Supplementary Information

The influence of hydroxy propyl β-cyclodextrin on the micellar to gel transition in F127 solutions investigated at macro and nanoscale level

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Fig. S1. Temperature dependence of storage modulus ($G'$) for samples 1-3 prepared in (a) H$_2$O and (b) D$_2$O at 10 Hz.
The behaviour of sample 1 described by data presented in Figure 2 in the main text is similar for all samples.

In particular for the sample 1, within the pretransition temperature range (293-303), G’ increased slower than G’’ did (at 293 and 298 K, G’ was kept pretty constant while G’’ rose), which means that the system has a viscoelastic behaviour close to the Newtonian one. Accordingly, the temperature ascending leads to increasing the viscous or loss part of the viscoelastic behaviour of the sample. Still, that G’ starts to increase when temperature evolved from 298 K to 303 K is in accordance to the system status closer to the gel transition.

In the temperature range 303-343 K, the sample starts to gel and then the gel becomes progressively strong as temperature increases. The G’ steeply rises reaching a plateau above 313 K and G’’ descends abruptly attaining a plateau beyond the same 313 K. This is equivalent to the prevalence of the elastic part over the viscous one of the sample viscoelasticity and, going further, to the increasing strength of the gel-like behaviour as a function of temperature in the range of 303-343 K. Generally, such behaviour of a viscoelastic material beyond its gel point, where G’>G’’ and the difference G’-G’’ becomes higher as strength gel increases, it is reported both for physically cross-linked gels [1-3] and chemically cross-linked ones [4,5].


Fig. S2. Dependence of loss modulus (G'') on angular frequency (ω) for the sample 1-H$_2$O at the inset temperatures;
**Fig. S3.** a) the experimental EPR spectrum of DT in 1-D$_2$O at 293 K - black continuous line, b) simulated spectrum – black dash line, c) component C1 – blue, d) component C2 – pink.

The software developed by Budil et al. on the basis of Liouville equation was used to simulate the two component spectra characteristic for DT in F127 solutions (this feature was observed only below the temperature values lower than cgt.$^a$

Magnetic parameters: $g_x = 2.0089$, $g_y = 2.0059$, $g_z = 2.0027$,

$A_{xx} = 6.8$G, $A_{yy} = 6.70$, $A_{zz} = 36.4$G,

$\beta_D = 90^\circ$

C1 88.7 %, C2 11.3 %

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Fig. S4. Variation of $\tau_c$ with $1/T$ for the spin probe DT in samples 1-3 prepared in H$_2$O and in D$_2$O.
Fig. S5a. Dependence of $\tau_c$ on temperature for spin probe MTCYC in samples 1-3 prepared in H$_2$O

The straight lines in figure S5a are guides to evidence the changes in slopes for variation of $\tau_c$ with temperature.
Fig.S6. The temperature dependence of the EPR spectra of L62NO in sample 1-D_2O
Fig. S7. The absolute-values Fourier transform ESEEM spectra of (a) L62NO, (b) MTCYC and (c) F127NO in samples 1-3 prepared in D$_2$O.
Fig. S8. Normalized fluorescence spectra of DT in H\textsubscript{2}O (red) and in sample 1-H\textsubscript{2}O (blue)

Fig. S9. Normalised (at 374 nm) emission spectra of pyrene (3 \textmu M) in sample1-H\textsubscript{2}O at 293 K (continuous line), 313 K (dotted line) and 333 K (dashed line). \( \lambda_{ex} = 335 \) nm