Primary Photoexcitations and the Origin of the Photocurrent in Rubrene Single Crystals

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By simultaneously measuring the excitation spectra of transient luminescence and transient photoconductivity after picosecond pulsed excitation in rubrene single crystals, we show that free excitons are photoexcited starting at photon energies above 2.0 eV. We observe a competition between photoexcitation of free excitons and photoexcitation into vibronic states that subsequently decays into free carriers, while molecular excitons are instead formed predominantly through the free exciton. At photon energies below 2.25 eV, free charge carriers are created only through a long-lived intermediate state with a lifetime of up to 0.1 ms and no free carriers appear during the exciton lifetime.

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In organic molecular crystals (OMCs) the small interaction between neighboring molecules naturally leads to the expectation that photoexcitation should result in localized transitions within individual molecules rather than in the delocalized interband transitions typical of covalently bound semiconductors. In fact, the photoinduced generation of free carriers in OMCs was thought for a long time to predominantly occur through the intermediary of localized excitonic states that would autoionize to create free carriers [1,2].

However, by probing the existence of free carriers through their effect on terahertz optical pulses it has recently become possible to detect the signature of a free-carrier density that appears to arise immediately after photoexcitation. As an example it has been possible to observe the appearance of free carriers within 0.5 ps after photoexcitation in pentacene [3]. These experiments seem to imply that free carriers can indeed be directly photoexcited in OMCs.

The question as to what is the most appropriate description of charge-carrier photogeneration in OMCs has not been answered yet in general, and there is an ongoing debate in the literature which also includes the nature of photoexcitations in conjugated polymers. In addition, the variety of excitonic states that can be excited in OMCs can make the photoexcitation picture in these materials quite complex [1,2,4–6]. The most obvious excitonic state is the equivalent of a Frenkel exciton, where photoexcitation leads to the promotion of the ground state electron onto one of the vibronic sublevels of the first excited state of a molecule. But it has also been shown that a purely electronic "frozen lattice" transition can result in what has been called a free exciton, and that local lattice deformations can lead to self-trapped excitons [2,4,7].

In this context, it is important to note that a spectral investigation can provide more relevant information on the nature of the primary photoexcitation than only time-resolved studies. Besides the obvious fact that different photon energies can create different excitations, the energetic structure of any primary excitation that is the main contributor to a given physical observable will be necessarily reflected in the excitation spectrum of that observable. This, in particular, also applies to the photocurrent amplitude. Its excitation spectrum would be different depending on if the principal mode of initial excitation is, e.g., a localized exciton or a band-to-band transition. Moreover, this applies even in the case where the relaxation from the initial excitation to other intermediary states is so fast that it cannot be directly detected with time-resolved techniques.

In this Letter, we investigate the primary photoexcitation mechanisms in rubrene single crystals. We observe a delayed photocurrent after pulsed illumination that directly indicates the existence of a long-lived intermediate state responsible for the creation of free charge carriers, and by an analysis of photoluminescence and photocurrent excitation spectra, we identify two different kinds of primary photoexcitation mechanisms, including a purely electronic transition that can be described as a free exciton. Rubrene has shown one of the highest carrier mobilities observed to date in organic crystals at room temperature [8], can be grown with a high purity, and has been successfully used as the transport layer in organic field-effect transistors (FETs) [9]. While its high mobility is well characterized in the FET geometry [10], and theoretical analysis of its transport properties has appeared [11], to our knowledge no experimental characterization of its optical and photoexcitation properties has been published yet.

In our experiments, a 1 mm thick rubrene sample was illuminated with 20 ps long laser pulses at a repetition rate of 10 Hz. A constant voltage of 700 V was applied to two 2 mm long silver contacts painted on the surface and spaced 4 mm apart along the *b* axis of the crystal. The illuminated area of 1.5 mm^2 was in the middle between the two contacts. These contacts have been previously found to provide nearly Ohmic current-voltage characteristics in

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rubrene [9], and the rubrene crystal has a high resistivity. We expect a negligible potential drop at the contacts and an essentially uniform electric field between them. The wavelength of the light pulses was tuned continuously in the spectral range between 420 and 680 nm. The pulse fluence was kept at 2 $\mu J/\text{cm}^2$ at all wavelengths. This fluence is in the range where the photocurrent response grows linearly with the pulse energy. The dynamics of the photoresponse was monitored by a 2 GHz/s sampling oscilloscope and averaged 150 times. Because of the small photocurrent necessitating a large shunt resistor, the response time of the detection was limited to $\sim 5\ \mu\text{s}$. The experimental setup allowed for the simultaneous detection of both the photoinduced luminescence transient and the photocurrent transient. It is important to note that the absorption in rubrene is already larger than about $50\ \text{cm}^{-1}$ around 600 nm, so that practically all the energy in our laser pulses is absorbed for wavelengths of 600 nm and below. The constant amount of deposited energy guarantees that all our excitation spectra directly correspond to the efficiency with which absorbed energy is converted into luminescence or current.

