P H Y S I C A L R E V I E W L E T T E R S

Role of Intermolecular Coupling in the Photophysics of Disordered Organic Semiconductors: Aggregate Emission in Regioregular Polythiophene

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We address the role of excitonic coupling on the nature of photoexcitations in the conjugated polymer regioregular poly(3-hexylthiophene). By means of temperature-dependent absorption and photoluminescence spectroscopy, we show that optical emission is overwhelmingly dominated by weakly coupled H aggregates. The relative absorbance of the 0−0 and 0−1 vibronic peaks provides a powerfully simple means to extract the magnitude of the intermolecular coupling energy, of approximately 5 and 30 meV for films spun from isodurene and chloroform solutions, respectively.

Regioregular poly(3-hexylthiophene) (rrP3HT) is a model material to explore the role of supramolecular order in the physics of polymeric semiconductors. In thin films, it self-organizes into two-dimensional π-stacked lamellar structures [1,2]. These structures allow for two-dimensional charge transport, resulting in field-effect mobilities of order 0.1 cm^2 (V s)$^{-1}$ [3], approaching those of amorphous silicon.

The degree to which rrP3HT forms these supramolecular structures depends upon processing conditions and molecular weight [4]. Morphology, in turn, affects electronic structure. Photoinduced and charge-modulation spectroscopy have provided evidence for delocalized polarons [5,6] but the nature of the primary *neutral* excitation has been the subject of debate [7–12]. A reasonable starting point is to consider a simple intrachain exciton [7]. However, the absorption and emission spectra cannot be fit using a simple Franck-Condon progression. Brown *et al.* proposed two emissive states close in energy, an *intra-* and an *interchain* state, both contributing to the absorption and emission spectra [8]. On the other hand, Kobayashi *et al.* proposed two intrachain emissive states, one with allowed transition to the ground state ($1B_u$) and one generally forbidden but weakly allowed due to vibronic coupling ($2A_g$) [9]. Others proposed that the first excited state is a single interchain H aggregate-type state [10,11]. One of us has recently built upon the latter idea with a theoretical model of *weakly interacting* H aggregate states [12]. We conclude here that this model describes comprehensively the photophysics of rrP3HT.

We are able to describe the rrP3HT absorption and emission spectra by invoking a single emitter and without the need to invoke more complicated models [8,9]. This is of general interest in other polymeric semiconductor systems exhibiting apparent non-Condon emission [13–16]. Using an analytical form of a weakly interacting H aggregate model, we describe unambiguously the shape of the

spectra from a micromorphological point of view. We demonstrate that the room-temperature bulk absorption spectrum contains microscopic detail of intramolecular order and interchain coupling energy in the solid state.

Solutions of rrP3HT (Plextronics) were made in isodurene and anhydrous chloroform (Aldrich) and heated to 70 °C for 30 min in N$_2$ atmosphere. Films were spin coated in N$_2$ atmosphere from hot solution and were subsequently heated to 100 °C for 30 minutes. Absorption spectra were measured with a Hewlett-Packard UV-VIS spectrometer in ambient conditions. Time-correlated single-photon counting was used to measure the photoluminescence (PL) lifetime of all samples, as well as the time-integrated PL spectra of the solutions using an apparatus described in detail elsewhere [17] and a pulsed diode laser (407 nm; 70 ps FWHM) as the excitation source. An argon-ion laser (488 nm) was used to measure steady-state PL spectra in films in a continuous-flow cryostat using an Oriel IV Instaspec spectrograph. Films of different thickness were measured to rule out self-absorption effects. Photoluminescence excitation (PLE) spectra were measured in vacuum with a Varian Cary Eclipse Fluorescence Spectrophotometer.

