

Precisely Examining the LUMO Levels of Organic Semiconductors

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Despite the importance, limited information is available for the unoccupied states (LUMO levels) of organic semiconductors because of lack of a suitable experimental method. The LUMO level is often estimated from the reduction potential of organic material measured in solution using cyclic voltammetry though the value does not include the solid state effect. For solid samples, the HOMO level and the energy gap determined by photoemission and UV-vis spectroscopies, respectively, is widely used. The estimated LUMO value is 0.5 or 1 eV lower than the electron transport level due to the exciton binding energy.

Inverse photoemission spectroscopy (IPES) is in principle the ideal techniques to examine the LUMO levels because the anionic state is measured in the solid state; mono-energetic electrons are introduced to the sample surface. By detecting emitted photons due to the radiative transition of electron to low-lying unoccupied states (including the LUMO level), the density of unoccupied states is mapped out. The onset with respect to the vacuum level corresponds to the electron affinity. In the previous IPES, however, introducing the electrons having kinetic energies of 5 - 15 eV results in damage to the organic samples and detecting the photons in the vacuum ultraviolet range limits the energy resolution to about 0.5 eV. Such instruments have been used without fundamental improvement since the late 1970s.

We have recently developed low-energy IPES (LEIPS), demonstrating the improved energy resolution and negligibly small sample damage [1]. To reduce the sample damage, the kinetic energy of electron is kept below 4 eV, the damage threshold of organic materials. As a result of lowering the electron energy, the emitted photon energy becomes lower than 5 eV. These near-ultraviolet photons can be analyzed using the multilayer band-pass filter improving the overall energy resolution by a factor of two. This means that the unoccupied states can be examined using LEIPS with an accuracy similar to the occupied states using photoemission spectroscopy. This novel technique has been applied to organic semi-conductors, e.g. typical materials used for the organic light-emitting diodes [2] and organic photovoltaic cells [3]. We also examined electron injection/collection barriers at the metal/organic interfaces [4,5] and orientation dependence of energy levels [6].

After presenting the principle and typical application of LEIPS, I will discuss the solid state effects on the behavior of charge carriers in organic semiconductors.

References

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