Ultrafast carrier dynamics in pentacene, functionalized pentacene, tetracene, and rubrene single crystals

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We measure the transient photoconductivity in pentacene, functionalized pentacene, tetracene, and rubrene single crystals using optical pump-terahertz probe techniques. In all of the samples studied, we observe subpicosecond charge photogeneration and a peak photoconductive response that increases as the temperature decreases from 297 down to 20 K, indicative of bandlike transport. Similar decay dynamics are observed at room temperature, but at low temperatures the decay dynamics measured in pentacene, rubrene, and tetracene crystals are much faster than those observed in functionalized pentacene crystals, revealing different charge trapping properties. © 2006 American Institute of Physics. [DOI: 10.1063/1.2193801]

Over the past decade, considerable efforts in organic synthesis and purification have resulted in improved organic semiconductors with room-temperature charge carrier mobilities well above 1 cm^2/V s.[1,2] A number of experimental and theoretical studies directed towards clarifying mechanisms of charge carrier generation and transport have also been carried out.[3–5] However, the exact nature of charge carrier photogeneration and transport in organic semiconductors is still not completely understood due to difficulties in assessing *intrinsic* properties that are often masked by impurities, contact effects, or grain boundaries. Recently, ultrafast optical pump-terahertz probe techniques[6] have been used to perform noncontact measurements of transient photoconductivity in organic single crystals and polycrystalline thin films over picosecond time scales,[7–10] making it possible to probe the intrinsic nature of mobile charge carriers before they are trapped at defect sites. In this letter, we compare the transient photoconductive properties of pentacene, functionalized pentacene, tetracene, and rubrene single crystals assessed using time-resolved terahertz pulse spectroscopy. In all samples, we observe fast (<400 fs) charge carrier photogeneration as well as bandlike charge transport characterized by an increasing charge carrier mobility as the temperature decreases. The decay dynamics due to carrier trapping are also explored, revealing, in particular, a transition to faster decay dynamics in pentacene single crystals below 70 K.

In our studies, we used single crystals of ultrahigh-purity pentacene (Pc),[2] pentacene derivative functionalized with triisopropylsilylethynyl (TIPS) side groups (FPc),[7,9,11] rubrene (Rub),[12,13] and tetracene (Tc). The Pc powder was purified using vacuum sublimation under a temperature gradient.[2] Rub, Tc, and Pc single crystals were obtained using physical vapor transport techniques as described in Refs. 2 and 12. The FPc single crystals were grown in a saturated tetrahydrofuran (THF) solution at 4 °C.[11] Eight FPc crystals and four Pc, Rub, and Tc crystals (each) were studied and yielded similar results.

A detailed description of the optical pump-terahertz probe experimental setup used in our studies can be found elsewhere.[14,15] The samples were mounted on 1–1.5 mm apertures in an optical cryostat (sample in helium vapor) and excited with 400 nm, 100 fs pump pulses from an amplified Ti:sapphire laser source (1.08 kHz). Both the terahertz probe and optical pump pulses were at normal incidence to the *a-b* plane of the single crystal samples. The optically induced negative differential transmission of the terahertz peak amplitude [$-(T-T_0)/T_0 \equiv -\Delta T/T_0$, where T_0 is the amplitude of the terahertz pulse transmitted through the unexcited sample] was monitored as a function of delay time (Δt) with respect to the optical pump pulse. The relationship between $-\Delta T/T_0$ and the transient photoconductivity has been discussed in Refs. 5, 7–9, and 15. Briefly, if the phase shift between the terahertz pulses transmitted through unexcited and optically excited sample is small, as was the case for all our samples, then $-\Delta T/T_0$ is directly proportional to the transient photoconductivity.[7–9] From the peak value of the photoconductive transient, the product of charge carrier mobility μ and charge carrier photogeneration efficiency η can then be calculated using $(-\Delta T/T_0)_{max} = \mu \eta F_a Z_0 \lambda / [hc(1+N)]$, where F_a is the *absorbed* fluence, Z_0 is the free space impedance, λ is the optical wavelength, h is Planck's constant, c is the speed of light, and N is the refractive index of the unexcited sample.[9,10,15] In all measurements reported here, the electric field of the optical and terahertz pulse was kept parallel to the highest mobility axis of the crystals. Upon azimuthal rotation of the crystals, we observed a photoconductivity an-

