Electronic Supplementary Material (ESI) for Soft Matter.

Urea *vs* carbamate groups: a comparative study in a chiral C_2 symmetric organogelator

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Electronic Supplementary Information

General details

The R_f values refer to aluminum sheets of silica gel 200 μm thick with a granulometry of 10-12 μm and a fluorescent label (Merck) used for TLC. For flash column chromatography separation, silica gel 60 40-63 μm granulometry (Merck) was used. Melting points were obtained with an Electrothermal apparatus. NMR spectra were acquired at r.t. with Varian Gemini apparatus with a resonating frequency respect to the ^1H nucleus of 200 MHz or 400 MHz. Chemical shift values are expressed in δ (ppm) respect to the tetramethylsilane (TMS) resonating frequency. Notation s, d, t, dd, m, bs are referred to the signal multiplicity, and mean respectively: singlet, doublet, triplet, doublet of doublet, multiplet, broad signal. The letter p before these notations means pseudo.

IR spectra were recorded with a Perkin-Elmer FT-IR881 spectrophotometer. All absorbance frequencies are expressed in wavenumbers ⍰ in cm^{-1}. Notations w, m and s, referred to the signal intensity, mean respectively weak, medium and strong.

For mass spectrometry measurements an LCQ-Fleet Thermo Scientific Electron Spry Ionization (ESI-MS) apparatus was employed. Values are reported in *m/z* and the intensity is expressed as percentage respect to the most intense peak.

Elemental analysis were realized with a Perkin-Elmer 240 analyser.

UV-Vis spectra were recorded with a Varian Cary 4000 with sample holders 1mm thick.

Specific rotation for chiral compounds were carried out with a Jasco-DIP370 Polarimeter and were referred to the sodium D line (589 nm), and to a 10 cm cell length (d=1). Solution concentration was expressed as c (c = 1 means 10.0 mg/mL). The reported values are the average of 30 measurements. $[\alpha]^T_D$ was calculated according to the following formula: $[\alpha]^T_D = (\alpha \cdot 100)/c \cdot l$.

Circular Dichroism (CD) measurements were performed with a Jasco J-715 spectropolarimeter equipped with a Jasco spectropolarimeter power supply PS-150J and a thermostatic bath Lauda Ecoline RE204. Sample holder consists in a thermostatable quartz cell with a path length of 0.01 cm. All CD spectra resulted from an average of 10 scans and were repeated after rotation of the cell in order to minimize or exclude the eventual contribution of LD (Linear Dichroism). Selected HT traces measured along with CD spectra are shown in Figure S5.

Small Angle X-Ray Scattering (SAXS) experiments were performed on the Hecus M. Braun X-ray System GmbH Graz. The X-ray beam was monochromated by a Seifert-Debye generator ID 303 to $\lambda CuK\alpha = 1.542$Å. The scattered X-rays were detected by a two-dimensional position sensitive detector (Hecus M. Braun) with a sample-to-detector distance of 275 mm.

Differential Scanning Calorimetry (DSC) measurements were performed with a TA Instrument DSC Q2000 apparatus. Steel pan were used. All reported results referred to scans with heating/cooling gradient of 1 °C/min. For all measurements weighted small amounts (balance sensibility 1/100 mg) of freshly prepared gels were transferred with a spatula in the steel pans, which, before the measurement were annealed heating from r.t. to boiling solvent temperature with a 5 °C/min heating gradient. The heat flux vs temperature was controlled using an exo-up configuration, i.e. the exothermic transitions merged as positive peaks from the baseline.

The samples for the AFM investigation were prepared by dropping 50 μL of gel on a freshly cleaved mica slide (Dumico, Rotterdam, The Netherlands) and directly mounted in the spin-coater (KW 4A Chemat Technology). Spinning has been carried out at 3000 rpm for 60 s. The obtained samples were dried under a dry nitrogen flux and then mounted in the sample holder of the microscope. AFM analysis was performed with a P47-PRO instrument (NT-MDT co. Zelenograd, Moscow, Russia) using a NSC36 silicon tip (MikroMasch, Tallinn, Estonia) having a resonating frequency of 155 kHz and a spring constant of 1,75 N/m. Semicontact mode (tapping mode) was used in order to avoid deformation or damage of the examined soft samples. All the images were processed using the WSXM 4.0 Nanotec software.[1]

Synthetic details

The synthesis of compound **5** was described elsewhere. [2]

