Supplementary Information for: Exclusive Ion Recognition Using Host-Guest Sandwich Complexes†

Nitesh Kumar[a*]

[a*] *Department of Chemistry, Washington State University, Pullman, WA, 99163*

E-mail: nitesh.kumar@wsu.edu

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Methodology

Table S 1: The compositions of the systems simulated in this study. Ligand represents the three different types of host molecules namely podand, 18-crown-6, and [2.2.2]-cryptand used in this study. Equilibrated box dimensions are provided for the systems with 18-crown-6.

H_2O	Cs^+	NO_3^-	Ligand	Equilibrated Box Dimensions
7205	130	130	40	58.43 × 58.43 × 70.69 Å^3
7205	130	130	60	59.03 × 59.03 × 71.41 Å^3
7205	130	130	80	58.85 × 58.85 × 74.04 Å^3
7205	130	130	100	60.03 × 60.03 × 72.62 Å^3
7205	130	130	130	61.01 × 61.01 × 73.79 Å^3
7205	130	130	160	61.66 × 61.66 × 74.59 Å^3
7205	130	130	260	57.29 × 57.29 × 97.02 Å^3

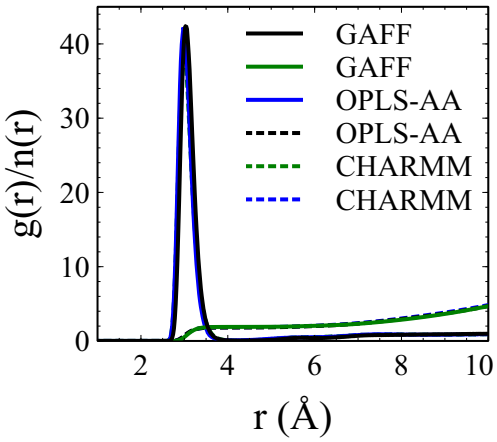

Figure S 1: Radial distribution (g(r)) and coordination number (n(r)) between Cs^+ and O_C (oxygen atoms of 18-crown-6) as a function of radial distance for different host force fields.

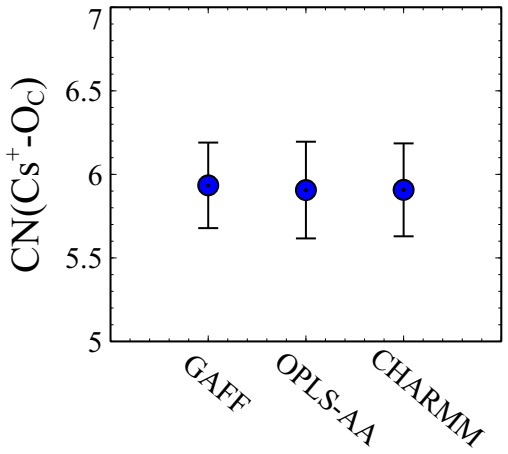

Figure S 2: Average Coordination number of interacting O_C (crown oxygen atoms) around central Cs^+ ions in systems with crown ether modelled using diffrent force fields. Note that only Cs^+ atoms that were directly interacting with the host molecules were taken into consideration for these calculations. The standard deviations of the coordination distributions of each host-guest system is shown as error bars.

Coordination Dynamics To probe the impact of the increase in host pre-organization and concentration on the dynamics of solvent and counter-anions in the guest coordination shells, we computed the lifetime distributions P(t) of H_2O and NO_3^- in Cs^+ coordination shells. Geometric cutoffs were used to compute the continuous time duration N(t,Δt) of atoms (O_W for water and O_N for nitrate) in the coordination shell.[1] The probability P(t) was defined as

$$P(t) = \frac{N(t, \Delta t)}{\sum_t N(t, \Delta t)} \tag{1}$$

and the corresponding residence time (τ) is,

$$\tau = \sum_{t=1}^{t_{max}} t\, P(t) dt. \tag{2}$$

where t_{max} is the maximum duration of continuous residence.

