Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Variable Temperature NMR of Organogelators : the Intensities of a Single Sample Describe the Full Phase Diagram

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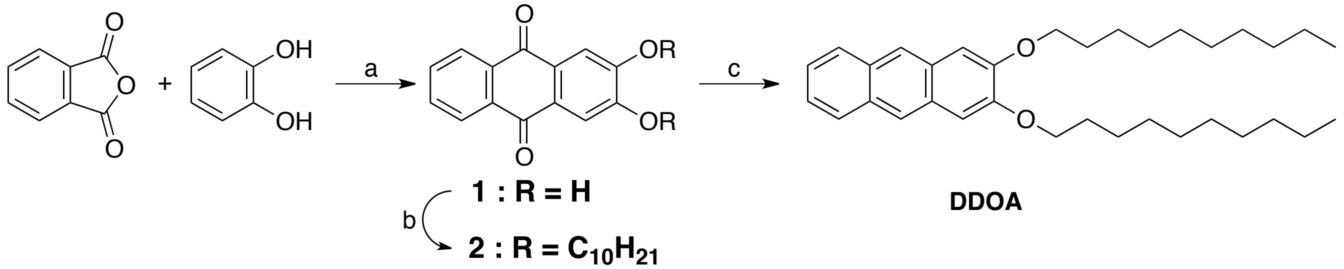
Electronic Supplementary Information

1. Synthesis of DDOA



Scheme 1. Synthetic scheme. a) AlCl3, 120 °C, 30%; b) $C_{10}H_{21}OSO_2CH_3$, K_2CO_3, Bu_4NBr, DMF, 55%; c) Zn, 40%.

2,3-dihydroxyanthracene-9,10-dione (1). $AlCl_3$ (100 g, 750 mmol) and NaCl (13 g, 222 mmol) were heated at 120 °C under mechanical stirring until the formation of the eutectic liquid. 1,2-Dihydroxybenzene (11.1 g, 101 mmol) and phtalic anhydride (15.0 g, 101 mmol) were added over 30 minutes and the solution was heated at 150 °C for 1 h 30. The reaction mixture was cooled and hydrolyzed with water first (150 ml) and then with hydrochloric acid (37%, 200 ml). The suspension was dissolved by reflux (160 °C) for 3 h. On cooling, a brown solid precipitated. It was filtered and dried under vacuum overnight. The precipitate was dissolved in sulfuric acid 95% (140 ml) and refluxed for 3 h. The solution was cooled mixed with water (300 mL) and the resulting precipitate filtered off and dried overnight under vacuum. The crude recrystallized in acetic acid to afford **1** as a black powder and used without further purification. (7.30 g, yield 30 %). M.p. > 270 °C (lit[1] 393-394°C); ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 10.65, (br s, OH), 8.18 (d, 2H, *J* = 5.9 Hz, 3.3 Hz, 5-H and 8-H), 7.90 (m, 2H, *J* = 5.9 Hz, 3.3 Hz, 6-H and 7-H), 7.57 (s, 2H, 1-H and 4-H); ^{13}C NMR ($(CD_3)_2SO$, 100 MHz) : δ 182.1 (C10, C9), 153.2 (C2, C3), 134.5 (C6, C7), 133.9 (C8a, C10a), 127.5 (C4a, C9a), 127.0 (C5, C8), 114.2 (C1, C4). FTIR (neat, ATR): ν_{max} (cm^{-1}) 3456 (br, s, νOH), 3207 (br, s, νC-OH), 1672 (s, νCO), 1575 (νCC aromatic), 1517, 1312, 1112, 971, 900, 793, 709; HRMS (ESI+): 241.0521, $M+H^+$ ($C_{14}H_8O_4$ requires 240.0495).

