Electronic Properties of Discrete NDI-T2 Oligomer Thin Films Using Photoelectron Spectroscopy and Low-energy Inverse Photoemission Spectroscopy

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The combination of photoelectron spectroscopy (PES) and low-energy inverse photoemission spectroscopy (LEIPES) is a valuable tool for the characterization of the density of occupied and unoccupied states in (organic) semiconductors. Their combination allows the transport or single particle bandgap to be determined. Especially for organic semiconductors, the possibility of such a measurement is crucial, as the transport bandgap is not only less accessible, but can significantly differ from the optical bandgap by 0.1 – 1 eV due to the correspondingly large Frenkel exciton binding energy that limits the charge separation in these materials. The low kinetic energy employed in LEIPES helps to avoid degradation due to the electron beam irradiation[1].

In this work, we combine PES and LEIPES with optical measurements, in particular spectroscopic ellipsometry to compare the transport and optical bandgaps of semiconducting discrete oligomers based on naphthalene diimide (NDI) and bithiophene (T2)[2] spin-coated on Ag substrates at different film thicknesses. Their thin films show optically anisotropic characteristics due to a preferential molecular orientation[3]. Here, for example in thin films of T2-$(NDI\text{-}T2)_2$, we observe an optical bandgap of 1.6 eV and a transport bandgap of 1.8 eV, suggesting an exciton binding energy of 0.2 eV. We reveal a transport bandgap narrowing effect at ultra-low film thicknesses, approaching the value of the optical bandgap, due to an energy shift in the onset position of the highest occupied molecular orbital. The potential roles of the substrate and the molecular orientation that lead to the results obtained are discussed.

Keywords: organic semiconductor, photoemission spectroscopy, low-energy inverse photoemission spectroscopy, transport bandgap, exciton binding energy, molecular orientation

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