Order Parameter The extent of order within the local water network is computed using Steinhardt order parameter[2] as

$$q_l^i = \left[\frac{4\pi}{2l+1} \sum_{m=-l}^{l} \left| \frac{1}{N} \sum_{j=1}^{N} Y_l^m(\vec{r}_j) \right|^2 \right]^{\frac{1}{2}} \tag{3}$$

where, Y_l^m is the spherical harmonics function. For angular momentum number $l = 6$, the magnetic quantum number ranges from -6 to 6. Here, $\vec{r}_j$ is the vector from reference i to nearest neighbour j. N is the number of nearest neighbours of the central atom j. Note that the values of the sixth order Steinhardt parameter $q_6 \sim 1$ represents an order solid-like and $q_6 \sim 0$ represents a disordered liquid-like molecular arrangement.

Results and Discussion

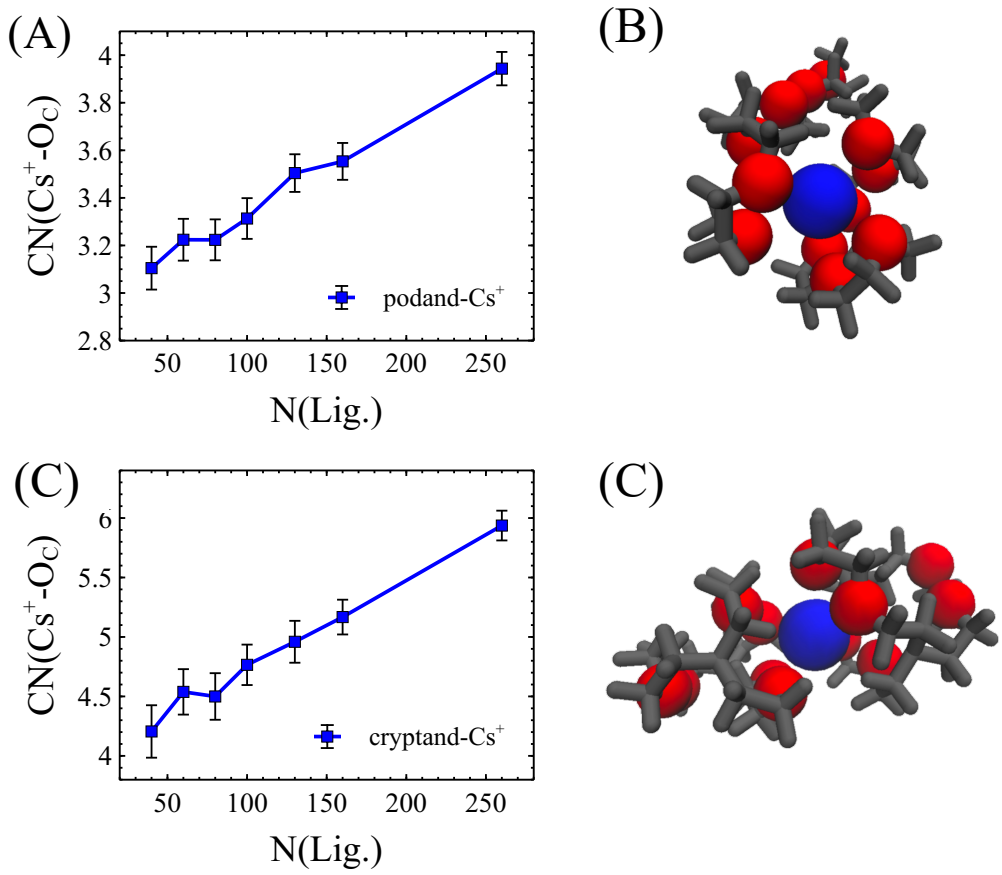

Figure S 3: (A) Coordination number of O_C (podand oxygen atoms) around central Cs^+ ions with increase in the podand concentration. (B) An illustration of a sandwich complex formed between podands and Cs^+ at n=260. Cesium ions are shown in blue, podand oxygen atoms are shown in red and all other atoms are colored grey. (C) The coordination number of O_C (cryptand oxygen atoms) around central Cs^+ ions with an increase in the cryptand concentration. (D) An illustration of a sandwich complex formed by cryptand with Cs^+ at n=260. Cesium ions are shown in blue, cryptand oxygen atoms are shown in red and all other atoms are colored grey. The standard deviations of coordination distributions of each host-guest system are shown as error bars.

