Electronic Supplementary Information for

The confluence of structure and dynamics in lanthanide(III) chelates: how dynamics help define structure in solution

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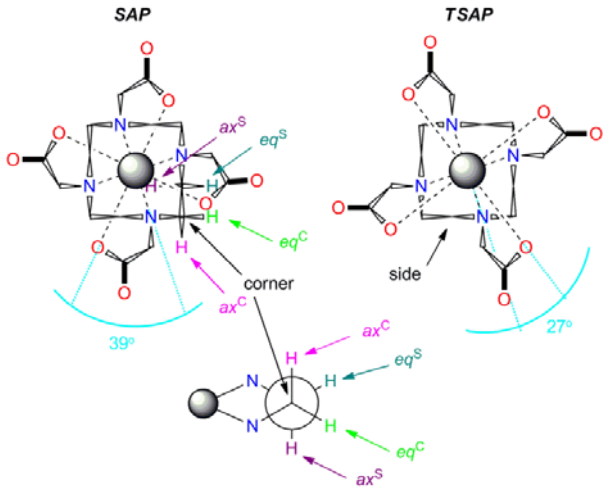

Figure S1. A description of lanthanide coordination in the SAP and TSAP coordination isomers and assignments of the macrocyclic ring protons in DOTA-type chelates.

Consideration of the effect of change in Yb^{3+} hydration on chemical shift

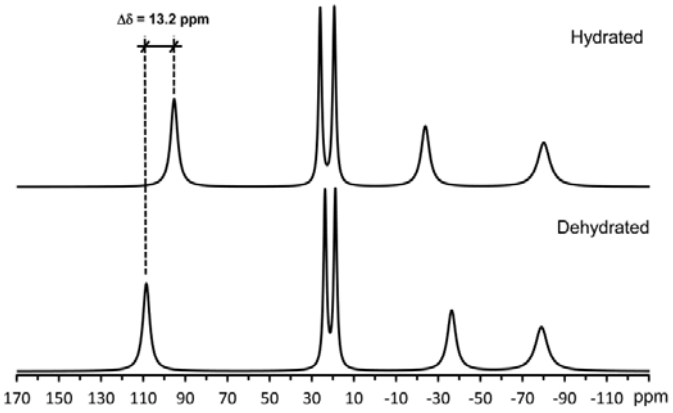

Figure S2. Simulations of the ^1H NMR spectra of the hydrated (top) and dehydrated (bottom) Yb^{3+} chelates of DO3AP(ABn).[J. Kotek, J. Rudovsky, P. Hermann and I. Lukeš, *Inorg. Chem.*, 2006, **45**, 3097-3102.]

On the basis of the crystal structures of YDO3AP(ABn) published by Lukeš and Hermann one can simulate a dipolar only ^1H NMR spectrum of the hydrated and dehydrated forms of a YbDOTA-type chelate. The positions of all protons in each of these structures are averaged and the dipolar shift calculated employing a ligand field parameter, *D*, value of 3600 for both chelates. The results show quite clearly that the spectrum of the hydrated and dehydrated chelates differ substantially. In this simulation there is a 13.2 ppm difference in the shifts of the ax^S protons. On this basis it is clear that if a hydrated and dehydrated form of a YbDOTA-type chelate existed simultaneously in solution then a different spectrum would be seen for each if they were not in rapid exchange on the NMR time-scale.

One should note that the ligand field parameter, *D*, may not take the same value in each form of the chelate. However, it is evident that increasing *D* in the hydrated chelate to equalize the shifts of the ax^S proton in both hydration states would simultaneously increase the shifts of other protons in the hydrated form which would increase the difference between the two state rendering both visible in the NMR spectrum. This exercise thoroughly debunks the notion that there are two hydration states of such chelates in slow or no exchange in solution. The two hydration states must be in fast exchange and given that a single sharp peak is observed for YbNB-DOTMA chelates at 600 MHz, that means exchange cannot be slower than 1×10^4 s^{-1}. The two hydration states must therefore exchange at the rate of water exchange, which is very rapid.

