How to Print a Crystal Structure Model in 3D

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Supporting Information

Instructions for Printing a 3D Model of an Interlocked Molecule: Cyanostars

Mechanically interlocked molecules such as rotaxanes and catenanes can also be easily printed in 3D. As long as the molecule is correctly designed and modeled, there is no need to assemble and glue the components after printing—they are printed inherently as mechanically interlocked molecules. We present the preparation of a cyanostar-based [3]rotaxane as an example.

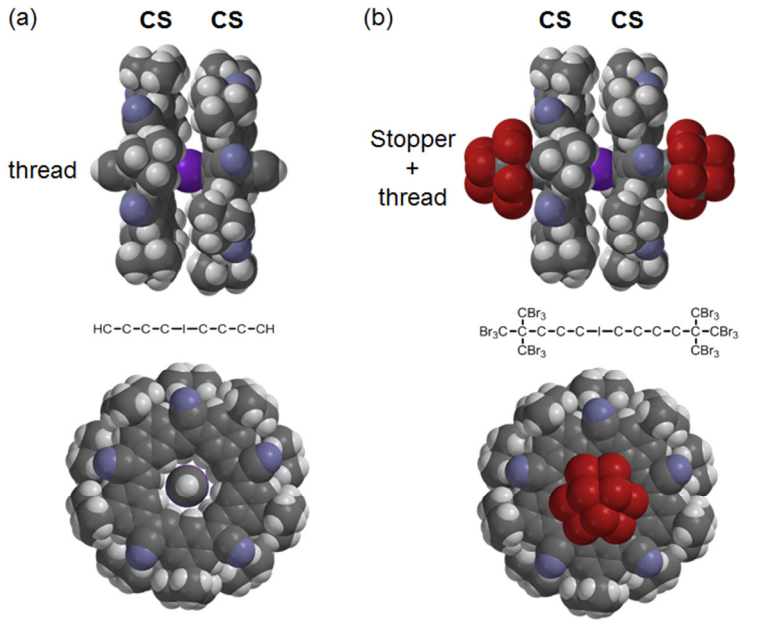

Figure S1. (*a*) Side and top view of two cyanostars (**CS**) threaded with a linear molecule. (*b*) Side and top view of a [3]rotaxane. Molecular models generated with Spartan '10.

A pair of sandwiched cyanostars[S1] (**CS**) derived from the crystal structure was "cleaned up" in the molecular computation software Spartan '10, i.e. disordered atoms were removed. A linear molecule was created and threaded through the cavity of two cyanostars (Figure S1a). Using a space filling view of the molecule, the three components were spaced sufficiently far apart to ensure that they did not make direct contact with each other when they are printed. Bulky stoppers were added to each end of the thread to form a [3]rotaxane (Figure S1b). The stopper size should be sufficiently large so that the cyanostars do not fall off. These design principles are strikingly similar to the chemical synthesis of rotaxanes. The thread and stoppers used in this model are employed as simple structural analogs. The designed molecular model was saved as a .pdb file.

The .pdb file was opened in PyMOL and modeled as spheres. Atom colors were adjusted as desired (Figure S2a). The spacing between each of the three components was double-checked to avoid direct contact between each other; particularly the central cavity of the

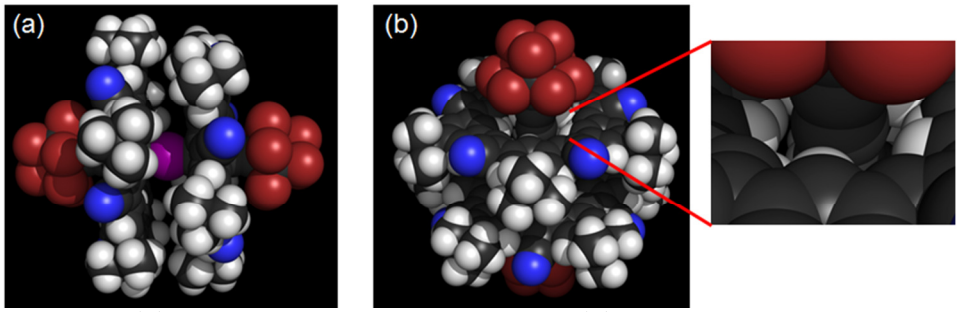

Figure S2. (*a*) Side view of the [3]rotaxane and (*b*) a tilted view with a zoom-in image of the cyanostar cavity. These images were generated in PyMOL.