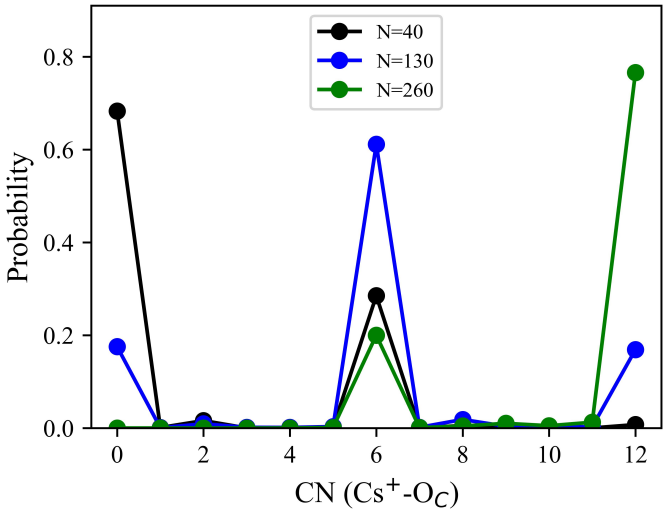

Figure S 4: Probability distribution of O_C (crown) around Cs^+ in the primary coordination shell at different crown concentrations.

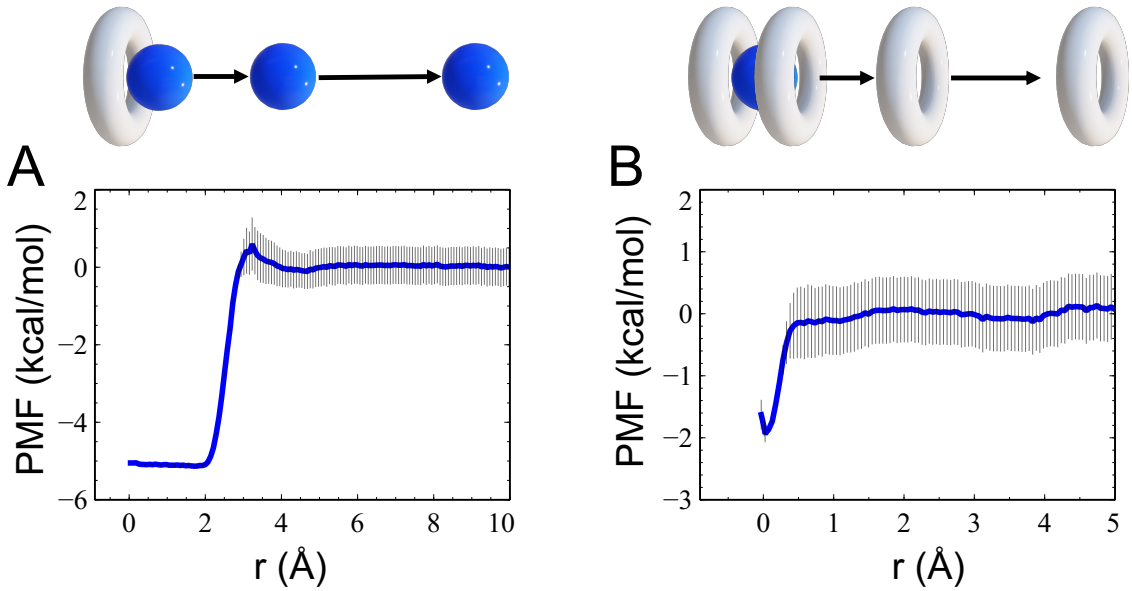

Figure S 5: Potential of mean force (PMF) between Cs^+ and crown with the Cs^+-crown distance as reaction coordinate from bound to unbound state in aqueous media. (A) PMF for Cs^+ binding to form 1:1 host-guest complex. (B) PMF for guest binding to form 2:1 sandwich complex. An illustration of host-guest complexes and the reaction coordinate is provided on the top of the respective PMFs.

