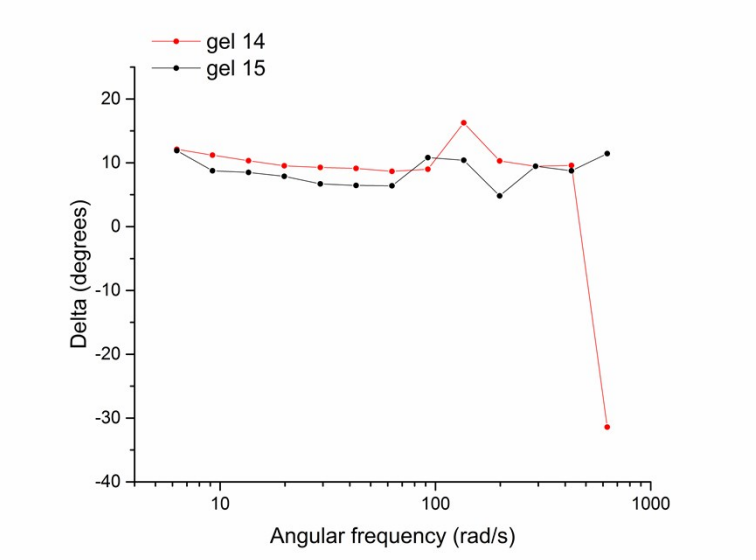


Figure S6: Angular frequency sweeps of gels **14**, **15**.

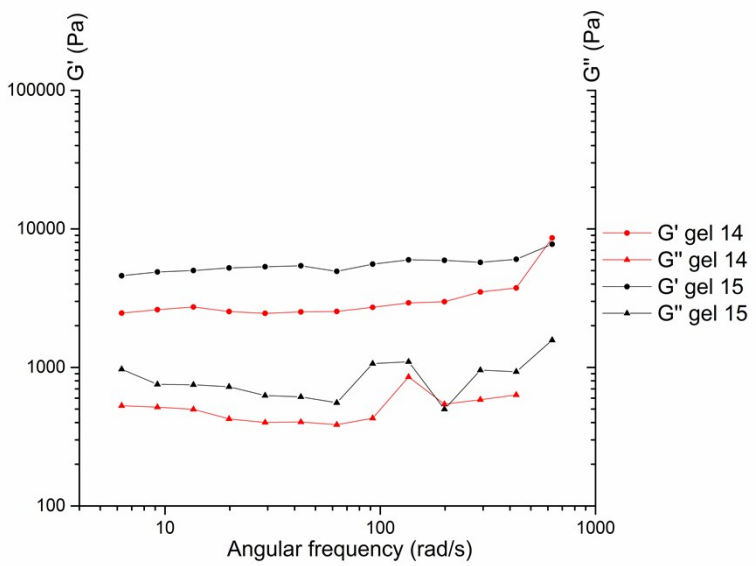


Figure S7: Angular frequency sweeps of gels **14**, **15** showing the storage moduli (G') and the loss moduli (G'').

6. Environmental SEM

The instrument used was a Philips XL–30. Samples were analysed together using a multiple pin sample holder. No sample coating was necessary. Accelerating voltage was 10.0 kV, while GSE (Gaseous Secondary Electrons) were collected in imaging mode to acquire images at 500x and 1000x magnification from each sample. Vacuum was considered established after 6 flushes of water vapour. WD (Working Distance) varied between 7.2 and 8.3 mm and spot size parameter was 5.0, while contrast and brightness were adjusted accordingly. No significant stigmatism was observed. Partial pressure of water in the chamber was kept 0.7 Torr.
Environmental SEM images were taken on xerogels obtained from gels **14**, **15** (20 mg mL^{-1}) in toluene. All gels were prepared following the procedure described in Section 3.

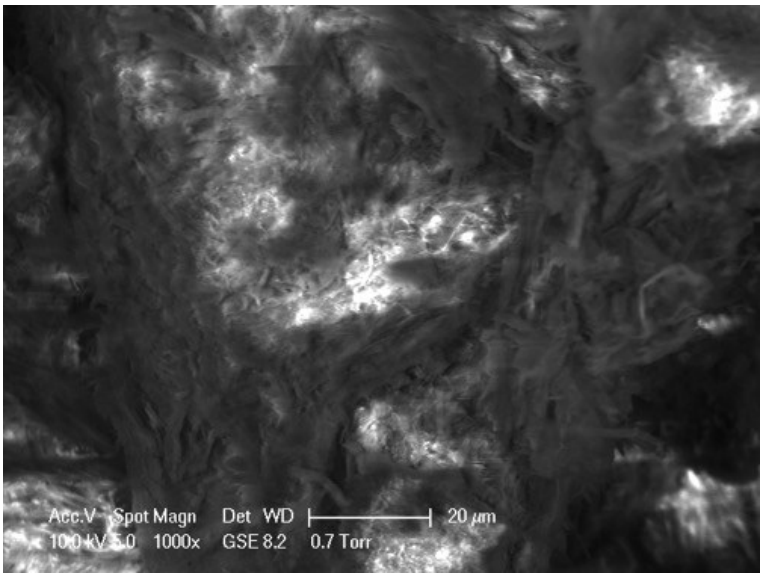


Figure S8: ESEM picture of xerogel **14** (1000x).

