Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Conformational preferences of TEMPO type radicals in complexes with cyclodextrins revealed by a combination of EPR spectroscopy, induced circular dichroism and molecular modeling

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Table S1

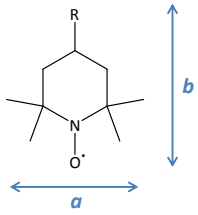
Dimensions (in Å) of cyclodextrins, according to ref.[S1]

Cyclodextrin	Internal diameter	External diameter	Height
α	5.7	13.7	
β	7.8	15.3	7.8
γ	9.5	16.9	

[S1] J. Szejtli, Introduction and general overview of cyclodextrin chemistry, *Chem. Rev.*, 1998, **98**, 1743–1754.

Dimensions (in Å) of TEMPO spin probes (DFT geometries)

Spin probe	*a*	*b*
TEMPO		4.2
4-amino-TEMPO	5.5	5.6
4-carboxy-TEMPO		6.1



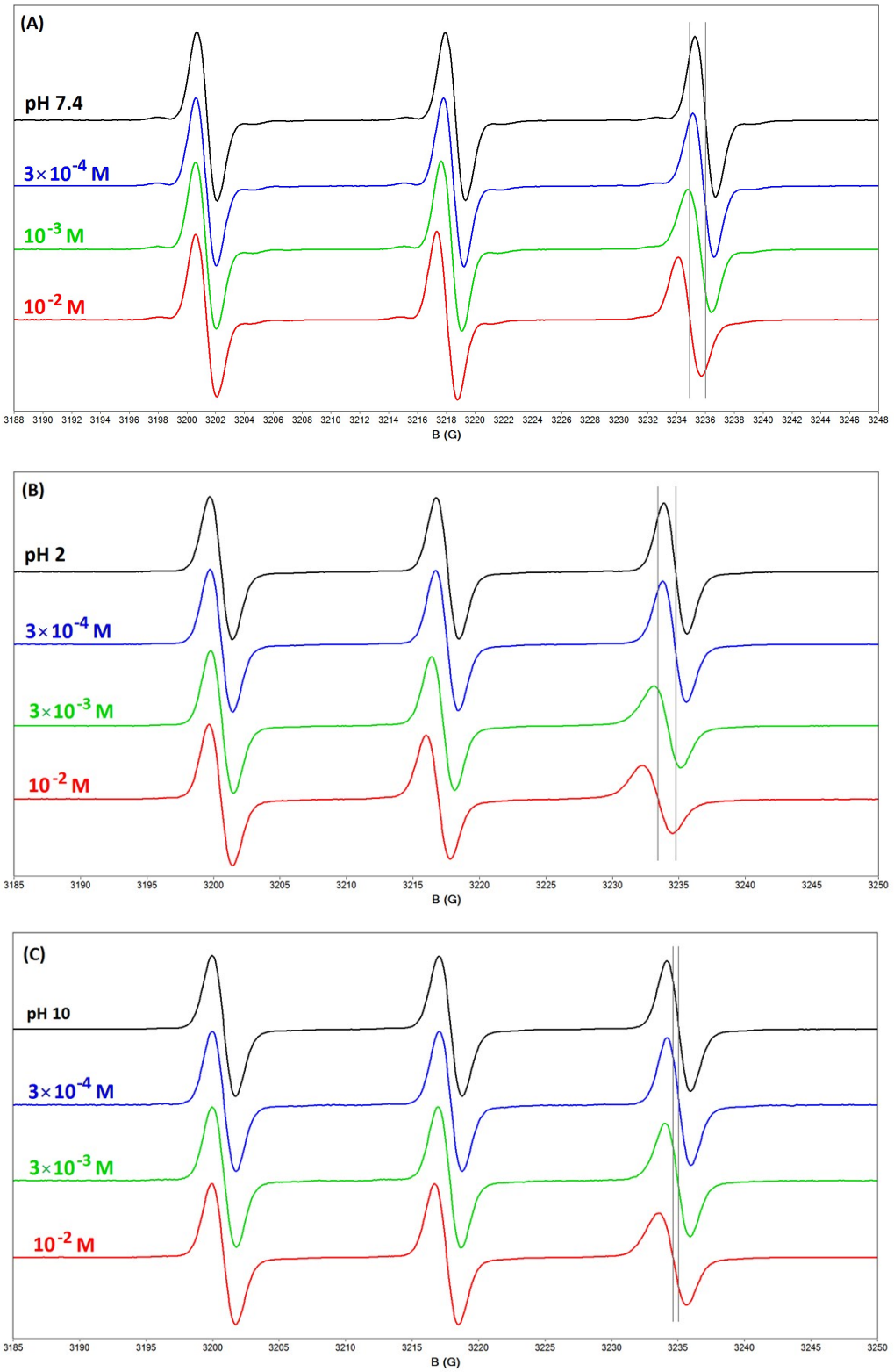


Fig. S1. The EPR spectra of (A) TEMPO, (B) 4-carboxy-TEMPO and (C) 4-amino-TEMPO in the presence of increasing concentrations of β-CD, at 298 K. The distance between the grey lines represents the $\Delta 2a_N$ parameter (in G).

