Electronic Supplementary Material (ESI) for Soft Matter

Hybrid Gels – Dynamic Self-Assembly Pathways in Two-Component Nanomaterials with both Responsive and Robust Nanoscale Networks

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SUPPLEMENTARY INFORMATION

Contents

1. General Experimental Methods.

All compounds required in the synthesis were purchased from standard commercial suppliers. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol 400 spectrometer (^{1}H 400 MHz, ^{13}C 100 MHz). A Bruker 500 (^{1}H 500 MHz) was used for kinetics experiments. Samples were recorded as solutions in deuterated NMR solvents as stated and chemical shifts (δ) are quoted in parts per million. Coupling constant values (*J*) are given in Hz. The level of assignment of ^{1}H NMR spectra was achieved using model compounds, literature data and standard knowledge of ^{1}H NMR. DEPT experiments were used to assist in the assignment of ^{13}C NMR spectra. Positive and negative ion electrospray mass spectra were recorded on a Bruker Daltonics MicroTOF mass spectrometer. IR spectra were recorded on a PerkinElmer Spectrum Two FT-IR spectrometer. Melting points were measured on a Stuart SMP3 melting point apparatus and are uncorrected. Circular dichroism spectra were recorded on a Jasco J810 CD spectrophotometer – concentrations were below the gelation threshold. T_{gel} values were recorded using a high precision thermoregulated oil bath. SEM was carried out on a LEO 1530 Gemini FEGSEM fitted with an Oxford Instruments 80mm X-Max SDD detector.

2. Images of Gels

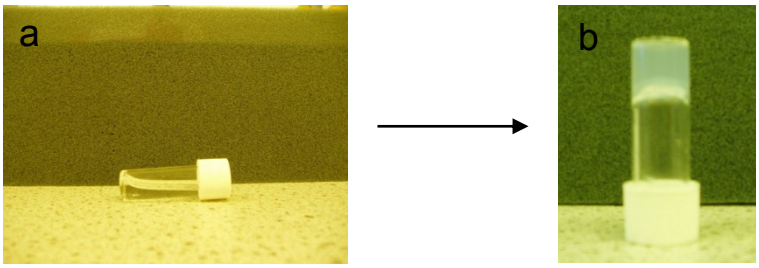

Figure S1. Formation of DBS-CO_2H hydrogel. Clear solution a) changes to translucent gel b) with decrease in pH brought about by hydrolysis of GdL.

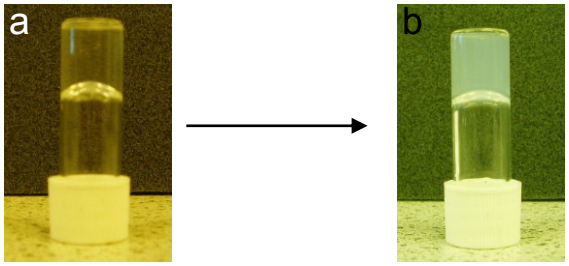

Figure S2. Formation of DBS-CO_2H/agarose hybrid gel. The change from clear gel a) to translucent gel b) indicates formation of DBS-CO_2H gelator network within agarose network.

3. T_{gel} data

Table 1 T_{gel} data for DBS-CO_2H and hybrid gels. "**>100**" signifies that the gel remained stable over the boiling point of the solvent; the collapse of the gel after this point can be attributed to the boiling of the solvent rather than a breakdown of the gel network.

% wt/vol DBS-CO_2H		**T_{gel} / °C**			
		DBS-CO_2H gel		Hybrid gel	
		6 mg GdL	8 mg GdL	6 mg GdL	8 mg GdL
0.15		**39**	**>100**	**>100**	**>100**
0.20		**47**	**>100**	**>100**	**>100**
0.25		**54**	**>100**	**>100**	**>100**
0.30		**>100**	**>100**	**>100**	**>100**

