**Supplementary material**

Table S1 : Number of $Cs^+$ cations "coordinated" (within 3.5 Å) to each $NBA^{4-}$ with different lifetimes (in ns) in solutions **A** (methanol : water) and **D** (pure water).

Table S2 : Average number CN of $M^+$ cations coordinated to $NBA^{4-}$ during the last 3 ns of dynamics (averaged over 3 ns for all $M^+$ ions).

Table S3 : Number of the $M^+$ ions ($Cs^+$, $Na^+$) within 3.5 Å, and of $Me_4N^+$ ions within 5 Å from $NBA^{4-}$ in solutions **A – D**.

Figure S1 : Chemical shifts δ from $^1$H-NMR titrations for NBA ($2.0 \times 10^{-3}$ mole.$L^{-1}$) in the presence of 2 equivalents of $K^+$ (a) and 2 equivalents of $Na^+$ (b) as a function of pH at 25.0 °C ($CD_3OD$:$D_2O$-80:20).

Figure S2 : Potentiometric titration curves of NBA ($1.5 \times 10^{-3}$ mole.$L^{-1}$), without and with various concentrations of $K^+$ (a) and $Na^+$ (b) cations.at 25.0 °C

Figure S3 : UV-Visible spectra variations at pH 9.9 for various $Cs^+$ to NBA (0 to 8) ratios.

Figure S4 : System **C** : $\phi_1$ (in red) and $\phi_2$ (in blue) angles (defined in Scheme 1) as a function of time (in ns) for each $NBA^{4-}$ ligand.

Figure S5 : **A** – **D** solutions: RDFs between the center- of -mass of $NBA^{4-}$ and the $M^+$ cations ($Cs^+$, $Na^+$). Averages over the 5 *EE* forms (in black) and 5 *ZZ* forms (in red) and corresponding integration numbers (within 10 Å).

Figure S6a : System **C** : Distances between the center of mass of each $NBA^{4-}$ (*ZZ*) molecule and $Cs^+$ (left) or $Na^+$ (right) cations as a function of time (last 2 ns of dynamics).

Figure S6b : System **C**: Distances between the center of mass of each $NBA^{4-}$ (*EE*) molecule and $Cs^+$ (left) or $Na^+$ (right) cations as a function of time (last 2 ns of dynamics).

Figure S7 : Initial (*left*), mixed (*middle*) and final (*right*) views of system **A**.

Figure S8 : $NBA^{4-}$ in a methanol:water 80:20 solution (**A** – **C)** and in pure water (**D**). Final views of the solvent boxes.

Figure S9: **A** – **D** solutions: RDFs $X^{+\cdots}O_{NBA}$ (first column), $X^{+\cdots}O_{wat}$ (red, second column), $X^{+\cdots}O_{MeOH}$ (black, second column), $N_{Me4N+}{}^{\cdots}O_{wat}$ (red, third column), $N_{Me4N+}{}^{\cdots}O_{MeOH}$ (black, third column).

Figure S10 : **F** – **K** aqueous solutions: NBA...NBA RDFs (between the center of mass of NBA's) in **F** (*black*), **H** (*red*), **I** (*green*), **J** (*blue*) and **K** (*pink*). Integration numbers within 15 Å.

Figure S11 : NBA systems in a methanol:water 80:20 solution (**A**,**E**) and pure water (**D**,**G**). Final views of the solvent boxes.

Figure S12 **:** Chemical shifts of the $H_3$ proton *vs* the NBA concentration in aqueous medium (pH = 8.3) at 25.0°C.

Figure S13 : Chemical shifts δ from $^{1}$H-NMR titrations for NBA ($2.0 \times 10^{-3}$ mole.$L^{-1}$) as a function of pH at 25.0 °C in aqueous solution

| | Lifetime | < 0.1 ns | 0.1 – 0.5 ns | 0.5 -1 ns | >1 ns | <> |
|---|---|---|---|---|---|---|
| | NBA | | | | | |
| | | **Solution A (methanol : water 80:20)** | | | | |
| 1 | *EE* | 0 | 1 | 0 | 1 | 1.8 |
| 2 | *EE* | 0 | 1 | 0 | 1 | 1.7 |
| 3 | *EE* | 1 | 1 | 0 | 2 | 2.1 |
| 4 | *EE* | 0 | 0 | 0 | 1 | 0.6 |
| 5 | *EE* | 0 | 0 | 0 | 1 | 1.0 |
| | <*EE*> | 0.2 | 0.6 | 0.0 | 1.2 | 1.4 |
| 6 | *ZZ* | 0 | 0 | 0 | 1 | 1.0 |
| 7 | *ZZ* | 0 | 0 | 0 | 1 | 1.0 |
| 8 | *ZZ* | 0 | 0 | 0 | 1 | 1.0 |
| 9 | *ZZ* | 1 | 1 | 1 | 1 | 2.2 |
| 10 | *ZZ* | 0 | 1 | 1 | 2 | 2.7 |
| | <*ZZ*> | 0.2 | 0.4 | 0.4 | 1.2 | 1.6 |
| | | **Solution D (pure water)** | | | | |
| 1 | *EE* | 4 | 1 | 1 | 0 | 1.2 |
| 2 | *EE* | 2 | 1 | 1 | 0 | 0.7 |
| 3 | *EE* | 3 | 1 | 1 | 0 | 0.6 |
| 4 | *EE* | 4 | 1 | 0 | 1 | 0.9 |
| 5 | *EE* | 5 | 1 | 1 | 0 | 1.1 |
| | <*EE*> | 3.8 | 1.0 | 0.8 | 0.2 | 0.9 |
| 6 | *ZZ* | 3 | 5 | 0 | 0 | 0.9 |
| 7 | *ZZ* | 2 | 4 | 0 | 0 | 1.4 |
| 8 | *ZZ* | 3 | 1 | 1 | 0 | 1.1 |
| 9 | *ZZ* | 4 | 2 | 1 | 0 | 1.1 |
| 10 | *ZZ* | 3 | 2 | 0 | 0 | 0.8 |
| | <*ZZ*> | 3.0 | 2.8 | 0.4 | 0.0 | 1.1 |

Table S1 : Number of $Cs^+$ cations "coordinated" (within 3.5 Å) to each $NBA^{4-}$ with different lifetimes (in ns) in solutions **A** (methanol : water) and **D** (pure water).

