

Hydration and Water-Mediated Binding of Superchaotropic *closo*-Dodecaborates

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The binding of *closo*-dodecaborates, $B_{12}X_{12}^{2-}$ with $X = H, Cl, Br, I$ (Fig.1a) to solutes, nanoparticles, polymers and interfaces has been copiously reported as a consequence of a water-mediated chaotropic effect.[1,2,3] However, the role of water has been inferred exclusively and indirectly from thermodynamic measurements. Herein, we use Raman spectroscopy in the O-H stretch region with multivariate curve resolution for solutions of $B_{12}X_{12}^{2-}$ in water to i) reveal their molecular hydration structure as illustrated in Fig.1b, ii) elucidate the temperature sensitivity of their hydration shell, and iii) report evidence for the water-release upon chaotropic binding. We find that all dodecaborates feature a sharp Raman band centered just below 3600 cm^{-1} – strongly blue-shifted compared to bulk water – that represents weakly H-bonded, “almost dangling” OH-groups in the hydration shell, see Fig.1c. Heating blue-shifts the hydration spectra less than the bulk water spectra, which makes hydration and bulk water at high temperature more similar and thus rationalizes the previously reported weaker chaotropic binding at high temperature. Hydration difference spectra along the binding isotherm with the non-ionic polymer hydroxypropylcellulose (HPC) further reveal the shedding of weakly H-bonded hydration water from $B_{12}X_{12}^{2-}$ as well as strongly H-bonded hydration water from $B_{12}X_{12}^{2-}$ and HPC as an associated process. The present study demonstrates weakly bound hydration water and a spontaneous release thereof as a hallmark of the superchaotropic behavior of dodecaborates.

Keywords:

chaotropic effect, nano-ions, ion specific effect, hydration, water, Raman MCR

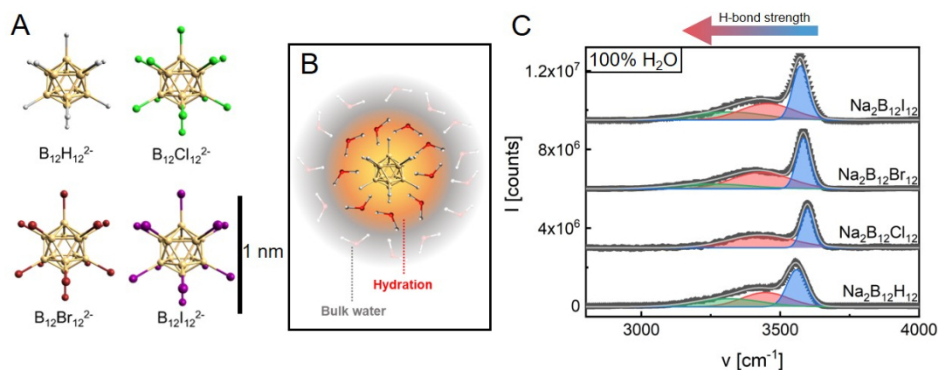


Figure 1. a) Molecular structure of $B_{12}X_{12}^{2-}$, b) Illustration of the hydration shell of $B_{12}H_{12}^{2-}$ c) Hydration spectra of $B_{12}X_{12}^{2-}$ in the OH-stretch region revealing a sharp blue-shifted peak.

References:

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