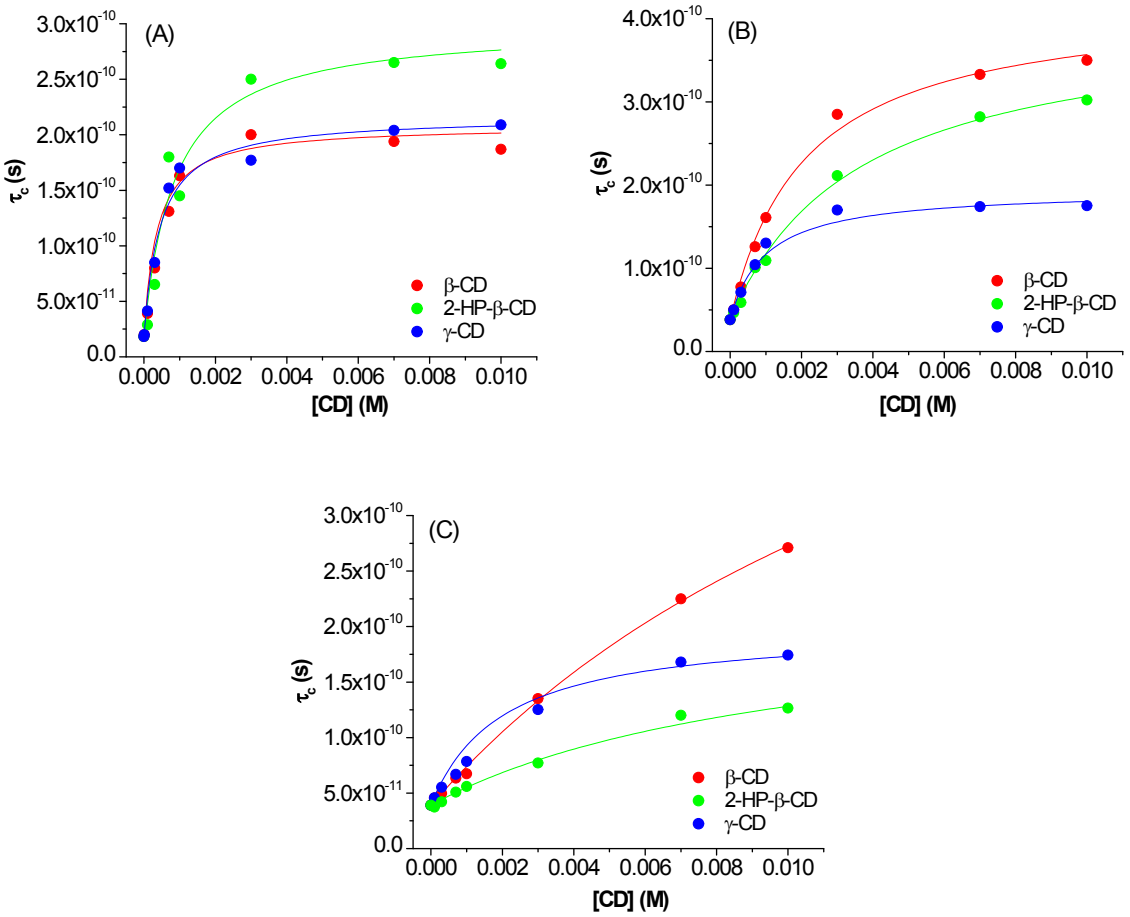


Fig. S2. Dependence of the rotational correlation time, τ_c, of (A) TEMPO (pH 7.4), (B) 4-carboxy-TEMPO (pH 2) and (C) 4-amino-TEMPO (pH 10) on the cyclodextrin concentration.

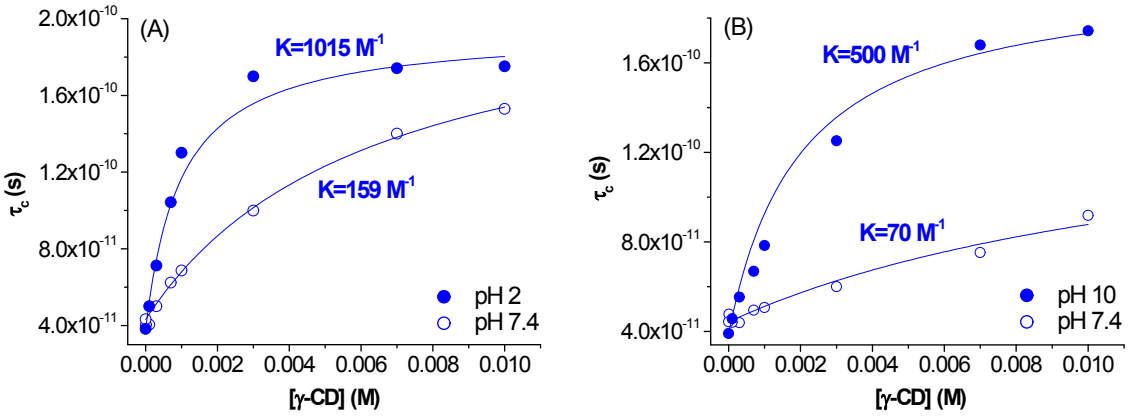


Fig. S3. Neutral *vs.* ionic species of (A) 4-carboxy-TEMPO and (B) 4-amino-TEMPO in interaction with γ-CD.