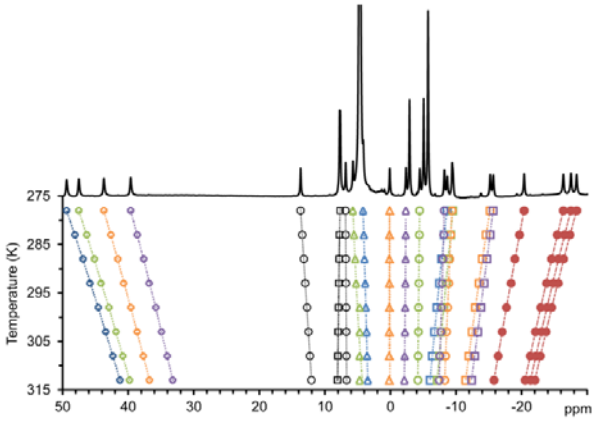

Figure S3. Variable temperature ^{1}H NMR spectra recorded in D_2O at 400 MHz of the 'corner' isomer Eu*S*-*RRRR*-NB-DOTMA. The spectral assignment from COSY data (reported in Webber and Woods, *Inorg. Chem.*, 8576 (2012)) allows each proton of each ethylene bridge to be shown in the same colour using open symbols according to the scheme: ax^{S} (diamonds); eq^{S} (squares); ax^{C} (triangles); eq^{C} (circles). The acetate protons, *ac*, are shown as closed red circles; the benzylic protons as black open circles; and the aromatic protons as black open squares. For clarity the temperature dependence of the methyl substituents is not shown.

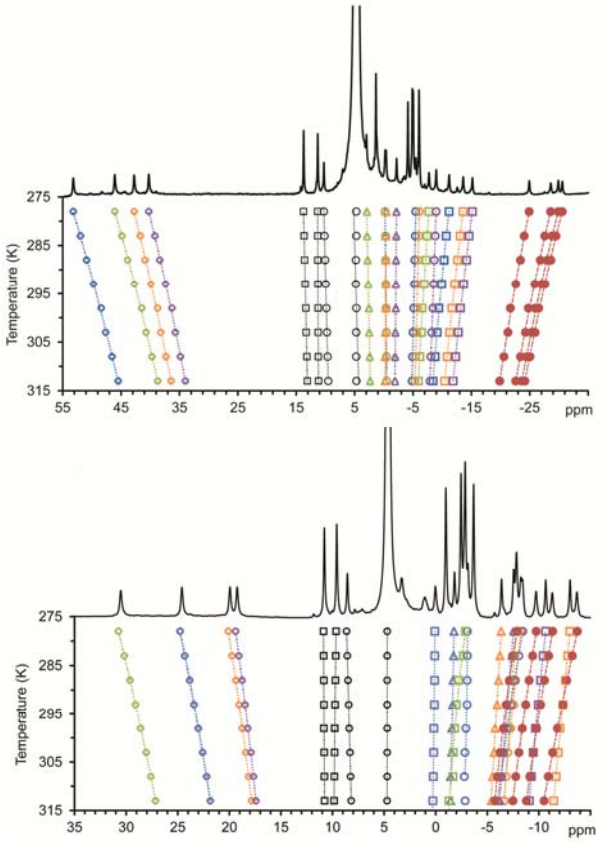

Figure S4. Variable temperature ^{1}H NMR spectra recorded in D_2O at 400 MHz of the 'side' isomers of Eu*S*-*RRRR*-NB-DOTMA (top) and Eu*S*-*SSSS*-NB-DOTMA (bottom). The spectral assignment from COSY data (reported in Webber and Woods, *Inorg. Chem.*, 8576 (2012)) allows each proton of each ethylene bridge to be shown in the same colour using open symbols according to the scheme: ax^{S} (diamonds); eq^{S} (squares); ax^{C} (triangles); eq^{C} (circles). The acetate protons, *ac*, are shown as closed red circles; the benzylic protons as black open circles; and the aromatic protons as black open squares. For clarity the temperature dependence of the methyl substituents is not shown.

