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## **Supporting Information:**

### **Solute Specific Perturbations to Water Structure and Dynamics in Tertiary Aqueous Solution**

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Pages	S1-S12
Figures	S1-9
Tables	S1-4

**List S1.** Samples list with isotopic makeup

- H2O
- D2O
- HDO
- H2O, 1.0 M H-TMAO
- D2O, 1.0 M H-TMAO
- HDO, 1.0 M H-TMAO
- H2O, 1.0 M D-TMAO
- D2O, 1.0 M D-TMAO
- HDO, 1.0 M D-TMAO
- HDO, 1.0 M HD-TMAO
- H2O, 0.2 M Mg(ClO<sub>4</sub>)<sub>2</sub>
- D2O, 0.2 M Mg(ClO<sub>4</sub>)<sub>2</sub>
- HDO, 0.2 M Mg(ClO<sub>4</sub>)<sub>2</sub>
- H2O, 1.0 M H-TMAO, 0.2 M Mg(ClO<sub>4</sub>)<sub>2</sub>
- D2O, 1.0 M H-TMAO, 0.2 M Mg(ClO<sub>4</sub>)<sub>2</sub>
- HDO, 1.0 M H-TMAO, 0.2 M Mg(ClO<sub>4</sub>)<sub>2</sub>
- H2O, 1.0 M D-TMAO, 0.2 M Mg(ClO<sub>4</sub>)<sub>2</sub>
- D2O, 1.0 M D-TMAO, 0.2 M Mg(ClO<sub>4</sub>)<sub>2</sub>
- HDO, 1.0 M D-TMAO, 0.2 M Mg(ClO<sub>4</sub>)<sub>2</sub>
- HDO, 1.0 M HD-TMAO, 0.2 M Mg(ClO<sub>4</sub>)<sub>2</sub>
- H2O, 2.7 M Mg(ClO<sub>4</sub>)<sub>2</sub>
- D2O, 2.7 M Mg(ClO<sub>4</sub>)<sub>2</sub>
- HDO, 2.7 M Mg(ClO<sub>4</sub>)<sub>2</sub>
- H2O, 1.0 M H-TMAO, 2.7 M Mg(ClO<sub>4</sub>)<sub>2</sub>
- D2O, 1.0 M H-TMAO, 2.7 M Mg(ClO<sub>4</sub>)<sub>2</sub>
- HDO, 1.0 M H-TMAO, 2.7 M Mg(ClO<sub>4</sub>)<sub>2</sub>
- H2O, 1.0 M D-TMAO, 2.7 M Mg(ClO<sub>4</sub>)<sub>2</sub>
- D2O, 1.0 M D-TMAO, 2.7 M Mg(ClO<sub>4</sub>)<sub>2</sub>
- HDO, 1.0 M D-TMAO, 2.7 M Mg(ClO<sub>4</sub>)<sub>2</sub>
- HDO, 1.0 M HD-TMAO, 2.7 M Mg(ClO<sub>4</sub>)<sub>2</sub>

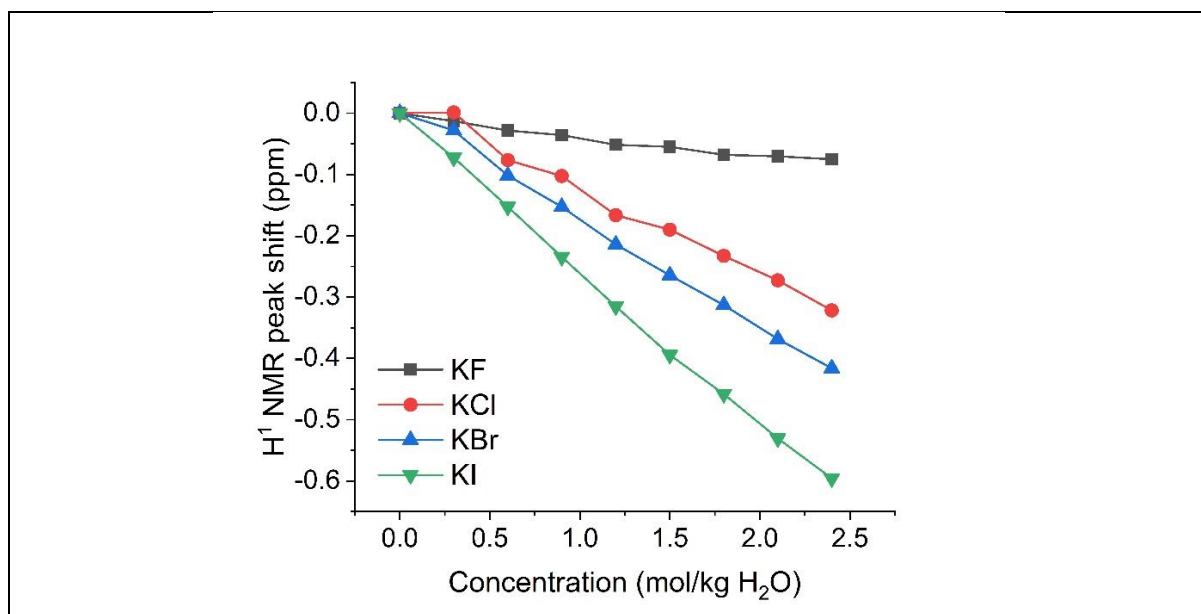
Atomic species	$\epsilon$ (kJ/mol)	$\sigma$ (Å)	Charge (e)
O <sub>w</sub>	0.65	3.166	-0.8476
H <sub>w</sub>	0.00	0.00	0.4238
C1	0.39	3.70	-0.2600

