MS34 Molecular recognition, supramolecular chemistry and crystal engineering

Chairs: Chiara Massera, Carl Henrik Görbitz

MS34-O1 Sense and flexibility: self-assembly, host-guest chemistry and solid state dynamic behaviour of cyclic peptoids

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The design and synthesis of artificial systems able to mimic biological functions is the aim of extensive research activity in the field of molecular nanotechnology. Cyclic peptoids for their biostability and potential diversity seem to be the ideal candidates to evoke biological activities and novel chemical properties [1].

Peptoids differ from peptides in the backbone position of the side chains, which are attached to the nitrogen atoms. Due to the lack of the amide proton, CH···OC hydrogen bonds and CH-π interactions, play a key role in the solid-state assembly of cyclic α-peptoids: face to face or side by side arrangement of the macrocycles mimick β-sheet secondary structure in proteins [2,3].

Interestingly, the side chains may act as pillars: they may extend vertically with respect to the macrocycle plane and determine the columnar arrangement of the peptoid macrocycles [3].

Moreover, the peculiar conformational flexibility of cyclic peptoids is the key to their solid state dynamic behaviour. A cyclic peptoid compound, strategically decorated with propargyl and methoxyethyl side chains, undergoes a reversible single-crystal-to-single-crystal transformation upon guest release/uptake (see figure). The extensive and reversible alteration in the solid state is connected to the formation of an unprecedented "CH–π zipper", which can reversibly open and close, thus allowing for guest sensing [4].

This contribution shows how easily tunable cyclic peptoids may lead to functional materials, that feature both robustness and adaptivity, at the frontier between materials science and biology.

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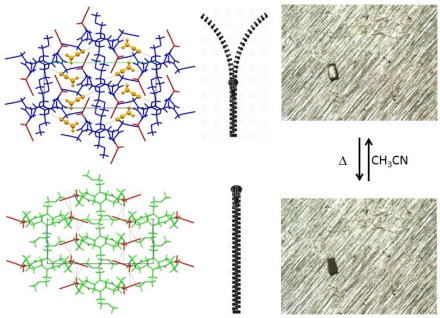

Figure 1. Single crystal to single crystal transformation upon acetonitrile release and uptake for the cyclic peptoid cyclo-(Nme-Npa$_2$)$_2$, Nme = N-(methoxyethyl)glycine, Npa = N-(propargyl)glycine. Open CH–π zipper in the acetonitrile inclusion compound and closed CH–π zipper in the desolvated form.

Keywords: Crystal Engineering, Host-Guest Chemistry, Cyclic Peptoids, CH-pi interactions