| NBA | | **A** | | **B** | | **C** | | | **D** | | **I** | | **J** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $Cs^+$ | $Me_4N^+$ | $Na^+$ | $Me_4N^+$ | $Cs^+$ | $Na^+$ | $Me_4N^+$ | $Cs^+$ | $Me_4N^+$ | $Cs^+$ | $Cs^{+\,a)}$ | $Cs^+$ | $Me_4N^+$ |
| 1 | *EE* | 1.8 | 0.7 | 3.0 | 0.9 | 0.5 | 1.0 | 3.1 | 1.2 | 1.2 | 0.2 | 1.6 | 0.2 | 2.3 |
| 2 | *EE* | 1.7 | 1.1 | 1.0 | 1.8 | 1.9 | 1.5 | 0.5 | 0.7 | 0.9 | 0.2 | 1.8 | 1.3 | 2.5 |
| 3 | *EE* | 2.1 | 0.8 | 0.0 | 3.0 | 2.2 | 1.8 | 0.8 | 0.6 | 1.7 | 0.2 | 1.2 | 1.6 | 1.7 |
| 4 | *EE* | 0.6 | 2.2 | 0.0 | 2.2 | 0.0 | 2.0 | 1.4 | 0.9 | 0.5 | 0.2 | 1.7 | 1.0 | 1.9 |
| 5 | *EE* | 1.0 | 1.7 | 2.0 | 2.2 | 2.8 | 0.0 | 0.6 | 1.1 | 1.1 | 0.3 | 2.0 | 1.5 | 2.1 |
| <*EE*> | | 1.4 | 1.3 | 1.2 | 2.0 | 1.5 | 1.3 | 1.3 | 0.9 | 1.1 | 0.2 | 1.7 | 1.1 | 2.1 |
| 6 | *ZZ* | 1.0 | 2.3 | 2.0 | 0.8 | 1.2 | 1.9 | 1.9 | 0.9 | 0.9 | 0.3 | 2.0 | 1.6 | 2.1 |
| 7 | *ZZ* | 1.0 | 1.8 | 1.0 | 1.8 | 1.0 | 0.0 | 1.4 | 1.4 | 0.6 | 0.2 | 1.9 | 1.8 | 0.7 |
| 8 | *ZZ* | 1.0 | 1.6 | 2.7 | 0.3 | 1.0 | 1.0 | 1.3 | 1.1 | 0.7 | 0.2 | 1.8 | 2.1 | 0.4 |
| 9 | *ZZ* | 2.2 | 0.6 | 2.0 | 0.9 | 1.9 | 1.0 | 1.5 | 1.1 | 0.7 | 0.2 | 1.4 | 1.4 | 0.7 |
| 10 | *ZZ* | 2.7 | 0.4 | 1.4 | 2.0 | 2.6 | 1.2 | 0.2 | 0.8 | 1.4 | 0.2 | 1.9 | 1.3 | 0.5 |
| <*ZZ*> | | 1.6 | 1.3 | 1.8 | 1.2 | 1.6 | 1.0 | 1.3 | 1.1 | 0.9 | 0.2 | 1.8 | 1.6 | 0.9 |

Table S2 : Average number CN of $M^+$ cations coordinated (within 3.5 Å) to $NBA^{4-}$ (within 3.5 Å) during the last 3 ns of dynamics (averaged over 3 ns for all $M^+$ ions).

| | **A** | **B** | **C** | | **D** |
|---|---|---|---|---|---|
| $M^+$ | $Cs^+$ | $Na^+$ | $Cs^+$ | $Na^+$ | $Cs^+$ |
| $M^{+\cdots}O_{NBA}$ | 2.1 | 2.4 | 1.6 | 1.6 | 1.1 |
| $M^{+\cdots}O_{methanol}$ | 2.7 | 2.4 | 3.0 | 2.8 | - |
| $M^{+\cdots}O_{wat}$ | 2.2 | 1.9 | 2.1 | 1.7 | 6.0 |
| $X^{+\cdots}O_{solvent}$ | 4.9 | 4.3 | 5.1 | 4.5 | 6.0 |
| $N_{NMe4+}{}^{\cdots}O_{methanol}$ | 6.3 | 6.2 | 6.2 | | - |
| $N_{NMe4+}{}^{\cdots}O_{wat}$ | 4.3 | 4.2 | 4.3 | | 14.0 |
| $N_{NMe4+}{}^{\cdots}O_{solvent}$ | 10.6 | 10.4 | 10.5 | | 14.0 |

Table S3 : Number of the $M^+$ ions ($Cs^+$, $Na^+$) within 3.5 Å, and of $Me_4N^+$ ions within 5 Å from $NBA^{4-}$ in solutions **A – D**.

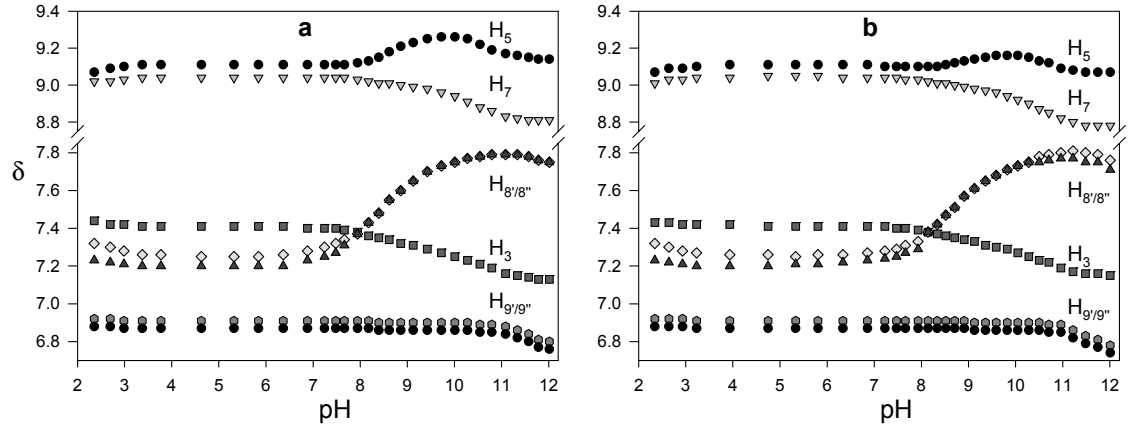


Figure S1 : Chemical shifts δ from $^1$H-NMR titrations for NBA (2.0 x $10^{-3}$ mole.$L^{-1}$) in the presence of 2 equivalents of $K^+$ (a) and 2 equivalents of $Na^+$ (b) as a function of pH at 25.0 °C ($CD_3OD$:$D_2O$-80:20).