H1	0.065	1.80	0.1100
N1	0.711	3.25	0.4400
O1	0.585	3.08	-0.6500
Mg	0.4593	0.90	2.0000
Cl <sub>p</sub>	0.566	4.19	2.3904
O <sub>p</sub>	0.65	3.166	-0.8476

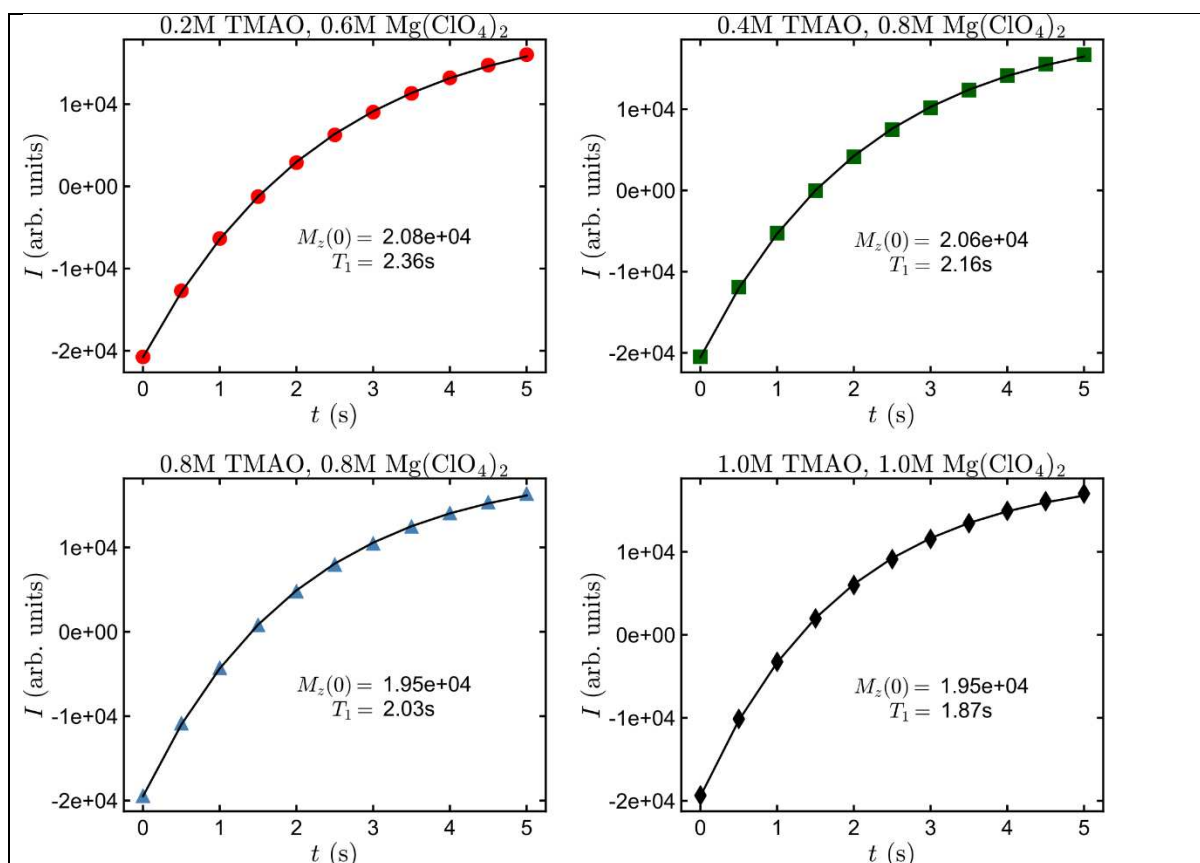
**Table S1.** Lennard-Jones and Coulomb parameters for atomic species present in simulation. W subscript indicates water atoms, 1 indicates TMAO, p indicates perchlorate ion

