

## Radical-Radical Templatation in Mechanically Interlocked Molecules

*Marco Frasconi*

Department of Chemical Sciences, University of Padova, Via Marzolo 1, Padova 35131, Italy

The self-assembly of molecular building blocks into the desired structures plays a fundamental role for the development of functional materials. The precise control of noncovalent bonding interactions has allowed to develop a variety of template-directed protocols and to explore the possibility of wholly synthetic molecules to perform advanced tasks, such as muscle-like contraction and expansion. Here, we highlight the introduction of radical-pairing interactions into mechanically interlocked molecules (MIMs), from the development of protocols for the template-directed synthesis of MIMs to their redox controlled actuation. The formation of reversible weak noncovalent  $\pi$ -homodimers by radical species, particularly by tetrathiafulvalene (TTF) and 1,1'-dialkyl-4,4'-bipyridinium (BIPY), has received much attention in the past half-century because of the ease of their preparation and well-organized assemblies. The tendency of bipyridinium units in their reduced radical-cation state to form inclusion complexes with the diradical dicationic cyclobis(paraquat-phenylene) ring has been investigated mechanistically and quantitatively. We have employed the remarkable stabilization associated with this inclusion complex for the development of radical template-directed strategies for synthesizing MIMs. By using these strategies, we have constructed BIPY-only based catenanes and rotaxanes. In addition to providing supramolecular assistance in the syntheses of MIMs, radical-pairing interactions introduce switching behaviour into the resulting MIMs along with optical, conducting, and magnetic properties. We have used chemical, electrochemical, and photochemical approaches to achieve the reversible actuation of BIPY-based MIMs. Electrochemical investigations performed on the rotaxanes indicate that their mechanically interlocked structures lead to the enforced interactions between the dumbbell and ring components, allowing them to contract in their reduced states and expand in their fully oxidized states as a result of Coulombic repulsions. The ability to tailor the properties of MIMs by radical-pairing interactions and the electrochemical modulation of their actuation paves the way for the investigation of more complex processes at the molecular and supramolecular levels, such as the operation of artificial molecular machines that function by transducing electrochemical energy into mechanical work at the nanoscale.