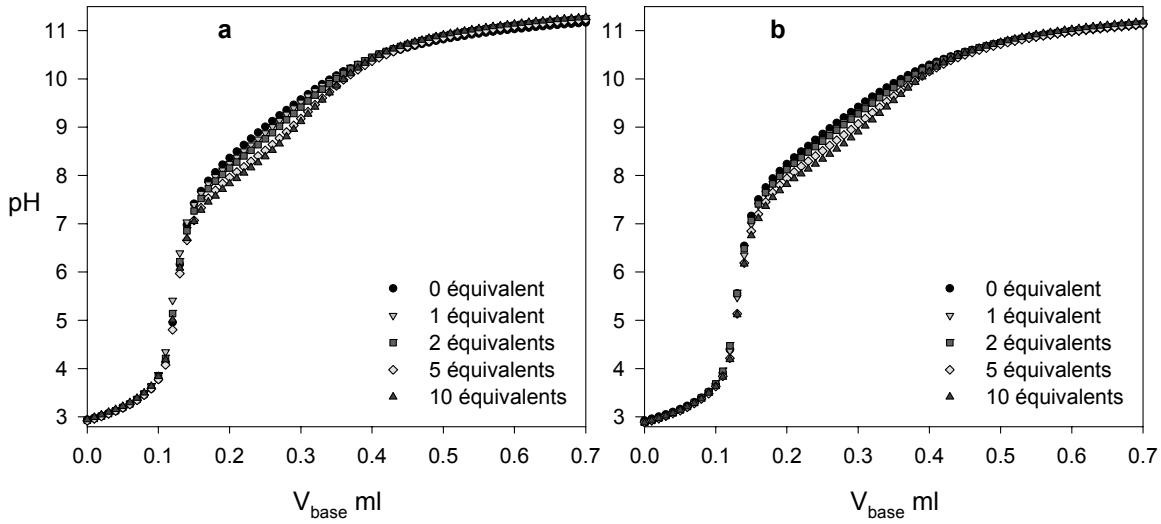


Figure S2 : Potentiometric titration curves of NBA (1.5 x $10^{-3}$ mole.$L^{-1}$), without and with various concentrations of $K^+$ (a) and $Na^+$ (b) cations.at 25.0 °C

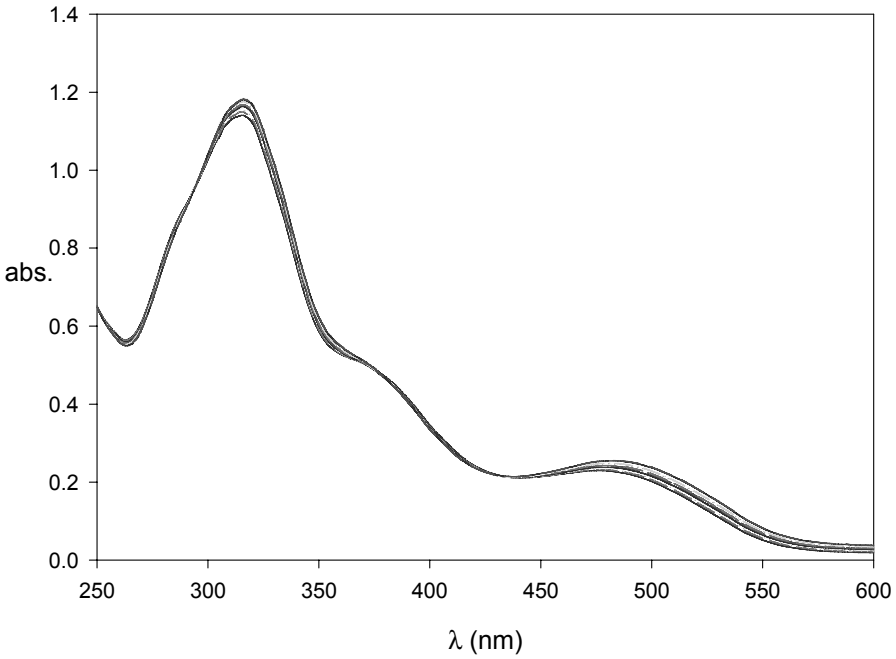


Figure S3 : UV-Visible spectra variations at pH 9.9 for various $Cs^+$ to NBA (0 to 8) ratios.