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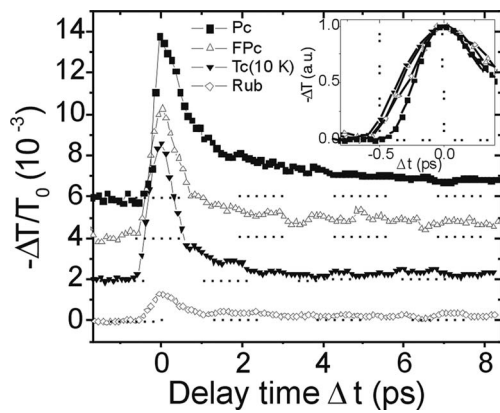
FIG. 1. Differential transmission of the terahertz pulse ($-\Delta T/T_0$) as a function of pump-probe delay time (Δt) obtained in Pc, FPc, and Rub crystals (all at room temperature) and in Tc (at 10 K) upon photoexcitation with 400 nm, 100 fs pump pulses. The transients are offset along the y-axis for clarity. The inset shows the differential transmission of the terahertz pulse normalized to its value at $\Delta t=0$ and illustrates subpicosecond charge photogeneration in all samples.

isotropy within a factor of $\sim 2-4$, a detailed study of which will be reported elsewhere.

Complete absorption of the 400 nm optical pump beam is observed in FPc, Tc, and Rub crystals, and $\sim 90\%$ absorption is achieved in Pc crystals. Figure 1 illustrates the differential terahertz transmission ($-\Delta T/T_0$) as a function of delay time (Δt) between the optical pump and terahertz probe pulses obtained in Pc, FPc, Tc, and Rub crystals upon photoexcitation with optical pulses with the fluence of ~ 0.5 mJ/cm^2. Transients shown for Pc, FPc, and Rub were obtained at room temperature (297 K), while that for Tc was taken at 10 K. The inset in Fig. 1 shows the onset of the photoresponse, normalized to its maximum value at $\Delta t=0$, and reveals a fast (<400 fs rise time limited by the time resolution of our setup) carrier photogeneration process in all crystals. Subpicosecond charge photogeneration has been previously observed in FPc and Pc single crystals[7,8] and thin films.[9,10] The similar trend observed in all crystals studied here (inset of Fig. 1) suggests that subpicosecond photogeneration of free carriers,[7–10,16] and not only of excitons,[3] in the absence of a static electric field is an intrinsic property of oligoacenes.

At room temperature, measurements of the peak value of $-\Delta T/T_0$ yielded $\mu\eta \sim 0.3-0.35$, $0.15-0.2$, $0.05-0.06$, and 0.03 cm^2/V s for Pc, FPc, Rub, and Tc crystals, respectively. (Note that if we assume $\eta=1$, then these $\mu\eta$ values provide a *lower estimate* for the carrier mobility μ. If $\eta<1$, then the mobility value is higher.) The observed difference in $\mu\eta$ could be due to the differences in (i) *intrinsic* carrier mobility, (ii) *initial* photogenerated free carrier yield, and (iii) carrier loss due to charge trapping or recombination occurring within 400 fs after photoexcitation (included in η), not resolved in our experiment. The comparison between the room-temperature (RT) values of $\mu\eta \sim 0.3-0.35$ cm^2/V s obtained in our *ultrapure* Pc single crystals and those measured in high-quality, but not extra purified, Pc single crystals of $\mu\eta \sim 0.2$ cm^2/V s using a similar optical pump-terahertz probe setup (Ref. 8) suggests that the factor (iii) has a relatively small contribution to the differences in $\mu\eta$ observed in various crystals at RT. This is supported by our previous observation of the $\mu\eta$ values measured in good quality FPc thin films reaching 30%–40% of those obtained
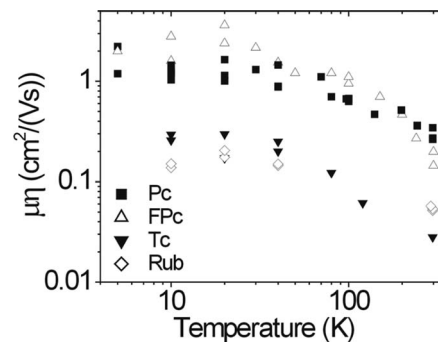
in FPc single crystals, in spite of the abundance of deep traps at the grain boundaries in thin films.[10] Therefore, the differences in the trapping properties of FPc, Pc, Rub, and Tc crystals most likely account only for a factor of up to ~ 2 in the differences in $\mu\eta$ values obtained in these crystals at RT, while further differences are due to factors (i) and (ii). For example, the lower transient photoconductivity observed in Rub compared to Pc single crystals at RT at 400 nm could be mostly due to the lower photogeneration efficiency [factor (ii)] in Rub, in qualitative agreement with Refs. 13 and 17.

