

CHEMISTRY

'All-in-one' strategy for metalla[3]catenanes and ring-in-ring complex

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Research into mechanically interlocked molecules, such as catenanes, rotaxanes and molecular knots, has been gaining momentum in recent decades, not only because of their intriguing structures and topological importance, but also because of their important applications as molecular machines and nanoscale devices [1,2]. In addition to traditional organic macrocycles based on covalent bonds, organometallic macrocycles or rectangles based on coordination self-assembly are promising alternative building blocks for the construction of molecular interlocked structures [3]. Some complicated interlocked molecules based on a reversible coordination bond have been realized by one-step processes. Obviously, the realization of this comprehensive protocol requires careful selection and elaborate design of the precursor and ligand. Despite extensive research and several stunning breakthroughs in the

synthesis of interlocked molecular species, linear [3] catenanes and the ring-in-ring complex are exceedingly rare, and their targeted synthesis remains a formidable challenge [4].

Recently, Prof. Guo-Xin Jin from Fudan University (Shanghai, China) made exciting progress and developed coordination self-assembly of metalla[3]catenanes, molecular Borromean rings (BRs) and a ring-in-ring complex using a simple π -donor unit [5].

In this work, the authors used bithiophenyl groups as building blocks to replace the widely used phenylene or polycyclic aromatic groups for enhancing the stacking interactions. In this way, a series of metalla[2]catenanes, linear metalla[3]catenanes and BRs based on an organometallic half-sandwich unit were realized by high-yield and one-step processes (Fig. 1). The bithiophenyl groups effectively enhance the strength of the

inter-ring interactions and play a crucial role in the formation of these homogeneous interlocked molecules.

Generally, macrocycle or cages based on coordination self-assembly commonly bear several positive charges and are more suitable for encapsulation of electroneutral or electron-rich guests than of electron-poor cations because of the Coulombic repulsion between host and guest. However, the authors took advantage of strong electrostatic interactions between electron-rich (π -donor, D) and electron-deficient (π -acceptor, A) aromatic groups to overcome the Coulombic repulsion and realized the introduction of the electron-deficient methylviologen cation into cationic metallarectangles. Following this logic, a heterogeneous D-A ring-in-ring complex was successfully prepared by threading a cationic metallarectangle based on an electron-deficient naphthalenediimide

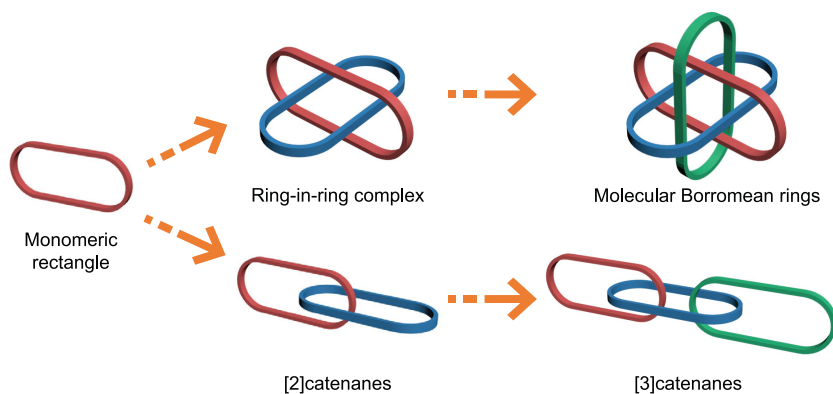


Figure 1. Various interlocked structures: monomeric macrocycle; ring-in-ring complex; Borromean rings; [2]catenanes; linear [3]catenanes.

(NDI) unit inside a metallarectangle based on electron-rich bithiophenyl groups. On this basis, the method for a heterogeneous D-A ring-in-ring complex was extended by use of a metallarectangle based on a pyrenyl group.

The work of Prof. Guo-Xin Jin's research group provided new ideas for designing the complicated topologic interlocked structures and will help

the understanding of coordination self-assembly and boost the development of organometallic assemblies. It demonstrates how the formation of the resulting structures can be well controlled and modulated by the incorporation of various types of noncovalent bonding interactions into complex self-assembly systems. Moreover, this self-assembly process takes us one step past efficient

construction to seeking possible applications through rational design.

Conflict of interest statement. None declared.

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