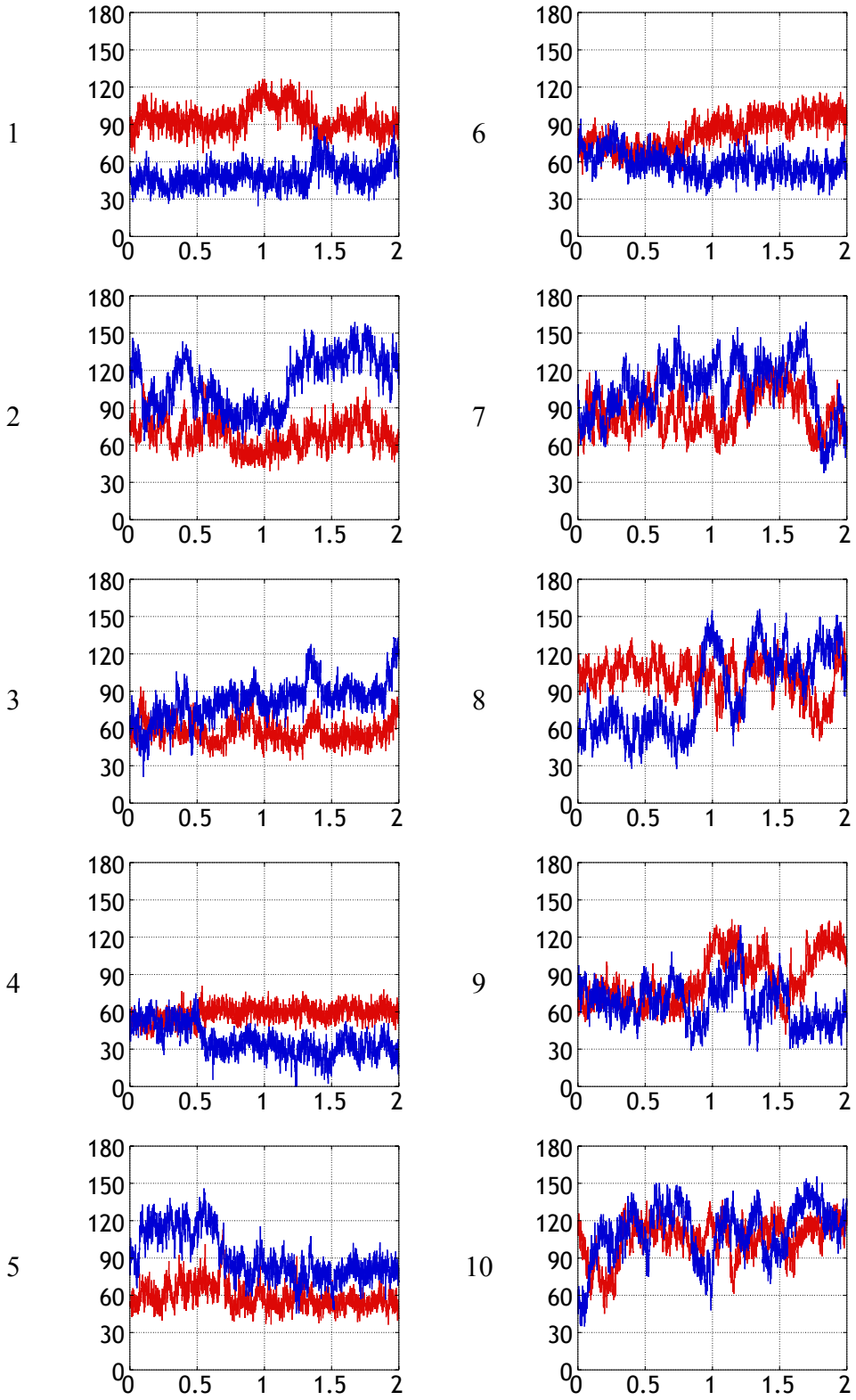


Figure S4 : System **C** : $\phi_1$ (in red) and $\phi_2$ (in blue) angles (defined in Scheme 1) as a function of time (in ns) for each $NBA^{4-}$ ligand.

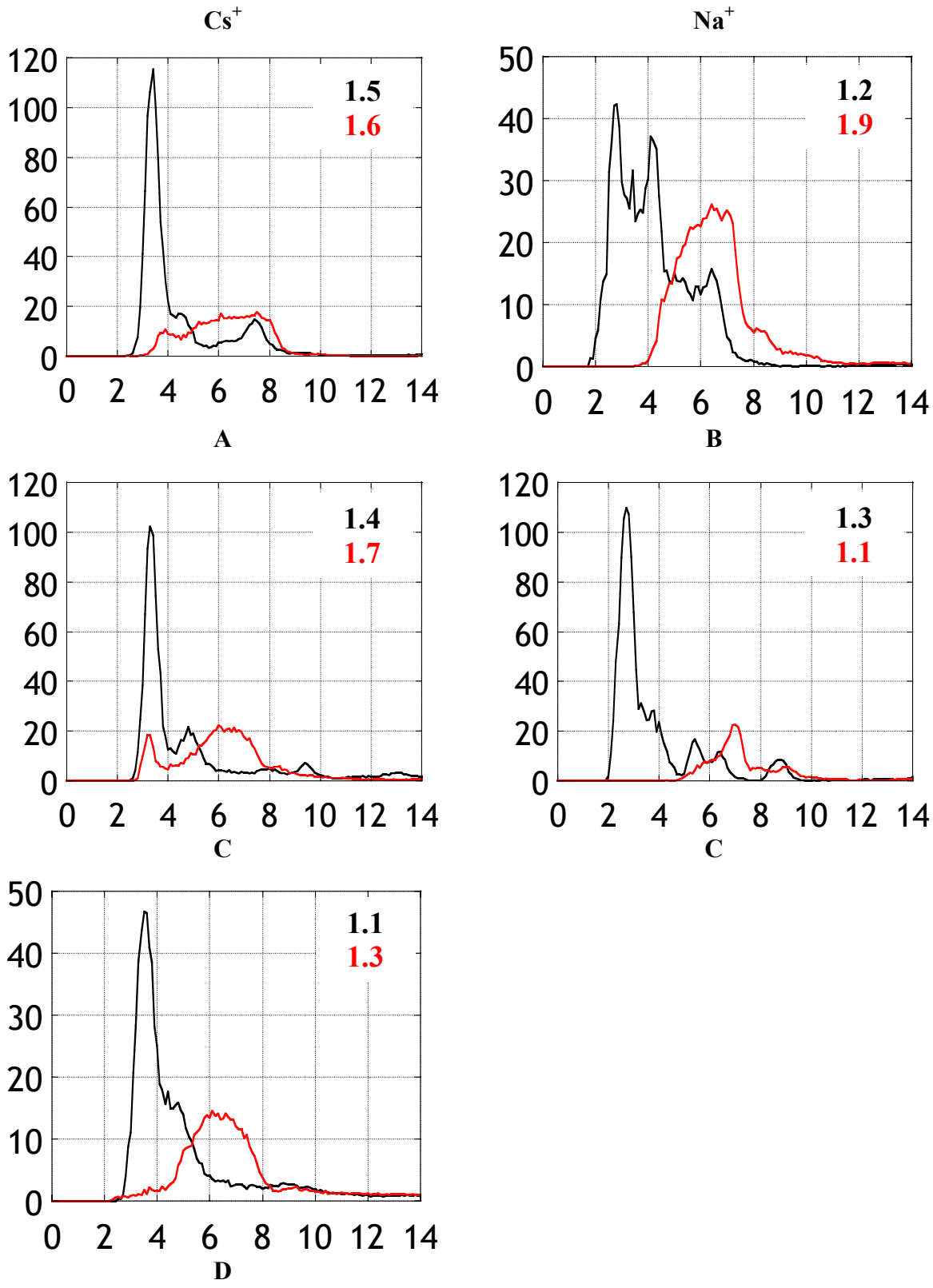


Figure S5 : **A** – **D** solutions: RDFs between the center- of -mass of $NBA^{4-}$ and the $M^+$ cations ($Cs^+$, $Na^+$). Averages over the 5 *EE* forms (in black) and 5 *ZZ* forms (in red) and corresponding integration numbers (within 10 Å).

