

Investigation of the Electronic Structure and Spectroscopy of Organometallic and Transition-metal Nanostructures

The realization of the nanomaterials with specific topology and supramolecular architecture useful for high-performance nanoscale devices is currently one of the main challenges in nanotechnology. Here we highlight our recent research activities on inorganic/organometallic functional materials for molecular electronics, light harvesting and photocatalysis.

Covalent and non-covalent donor-acceptor (D-A) assemblies were intensively studied during the last several decades due to their potential use in solar energy to electricity conversion. In order to archive the high efficient solar energy conversion, the formation and stability of the long-living charge-separation state, which can be controlled by the electronic structure, type of the linking group, and geometric orientation of the light-harvesting donor and electron acceptor, is required. The D-A assemblies with covalent bonds can be controlled by the nature of the linking group. However, the preparation often requires several additional synthetic steps, which make such structures less attractive for industrial applications. An alternative approach is the formation of well-organized non-covalent assemblies, which can be controlled by dispersion interactions.

We have prepared the non-covalent complexes formed between C_{60} and C_{70} fullerenes and substituted boron subphthalocyanines (Fig. 1a) and examined the tunability of the subphthalocyanine core toward finding a stronger binding fullerene receptor, which improve photovoltaic characteristics of heterojunctions by facilitating the electron-transfer from subphthalocyanine to fullerene [1]. It has been found that the hexathiophenol-containing receptor shows the largest interaction energy with fullerenes that confirmed by UV-vis data (Fig. 1b) and extensive DFT calculations (Fig. 1c).

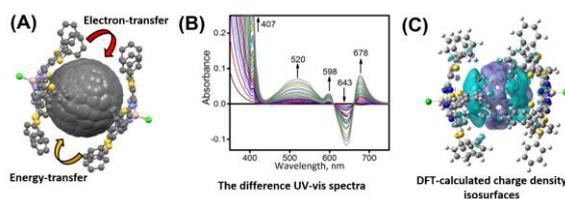


Fig.1: Non-covalent complex formation in subphthalocyanine/fullerene system.

These systems were thought as a low-cost alternative to the traditional organic light-harvesting modules for organic

photovoltaics.

New trinuclear Fe-Ru-Fe tetraphenylporphyrin complexes axially coordinated with various ferrocene-based ligands, were prepared and characterized [2]. It was observed that the first oxidation process was attributed to the reversible oxidation of the Ru^{II} center, which is important for their application as molecular wires (see Fig. 2). DFT and time-dependent DFT calculations aided in correlating the spectroscopic and redox properties of studied complexes with their electronic structures.

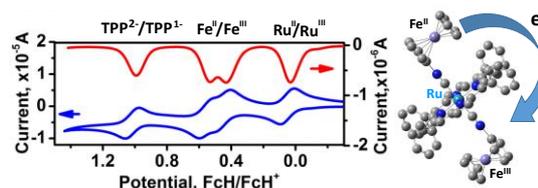


Fig.2: Trinuclear porphyrin/ferrocene complexes [2].

New spherical organic-inorganic ferrocene-tin hydroxide clusters of general formula $[(FcSn)_{12}O_{14}(OH)_6]X_2$ were prepared and analysed [3]. DFT and TDDFT calculations suggest that the organometallic substituents in the $[(FcSn)_{12}O_{14}(OH)_6]^{2+}$ core are rather isolated from each other, and thus such a cluster can be potentially used as an electron reservoir, which can provide up to 12 electrons toward chemical processes.

References

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