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Molecular and Supramolecular Multiredox Systems

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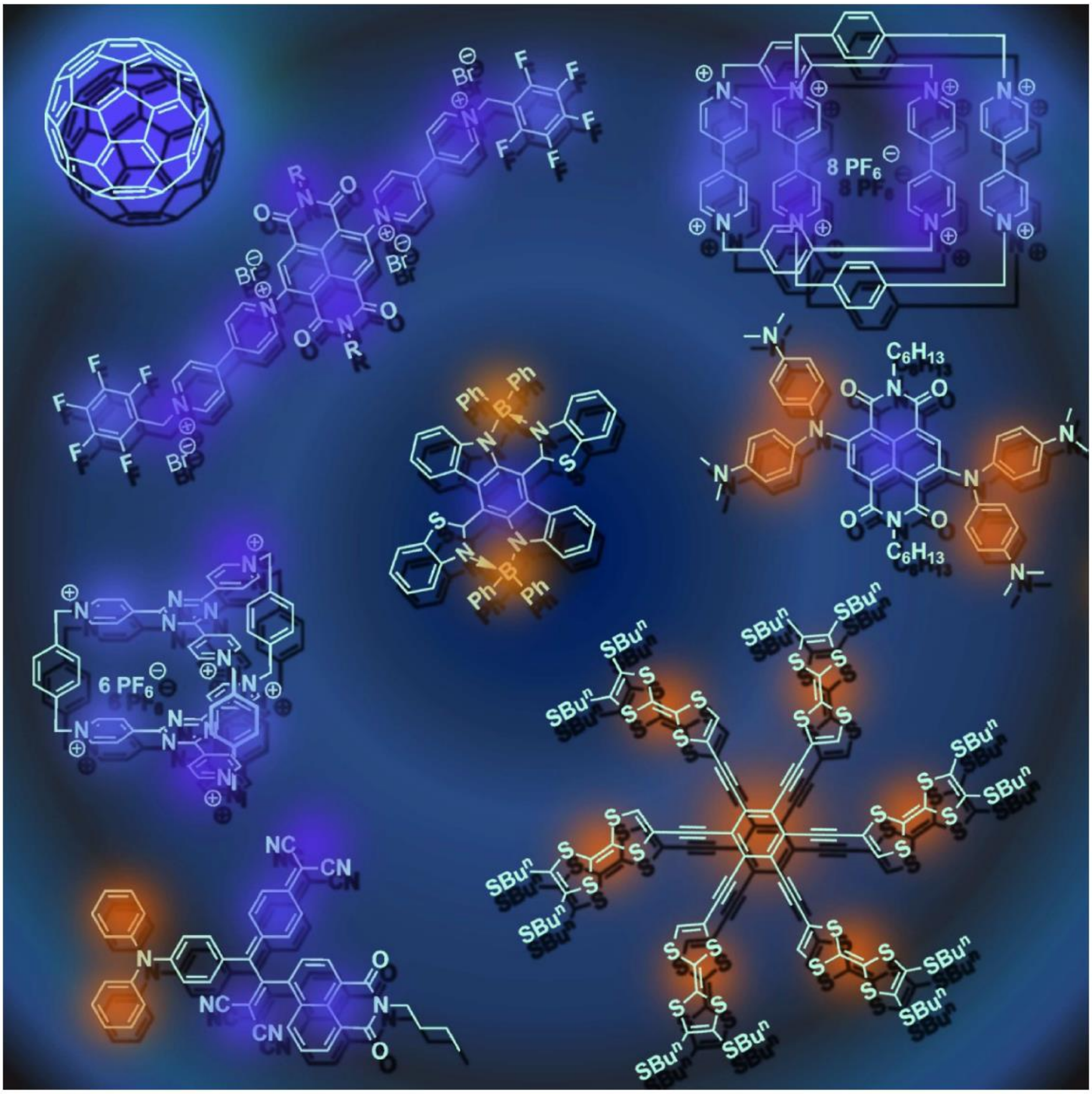

