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Self-Organisation Effects in Dynamic Nanoscale Gels Self-Assembled from Simple Mixtures of Commercially Available Molecular-Scale Components

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SUPPORTING INFORMATION

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1. Synthesis of Lauric Hydrazide

Although commercially available from Chinese suppliers, we synthesised lauric hydrazide using a modification of a procedure previously described in the literature.[1] Methyl laurate (5.2 g, 24.26 mmol) was placed in a round bottom flask along with ethanol (65 mL). Hydrazine monohydrate was added to the mixture through a syringe. The solution was stirred at 80 °C for 5 hours, and left to stir at room temperature overnight, after which a white crystalline precipitate had appeared which was filtered off to give the product in essentially quantitative yield. Yield: 5.2 g (100 %); m.p. 105-106 °C, ^{1}H NMR ($CDCl_3$-*d*, 400 MHz) δ 0.87 (t, 3H, *J* = 6.8 Hz), 1.25-1.29 (m, 16H), 1.62-1.65 (m, 2H), 2.14 (m, 2H), 3.89 (bs, 2H), 6.69 (bs, 1H). ^{13}C NMR ($CDCl_3$-*d*, 100 MHz) δ 14.10, 22.66, 25.48, 29.26, 29.28, 29.30, 29.44, 29.57, 31.88, 34.58, 174.01. ESI-MS (m/z) calculated value for C12H27N2O [M] requires: 215.2118; (ES^+) found: 215.2117 (100%, $[M+H]^+$).

2. Thermal Stability of Gels and Gel Mixtures

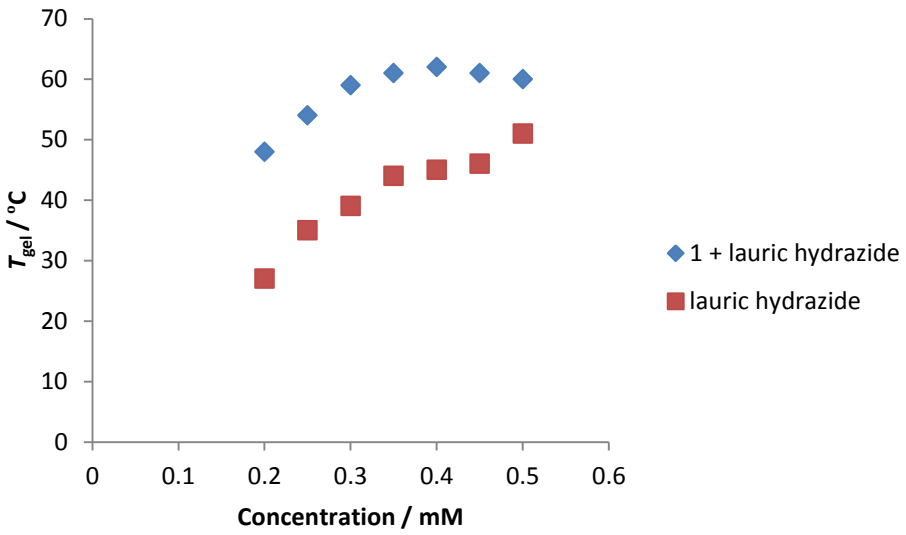

Fig. S1. T_{gel} data obtained from tube inversion experiments showing that reaction between undecanal (**1**) and lauric hydrazide forms the acyl hydrazone which leads to a more thermally stable gel network.

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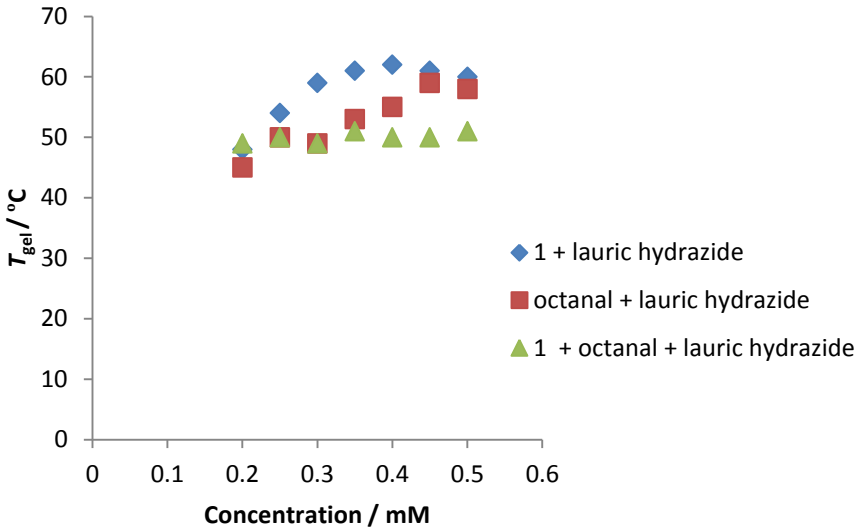