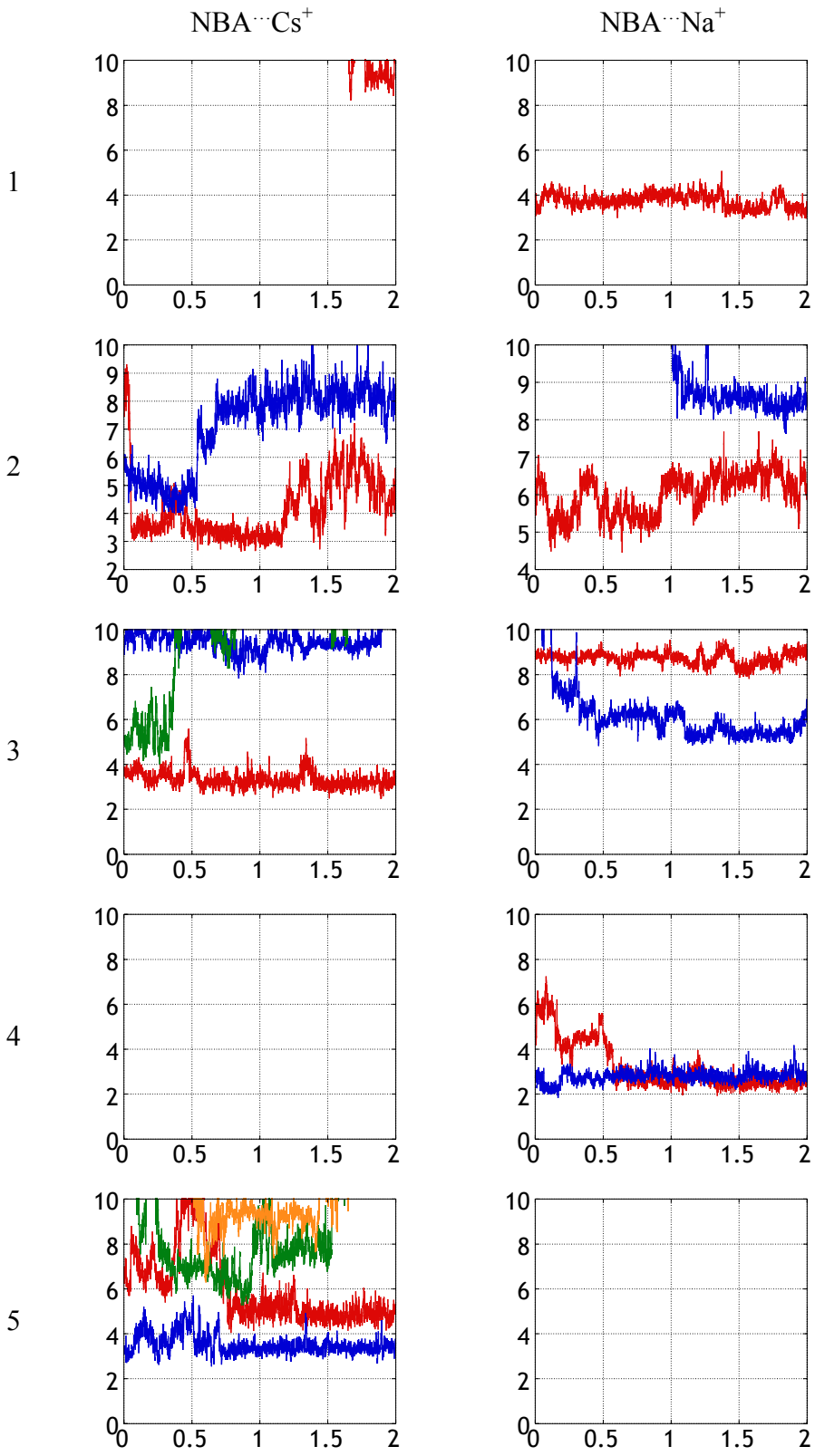


Figure S6a : System **C** : Distances between the center of mass of each $NBA^{4-}$ (*ZZ*) molecule and $Cs^+$ (left) or $Na^+$ (right) cations as a function of time (last 2 ns of dynamics).

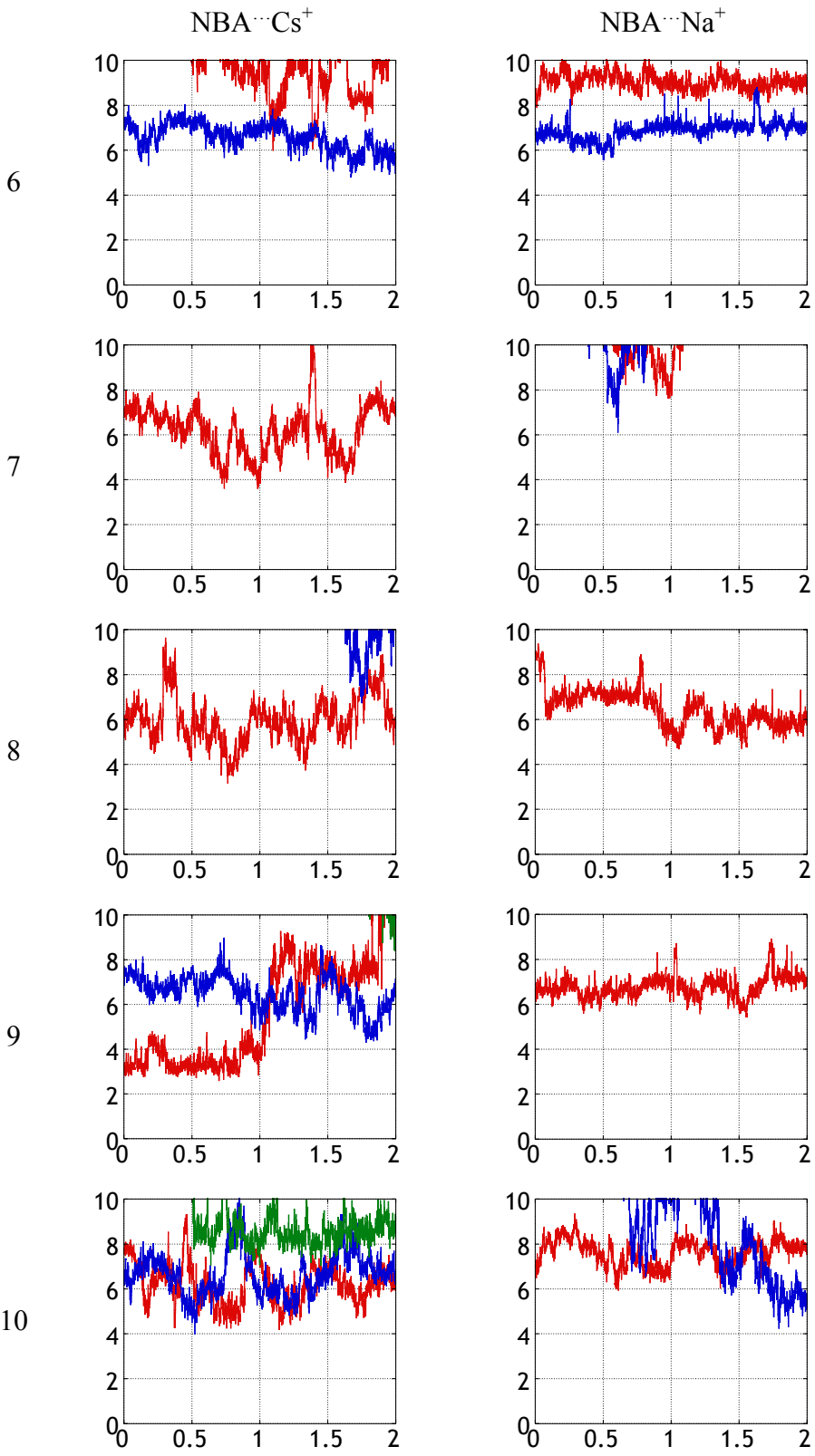


Figure S6b : System **C**: Distances between the center of mass of each $NBA^{4-}$ (*EE*) molecule and $Cs^+$ (left) or $Na^+$ (right) cations as a function of time (last 2 ns of dynamics).