4. ^{1}H NMR spectra of gels

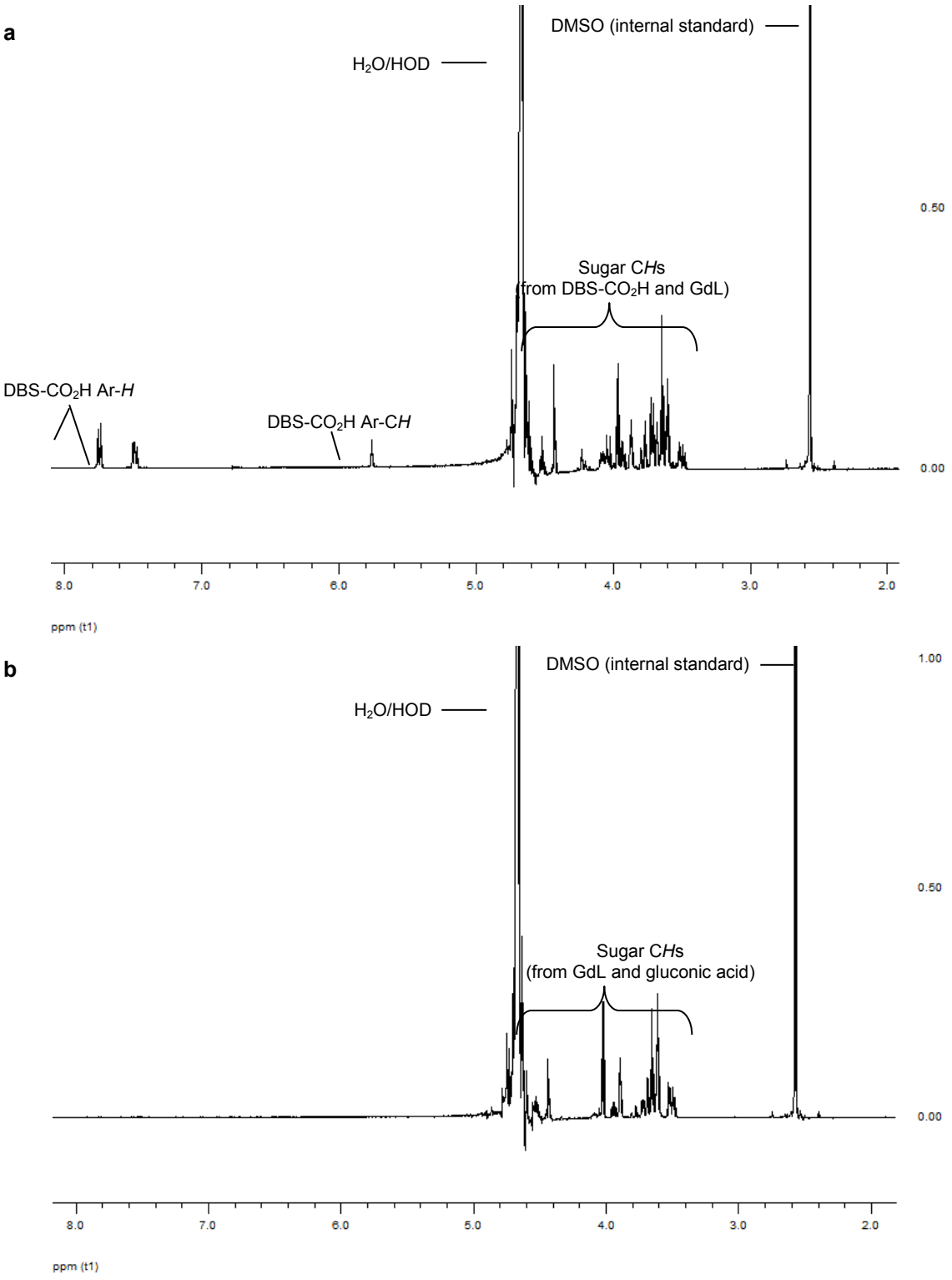

Figure S3. ^{1}H NMR spectra (400 MHz, D_2O) of DBS-CO_2H gel (0.2% wt/vol) at (**a**) start of gelation and (**b**) end of gelation; the absence of signals related to DBS-CO_2H in (**b**) indicates that all of the gelator has been incorporated into a sample-spanning solid-like network.

