DIPARTIMENTO DI CHIMICA

SAPIENZA
UNIVERSITÀ DI ROMA

Seminario di Dipartimento
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Geometrical and Topological Effects in Molecular Recognition and Self-Assembly Processes

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The topology of molecules has been conjectured to play a fundamental role in a wide range of physicochemical and functional properties of molecules.[1] Despite the significant implications of topology, this aspect has not been explored significantly yet by chemists. By contrast, the practical importance of topology has been demonstrated in the field of polymer science, where the topological effects have been mastered in order to control the mechanical properties of polymers. Here, we highlight the significance of mechanical bonding and topology on the close interactive disposition of radical cation dimers of (i) singly oxidized tetrathiafulvalene (TTF) and (ii) singly reduced bipyridinium ($BIPY^{2+}$) units. We report how topology, within the context of mechanical bonding in a [3]- and a doubly interlocked [2]catenane (a molecular Solomon link), controls the redox properties and the radical dimerization of two TTF units within the isomeric molecular frameworks. The complete collection of experimental data in solution and in the solid state points to a fundamental connection between the topology of the molecules and their geometries and properties. 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 also investigated mechanistically and quantitatively. The remarkable stabilization associated with this supramolecular entity has been employed in the template-directed synthesis of mechanically interlocked molecules[2] as well as a means to control inter- and intramolecular mechanical motions.[3] The ability to tailor the properties of unnatural molecules by controlling their topologies paves the way for the investigation of more complex processes at the molecular and supramolecular levels, such as the actuation of artificial molecular machines[4] that functions by transducing electrochemical energy into mechanical energy at the nanoscale.

References

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