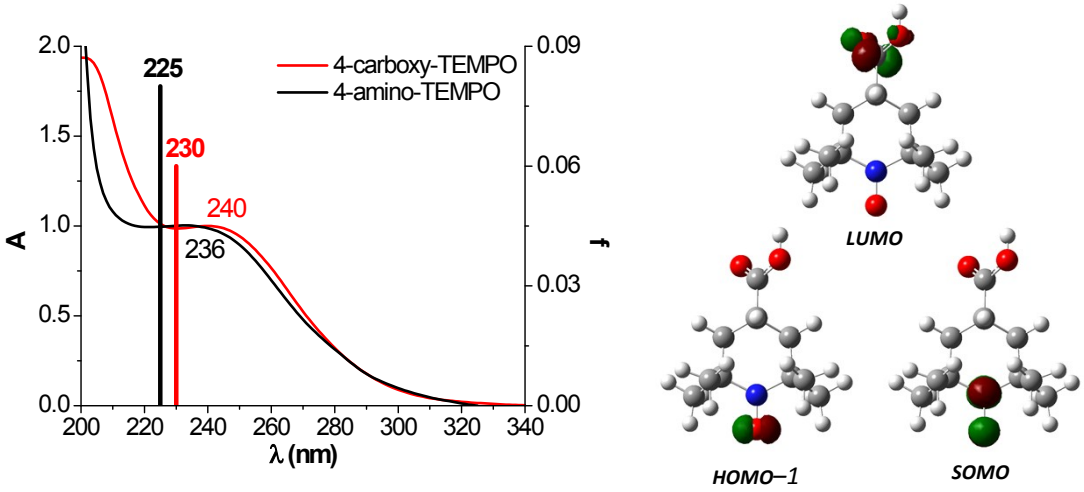


Fig. S4. Left: Normalized experimental absorption spectra of 4-carboxy-TEMPO and 4-amino-TEMPO at pH 2 and 10, respectively. The absorption maxima calculated at the B3LYP/6-311++G(d,p) level by reconvolution of individual spectra of conformers weighted by their Boltzmann