Electronic Supplementary Material (ESI) for Soft Matter


# Self-Sorting Gels – Mixing and Ageing Effects in Thermally Addressable Supramolecular Soft Nanomaterials

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## SUPPLEMENTARY INFORMATION

### Contents

## 1. Materials

Organogelator **1** was purchased from AK scientific, organogelator **2** was synthesised according to the method previously reported in the literature.[1] 1,2-Dichlorobenzene (DCB)-$d_4$ was purchased from Aldrich.

## 2. Differential Scanning Calorimetry

Transition enthalpies were determined using a Mettler Toledo 822e differential scanning calorimeter, calibrated against pure indium. Heating and cooling rates of 10°C $min^{-1}$ were employed over a range of 10-160°C. Sample weights were of the order of 8 mg, and experiments were performed using 40 µL aluminium pans. The samples were made in 1 mL 1,2-DCB and left to stand overnight. The gels were made at the concentrations shown in Table 1. Tables 2-5 present the DSC data.

**Table 1** Concentrations used in DSC samples of gelators **1** and **2**, and their 1:1 mixture

| Gelator | Mass of Gelator /mg | Conc of Gelator /mM |
|---|---|---|
| **1** | 22.9 | 59.2 |
| **2** | 40 | 79.0 |
| **1** + **2** | 22.9 + 30 | 59.2 |

**Table 2** Data from DSC curve of Gelator **1**

| | Heat 1 | Heat 2 | Cool 1 | Cool 2 |
|---|---|---|---|---|
| **Onset temperature/ºC** | 118.97, 148.06 | 111.74, 149.56 | 124.24 | 124.01 |
| **Peak Maximum/ºC** | 133.08, 153.19 | 124.52, 152.51 | 120.81 | 116.22 |
| **Peak Integral/mJ** | 5.56, 1.54 | 1.11, 0.50 | -11.16 | -6.46 |

**Table 3** Data from DSC curve of Gelator **2**

| | **Heat 1** | **Heat 2** | **Cool 1** | **Cool 2** |
|---|---|---|---|---|
| **Onset temperature/ºC** | 51.04, 148.91 | 41.09 | 56.53 | 56.91 |
| **Peak Maximum/ºC** | 60.66, 149.45 | 64.13 | 54.10 | 54.15 |
| **Peak Integral/mJ** | 5.82, 18.96 | 5.68 | -4.38 | -4.49 |

**Table 4** Data from DSC curve of Gelator **1** + **2**

| | **Heat 1** | **Heat 2** | **Cool 1** | **Cool 2** |
|---|---|---|---|---|
| **Onset temperature/ºC** | 50.32, 119.32, 131.06 | 46.50, 117.81, 137.89 | 45.56, 117.81, 137.89 | 52.33, 123.93 |
| **Peak Maximum/ºC** | 61.10, 133.89, 143.11 | 63.34, 126.67, 147.03 | 48.14, 119.89 | 47.99, 119.83 |
| **Peak Integral/mJ** | 5.14, 11.28, 3.79 | 4.81, 0.99, 5.34 | -4.24, -4.29 | -3.90, -5.69 |

**Table 5** Data from DSC curve of Gelator **1** + **2** after ageing for 2 weeks.

| | **Heat 1** | **Heat 2** | **Cool 1** | **Cool 2** |
|---|---|---|---|---|
| **Onset temperature/ºC** | 34.47, 140.01 | 45.56, broad | 51.66, 129.15 | 51.72, 127.09 |
| **Peak Maximum/ºC** | 63.31, 143.45 | 64.10, broad | 49.23, 113.08 | 48.75, 118.92 |
| **Peak Integral/mJ** | 4.20, 1.63 | 3.96 | -4.18, -1.86 | -4.12, -5.04 |

## 3. Variable Temperature NMR

VT NMR experiments were performed using Jeol ECX spectrometer, operating at 400 MHz.

### VT NMR of Gelator 2

Gelator **2** (50 mg) was dissolved in 1,2-DCB-$d_4$ (0.75 mL) in an NMR tube and left to stand overnight. A variable temperature NMR run was carried out between 30-100°C. The stacked plot is shown in Figure 1.

