Rim Binding of Chemically Modified γ-cyclodextrins to Hydrophobic Surface

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Cyclodextrins (CDs) are widely applied in industry because they recognize and solubilize various hydrophobic molecules. The molecular recognition of CDs has been regarded as only cavity binding. However, our group recently found rim binding modes of CDs, in which CDs recognized guests larger than their cavity size on their rims in a size-selective manner (Figure a), using atomic-resolution transmission electron microscopy (TEM). The rim binding has a potential for new application of CDs to solubilize large molecules and materials selectively. We herein synthesized several γ-CD derivatives in which the hydroxy groups at the lower rim are fully acylated (Figure b), and found that the introduction of the hydrophobic substituents to the lower rim of γ-CD enhances rim binding and suppress cavity binding to hydrophobic guests in water. Statistical analysis of TEM images of the complex of CD derivatives and conical carbon nanotubes (Figure c) reveals that the rim binding rate of Php-γ-CD was doubled from that of native-γ-CD and the cavity binding (to nanotubes smaller than 0.60 nm) has completely disappeared. The large functional groups are the key of the difference in size selectivity; the alkyl chain and phenyl group possess various interaction (e.g. C-H···π, π···π), then the structure gives the host high affinity to the surface the guest. In addition to that, the bulkiness of the structure prevents carbon nanotubes penetrating into the CD cavity. We conducted the thermodynamic analysis (Figure d) and confirmed that the rim modification alters the thermodynamics of the complexation. The complexation between Php-γ-CD and the guest becomes more enthalpically favorable through π···π interaction when compared with Bu-γ-CD.

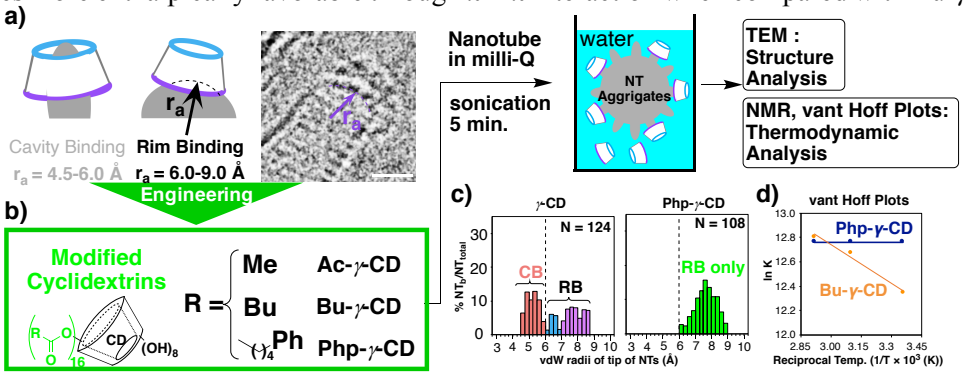

Figure. Rim binding of modified γ-CDs. a) Schematic image of cavity binding and rim binding (left) and TEM image of CD on a conical carbon nanotube (right scale bar = 1nm). b) Chemical structure of γ-CD derivatives. c) Size distribution of van der Waals radii of γ-CD- and Php-γ-CD-bound carbon nanotubes. d) van't Hoff plots of binding of Php-γ-CD (blue) and Bu-γ-CD (orange) to carbon nanotubes.