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	Water Diluted	**Water Concentrated**	**Methanol Concentrated**
NBu_4^+	-230	-201	-150
Cs^+	-391	-373	-225
H_3O^+	***	-346	***
$H_5O_2^+$	***	-336	***
UO_2^{2+}	-365	-330	-183
Eu^{3+}	-375	-340	-150
Eu^{3+} (H_2O SPCE)	***	-338	***

TABLE S1: Average interaction energy of one PW^{3-} with the solvent (Averages taken over the last 2 ns of dynamics and over all PW^{3-} anions).

	Water Diluted	**Water Concentrated**	**Methanol Concentrated**
NBu_4^+	4802 (171)	28920 (152)	26263 (138)
Cs^+	3678 (131)	24017 (126)	24782 (130)
H_3O^+	***	26094 (137)	***
$H_5O_2^+$	***	26275 (138)	***
UO_2^{2+}	3924 (140)	26454 (139)	25405 (133)
Eu^{3+}	3798 (136)	26794 (141)	27090 (143)
Eu^{3+} (H_2O SPCE)	***	26736 (140)	***

TABLE S2: PW^{3-} - PW^{3-} interaction energies (kcal/mol). Averages over the last 2 ns of dynamics. In brackets average per PW^{3-}…PW^{3-} pair.

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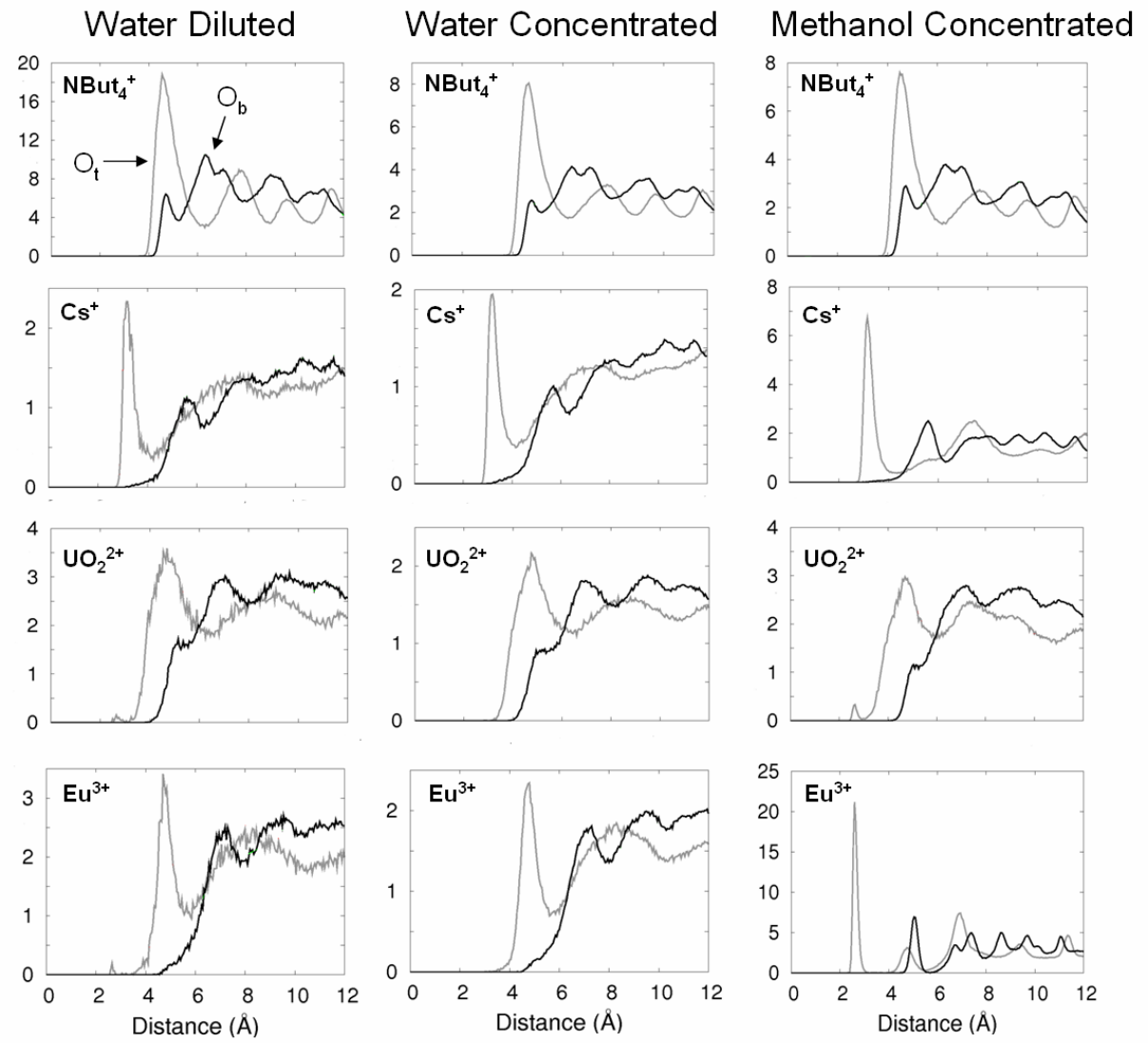
	Water Diluted	**Water Concentrated**	**Methanol Concentrated**
NBu_4^+	-1592 (-66)	-3294 (-54)	-3019 (-50)
Cs^+	-1157 (-48)	-2873 (-48)	-2789 (-46)
$H_5O_2^+$	***	-2897 (-48)	***
H_3O^+	***	-2879 (-48)	***
UO_2^{2+}	-1244 (-103)	-2928 (-97)	-2898 (-97)
Eu^{3+}	-1202 (-150)	-2956 (-147)	-3112 (-155)
Eu^{3+} (H_2O SPCE)	***	-2969 (-148)	***

