# Atomistic Insights into Structure–Morphology Relationships in Hydrated Poly(benzimidazolium) and Poly(bis-arylimidazoliums) Ionene Membranes

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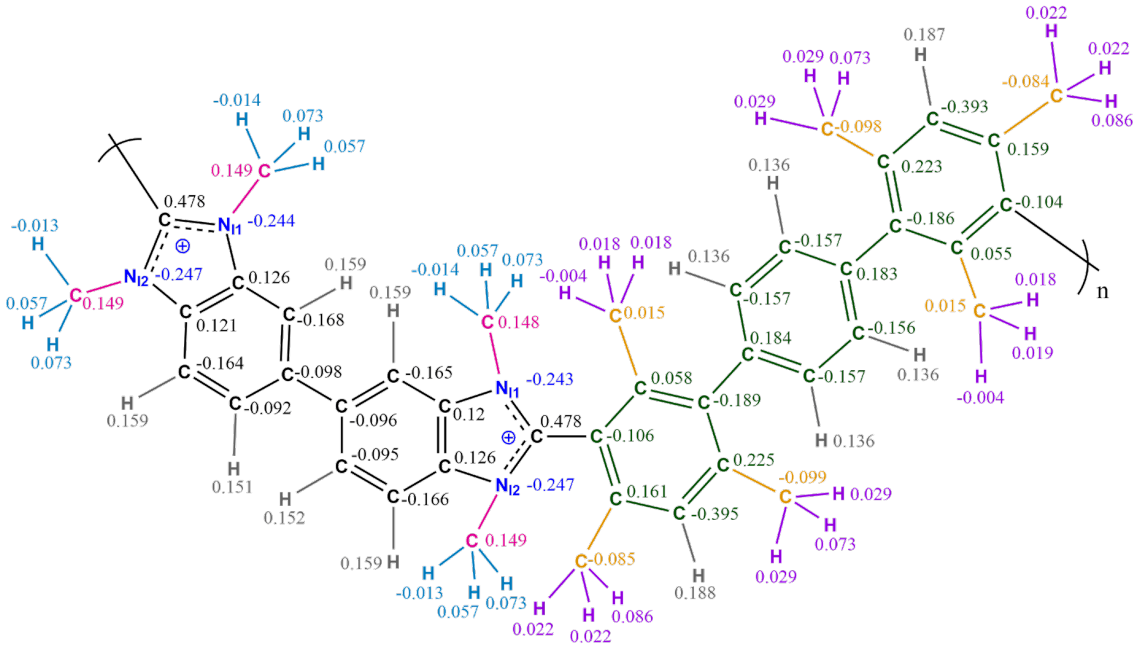
## Supporting Information:

**Table S1:** Coordination numbers calculated from a 40 ns NVT production run at 300 and 333 K for HMT-PMBI and PAImMM for various atom–atom interactions (Cutoff distance of the first solvation shell is given in parentheses).

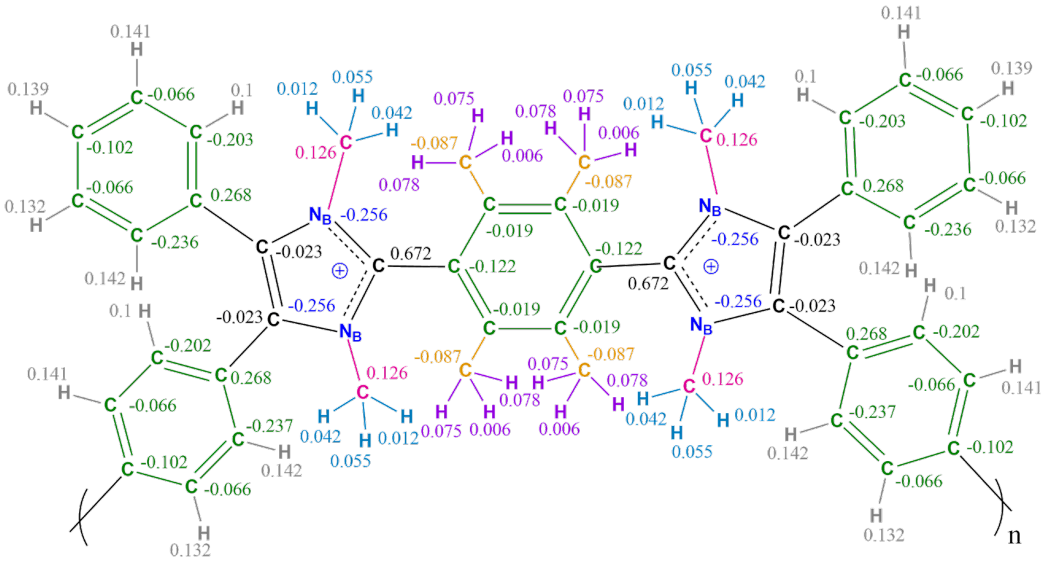
| System | Temperature (K) | N–OH (Å) | N–OW (Å) | OH–OW (Å) | N–N (Å) | OH–OH (Å) | OW–OW (Å) |
|---|---|---|---|---|---|---|---|
| HMT-PMBI | 300 | 3.32, 3.12 (7.9Å) | 6.22, 5.56 (5.5Å) | 5.88 (3.6Å) | 3.99, 2.14 (9.3Å, 8.2Å) | 1.23 (5.3Å) | 5.82 (4.3Å) |
| | 333 | 3.18, 3.09 (7.9Å) | 5.8, 5.2 (5.5Å) | 5.6 (3.6Å) | 3.82, 2.07 (9.3Å, 8.2Å) | 1.06 (5.3Å) | 5.6 (4.3Å) |
| PAImMM | 300 | 2.91 (8Å) | 4.87 (5.4Å) | 5.79 (3.6Å) | 1.83 (7.2Å) | 1.1 (5.3Å) | 5.65 (4.3Å) |
| | 333 | 2.89 (8Å) | 4.65 (5.4Å) | 5.55 (3.6Å) | 1.79 (7.2Å) | 0.96 (5.3Å) | 5.47 (4.3Å) |