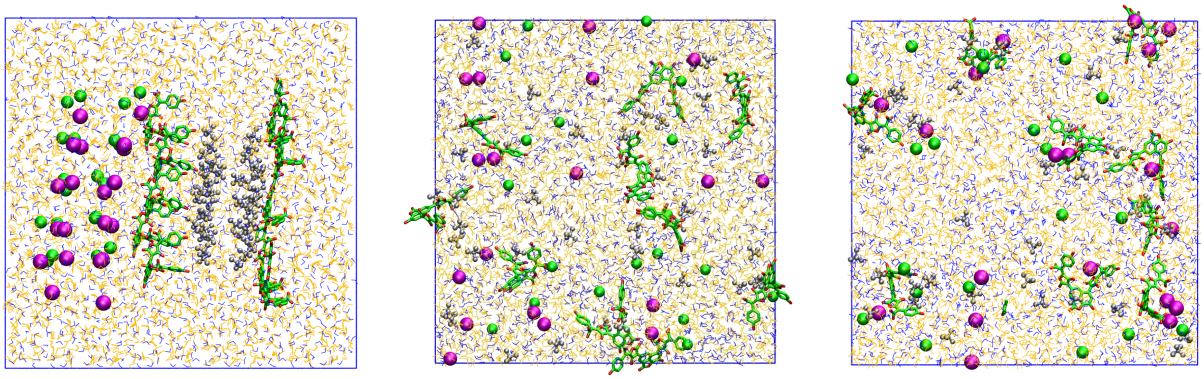

Figure S7 : Initial (*left*), mixed (*middle*) and final (*right*) views of system **A**.

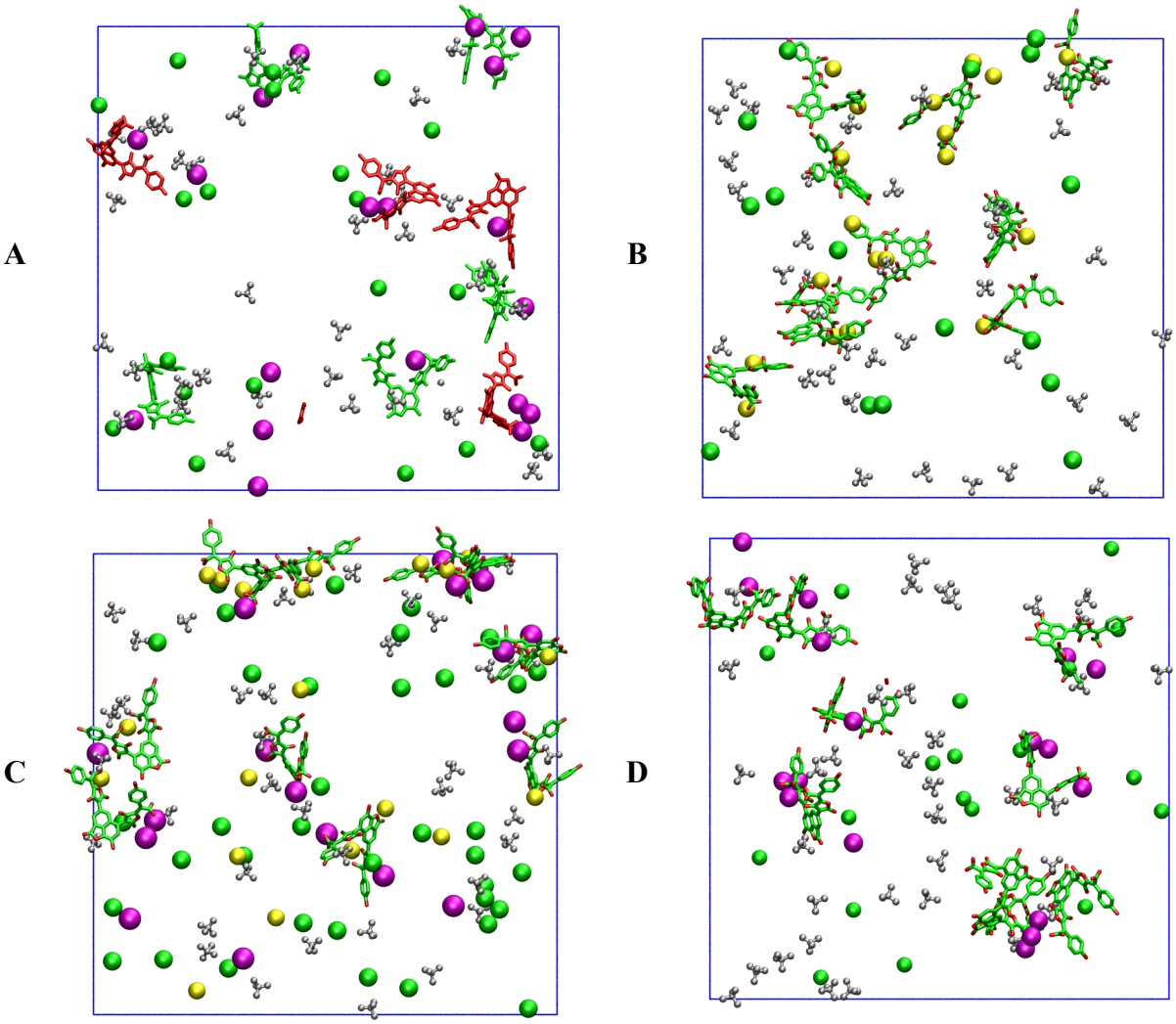


Figure S8 : $NBA^{4-}$ in a methanol:water 80:20 solution (**A** – **C**) and in pure water (**D**). Final views of the solvent boxes.