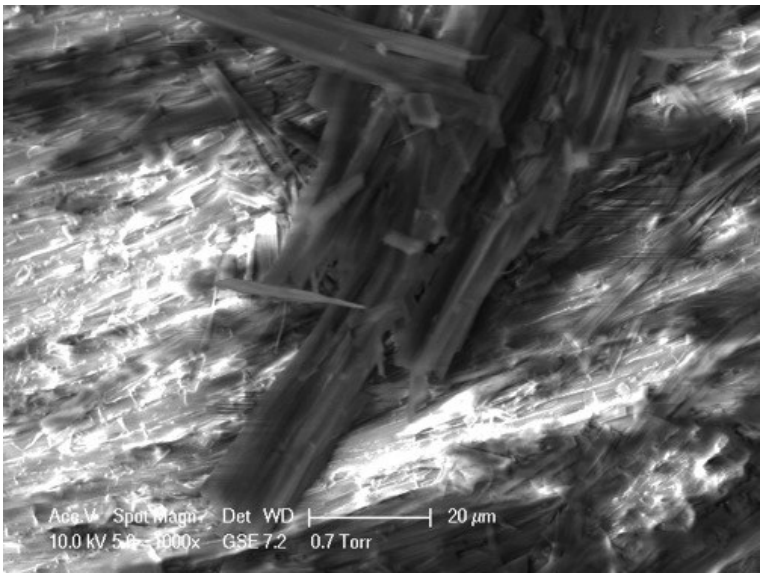


Figure S9: ESEM picture of xerogel **15** (1000x).

7. Molecular modelling

7.1. Crystal Structure Prediction

A computational crystal structure prediction (CSP) study, as we have performed it, involves surveying the landscape of potential crystal structures, which correspond to local minima on the lattice energy surface, and calculating the lattice energy of each. As has been described in the text, we performed a rigid-molecule search, and also a flexible-molecule search, for both gelators **14** and **15**.

To perform the rigid molecule search, we optimised the molecular geometry of each molecule with density functional theory (DFT), specifically B3LYP with Grimme's D3 Becke-Johnson damped dispersion correction,[1] with a 6-311G(d,p) basis set, and all DFT calculations herein were performed with this level of theory using the Gaussian09 software.[2] The urea group was constrained to a planar geometry throughout and, by starting with the $–OCH_3$ group of gelator **15** in two positions, we located two energy minima (conformers) for this molecule. Both gelator **15** structures were used as a basis for a rigid search, and including gelator **14** as well, this made three independent searches in total.

The rigid molecule search was based upon our in-house Global Lattice Energy Explorer (GLEE) code,[3] which applies a quasi-random method, based on Sobol sequences.[4] All relevant degrees of freedom for the position and orientation of the molecules in the asymmetric unit, and the lengths and internal angles of the unit cell, were sampled. For each starting molecule or conformation, we generated 5000 structures in each of 16 space groups: $P1$, $P\bar{1}$, $P2_1$, $C2$, Cc, $P2_1/c$, $C2/c$, $P2_12_12$, $P2_12_12_1$, $P4_12_12$, $C222_1$, $Pna2_1$, $Pbcn$, $Pbca$, $Pnma$ and $R\bar{3}$.

Using the program DMACRYS,[5] each structure was lattice energy minimised according to a quasi-Newton Raphson scheme, keeping the molecular geometry rigid. The force field consisted of atomic multipoles (up to hexadecapole on each atom) derived from a DFT calculation, by the distributed multipole analysis method of Stone,[6] and a Buckingham potential parameterized according to a revision of Williams' methodology.[7] The pair potentials for van der Waals forces, and multipole interactions beyond the dipole to dipole summed up to a cut-off of 15 Angstroms. Duplicate structures were removed by our own clustering methodology.[3] Longer-range electrostatic interactions were summed using Ewald summation.

The inclusion of molecular flexibility within the scheme described above requires a few extensions. In the initial sampling, we lengthen the Sobol quasi-random variate to include three additional variables, which relate to the intra-molecular degrees of freedom as described in the main text (describing flexibility around the urea group and the $–NO_2$ or $–OCH_3$ substituent). The mapping from quasi-random numbers to displacements of the molecule is achieved by sampling distortions whose energy does not exceed 22 kJ $mol^{–1}$ from the lowest energy conformation of each molecule. The sampling for gelator **14** was based on a distorted hypersphere, as is described in [10], but as we wished to sample a space of distortions of gelator **15** which would, approximately, include both conformers from the rigid search concomitantly, a method based around a single, distorted hypersphere was inappropriate. Our solution was to take a training set of (443) points within the energetically accessible region of space by rejection sampling, and use a method based on inverse transform sampling to relate randomly drawn points of the cumulative probability distribution along each degree of freedom to predicted points in the full space of distortions. Our model was fitted using Gaussian process regression, and improved results were obtained by rotating the distribution into the space spanned by the eigenvectors of the (massless) inertia matrix; this method, and developments thereof, will be described in future work.

