

ELECTRON TRANSFER IN HALOGEN BONDED CO-CRYSTALS

Alva D. Dillon, Glake Hill and Wojciech Kolodziejczyk

Department of Chemistry and Biochemistry, Jackson State University, 1400 J.R. Lynch Street, Jackson, Mississippi 39203, USA

Abstract: Organic electronics are at the forefront of research to produce more cost efficient and effective products. Though, not as efficient, they give the possibility of lighter flexible electronic devices vs inorganic materials. Conductive organic materials fall into the category of polymers or molecular solids and salts. Model molecular solids consist of small molecules like pentacene and anthracene. One early discovery of a charge transfer complex, include pyrene and halogens which form charge transfer salts with semiconducting behavior. The molecules under question are bithiophene-pyridine derivatives, acting as a halogen bond donor, along with a halogen bond acceptors derived from 1-iodoethenylbenzene. Computational methods are used to answer the question of how efficient is charge transfer in these co-crystals with Marcus theory of Electron Transfer and what molecular properties make them efficient. Marcus theory consist two key parameters: the electronic coupling term and reorganization energy. Reorganization energies have been evaluated in the adiabatic and nonadiabatic cases. Modeling reorganization energies are done by calculating transition states, in the non-adiabatic case, and evaluating the sum of two relaxation energy terms, in the adiabatic case. Electronic coupling terms evaluated using the energy splitting of dimers which measures the coupling of the orbitals of interest and a direct method which uses the Fock matrix of the dimer system and molecular orbital vectors of non-interacting monomers to obtain the Fock transfer integral. Our molecules were specifically engineered to produce a significant sigma hole on the halogen to strengthen the interaction with the donor. The donor molecule consists of three conjugated rings, where one ring acts as an acceptor and the other two as donors. In the ground state these systems are perpendicular, however, upon excitation there is a planarized intramolecular charge transfer (PICT) between the two ring systems resulting in a planar configuration. When this rotation occurs, it couples the π systems, therefore, in experiment upon excitation quantum yields for the observation of fluorescence should be high. Analyzing the theoretical mobility values, reorganization energies, electronic coupling terms, and planarized intramolecular charge transfer energetics will characterize whether the molecules have the potential to be dominantly n- or p- type semiconductors. Frequency calculations were carried out in ground states and the excited states to verify stationary points. All calculations were done at the density functional level (DFT) of theory using Gaussian basis sets including diffuse and polarization functions for calculations on dimers. To tie off the characterization, in the crystal structure our molecules have restricted intramolecular motion. With the restriction of molecular motion different properties of the crystal structures will be revealed.

Keywords: Charge transfer, halogen bonds, Marcus theory, computational chemistry, density functional theory