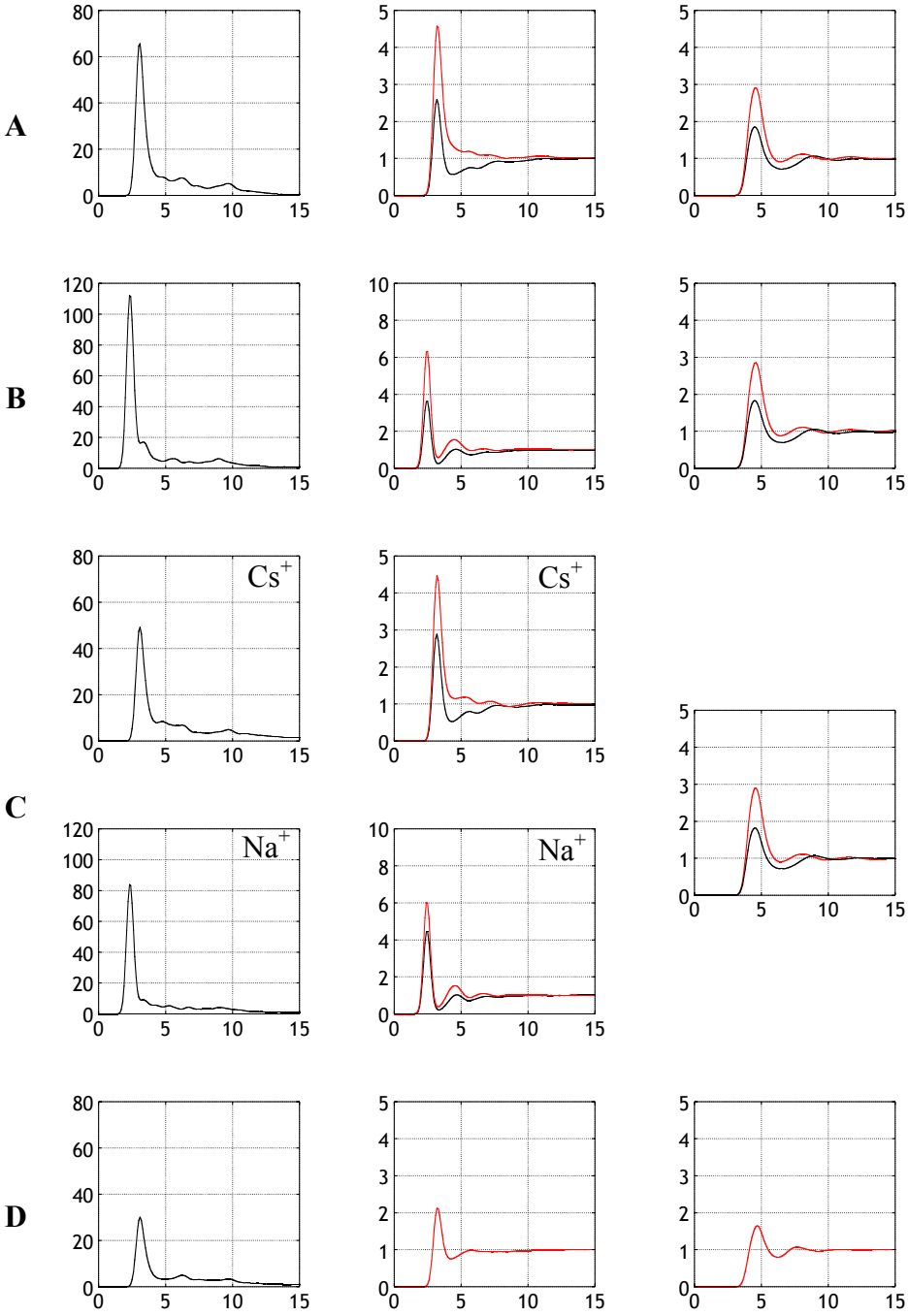


Figure S9 : **A** – **D** solutions: RDFs $X^{+}\cdots O_{NBA}$ (first column), $X^{+}\cdots O_{wat}$ (red, second column), $X^{+}\cdots O_{MeOH}$ (black, second column), $N_{Me4N+}\cdots O_{wat}$ (red, third column), $N_{Me4N+}\cdots O_{MeOH}$ (black, third column).

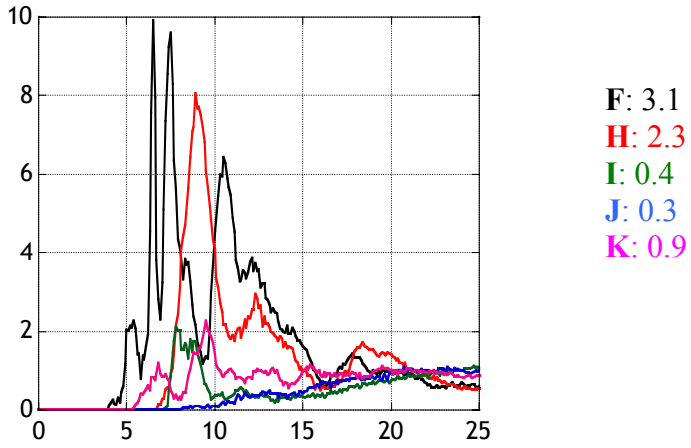


Figure S10 : **F** – **K** aqueous solutions: NBA···NBA RDFs (between the center of mass of NBA's) in **F** (*black*), **H** (*red*), **I** (*green*), **J** (*blue*) and **K** (*pink*). Integration numbers at 15 Å.