To proceed, we consider the change in intra-molecular energy, and this is achieved by fitting DFT energies of a series of trial geometries with another Gaussian process regression model. The number of training points required for the gelator **14** and **15** models were 900 and 1200 points

respectively. The same data sets were used to train a model, which related partial charges on each atom, as calculated with the Mulfit program,[8] based on the CHELPG procedure,[9] to the intra-molecular degrees of freedom. All details pertaining to our method of performing a flexible CSP search, including further references, are set out in another paper.[10]
Again, 5000 structures are generated per space group in the same space groups as the rigid molecule search. By including flexibility around the $–OCH_3$ group, we only use the lower energy conformer for gelator **15**, rather than both, as was done with the rigid search. The crystal structures thus generated are minimised, again with DMACRYS, and the same settings as above were used. The differences in the schemes were that the force field used an electrostatic model based on fitted partial charges, as has been described above, and that multiple rigid minimisations were performed within the framework of a heuristic scheme. This wrapper sampled intra-molecular flexibility according to a simplex algorithm, allowing the crystal to relax at each stage,[10] and thus converge to minima in both intra- and inter-molecular phase space.
The lowest, unique, structures from this methodology were reminimised with multipoles up to the rank of hexadecapole; i.e. the final energies are calculated with the same force field and settings as had been used in the rigid CSP, and hence the lattice energies of the flexible and rigid CSP structures are comparable amongst each other.

7.2. NMR calculations

Periodic DFT geometry optimisations and chemical shift calculations were carried out on sets of the lowest energy predicted crystal structures of **14** and **15** using the program CASTEP,[11] using a planewave basis set, and ultra-soft pseudo-potentials generated on-the-fly. We included the two lowest energy predicted crystal structures of each molecule, in addition to other low energy structures (4 for gel **14**, 5 for gel **15**) whose simulated PXRD patterns were similar to the observed PXRD from the gels. The crystal structures were first geometry-optimised, allowing all atomic positions and lattice parameters to relax. The GIPAW method[12] was then used for the calculation of chemical shielding tensors for all atoms. All calculations were performed using the PBE functional, a 700 eV plane wave energy cut-off and a Monkhorst–Pack grid of k-points corresponding to a maximum spacing of 0.05 $Å^{-1}$ in reciprocal space.

(1) S. Grimme, S. Ehrlich, and L. Goerigk. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J. Chem. Phys. 2010; 132;154104
(2) Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
(3) D. Case, J. Campbell, P. J. Bygrave and G. M. Day. *J. Chem. Theory Comput.* (2015), in press, DOI: 10.1021/acs.jctc.5b01112.
(4) I. Sobol. USSR Computational Mathematics and Mathematical Physics. 1977;16;236
(5) M. Leslie. Advanced Users DMACRYS manual. Manual release July 2013, referring to Program release. DMACRYS 2.0.8. 2013
(6) A. Stone. Distributed Multipole Analysis of Gaussian Wavefunctions. GDMA version 2.0.02

(7) D. Williams. Improved intermolecular force field for crystalline oxohydrocarbons. J. Comp. Chem. 2001;22;1
(8) P. Winn, G. Ferenczy, and C. Reynolds. J. Phys. Chem. A. 1997; 101;5437
(9) C. Breneman, K. Wiberg. Determining atom-centered monopoles from molecular electrostatic potentials. The need for high sampling density in formamide conformational analysis. Comp. Chem. 1990; 11 (3); 361
(10) D. Case, P. Bygrave, T. Gee, and G. M. Day. In preparation.
(11) S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson and M. C. Payne, Z. Kristallogr., 2005, 220, 567.
(12) C. J. Pickard and F. Mauri, Phys. Rev. B: Condens. Matter Mater. Phys., 2001, 63, 245101.

8. Powder X-ray Diffraction

Powder X-Ray Diffraction (PXRD) measurements were performed using a Thermo Scientific ARL XTRA Powder Diffractrometer by transferring *ca.* 1000 μL of the gel or reference solid powder onto a stainless steel sample holder. Samples were analysed under a Cu Kα (λ = 1.54 nm) radiation in the 2θ range of 3 to 36º, a step size of 0.01º and a scan time of 4 s.

