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

ESI for: Solvation Structure of Lanthanide(III) Bistriflimide Salts in Acetonitrile Solution: a Molecular Dynamics Simulation and EXAFS Investigation

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Spatial distribution function calculation details

Ln^{3+} coordination geometry in pure acetonitrile

To identify the geometry of the coordination polyhedron for the 10-fold structures of La^{3+} and Dy^{3+} ions in pure acetonitrile we have resorted to build an internal reference system centered on the cation and to calculate a spatial distribution function (SDF) of solvent molecules in this reference system. The internal reference system was based on the instantaneous positions of the 8th and 9th solvent molecule in order of distance from the central ion. A reliable SDF can be obtained only if the mutual arrangement of these molecules is well defined, i.e. if the ligands play well defined roles inside the first shell polyhedron.

To verify if this is the case, we have calculated a combined distribution function (CDF) combining the distribution of the distance between the Ln^{3+} ion and the nitrogen atom of the 8^{th} acetonitrile molecule nearest to the ion (r_{Ln-N_8}), and the distribution function of the $\psi_{N_8-Ln-N_9}$ angle calculated between the 8^{th} and 9^{th} acetonitrile molecule. The CDFs are shown in the left panels of Figures S1 and S2 for the La^{3+} and Dy^{3+} ions, respectively, and in both cases two well defined peaks are found centered at angle values of about 60° and 120°. Note that in this and in the following analyses we have used only those simulation frames in which the ion first solvation shell is formed by 10 acetonitrile molecules.

We have then calculated another CDF using the same angle ($\psi_{N_8-Ln-N_9}$) and the distance between the 8^{th} and 9^{th} acetonitrile molecule ($r_{N_8-N_9}$) (right panels of Figures S1 and S2 for the La^{3+} and Dy^{3+} ions, respectively). Also in this case two separated peaks are found showing that when $r_{N_8-N_9}$ is shorter than 4.0 Å the $\psi_{N_8-Ln-N_9}$ angle is below 90°, while for $r_{N_8-N_9}$ distances longer than 4.5 Å, angles larger than 100° are formed.

The 8th and 9th acetonitrile molecules have thus well defined positions respect to each other inside the coordination polyhedron so that they can be used to build an internal reference system based on their instantaneous positions. In particular, two unit vectors have been defined, the former along the direction between the Ln^{3+} ion and the nitrogen atom of the 8th acetonitrile molecule, the latter along the same direction involving the 9th molecule. We have selected for this analysis only those MD configurations in which the ions form a ten-fold complex and where the $r_{N_8-N_9}$ distance is larger than 4.50 Å, to include only the frames where the 8th solvent molecule is on the opposite side of the 9th acetonitrile molecule with respect to the central ion. Note that the percentage of simulation frames simultaneously satisfying these two conditions is 36% and 41% for La^{3+} and Dy^{3+}, respectively.

Ln^{3+} coordination geometry in acetonitrile solution of $Ln(Tf_2N)_3$ salts

To identify the geometry of the 10-fold complexes formed by the La^{3+} and Dy^{3+} ions in acetonitrile solution of $Ln(Tf_2N)_3$ salts, we have applied the same procedure used for Ln^{3+} ions in pure acetonitrile based on the calculation of a SDF in an internal reference system centered on the Ln^{3+} cation. We have thus calculated from the MD simulation of $Ln(Tf_2N)_3$ acetonitrile solutions the CDF combining the distribution of Ln-X_8 distances r_{Ln-X_8} (where X_8 belongs to the 8th species nearest to the ion that can be either the O atom of the Tf_2N^- anions or the N atom of the acetonitrile molecules) and the distribution functions of the X_8-Ln-X_9 angles between the 8th and 9th species ($\psi_{X_8-Ln-X_9}$). Note that in all of the following analyses only the simulation frames corresponding to 10-fold clusters have been considered.

