

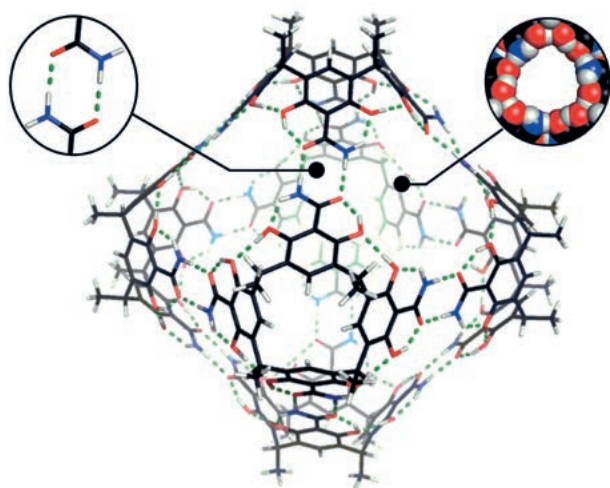
Concentration-dependent self-assembly of an unusually large hexameric hydrogen-bonded molecular Cage

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Over the last decades, the self-assembly of molecular capsules and cages using non-covalent interactions (*e.g.* hydrogen bonds, halogen bonds or hydrophobic interactions) has been intensively studied. In the case of the hydrogen-bond-based systems, the size of the assemblies formed has remained rather modest (largest volumes 1400–2300 Å³). In this work, the authors report a rational design and synthesis of a new hexameric cage with a cavity volume of ~2800 Å³. This assembly is larger than any previously known capsule/cage structure relying exclusively on hydrogen bonds. Remarkably, it is held together by only 24 intermolecular hydrogen bonds all based on simple amide–amide dimerization with a porous structure, whereas most other assemblies of this class feature a much more complex hydrogen-bonding network. This work is expected to aid rational development of future systems and provides important lessons for the design of new, more sophisticated assemblies in order to overcome the current limitations.

Authors' comments:

“Although we were able to predict the structure of the hexameric assembly, its host–guest behaviour remains puzzling: in contrast to other hexameric assemblies, it only binds fullerenes. Work to elucidate the reasons for this is ongoing.”



- Large Hydrogen-bonded Cage ($V \approx 2800 \text{ \AA}^3$)
- Concentration-dependent Self-assembly
- Encapsulation of Fullerenes

Shear stress-responsive polymersome nanoreactors inspired by the marine bioluminescence of dinoflagellates

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The light emission in response to flowing water is a phenomenon that happens in marine plankton and has been harnessed in this work to activate biocatalytic reactions. Polymersomes were formed from amphiphilic copolymers that carry complementary nucleobases in their membrane. Under turbulent mixing or flow conditions, the nucleobase pairs in the hydrophobic leaflet separate exposing their hydrogen bonding motifs and making the membrane more hydrophilic. Thus, the permeability to water-soluble compounds is highly improved. By encapsulating enzymes, nanoreactors could be generated for a variety of biocatalytic reactions, such as enzymatic polymerisations or chemo luminescence, to be controlled by external stimuli. These results open new opportunities for innovative applications such as 3D printing or force-responsive drug delivery systems.

Authors' comments:

“The work shows a transient activation of polymersome nanoreactors by mechanical forces and is a first example of force-responsive polymersomes. The ability to switch on enzymatic reactions by shear forces allows to create biocatalytic systems that mimic phenomena and reaction cascades observed in nature.”