populations are depicted as lines. Right: Localization of the frontier molecular orbitals for the minimum energy conformer of 4-carboxy-TEMPO (τ = −20 deg).

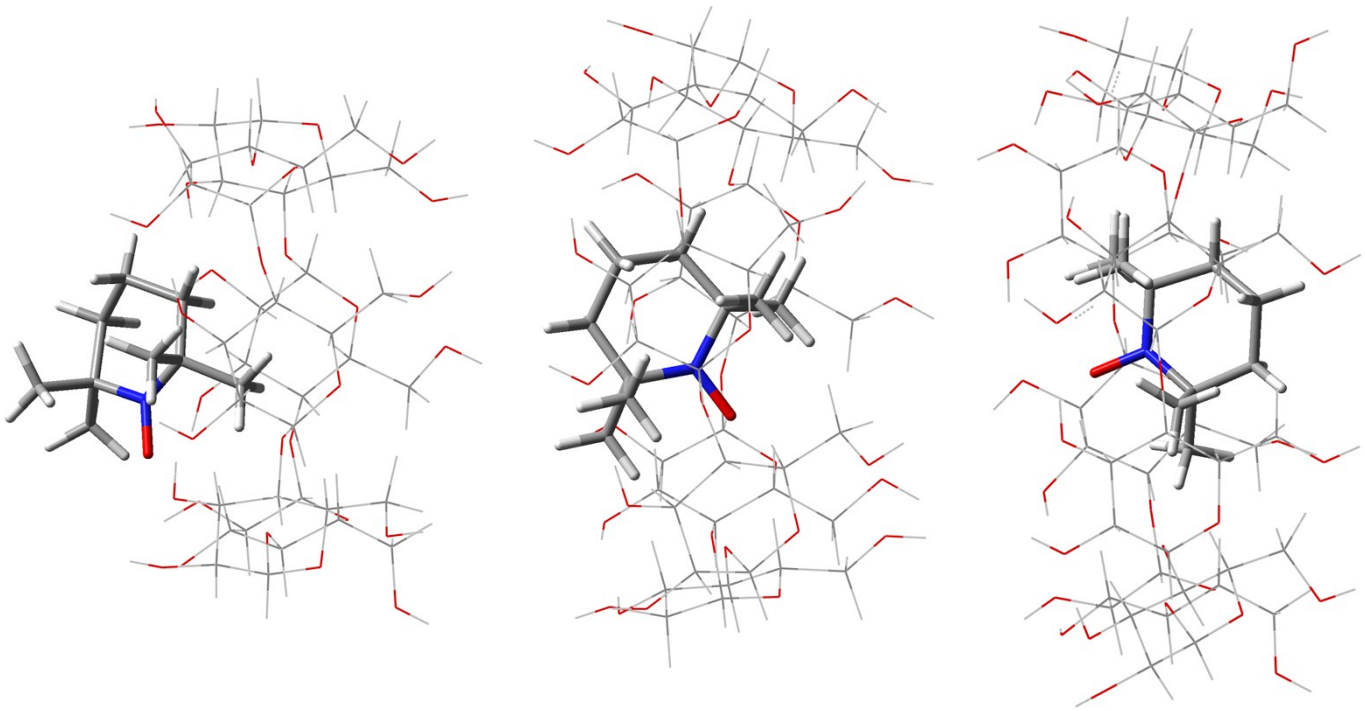


Fig. S5. Proposed structures (lateral view) of the inclusion complexes of TEMPO with (A) α-CD, (B) β-CD and (C) γ-CD.

