

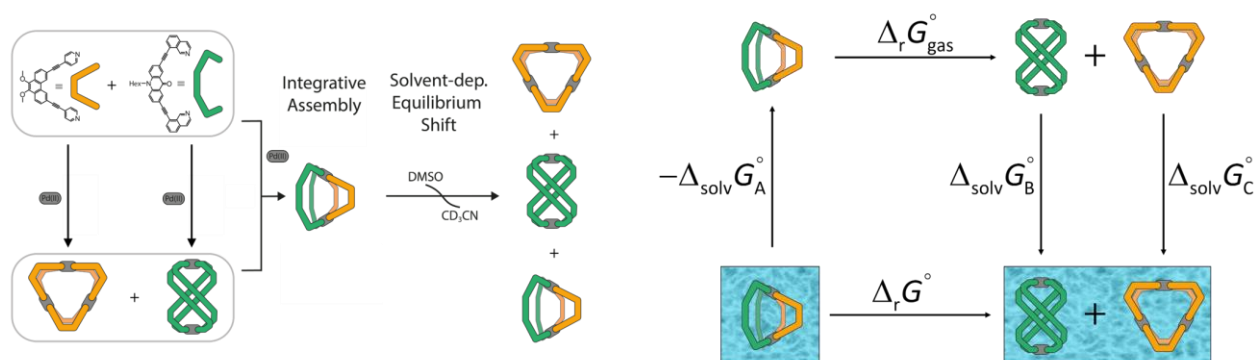
Solvent-controlled separation of integratively self-sorted supramolecular coordination cages

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In the field of metallosupramolecular coordination cages several strategies, e.g., the method of shape complementary assembly, have been established to achieve the formation of heteroleptic cage species. [1-3] Hereby the aim is to assemble only a single complex structure of a well-defined size and shape and avoid statistical product mixtures. This goal can be realized by focusing on the cage formation reaction thermodynamics. Besides the release of strain and reduction of assembly nuclearity, the influence of solvent on the cage equilibria plays a major role which must be considered. [4-6]

We here present a joint experimental and theoretical investigation of a system of integrative self-sorting palladium cages whose equilibrium is determined by the chosen solvent. [7] While only the heteroleptic cage species forms in dimethyl sulfoxide, a mixture of the latter with two homoleptic species is observed in acetonitrile. To understand the driving force of these reactions, cage assembly thermodynamics was characterized experimentally and by calculations using liquid-state integral-equation theory. Both, a high-level quantum-mechanical (QM) approach using the embedded cluster reference interaction site model (EC-RISM), and a force field (FF) model based on the three-dimensional RISM were used to model the reaction. [8]



The joint ansatz yields deep insight into the reaction thermodynamics on a molecular level. Both the QM and FF-based methods reproduce the experimental reaction Gibbs energy well. With the RISM-based approaches, guided by an experimental van't Hoff analysis, the reaction thermodynamics could be further decomposed into energetic and entropic contributions. The results indicate that the solvation entropy is the driving force due to changes in solvent-accessible volumes of the reaction partners. A more detailed solvent-structure analysis was enabled by RISM-calculated three-dimensional and radial solvent distribution functions within and around the cages.

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