TABLE S3: Average interaction energy between one PW^{3-} and all M^{n+} counterions (kcal/mol). Averages over the last 2 ns of dynamics and over all PW^{3-}. In brackets: average interaction energy per PW^{3-} - M^{n+} pair.



Aqueous solutions of $PW_{12}O_{40}^{3-}$ with proton hydrates

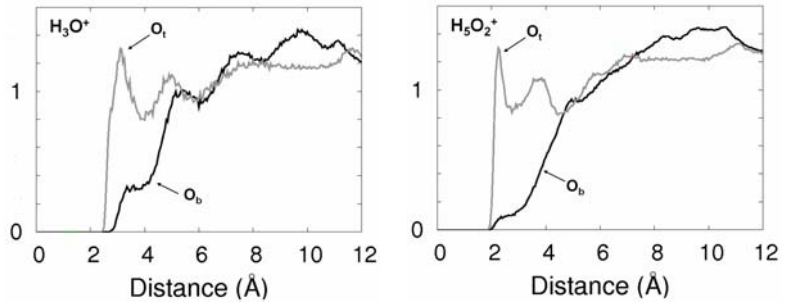


FIGURE S1: O_t …M^{n+} (grey) and O_b …M^{n+} (black) RDFs in diluted and concentrated aqueous solutions and in methanol.

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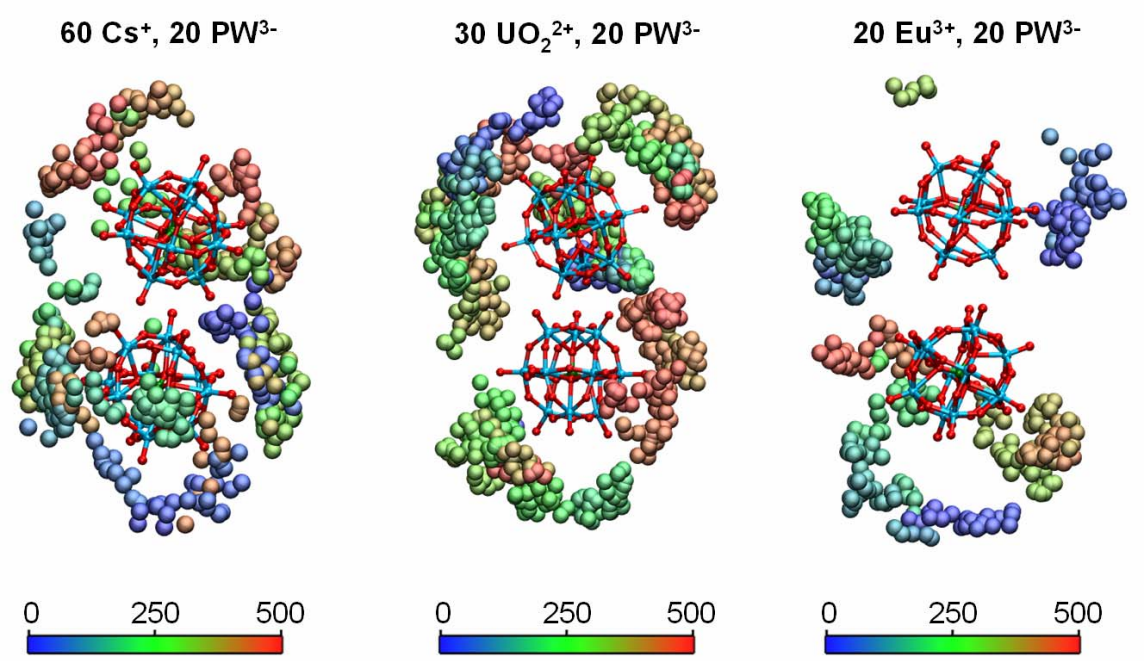