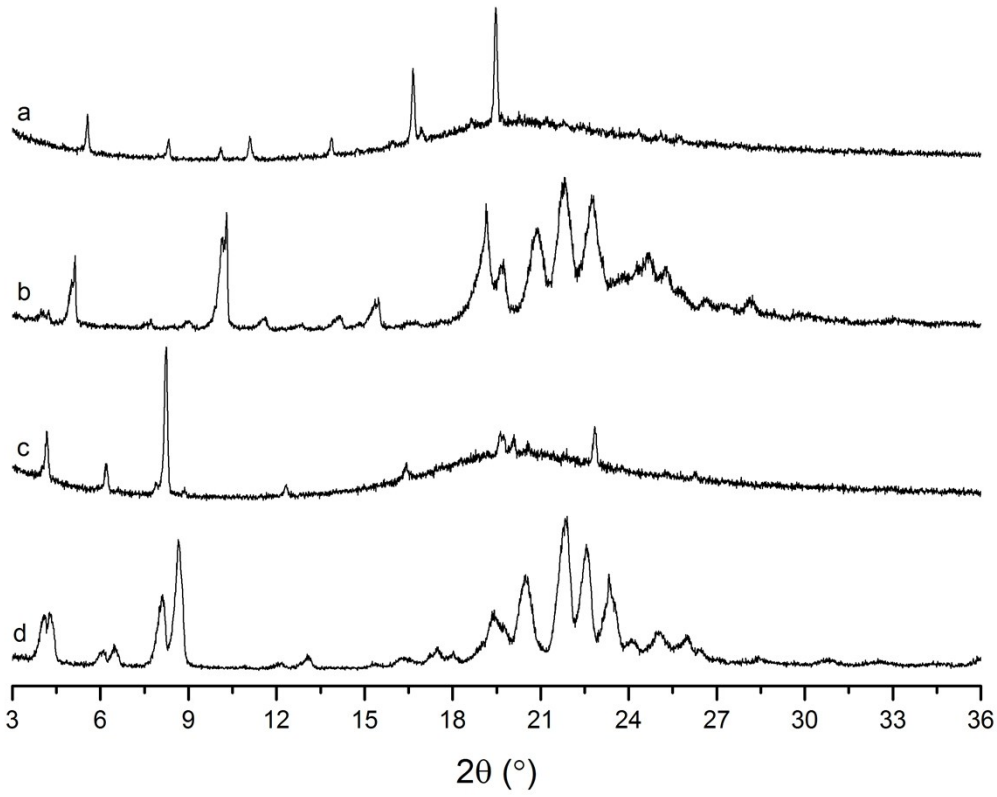


Figure S10: PXRD patterns of gels a) **14** and c) **15** in DMSO and reference solid powders of gelators b) **14** and d) **15**.

