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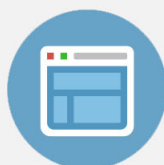
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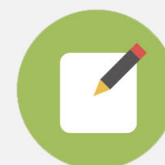


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Observation of Frenkel and charge transfer excitons in pentacene single crystals using spectroscopic generalized ellipsometry

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We report on the emerging and admixture of Frenkel and charge transfer (CT) excitons near the absorption onset in pentacene single crystals. Using high energy-resolution spectroscopic generalized ellipsometry with in-plane polarization dependence, the excitonic nature of three lowest lying excitations is discussed. Their distinct polarization dependence strongly indicates the presence of both Frenkel and CT types of excitons near the excitation onset. In particular, the peculiar polarization behavior of the second excitation can only be rationalized by taking into account the inherent CT transition dipole moment. This observation has important implications for the pentacene-based optoelectronic devices. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4811758>]

Organic semiconductors comprising π -conjugated organic molecules or polymers have attracted intensive attention for low-cost, large-scale, and flexible electronic device applications.^{1,2} Increasing research efforts have been devoted to organic electronic devices made from organic single crystals not only due to their superb device performance³ but also due to their fundamental importance to the understanding of the underlying charge transport mechanism in general organic semiconductor materials.⁴ However, despite the breakthroughs in the technology of organic electronics, the physics of organic crystals is comparatively little understood. In particular, the microscopic understanding of the electronic excitations remains elusive and often controversial despite its fundamental importance for organic optoelectronics.

Pentacene (C₂₂H₁₄) is regarded as an archetypical organic semiconductor materials and has been the subject of widespread research efforts in view of its superior device performances in applications such as organic field-effect transistors³ and organic photovoltaic cells.⁵ The pentacene crystal (Figs. 1(a) and 1(b)), like most organic molecular crystals, is made of weakly interacting molecules. Consequently, the electronic excitations are frequently described in terms of intramolecular Frenkel excitons (Fig. 1(c)), in which the excited electron-hole (e - h) pairs are confined to the same molecule, and intermolecular charge transfer (CT) excitons, for which the excited e - h pairs are located on adjacent molecules (Fig. 1(d)).^{6,7} The CT excitons, due to their much smaller oscillator strength, are not easily probed experimentally, and usually occur at higher energies above the absorption onset. In spite of extensive characterization of its electrical properties, the interpretation of electronic excitations in pentacene solids, in particular the

nature of the lowest excitations, is still conflicting. While earlier work described them as mainly molecular Frenkel excitons without CT excitation contribution,^{7,8} recent experimental studies using reflectivity measurements and electron energy-loss spectroscopy^{9,10} as well as sophisticated theoretical approaches¹¹ suggest CT-like excitonic contributions near the onset of absorption. Clarifying the CT contribution in the absorption onset has practical implications for organic photovoltaic devices, since CT exciton is generally considered as an important precursor in the creation of free charge carriers by light absorption. Moreover, in recent years singlet exciton fission in molecular solids, a process in which one singlet exciton is converted to a pair of triplet excitons, has received considerable interest, as it provides great potential to improve the power conversion efficiency of solar cells even beyond the Shockley-Queisser limit.¹² Pentacene has been shown to undergo highly efficient singlet fission,^{13,14} and solar cells made from pentacene/C₆₀¹⁵ and pentacene/nanocrystals^{16,17} bilayer structures have been demonstrated to exhibit very high quantum efficiencies. However, the mechanism of this process remains elusive,¹² and there has been on-going discussion on the CT character of the intermediate state that precedes the fission into separate triplet excitons.^{18–20} Consequently, identifying electronic excitations with CT character near the absorption onset is crucial to understand the singlet fission process.

In this Letter, we present the studies of the dielectric function of pentacene single crystals with full polarization dependence in the crystal a - b plane using a high energy-resolution spectroscopic ellipsometer. Spectroscopic ellipsometry has a unique advantage that it can directly obtain dielectric functions without the need of Kramer-Kronig analysis (KKA), which is known to suffer from limited energy window issue. We are able to resolve the contributions from both Frenkel- and CT-type excitons to the lowest electronic excitations.