Syntheses of compounds **6** or *ent*-**6**.[3] Compound **5** (or *ent*-**5**) (1.00 g, 5.20 mmol, 1.0 equiv.) was dissolved in dry CH_2Cl_2 (28.9 mL); the solution was cooled at 0 °C; then dry TEA (1.25 g, 12.4 mmol, 1.73 mL, d = 0.72 g/mL, 1.2 equiv.) and methanesulfonyl chloride (1.42 g, 12.4 mmol, 0.96 mL, d=1.48 g/mL, 1.2 equiv.) were added. The mixture was stirred for 6 hours at that temperature. After that the mixture was washed with a saturated solution of $NaHCO_3$ (2 x 25 mL), with brine and finally the organic phase was dried over Na_2SO_4 and concentrated to give a pale yellow solid with a 98% yield (R_f =0.26 Petroleum Ether/Ethyl Acetate 2:1), which was employed for the next step without further purification.
^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.31 (m, 5H, Ph ring), 5.13 (pt, J = 4.4 Hz, 2H, *H*CO), 3.67 (s, 2H, CH_2-Ph), 3.09 (m, 8H, SO_2CH_3 and NCH_2) 2.80 (dd, ^3J=4.2 Hz, ^2J = 11.3 Hz, 2H, NCH_2) ppm.

Synthesis of compounds **7** or *ent*-**7** [3]
Compound **6** (or *ent*-**6**) (0.60 g, 1.72 mmol, 1.0 equiv.), was dissolved in dry DMF (8.60 mL). The solution, kept under nitrogen atmosphere, was added with NaN_3 (0.34 g, 5.23 mmol, 1.5 equiv.) and heated at 100 °C for 18 hours. Then the solution was diluted with water (20 mL) and extracted with ethyl acetate (3 x 20 mL). The collected organic layers were washed with brine, dried over Na_2SO_4 and concentrated to give a yellow oil as the product (quantitative yield, R_f = 0.88 Petroleum Ether/Ethyl Acetate 2:1).
^{1}H-NMR (200 MHz, $CDCl_3$): δ= 7.27 (m, 5H, Ph ring), 3.83 (pt, J = 4.2 Hz, 2H, *H*CO), 3.60 (AB system, 2H, CH_2Ph), 2.98 (m, 2H, NCH_2) 2.56 (dd, ^3J = 4.6 Hz, ^2J = 10.3 Hz, 2H, NCH_2) ppm.
Safety warnings: Compounds **7** and *ent*-**7** are diazides. Organic azides azides are known to be potentially explosive compounds, whose explosions are caused by frictions, and their handling requires careful consideration of the risks.[4] Keep in mind the equation:

$$(N_C+N_O)/N_N >3 \qquad \text{[eq. S1]}$$

for safe organic azides[5], where N_C N_O and N_N are respectively the number of carbon, oxygen and nitrogen atoms present in the molecule. Diazide **7** has a value < 3 and should be treated with special precautions although, in our laboratory, we did not experience any problem in several repeated syntheses.
Still, we suggest to not exceed the scale we used (0.6 g of starting material) and, as we did, to use a safety shield in front of the reaction flask during manipulations (insertion/removal from the rotavapor, use of glass stoppers, connectors or joints…) and to wear proper gloves and a protective mask.

Synthesis of compounds **8** or *ent*-**8**[6]
Compound **7** (or *ent*-**7**) (170 mg, 0.70 mmol) was dissolved in EtOH (1 mL) and was added with Pd/C catalyst (10% Pd) (25 mg). The reaction flask was purged with a nitrogen flux and then a hydrogen atmosphere was created. The resulting mixture was stirred at r.t. for 6 hours, then it was filtrated on celite, which was washed with MeOH. The filtrate was concentrated to dryness to give the product (92% yield). The product should be preserved from air and used as soon as possible.
^{1}HNMR (200 MHz, $CDCl_3$): δ = 7.28 (m, 5H, Ph ring), 3.63 (m, 2H, *H*CO), 3.48 (s, 2H, CH_2Ph), 2.88 (m, 2H, NCH_2) 2.43 (m, 2H, CH_2) ppm.

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[1] free download from http://www.nanotec.es/

[2] D. Rejman, P. Kočalka, M. Buděšínský, R. Pohl, I. Rosenberg, *Tetrahedron*, 2007, **63**, 1243

[3] T. Kano, Y. Hato, A. Yamamoto, K. Maruoka, *Tetrahedron*, 2008, **64**, 1197.

[4] S. Bräse, C. Gil, K. Knepper, V. Zimmermann, *Angew. Chem. Int. Ed.* 2005, **44**, 5188.