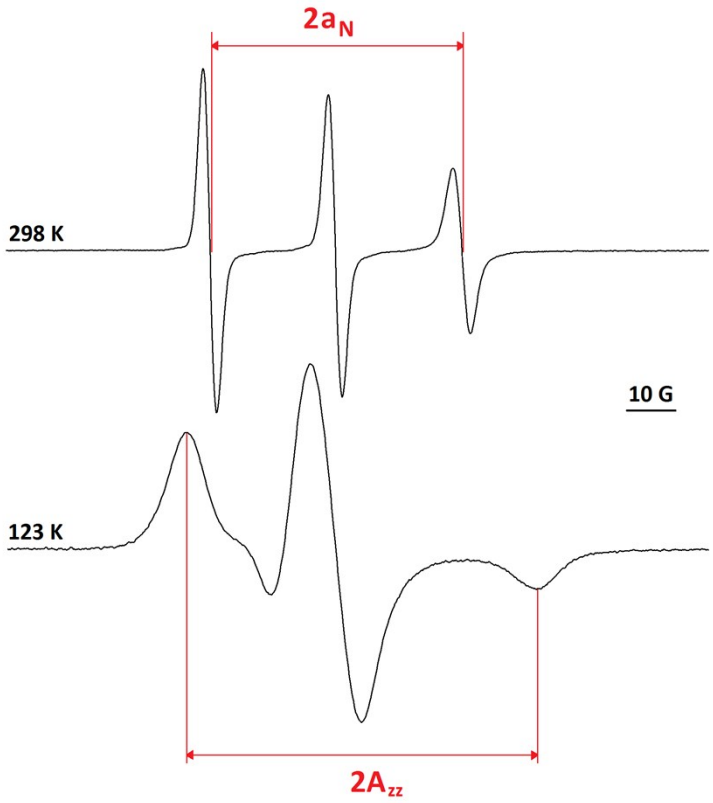


Fig. S6. Typical EPR spectra of a spin probe–cyclodextrin complex at different temperatures. The values of the hyperfine splitting constant (a_N, isotropic; A_{zz} anisotropic, parallel component) are obtained directly from the spectra, as indicated by the red lines.

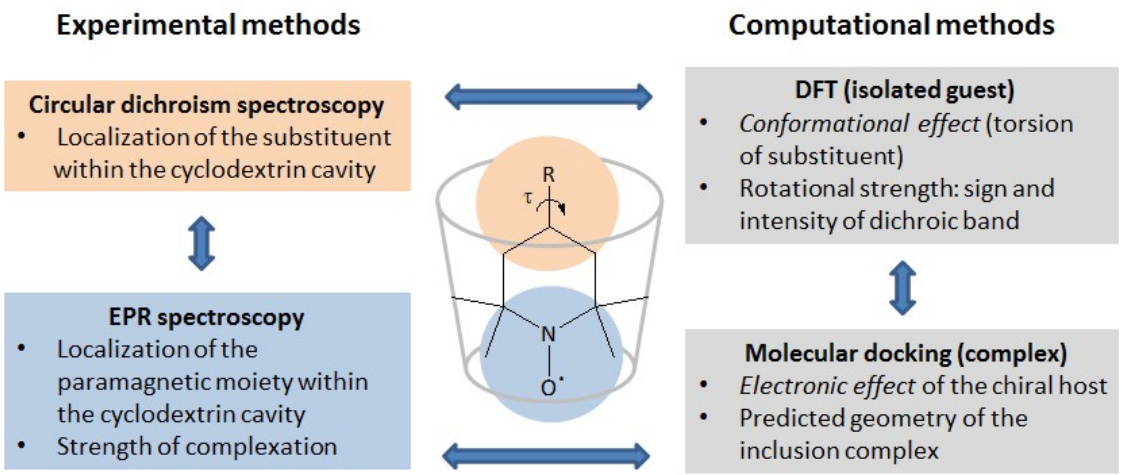


Fig. S7. Diagram illustrating the interplay of experimental and theoretical methods used in this study, and the information that can be extracted from each method.