**Table S2:** Self-diffusion coefficients (D $\times 10^{-5}$ $cm^2/s$) of hydroxide ions and water molecules calculated from the 40 ns NVT production run. Values in parentheses represent standard deviations.

| System | Temperature (K) | D (Hydroxide ion) | D (Water) |
|---|---|---|---|
| HMT-PMBI | 300 | 0.093 ±0.0084 | 0.6513 ±0.0248 |
| | 333 | 0.2337 ±0.014 | 1.3321 ±0.0214 |
| PAImMM | 300 | 0.0545 ±0.002 | 0.5577 ±0.0305 |
| | 333 | 0.147 ±0.0065 | 1.1912 ±0.0086 |



**a) HMT-PMBI**



**b) PAImMM**

**Figure S1:** The calculated CHELPG charges for (a) HMT-PMBI and (b) PAImMM.

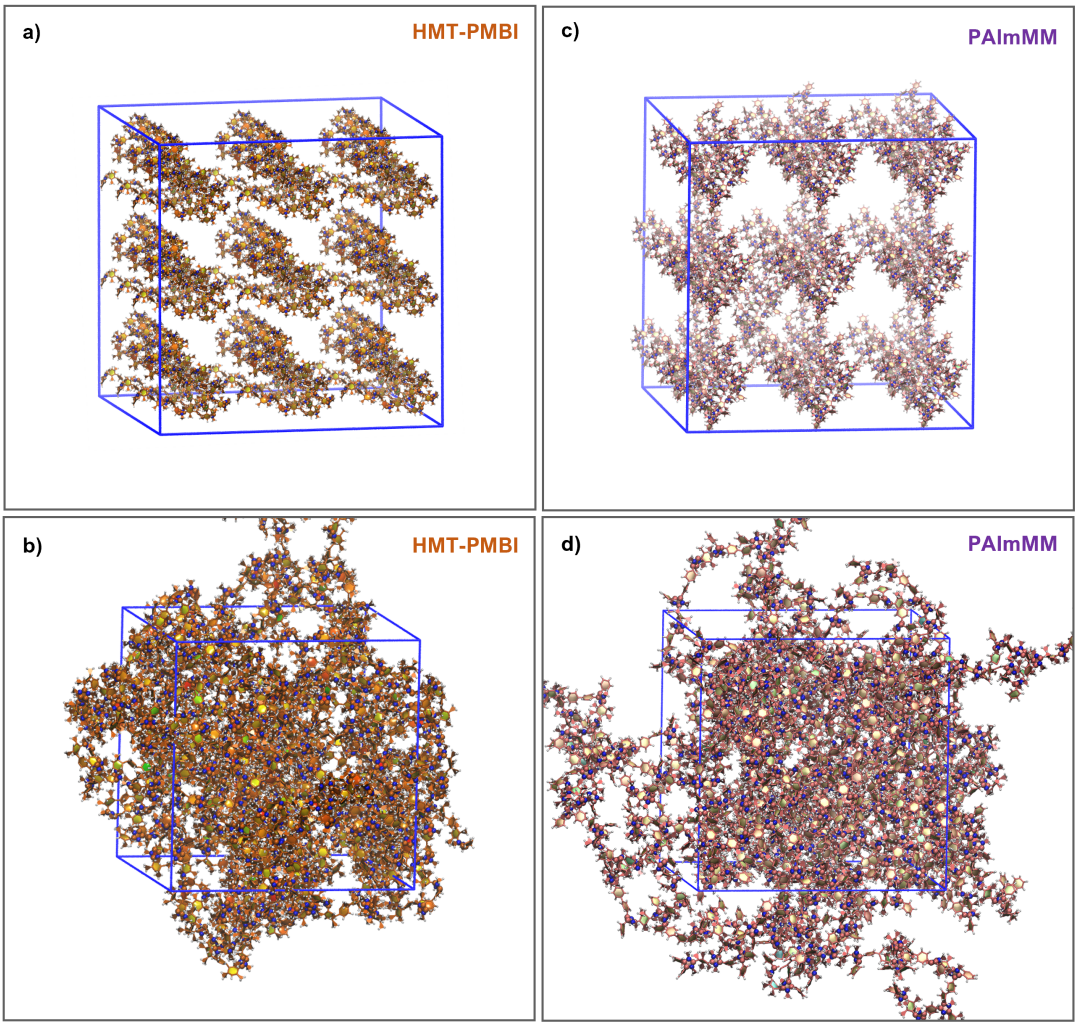



**Figure S2:** Snapshots of the simulation box showing the replicated and simulated annealed geometries for HMT-PMBI in panels (a) and (b), and for PAImMM in panels (c) and (d), respectively.

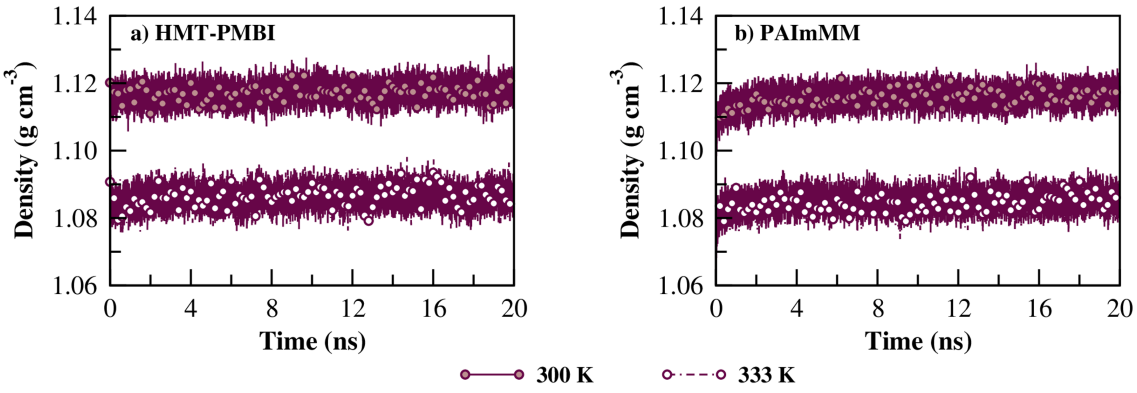



**Figure S3:** Density fluctuations during a 20 ns NPT equilibration run of the hydrated polymer matrices: (a) HMT-PMBI and (b) PAImMM at 300 K and 333 K.