[5] H. C. Kolb, M.G. Finn, K.B. Sharpless, *Angew. Chem. Int. Ed.* 2001, **40**, 2004.

[6] J. Skarżewski, A. Gupta, Tetrahedron: Asymmetry, 1997, **8**, 1861.

Gelation experiments

All gelation experiments were performed at r.t. with the following procedure:
1. Keep a weighted amount (balance sensitivity=0,0001g) of organogelators compound in a capped vial.
2. Add a measured volume of solvent (sensitivity = 0,01 mL) in order to reach the desired final concentration for the organogelator. If the organogelator is soluble in the tested solvent, then no gel formation can occur, vice versa if the organogelator is not soluble in the solvent gelation may occur.
3. The vial is then heated with a heating gun, maintaining the cap lean on its top, till the solvent started to reflux and an homogeneous solution is obtained. Then the vial was sealed and allowed to cool to r.t. If the solution is not homogeneous, further solvent is added and heating is repeated.
4. During the cooling process the sample was held in rest for a time which depends on (i) the organogelator molecule, (ii) the solvent and (iii) the concentration of the sample, ranging from few minutes (just the time required to cool from the boiling temperature of the solvent to r.t.) to several hours.
5. Gelation was recognized by the "test-tube inversion"[7]

The minimum gelling concentration (MGC) represent the lower limit of the concentration that allows the formation of a gel stable towards “test-tube inversion”. Below this concentration only solutions or viscous systems unstable towards “test-tube inversion” are obtained. The upper gelation limit is given by the solubility of the organogelator in the hot boiling solution of the chosen solvent. Above this concentration gels are obtained, but they are not homogeneous, since they contains traces of undissolved organogelator. For this reasons they are not suitable for characterization.

DSC graphics, IR and UV and CD and SAXS spectra

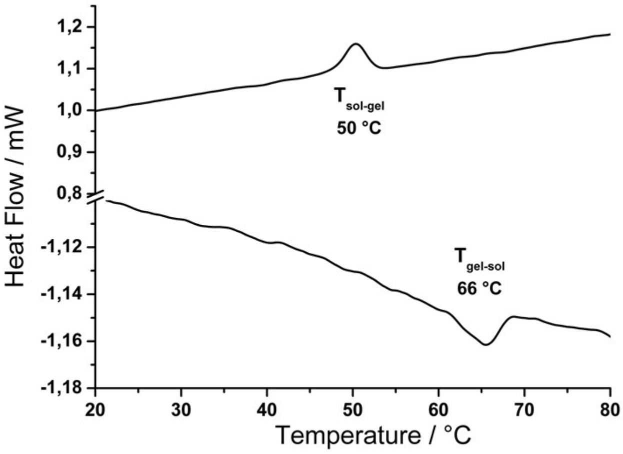

Figure S1: Calorimetric scan of a 10.0 mg/mL cyclohexane gel of **3**.

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[7] S. R. Raghavan, B. H. Cipriano, Gel Formation: phase diagrams using tabletop rheology and calorimetry. In Molecular Gels, Materials with Self-Assembled Fibrillar Networks, R. G. Weiss, P. Terech Eds, Springer, Dordrecht, The Netherlands, 2006, 239-274.

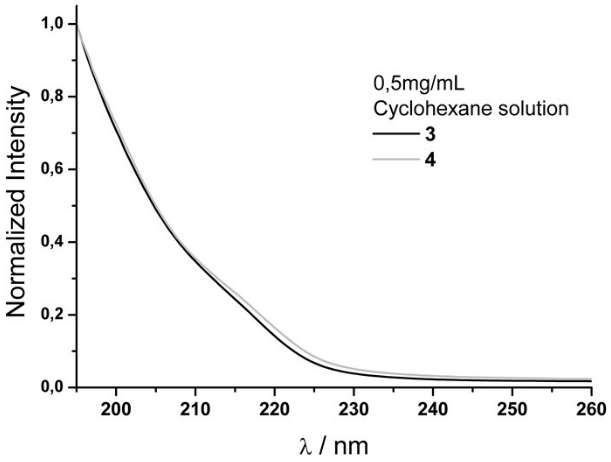

Figure S2. UV-Vis spectra of 0.5 mg/mL solution of urea organogelators.