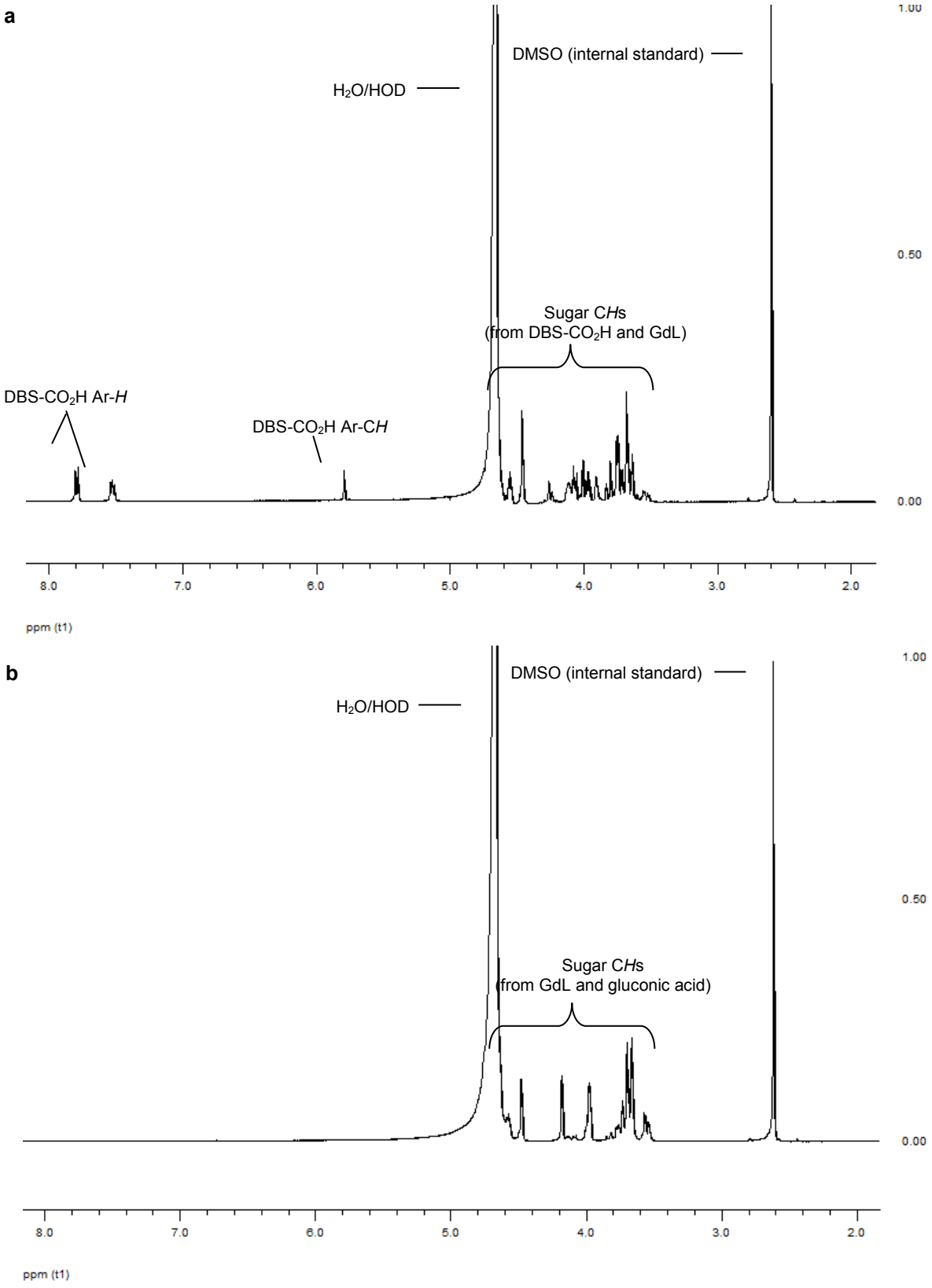

Figure S4. ^{1}H NMR spectra (400 MHz, D_2O) of DBS-CO_2H/agarose hybrid gel (0.2% + 0.5% wt/vol) at (**a**) start of gelation and (**b**) end of gelation, demonstrating that DBS-CO_2H is capable of assembling into solid-like fibres in the presence of agarose.