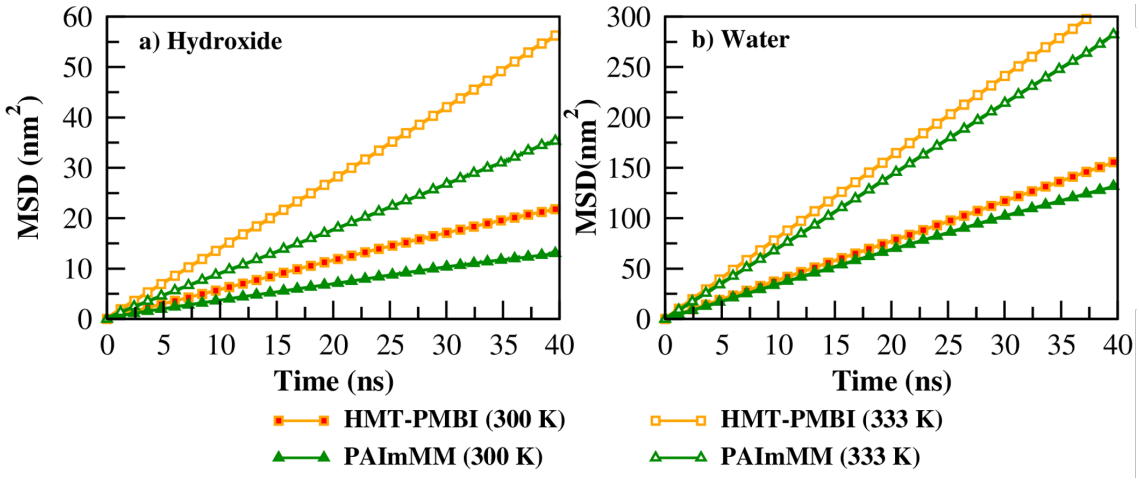



**Figure S4:** Mean square displacement (MSD) versus time plots obtained from a 40 ns NVT production run at 300 K 300 K (solid filled symbols) and 333 K (unfilled symbols) for (a) hydroxide ions and (b) water molecules.

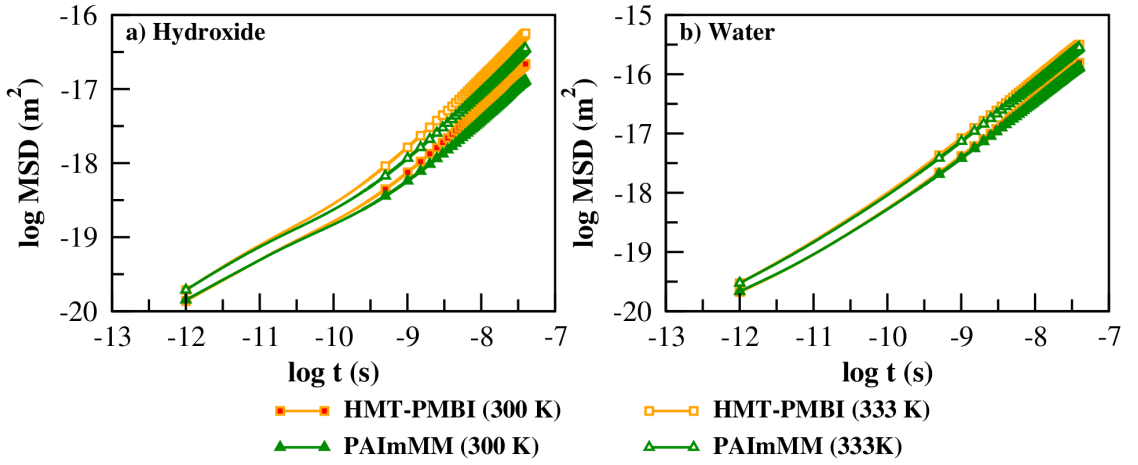



**Figure S5:** Log–log plots of mean square displacement (MSD) versus time for (a) hydroxide ions and (b) water molecules, obtained from a 40 ns NVT production run at 300 K (solid filled symbols) and 333 K (unfilled symbols).

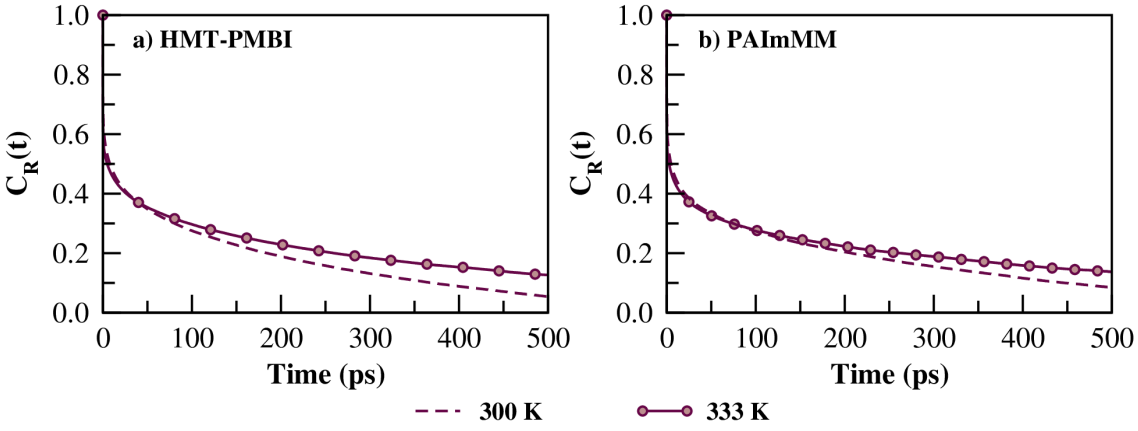



**Figure S6:** Time correlation functions for hydroxide ions located in the first solvation shell of the nitrogen atom at the functional active site of the polymer chain for (a) HMT-PMBI and (b) PAImMM at 300 K (solid line) and 333 K (dashed line).