Supplementary data for
Small-angle neutron scattering study of specific interaction and
coordination structure formed by mono-acetyl substituted
dibenzo-20-crown-6-ether and cesium ions

Computational method

All computations reported in this work were carried out in the Kohn-Sham formalism of the density functional theory (DFT) [1], including gradient corrections to the exchange-correlation functional after Perdew, Burke, and Ernzerhof [2] as implemented in the CPMD code [3]. The valence-core interaction was described by a von Barth-Car pseudopotential (PP) [4] for H, a norm-conserving Troullier-Martins PP [5] for C and O, and a Goedecker PP [6] for Cs, where semicore states of Cs were included as valence states. Valence orbitals were expanded in a plane wave (PW) basis set with an energy cutoff of 80 Ry. The Brillouin zone was sampled at the Γ point only. Relativistic effects were taken into account at the scalar relativistic level of theory via the Goedecker PPs generated based on the fully relativistic electronic structure calculations of a single atom. Our PW-DFT approach was validated by examining the ion-oxygen distance and related hydration energy for $\text{Cs}^+/\text{H}_2\text{O}$ complex as described

elsewhere [7]. For the present calculations we used a cubic simulation box of length $L = 21.167 \text{ \AA}$ under periodic boundary conditions. The excess charge of the system was compensated by a uniform background charge. During geometry optimization, all atoms were fully relaxed until residual forces on constituent atoms were smaller than $0.025 \text{ eV/\AA}$.

Energy levels of optimized ace-DB20C6/Cs

Fig. S1 shows Kohn-Sham energy levels and the first-fourth highest lying occupied orbitals (HOMO, HOMO-1, HOMO-2, HOMO-3) for our optimized ace-DB20C6/Cs. As shown in **Fig. S1**, HOMO of our optimized ace-DB20C6/Cs is localized on the acetyl group, while HOMO-1, HOMO-2, and HOMO-3 correspond to the bonding orbitals, consisting mainly of π -orbitals of the two benzene rings and d orbitals of a Cs^+ ion located above the center of the ether oxygen ring. The binding energy of ace-DB20C6/Cs in our optimized structure estimated as -40.3 kcal/mol is found to be much larger in magnitude than that for $\text{Cs}^+/\text{H}_2\text{O}$ complex (-13.8 kcal/mol), suggesting that ace-DB20C6/Cs in our optimized structure is rather stable.

Figure S1. Kohn-Sham energy levels and the first-fourth highest lying occupied orbitals (HOMO, HOMO-1, HOMO-2, HOMO-3) for our optimized ace-DB20C6/Cs. The energy levels of occupied and unoccupied Kohn-Sham orbitals are represented as solid and dashed lines, respectively.

References

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