Size-sensitive Recognition of Nanometer-sized Guest by Rim-extended Cyclodextrins

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Size-selective guest inclusion to a cavity of a macrocyclic molecule is widely applied in separation chemistry and supramolecular chemistry. In contrast to the size-selective recognition of a single atom ion and a small molecule, size-selective recognition of a nm-sized guest is still difficult due to the general difficulty in synthesizing a large macrocyclic host and a large entropy loss associated with the guest binding. Our group recently reported structural identification of the binding of cyclodextrins (CD) to various sizes of hydrophobic tips of conical carbon nanotubes (NTs) by single-molecule atomic-resolution time-resolved electron microscopy (SMART-EM)[1]. CDs recognize guests by size-sensitive binding using the two rims (narrow and wide rims) in addition to the cavity (Fig.a left). We surmise that the nm-size selectivity in guest binding can be achieved by enhancing the wide rim binding (wRB) over narrow rim binding (nRB) and suppressing the cavity binding (CB) by modification of the wide rim with hydrophobic groups (Fig. a right). For this purpose, we designed rim-extended γ-CD, in which secondary hydroxy groups at the wide rim are partially acylated to maintain water solubility (Fig. b).

We synthesized three rim-extended CDs (Ac-γ-CD, Pn-γ-CD, and Php-γ-CD) bearing different hydrophobic groups and examined the binding of these CDs to the NT library by SMART-EM. The overall shape of CD in an EM image matches well with the structural model based on wRB of rim-modified γ-CDs (Fig. c). The radius-selectivity data of γ-CD and the rim-extended γ-CDs shows that binding-selectivity spectrum shifts to larger guests by introduction of longer substituents due to enhanced hydrophobic and van der Waals interactions with NTs (Fig. d). Elongation of the alkyl group (Pn-γ-CD) completely suppressed the CB binding by the steric hindrance, and installation of phenyl group (Php-γ-CD) further enhances the CD-NT interaction to show unimodal distribution ranging from 6 to 9 Å in NT diameter by rim binding.

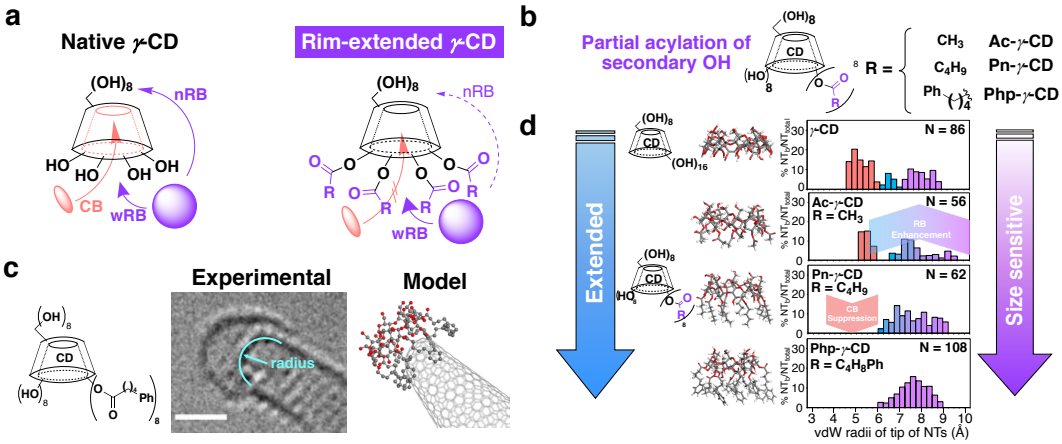

Figure. Molecular recognition by rim-extended CDs. a) Control of guest binding by acylation of secondary hydroxy groups at the wide rim. b) Chemical structure of rim-extended γ-CDs. c) TEM image of Php-γ-CD on an NT in wRB mode (left, exposure time = 250 ms Scale bar: 1 nm) and the corresponding atomic-number-correlated molecular model[2] (right). d) Histograms of the percentage of CD-bound NT per total number of NTs.

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