Supplementary Material (ESI) for PCCP

Mobility of spin probes in vitrified cyclodextrin inclusion complexes

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SUPPLEMENTARY INFORMATION.

Table of contents.

Figure S1. Host-guest equilibrium between spin labels and cyclodextrin.

The spectra in the figure show solution of TEMPO (5×10^{-4} M) and β-cyclodextrin (7.5×10^{-4} M) in aqueous glycerol at 210 K immediately (e.g., 10 min) after mixing (blue line) and after 1 h at 210 K (purple line). The spectra appear identical which suggests that the equilibrium is established very rapidly.

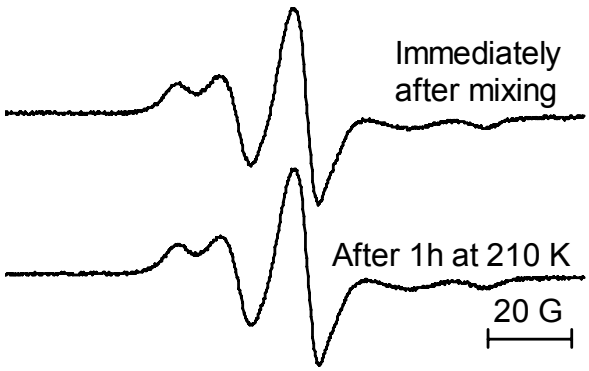


Figure S2. Effect of pH on the EPR spectra of complexed **TNH_2**.

The spectra were recorded for solutions of **TNH_2** (5×10^{-4} M) and β-cyclodextrin in aqueous glycerol at 210 K at pH 2 and pH 10.

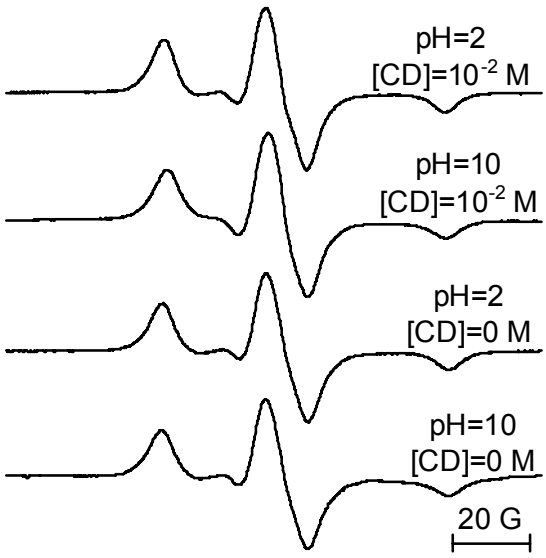


Figure S3. Calculation of equilibrium constants for the host-guest complex formation between **T** and β-cyclodextrin.

Experimental spectra at different cyclodextrin concentration were fitted to a mixture of two components corresponding to free and complexed **T**. The ratio of the two components was optimised using a least square method. The relative weighting of two components was used to calculate the equilibrium constants.

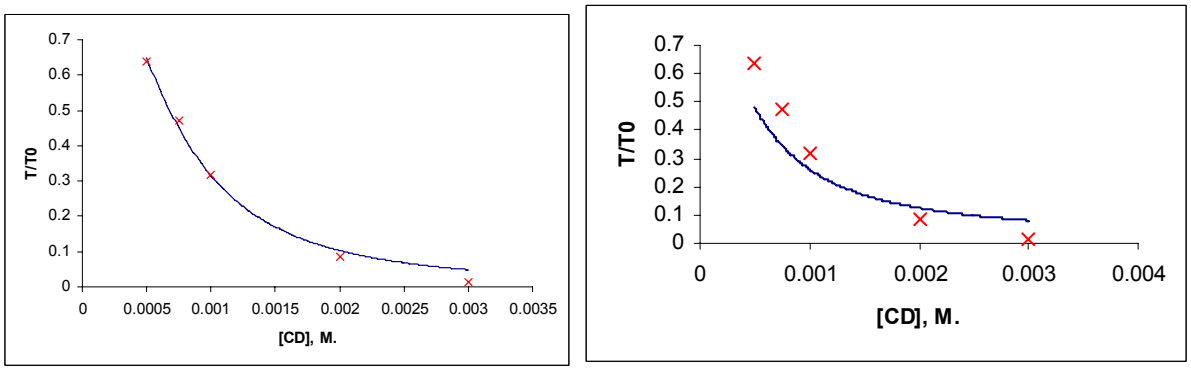
As the speciation curves for the formation of 1:2 complexes involve cubic equations which cannot be solved analytically, the plots below were prepared assuming large excess of cyclodextrin in the mixture (equation 1). This approach is incorrect at lower concentrations of cyclodextrin but gives a good visual indication of the appropriateness of fit.

