

F is the electric field, $\tau_f = k_f^{-1}$ the exciton lifetime, μ the sum of electron and hole mobilities. The field dependent dissociation rate $k_d(F) = \mu\kappa_d(F)$ is

$$k_d(F) = \frac{3\gamma}{4\pi r_s^3} \exp\left(-\frac{E_b}{kT}\right) \frac{J_1(2\sqrt{-2b})}{\sqrt{-2b}} \quad (2)$$

where $\gamma = q\mu/\epsilon\epsilon_0$ is the Langevin recombination factor,²³ r_s is the initial exciton radius, $E_b = e^2/(4\pi\epsilon\epsilon_0 r_s)$ is the exciton binding energy, kT the thermal energy, J_1 the Bessel function of order one, and $b = e^3 F/(8\pi\epsilon\epsilon_0 (kT)^2)$. F is the electric field, e is the elementary charge, and $\epsilon\epsilon_0$ the effective dielectric constant of the organic semiconductor blend.

Using the OB model with $\mu\tau = 5 \cdot 10^{-16} \text{ m}^2/\text{V}$, $\epsilon = 3.4$ and a maximum quenching of 9%, we could achieve a reasonable fit to our experiment, yielding $E_b = 0.42 \text{ eV}$ as shown in Fig. 4. The discrepancy between the shoulder at low fields in the experimental data and the fit can be explained by the reasonable assumption that the exciton binding energies are distributed over a finite energy range. We attribute the different magnitudes of experimental and modelled the field dependent photoluminescence quenching to higher energy transitions from singlet exciton to polaron pair, which are beyond our measurement range.

Using the Einstein relation, the $\mu\tau$ product can also be expressed in terms of a diffusion length L_D ,

$$L_D = \sqrt{D\tau} = \sqrt{\frac{kT}{e}} \mu\tau, \quad (3)$$

D being the diffusion coefficient. For $\mu\tau = 5 \cdot 10^{-16} \text{ m}^2/\text{V}$, L_D becomes 3.5 nm. Using the singlet exciton lifetime as determined recently for regioregular P3HT,²⁴ $\tau = 0.4 \text{ ns}$, we determine a mobility of the strongly bound charges of about $1.3 \cdot 10^{-6} \text{ m}^2/\text{Vs}$ from the above mentioned $\mu\tau$ product used to describe the data in Fig. 4.

IV. DISCUSSION

TABLE I. Experimentally determined energy levels of regioregular P3HT. The corresponding energies are shown and explained in Fig. 1.

Energy	[eV]	Method
$E_{g,s}$	2.6	PES/IPES
LUMO ⁻ relative to E_F	1.85	PES/IPES
HOMO ⁺ relative to E_F	-0.75	PES/IPES
$E_{g,abs}$	1.85	absorption
$E_{g,s}$	2.58	EQE
$E_{g,abs}$	1.88	EQE
$\Delta E_{S \rightarrow PP}$	≥ 0.42	field dependent PL
$\Delta E_{S \rightarrow P}$	≈ 0.7	PES/IPES vs. absorption, EQE

The experimentally determined energy levels of regioregular P3HT, schematically shown and explained in Fig. 1, are

summarized in Tab. I. A central result is the finding that the transport gap $E_{g,s}$ of 2.6 eV directly corresponds to the energy needed for achieving an efficient photocurrent. We point out that the two independent methods involved in determining this single particle gap—photoemission spectroscopy and external quantum efficiency—rely on very different principles. The former is very surface sensitive and is performed on thin films, whereas the latter relies on charge generation and transport in the bulk of a device. The nevertheless same resulting energy for the transport gap is consistent with former work.²⁵ The difference between $E_{g,s}$ and the absorption onset $E_{g,abs} = 1.85 \text{ eV}$ can be attributed to the exciton binding energy $\Delta E_{S \rightarrow P} \simeq 0.7 \text{ eV}$. Sakurai et al.¹² investigated poly(3-octylthiophene) and found the 1A_g polaron pair state 0.5 eV above the 1B_u exciton by electroabsorption and two-photon absorption. Using electroabsorption, Liess et al.¹¹ determined 0.6 eV for the transition from the 1B_u exciton state to the $^m A_g$ state of another poly(3-alkyl thiophene), pointing out that this might be lower limit for the continuum band threshold. Van der Horst *et al.* calculated 0.61 eV for the latter transition.¹³ We note that our experimental approach, in contrast to Sakurai *et al.*, Liess *et al.* and van der Horst *et al.*, probes the transition from singlet excitons to free polarons, thus giving the exciton binding energy relevant for applications such as photovoltaics.

The apparently lower exciton binding energy found by PL(F) measurements, 0.42 eV instead of 0.7 eV, can be understood as follows. In order to quench the PL, it is sufficient to separate the constituents of the exciton partly, i.e., generating a—still bound—polaron pair. Therefore, not the full energy to generate a free polaron from the exciton has to be invested. In other words, the PL quenching experiment determines the energy of the transition from singlet exciton to polaron pair, $\Delta E_{S \rightarrow PP} \geq 0.42 \text{ eV}$. Note that from the levelling off of the field dependent PL shown in Fig. 4 it is clear that only a fraction of the singlet exciton radiative decay is suppressed. This effect is probably related to the semicrystalline regions in P3HT,²⁶ leading to self-quenching of PL even at zero field. Also, the exciton binding energy, and specifically the exciton to polaron pair transition, is probably distributed in energy. The experimentally determined value of 0.42 eV thus presents a lower limit for the exciton-to-polaron-pair transition energy. It corresponds well with the density functional theory calculations of van der Horst¹³ for polythiophene, where 0.45 eV were determined for this transition, and the photophysical experiments of Sakurai et al.¹² on poly(3-alkyl thiophene) (0.55 eV).

The remaining energy difference between polaron pair and free polaron, which is necessary to create a photocurrent, can be expressed as $\Delta E_{S \rightarrow P} - \Delta E_{S \rightarrow PP}$. Experimentally, we find that $\leq 0.3 \text{ eV}$ are needed for this transition. This energy difference corresponds to a Coulomb binding energy. Assuming a dielectric constant $\epsilon = 3.4$, an electron-hole distance of about 1.4 nm can be derived, which is similar to the d-spacing of 1.6 nm found in X-ray diffraction.²⁷ The latter can be attributed to twice the hexyl side chain length of P3HT, representing the stacking of different molecular units.

We point out that our results suggest that the interpretation of Österbacka et al.²⁸ concerning polaron transitions observed in P3HT by photoinduced absorption spectroscopy might need