2,3-bis(decyloxy)anthracene-9,10-dione (2) : A solution of **1** (1.01 g, 6.35 mmol), $C_{10}H_{21}OSO_2CH_3$ (2 g, 12.7 mmol, 2 equiv.) and Bu_4NBr (680 mg, 3.15 mmol, 0.50 equiv.) in DMF (100 mL) was stirred at 60 °C and K_2CO_3 (2.93 g, 21.1 mmol, 3.32 equiv.) was added slowly. The reaction was stirred for 12 h at 60 °C, cooled at RT and mixed with aqueous HCl (1 M, 1 L). The resulting precipitate was recovered by filtration and purified by chromatography (SiO_2, CH_2Cl_2/heptane : 2/1) to afford pure **2** as a yellow powder (1.21 g, 55 % yield). M.p. 100 °C (lit (1) 101°C); ^1H NMR (400 MHz, $CDCl_3$) : δ 8.26 (2H, dd, *J* = 5.9 Hz, 3.3 Hz, C8, C5), 7.74 (2H, dd, *J* = 5.9 Hz, 3.3 Hz, C6, C7), 7.68 (2H,s, C1, C4), 4.20 (4H, t, *J* = 6.6 Hz, $OCH_\mathbf{2}$), 1.89 (4H, p, *J* = 7.2 Hz, $OCH_2C\mathbf{H_2}$), 1.50 (4H, m, $OCH_2CH_2C\mathbf{H_2}$), 1.43-1.21 (24H, m, $OCH_2CH_2CH_2(C\mathbf{H_2})_6CH_3$), 0.88 (6H, t, *J* = 7.0 Hz, $C\mathbf{H_3}$). ^{13}C (100 MHz, $CDCl_3$) : δ 182.6 (C9, C10), 153.8 (C2, C3), 133.7 (C6, C7), 133.69 (C8a, C10a), 128.1 (C9a, C4a), 126.9 (C8, C5) 109.3 (C1, C4), 69.4 (OCH_2), 31.9 ($OCH_2\mathbf{C}H_2$), 29.7, 29.6, 29.5, 29.4, 28.9, 26.0 ($\mathbf{C}H_2CH_2CH_3$), 22.7 ($\mathbf{C}H_2CH_3$), 14.1(CH_3). FTIR (neat, ATR diamond): ν_{max} (cm^{-1}) 3070, 2917 ($\nu_{as}CH_2$ alkyl), 2849 (ν_sCH_2 alkyl), 1689 (ν_sCO), 1574 (νCC aromatic), 1513, 1466, 1377, 1307, 1219, 1111, 1087, 885, 711, 621. HRMS (ESI+): 521.3641 $M+H^+$ ($C_{34}H_{48}O_4$ requires 520.3625). Anal. Found: C, 78.48; H, 9.33. Calcd. for $C_{34}H_{48}O_4$: C, 78.4; H, 9.29.

2,3-bis(decyloxy)anthracene (DDOA) : anthraquinone 2 (550 mg, 1.06 mmol), zinc powder (1.40 g, 21.4 mmol, 20.2 equiv.) and aqueous NaOH (10%, 50 ml) were heated at 100 °C for 24 h. The solution was cooled, filtered to remove the powder and extracted with dichloromethane (2 x 75 mL). The organic layer was dried (Na_2SO_4) and concentrated under vacuum. The crude solid was purified by column chromatography (C_6H_{12}/EtOAc 9/1) to afford pure DDOA as a white powder (207 mg, 40% yield). M.p. 85 °C (lit (1) 84°C); NMR ^1H (400 MHz, $CDCl_3$) : δ 8.16 (H, s, C9, C10), 7.89 (2H, dd, *J* = 6.4 Hz, 3.2 Hz, C8, C5), 7.37 (2H, dd, *J* = 6.4 Hz, 3.2 Hz, C6, C7), 7.16 (2H, s, C1, C4), 4.13 (4H, t, *J* = 6.6 Hz OCH_2), 1.91 (4H, p, *J* = 7.2 Hz $OCH_2C\mathbf{H_2}$) 1.52 (4H, m, $OCH_2CH_2C\mathbf{H_2}$), 1.44-1.27 (24H, m, $OCH_2CH_2CH_2(C\mathbf{H_2})_6CH_3$), 0.88 (6H, t, *J* = 7.0 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) : δ 150.0 (C2, C3), 130.7 (C8a, C10a), 128.7 (C8, C5), 127.6 (C6, C7), 124.4 (C9, C10), 123.7(C1, C14), 105.9 (OCH_2) , 68.7 (OCH_2CH_2), 32.0, 29.7, 29.6, 29.5, 29.4, 29.1, 26.2, 22.7 (CH_2CH_3), 14.2 (CH_3). FTIR (neat, ATR diamond): ν_{max} (cm^{-1}) 3046 (s, νCH aromatic), 2916 ($\nu_{as}CH_2$ alkyl), 2850 (ν_sCH_2 alkyl), 1668, 1629, 1568, 1491, 1466, 1287, 1222, 1164, 1013, 891, 739, 593. HRMS (ESI+): 497.398 $M+Li^+$ ($C_{34}H_{50}O_2$ requires 497.397).