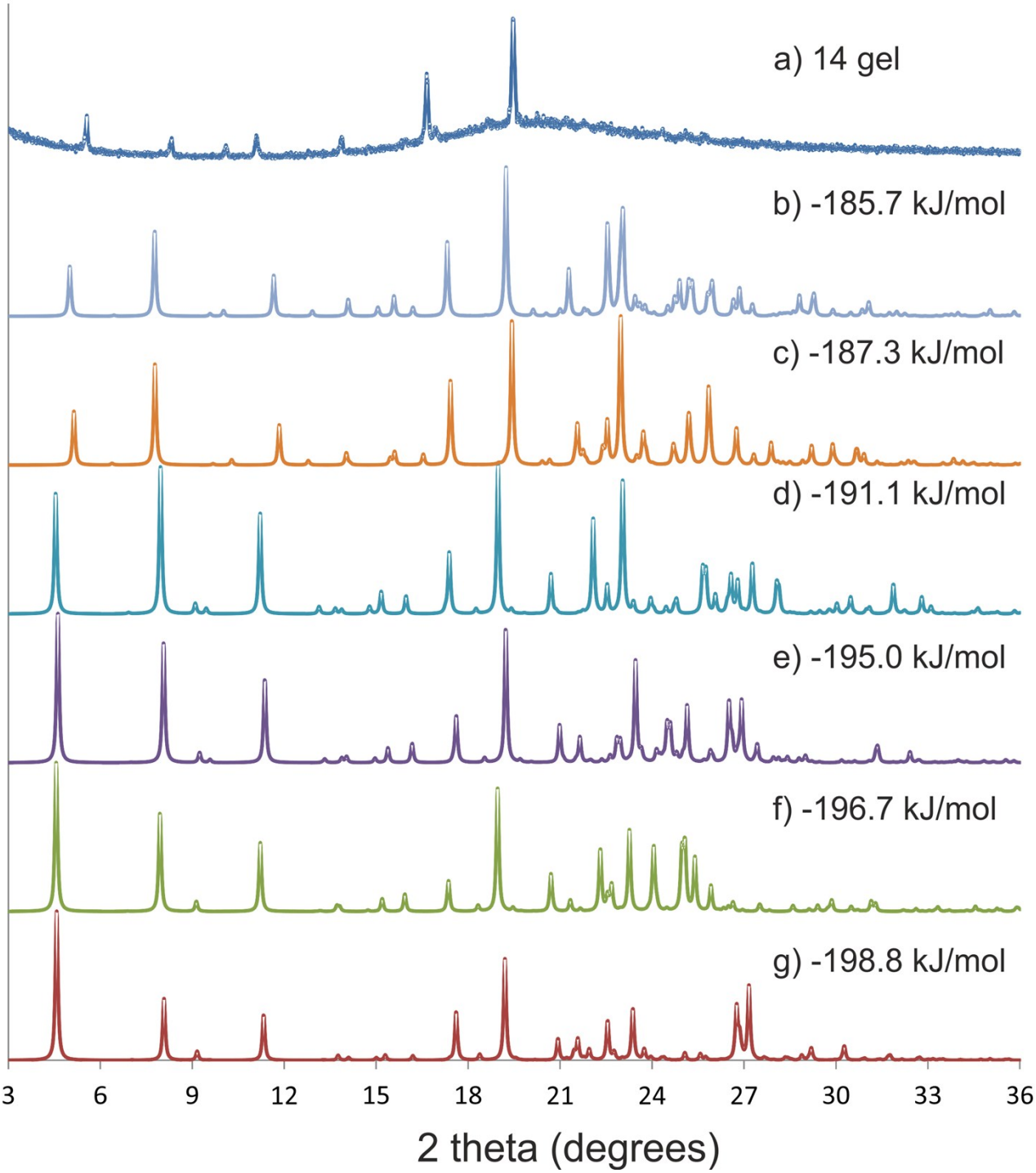


Figure S11. Comparison of PXRD from a) a gel sample of **14** with simulated PXRD patterns from six of the lowest energy predicted crystal structures (b – g), all of which contain urea-nitro (N-H…O) hydrogen bonding. The pattern (g) corresponds to the structure shown in Figure 4a.