The design and synthesis of molecular and supramolecular multiredox systems have been summarized. These systems are of great importance as they can be employed in the next generation of materials for energy storage, energy transport, and solar fuel production. Nature provides guiding pathways and insights to judiciously incorporate and tune the various molecular and supramolecular design aspects that result in the formation of complex and efficient systems. In this review, we have classified molecular multiredox systems into organic and organic-inorganic hybrid systems. The organic multiredox systems are further classified into multielectron acceptors, multielectron donors and ambipolar molecules. Synthetic chemists have integrated different electron donating and electron withdrawing groups to realize these complex molecular systems. Further, we have reviewed supramolecular multiredox systems, redox-active host-guest recognition, including mechanically interlocked systems. Finally, the review provides a discussion on the diverse applications, e.g. in artificial photosynthesis, water splitting, dynamic random access memory, etc. that can be realized from these artificial molecular or supramolecular multiredox systems.

1. Introduction

Multiredox systems have major importance in wide ranging areas such as high energy density batteries, solar fuel production, catalysis, sensors, photosynthesis, and cellular respiration. Research progress in synthetic and supramolecular chemistry has led to complex artificial systems that can attempt to mimic intricate biological processes.[1] Countless biological processes require multielectron transfer reactions for conversion of energy that can be utilized for chemical transformations.[2] These processes involve proton and electron tunneling, light absorption, excited electronic state formation and excited state energy transfer. These processes occur in cellular respiration, photosynthesis, DNA UV-damage repairs, neurotransmitters and many other complex biological reactions.[3] Multiple electron transfer reactions can also have great importance in those biological processes which require stable reduced and oxidized intermediate states of organic molecules.[4]

Most of the practically important electrochemical reactions such as photosynthesis, proton reduction, CO_2 splitting and water oxidation are multi-electronic in nature and have substantial kinetic barriers for electron transfer.[5,6] Therefore, for the practical sense of required energy input, we need to design the electrode surface in such a way that can increase the electron transfer rate. Thermodynamically simple processes like, hydrogen oxidation and dioxygen reduction also have multi-electronic nature and requires multiredox active electrocatalysts to accelerate the reaction rate. Nature gives us valuable lessons about how to assemble such complex self-assemblies with precisely defined functional components.[7]

There is a significant challenge for material and biological scientists to design and synthesize such complex molecular materials which can store and transfer multiple electrons at low operational potentials to the substrate and are stable under ambient condition.[7c] In this review article, we make an effort to provide a concise overview of the recent multiredox systems.

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2. Classification of Multiredox Systems

A large class of molecular and supramolecular redox systems have been synthesized having attractive optical and electronic properties. The multiredox systems of interest, in this review, are that can perform at least four-electron transfer processes. We have classified multiredox systems in three broad categories:

1. Organic multiredox molecules
2. Organic-Inorganic Hybrid multiredox molecules
3. Supramolecular multiredox systems

2.1. Organic Multiredox Molecules

Construction of multiredox active organic molecules are of particular interest owing to their importance in advanced functional materials and also as molecular catalysts for multi-electron transformation processes.[8] These multiredox active organic scaffolds can vary from small molecules, dendrimers to oligomers and polymers.[9] Depending on their electronic properties, these multiredox active molecues can be further categorized into three classes: I. Multielectron acceptors, II. Multielectron donors, and III. Multielectron ambipolar systems, which can donate and accept the multiple electrons simultaneously.

2.2. 1. Organic Multi-electron Acceptors

For the past three decades, synthesis of organic molecules with strong electron accepting and n-type semiconducting properties have been stimulated by the global need for efficient and cheap electronic devices to access renewable energy sources.[10] Towards this endeavour, an understanding of the elementary relationship between the molecular and supramolecular structures and their opto-electronic properties are needed. In general, the multielectron acceptors are constructed by con-