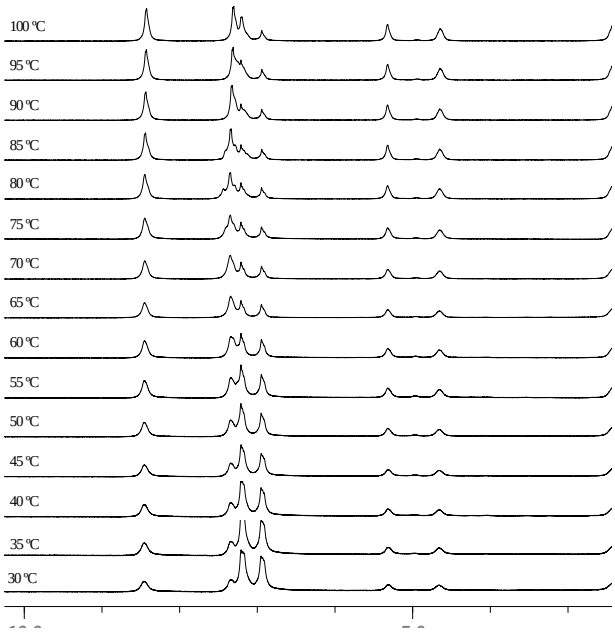


**Figure 1** Stacked plot of VT NMR spectra of organogelator **2**

**VT NMR of Gelator 2 + 1**

Gelator **1** (1 mg) and gelator **2** (1.30 mg) were dissolved in 1,2-DCB-$d_4$ (0.75 mL) in an NMR tube with heat/sonication, and left to stand overnight. A variable temperature NMR run was carried out between 25-100°C. The stacked plot is shown in Figure 2.

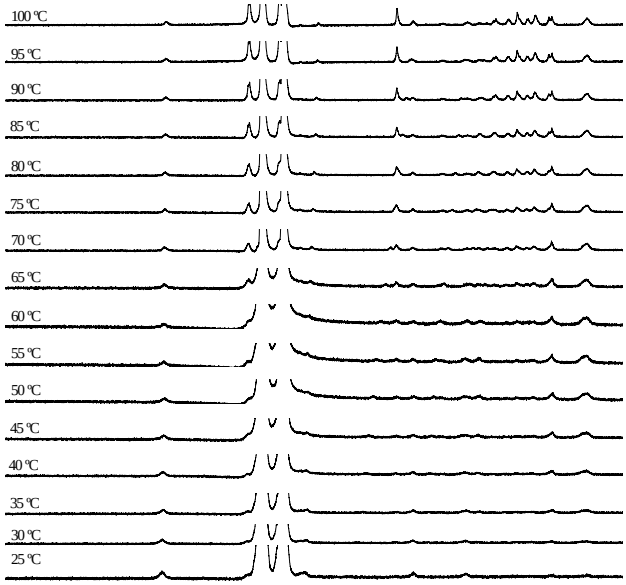


**Figure 2** Stacked plot of VT NMR spectra of organogelator **2 + 1**

## 4. SEM

Gels were made in glass vials, left to settle overnight and then a small sample was taken and spread onto an SEM stub where it was left to dry under ambient conditions overnight.

