Spiralinės orbitalės ir sukinio-orbitos sąveika paprastose angliavandenilio molekulėse

Helical molecular orbitals to induce spin-orbit coupling in simple hydrocarbon molecules

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Spin-orbit coupling (SOC) is a relativistic interaction between the spin and orbital motion of an electron that unlocks transitions between singlet and triplet states. [1] Strong SOC is a desirable property in organic molecules as it mediates intersystem crossing (ISC) in photosensitizers for phtotodynamic therapy and reverse ISC in emitters for organic light emitting devices (OLED). Generally, spin-flip probability depends on the magnitude of magnetic moment arising from electron’s orbital motion in the electric field of a nucleus, thus SOC is proportional to Z^4, where Z is an atomic number. However, significant SOC can be achieved in molecules composed of light elements when spin-flip is induced by large enough orbital momentum created by mixing of orthogonal molecular orbitals (MOs).

Recently, SOC was suggested to appear in chiral hydrocarbon systems due to electron‘s motion in helical potential. Geometric SOC due to helical potential was identified in chiral structures such as DNA. While SOC interactions were only explored in chiral molecular structures, helical potential also appears on a smaller scale as helical molecular orbitals (hel-MOs) in linear carbon chains (oligoynes). The formation of helical π-system is enabled by overlap of orthogonal p orbitals in sp hybridized carbons where nodal plane rotates around the axis of chain (unlike sp2 carbons that form a planar nodal plane). The importance of evaluating spin-orbit coupling in carbon wires is significant due to recent advances in chemistry of oligoynes.

In this work, we use a combination of ultrafast spectroscopy and quantum chemical calculations to relate enhanced ISC rate to hel-MOs in oligoyne-bridged bifluorene derivative (Figure 1). We demonstrate that simple modification of the bifluorene bridge unit from alkyne to diyne, leads to emergence of distinct helical orbitals together with activation of strong ISC pathway. Transient absorption studies showed singlet-to-triplet ISC rate of up to 6 ns^{-1} resulting in 0.84 triplet yield. Density functional theory (DFT) computations suggested strong SOC between singlet and triplet states of ππ* character, which expands the use of El-Sayed rules and interpretation of spin-orbit coupling in simple hydrocarbons. These findings suggest that oligoyne bridge units could be implemented in the design of new organic photosensitizers or emitters aiming to achieve substantial spin-orbit coupling. [2]

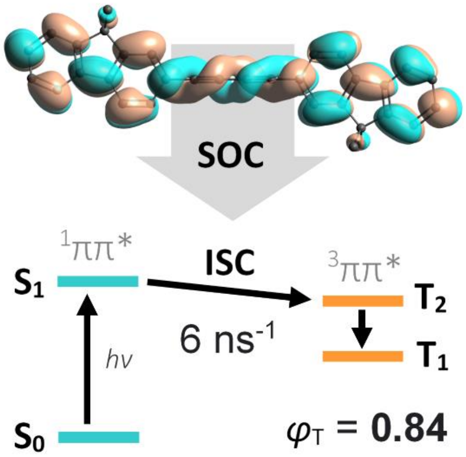

Fig. 1. Molecular orbitals of oligoyne bridged bifluorene and the corresponding energy level diagram.

Literatūra

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