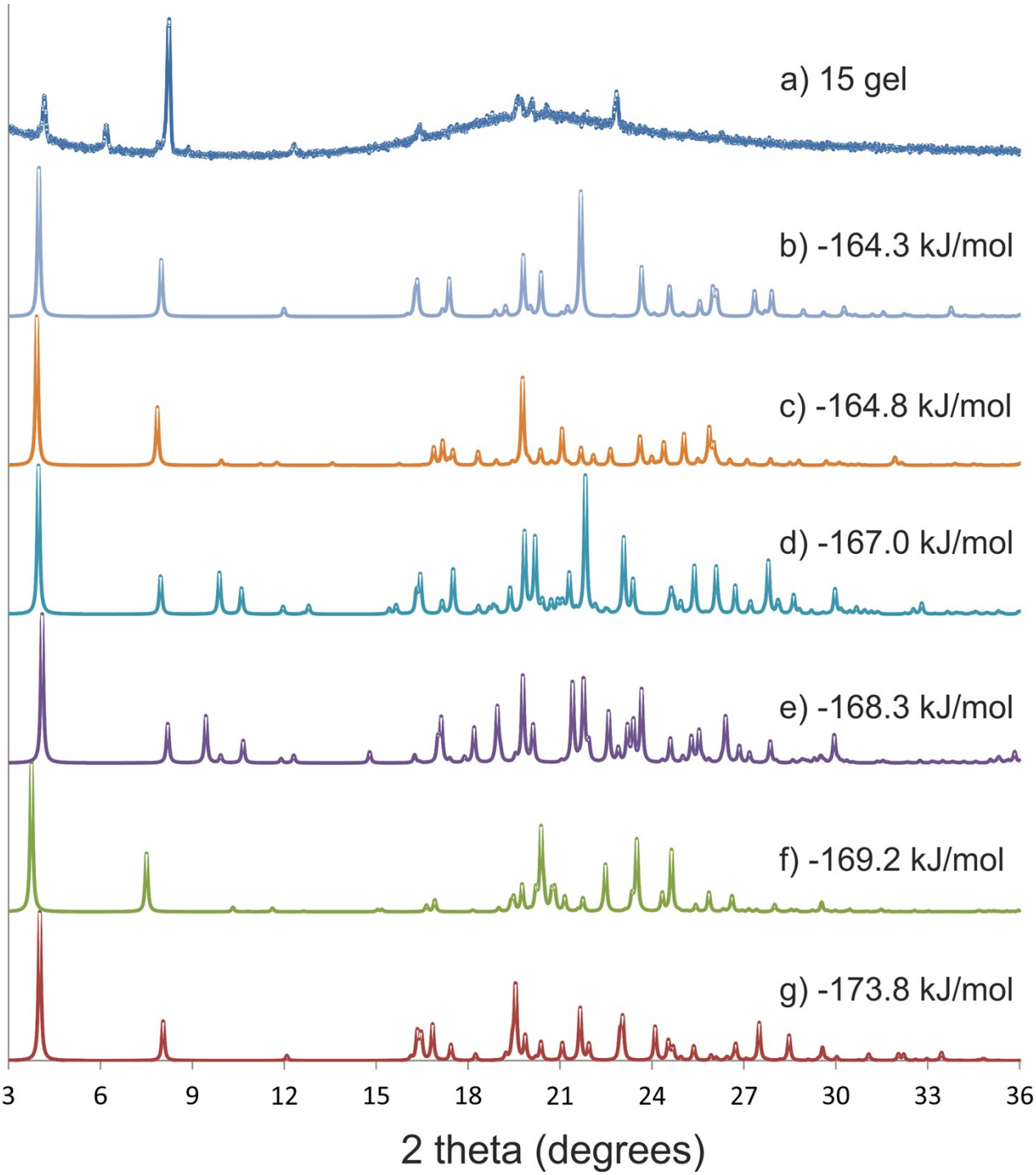


Figure S12. Comparison of PXRD from a) a gel sample of **15** with simulated PXRD patterns from six of the low energy predicted crystal structures (b – g), all of which contain urea-urea hydrogen bonding. The pattern (g) corresponds to the structure shown in Figure 4e.

9. NMR spectroscopy

Hot solutions (60 mg mL^{-1} in DMSO-d_6) were transferred into NMR tubes or plastic inserts and allowed to cool down to room temperature, after which gels were obtained.
Solution state NMR experiments were performed at 25 °C using a Bruker Avance III spectrometer at ^1H frequency of 800.23 MHz equipped with a 5 mm probe.
2D ^1H–^1H NOESY experiments with WATERGATE for solvent suppression (noesygpph19), as the samples contained significant amounts of residual DMSO, were recorded at variable mixing times, τ_m (0.0025, 0.005, 0.01, 0.025, 0.05, 0.1, 0.25, 0.5, 0.75 and 1 s), with a recycle delay of 2 s and 32 scans. Internuclear distances were calculated according to the Initial Rate Approximation, which establishes that the initial build-up of NOE enhancements with mixing time is approximately linear.[1] The cross-relaxation rate could therefore be determined from the initial slope of the build-up curve (I_{IS} as function of τ_m), where the NOE enhancement (I_{IS}) was defined as the ratio between the intensity of the cross-peak at a certain mixing time and the intensity of the diagonal peak at zero mixing time $\left(I_{IS} = \frac{I_z}{I_{eq}}\right)$, approach that has been applied to organogels by Canet *et al*.[2] In turn, the cross-relaxation rate was proportional to the inverse sixth power of the internuclear distance (r_{IS}^{-6}), $\sigma_{IS} = \zeta r_{IS}^{-6}$. This relationship between intensity and distance allowed the observed NOE intensities to be calibrated relatively to a known internuclear distance (H_c–H_d) within the supramolecular system.[1–3]

Solid-state NMR experiments were performed using a Bruker Avance III spectrometer at ^1H frequency of 400.23 MHz equipped with a 4 mm triple resonance probe. ^1H-^{13}C CP/MAS NMR experiments of powder references were acquired using 256 scans at 25 °C and a magic-angle spinning (MAS) rate of 10 kHz with a recycle delay of 20 s and contact time of 2 ms. The spectra of gel samples were acquired using 2048 scans at 25 °C and a MAS rate of 1 kHz with a recycle delay of 10 s and contact time of 2 ms. The spectra of frozen gel samples were acquired using 1024 scans at 0, 5, 10 and 15 °C and spinning rates of 1, 4 and 8 kHz with a recycle delay of 20 s and contact time of 2 ms.

(1) Neuhaus D, Williamson MP. The nuclear Overhauser effect in structural and conformational analysis: VCH New York; 1989.
(2) Bouguet-Bonnet S, Yemloul M, Canet D. New Application of Proton Nuclear Spin Relaxation Unraveling the Intermolecular Structural Features of Low-Molecular-Weight Organogel Fibers. Journal of the American Chemical Society. 2012;134(25);10621-7.
(3) Butts CP, Jones CR, Towers EC, Flynn JL, Appleby L, Barron NJ. Interproton distance determinations by NOE–surprising accuracy and precision in a rigid organic molecule. Organic & biomolecular chemistry. 2011;9(1);177-84.

Experimental and calculated ^{13}C chemical shifts for gels **14** and **15** are reported in the table below. Calculated isotropic chemical shieldings were converted to chemical shifts by matching the chemical shift of the CH_3 carbon to that of the gel at 0 ºC.

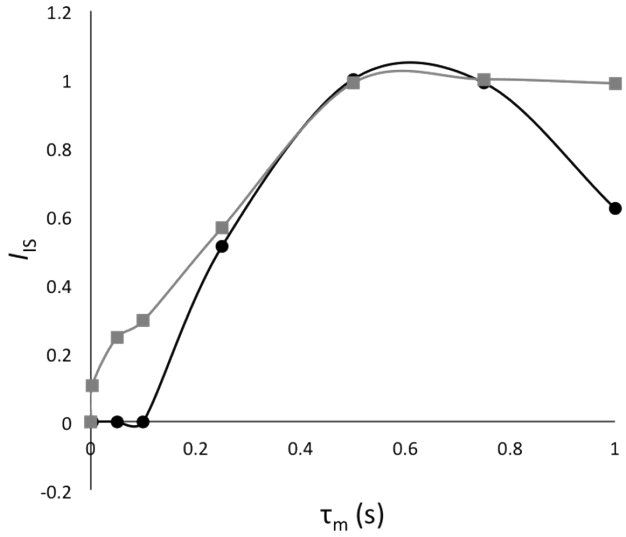


Figure S11: Evolution of normalised NOE enhancements (I_{IS}) with mixing time (τ_m) for the cross-peaks between H_c-H_d (grey squares) and NH_2-H_d (black circles), highlighting the characteristic lag time of indirect NOE enhancements.