FIGURE S2: $(PW^{3-})_2$ dimers with Cs^+ , UO_2^{2+} or Eu^{3+} counterions within 3 Å: cumulated views over 1 ns. Different regions of same color correspond to different cations at a given time.

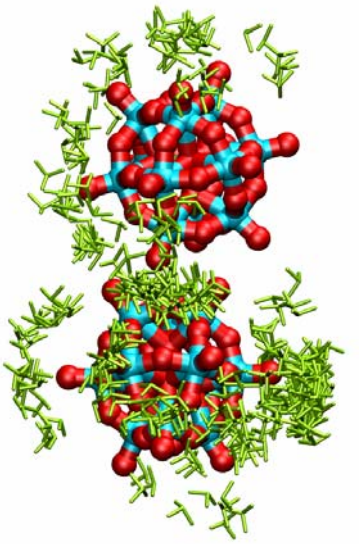
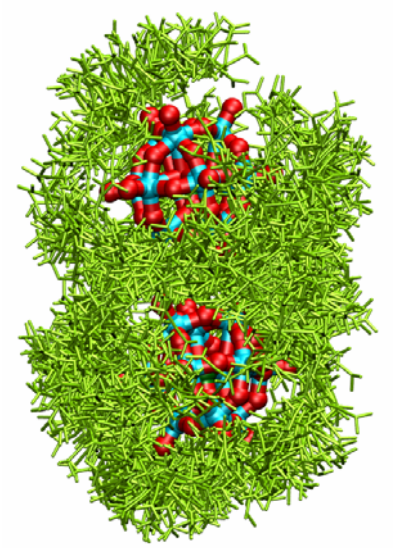
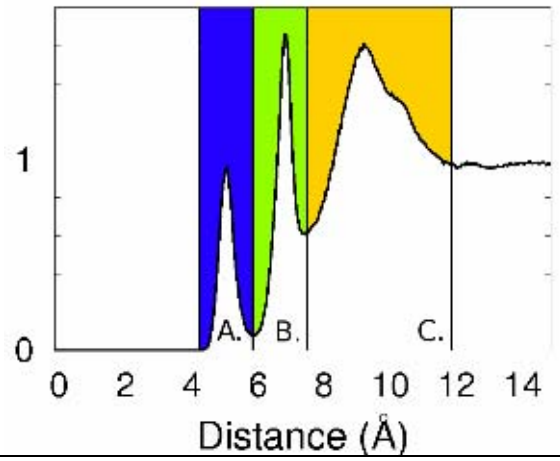
H_3O^+	$H_5O_2^+$
	

FIGURE S3: $(PW^{3-})_2$ dimer with H_3O^+ vs $H_5O_2^+$ counterions in water: cumulated views of first shell M^+ counterions.

	A	B	C
Eu^{3+}	2.5	11.4	90.4
UO_2^{2+}	2.5	11.0	87.0
Cs^{+}	2.9	11.5	84.5
NBu_4^{+}	1.2	7.2	60.0



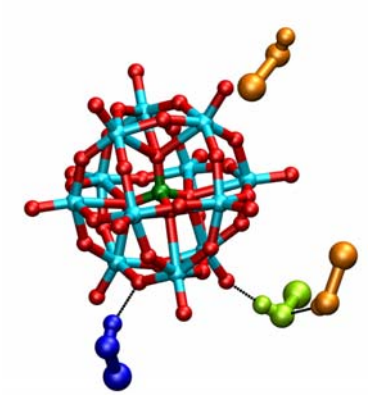


Figure S4: PW^{3-} with NBu_4^{+}, Eu^{3+}, UO_2^{2+} and Cs^{+} counterions in methanol. *Right:* P...H_{MeOH} RDFs, and snapshots of typical solvation patterns. *Table left*: Integration of the *A – C* peaks of the RDFs for the different salts.