$$T = \frac{T_0}{K \times CD_0^{\,2} + 1} \qquad (1)$$

Here T_0 and T are equilibrium and initial concentration of the spin label, CD_0 is the initial concentration of cyclodextrin, and K is the equilibrium constant.

The plot below shows fitting the experimental T/T_0 ratio *vs.* cyclodextrin concentration assuming 1:2 (a) and 1:1 (b) **T** to β-cyclodextrin stoichiometry in the complex using equation (1). Least square method was used for fitting. Experimental points (crosses) and fitting lines (solid line) are shown. It is clear that fitting is much better for the 1:2 model.

(a) (b)



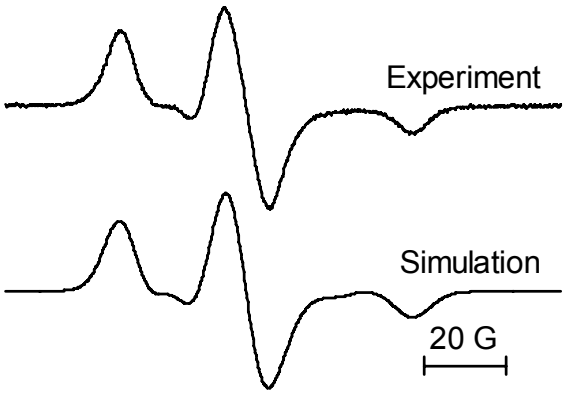
As the equation (1) is inaccurate at low cyclodextrin concentrations, the values of equilibrium constants were calculated for each concentration using equation (2) which is accurate for all concentrations. The equilibrium constants thus calculated for every concentration were averaged to obtain values quoted in the text.

$$K = \frac{T_0 - T}{T \times [CD_0 - 2(T_0 - T)]^2} \qquad (2)$$

Figure S4. Simulation and fitting of slow motion EPR spectra.

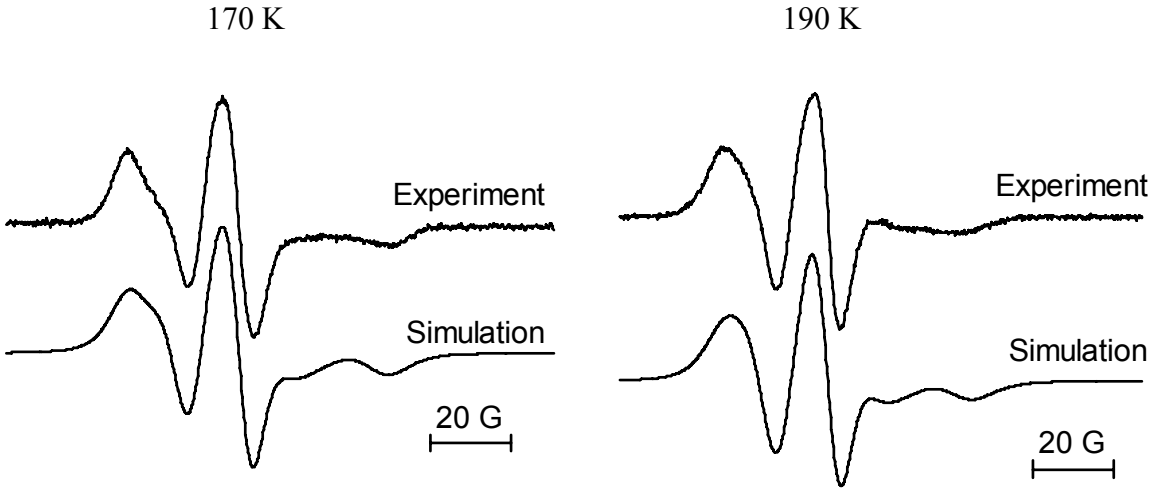
The spectra were simulated using NLSL software (ref. 14 in the main text) assuming anisotropic Brownian diffusion of the axially-symmetric spin label. The following magnetic parameters were obtained by fitting of a frozen **T** solution at 110 K to a powder pattern spectrum and were used for dynamics simulations:

