Relationship between Structure and Property in Organic Semiconductors by an Electron Density Analysis

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Organic semiconductors have received an intensive academic and commercial interest due to their promising optoelectronic and charge transfer properties to develop all organic or hybrid organic-inorganic electronic devices such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and photovoltaic cells.[1] Rubrene (5,6,11,12-tetraphenyltetracene, RUB) is one of the most explored compound in the context as it has nearly 100% fluorescence quantum efficiency in solution and high p-type mobility up to 20cm^2/Vs.[2] The high charge-carrier mobilities is attributed to π···π interactions between tetracene backbones in the crystal packing. However, an exact mechanism of the charge carrier transport and charge injection in organic semiconductors remains unknown. In the same time, rubrene undergoes an oxidation in the presence of light to form rubrene endoperoxide (RUB-OX).[3] RUB-OX molecules show reduced semiconducting properties due to the lack of π···π interactions between the RUB-OX molecules.

We have determined the electron density distribution on RUB and RUB-OX using the combination of X-ray and neutron diffraction data. The ADPs of hydrogens were obtained from the SHADE server[4] in the absence of neutron data. The presence of $C_\pi \cdots C_\pi$ interactions between neighboring tetracene backbones of the RUB molecules is experimentally demonstrated from a topological analysis of the electron density, Non-Covalent Interaction (NCI) analysis (Fig. 1) and the calculated interaction energy of molecular dimers. In addition, a significant contribution to the lattice energy of the crystal is provided by H–H interactions. We bring out the structural differences between RUB and RUB-OX to correlate with their semiconducting properties in the crystalline state.

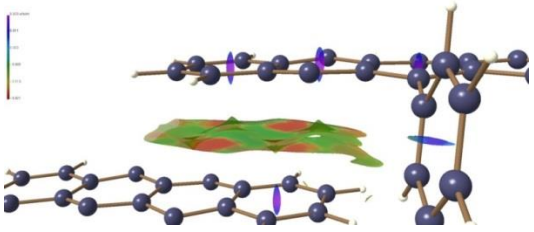

Fig 1: RDG-based NCI isosurfaces for π···π stacking interactions obtained from the experimental ED model.

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