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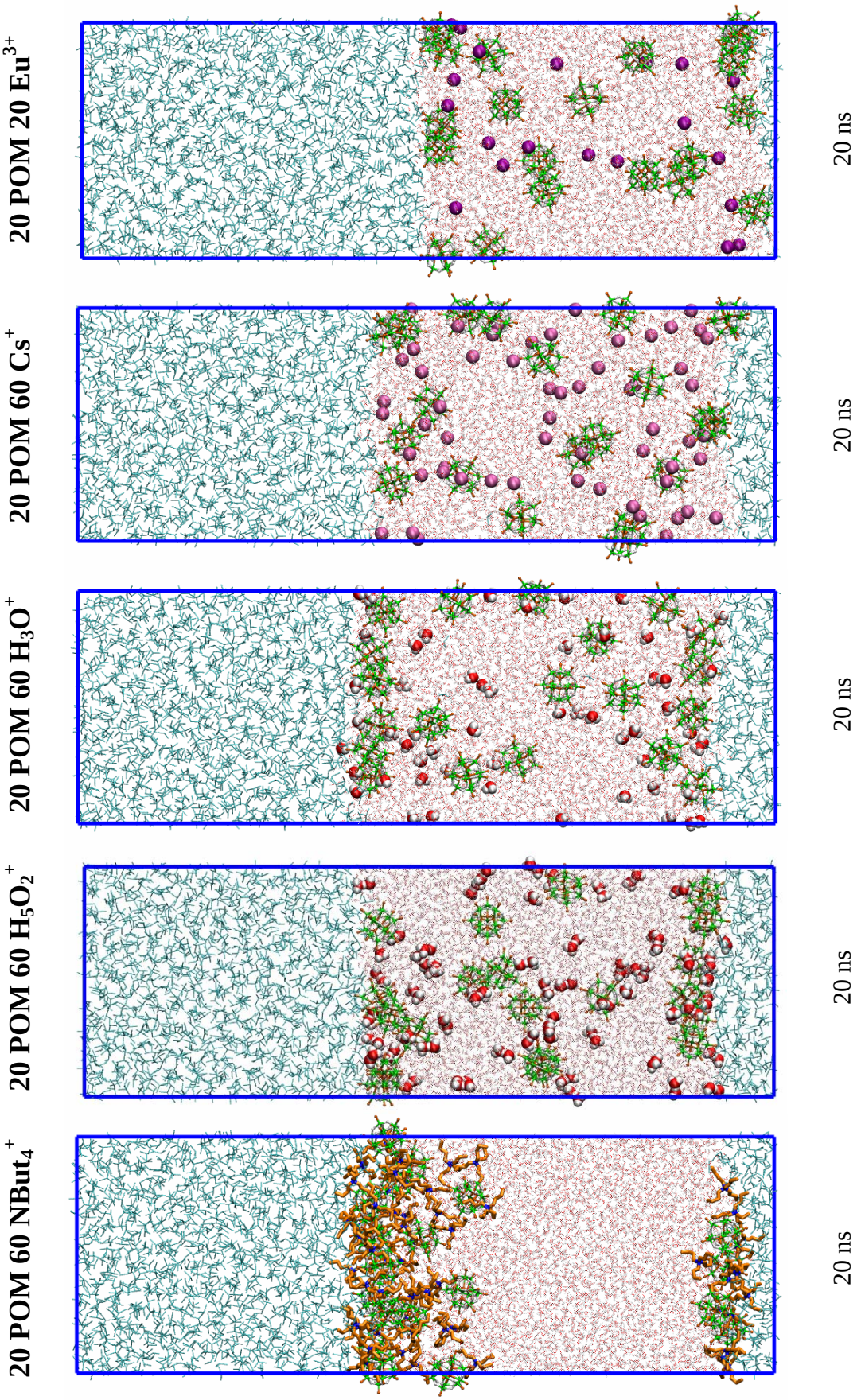

Figure S5: 20 PW^{3-} with either Eu^{3+}, Cs^{+}, H_3O^{+}, $H_5O_2^{+}$ or NBu_4^{+} as counterions at the chloroform / water interface.