2. NMR experiments.

Materials. BHPB10 was synthesized according to a published procedure.[1] HSA was purchased from Aldrich and used as is. DDOA was synthesized by a modified procedure from the literature[2] (see supp. info).

Variable temperature NMR. The NMR spectra were measured at different temperatures on a Bruker Avance III spectrometer operating at 600 MHz. The temperature of the probe was calibrated by two methods : with a thermocouple inserted in a sample; from the shifts of methanol at different temperatures.[3] both methods yielded the same temperatures within ± 0.4 °C.

In a typical experiment, the required amount of the gelator was weighed on a precision balance (accuracy ± 20 µg) in a NMR tube. A standard bis(trimethylsilyl)acetylene (BTMSA) was introduced by adding a weighed amount (20 mg) of a solution in the deuterated solvent (2 wt. % solution). The rest of the deuterated solvent (about 0.5 mL) was weighed in the tube to match the desired wt. concentration.

The temperature was incremented by steps of 1 or 2 °C. After each heating steps, the sample temperature was allowed to stabilize and equal the targeted temperature within ± 0.1 °C, at least during 40 s and the sample was let equilibrate at this temperature for additional 3 to 4 min. The FID were measured only after this delay. The overall heating rate was about 0.25 °C/min.

The recycling times and pulse angles were tuned to reach a good compromise between experiment duration and minimizing errors of integration. For instance, longitudinal relaxation times T_1 of the proton of HSA at 3.6 ppm (Fig. 2) T_1 varies from 6.3 to 1.5 s when the temperature increases, and for the protons of the standard T_1 varies from 3.3 to 6.1 s. The recycling time has been set to 18 s and the pulse angle at 30°. The resulting error has been taken into account to estimate the overall errors (see below).

The measured intensities I_m were normalized to the integrals of the peaks of the standard I_{st} (Fig. S1). The normalized intensities are noted I ($I = I_m/I_{st}$). It was ensured that the ratio between this signal and that of the residual protonated solvent was constant. Therefore, when the signals of the solvent did not overlap with that of the gelators, it was possible to normalize the spectra by their intensities. The intensities of several peaks of the gelator were measured either by direct integration, either by fitting the peaks with lorentzian peaks. When the gel was melted, the intensities of the peaks reached a plateau. The values of the intensities of the plateau were averaged and the average value was taken as $I_{\max}$. The uncertainty on the average of the plateau estimated as the peak-to-peak deviation (about 2 %).

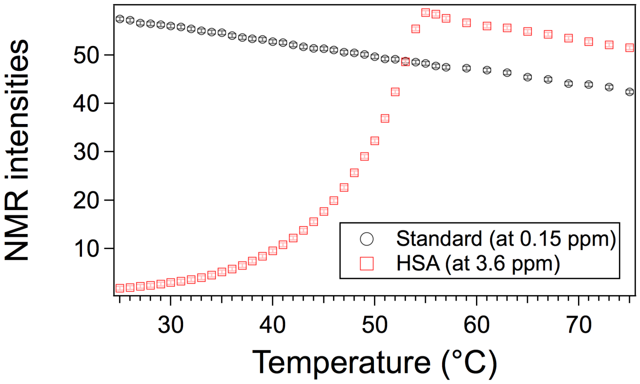


Figure S1. NMR integrals of the peak at 3.6 ppm of HSA and the peak of the standard (BTMSA).

