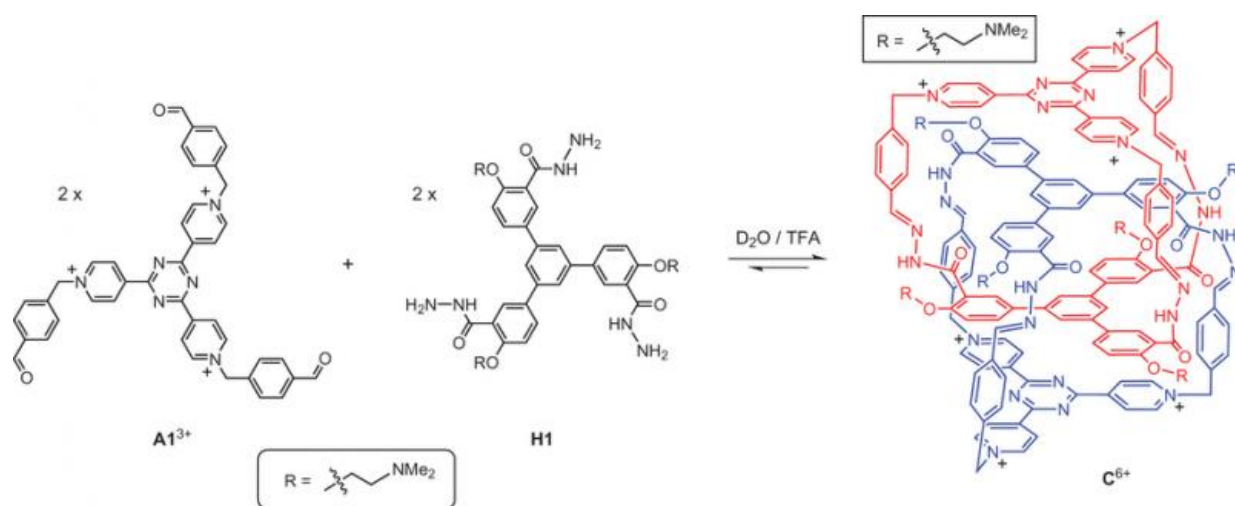


Organic catenane self-assembles in acidic water

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Structural formulae of precursors $A13^+$, $H1$ and the [2]catenane $C6^+$. Credit: (c) 2015 *Nature Chemistry* (2015). DOI: 10.1038/nchem.2392

(Phys.org)—There are many naturally-occurring supermolecular structures. Among them are catenanes. From the Latin for "chain", a catenane is comprised of two interlocked molecules, and have been found in the mitochondrial DNA of HeLa and leukemia cells. Researchers are interested in synthetically deriving catenanes using naturally-occurring conditions in an effort to understand how they formed in natural as well as exploit their unique architecture for biological and technological uses.

Catenane chemistry is typically done in organic solvents, but biological applications are predominantly in aqueous environments. Hao Li, Huacheng Zhang, Aaron D. Lammer, Ming Wang, Xiaopeng Li, Vincent M. Lynch, and Jonathan L. Sessler from Zhejiang University, The University of Texas at Austin, Texas State University, and Shanghai University have isolated and characterized an organic catenane that was made using a one-step synthesis in an aqueous acidic solvent and in relatively high yields. Furthermore, they demonstrated that their catenane is environmentally tunable and highly stable. Their work appears in the recent edition of *Nature Chemistry*.

Li, et al. built their catenane by employing organic functional groups that were not only water soluble, but would also promote self-assembly. They combined an aldehyde compound with a hydrazine in D₂O and trifluoroacetate to produce a hydrazone (-C=N-N) linkage. This synthesis was carried out over eight hours at 70°C, and evidence from HPLC-MS indicated that the resulting [2]catenane was produced in near quantitative yields.

In order to verify that they made the target [2]catenane, C⁶⁺, Li, et al. used NMR, X-ray diffraction, and mass spectrometry. NMR studies of the product compared to the starting materials demonstrated the expected proton shift for an aldehyde-amino condensation reaction. Additionally, shifts in the tetraphenyl protons indicated that they are more shielded than in the starting materials, providing evidence for placement within the cavity of the catenane.

Crystal studies confirmed the three-dimensional structure of C⁶⁺, as well as provided insights into which parts of the interlocked structure were likely stabilized by pi-pi interactions. Two different crystals were grown based on differing counterions, C⁶⁺ • 6CF₃CO₂⁻ and C⁶⁺ • 6Cl⁻. Both are made using the same synthetic procedure except for using DCl instead of trifluoroacetate. C⁶⁺ • 6Cl⁻ produced a better crystal and was used to

determine structural characteristics. This study confirmed that the structure is comprised of two interlocking cage-structures. Additionally, ESI-MS showed distinctive mass peaks for the [2]catenane.

The high yield and relative stability of C^{6+} indicates that it is thermodynamically favored over the non-[interlocked molecules](#), likely due to hydrophobic effects and pi-pi donor-acceptor interactions. To see how C^{6+} behaves in differing environments, Li, et al. added DMSO to their reaction mixture in varying ratios of water-to-DMSO. They found that as DMSO increased, the catenane dissociated into oligomers. Precipitating these oligomers and re-dissolving them in D_2O and trifluoroacetate retrieved the [2]catenane. They also determined that C^{6+} is stable at room temperature for eight hours in neutral and weakly basic solvent.

This research shows, for the first time, the synthesis and characterization of a purely organic three-dimensional catenane in aqueous media using self-assembly methods. Furthermore, the pH tunability of this catenane opens the door for biologically relevant studies in water using mechanically interlocked molecules.

More information: Hao Li et al. Quantitative self-assembly of a purely organic three-dimensional catenane in water, *Nature Chemistry* (2015). [DOI: 10.1038/nchem.2392](https://doi.org/10.1038/nchem.2392)

Abstract

Self-assembly by means of coordinative bond formation has opened up opportunities for the high-yield synthesis of molecules with complex topologies. However, the preparation of purely covalent molecular architectures in aqueous media has remained a challenging task. Here, we present the preparation of a three-dimensional catenane through a self-assembly process that relies on the formation of dynamic hydrazone linkages in an acidic aqueous medium. The quantitative synthesis

process and the mechanically interlocked structure of the resulting catenane were established by NMR spectroscopy, mass spectrometry, X-ray crystallography and HPLC studies. In addition, the labile hydrazone linkages of the individual [2]catenane components may be 'locked' by increasing the pH of the solution, yielding a relatively kinetically stable molecule. The present study thus details a simple approach to the creation and control of complex molecular architectures under reaction conditions that mimic biological milieux.

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