Supramolecular self-sorting: A route to sophisticated multi-interlocked molecular muscles

Interlocked molecular machines are promising targets in the domain of nanotechnology. Among molecular machines, the doubly interlocked “molecular muscle” architecture (Fig. 1) is of particular interest. It consists of the interweaving of two so-called “hermaphrodite” monomers: since theses monomers each possess a macrocycle linked to a molecular tail that contains a recognition site for the macrocycle itself, two monomer units can self-assemble into the peculiar interlaced structure.

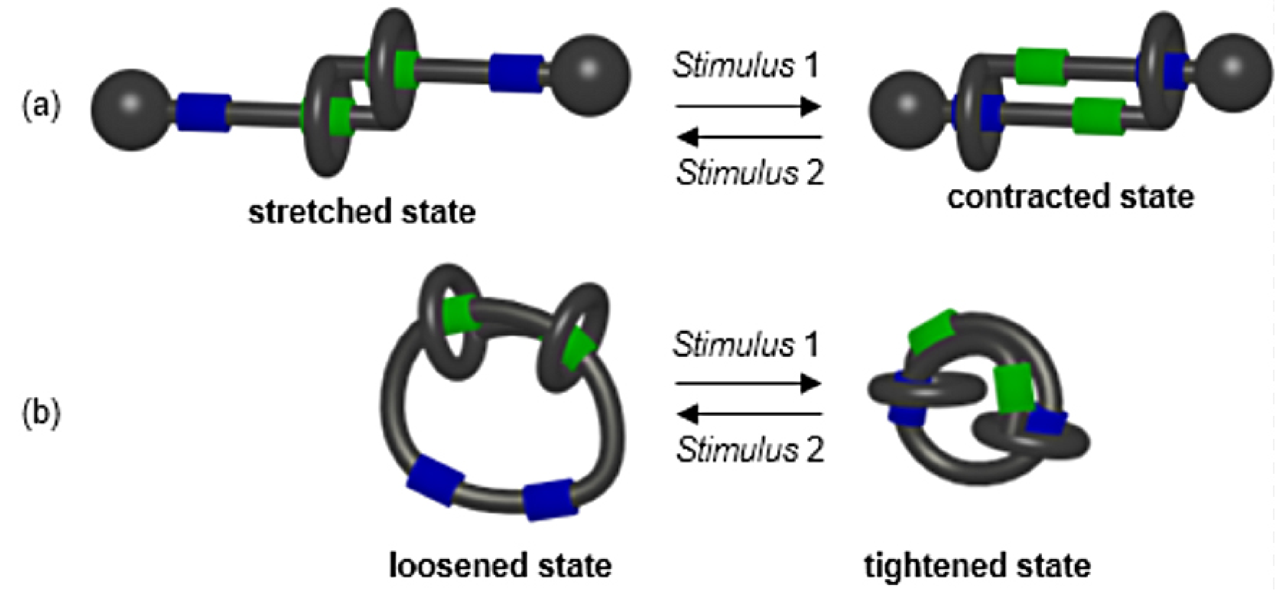

Fig. 1. Cartoon representations of: (a) a linear molecular muscle, (b) a cyclic molecular muscle

When the molecular axle contains several sites of recognition of different affinities for the macrocycle, the doubly interlocked molecule (*i.e.* a rotaxane dimer) can behave as a molecular muscle that has the possibility to tighten and stretch depending on an external *stimulus*. This motion, if accurately controlled, can lead to molecules of different shapes with different physical and/or chemical properties, which is of real high interest. Since the first synthesis of an interlocked molecular muscle was reported by J.-P. Sauvage in 2000, only a few original examples of such an architecture have been reported, probably because of their challenging synthesis. Figure 1 reports the two [c2]daisy chain-based linear and cyclic molecular muscle architectures known to date.

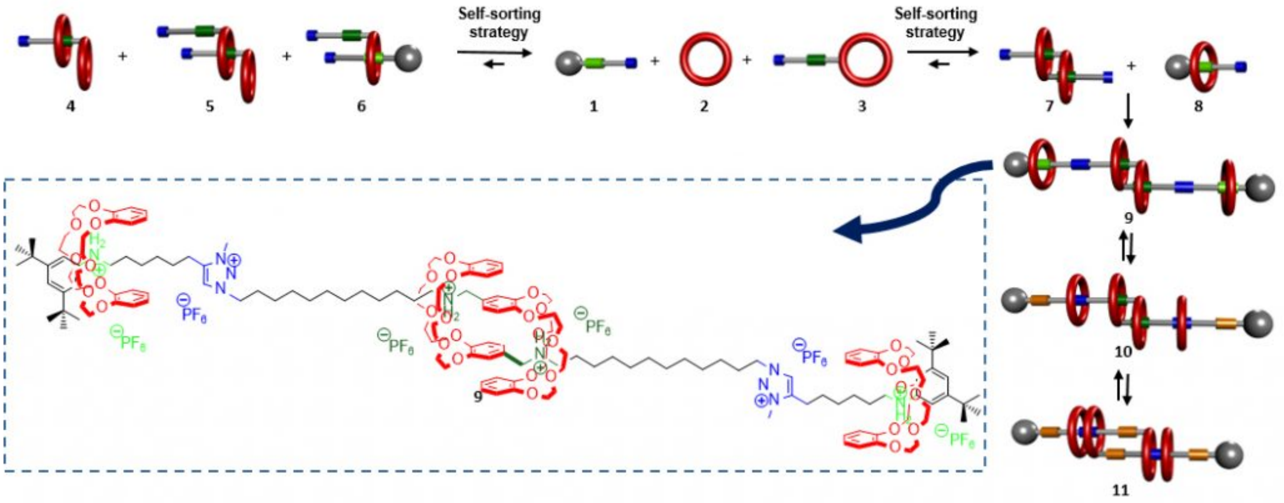

Fig. 2. Self-sorting strategy toward the hetero[4]rotaxane molecular machine

In the published paper, we investigated a new route to a more sophisticated pH-sensitive tetra-interlocked molecular muscle that we can call a hetero[4]rotaxane. The novel architecture combines a doubly interlocked rotaxane dimer (*i.e.* a molecular muscle moiety) linked to two [2]rotaxane arrangements (Fig. 2, compounds 9, 10 and 11). Combining the gliding motions of macrocycles along threads in respectively a rotaxane dimer and two separate rotaxane units in a sole molecule has never been realized so far. It certainly provides supplementary information in the molecule since more *co*-conformational states (*i.e.* shapes) of the molecule can be envisaged. The molecular precursors 1, 2 and 3 have been designed so that affinities of the considered molecular axles for macrocyles could selectively yield the supramolecular species **7** and 8. Indeed, the molecular axle 1 prefers to be threaded by the sole macrocycle 2 (to give the semi-rotaxane 8), while “hermaphrodite” monomer 3 prefers to self-assemble to provide the rotaxane dimer scaffold **7**. No other supramolecular species (*i.e.* 4, 5 and 6) was detected in the mixture. Connecting the compounds **7** and 8 very efficiently led to the tetra-interlocked molecular target 9. The subsequent reversible pH-sensitive molecular machinery was also reported and demonstrated the possibility of several co-conformational states. Taking advantage of such sophisticated structures in various investigation fields is under way.

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