アミドシクロデキストリンが疎水基に応じてリン酸アニオンを認識する機構

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Mechanism of Amide Cyclodextrin to Recognize Phosphate Anions Depending on Their Hydrophobic Groups

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An amide cyclodextrin derivative[1)] **1**$^{7+}$ bearing *N*-methyl pyridinium groups exhibited distinctive recognition modes for phosphate anions with different hydrophobic groups. Analysis by NOESY, ITC measurements and MD simulation revealed that phenyl phosphate was positioned slightly "upper" (closer to the pyridinium amide side) in **1**$^{7+}$ with the oxygen of phosphate ester R-O-P involved in the hydrogen bonds with amide N-H, and configurational entropy plays a key role in the inclusion. Meanwhile, adamantyl phosphate was positioned "lower" (closer to the methoxy rim of CD) with terminal -PO_3^{2-} forming hydrogen bonds with amides, and the hydrophobic effect is a major contributing driving force of the inclusion.

Keywords : Molecular Recognition; Amide; Cyclodextrin; Supramolecule; Hydrogen Bond

N-メチルピリジニウム基をもつアミドシクロデキストリン誘導体[1)] **1**$^{7+}$が、異なる疎水基をもつリン酸アニオンに対してそれぞれ特徴的な認識様式を示すことがわかった。NOESY や ITC 測定、MD 計算による解析から、フェニルリン酸はリン酸エステル R-O-P の酸素原子がアミド N-H による水素結合に関与することで **1**$^{7+}$の内孔のやや上方 (ピリジニウムアミド基に近い側) に位置し、配置エントロピーが包接において重要な役割を果たしていることがわかった。一方、アダマンチルリン酸は末端の-PO_3^{2-}がアミドと水素結合を形成してやや下方 (CD のメトキシ基に近い側) に位置し、疎水効果が包接における主たる駆動力となっていた。

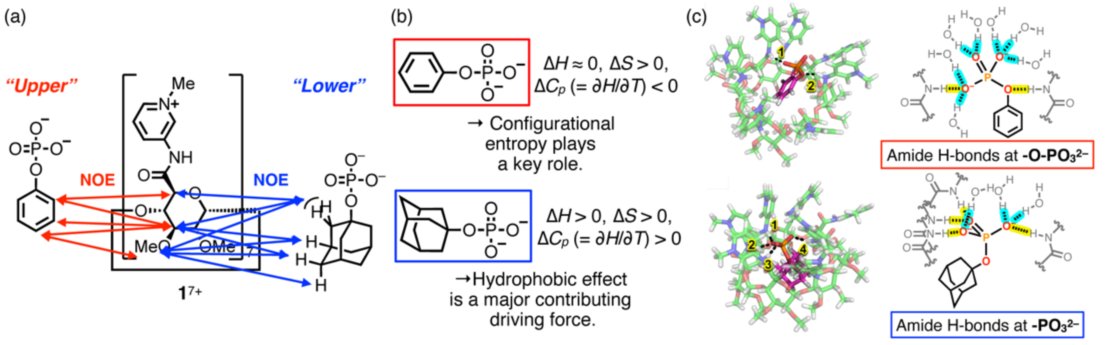

Figure. (a) NOE correlations between **1**$^{7+}$ and phosphate. (b) Results of isothermal titration calorimetry (ITC) measurements. (c) Hydrogen bonding in a snapshot of MD simulation.

1) H. Takayanagi, M. Nakahata, G. Watanabe, T. Nakamura, *103rd CSJ Annual Meeting*, K606-1am-02, **2023**.