Fig. S2. T_{gel} data obtained from tube inversion experiments showing that undecanal (**1**) and lauric hydrazide (blue diamonds) form a more stable gel than octanal and lauric hydrazide (red squares). Both 'pure' gelation systems are more effective than the mixed system (green triangles) – indicative of co-assembly.

3. NMR Analysis of Gels

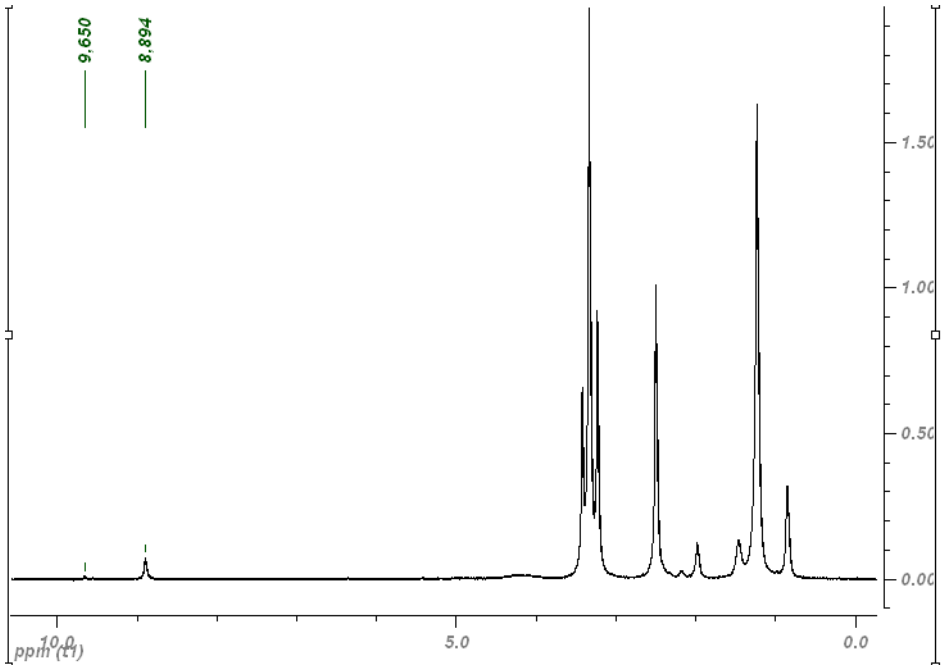

Fig. S3. ^{1}H NMR spectrum of gel formed from undecanal (**1**) and lauric hydrazide at 25ºC. Only peaks associated with the two 'starting materials' can be observed.