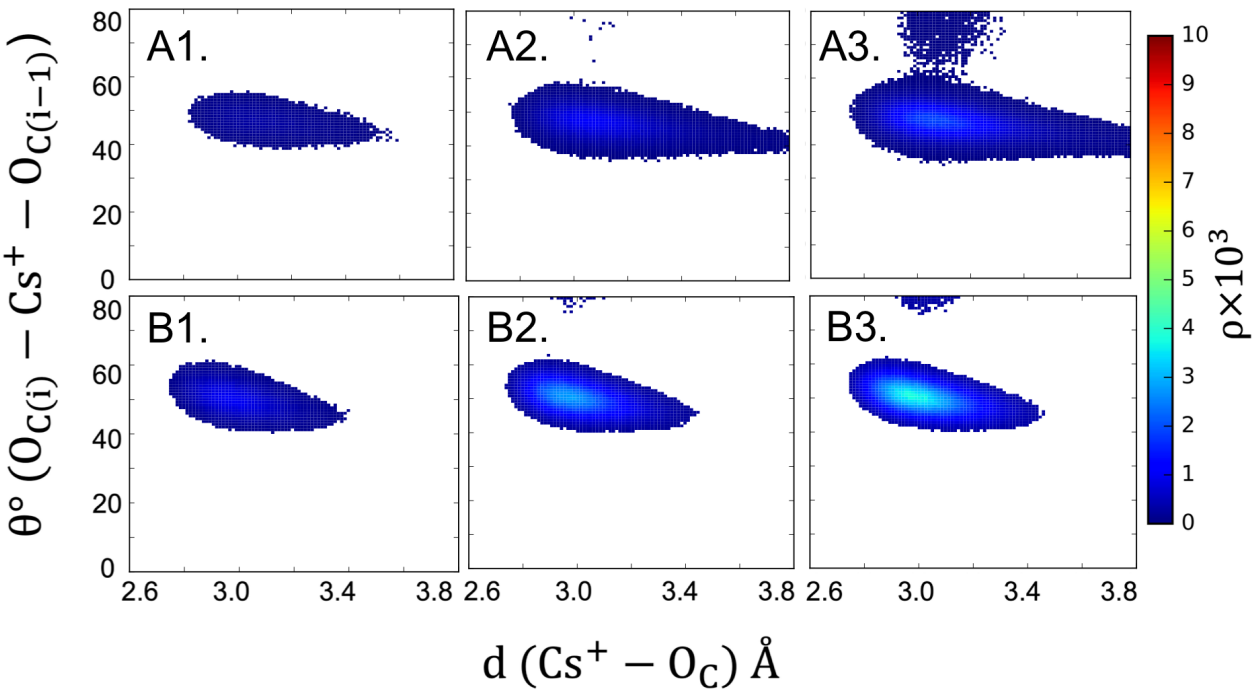

Figure S 6: Combined angular/spatial distributions of $O_{C(i)}$-Cs^+-$O_{C(i-1)}$ angle and Cs^+-$O_{C(i)}$ distances between Cs^+ ions and crown oxygen atoms in systems with (A1.) 40 (A2.) 130 (A3.) 260 podand and (B1.) 40 (B2.) 130 (B3.) 260 cryptand molecules.

