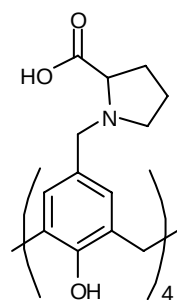


## Proline-Functionalised Calix[4]arene: An Anion-Triggered Hydrogelator – Supplementary information

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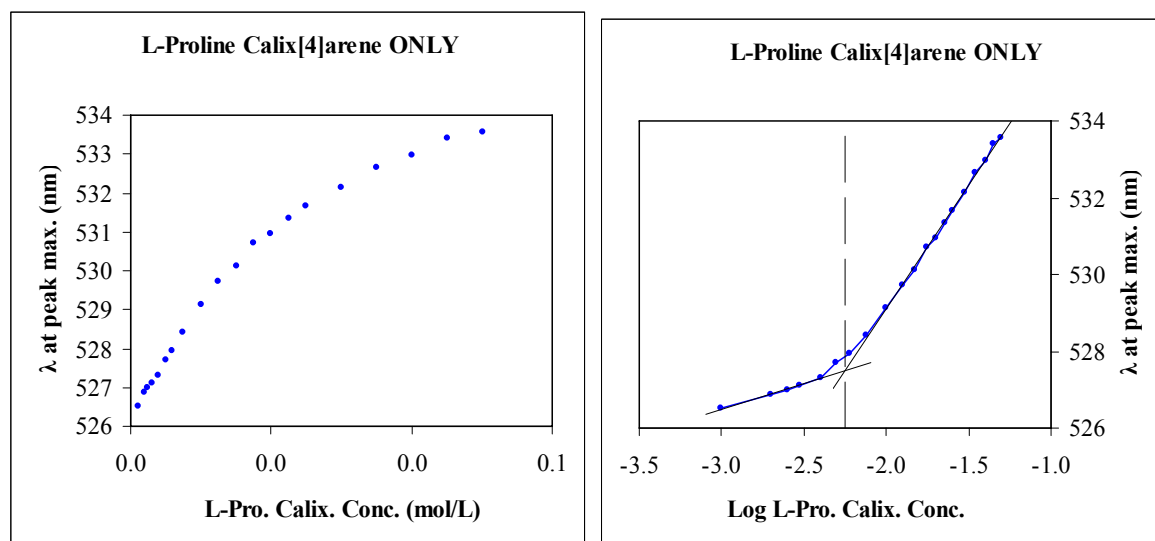
### Synthesis of Proline Functionalised Calixarene 1



Calix[4]arene (2.0 g, 4.8 mmol), tetrahydrofuran (45 mL), L-proline (2.9 g, 25 mmol) dissolved in water (7 mL), glacial acetic acid (5.6 mL) and formaldehyde (2.0 mL, 37% w/v, 27 mmol) were combined and left stirring for 72 hours. The liquid was decanted and drained well from the product that deposited on the flask wall. The flask was triturated with acetone and the solution then filtered. The precipitate was washed with acetone and then recrystallised from water/ethanol(1:1)-acetone to yield a white solid (3.7 g; yield, 77%), m.p. 340°C (dec.),  $[\alpha]_D +7.3$  (c = 3.0, H<sub>2</sub>O). Anal. Calcd for C<sub>52</sub>H<sub>60</sub>N<sub>4</sub>O<sub>12</sub>·4H<sub>2</sub>O C, 62.1; H, 6.8; N, 5.6. Found: C, 62.0; H, 6.8; N, 5.5. <sup>1</sup>H NMR (D<sub>2</sub>O): δ, 1.40-1.82 (broad m, 12H CHCH<sub>2</sub>), 1.82-2.20 (broad m, 4H, CHCH<sub>2</sub>), 2.75-2.98 (broad m, 4H, CH<sub>2</sub>N), 3.18-3.35 (broad m, 4H, CH<sub>2</sub>N), 3.54-3.67 (broad t, 4H, NCH), 3.67-3.82 (broad s, 8H, ArCH<sub>2</sub>N), 3.83-3.88 (broad s, 8H, ArCH<sub>2</sub>Ar), 7.03 (s, 8H, ArH). <sup>13</sup>C NMR (D<sub>2</sub>O): δ, 20.9, 29.9 (2 x CH<sub>2</sub>), 28.7 (ArCH<sub>2</sub>Ar), 52.4, 55.9 (2 x CH<sub>2</sub>N), 66.1 (CHN), 121.4, 127.8, 129.5, 149.4 (Ar), 171.8 (C=O).