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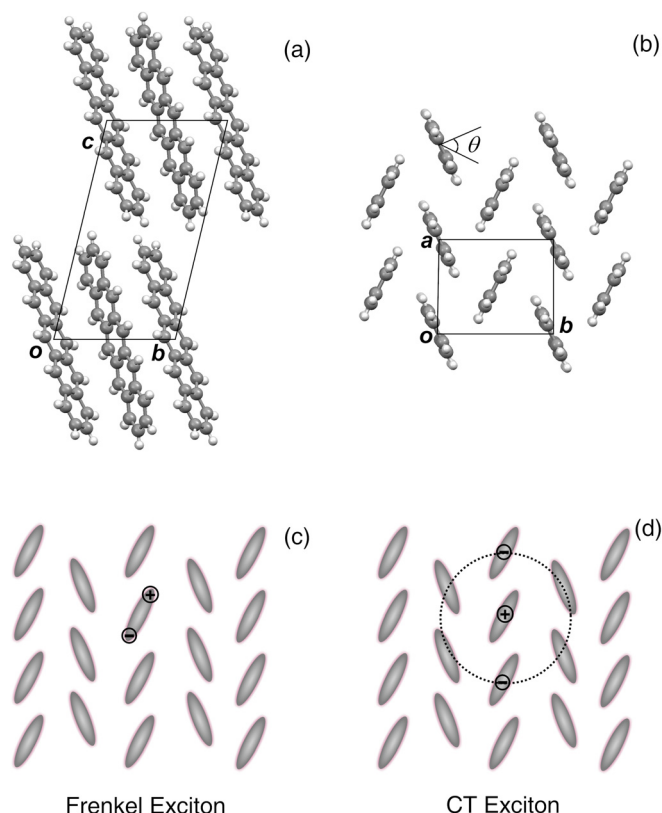


FIG. 1. Crystal structure of pentacene viewed from (a) the *b-c* plane, and (b) the projection of the *a-b* plane perpendicular to the long molecular axis showing the herringbone packing structure. The herringbone packing angle θ of pentacene crystals is defined as the angle between the normal vectors to the molecular planes of the two translationally non-equivalent molecules. (c) and (d) are schematic illustrations of the electronic excitations in molecular crystals in the form of Frenkel excitons and CT excitons, respectively.

High purity pentacene single crystals were grown using physical vapor transport method. To achieve the highest purity, the pentacene source (Sigma-Aldrich) is prepurified by vacuum sublimation under temperature gradient. Details on the purification and crystal growth steps have been described elsewhere.²¹ Large single crystals were achieved with a size of 4×4 mm and thickness of 15–20 μm . Transport measurement for pentacene single crystals grown in this methods typically show high hole mobility up to $35 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ supporting the high purity of the single crystals.²¹ The crystal structure was determined with X-ray diffraction (XRD) showing typical single crystalline phase of pentacene²² with (001) surface orientation. The real (ϵ_1) and imaginary (ϵ_2) parts of dielectric function were determined using an extended Sentech SE850 spectroscopic generalized ellipsometer.²³ Ellipsometry is a direct technique to measure the changes of amplitude and phase upon reflection of light from a sample. From these, the complex dielectric function ($\epsilon_1 + i\epsilon_2$) was directly derived without performing any KKA. In an anisotropic material the dielectric function is represented by a dielectric tensor. The components of the dielectric tensor correspond in a good approximation to the pseudo-dielectric function plotted in Figs. 2 and 3. All experiments were done at room temperature.

In Fig. 2(a), we show a representative ellipsometry measurement of ϵ_2 of pentacene molecular crystals for light polarization E parallel to a certain in-plane direction away from its crystallographic axis *a* and *b*. The overall spectral

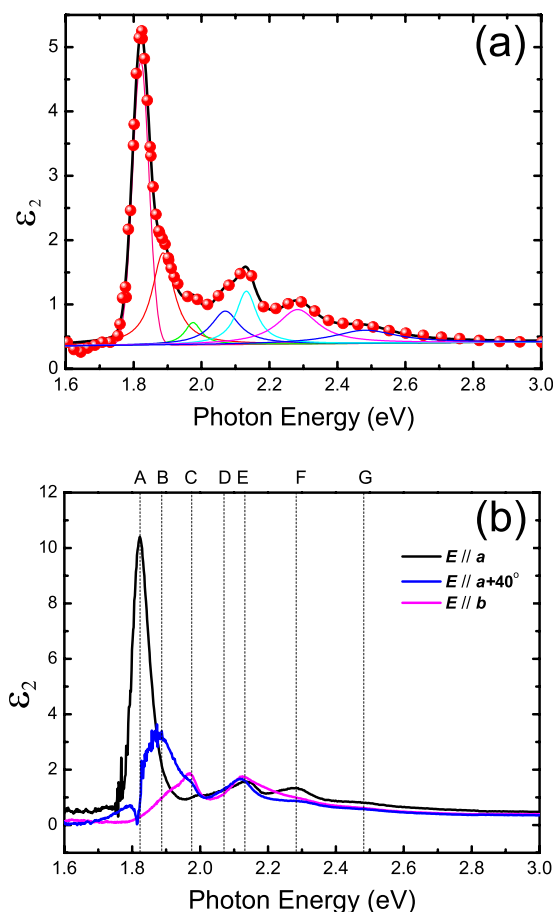


FIG. 2. Imaginary part of the dielectric function ϵ_2 of pentacene single crystals with (a) light polarization E direction in 20° offset from crystallographic axis *a*, and (b) E direction parallel to various in-plane directions. The spectrum in (a) is fitted by Lorentzian shape functions (thin colored lines). The thick black line is the cumulative fit curve. Representative experimental data are shown in solid red balls. The actual experimental data points are much denser with an average energy step less than 3 meV.