Sample	Water Molecules	TMAO Molecules	Mg <sup>2+</sup> ions	ClO <sub>4</sub> <sup>-</sup> ions	Box dimension (Å)
H <sub>2</sub> O	1000	-	-	-	31.0723
1.0 M TMAO	4104	80	-	-	51.0434
0.2 M Mg(ClO <sub>4</sub> ) <sub>2</sub>	4104	-	16	32	49.9840
1.0 M TMAO, 0.2 M Mg(ClO <sub>4</sub> ) <sub>2</sub>	4104	80	16	32	51.2654
2.7 M Mg(ClO <sub>4</sub> ) <sub>2</sub>	4224	-	260	520	54.4902
1.0 M TMAO, 2.7 M Mg(ClO <sub>4</sub> ) <sub>2</sub>	4224	80	260	520	55.5774

**Table S2.** Number of molecules used in each simulation box and length of cubic box



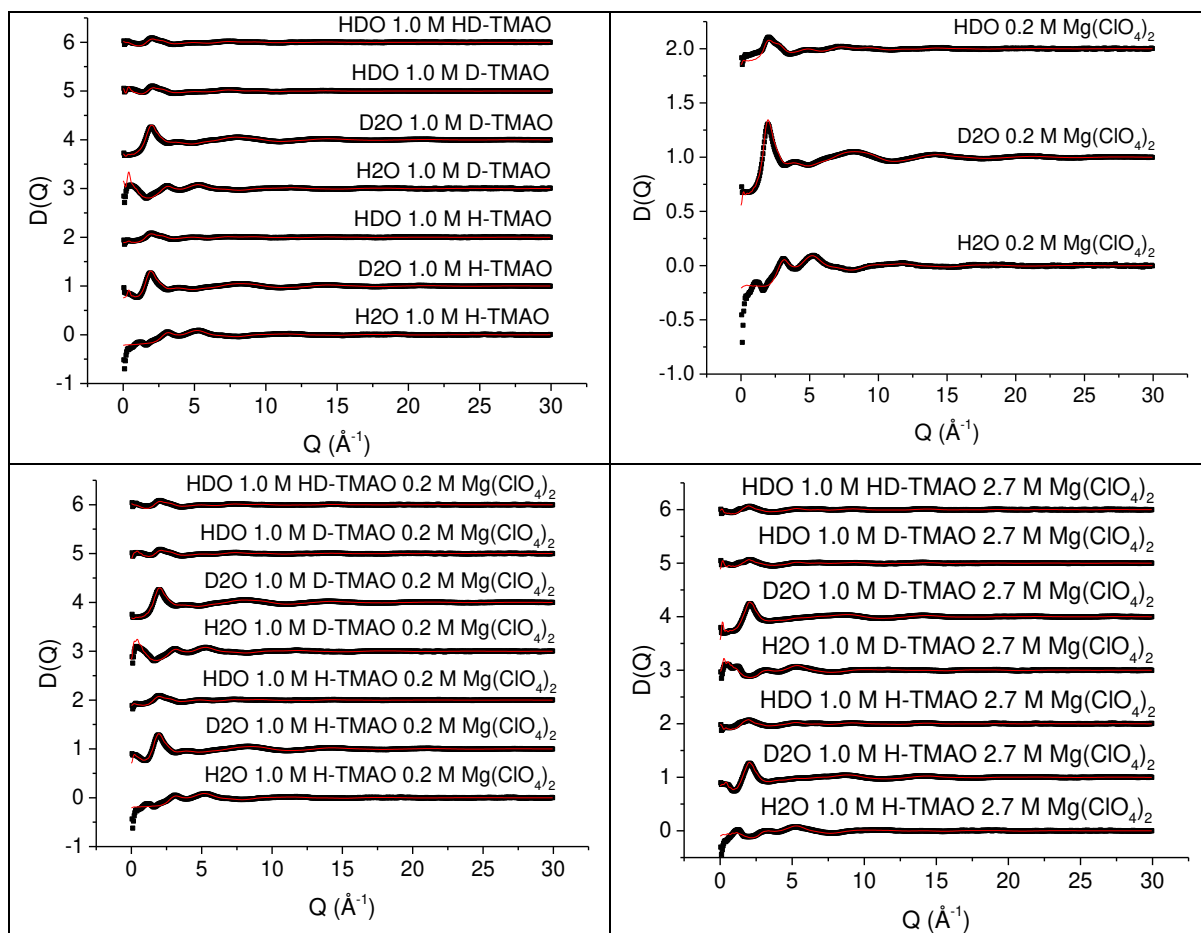
**Figure S1.** H<sup>1</sup> NMR peak shift for water as a function of increasing concentration of the potassium halide salts: KF, KCl, KBr, KI.