The photoluminescence (PL) emission spectrum of rubrene determined under continuous wave (cw) excitation is shown in Fig. 1, together with the rubrene absorption spectrum, which shows clear vibronic bands with a separation of about 0.18 eV. This agrees with the largest Raman line at $1430\ \text{cm}^{-1}$ that we observed in Rubrene crystals, and that can be attributed to a C-C stretching vibration (see, e.g., Ref. [6]). One notes a typical mirrorlike relationship between PL emission at 620 nm and above and its cw excitation spectrum (and the absorption spectrum) with the energies of the first vibronic resonances in excitation and absorption almost symmetrical with respect to the 2.17 eV energy, which corresponds to the weaker, higher energy PL band near 570 nm. This band may seem to play the role of a zero-phonon line, but its excitation spectrum is markedly different from the excitation spectrum of the PL emitted at all wavelengths above 600 nm, while it would need to have the same excitation spectrum if it was a zero-phonon transition belonging to the same family of vibronic levels. It follows that the 570 nm emission band must be due to a different emitting species. Among other reasons that we will discuss below, the overlap of the excitation spectrum of the 570 nm band with its emission spectrum leads us to associate it with a purely electronic, frozen lattice transition, which can be assigned to a free exciton [4,12]. The 620 nm band and its vibronic structure, on the other hand, can be assigned to a (probably self-trapped) molecular exciton [4].

An important result, which contrasts with the cw results discussed above, is that the excitation spectrum of the PL transient after pulsed excitation is the same for the 570 nm band and for the 620 nm band. The PL dynamics is characterized by an exponential decay with a time constant of $1.05 \pm 0.2\ \mu\text{s}$ that follows a fast transient in the first 10 ns after illumination [see inset of Fig. 2(a)]. Figure 1 shows the excitation spectrum obtained by monitoring the PL at 620 nm and 1 μs after photoexcitation. This spectrum is very similar to the cw excitation spectrum of the 570 nm band in the wavelength range where they can be compared, and it shows modulations that are opposite to those of the first vibronic resonances of the absorption near 2.3, 2.5, and 2.66 eV. This ''anticoincidence'' between the PL excitation spectra of the 570 nm band and the absorption is consistent with our assignment of this emission band to a free exciton. The excitation to a free-exciton continuum, according to Toyozawa's description [7], is expected to be a relatively smooth function of the photon energy when compared to the excitation to vibronic levels. Since the total number of absorbed photons is always the same, the two effects

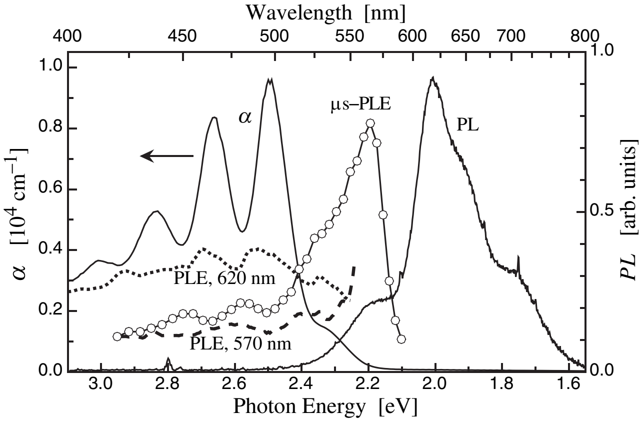

FIG. 1. *b*-polarized absorption spectrum (α), photoluminescence spectrum (PL), cw luminescence excitation spectrum (PLE) monitored at 570 nm (dashed line) and 620 nm (dotted line), and excitation spectrum of the microsecond luminescence transient induced by *b*-polarized light (open circles).