Figure 1(a) shows room-temperature (RT) PL and absorption spectra of a 0.0001% by weight solution of rrP3HT in isodurene (a ''bad'' solvent). At such low concentration we do not observe a solvent dependence on the spectral shape. These spectra are attributed to intrachain excitations and are therefore reproduced with a Franck-Condon model where the relative intensity of the vibronic replica is given by

$$I_{0\to m} \propto (\hbar\omega)^3 n_f^3 \frac{S^m \exp(-S)}{m!}, \qquad (1)$$

where n_f is the real part of the refractive index at photon energy $\hbar\omega$ and m denotes the vibrational level. S is the
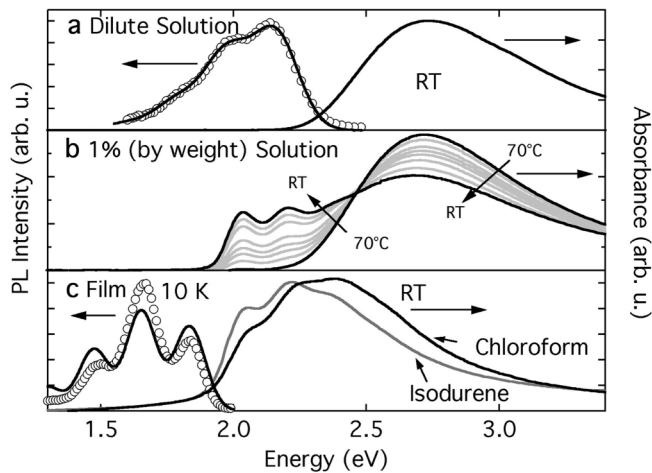
FIG. 1.   (a) Normalized room-temperature (RT) absorption and
PL spectra of rrP3HT in a 0.0001 wt % isodurene solution. Solid
line through PL is a Franck-Condon fit. (b) Temperature-
dependent absorption spectra of 1 wt % isodurene solution.
(c) Normalized absorption spectra of a film spun from 1 wt %
isodurene and chloroform solutions. The PL spectrum of a
chloroform film is also shown (○) with a Franck-Condon best
fit (solid curve). The PL spectrum was measured at 10 K whereas
absorption spectra were measured at RT.

Huang-Rhys factor, which gives a measure of the coupling
between the electronic transition and a phonon mode [13].
    We fit the dilute PL spectrum in Fig. 1(a) assuming that
the C = C symmetric stretch at 0.18 eV dominates the
coupling to the electronic transition [18,19]. For simplicity
we used a Gaussian line shape with the same width for each
of the vibronic transitions. The refractive index of the
solvent was taken to be constant across the examined range
[20]. The fit is shown as the solid line in Fig. 1(a) and gives
$S = 1.00 \pm 0.05$.
    At significantly higher concentration (1 wt %) the ab-
sorption spectrum exhibits additional structured compo-
nents at lower energy, which disappear upon heating the
solution to 70 °C [Fig. 1(b)]. The emergence of the red-
shifted species is correlated with the formation of crystal-
lites as the chains extend and planarize [21–23]. A
corresponding reduction in PL efficiency [21] suggests
formation of weakly emissive aggregates. The low-energy
absorption observed in solution at high concentration
dominates the spectrum in the solid state [Fig. 1(c)]. The
absorption spectrum of a film spun from chloroform, a
good solvent, is similar to that spun from isodurene, but
the relative intensity of the 0–0 and 0–1 peaks is solvent
dependent. We note that we cannot fit the solid-state PL
spectrum using a standard single-oscillator Franck-Condon
progression at any temperature studied (in the range 10–
300 K), as shown in Fig. 1(c) for the spectrum at 10 K (see
also Ref. [8]). We conclude from these observations that
most of the polymer chains self-organize to form aggre-
gates in the film.
    We now consider whether there is evidence for more
than one emissive species. The solid-state PL excitation