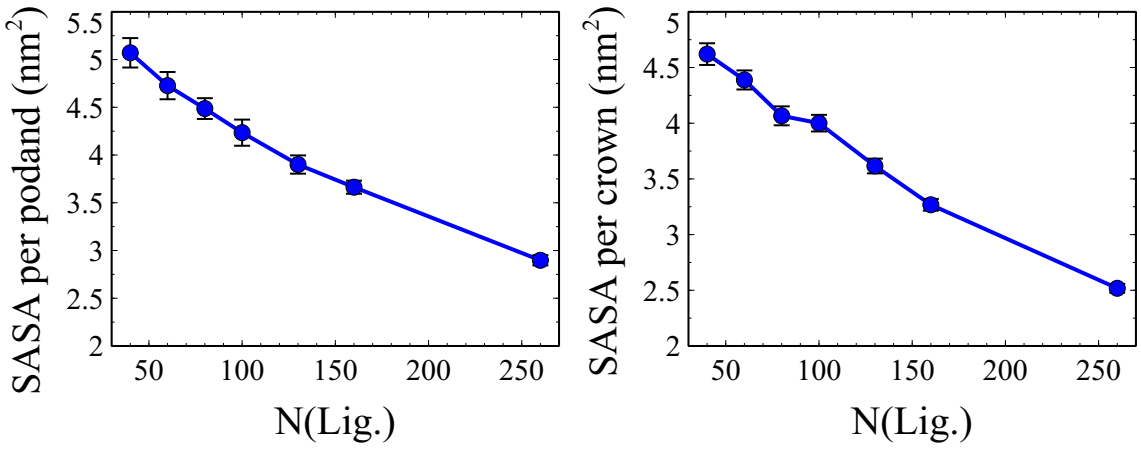

Figure S 7: Solvent accessible surface area (SASA) of podand and crown at different host concentrations.

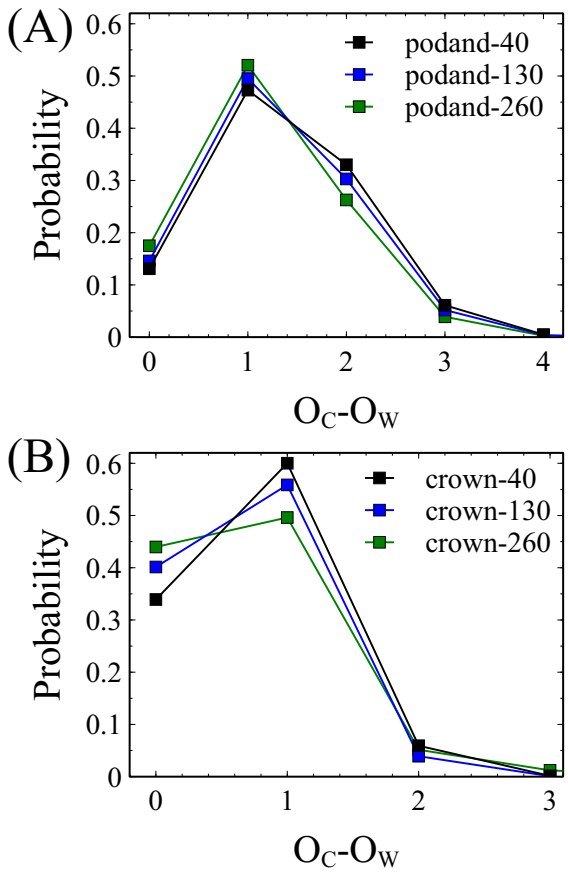

Figure S 8: Probability distribution of O_W (water oxygen atoms) around O_C (host oxygen atoms) of (A) podand and (B) 18-crown-6 molecules at different concentrations.

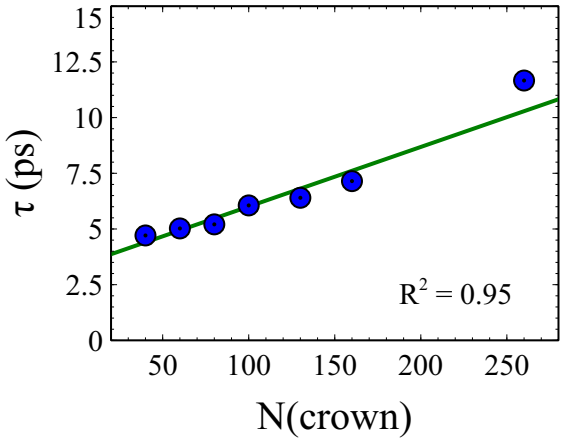

Figure S 9: Ensemble average residence times of the H_2O molecules in primary Cs^+ coordination shells in systems with 18-crown-6. The lifetimes were fitted to the linear regression model to probe the linear dependence of solvation dynamics on system composition.