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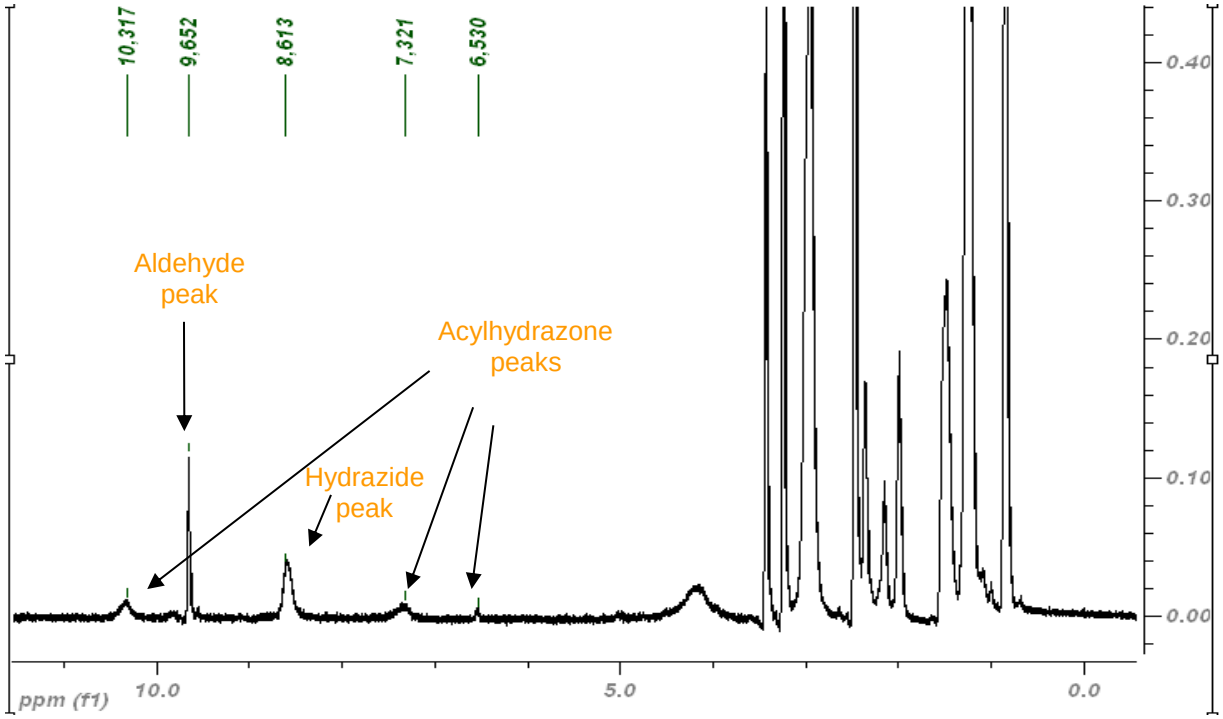

Fig. S4. ^{1}H NMR spectrum of sol formed from undecanal (**1**) and lauric hydrazide at 110ºC. In addition to the peaks for the aldehyde and hydrazide, peaks associated with the mobile acylhydrazone product can also now be observed. The peaks are broad owing to the fact the acylhydrazone is still undergoing some aggregation even in the sol at NMR concentrations.

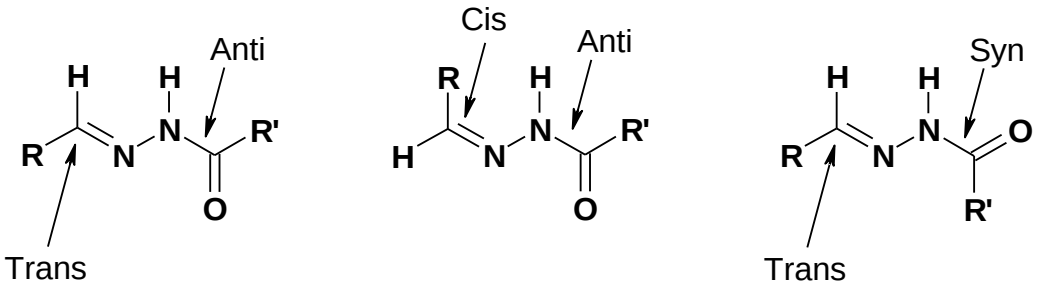

Fig. S5. Schematic diagram showing how acyl hydrazones can exist in a number of different conformations at elevated temperature.

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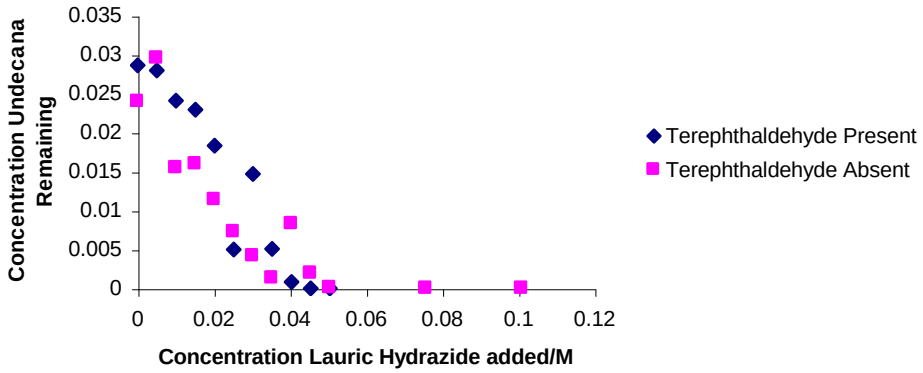

Fig. S6. NMR assessment of concentration of undecanal (**1**) on the addition of lauric hydrazide, demonstrating (pink squares) that it reacts in an equimolar manner with lauric hydrazide. In the presence of terephythaldehyde (blue diamonds), the undecanal is still depleted in a similar way.