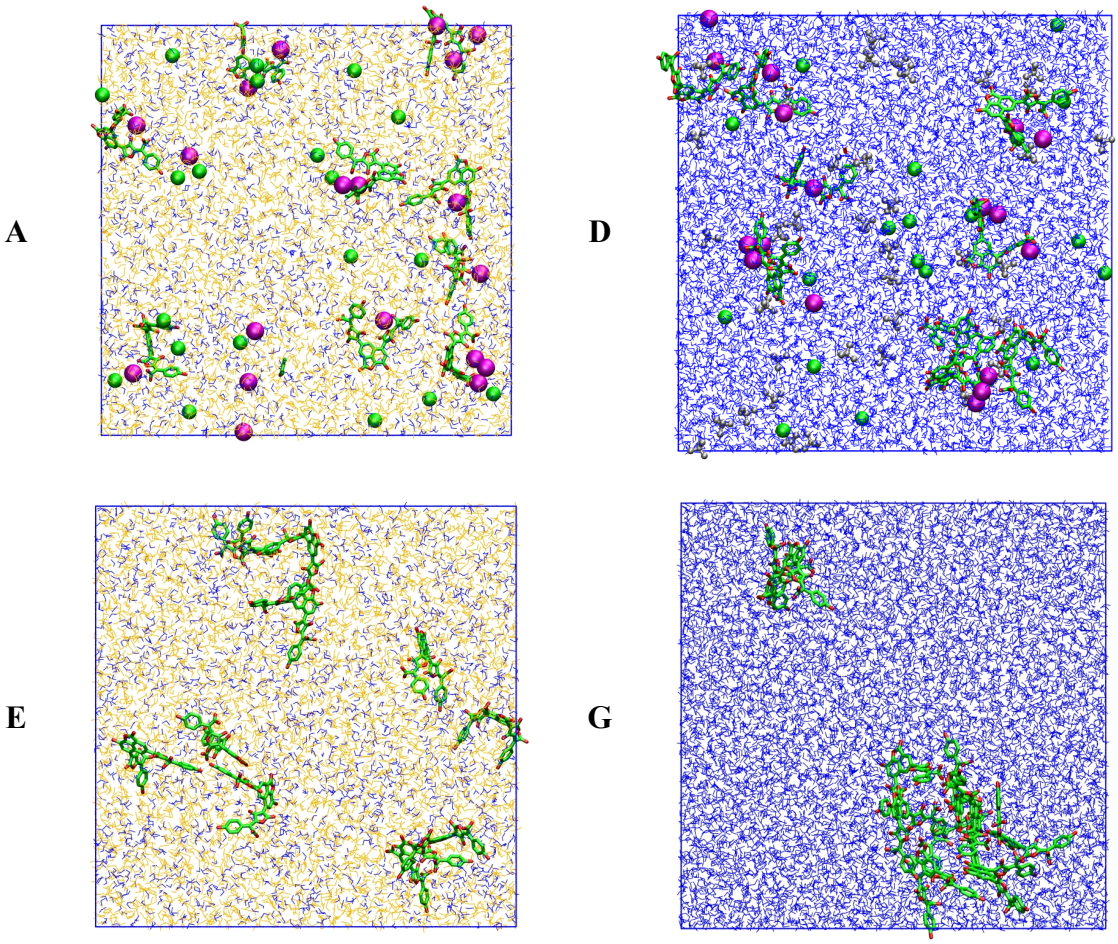


Figure S11 : NBA systems in a methanol:water 80:20 solution (**A**,**E**) and pure water (**D**,**G**). Final views of the solvent boxes.

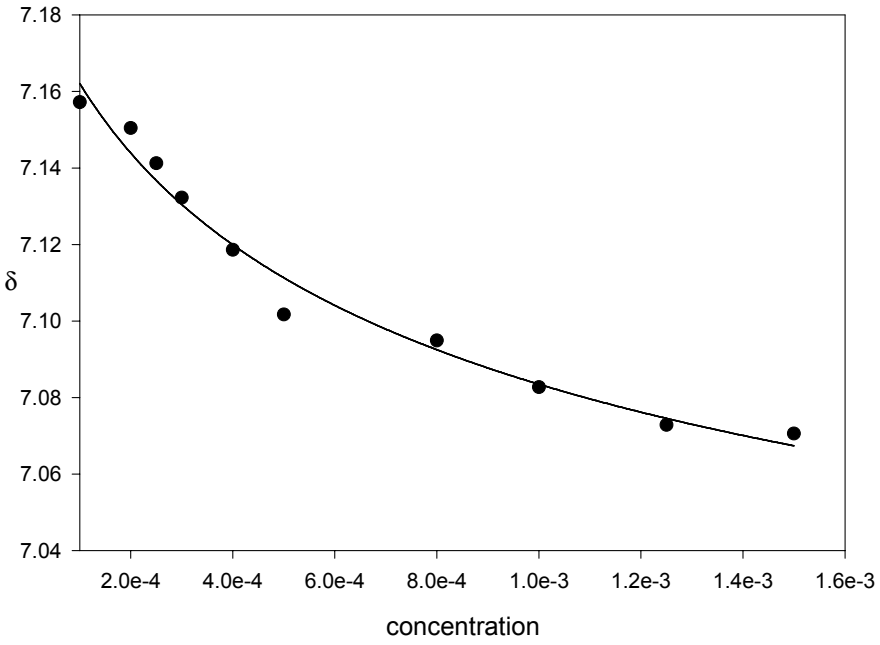


Figure S12 : Chemical shifts of the $H_3$ proton *vs* the NBA concentration in aqueous medium (pH = 8.3) at 25.0°C.

The dimerisation constant $K_d$ has been calculated according the equation [a)]

$$\delta = \delta_m + (\delta_d - \delta_m)\left(\frac{4K_d x + 1 - \sqrt{8K_d x + 2}}{4K_d x}\right)$$

where $x$ is the total concentration of NBA

$K_d$ the dimerisation constant

$\delta_m$ the chemical shift for the nucleus in the monomer

$\delta_d$ the chemical shift for the nucleus in the dimer

a) From D. B. Davies, L. N. Djimant, A. N. Veselkov, *J. Chem. Soc. Faraday Trans.*, 92 (**1996**) 383-390.

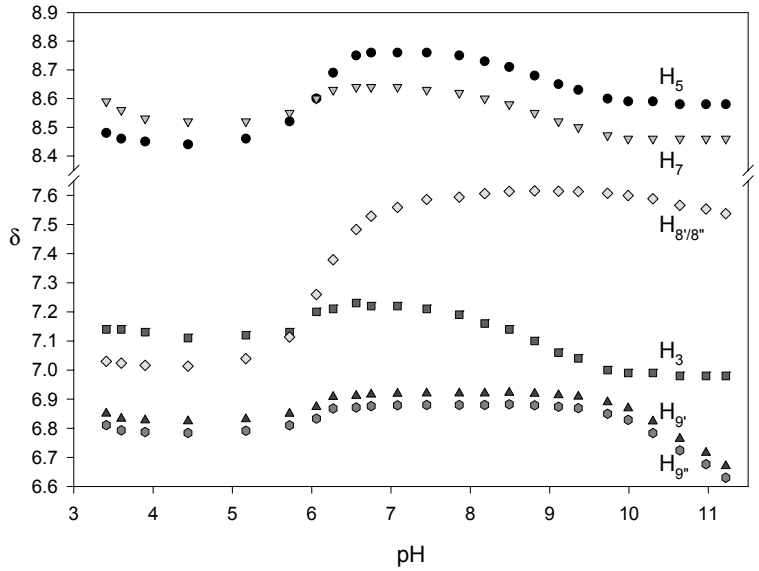


Figure S13 : Chemical shifts δ from $^{1}$H-NMR titrations for NBA (2.0 $10^{-3}$ mole.$L^{-1}$) as a function of pH at 25.0 °C in aqueous solution.