shape agrees well with previous optical measurements^{9,24–27} as well as theoretical calculation¹¹ on pentacene solids, showing several pronounced excitation features below 2 eV and weak excitations at higher photon energies coupled to vibrations. By performing least-square fits of the spectrum, we can clearly reveal the presence of seven individual excitations in the energy range between 1.8 and 2.8 eV (labeled A to G). In particular, in addition to the commonly reported excitation A (at 1.821 eV) and C (at 1.975 eV), we have discovered the emerging of another electronic excitation B centered at 1.887 eV. These three low-lying excitations are indisputably excitonic in nature considering the transport energy gap E_g of 2.2 eV for pentacene solids.²⁸

In order to further determine the microscopic origin of these excitons (i.e., intramolecular Frenkel excitons versus intermolecular CT excitons), polarization dependence of the observed electronic excitations is carried out. Figure 2(b) reports the dielectric function for the light polarizations E parallel to the in-plane lattice vector *a*, *b*, and in a direction with 40° offset with respect to *a*, respectively. Immediately one will find the peaks A, B, and C below the gap are strongly polarization dependent with significant anisotropies of spectral shapes and intensities. The lowest excitation peak A exhibits the highest intensity when light polarization $E \parallel a$,

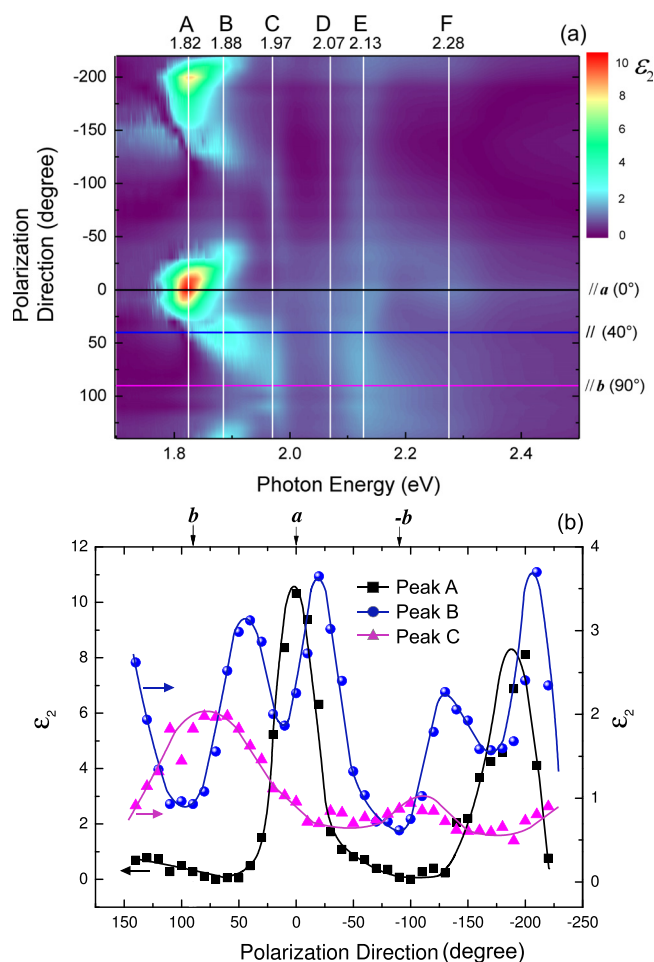


FIG. 3. (a) Contour plot of the imaginary part of the dielectric function ϵ_2 as a function of photon energy and full in-plane light polarization direction in the a - b plane for pentacene single crystals. The three horizontal lines correspond to the plots in Fig. 2(b). (b) Vertical cut of the contour plot at the photon energy of peak A, B, and C show the polarization dependent dielectric function of corresponding excitons. Solid lines through points are guide for eyes only.

whereas it virtually vanishes when $E//b$. In contrast, an opposite polarization dependence of excitation C is observed. In a pentacene molecule, the intramolecular Frenkel exciton corresponds to the electronic transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), whose symmetries determine the orientation of associated transition dipole moment to be polarized along the short molecular axis.¹¹ Meanwhile, the intermolecular interactions between two translationally non-equivalent molecules in a unit cell lift the degeneracy of the molecular energy states, giving rise to two distinct excitation bands with finite band widths,⁷ or the so-called Davydov splitting.²⁹ Both Davydov components are predicted to be polarized perpendicular to each other and almost coincide with the crystallographic axis a and b , respectively.^{7,29} Consequently, when the polarization of the incident light switches between a and b , one of the Davydov components should nearly vanish. This canonical description of molecular Frenkel exciton and its associated Davydov split component is fully consistent with the present polarization dependent behavior of excitations A and C, and therefore they are predominantly attributed to intramolecular Frenkel excitons. In contrast, the intensity of excitation B appears to be diminished when E is parallel to a and b , whereas it is

significantly enhanced when the polarization direction is tuned in-between a and b .