Samples of the side and corner isomers of Eu*S*-*SRRR*-NB-DOTMA (both SAP isomers) were also isolated from the preparation of Eu*S*-*RRRR*-NB-DOTMA. The temperature dependence of these two isomers is comparable to that of the two isomers of Eu*S*-*RRRR*-NB-DOTMA and is shown in Figure S2 and S3.

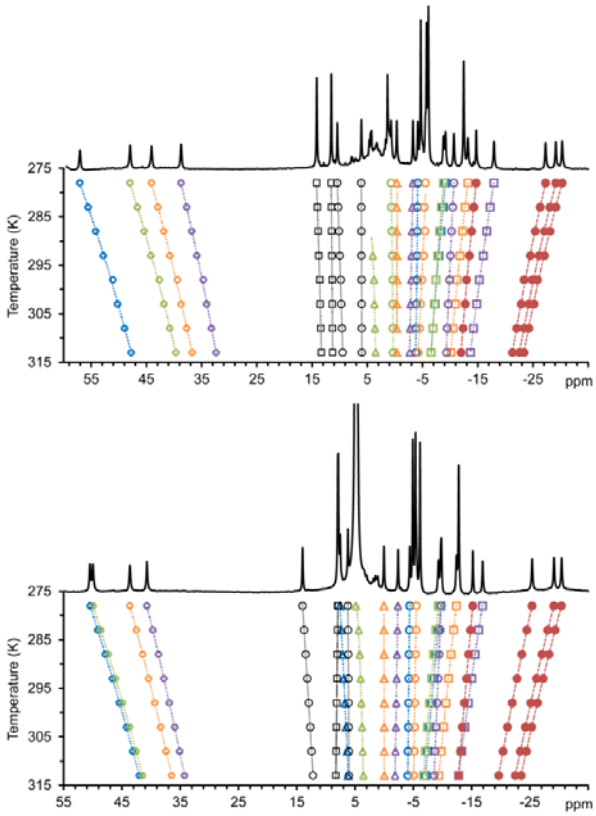

Figure S5. Variable temperature ^{1}H NMR spectra recorded in D_2O at 400 MHz of the 'side' (top) and 'corner' (bottom) isomers of Eu*S*-*SRRR*-NB-DOTMA. The spectral assignment from COSY data (reported in Webber and Woods, *Inorg. Chem.*, 8576 (2012)) allows each proton of each ethylene bridge to be shown in the same colour using open symbols according to the scheme: ax^{S} (diamonds); eq^{S} (squares); ax^{C} (triangles); eq^{C} (circles). The acetate protons, *ac*, are shown as closed red circles; the benzylic protons as black open circles; and the aromatic protons as black open squares. For clarity the temperature dependence of the methyl substituents is not shown.