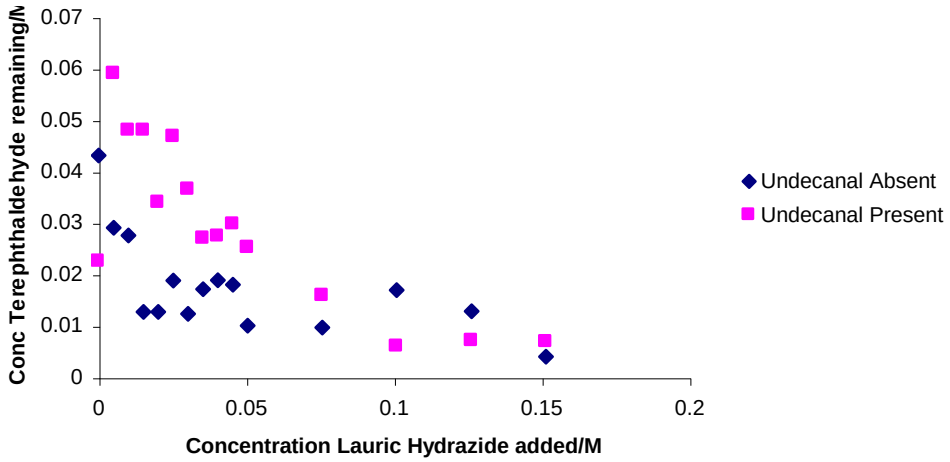

Fig. S7. NMR assessment of concentration of terephthaldehyde (**4**) on the addition of lauric hydrazide, demonstrating (blue diamonds) that it reacts with lauric hydrazide. In the presence of undecanal (pink squares), the terephthaldehyde is not depleted in the same way, and is only fully depleted once all of the undecanal has reacted. However, this does show that some reaction is taking place between terephthaldehyde and lauric hydrazide.

4. Differential Scanning Calorimetry

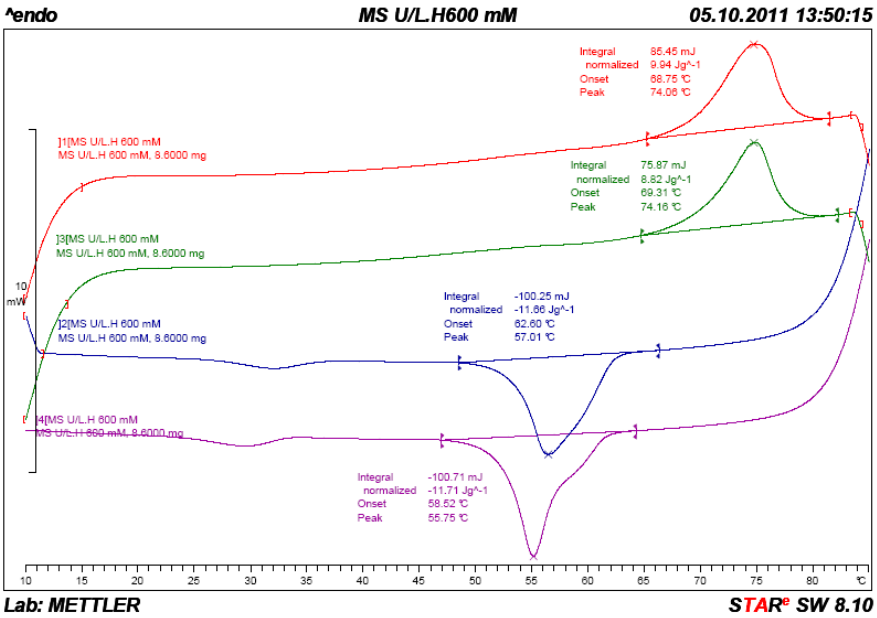

Fig. S8. Differential scanning calorimetry for undecanal (**1**) and lauric hydrazide (both 600 mM) in DMSO (total sample mass 8.60 mg). Endotherm peaks (gel-sol) at 74.1ºC on both cycles, exotherm peaks (sol-gel) at 57.0 ºC and 55.8ºC on cycles 1 and 2 respectively.