The obtained CDFs are shown in the left panels of Figure S3 and S4 for the La^{3+} and Dy^{3+} ions, respectively. In both cases two well defined peaks at about 60° and 120° are found but in the La^{3+} complex an additional contribution at 180° can be also observed. We have then calculated the CDFs using the same angle and the distance between the 8th and 9th species from the ion $r_{X_8-X_9}$ (see right panels of Figures S3 and S4 for La^{3+} and Dy^{3+}, respectively). Two separated peaks are found in both La^{3+} and Dy^{3+} solutions, the former at low distances and angles ($r_{X_8-X_9}$ <4.0 Å, $\psi_{X_8-Ln-X_9}$ <100°), the latter at large distances and angles ($r_{X_8-X_9}$ >4.0 Å, $\psi_{X_8-Ln-X_9}$ >100°). However, in the La^{3+} case additional contributions at about 180° are also present when the 8th and 9th species from the La^{3+} ion are far from each other ($r_{X_8-X_9}$ >5.25 Å). In order to calculate a reliable SDF and to select simulations frames in which the mutual arrangement of the 8th and 9th species from the ion is well defined, we have considered for Dy^{3+} only those 10-fold configurations where the $r_{X_8-X_9}$ was larger than 4.0 Å. For La^{3+} we have added an additional conditions by using also an upper cutoff on the $r_{X_8-X_9}$ distances to avoid the spurious contributions giving rise to the X_8-Ln-X_9 angles at 180° (4.0 Å<$r_{X_8-X_9}$ <5.25 Å). It is important to stress that 39% of the total simulation frames satisfy the adopted conditions for both La^{3+} and Dy^{3+}. We have thus built an internal reference system based on the instantaneous positions of the 8th and 9th species from the ion by defining two unit vectors: the former along the direction between the Ln^{3+} ion and the nearest atom of the 8th species in order of distance from the ion, the latter along the same direction involving the 9th species. Note that in this analysis the Tf_2N^- anions and the acetonitrile molecules are indifferently treated so that the atoms considered to define the unit vectors can be either the Tf_2N^- O atom (when the 8th or 9th species is the anion) or the acetonitrile N atom (when the 8th or 9th species is the acetonitrile molecule).

La^{3+}				
	La-N		La-O	
system	c_N^{inner}	c_N^{outer}	c_O^{inner}	c_O^{outer}
pure CH_3CN	0.00-3.30	3.30-4.30		
Tf_2N^-+CH_3CN	0.00-3.30		0.00-4.16	
Dy^{3+}				
	Dy-N		Dy-O	
system	c_N^{inner}	c_N^{outer}	c_O^{inner}	c_O^{outer}
pure CH_3CN	0.00-3.00	3.00-4.20		
Tf_2N^-+CH_3CN	0.00-3.10	3.10-4.20	0.00-3.00	3.00-4.16

Table S1. Cutoff values used to calculate the coordination numbers of the inner (c^{inner}) and outer (c^{outer}) solvation shells of the La^{3+} and Dy^{3+} ions from the MD simulations of $La(Tf_2N)_3$ and $Dy(Tf_2N)_3$ in acetonitrile or of the La^{3+} and Dy^{3+} ions in pure acetonitrile. The cutoff values have been chosen based on the Ln-N and Ln-O $g(r)$ results shown in Figure 2 and 6 of the manuscript. Note that N is the nitrogen atom of the acetonitrile molecules and O is the oxygen atom of the Tf_2N^- anions.

