Alleno-Acetylenic Cage (AAC) Receptors: Chiroptical Switching and Enantioselective Complexation

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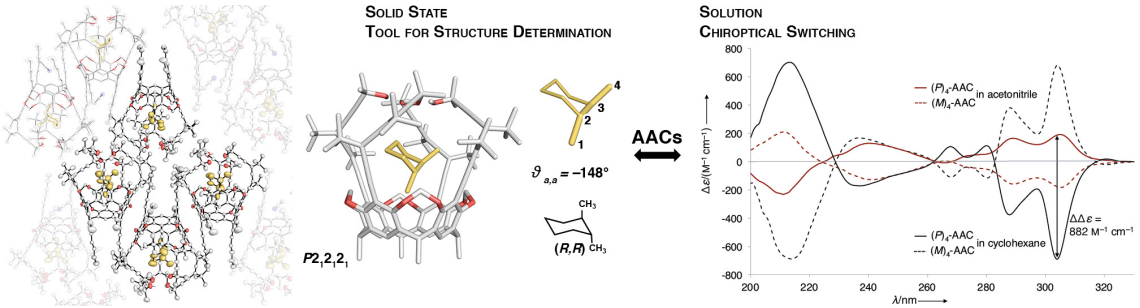
Molecular recognition in its modern definition implies that two molecules interact with each other in a specific way, with the result that their pairwise potential energy decreases more significantly than in any other interaction mode.[1] Studies on model systems have greatly helped to decipher and quantify interactions that drive enantioselective binding of chiral guests by natural and artificial host systems, establishing fundamental concepts, such as Fischer's shape complementarity and the three point interaction model.[2]

Herein, we present enantiomerically pure alleno-acetylenic cage (AAC) receptors which undergo solvent-dependent binary conformational switching in solution between a closed cage form, stabilized by a fourfold H-bonding array, and an open form.[3] Controlled switching between the open and closed state, combined with strong conformational dependence of the chiroptical properties allows for selective complexation and quantification of small molecule complexation. The highly confined chiral cavity of the closed conformation renders AACs an ideal model system to study the subtle interplay between space occupancy, conformation and chiral recognition. This system enabled the first enantioselective inclusion complex of a chiral alicyclic hydrocarbon based purely on dispersive interactions and optimal space filling, confirming the validity of the 55 % occupancy rule.[4]

AACs assemble in the solid state to a porous network forming inclusion complexes with otherwise non-crystalline small molecules allowing for the first time the structural elucidation of 1,2-substituted cyclohexanes in their (di)axial conformation in the solid state. In combination with solution studies and computational studies this allows for the investigation and quantification of interaction and conformation at the molecular level [5].



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