(PLE) spectra [Fig. 2(a)] show no dependence on detection
wavelength and resemble the absorption spectrum. The PL
lifetime is the same at the 0–0 and 0–1 energies at all
temperatures [Fig. 2(b)]. We conclude that there is a single
emissive species in the solid state.
    To elucidate the nature of the emissive species, we
measured temperature-dependent and time-dependent PL
spectra (Fig. 3). Figure 3(a) shows temperature-dependent
PL spectra of a film from 10 K to 300 K. As the tempera-
ture increases, the spectra blueshift and broaden, and the
0–0 peak becomes relatively more intense. Temperature-
dependent PL spectra of *intramolecular* excitations gener-
ally show a blueshift and broadening upon increasing
temperature, but no change in relative intensities of vi-
bronic peaks [13]. Figure 3(b) displays time-dependent PL
spectra at 10 K, normalized to the 0–1 peak intensity. The
0–0 peak becomes relatively less intense with time, and we
observe a dynamic spectral redshift.
    We demonstrate here that such temperature dependence
and temporal evolution is consistent with an H aggregate
model in the weak intermolecular coupling regime. In H
aggregates the transition from (to) the ground state to
(from) the first excited state is forbidden. Intermolecular
coupling is taken to be resonant Coulomb (excitonic)
coupling, denoted J. At 3.8 Å π-stacking distance in
rrP3HT [2], we might expect a large J [24]; however, the
long conjugation length in rrP3HT (estimated to be be-
tween 20–25 thiophene units from x-ray studies [2]) also
plays an important role. Quantum chemical calculations
have shown that increasing the conjugation length reduces
J [25,26]. This has been recently demonstrated experimen-
tally in oligothiophenes [27], leading to the conclusion that
in the long polythiophene chain J could be small. In the
"weak" excitonic coupling regime J is smaller than the
vibrational relaxation energy and the interchain interaction
leads to vibronic bands as shown in Fig. 3(c). The free
exciton bandwidth is $W = 4J$ [12].
    In such an H aggregate, absorption of light is to the top
of the vibronic bands. In accordance with Kasha's rule,
emission is from the lowest excited state, with zero oscil-
lator strength for the 0–0 transition in the absence of
disorder. In contrast, the sideband transitions are allowed.
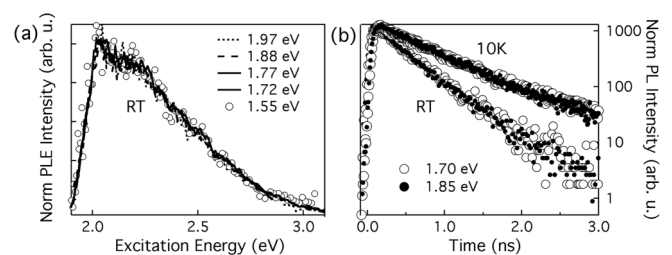In the weak coupling limit the intensities of the 0–1 and

FIG. 2.   (a) Normalized PLE spectra at room temperature (RT)
of a film spun from a chloroform solution at different detection
photon energies. (b) PL decay at two photon energies measured
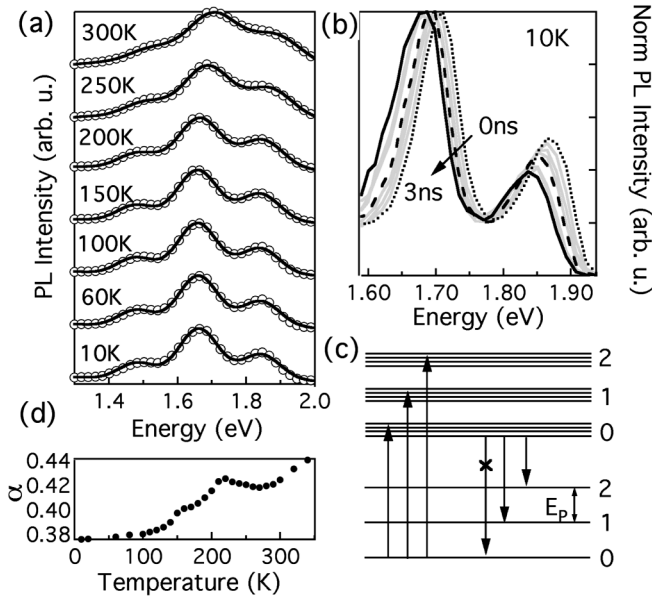at RT and 10 K.