5. Avrami Plots

The Avrami model expressed in [1],[1] in which $X(t)$ represents the volume fraction of the gel phase, K is a temperature dependent constant (similar to a rate constant), n is the Avrami exponent (which reflects the dimensionality of 'crystal' growth) and t is time, can be rearranged into equation [2]:

$$1 - X(t) = \exp(-Kt^n) \quad [1]$$

$$\ln(\ln(1/1-X(t)) = \ln K + n\ln(t) \quad [2]$$

$$X(t) = (I(\infty) - I(t))/(I(\infty)-I(0)) \quad [3]$$

The volume fraction of the gel phase $X(t)$ can be expressed in terms of NMR signal intensity at equilibrium ($I(\infty)$), at time t ($I(t)$) and at the start of the experiment ($I(0)$) using equation [3]. This relationship enables linear fitting of equation [2] to calculate the Avrami exponent n by plotting $\ln[-\ln(I(\infty) - I(t))/(I(\infty) - I(0))]$ versus ln(t), where n is the gradient.[2]

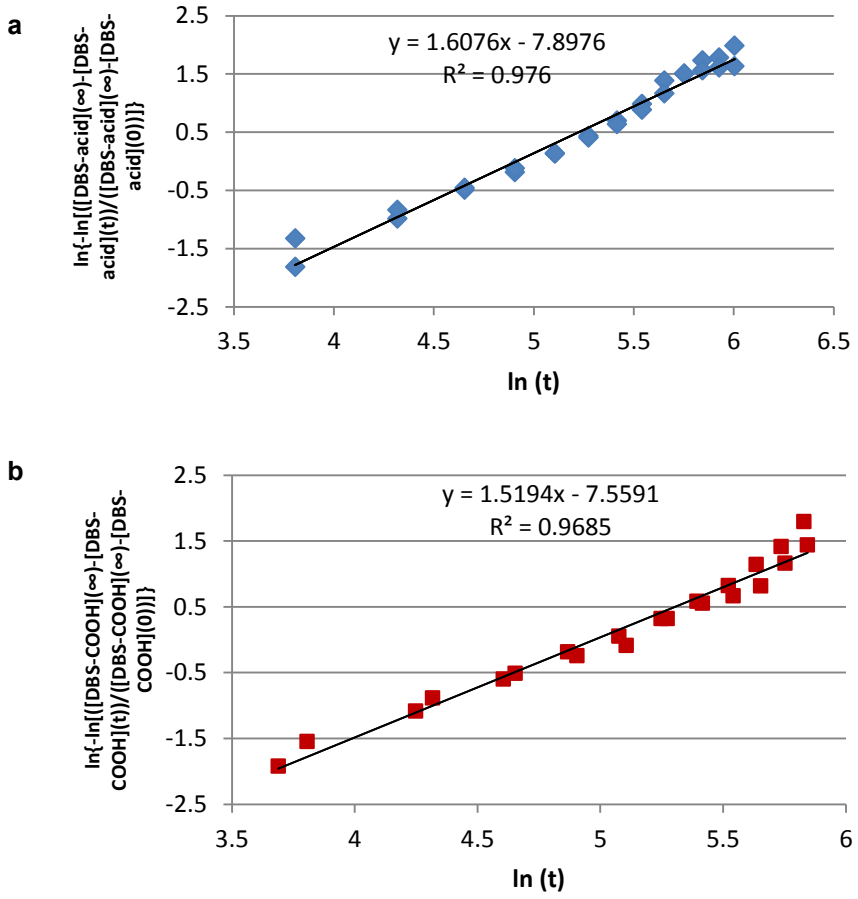

Figure S5. Avrami plots for DBS-CO_2H in (**a**) the absence of agarose and (**b**) the presence of agarose.

