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14. ABSTRACT

Density functional calculations were performed for polymers including PBTTT, P3HT, and PQT. To understand the origin of the high mobility and molecular ordering in PBTTT, the atomic and electronic structure was calculated. The calculations predicted that the conjugated planes exhibit a rotation (tilt) around the polymer axis. The degree of tilting depends on the alkyl-side-chain length. Tilting reduces the inter-chain molecular overlap, and this lowers the hole mobility. Calculations for PQT and P3HT show that tilting occurs in these materials also. This discovery led to a natural interpretation of NEXAFS data, which confirms the predicted tilt. It was shown that backbone tilt is a consequence of electrostatic energy reduction. A simple model of scattering indicates the mobility could be reduced by 60 percent by the tilt. Ozone was investigated as an impurity in PQT. Calculations show that ozone molecules that are weakly attached to the conjugated chains give rise to acceptor levels in the gap. This shows that ozone can dope the material p-type, and must be prevented from interacting with organic semiconductor devices. An expt./theoretical study of O2 in pentacene indicated that a positive gate voltage can cause dissociative interaction of O2 with pentacene.

15. SUBJECT TERMS

organic semiconductors, PBTTT, P3HT, PQT, polythiophenes, pentacene, defects, mobility

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Annual accomplishments: We performed calculations of the atomic and electronic structure for the organic semiconductor poly(3,6-dialkylthieno[3,2-b]thiophene-*co*-thieno[3,2-b]thiophene), which we refer to as PATT. The construction of PATT is such that the separation between the alkyl side-chains is intermediate between the separations in P3HT and PBTTT. An objective was to test whether this intermediate side-chain separation leads to increased bonding strength between layers, and perhaps promotes greater crystalline order and mobility. Density functional calculations for interdigitated and non-interdigitated structures of PBTTT and PATT were performed which indicate that the binding is indeed larger in PATT than in PBTTT (by 40%). Colleagues at PARC and Imperial College (Iain McCulloch) have characterized the properties of PATT and a paper including theoretical and experimental results (mobility, structure, and thermal properties) was submitted for publication. (J. E. Northrup, M. L. Chabinyc, R. Hamilton, I. McCulloch and M. Heeney, *Theoretical and experimental investigations of a poly-alkylated-thieno[3,2-b]thiophene semiconductor*.)

We have argued that the energetic instability of perfectly cofacial (i.e. untilted) polymer backbones is a general characteristic. Therefore, a general mechanism must underlie this property. We developed a model that explains the origin of the backbone rotation: We showed that the driving force for the rotation is the reduction in electrostatic energy that occurs upon tilting of the backbones.

Detailed investigations of the interaction of O_2 molecules with pentacene were performed. Based on calculations of formation energies of charged defects a model was developed which explains why a positive gate voltage, which attracts electrons to the semiconductor/dielectric interface, leads to the formation of *acceptors*. This model explains for the first time why exposure of pentacene to oxygen *in the presence of an electric field* leads to p-type doping of the pentacene.

Archival publications:

(1) J. E. Northrup, *Atomic and electronic structure of polymer organic semiconductors: P3HT, PQT, and PBTTT.* Phys. Rev. B **76**, 245202 (2007).

Change in research objectives (if any): None

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