Localization/Delocalization of Charge Carrier in Organic Semiconductor via Temperature Dependent-Electronic Polarization Energy

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It is widely believed that a charge carrier (electron/hole) is localized on a single molecule and incoherently transported by the hopping mechanism assisted by thermal energy in most of organic semiconductors (e.g., copper phthalocyanine (CuPc) and C60). However, a charge carrier is delocalized and coherently transported by the band-like mechanism in some OSCs with high charge carrier mobility (e.g., pentacene and rubrene).

A localized charge carrier with a charge e should be stabilized by electronic polarization (D) as much as 1 eV. When the charge carrier delocalized with radius (r), D should decrease. The magnitude of D as a function of r can be estimated by Born equation of solvation energy, $D = e^2 (1-1/\varepsilon_r) / (8\pi\varepsilon_0 r)$ if dielectric response of surrounding molecules is approximated by a continuum dielectric with a relative permittivity ε_r.

The molecules used in this experiment are CuPc, C60 and pentacene. As previously reported[1], the electronic polarization energy can be determined by probing its ionization energy (IE_s) and electron affinity (EA_s). IE_s and EA_s were measured by ultraviolet photoelectron spectroscopy (UPS) and low energy inverse photoelectron spectroscopy (LEIPS)[2] respectively. As the localization or delocalization of the charge carriers should depend on the temperature due to the phonon induced scattering effect, we examined D value as a function of temperature.

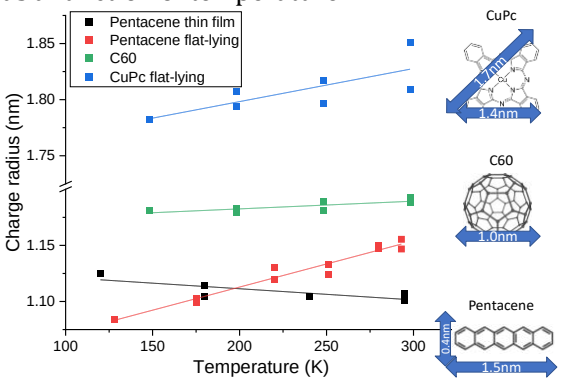

Figure 1. Charge radius vs temperature graph with its slope equation on the left, and the molecules with their approximate dimension on the right.

As shown in Figure 1, the charge radius r has a similar dimension to the respective molecule indicating that the charge carrier is localized only on a single molecule. Furthermore, from the temperature dependence, C60, CuPc and flat-lying pentacene shows that the charge carriers possess a thermal-activated hopping transport, while pentacene thin film shows a band-like transport, supporting the temperature dependent mobility experiment[3].

In summary, we found that charge carrier radius is localized on a single molecule from the viewpoint of electronic polarization energy. And the temperature dependence suggest that a localized charge carrier also has a tendency to transport coherently.

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