## CMC Determinations

(a)



(b)

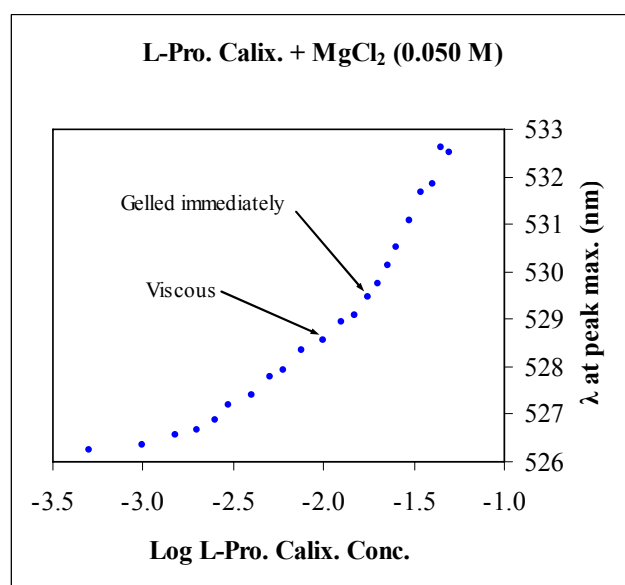


Figure S1. (a) CMC determination for L-Proline calix[4]arene using Rhodamine 6G as the probe (reference 13). The intersection gives a CMC of 5.6 mM. (b) Results of the same experiment, but in the presence of magnesium chloride.

## Atomic Force Microscopy Procedure and Additional Results

Characterisation of the gels was achieved using a Dimension 3100 Atomic Force Microscope (Digital Instruments, Santa Barbara, USA). A thin film of the wet gel was placed on a freshly cleaved mica substrate and imaged in Tapping Mode with a Silicon cantilever (type NSC-15,

Mikromasch, Spain). The cantilevers used were cleaned with an UV/ozone cleaner prior to the measurements.

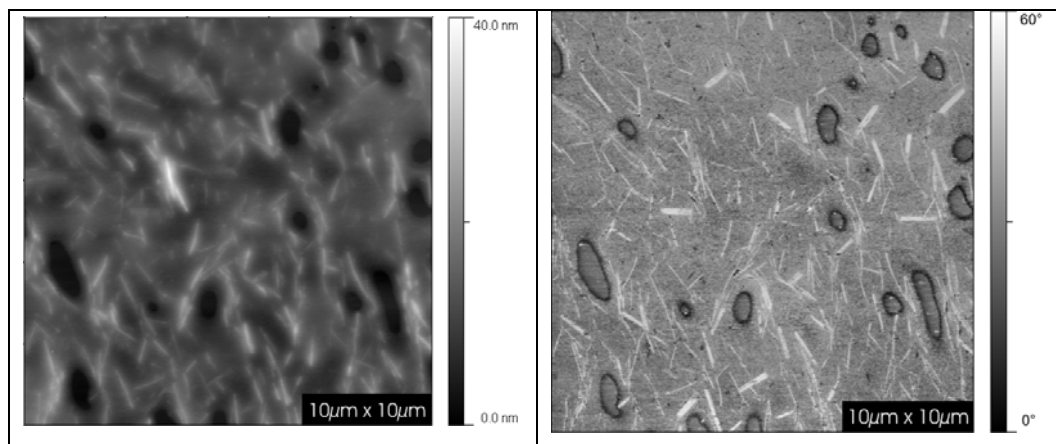


Figure S2. **1** /  $\text{Mn}(\text{NO}_3)_2$  gel imaged after crystallisation commenced. (left: topography, right: phase image)

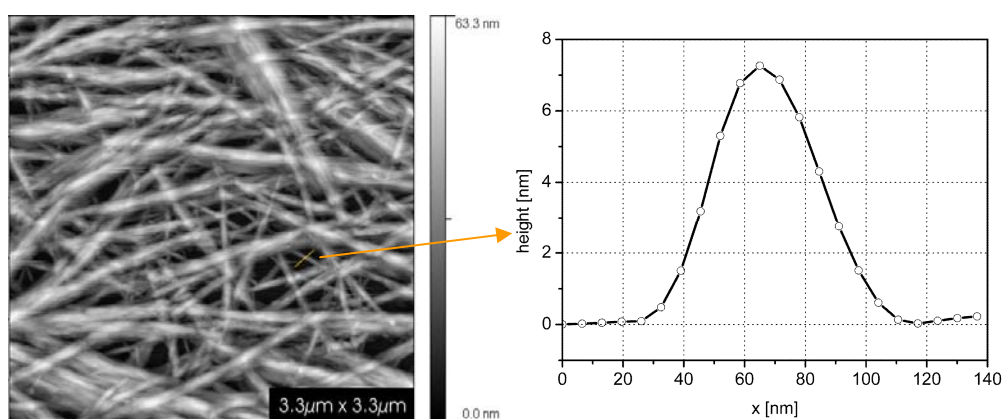


Figure S3. **1** /  $\text{MgCl}_2$  gel; topographic image and needle cross section.