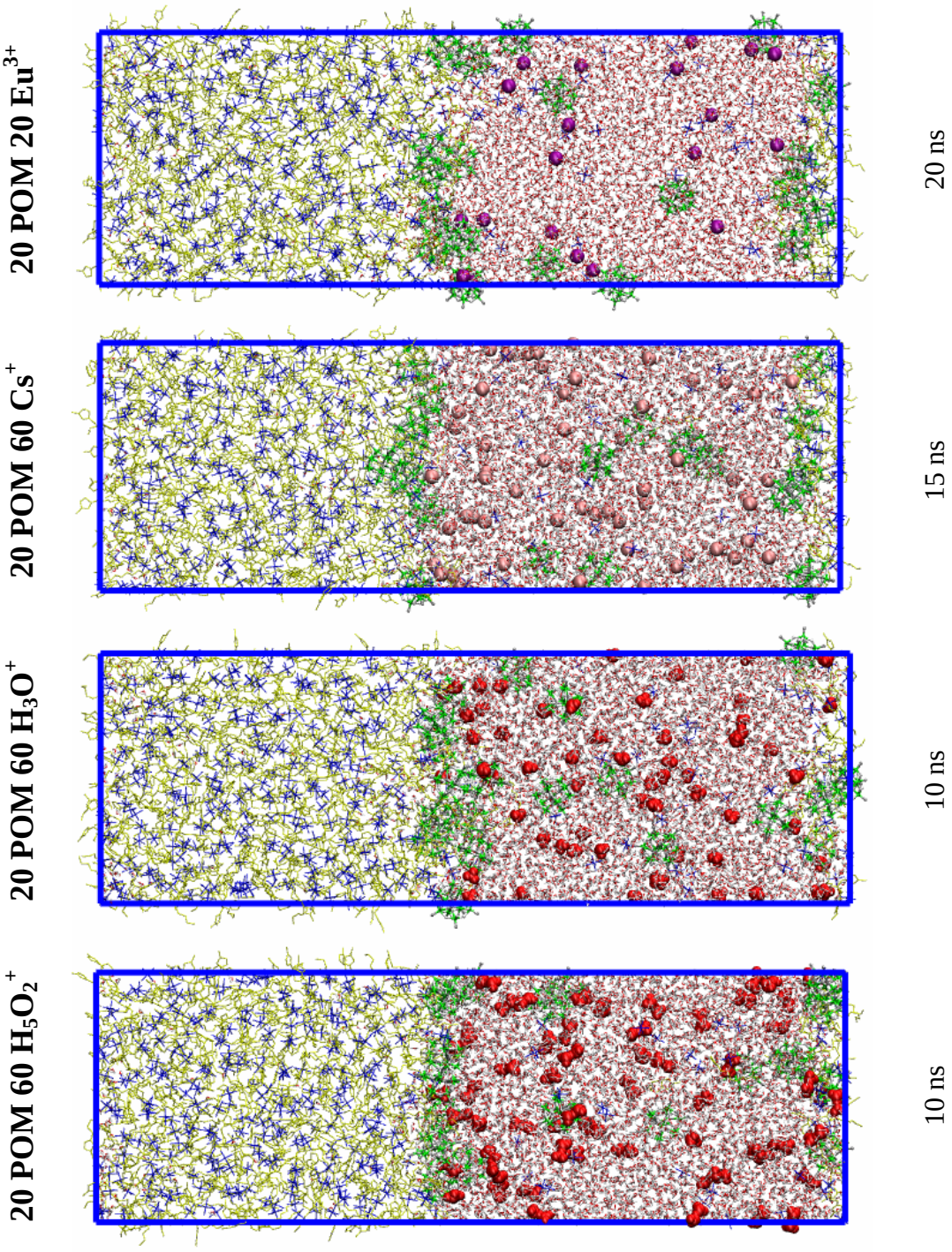

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Figure S6: 20 PW^{3-} with either Eu^{3+}, Cs^{+}, H_3O^{+} or $H_5O_2^{+}$ as counterions at the aqueous interface with the [OMI][PF_6] room temperature ionic liquid (based on the octyl-methyl imidazolium OMI^{+} cation and the PF_6^{-} anion).