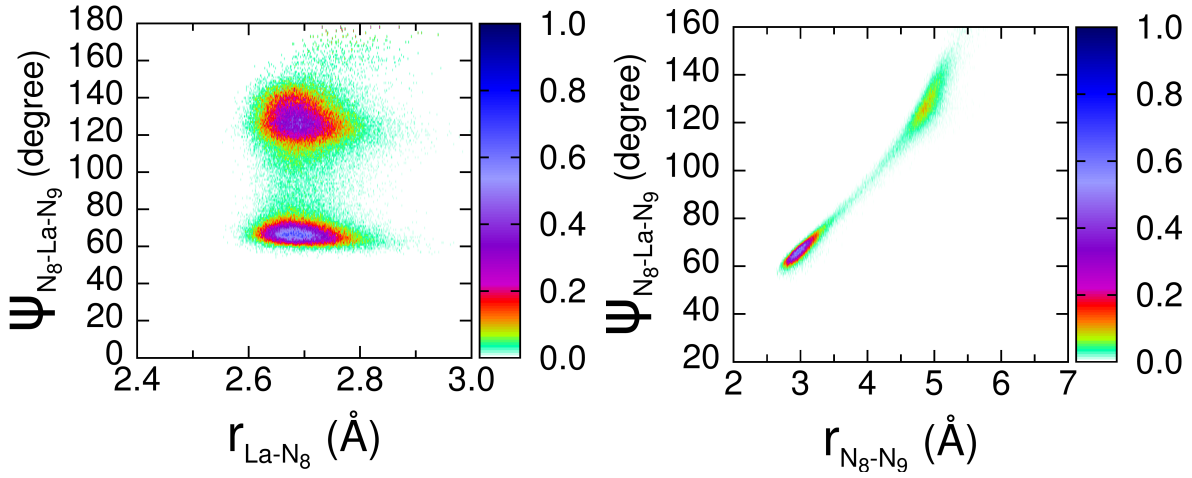

Figure S1. Combined distribution functions (CDFs) calculated from the MD simulation of La^{3+} ion in pure acetonitrile. Left panel: CDF obtained combining the distance between the La^{3+} ion and the nitrogen atom of the 8th acetonitrile molecule nearest to the ion (r_{La-N_8}) and the distribution function of the N_8-La-N_9 angle ($\psi_{N_8-La-N_9}$) calculated between the 8th and 9th acetonitrile molecules. Right panel: CDF obtained combining the distance between the nitrogen atoms of the 8th and 9th acetonitrile molecule in order of distance from the ion ($r_{N_8-N_9}$) and the distribution function of the $\psi_{N_8-La-N_9}$ angle.

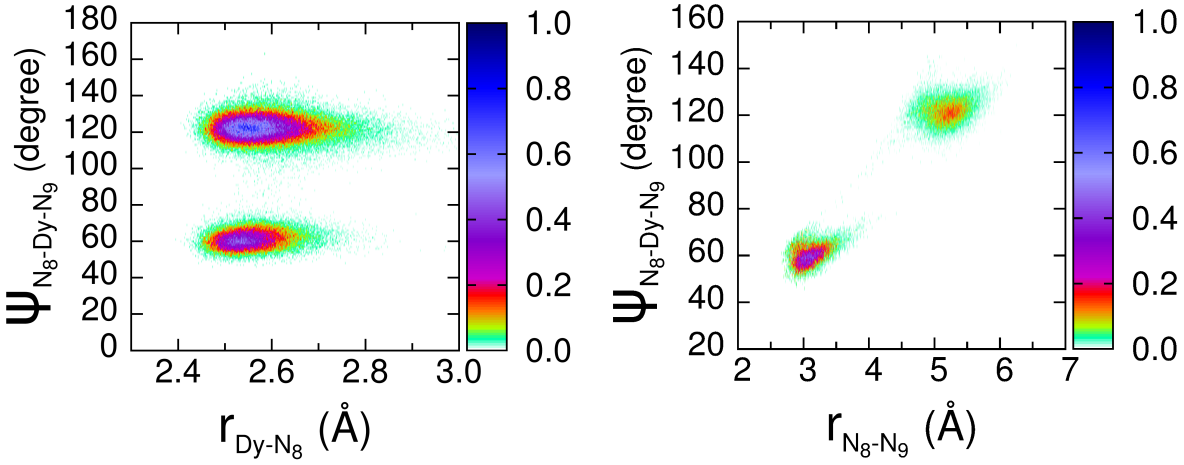

Figure S2. Combined distribution functions (CDFs) calculated from the MD simulation of Dy^{3+} ion in pure acetonitrile. Left panel: CDF obtained combining the distance between the Dy^{3+} ion and the nitrogen atom of the 8th acetonitrile molecule nearest to the ion (r_{Dy-N_8}) and the distribution function of the N_8-Dy-N_9 angle ($\psi_{N_8-Dy-N_9}$) calculated between the 8th and 9th acetonitrile molecules. Right panel: CDF obtained combining the distance between the nitrogen atoms of the 8th and 9th acetonitrile molecule in order of distance from the ion ($r_{N_8-N_9}$) and the distribution function of the $\psi_{N_8-Dy-N_9}$ angle.

