

Electronic Supplementary Information

Binary twinned-icosahedral [B₂₁H₁₈]⁻ interacts with cyclodextrins as a precedent for its complexation with other organic motifs

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Methods

High-resolution mass spectrometry –FT–ICR

The experiments were performed on a high-resolution and high-sensitivity mass spectrometer MS–ESI/FT–ICR (Fourier Transform Ion Cyclotron Resonance) Agilent/Varian-920, provided with a 7.0-T actively-shielded superconducting magnet, in line with a triple quadrupole MS Agilent/Varian 320 equipped with an electrospray ionization (ESI) source. The sample of **KB21** was diluted in a mixture of acetonitrile and water in a 1:1 (vol/vol) ratio, and approximately 4×10^{-5} M samples of α -, β -, and γ -CD were added in a 1:1 molar ratio to obtain each of the three complexes. Fresh solutions were directly infused into the ESI source at a flow rate of 10 mL/min. Quadrupole and hexapole ion guides, accumulation ion hexapole and other key components were optimized in order to maximize the detection of signals in m/z ranges within 100–1700 Da. Commercial beer malto-oligosaccharides were used as mass calibrants and tuning standards in both the positive and negative ion modes.^{1,2}

Computations

The starting structures of the complexes were generated by potential energy surface (PES) scans of **B21** moving along the z-axis of CD at the DFT-D3³ (TPSS/TZVPP) level. From the minimum-energy structures, force-field-based molecular dynamics (MD) simulated annealing (for details, see SI) was started. The energies of the obtained structures were evaluated by the more reliable but also more computationally demanding quantum mechanical (QM) method.

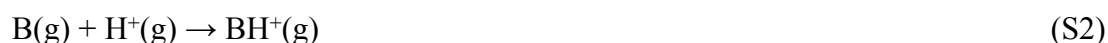
Force field parameters for the hosts were taken from the general AMBER force field (GAFF)⁴ using restrained fit to the electrostatic potential (RESP)⁵ partial atomic charges at the HF/6-31G* level. The parameters for K⁺ were taken from ff14SB.⁶ For **B21**, equilibrium bond

distances from QM optimization were used. Nonbonded parameters were transferred from the universal force field (UFF).⁷

The geometries resulting from MD were optimized by means of DFT-D3 (TPSS/TZVPP level) using TURBOMOLE 6.6⁸ in the Cuby 4⁹ framework. The interaction-energy (ΔE) values of the binary complexes were calculated as the energy difference between the energy of the optimized complex and the energies of the optimized subsystems (with deformation energy being included) (Eq. S1). The correction for the basis set superposition error (BSSE) was not considered as it is partially covered by the parameterization of the D3 correction (DFT-D3):

$$\Delta E = E_{(A,B)} - (E_{(A)} + E_{(B)}) \quad (\text{S1})$$

The gas-phase basicity (or intrinsic basicity) of a base B, $GB(B)$, is defined as the Gibbs free energy for the hypothetical acidification reaction:¹⁰



Electronic structure computations for this purpose were carried out with the Gaussian 09 program¹¹ using the MP2/6-31G* model chemistry. Second-derivative analyses were run with the same program package. Electrostatic potential (ESP) was computed using the Gaussian 09 and Molekel4.3¹² programs.

Results

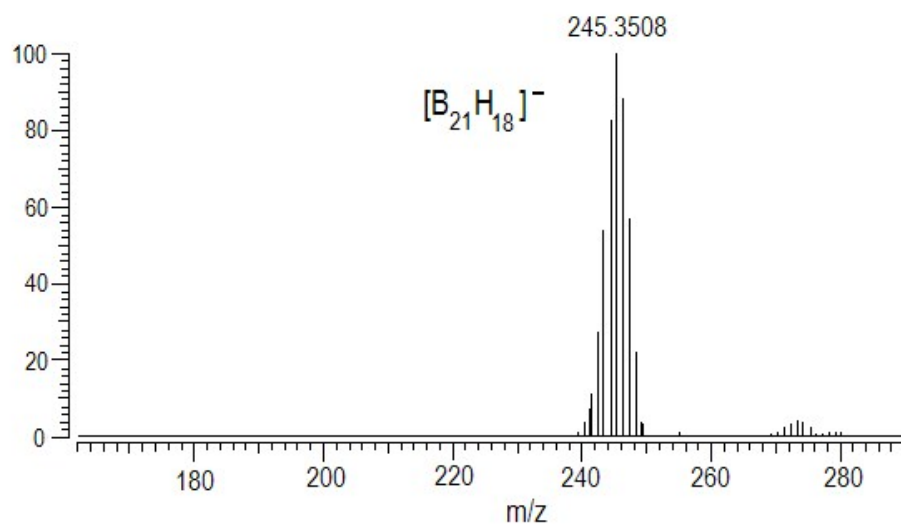


Fig. S1 ESI FT-ICR spectrum, in the negative mode, of $KB_{21}H_{18}$ (ACN: water) for range of $m/z < 300$