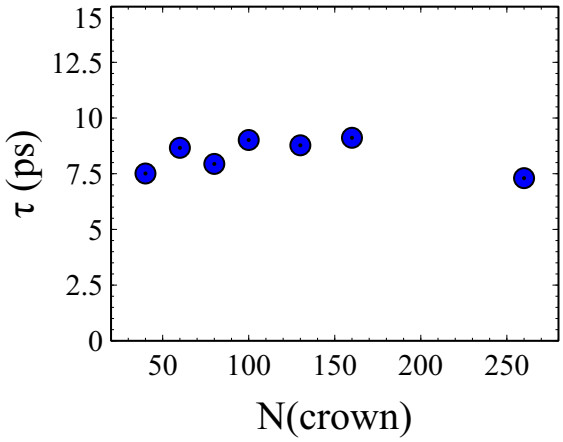

Figure S 10: Residence time of O_N (nitrate oxygen atoms)in the primary coordination of Cs^+ atoms as a function of host concentration.

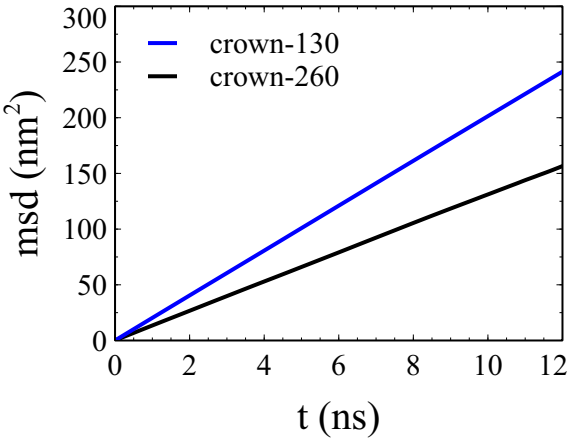

Figure S 11: Mean square displacements of host molecules at different host concentrations.

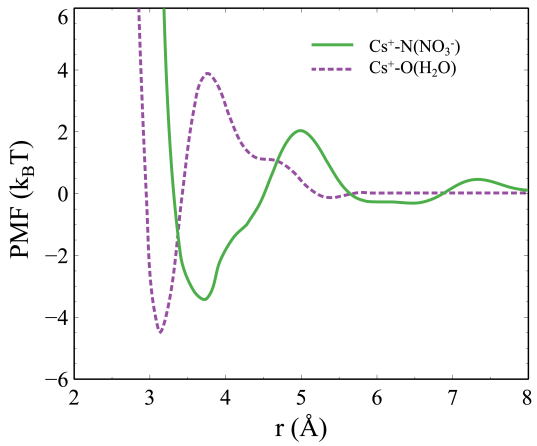

Figure S 12: Potential of mean forces between Cs^+-$N(NO_3^-)$ and Cs-$O(H_2O)$ with the radial distance as reaction coordinate.

Impact of Host-Guest Interactions on Water Structure The influence of host pre-organization and concentration on solvent topology has been analyzed utilizing pair-correlation functions, the inter-molecular hydrogen-bonding network, and the q_6 order parameter (Figure S13). It is observed that the pre-organization of the host exerts negligible perturbation on the structural configuration and local ordering of water. This conclusion is drawn from the observation that water (O_W) pair-correlation functions and the primary solvation coordination number distributions remain consistent across podand, crown, and cryptand host systems. Notably, the distributions across these systems consistently revealed that water exhibits the highest propensity to establish four inter-molecular connections (Figure S13 B). On the other side, host concentration alters the topology of the water H-bonding network due to enhanced crown clustering on the addition of host molecules. In particular, the increased host concentration generated a disorder within the water network, resulting in a shift in q_6 to a lower value (Figure S13 C).