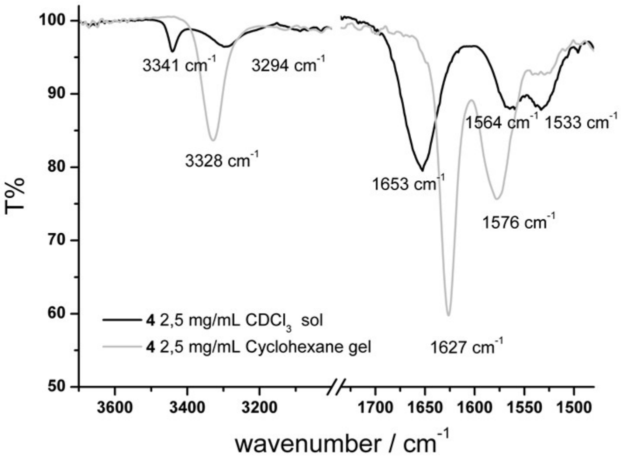

Figure S3. FT-IR spectra of 2.5 mg/mL samples of **4**.

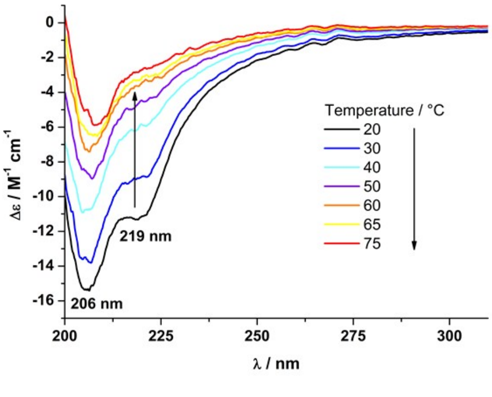

Figure S4. Left. CD spectra of a 10 mg/mL cyclohexane gel of **4** as a function of temperature from 20 °C to 75 °C. Temperature steps 5 °C. Because of experimental limit the melting temperature was not reached.

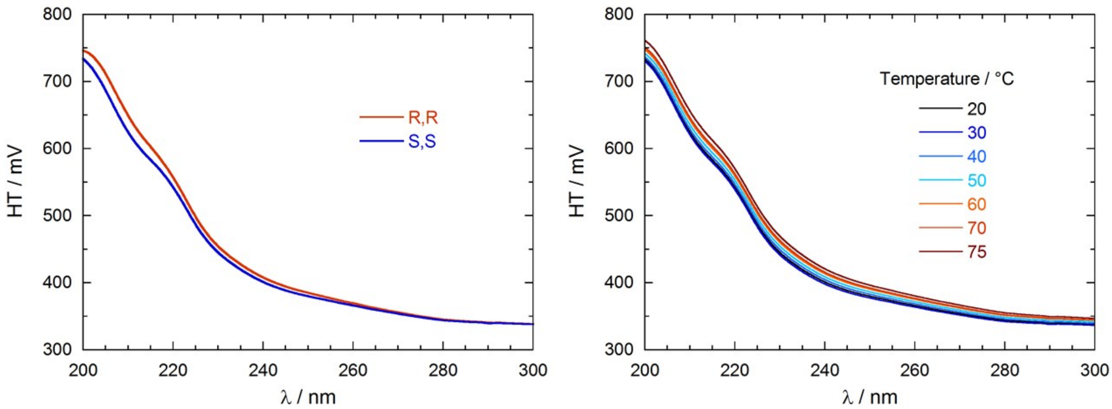

Figure S5. HT (transmittance) traces measured along with the CD spectra of the gels of **3** and *ent*-**3** (left, corresponding to the spectra of pure enantiomers in Figure 9 in the main text) and with the variable-temperature CD spectra of the gel of **3**, in cyclohexane (right, corresponding to Figure 4a in the main text).

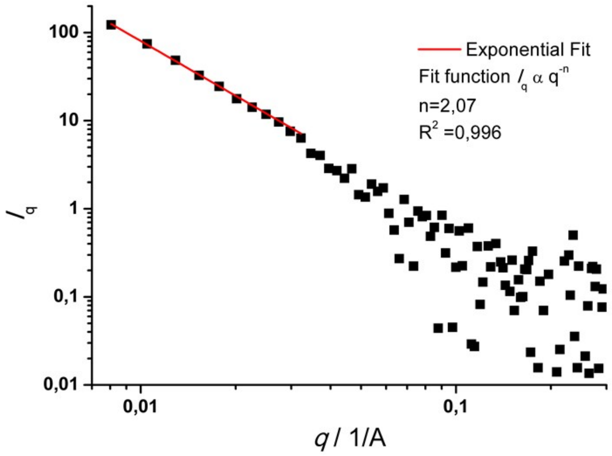

Figure S6. SAXS spectra of a cyclohexane gel of **3** (5 mg/mL). It is also reported the fit of the low-*q* region that follows a power-low decay.

