

Active Roles of Water in Aqueous Assembly of Macromolecules [†]

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Abstract: Aqueous self-assembly customarily focuses on the molecular interactions of assembling building blocks; the role of water is barely studied. The hydration of hydrophobic P^+X^- (P^+ : macromolecular phosphonium cation, X^- : anion) is dependent on the ionic end groups, which is responsible for the consequent assembling behavior. The water interaction with the backbone was analyzed by FT-IR, and the dynamics were measured by low field-NMR spectroscopy. The combination of these two techniques reveals the effect of X^- on hydration. When X^- is I⁻, the ionic end group ordered water molecules that exerted a detectable long-range effect de-hydrating the backbone. The consequent hydrophobic interaction drove the aqueous assembly of P^+I^- into micelle-like aggregates with the ionic group exposed to water. In contrast, the ion pair with a hydrophobic anion of $[BPh_4]^-$ was not able to hold water and did not deplete the hydration water. The hydrated backbone of $P^+[BPh_4]^-$ assembled into vesicles that were driven by hydration interactions. This elucidation at the molecular level is craved to progress aqueous supramolecular chemistry.

Keywords: aqueous assembly; hydrophobic effects; macromolecules.

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Conflicts of Interest

The authors declare no conflict of interest.