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Understanding the effect of thionation on naphthalene diimide using first-principles predictions of near-edge x-ray absorption fine structure spectra

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Conjugated organic materials, such as semiconducting polymers and small molecules, have shown great potential for electronic applications, boasting favorable properties such as being mechanically flexible and having low processing temperatures. Additionally, the organic components comprising semiconducting polymers and small molecules are interchangeable, resulting in a high degree of synthetic control over the electronic properties of conjugated semiconductors. For example, it has recently been shown that an increasing degree of thionation – the replacement of oxygen atoms with sulfur atoms – results in a systematic shift in the NEXAFS spectra of naphthalene diimide (NDI)-based molecules. While such changes are systematic, it is difficult to directly connect the changes to the measured C 1s to ⍰* manifold to the electronic properties of the molecule since the NEXAFS spectrum obtained contains transitions from carbon atoms in different environments and hence different core levels. In this study, we have used a first-principles approach, the eXcited Core Hole (XCH) model, in order to resolve individual atomic contributions to the NEXAFS spectrum of a series of NDI molecules with increasing thionation. The simulations yield an excellent correspondence with the experimentally measured NEXAFS spectra. Furthermore the calculations of both the x-ray absorption spectra, as well as the neutral and excited molecular orbital density distributions, indicate that the sulfur substitution decreases the core level shift of the molecule, lowering the energy required to excite an electron from a core level. The simulations also reveal how changes in the symmetry of the molecule with thionation affect the resulting molecular orbitals and hence electronic transitions. The successful application of computational methods to explain the rich fine structure observed experimentally thus enables direct connection between measurement and the underlying molecular transitions. Such insights are important for underpinning the application of NEXAFS spectroscopy and related soft x-ray techniques in characterizing the microstructure of organic semiconductor films, which in turn are being used to optimize the performance of organic electronic devices.

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