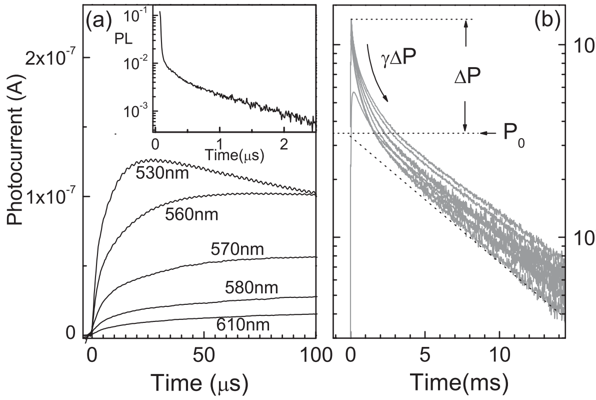

FIG. 2. (a) Detail of the photocurrent buildups for long wavelength excitation. The inset shows the time dynamics of the photoluminescence after the pulsed excitation. (b) Photocurrent transients in the shorter wavelength region, taken every 20 nm between the excitation wavelengths of 570 (lowest curve) and 430 nm. The parts of the decays that correspond to the amplitudes ΔP and P_0 are indicated.

compete: less free excitons are created when more photons are lost to excitation of vibronic levels. But since the transient PL arising from the molecular exciton has the same excitation spectrum as the free exciton, it follows that the molecular excitons that decay radiatively on the microsecond time scale are predominantly created by a transition from a free-exciton state. Whatever excitation is left by the illumination pulse in the molecular vibronic levels, it *does not* directly decay by multiphonon relaxation to the ground state of the molecular exciton. From the fact that photoexcitation in correspondence with the vibronic levels *does* lead to an increased luminescence when measured under cw conditions, it follows that there must be an important, slow contribution to the creation of molecular excitons that is enhanced by absorption into vibronic levels and that dominates the PL in cw experiments while emitting a too low photon flux to be detected as a transient. We argue that such a photoluminescence must be due to photoexcited electrons and holes that meet at a later time to form a molecular exciton and radiatively recombine. The main conclusion is that when vibronic levels are photoexcited, the system has a higher probability of generating free carriers than of reaching the ground state of a molecular exciton.

The transient photoconductivity curves that we determined together with the luminescence are shown in Fig. 2 for different excitation wavelengths. Since rubrene is known to be a hole dominated material, we associate the observed photocurrent with holes. From this data one can derive a total number of carriers $P(t)$ that is contributing to the current from $P(t) = I(t)d^2/e\mu V$, where I is the photocurrent, d is the interelectrode distance, e is the unit charge, V is the applied voltage, and μ is the hole mobility, which is taken to be 10 $\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ [13].

Apart from an initial transient, which is significant only at shorter wavelengths where it is recognized as a quadratic (hyperbolic) decay, the photocurrent decays exponentially with a millisecond time constant which shows little variation with the wavelength of the pulsed excitation and which must be associated with an average effective lifetime of the photoexcited carriers. It may be due to the influence of impurities that provide recombination through a trap state in the band gap. Since this relaxation process does not affect the measurements on the shorter time scales and the initial amplitude of the exponential decay, we do not discuss it further here.

In Fig. 3 we plot separately the excitation spectra corresponding to the amplitude of the initial quadratic decay (ΔP) of the photocurrent and the amplitude of the exponential decay (P_0), together with the rise time of the photocurrent. When compared to the number of photons in the laser pulse, the peak number of excited holes is about 10^4 times smaller. This means that the quantum efficiency for hole generation is of the order of 10^{-4}, consistent with the results of Ref. [14].

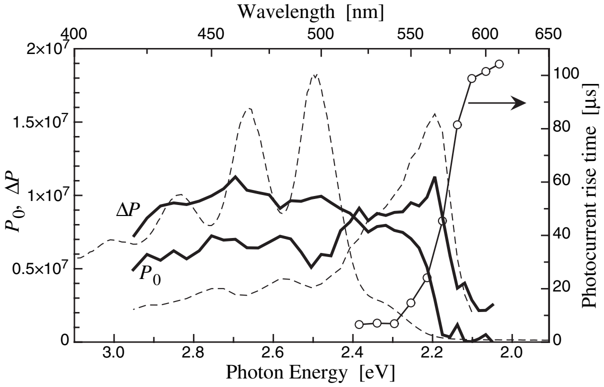

FIG. 3. Spectral dependencies of the amplitudes of the quadratic (ΔP) and exponential (P_0) components of the photocurrent, together with its exponential rise time (open circles). The absorption spectrum and the transient luminescence excitation spectrum of Fig. 1 are shown as a reference (thin dashed lines).