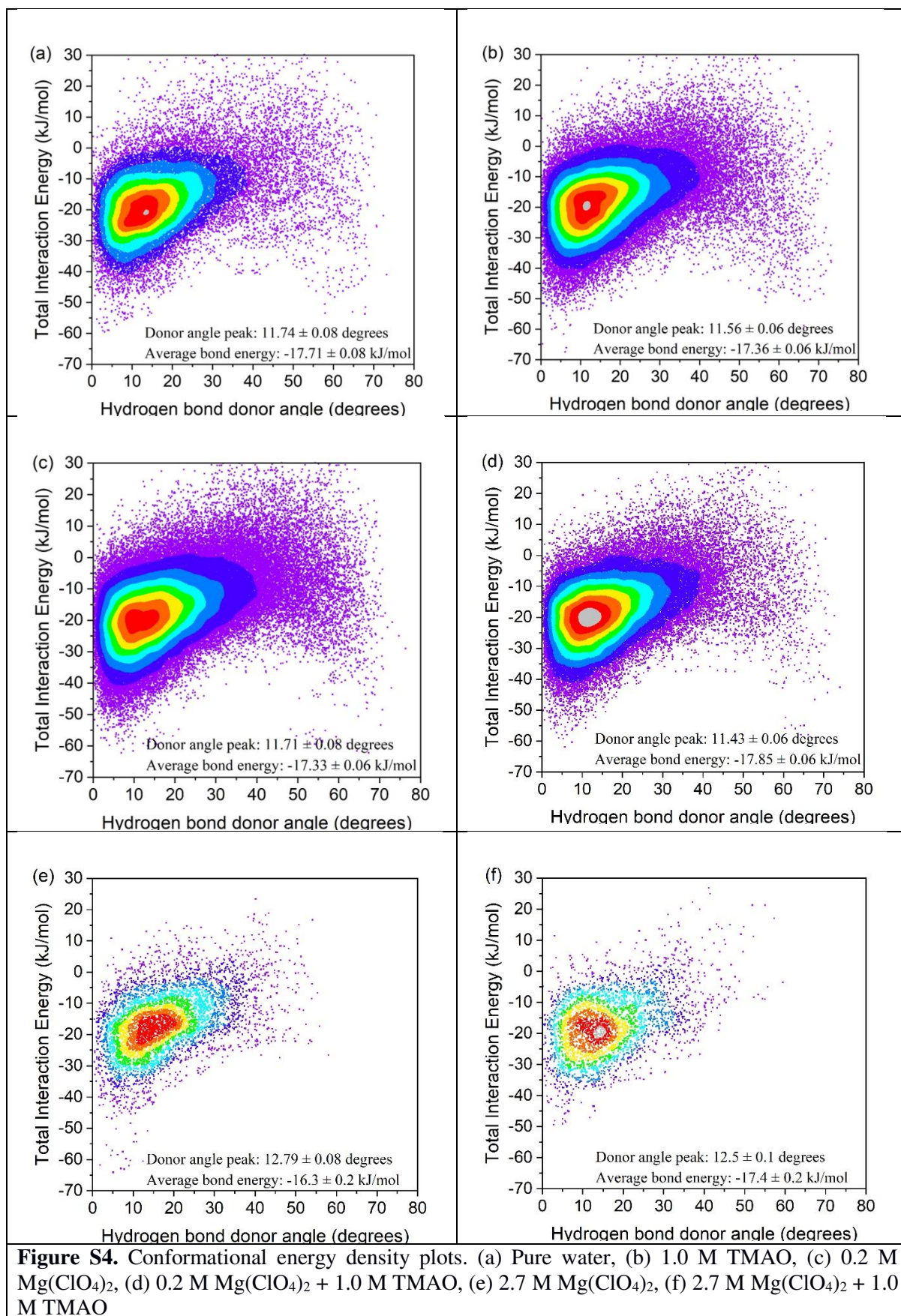
**Figure S2.** Net magnetization in the z direction following a  $180^\circ$  pulse for four example datasets. The data are all extremely well described using a single exponential decay term, indicating that any dynamic heterogeneities in the sample are minimal.

