MS29 Crystal engineering: structural flexibility, phase transitions and non-standard manipulation of synthons

MS29-05

Less is more: how the lack of strong hydrogen bonds highlights the role of weak interactions.

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Abstract

Peptoids are N-substituted polyglycines with useful biological activities and interesting chemical properties both in solution and in the solid state [1].

Recently, our group evidenced how environmental changes such as temperature, humidity, gas pressure, etc.) may trigger the dynamic behaviour of cyclic peptoids in the solid state [2]. We established the solvatomorphic behaviour of a cyclic hexapeptoid decorated with four propargyl and two methoxyethyl side chains, which led to the discovery of two pure crystalline forms and four solvates [2,3]. Interestingly, the methanol solvate and the hydrate form result in a stable porous molecular framework, which adsorbs gases as propyne or carbon dioxide, but not methane [4].

By conformational energy and lattice energy calculations we demonstrated that intermolecular CH···OC backbone-to-backbone interactions are able to tighten a peptoid porous framework upon guest release by triggering a reversible single crystal to single crystal transformation at above 40°C. Thus, two propargyl side chains move by 113° and form an unprecedented "CH-π zipper", which may be unzipped by new CH···OC and CH-π interactions by exposure to guest vapors [5].

We also evidenced that the formation of stable porous frameworks based on cyclic peptoids can be triggered by strategic choice of appropriate side chains. We demonstrated that substitution of distal propargyl side chains with methoxyethyl groups in a fully propargylated cyclic octamer peptoid greatly improves the solid state stability inducing permanent one-dimensional porosity of the compound [6]. More recently we evidenced the role of intramolecular backbone-to-backbone CO···CO interactions and CH···OC hydrogen bonds in the stabilization of enantiomorphic right- and left-handed polyproline type I helices in cyclic dodecapeptoids [7].

In this contribution we will show how the lack of the amide proton prevents the formation of NH···CO hydrogen bonds and makes peptoids the ideal platform for evidencing the influence of weak interactions, as CH···OC and CO···OC interactions, in stabilizing molecular conformations, triggering conformation polymorphism and phase transitions, and ultimately determine their dynamic solid state behaviour.

References

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