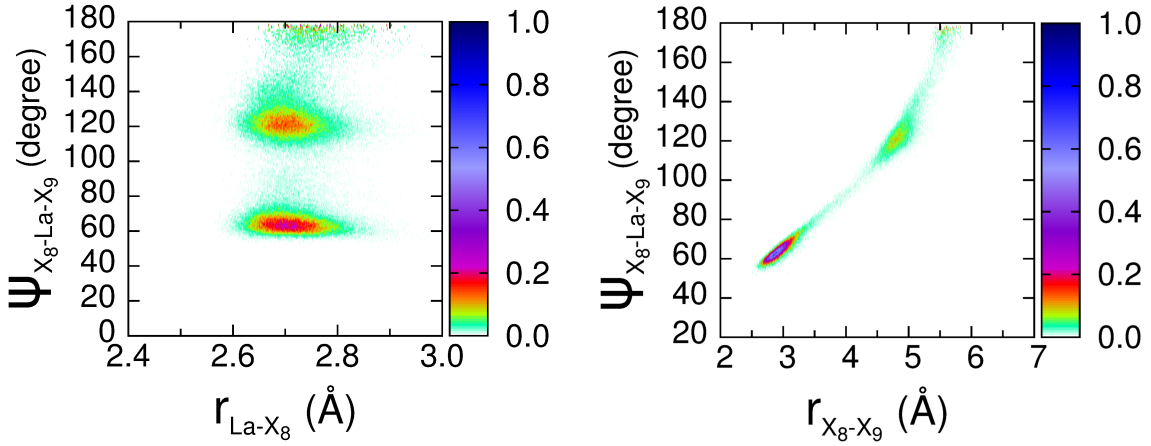

Figure S3. Combined distribution functions (CDFs) calculated from the MD simulation of $La(Tf_2N)_3$ acetonitrile solutions. Left panel: CDF obtained combining the distance between the La^{3+} ion and the distribution of La-X_8 distances r_{Ln-X_8} (where X_8 belongs to the 8th species nearest to the ion being either the O atom of the Tf_2N^- anions or the N atom of the acetonitrile molecules) and the distribution functions of the X_8-La-X_9 angles between the 8th and 9th species in order of distance from the ion ($\psi_{X_8-La-X_9}$). Right panel: CDF obtained combining the distance between the 8th and 9th species from the ion $r_{X_8-X_9}$ and the $\psi_{X_8-La-X_9}$ angle.

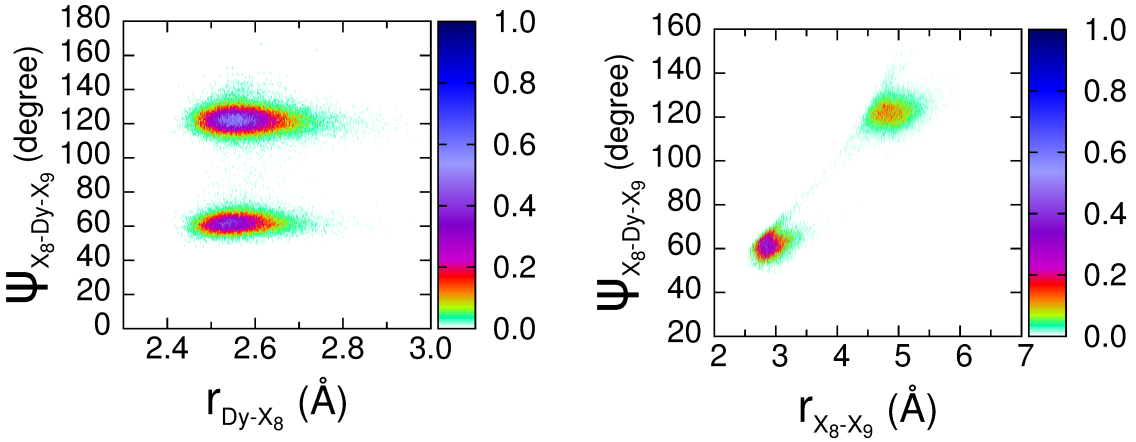

Figure S4. Combined distribution functions (CDFs) calculated from the MD simulation of $Dy(Tf_2N)_3$ acetonitrile solutions. Left panel: CDF obtained combining the distance between the Dy^{3+} ion and the distribution of La-X_8 distances r_{Dy-X_8} (where X_8 belongs to the 8th species nearest to the ion being either the O atom of the Tf_2N^- anions or the N atom of the acetonitrile molecules) and the distribution functions of the X_8-Dy-X_9 angles between the 8th and 9th species in order of distance from the ion ($\psi_{X_8-Dy-X_9}$). Right panel: CDF obtained combining the distance between the 8th and 9th species from the ion $r_{X_8-X_9}$ and the $\psi_{X_8-Dy-X_9}$ angle.