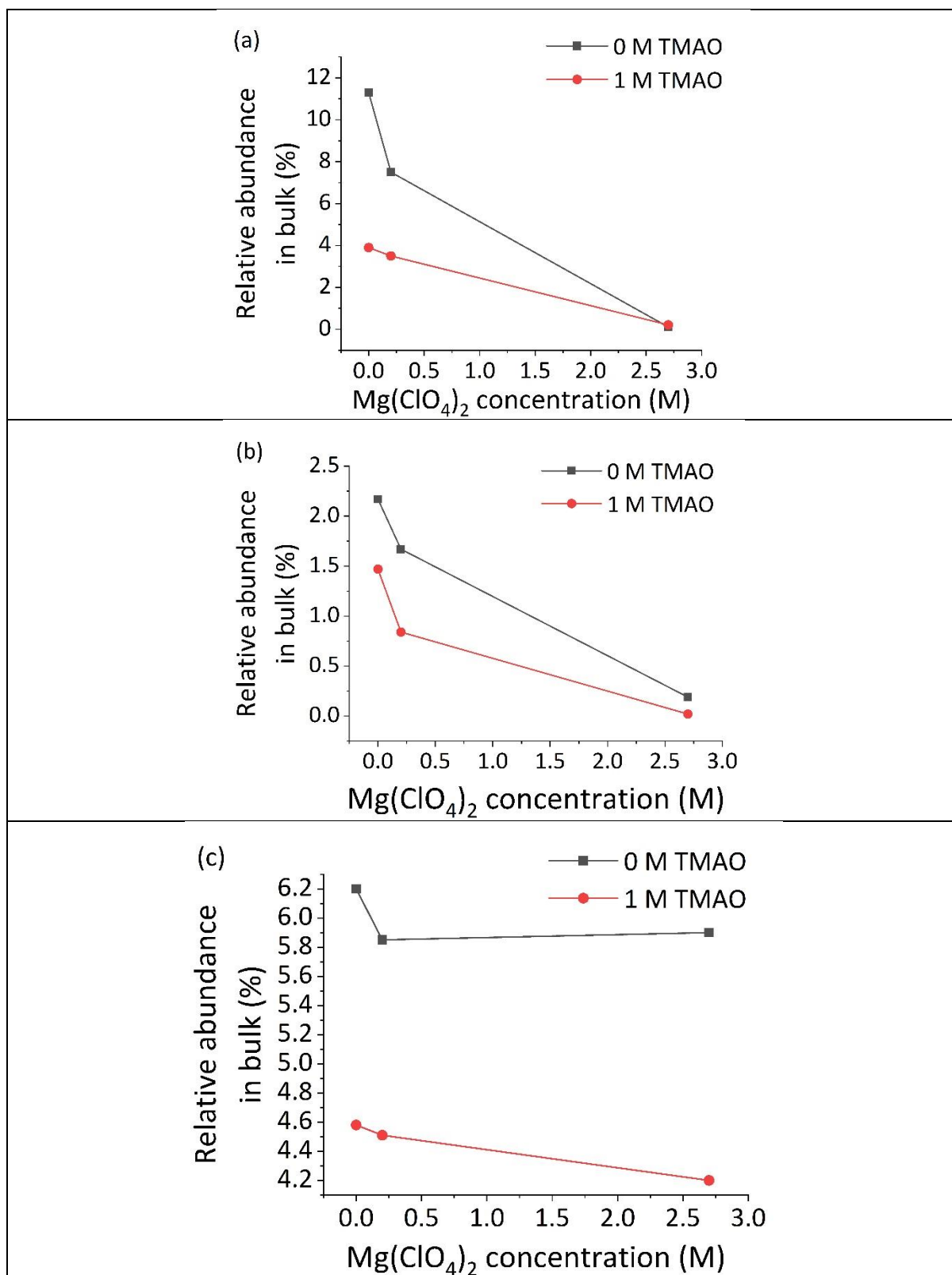
Solute pair	1.0 M TMAO	0.2 M $\text{Mg}(\text{ClO}_4)_2$	0.2 M $\text{Mg}(\text{ClO}_4)_2$ + 1.0 M TMAO	2.7 M $\text{Mg}(\text{ClO}_4)_2$	2.7 M $\text{Mg}(\text{ClO}_4)_2$ + 1.0 M TMAO
Cl <sub>p</sub> - Mg	-	0.03 (3.50 Å)	0.03 (3.50 Å)	0.58 (3.50 Å)	0.55 (3.50 Å)
N1 - Cl <sub>p</sub>	-	-	0.24 (6.28 Å)	-	3.45 (6.61 Å)
N1 - Mg	-	-	0.03 (3.50 Å)	-	0.2 (3.50 Å)
N1 - N1	0.70 (7.04 Å)	-	1.00 (7.82 Å)	-	0.33 (6.24 Å)

**Table S3.** Coordination numbers for solute – solute interactions present in samples. Distance used to calculate solute – solute coordination number correspond to the location of the first minima in the associated RDF, shown in brackets.