FIG. 3.   (a) PL spectra of a film spun from chloroform solution at various temperatures. The solid lines through the data are fits to Eq. (2). (b) Time-resolved PL spectra measured at 10 K, normalized to the 0–1 peak. Spectra are integrated over 0.25-ns windows and presented here from 0–3 ns. (c) Jablonski diagram showing the exciton energy level structure. (d) Variation of α with temperature [see Eq. (2)].

subsequent replicas are somewhat diminished from their single molecule values [12,14], consistent with the aggregation-induced reduction in quantum yield. However, the sidebands retain the same *relative* intensities as the single molecule spectrum [12]. Hence, the aggregate emission spectrum should have a weak, disorder-allowed 0–0 component followed by a Franck-Condon progression of sidebands. Accordingly, the PL spectrum can be modeled as a modified Franck-Condon progression with a variable 0–0 amplitude:

$$I(\omega) \propto (\hbar\omega)^3 n_f^3 e^{-S}$$
$$\times \left[\alpha \Gamma(\hbar\omega - E_0) + \sum_{m=1} \frac{S^m}{m!} \Gamma(\hbar\omega - (E_0 - mE_p)) \right].$$

$$(2)$$

We define n_f, m, and S as in Eq. (1). E_0 is the 0–0 transition energy, E_p is the phonon energy of the C = C symmetric stretch (0.18 eV), Γ is the line-shape function (simplified to be purely Gaussian with constant width), and α is a constant whose amplitude is allowed to vary during the fit. As shown in [12], α is a strong function of the disorder width and spatial correlation length. Fits with Eq. (2) are shown as solid curves in Fig. 3(a) with $S = 1$ (5% uncertainty) at all temperatures; α as a function of temperature is shown in Fig. 3(c). We note that $S \approx 1$ in noninteracting planar polythiophene chains [23] and should not change upon aggregation in the weak coupling regime. Upon increasing temperature the PL spectra blue-

shift and broaden due to increasing thermal disorder. We also observe a systematic increase of the 0–0 peak intensity (α) with temperature due primarily to thermally excited, less-forbidden levels higher up in the lowest vibronic band, a distribution typical of H aggregates. Thermal disorder may also lead to a relaxation of the selection rule making the 0–0 transition more allowed. Invoking the first mechanism with the model of Ref. [12] leads to a spectral blueshift and 0–0 peak enhancement with temperature in good qualitative agreement with experiment. Furthermore, the dynamic redshift (even at 10 K) and the loss of 0–0 peak intensity with time indicates energy diffusion to more ordered domains which carry lower 0–0 intensity. We conclude that H aggregates are the only emissive species in rrP3HT.

Having established that weak intermolecular electronic coupling gives rise to the spectral properties presented here, we can use these properties to quantify the magnitude of the electronic coupling. Within an H aggregate model, the magnitude of the interchain coupling can be estimated from the ratio of the 0–0 and 0–1 absorbance peaks [12] [Fig. 1(c)]. With $S = 1$, one finds

$$\frac{A_{0-0}}{A_{0-1}} \approx \frac{n_{0-1}}{n_{0-0}} \left(\frac{1 - 0.24W/E_p}{1 + 0.073W/E_p} \right)^2, \quad (3)$$

where n_{0-i} is the real part of the refractive index at the 0–i peak. E_p is the phonon energy of the main oscillator coupled to the electronic transition. Using $E_p = 0.18$ eV, a refractive index ratio of ~0.97 [8], and the experimental absorbance ratios shown in Fig. 1(c), Eq. (3) gives the free exciton bandwidths, W, of ~120 meV for the film spun from chloroform and ~20 meV from isodurene. We note that the absorbance vibronic peak spacing predicted by the model is not uniform owing to second order effects [28]. This is in qualitative agreement with experimental data [8].

Using this analysis, we can construct a microscopic picture of polymer structure. Assuming similar interchain order in these films, the conjugation length and intrachain order play a role in the degree of interchain coupling [12]. Remembering that increasing the conjugation length reduces J, we see that the chloroform-spun film, with $J \sim$ 30 meV, displays lower intrachain order than the isodurene film, $J \sim 5$ meV. Furthermore, J can be used to determine the average conjugation length by comparing it to quantum mechanical calculations on pairs of variable-sized oligomers. Crude estimates implementing Zerner's Intermediate Neglect of Differential Overlap (ZINDO) method predict the conjugation length in chloroform films to be 20–30 monomers. Isodurene films, with significantly smaller J, are expected to have conjugation lengths at least twice as large.