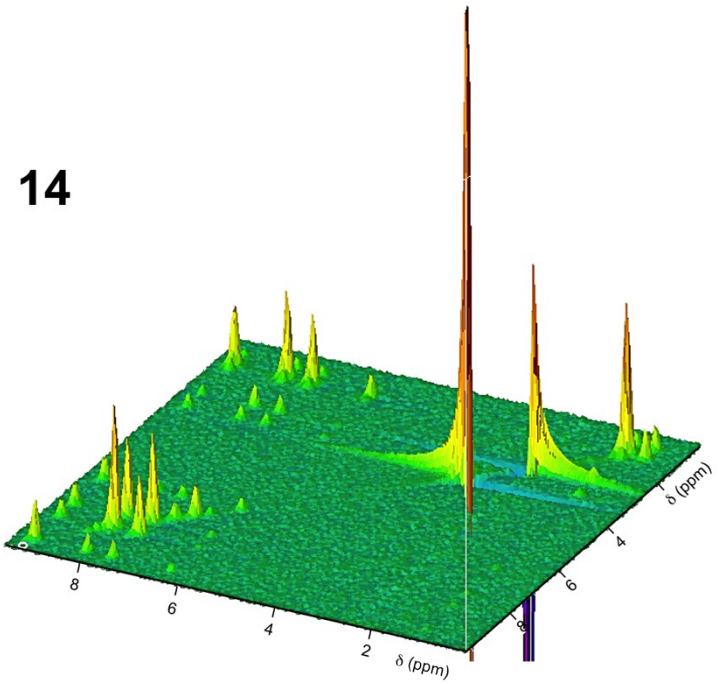


Figure S12: 2D ^1H–^1H NOESY spectra of gel **14**, 3D rendering of Fig. 4 (left).

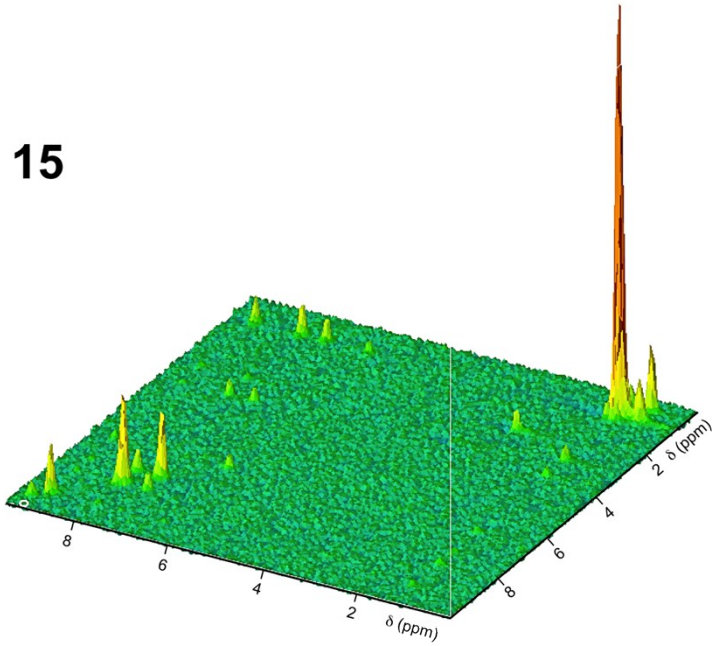


Figure S13: 2D ^{1}H–^{1}H NOESY spectra of gel **15**, 3D rendering of Fig. 4 (right).

