Mechanically interlocked daisy-chain-like structures as multidimensional molecular muscles

Daisy chains are garlands of flowers often worn as bracelets or necklaces (Figure 1). Because of their beautiful structures and possibly muscle-like motions, cyclic molecular daisy chains ([*cn*]DCs, where *n* is the number of repeating units) have long been attractive synthetic targets for supramolecular chemists. The significant entropic preference for small [*c2*]DCs has meant, however, that the selective assembly of higher-order homologues ($n \geq 3$) remains highly challenging.

Figure 1. A [*c7*]DC made from flowers.

Recently, a research team led by Professor Sheng-Hsien Chiu in the Department of Chemistry at NTU described the first successful exclusive assembly of [*c3*]- and [*c4*]DCs from simple hermaphroditic monomers. They characterized these novel structures using NMR spectroscopy, mass spectrometry, and X-ray crystallography. Having assembled [*c3*]- and [*c4*]DCs selectively in solution, they prepared interlocked versions of these novel interwoven structures in respectable yields of 58 and 64%, respectively. X-ray crystallography revealed the first ever examples of the solid-state structures of molecular [*c3*]- and [*c4*]DCs (Figure 2).

These interlocked [*c3*]- and [*c4*]DCs function as artificial muscles that perform work in multiple dimensions on the molecular level. Indeed, each exists in two states characterized by the distance between the stoppering termini: "stretched" (longer) and "contracted" (shorter) forms. Switching from one state to the other occurs with the simple application of a chemical stimulus (addition and removal of Zn^{2+} ions).

The three components of the [*c3*]DC undergo their contraction and stretching events in the same plane; therefore, the [*c3*]DC moves similar to a two-dimensional molecular muscle (Figure 3a). When the [*c3*]DC switches between its planar stretched and contracted triangular forms, it changes in size by approximately 23% (as measured by the distance between its termini). The contraction/stretching motion can be reversed by adding or removing Zn^{2+} ions.

For the interlocked [*c4*]DC, the stretched and contracted states have square and tetrahedral structures, respectively. Therefore, its switching events occur with an overall three-dimensional motion. The change in distance between the termini (36%) and the change in the radius of the circumscribed sphere (18%) upon moving from the stretched to the contracted state of the [*c4*]DC make it a good mimic of biological muscle, the one-dimensional (1D) movement of which occurs with a change in size of approximately 27%. Therefore, these new structures can be considered artificial molecular muscles. Unlike 1D biological muscles, however, these compounds contract and stretch in two or three dimensions, which opens up interesting possibilities for molecular machines capable of performing mechanical work in multiple dimensions. If the muscle-like motion of such a structure could be selectively controlled in one or more dimensions, it might function as a smart (i.e., stimuli-responsive) material capable of precisely changing size or shape in 3D space on a macroscopic level; therefore, such a material would be totally and reversibly moldable at will.

The research team, which consisted of Jia-Cheng Chang, Shin-Han Tseng, Yi-Hung Liu, Shie-Ming Peng, and Sheng-Hsien Chiu of National Taiwan University and Chien-Chen Lai of National Chung Hsing University and China Medical University Hospital, published their results in *Nature Chemistry* (DOI. 10.1038/nchem.2608) in September (2016).

Reference
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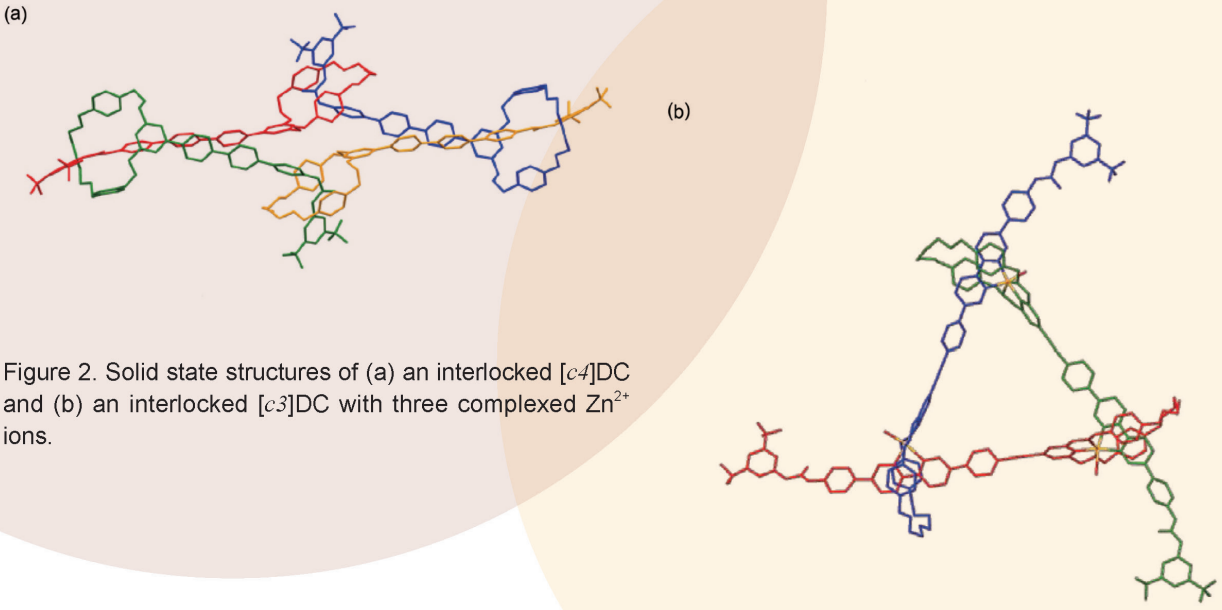

Figure 2. Solid state structures of (a) an interlocked [*c4*]DC and (b) an interlocked [*c3*]DC with three complexed Zn^{2+} ions.

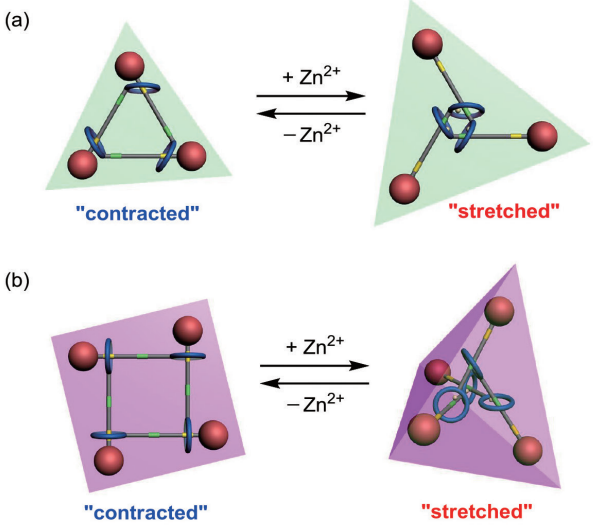

Figure 3. Switching (a) [*c3*]- and (b) [*c4*]DCs between stretched and contracted states through the addition and removal of Zn^{2+} ions.