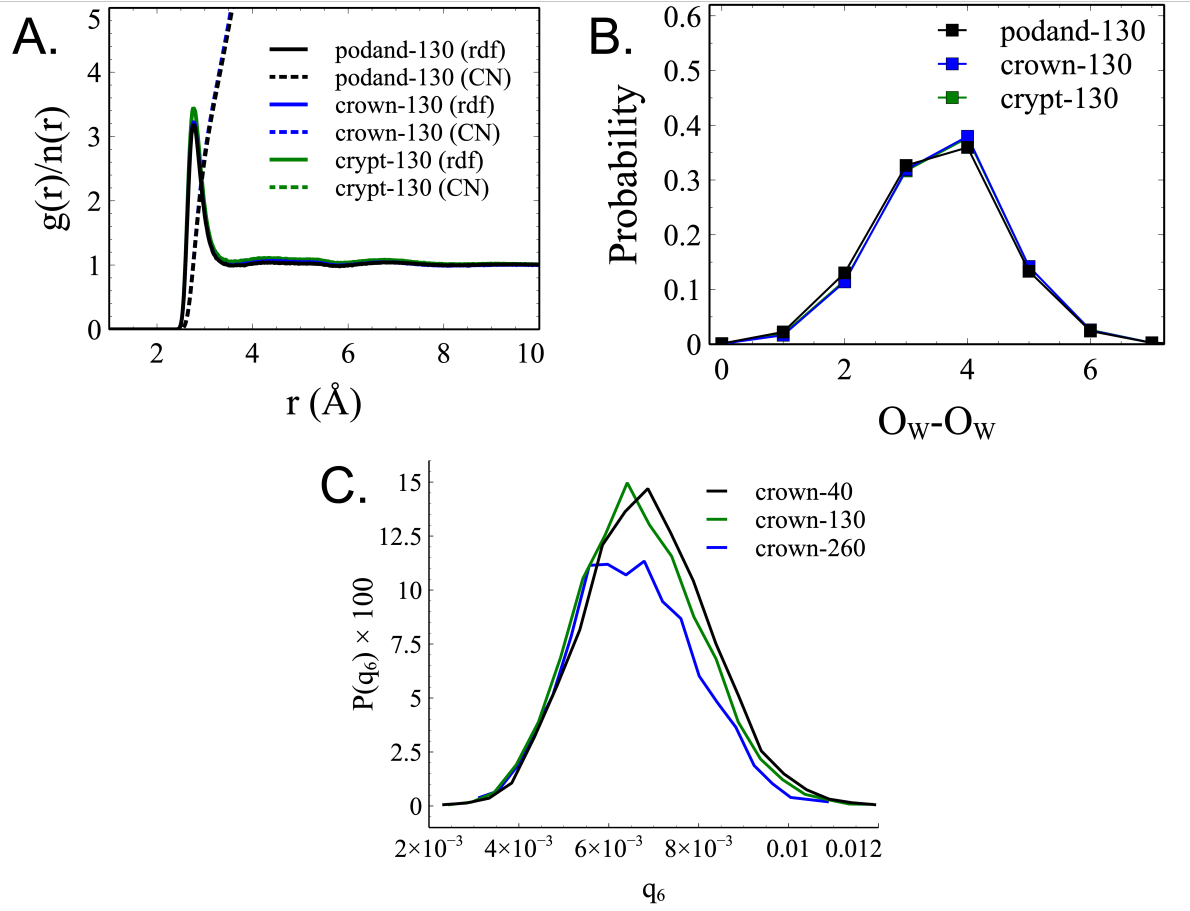

Figure S 13: (A) Radial distribution and coordination number as a function of the radial distance between oxygen atoms within different host-guest systems. (B) Probability of different water (Ow) coordination in the systems with different host molecules. A 3.5 Å cutoff is used to obtain the water-water coordination numbers. (C) The sixth order Steinhardt parameter q_6 probability distributions for water ordering in systems with 18-crown-6 as host. Note that O(H_2O) atoms were considered as the reference for the computation.

References

(1) Michaud-Agrawal, N.; Denning, E. J.; Woolf, T. B.; Beckstein, O. MDAnalysis: A Toolkit for the Analysis of Molecular Dynamics Simulations. *Journal of Computational Chemistry* **2011**, *32*, 2319–2327.

(2) Lechner, W.; Dellago, C. Accurate Determination of Crystal Structures based on Averaged Local Bond Order Parameters. *The Journal of Chemical Physics* **2008**, *129*, 114707.