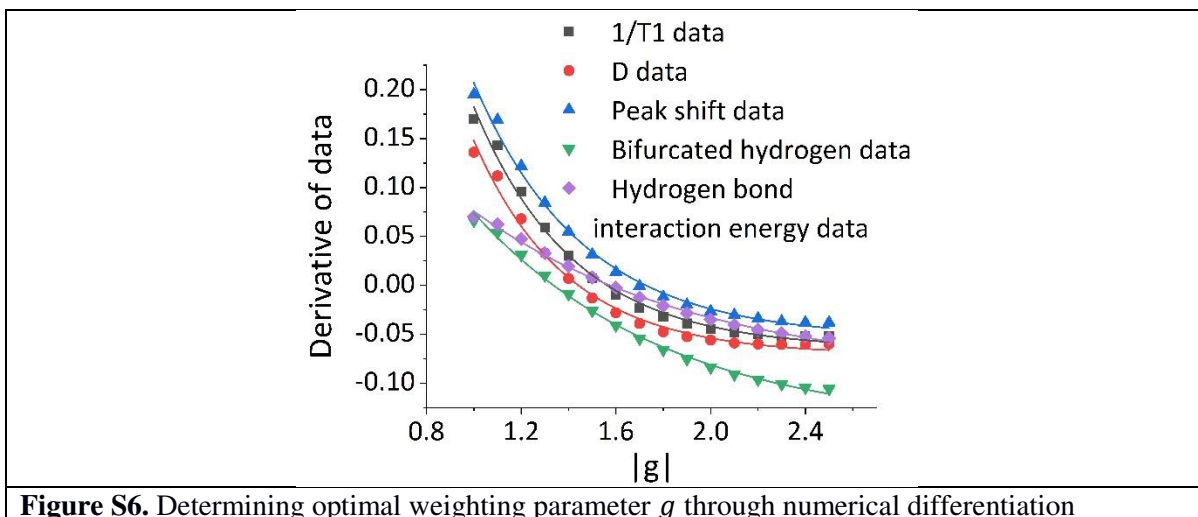


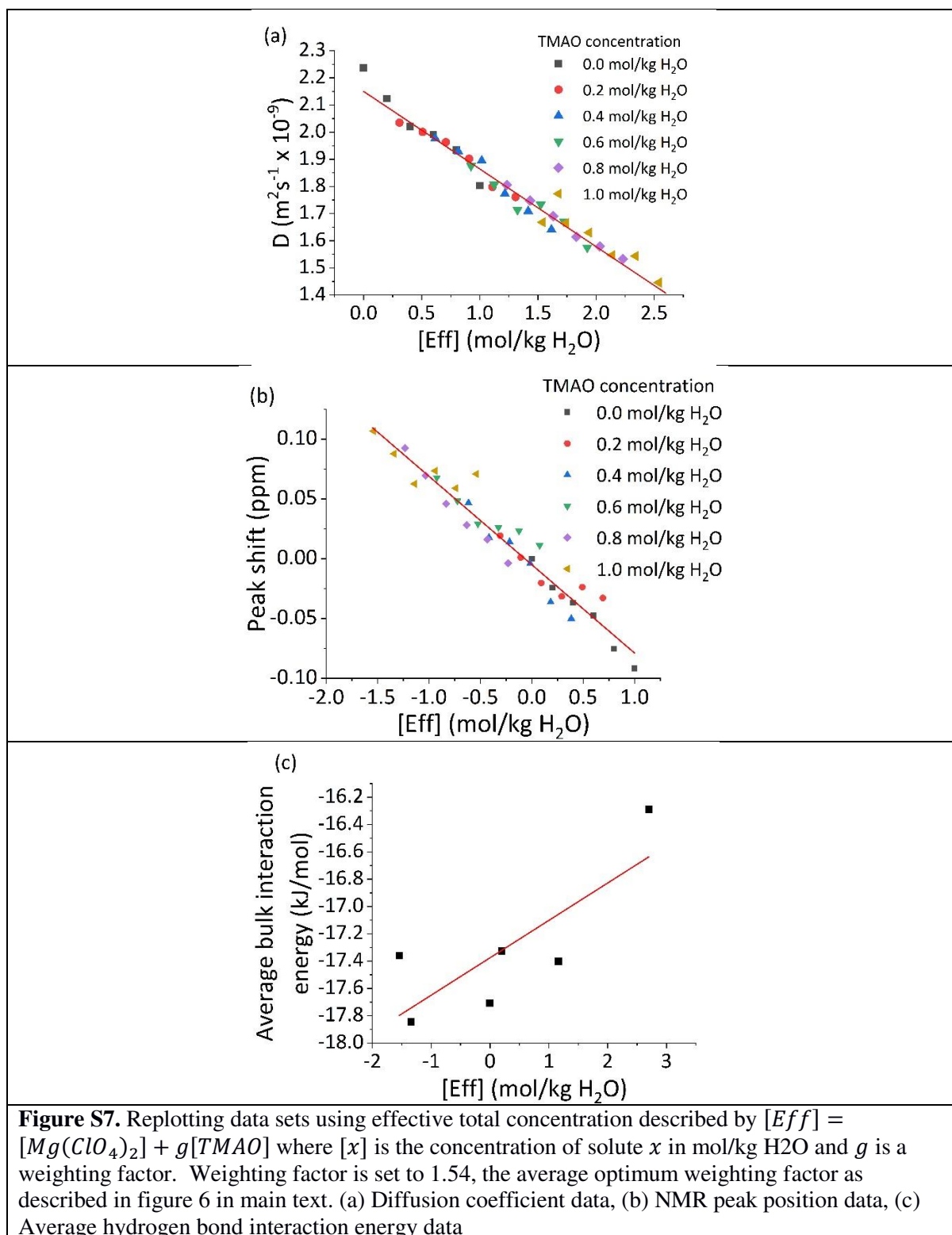
**Figure S3.** EPSR fits (red lines) to corrected diffraction data (black points) for 1.0 M TMAO (top left), 0.2 M  $\text{Mg}(\text{ClO}_4)_2$  (top right), 1.0 M TMAO + 0.2 M  $\text{Mg}(\text{ClO}_4)_2$  (bottom left), 1.0 M TMAO + 2.7 M  $\text{Mg}(\text{ClO}_4)_2$  (bottom right).