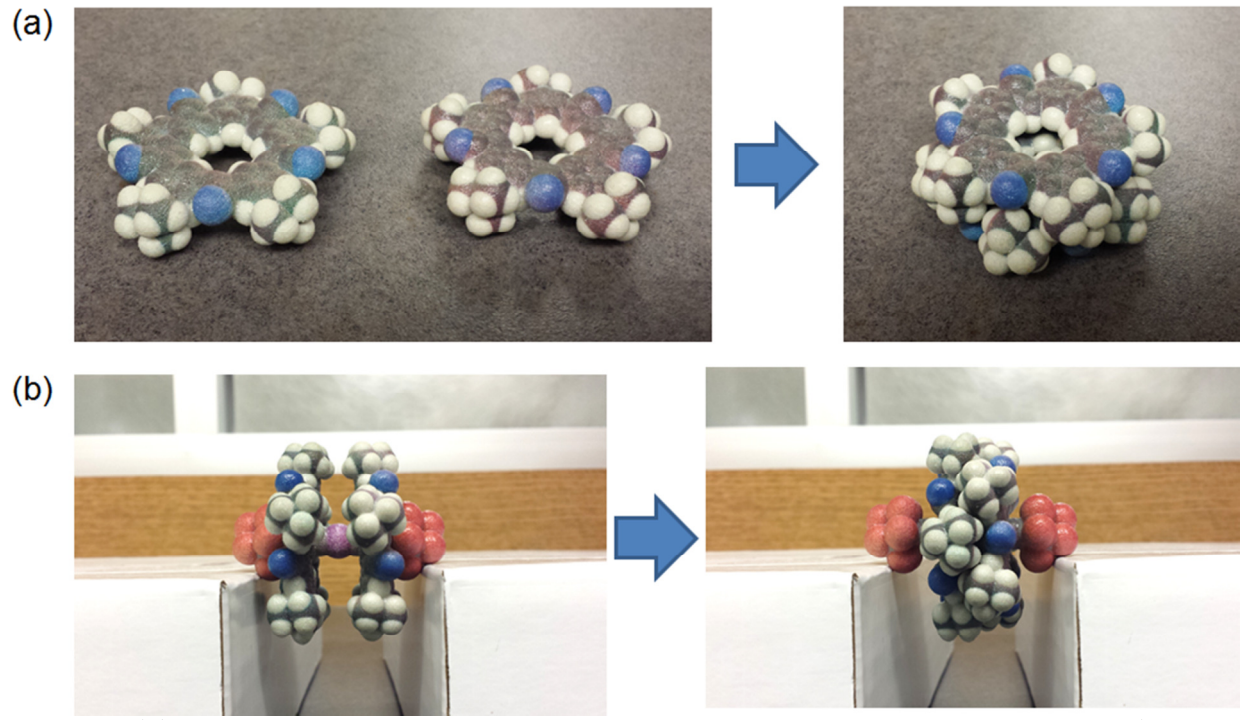

Figure S3. (*a*) Demonstration of a sandwich formation using 3D printed cyanostar models (see also movie S1) that relies upon complementarity between the curved chiral faces and steric gearing between *t*-butyl substituents. (*b*) A [3]rotaxane with movable and rotatable cyanostars (see also movie S2 for the movements and circumrotational spinning of the cyanostar macrocycles).

cyanostars (Figure 2b) to ensure the thread is not eclipsing or touching the inner cavity of the CS macrocycle. The sphere sizes can be adjusted when needed (see http://www.pymolwiki.org/index.php/Spheres). The model was saved as a .wrl file (*File* > *Save Image As* > *VRML2*) that was submitted for printing.

Instructions for Printing a "Molecular Spinning Top" in 3D: Triazolophanes

Triazolophanes[2] are rigid, shape persistent macrocycles. Their geometry minimization was performed using density functional theory,[3] and revealed completely planar structures upon halide (Cl^- or Br^-) binding to their central cavities. A 3D model can be made and printed (Figure S4) as described above for the rotaxane. Selection of Br^- (colored red) instead of Cl^- allows for a spinning top to be made, thus combining visualization with game play. The Br^- has a slightly large size (r_{ionic} = 1.91 Å) that allows it to breach the plane of the macrocycle defined by carbon (r_{vdW} = 1.70 Å) and

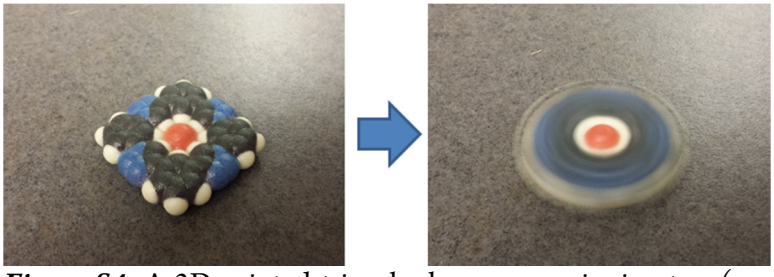

Figure S4. A 3D printed triazolophane as a spinning top (see also movie S3 of the spinning).

nitrogen (r_{vdW} = 1.55 Å) atoms. The protective coating allows it to be enjoyed equally by adults (pedagogy) and children (game play) when handled in various situations.

References

(1) S. Lee, C.-H. Chen and A. H. Flood, *Nat. Chem.*, 2013, **5**, 704–710.

(2) Y. Li and A. H. Flood, *Angew. Chem. Int. Ed.*, 2008, **47**, 2649–2652.

(3) I. Bandyopadhyay, K. Raghavachari and A. H. Flood, *ChemPhysChem*, 2009, **10**, 2535–2540.