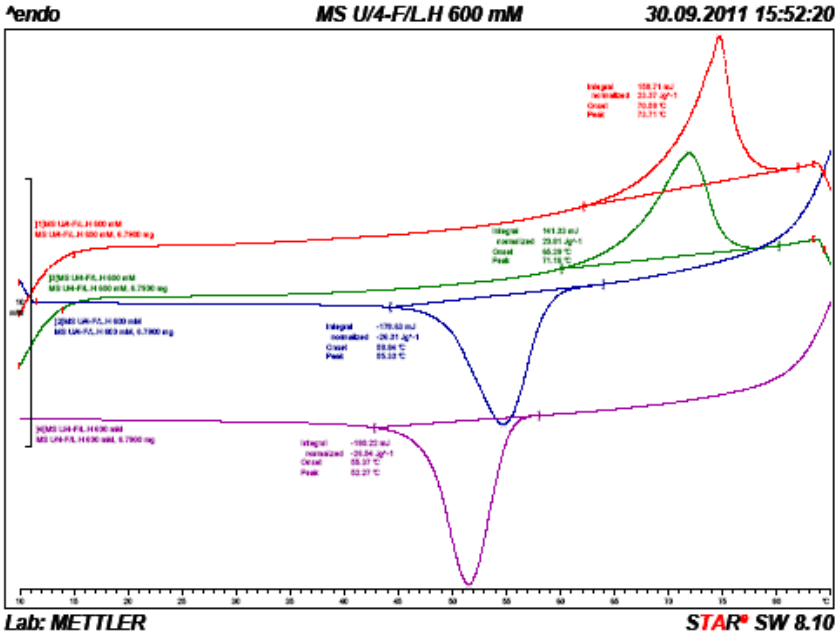

Fig. S9. Differential scanning calorimetry for undecanal (**1**), 4-fluorobenzaldehyde (**2**) and lauric hydrazide (all 600 mM) in DMSO (total sample mass 6.79 mg). Endotherm peaks (gel-sol) at 73.7ºC and 71.2ºC, exotherm peaks (sol-gel) at 55.3ºC and 50.2ºC on cycles 1 and 2 respectively.

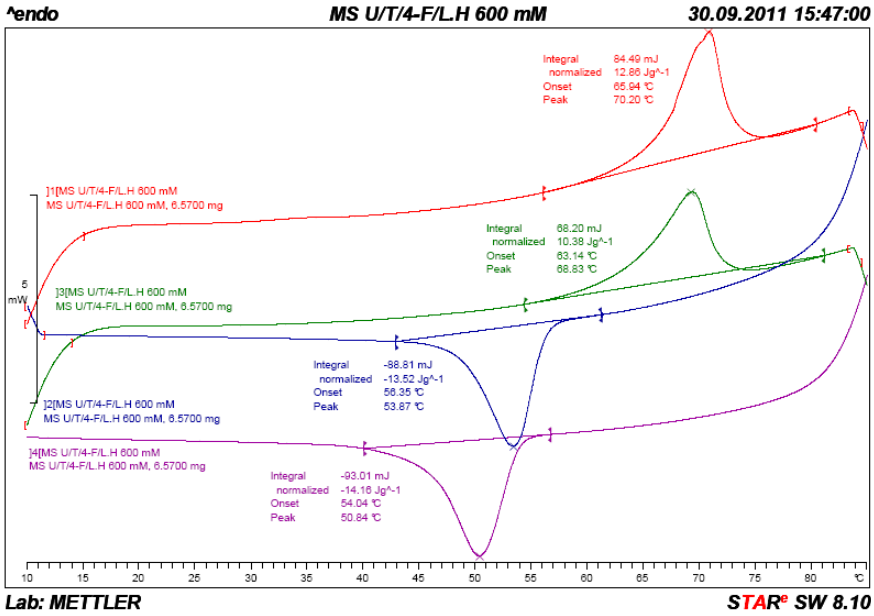

Fig. S10. Differential scanning calorimetry for undecanal (**1**), 4-fluorobenzaldehyde (**2**), terephthaldehyde (**4**) and lauric hydrazide (all 600 mM) in DMSO (total sample mass 6.57 mg). Endotherm peaks (gel-sol) at 70.2ºC and 68.8ºC, exotherm peaks (sol-gel) at 53.9ºC and 50.8ºC on cycles 1 and 2 respectively.