Field-effect transistors fabricated with rrP3HT films spun from high boiling point solvents, such as isodurene, display increased A_{0-0}/A_{0-1} ratio and higher field-effect mobility than those from lower boiling point solvents such as chloroform [29]. This indicates that intramolecular or-
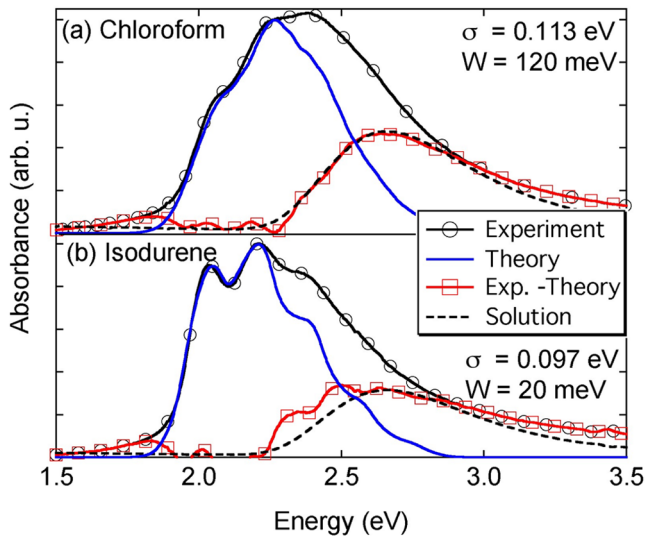
FIG. 4 (color online). Experimental and simulated absorption spectra measured at room temperature for films spun from (a) chloroform and (b) isodurene. Calculations were performed on π stacks containing 12 polymers, large enough to ensure spectral convergence. Transition frequency offsets were chosen randomly from a Gaussian distribution with $(1/e)$ full width of 2σ and spatial correlation length $l_0 = 3$. The final absorption spectrum was averaged over 1500 disorder configurations. For further details, see [12].

der, which is related to J, is of overriding importance to optimize charge mobility. This simple procedure for estimating J, and thus the conjugation length and degree of intrachain order, is a powerful tool for materials development and processing efforts.

To further explore the physical validity of the weakly interacting H aggregate model, we present a more detailed analysis of the absorption spectra of films spun from chloroform and isodurene (Fig. 4). Alongside the experimental spectra we also plot the calculated spectra using a Holstein-like Hamiltonian with correlated site disorder [12]. The solid curves (no markers) are the attenuation, $\mathbb{Im}[\epsilon(\omega)]/\mathbb{Re}[n(\omega)]$, where the numerator is the imaginary part of the dielectric constant and the denominator is the real part of the refractive index. The evaluation of $\mathbb{Im}[\epsilon(\omega)]$ [denoted $A(\omega)$ in [12]] is described in detail in Ref. [12]. For the frequency dependent index we utilized the measured value. The ratio of the 0–0 to 0–1 peak absorbance is in excellent agreement with the measured ratio, a consequence of the validity of Eq. (3). The stronger absorption measured for energies greater than approximately 2.3 eV is due to unaggregated molecules or short oligomers, both of which are substantially blueshifted compared to the π-stacked aggregate. To test this idea we subtracted the theoretical curves from the experimental ones, obtaining the differential curves (square markers). These agree very well with the low-concentration solution spectra in both samples, suggesting an important contribu-

tion of unaggregated polymers in the absorption spectra. However, as demonstrated in this Letter, a single species comprised of aggregates is responsible for emission.

We have shown that the emission in rrP3HT arises from weakly coupled H aggregates with no significant contribution from intrachain excitons. We can probe the microscopic order in thin films of rrP3HT using the 0−0 and 0−1 peaks of the PL and absorption spectra. This provides an exciting opportunity to explore the interplay between processing, order, and ultimately device performance, and a general framework to unravel interchain effects in semiconductor polymers [13−16].

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