### Additional SEM images

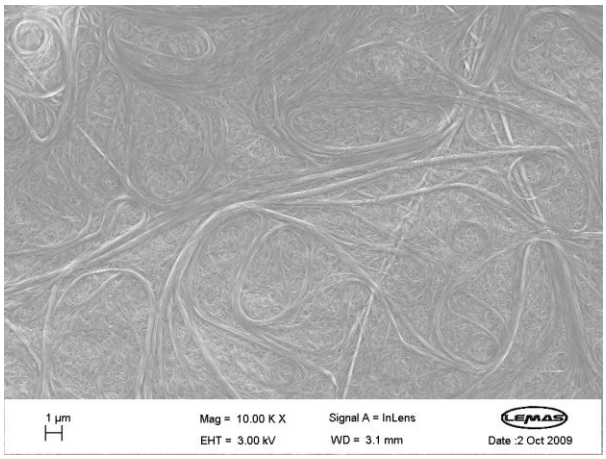


**Figure 3.** SEM image of 50 mg gelator **2** aged for 24 h. Scale bar = 1 μm.

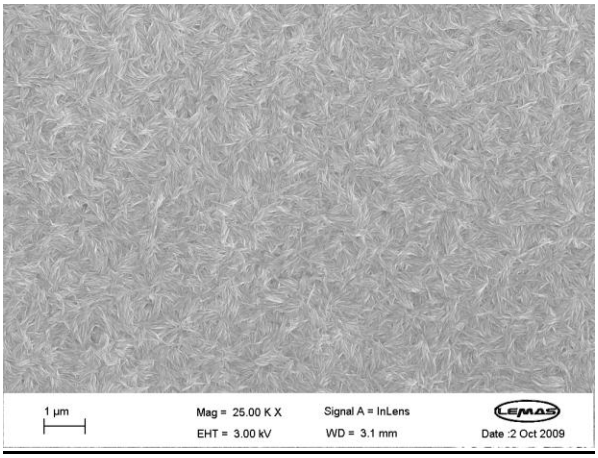


**Figure 4.** SEM image of 50 mg gelator **2** aged for 21 days Scale bar = 1 μm.

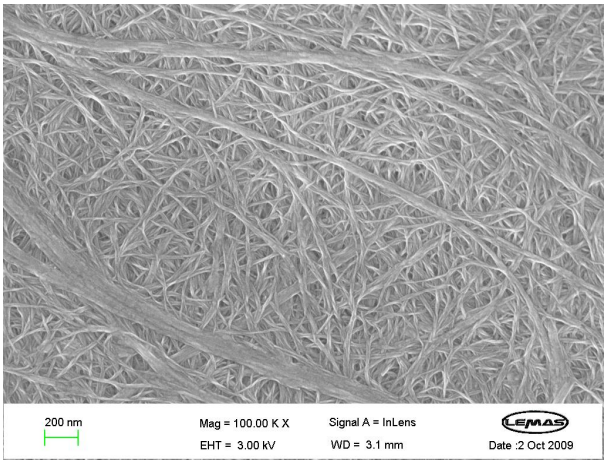


**Figure 5.** SEM image of 50 mg gelator **2** + 1 eq. gelator **1** aged for 24 h. Scale bar = 200 nm.

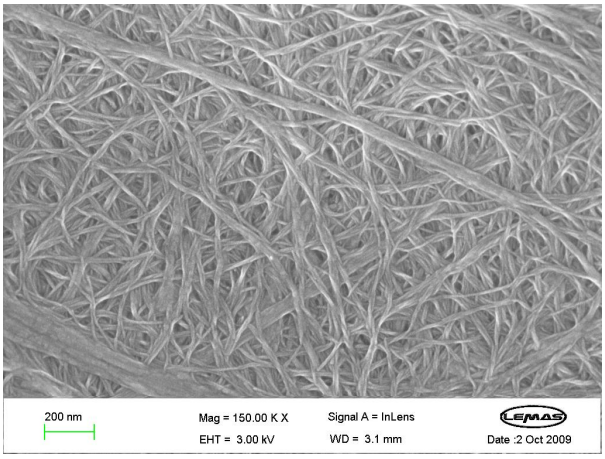


**Figure 6.** SEM images of 50 mg gelator **2** + 1 eq. gelator **1** aged for 24 h. Scale bar = 200 nm.

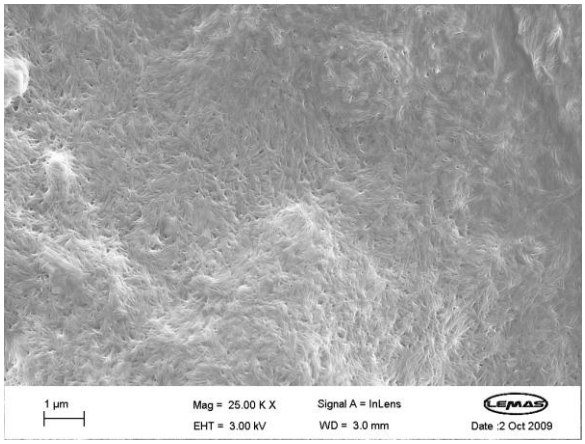


**Figure 7.** SEM images of 50 mg gelator **2** + 1 eq. gelator **1** aged for 21 days. Scale bar = 1 μm.

## 5. References

1. S. Malik, S. Kawano, N. Fujita and S. Shinkai, *Tetrahedron*, 2007, **63**, 7326-7333.