6. CD Spectra

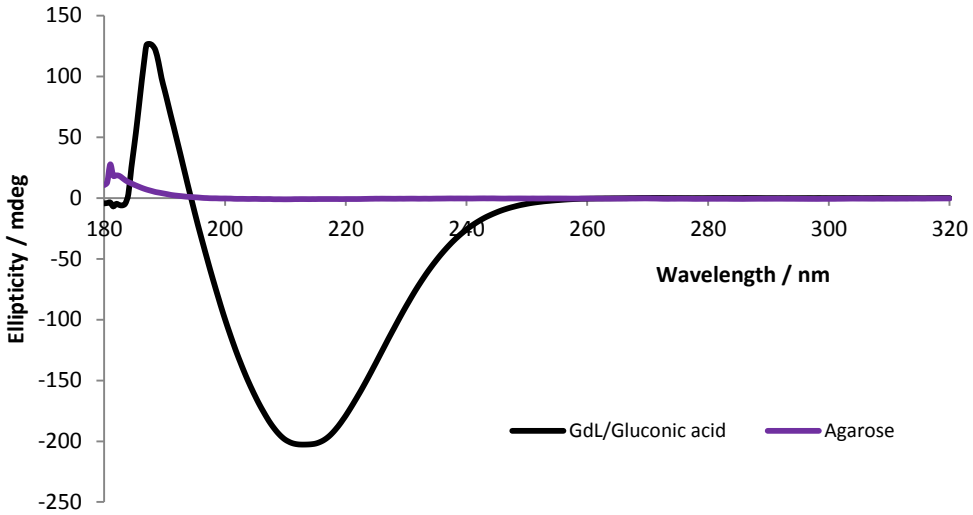

Figure S6. CD Spectra of GdL (gluconic acid, black) and agarose (purple) showing that they do not have signals in the same region of the spectrum as DBS-CO_2H (ca. 260 nm)

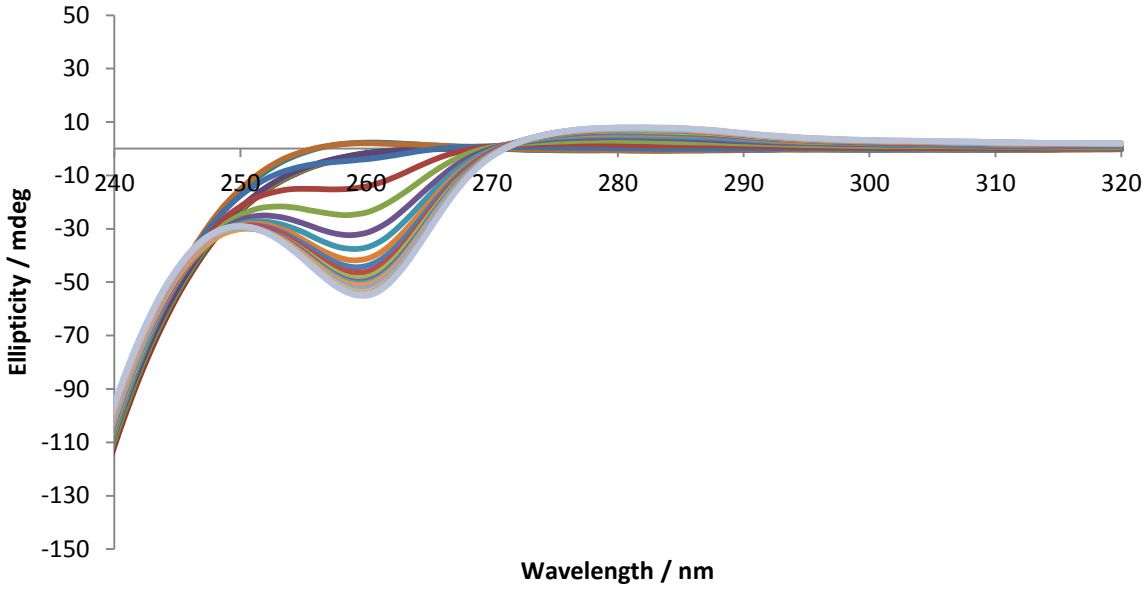

Figure S7. Evolution of CD Spectrum of DBS-CO_2H (0.02% wt/vol) over a two hour period in the absence of agarose