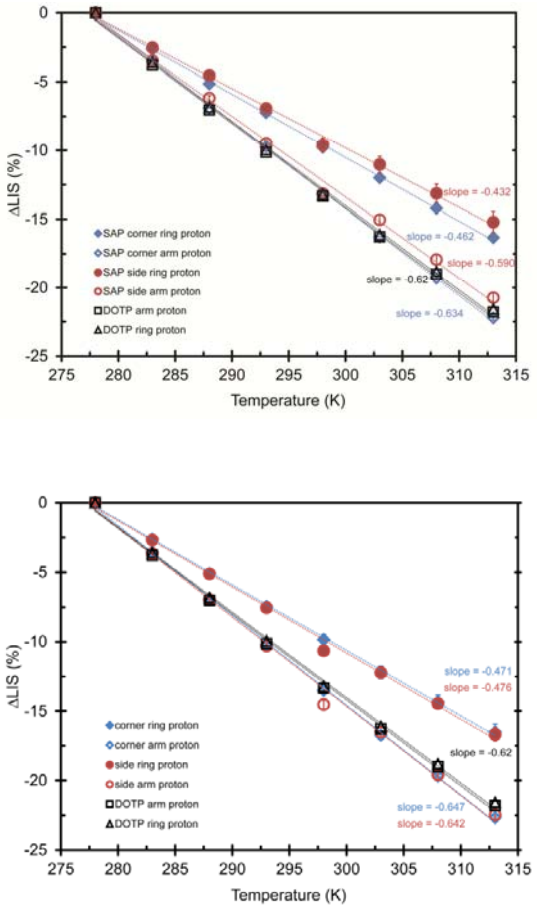

Figure S6. The change in experimentally observed lanthanide induced shift (LIS) with changing temperature for the ring proton (ax^S) and pendant arm proton (*ac*) of the 'side' and 'corner' isomers of Eu*S*-*RRRR*-NB-DOTMA (top) and Eu*S*-*SRRR*-NB-DOTMA (bottom) (both SAP isomers) expressed as a percentage of the shift at 278 K. The error bars represent the experimentally observed deviation from the average value for each data point. The data are shown against those obtained for EuDOTP for comparative purposes.

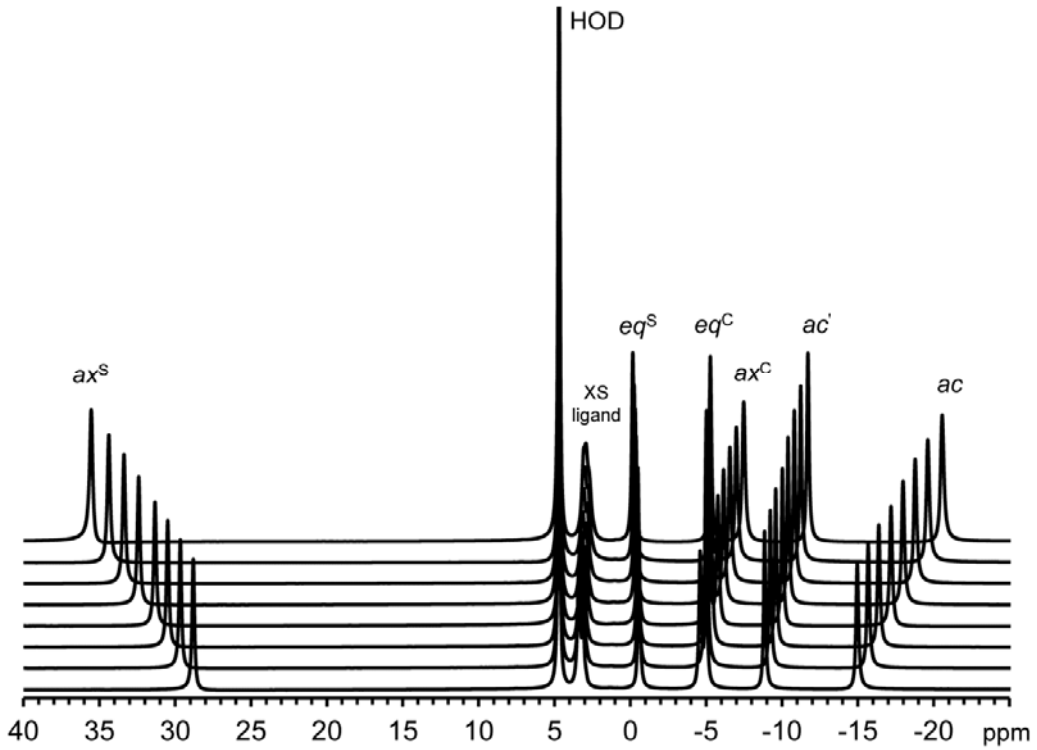

Figure S7. A stacked plot of variable temperature ^{1}H NMR spectra of EuDOTP recorded in D_2O at 400 MHz from 278 K (top) to 313 K (bottom) in 5 K increments.