The distinct dependence on the light polarization of these low-energy excitations is more clearly seen in Fig. 3(a), which shows the contour plot of ϵ_2 as a function of photon energy and in-plane light polarization direction. Closer inspection of the anisotropy of excitation A-C reveals significantly dissimilar polarization dependence, more clearly seen in the variation of dielectric function at peak positions as a function of polarization direction (Fig. 3(b)). The excitation intensities of exciton A and C complement each other, showing maximum values at $E//a$ and $E//b$ directions, respectively, and diminishing at the corresponding perpendicularly polarized direction, which is due to their Frenkel exciton nature as discussed above. In contrast, the intensity of excitation B exhibits a more complex polarization-dependence, displaying two maxima at polarization directions away from the main crystallographic axes. Such distinct polarization dependence of excitation B most likely suggests the occurrence of a more complex exciton character.

First, we can safely exclude the possibility that excitation B is the vibronic replica of the lowest excitation A, because the dominant molecular vibration mode in pentacene is at around 175 meV.²⁵ In addition, we would expect to observe a similar polarization-dependence of peak B as that of excitation A, if it originates from the associated vibrational coupling. The second possibility of the origin of excitation B is the admixture of intermolecular CT excitons. Although several CT excitons corresponding to different e - h pair configurations were identified by electroabsorption in pentacene solids with excitation energy higher than 2.0 eV,²⁵ it was recently suggested that CT excitons could lie at lower energies close to the absorption onset.⁹⁻¹¹ The excitation energy of CT exciton (E_{CT}) with respect to the band gap E_g (~ 2.2 eV) can be crudely estimated by a simple point-charge model⁷ as $E_{CT} = E_g - \frac{e^2}{4\pi\epsilon_0\epsilon_r r_{CT}}$, in which r_{CT} denotes the intermolecular distance of the charge-transfer molecular pairs and ϵ_r (~ 2.5) is the relative dielectric constant of pentacene,¹² yielding CT exciton at energies close to the observed excitation B. More advanced calculations by including e - h interactions give rise to lowest CT exciton (in the spin singlet state) in pentacene solids with a binding energy of 300 meV,¹¹ which is agreeing surprisingly well with the binding energy of the exciton B. Hence, it is very likely that our experimental observation of the excitation B essentially suggests the intermolecular CT exciton parentage. However, it must lose its pure CT character, as it gains significant oscillator strength by borrowing spectral weight from the intramolecular Frenkel excitations,³⁰ as evidenced by its unusually high absorption intensity for a typical CT exciton. Moreover, the mixed character of CT and Frenkel excitons in excitation B is expected to lead to rather complex polarization dependence different from that of Frenkel excitons. As shown in Fig. 3(b), excitation B peaks in intensity at polarization directions separated by $60^\circ \pm 10^\circ$. Intriguingly, this angular separation is not far from the herringbone packing angle θ of 51.9° of pentacene crystals (Fig. 1(d)).²² This closeness to the herringbone angle of molecules may reflect the intrinsic electronic transition dipoles of the CT exciton.

Indeed, the calculated wavefunction of CT singlet exciton exhibits the special spatial correlation of electron and hole states: they prefer to be distributed in the adjacent parallel molecules.¹¹ It is therefore expected to have two sets of CT excitation along each non-equivalent molecule by tuning the polarization vector of incident light. Therefore, we must include this inherent CT transition dipole moment into the excitation B in order to explain its polarization behavior.³¹ It is worth mentioning here that having CT excitons close to the lowest singlet excitation energy (and therefore twice its triplet energy) in pentacene also supports the involvement of CT intermediate state in the singlet fission process.²⁰ It is therefore highly desired to perform detailed calculations in future to support the CT mixing character in the excitation B and its involvement in the singlet fission process.

In conclusion, using high-resolution spectroscopic generalized ellipsometry with full polarization dependence, we have studied the excitonic nature of low lying electronic excitations in pentacene single crystals. Admixture of intramolecular Frenkel excitons (including its Davydov splitting) and intermolecular CT exciton are identified in the lowest electronic excitations based on their distinct exciton binding energy and polarization dependence. The coexistence of different types of excitons in low-lying excitations indicates that a more general framework including both types of excitons is indispensable to make a successful description of electronic excitations and modeling of charge dynamics in organic molecular solids.

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