

MS33 Supramolecular recognition

MS33-01

Host-guest chemistry in the solid state: stories on concomitant and sequential crystallization

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Abstract

The molecular recognition between protein and ligand is a delicate balance of multiple attractive and repulsive interactions affected by solvation/desolvation phenomena and conformational changes of one or both molecular partners. The same can refer to the simpler supramolecular host-guest systems composed of flexible partners with multiple binding interactions.[1] In reality at least some of the aqueous host-guest complexes are characterized not by one single crystal structure, but by ensemble or snap shots of various host-guest crystal forms. These crystal forms can differ in the supramolecular interactions, conformation of host or guest, and even host-guest stoichiometry. The situation is additionally complicated by solute-solvent interactions, as in aqueous supramolecular chemistry water cannot be treated as pure spectator in the host-guest complexation and crystallization. Unfortunately, the experimental crystal structure data on the host-guest supramolecular recognition rarely mirror the whole structural landscape.

Here the host-guest systems of bizarre crystallization behaviour will be discussed. The host-guest complexes with competing sets of strong non-covalent interactions and/or constrictive binding can exhibit two-step complexation and crystallization. Some cucurbit[6]uril host-guest systems reveal sequential or concomitant crystallization of metastable and equilibrium host-guest complexes. These crystal forms differ in the host-guest interaction and hydration mode. The metastable crystal complexes interconvert spontaneously into stable crystal forms *via* the solution-mediated transformation at ambient conditions. The host-guest system of carboxylated pillar[5]arene with bis-amidinium guest pentamidine is manifested as an ensemble of three host-guest crystal forms. These crystal complexes, although all based on the cavity inclusion of guest inside host, differ in the supramolecular interactions and solvation type.

Our results show that there are many challenges in terms of ruling out the principles and conditions for the concomitant or sequential crystallization of the host-guest complexes. But they also open up an exciting opportunity in terms of more holistic models of the host-guest systems. It is time to shift our focus from 'visible interactions' in one crystal structure to the appreciation of many subtle effects playing combined role in the host-guest complexation and crystallization.

References

[1] Yang, L. P.; Zhang, L.; Quan, M.; Ward, J. S.; Ma, Y.-L.; Zhou, H.; Rissanen, K.; Jiang, W. A Supramolecular System that Strictly Follows the Binding Mechanism of Conformational Selection. *Nat. Commun.* 2020, 11, 2740.