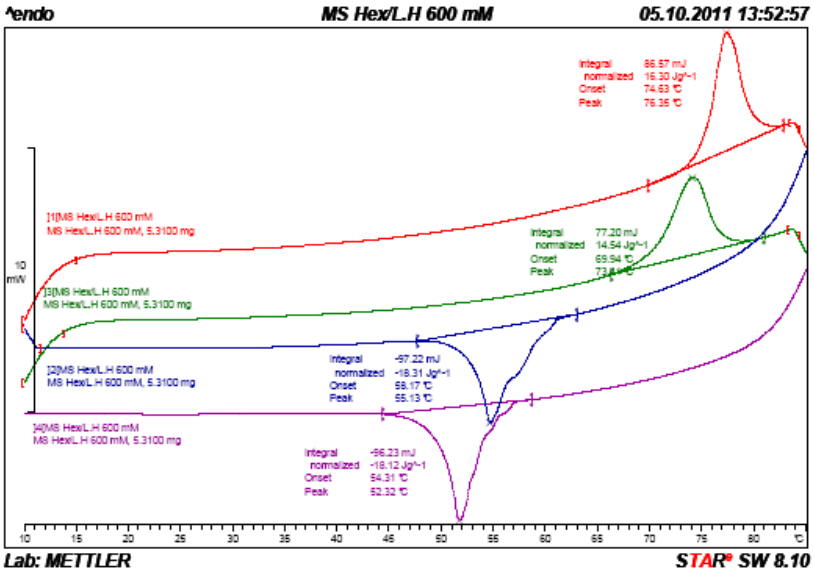

Fig. S11. Differential scanning calorimetry for hexanal (**5**) and lauric hydrazide (all 600 mM) in DMSO (total sample mass 5.31 mg). Endotherm peaks (gel-sol) at 76.4ºC and 73.3ºC, exotherm peaks (sol-gel) at 55.1ºC and 52.3ºC on cycles 1 and 2 respectively.

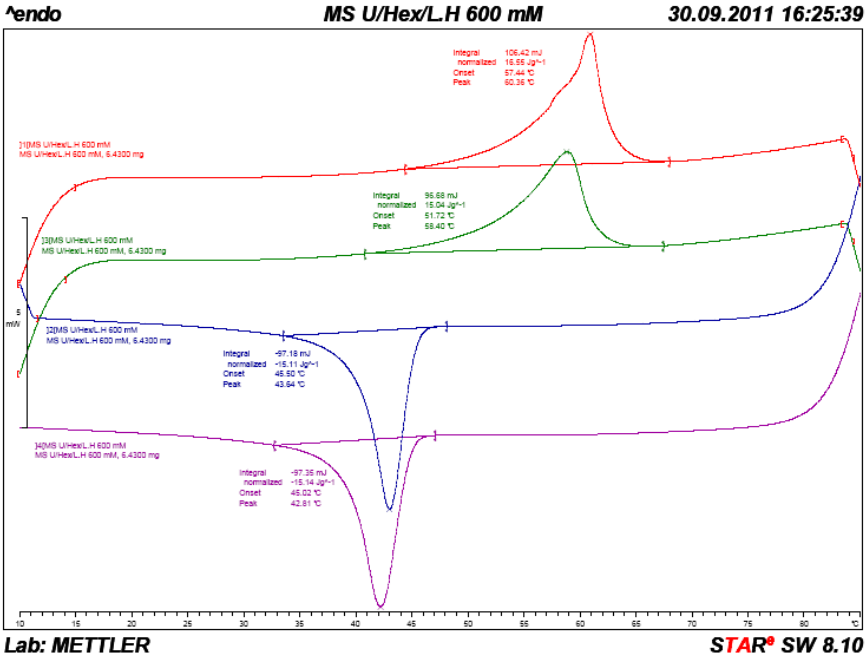

Fig. S12. Differential scanning calorimetry for undecanal (**1**), hexanal (**5**) and lauric hydrazide (all 600 mM) in DMSO (total sample mass 5.31 mg). Endotherm peaks (gel-sol) at 60.4ºC and 58.4ºC, exotherm peaks (sol-gel) at 43.6ºC and 42.8ºC on cycles 1 and 2 respectively.

5. References

1 S. Awasthi, P. Rishishwar, A. N. Rao, K. Ganesan, R. C. Malhotra, *J. Kor. Chem. Soc.*, 2007, **51**, 506.