MD simulation revealed subunits-based complexes optimized at the DFT level

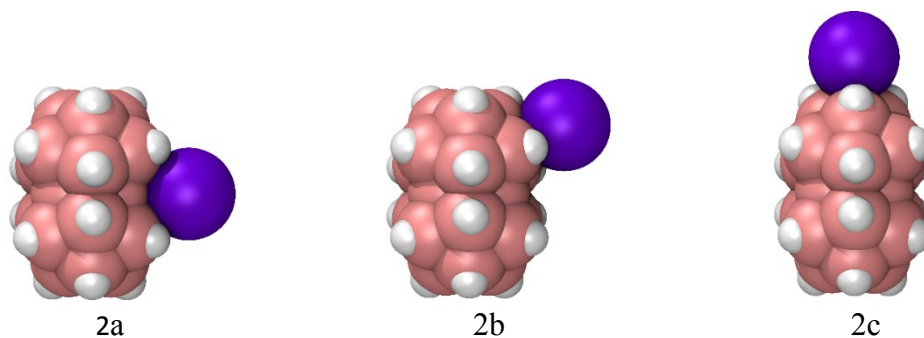


Fig. S2 Optimized geometries of KB_{21} . Three possible positions of K^+ are taken from MD snapshots. Interaction energies between B_{21} and K^+ are -82.9, -77.9 and -78.0 kcal/mol for the forms 2a, 2b, and 2c, respectively.

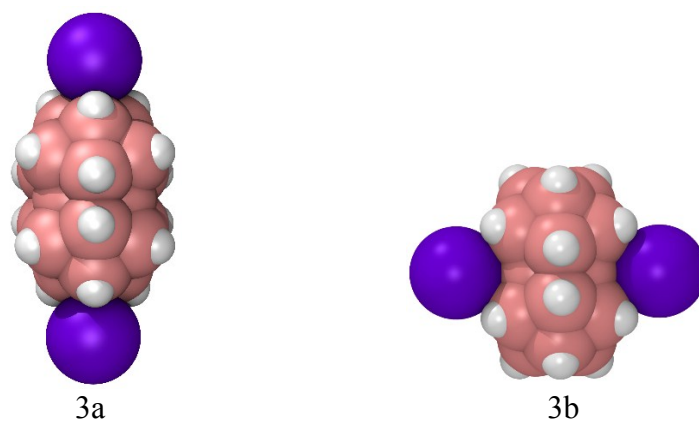


Fig. S3 The most stable computed structures of the $\text{KB21} \cdots \text{K}^+$ complexes. Interaction energies are computed to be and -30.0 and -29.7 kcal/mol for 3a and 3b, respectively when KB21 interacts with K^+ .

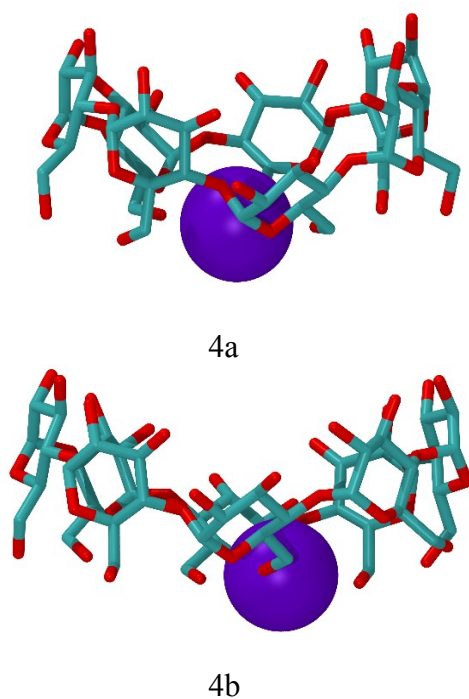


Fig. S4 The most stable computed structures of the $\beta\text{-CD} \cdots \text{K}^+$ (4a) and $\gamma\text{-CD} \cdots \text{K}^+$ (4b) complexes. Interaction energies are computed to be -50.7 and -65.0 kcal/mol for 4a and 4b, respectively.



Fig. S5 The most stable computed structures of the β -CD \cdots B21 (5a) and γ -CD \cdots B21 (5b) complexes. Interaction energies are computed to be -24.8 and -31.0 kcal/mol for 5a and 5b, respectively.

Table S1 Interaction energies (ΔE) of the studied complexes in kcal/mol

Complex	ΔE
B21 \cdots K ⁺	-82.9
KB21 \cdots K ⁺	-30.0
β -CD \cdots K ⁺	-50.7
γ -CD \cdots K ⁺	-65.0
β -CD \cdots B21	-24.8
γ -CD \cdots B21	-31.0
KB21 \cdots [β -CD + K] ⁺	-51.8
KB21 \cdots [γ -CD + K] ⁺	-51.1

Notes and References

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