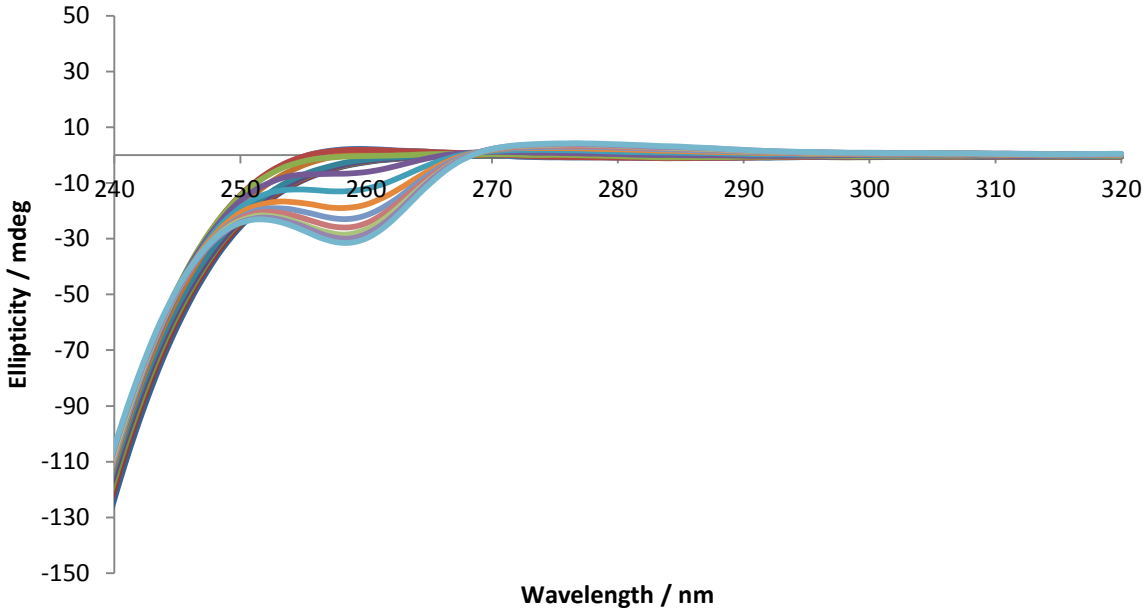

Figure S8. Evolution of CD Spectrum of DBS-CO_2H (0.02% wt/vol) over a two hour period in the presence of agarose (0.05% wt/vol).

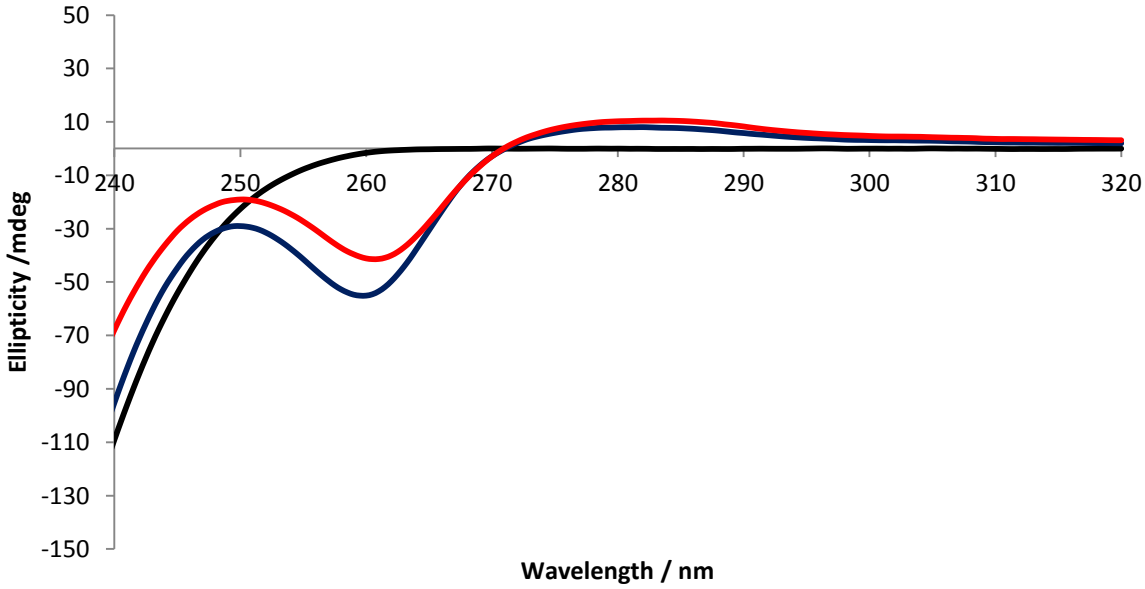

Figure S9. CD Spectra of DBS-CO_2H at 0 h (black), 2 h (blue) and 5 h (red) illustrating further slow reorganisation and decrease in CD ellipticity after 2 h.

7. References

1. a) M. Avrami, *J. Chem. Phys.* **1939**, *7*, 1103-1112; b) M. Avrami, *J. Chem. Phys.* **1940**, *8*, 212-224; c) M. Avrami, *J. Chem. Phys.* **1941**, *9*, 177-184.
2. X. Huang, P. Terech, S. R. Raghavan, R. G. Weiss, *J. Am. Chem. Soc.* **2005**, *127*, 4336-4344.