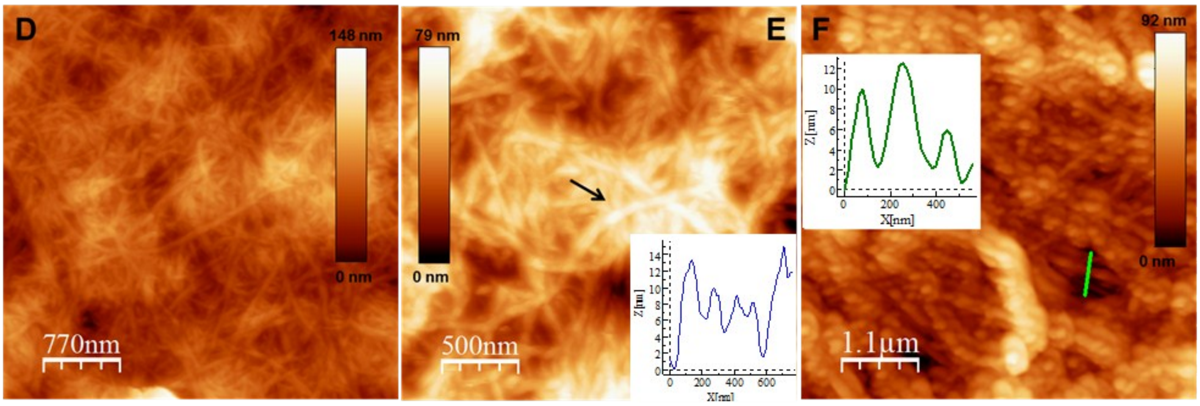

Figure S7. AFM topographic images of 5.0 mg/mL cyclohexane gel of *ent*-**3** (D,E) and **4** (F) with relative height profiles. In panel E the inset show the profile of the fiber indicated by the black arrow.

Description of the nucleation-elongation model

The aggregation process of organogelator molecules may be described by means of a nucleation-growth model, which is characterized by a first slow formation of nuclei of a critical size, followed by a faster elongation process during which the nuclei grow progressively to lead to larger aggregates. The (average) transition between the two regimes occurs at the elongation temperature T_{el}.

In the elongation regime, i.e. when $T < T_{\mathrm{el}}$, the fraction of aggregated molecules at temperature T is described by the following equation:[8]

$$\alpha_{\mathrm{agg}} = \alpha_{\mathrm{SAT}} \left\{ 1 - \exp\left[-\frac{h_{\mathrm{el}}}{R T_{\mathrm{el}}^{2}} (T - T_{\mathrm{el}}) \right] \right\} \qquad \text{[eq. S2]}$$

where h_{el} is the the intermolecular interaction enthalpy, and α_{SAT} is a parameter used to prevent the ratio $\alpha_{\mathrm{agg}}\alpha_{\mathrm{SAT}}$ exceeding unity. In the fitting of CD data, α_{agg} was set to 1 for the $\Delta\varepsilon_{\mathrm{max}}$ measured at 20°C (318K), so that at each temperature T it holds $\alpha_{\mathrm{agg}}(T) = \dfrac{\Delta\varepsilon_{\mathrm{max}}(T)}{\Delta\varepsilon_{\mathrm{max}}(318K)}$. The values of $\alpha_{\mathrm{agg}}(T)$ were plotted against T and fitted according to equation S1 using a non-linear least squares procedure which yielded, among other things, the value of T_{el}. The results of the fitting for the 4 curves shown in Figure 4 (main text) are summed in the table below.

	203 nm Cooling	218 nm Cooling	203 nm Heating	218 nm Heating
α_{SAT}	1.00 ± 0.03	1.02 ± 0.03	1.00 ± 0.03	1.00 ± 0.01
T_{el} (K)	366.0 ± 0.7	365.0 ± 0.6	368.9 ± 0.2	369.1 ± 0.1
h_{el} (kJ/mol)	−110 ± 14	−123 ± 17	−244 ± 19	−226 ± 11

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[8] a) M. M. J. Smulders, A. P. H. J. Schenning and E. W. Meijer, *J. Am. Chem. Soc.,* 2008, **130**, 606; b) U. Mayerhöffer, Würthner, F. *Chem. Sci.,* 2012, **3**, 1215.