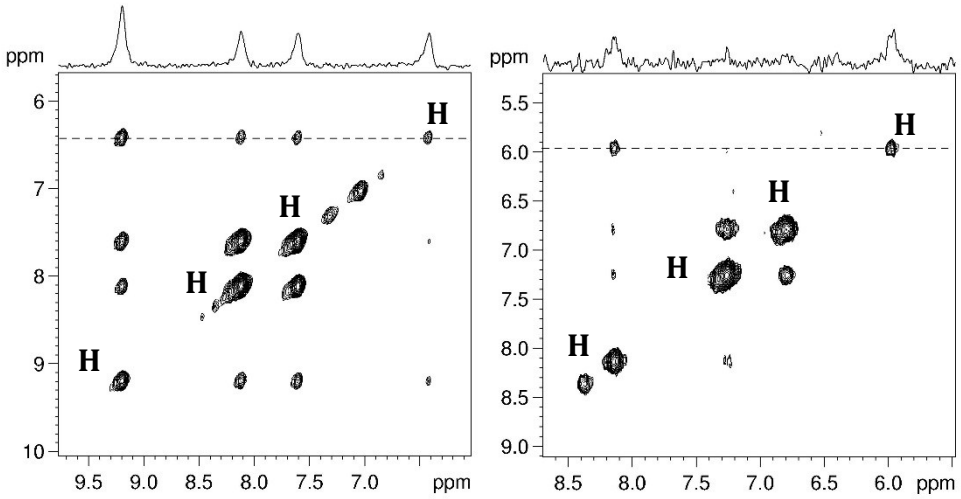
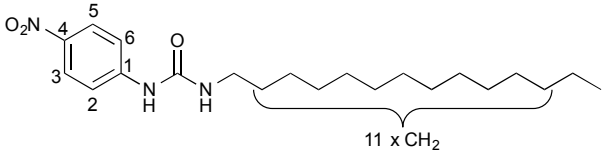
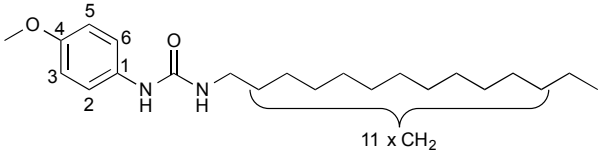


Figure S14: Expansions of 2D ^{1}H-^{1}H NOESY spectra of gels **14** (left) and **15** (right) (60 mg mL^{-1} in DMSO-d_6, 25 C, 500 ms, 800.23 MHz; cf. Fig.6 main text). The horizontal dotted line at the frequency of proton Ha indicates the slice of the spectra shown at the top. Only **14** shows an unambiguous NOE supporting the intermolecular short distance Ha-Hd.

14



15



Assignment	**14** δ (ppm)							
	Reference solid powder	Gel 0 °C 8 kHz	Calculated structures (kJ mol^{-1})					
			-198.84	-196.70	-195.02	-191.14	-187.27	-185.73
Carbonyl	155.5	155.7	149.2	151.4	153.0	152.2	148.5	148.7
C1	145.5	146.3	148.8	149.9	152.2	150.9	148.4	147.7
C4	141.2	141.3	137.7	137.5	139.7	138.0	135.4	135.7
C2	127.7	125.9	127.7	129.5	130.9	129.9	126.6	126.0
C6	126.4		126.9	128.1	129.0	128.2	126.1	125.7
C3	120.1	117.5	118.8	118.8	120.0	118.3	116.0	117.0
C5	113.5		118.1	117.4	122.0	120.2	117.2	116.8
$NH\underline{C}H_2$	42.7	41.7	41.4	41.7	42.1	41.5	40.3	38.5
11 x CH_2	33.7	34.4	33.9	34.2	35.5	35.4	32.5	33.0
$\underline{C}H_2CH_3$	25.1	26.3	26.1	27.5	29.1	28.3	24.9	24.9
CH_3	15.9	16.5	16.5	16.5	16.5	16.5	16.5	16.5
RMSD	-	-	*1.83*	*2.13*	*2.62*	*2.33*	*2.57*	*2.37*

Assignment	**15** δ (ppm)							
	Reference solid powder	Gel 0 °C 8 kHz	Calculated structures (kJ mol^{-1})					
			-173.78	-173.69	-169.17	-168.26	-167.00	-164.75	-164.33
Carbonyl	155.5	154.8	153.6	155.2	156.9	155.9	157.7	154.4	158.9
C4	158.2	158.2	155.2	156.7	157.2	157.1	160.8	155.9	158.4
	157.1	157.0							
C1	131.6	131.5	130.9	131.9	135.5	132.6	136.0	135.0	134.4
C2	128.1	127.9	123.2	127.5	130.2	125.6	126.1	125.6	127.6
	125.0	125.0							
C6	120.7	120.7	122.1	121.5	125.4	124.9	125.1	122.9	124.5
C3	116.6	118.8	116.9	121.3	121.8	121.2	123.1	121.6	121.8
		117.4							
C5	111.3	111.3	110.1	117.4	116.2	116.3	119.0	112.9	115.3
OCH_3	55.1	54.9	54.9	56.1	58.6	59.2	61.0	57.6	59.1
$NH\underline{C}H_2$	43.9	43.8	40.9	42.7	45.9	42.1	46.8	42.7	44.6
11 x CH_2	34.7	34.7	34.7	34.1	35.2	35.3	38.7	35.5	38.2
$\underline{C}H_2CH_3$	26.3	26.3	26.3	22.7	30.4	29.2	34.1	30.4	31.6
CH_3	15.6	15.5	15.5	15.5	15.5	15.5	15.5	15.5	15.5
RMSD	-	-	*1.44*	*1.84*	*2.64*	*3.19*	*4.44*	*1.92*	*3.43*