$g_x = 2.0098$
$g_y = 2.0061$
$g_z = 2.0020$
$A_x = 6.80$ G
$A_y = 6.70$ G
$A_z = 36.29$ G



Only rotational diffusion parameters (RPRP and RPLL) and isotropic Gaussian linewidth (gib0) were varied. The values of these parameters were optimised using a least square method. Although the quality of fitting was only adequate, we believe the errors in diffusion parameters are small compared to their variation with temperature. We felt that improvement of fit by using more complex models (e.g., anisotropic line widths, orienting potential etc) is not justified.

The plots show experimental and simulated spectra for solutions of **T** (5×10^{-4} M) and β-cyclodextrin (1×10^{-2} M) in aqueous glycerol.



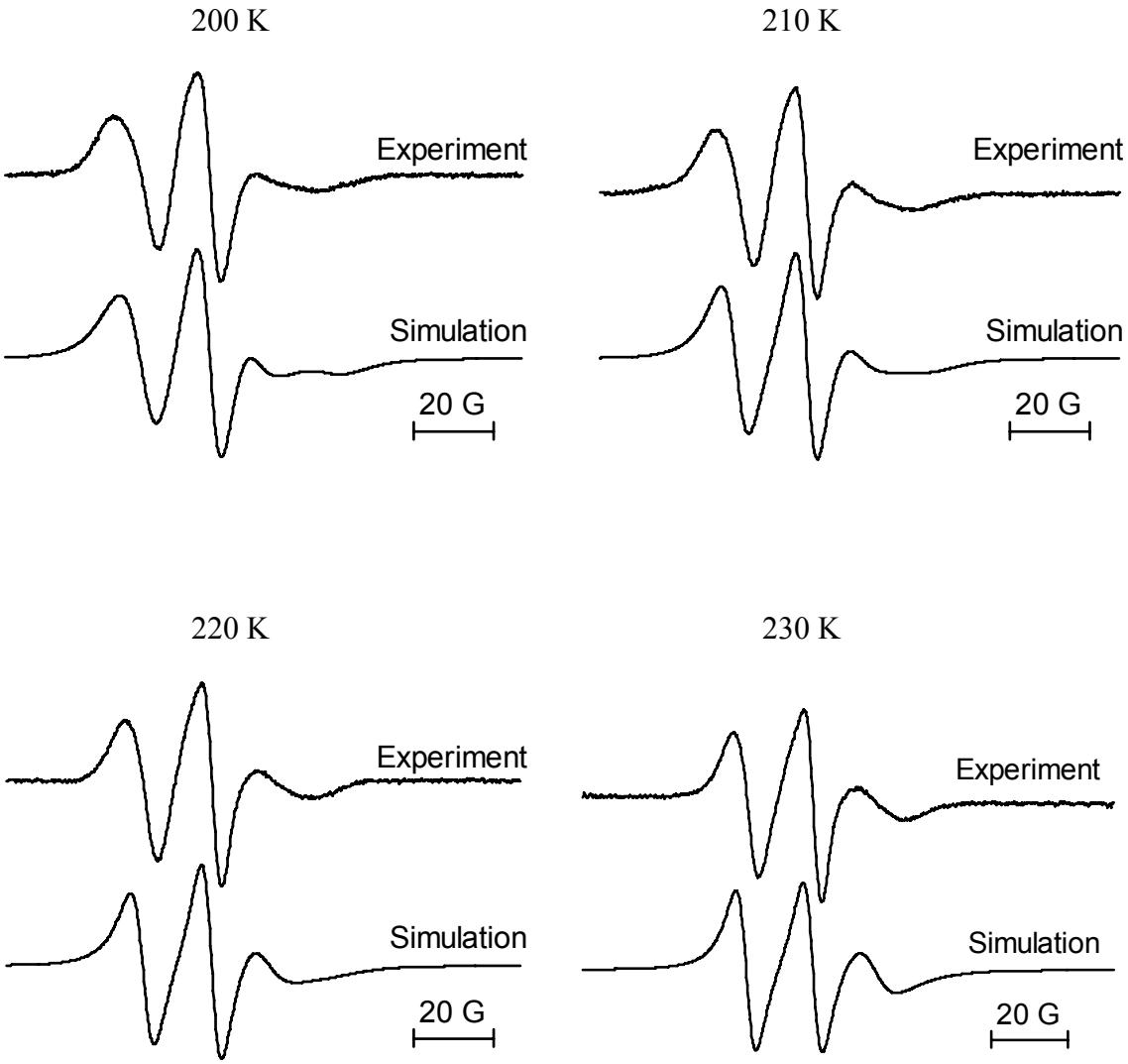


Figure S5. EPR spectra of hydrated and dehydrated solvent-free, solid complex between **T** and β-cyclodextrin.

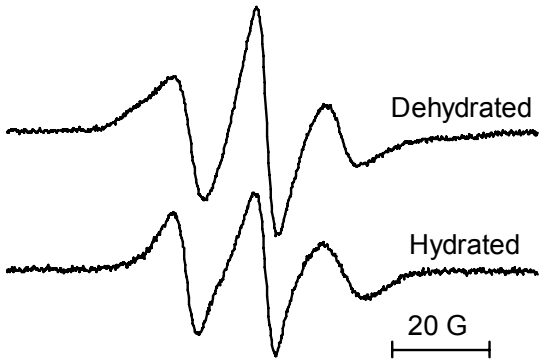


Figure S6. EPR spectra of **TOH** and **CT** in water:glycerol (8:2 w/w) at different β-CD concentrations at 210 K.

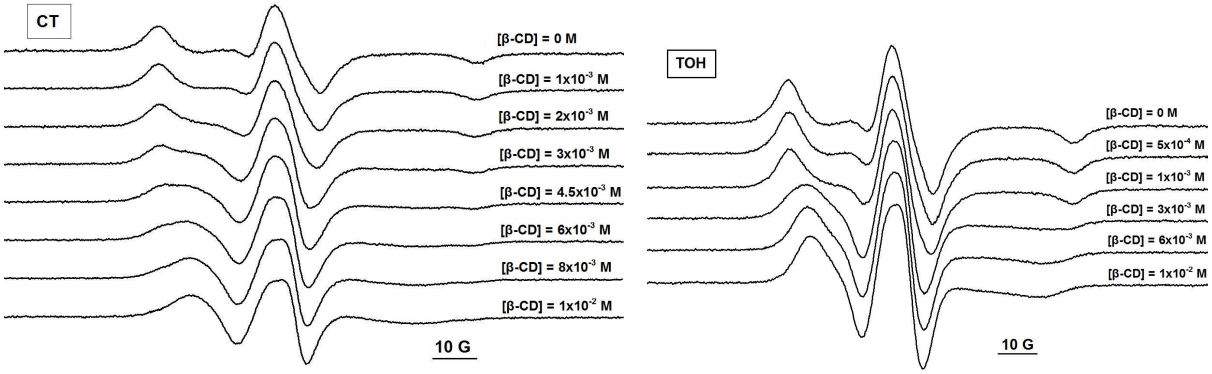


Figure 7. EPR spectra of **T** solution in aqueous glycerol at different temperatures.