The intensities I of the peaks of the gelators were converted to the weight concentrations with eq. 1.

$$c = c_t \frac{I}{I_{\max}} \Bigg/ \left[1 + c_t\left(\frac{I}{I_{\max}} - 1\right)\right] \qquad (1)$$

where c_t is the total wt. concentration of the gelator, $I_{\max}$ is the averaged intensity of the peak in the plateau. $I_{\max}$ has been measured after averaging the intensities in the plateau. For low concentrations, c can be approximated by eq. 2 with an uncertainty less than 0.5 %.

$$c = c_t \frac{I}{I_{\max}} \qquad (2)$$

Equal weight fractions in deuterated and protonated solvents do not represent the same molar concentration. Therefore, the plots mixing results in deuterated solvent with results in protonated solvent were represented with molar fractions in abscissa. The molar fractions X were calculated form the NMR intensity according equation (3)

$$X = X_t \frac{I}{I_{\max}} \Bigg/ \left[1 + X_t\left(\frac{I}{I_{\max}} - 1\right)\right] \qquad (3)$$

where X_t is the total molar fraction. For low concentration X can be approximated by an equation similar to eq. 2.

The calculation of the concentrations gave similar results with intensities measured by integrations or by fitting, within less than 1% error for higher temperatures and less than 5 % for the lower temperatures. The uncertainty of c or X was appraised by taking into account the signal/noise ratio (SNR), the incomplete integration range (~ 2%),[4] the uncertainty on mass (~ 1%), the error due to incomplete relaxation. The error due to SNR is about constant with temperature, therefore the uncertainty on the NMR intensities decreases from 1% at the plateau to large values at low T and c. The lower concentrations, with a high uncertainty (> 50 %) have been discarded (although in line with higher c values).

3. DSC. The thermograms were recorded with a SETARAM III microcalorimeter. The measuring cell was filled with a gelator/solvent mixture (between 100 and 200 mg). The reference cell was filled with a mass of pure solvent equal to that of the first cell within 0.1 mg. The gel was formed during a first cycle of heating at 1 °C/min and cooling at 0.3 °C/min. The thermograms were measured during a second cycle at heating and cooling rates close to the overall rate of the NMR experiments (0.25 °C/min).

4. Rheology. The real and imaginary parts of the shear modulus were measured as a function of temperature as described previously.[5] The temperature of gel-to-sol transition is defined by the temperature for which the elastic modulus G' and loss modulus

G″ cross over. Each transition temperature was measured for decreasing stress values and the temperature was deduced from a null stress extrapolation. This caution avoids measuring a decrease of *G′* because it flows under a high stress.

5. Solubility assays.

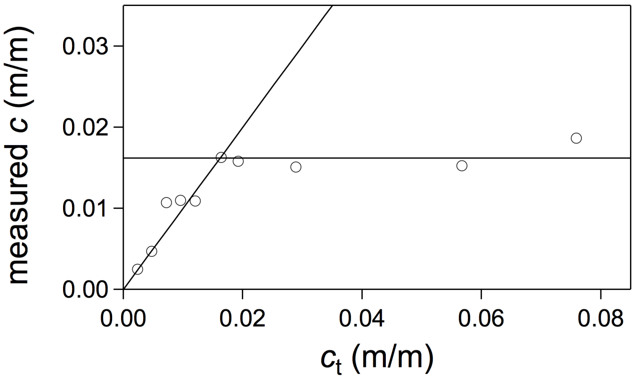


Figure S2. Saturation experiment at 48 °C with Hirst *et al*. method[2]
Measured NMR intensities against total concentration c_t.

6. Bibliography

(1) Pozzo, J.-L.; Clavier, G. M.; Colomes, M.; Bouas-Laurent, H. Different Synthetic Routes towards Efficient Organogelators: 2,3-Substituted Anthracenes. *Tetrahedron* **1997**, *53*, 6377–6390.

(2) Hirst, A. R.; Coates, I. A.; Boucheteau, T. R.; Miravet, J. F.; Escuder, B.; Castelletto, V.; Hamley, I. W.; Smith, D. K. Low-Molecular-Weight Gelators: Elucidating the Principles of Gelation Based on Gelator Solubility and a Cooperative Self-Assembly Model. *J. Am. Chem. Soc.* **2008**, *130*, 9113–9121.