From the photocurrent spectra in Fig. 3 one sees that the amplitude $P_0(\lambda)$ of the exponential decay in the free-carrier number increases as soon as the photon energy approaches the free-exciton band at 570 nm and peaks close to the maximum of the free-exciton transition. $P_0(\lambda)$ dominates the number of photoinduced carriers until the amplitude $\Delta P(\lambda)$ of the quadratic decay becomes significant. This happens when the linear absorption is so strong that it confines the excitation close to the surface of the sample, creating a larger carrier density and hence a stronger quadratic recombination. Since the total number of absorbed photons is constant, whenever $\Delta P(\lambda)$ increases (especially in correspondence with the vibronic absorption lines), $P_0(\lambda)$ decreases. By fitting the photocurrent time dynamics at the shorter wavelengths and calculating the carrier density using the absorption data plotted in Fig. 1 and the total number of carriers in Fig. 3, it is possible to determine a quadratic recombination coefficient of $(4 \pm 1.5) \times 10^{-10}$ $\mathrm{cm}^3\,\mathrm{s}^{-1}$. This value is remarkably constant in the wavelength interval between 510 and 420 nm where the quadratic recombination is clearly observed. The increased quadratic recombination after pulsed illumination leads to an effective decrease of the number of carriers left behind in the crystal for optical energies corresponding to the vibronic resonances. But under cw excitation, quadratic recombination does not play a role, and excitation in coincidence with the vibronic resonances will lead to an enhanced creation of free electron and hole pairs that will then be able to recombine at a later time to form molecular excitons, and consequently lead to the increased PL efficiency.

A surprising feature of the photocurrent dynamics appears for excitation energies below 2.25 eV: the illumination pulse does not immediately create any free carriers and the photocurrent grows quite slowly after photoexcitation, long after the microsecond decay of the photoluminescence. This means that free carriers start being generated after the excitons responsible for the PL have recombined. The buildup time of the photocurrent has an almost constant value of the order of 0.1 ms in the wavelength range between 610 and 590 nm (2.04–2.10 eV). This time must correspond to the lifetime of an intermediate state that autoionizes into electrons and holes and that must be formed starting from the free exciton. At higher excitation energies, the rise time of the current, and hence the intermediate state lifetime, shortens until, at excitation energies larger than 2.25 eV, we cannot resolve the buildup time of the photocurrent anymore. For these higher excitation energies, we cannot exclude an instantaneous contribution to the photocurrent through creation of delocalized electrons and holes, especially when the excitation energy corresponds to the vibronic resonances, as mentioned above. But in the range of photoexcitation energies between 2.0 and 2.25 eV, the general coincidence between the excitation spectrum $P_0(\lambda)$ and the free-exciton spectrum indicates that the free exciton must play a role in the creation of electrons and holes. In this spectral region, we have very clear proof that photoexcitation does not create any electron-hole pairs either directly or through ionization of the free exciton. Instead, the free exciton ultimately decays into a longer-lived intermediate state that then autoionizes into free carriers. Such an intermediate state may be associated with the triplet exciton that can be formed through intersystem crossing in many organic systems [1,15,16].

Finally, the observation of a free exciton and the fact that it can be photoexcited over a wide spectral range raise the question as to weather the terahertz absorption signal observed in Ref. [3] in pentacene may not be due to transitions induced by the terahertz field between the closely spaced sublevels of the free exciton [7,12], similar to the microwave transitions that have been observed to occur between free-exciton sublevels in other organic materials [16], which brings us back to the initial question about the nature of the primary photoexcitation in OMCs. Additional insights into this question and into the electronic states of Rubrene single crystals will be obtained by a further investigation of the effects presented here, such as of their temperature quenching properties.

In conclusion, we have shown that the primary photoexcitation in rubrene single crystals consists of free excitons starting at photon energies above ~2.0 eV, with also some excitation of vibronic levels at higher photon energies. The free exciton can radiatively recombine to emit a PL band centered at 570 nm, can convert into a molecular exciton that radiates the PL band that peaks at 620 nm, or can lead (possibly through the molecular exciton) to an intermediate state with a lifetime of up to 0.1 ms, which then self-ionizes into electrons and holes. Important highlights of this work are (1) the observations that the excitation in the vibronic resonances does not decay to the ground state of a molecular exciton but leads instead to delocalized carriers that only later meet to form a molecular exciton and radiatively recombine, and (2) the clear and direct evidence, provided by the observed delayed onset of the photocurrent, that it is impossible to obtain free carriers directly at optical excitation energies lower than 2.25 eV, where free carriers are exclusively formed by autoionization of a long-lived intermediate state originating from the initial creation of a free exciton.

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