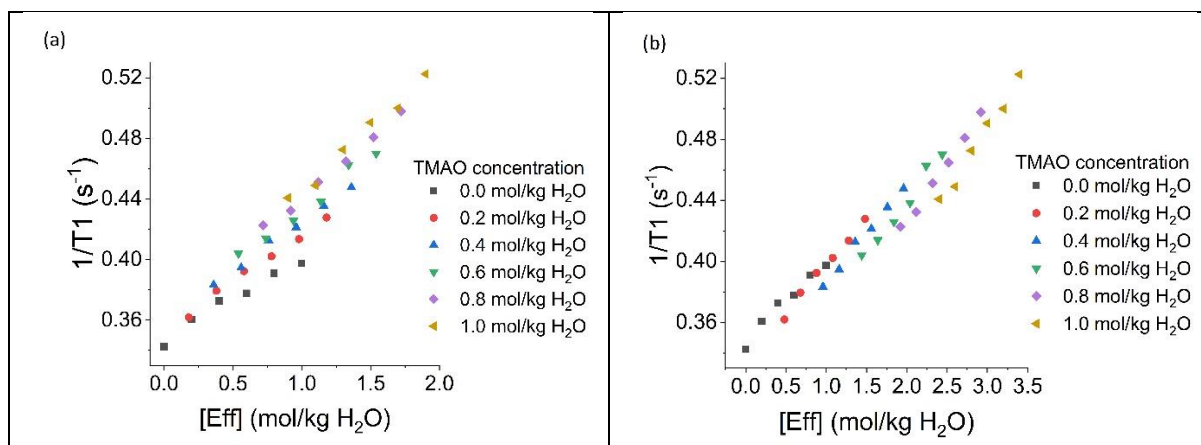




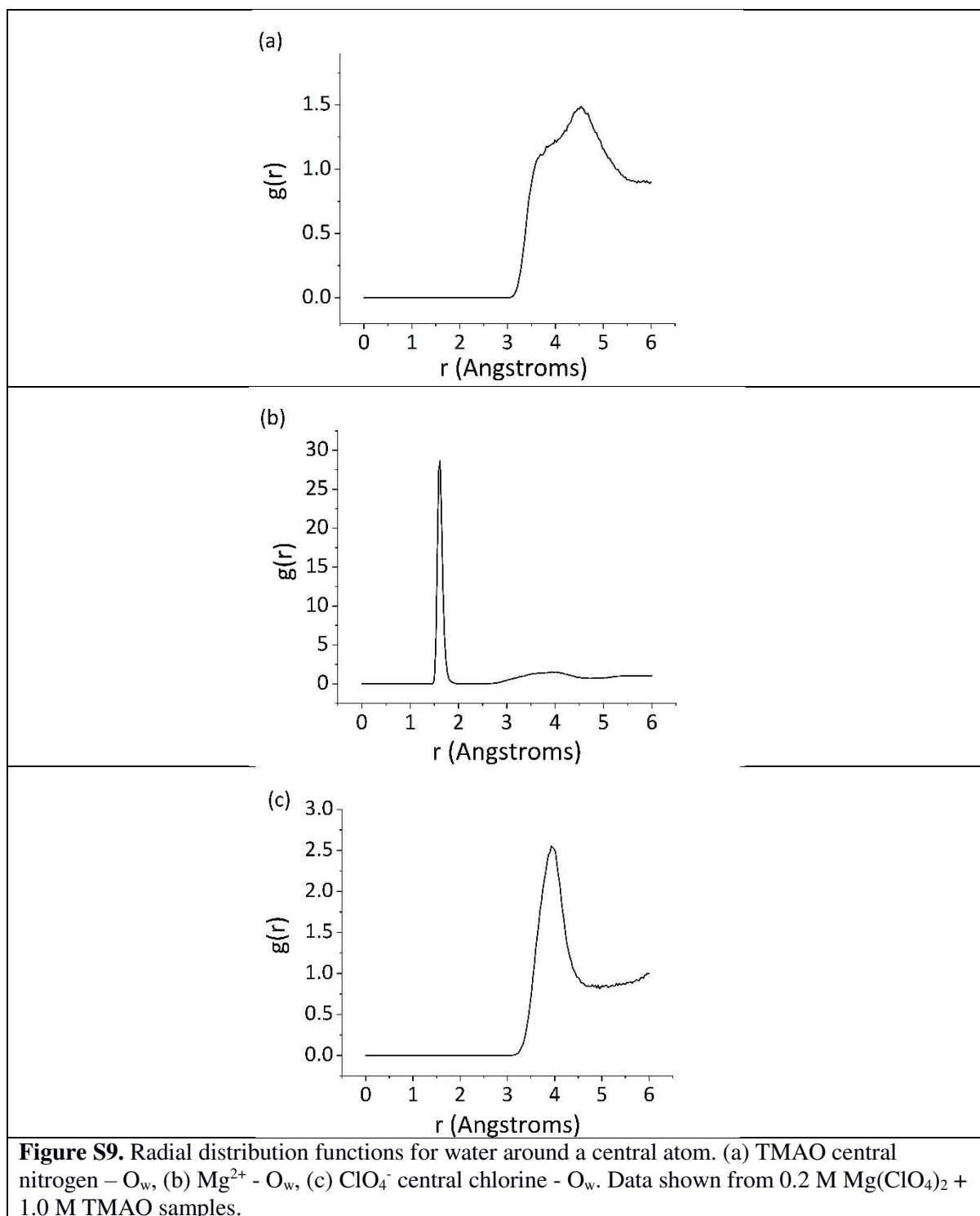
**Figure S5.** Abundance of specific hydrogen bonded conformations. (a) cyclic dimers, (b) bifurcated oxygens, (c) hydrogen bonded molecules with positive total interaction energy.







**Figure S8.** Replotting inverse  $T_1$  data using effective total concentration described by  $[Eff] = [Mg(ClO_4)_2] + g[TMAO]$  where  $[x]$  is the concentration of solute  $x$  in mol/kg H<sub>2</sub>O and  $g$  is a weighting factor. Weighting factor is set to the extreme limits used to determine the optimum weighting parameter: 0.9 (a) and 2.4 (b).



### Derivation S1. Determination of Excluded Volume

Here we make the very basic assumption that the excluded volume of a solute molecule is equivalent to the volume of a sphere whose radius corresponds to the distance from the solute molecule's central atom to the first peak of the central atom – water RDF. Table below shows the location of the first peak of the radial distribution functions for water around a central atom X (RDFs shown in figure S9) and the volume of the corresponding sphere.

Central atom X	X- $O_w$ RDF first peak location (Å)	Effective volume (Å <sup>3</sup> )
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Central TMAO nitrogen	4.52	387
Mg <sup>2+</sup>	1.61	18
Central ClO <sub>4</sub> <sup>-</sup> chlorine	3.94	256
<b>Table S4.</b> Location of the first peak in the X-O <sub>w</sub> radial distribution function where X is the central atom of a solute molecule/ion and the volume of a sphere described by this distance. Data taken using the 0.2 M Mg(ClO <sub>4</sub> ) <sub>2</sub> + 1.0 M TMAO sample to minimise effects of hydration shell overlap.		

A TMAO molecule therefore has an effective volume of 387 Å<sup>3</sup>, and a completely dissolved Mg(ClO<sub>4</sub>)<sub>2</sub> molecule therefore has an effective volume of 530 Å<sup>3</sup>. If the weighting parameter  $g$  were solely due to excluded volume effects it would therefore be equal to the ratio of the TMAO effective volume to the Mg(ClO<sub>4</sub>)<sub>2</sub> effective volume, which is 0.73.