Figure 2 shows the temperature dependence of $\mu\eta$ measured in Pc, FPc, Tc, and Rub single crystals. As the temperature *decreased* from 297 to about 20 K, $\mu\eta$ *increased* in all samples by a factor of 3–10, depending on the crystal. A slight decrease in $\mu\eta$ is observed below 20 K, which may be due to impurity scattering at low temperatures.[18] Assuming η does not increase as the temperature decreases, we can attribute the temperature dependence of $\mu\eta$ shown in Fig. 2 to bandlike charge carrier transport,[7–10,18] which has not been previously observed over such a *wide* temperature range in Tc and Rub single crystals.[13,19,20] The initial increase of $\mu\eta$ by a factor of 1.5–3 (depending on the crystal) as the temperature is lowered from 297 to about 150 K (Fig. 2) is consistent with the increase in charge carrier mobility observed from field-effect measurements in Rub (Ref. 13) and from space-charge-limited-current measurements in Pc (Ref. 2) and Tc (Ref. 19) single crystals over the same temperature range. Interestingly, in our ultrapure Pc crystals, the temperature dependence of $\mu\eta$ ($\mu\eta \sim 0.3$ cm^2/V s at 297 K and $\mu\eta \sim 1.5$ cm^2/V s at 10 K) is much stronger than that obtained in Pc crystals in Ref. 8 ($\mu\eta \sim 0.2$ cm^2/V s at 297 K and $\mu\eta \sim 0.4$ cm^2/V s at 10 K) under similar conditions. This suggests that the contribution from carrier loss due to charge trapping within 400 fs after photoexcitation to the measured $\mu\eta$ values is more substantial at low temperatures, which is expected due to higher charge carrier mobility at low temperatures. Surprisingly, the solution-grown FPc crystals exhibit a temperature dependence for $\mu\eta$ similar to that seen in the ultrapure Pc crystals grown by vapor transport methods.

Decay dynamics of the transient photoconductivity provide further information about charge transport and trapping processes.[9,10,21] Figure 3 compares dynamics of the transient photoconductivity normalized to its value at $\Delta t=0$, obtained at 297 K [Fig. 3(a)] and 10 K [Fig. 3(b)]. At 297 K, all the crystals exhibited similar decay dynamics, at least for Δt
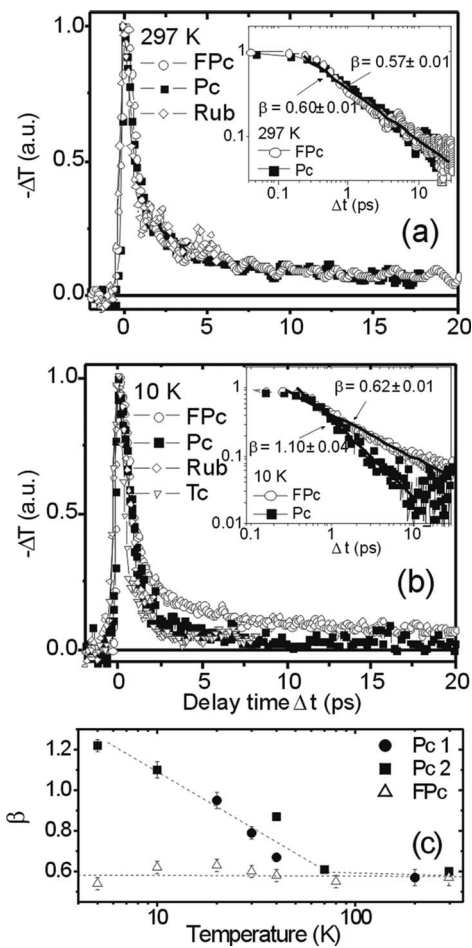

FIG. 2. Temperature dependence of the product of mobility (μ) and photogeneration efficiency (η) calculated from the peak value of $-\Delta T/T_0$ in Pc, FPc, Tc, and Rub samples. The minimum detectable $\mu\eta$ product is 0.01 cm^2/V s.

FIG. 3. Differential transmission of the terahertz pulse normalized to its value at $\Delta t = 0$ in the case of (a) FPc, Pc, and Rub samples at 297 K and (b) FPc, Pc, Rub, and Tc samples at 10 K. Insets show the FPc and Pc data replotted on a log-log scale and fitted with the power-law function $\sim(\Delta t)^{-\beta}$ (thick solid lines) with (a) $\beta = 0.57$ and 0.6 for FPc and Pc, respectively, at 297 K and (b) $\beta = 0.62$ and 1.1 for FPc and Pc, respectively, at 10 K. (c) Power-law exponents (β) obtained from fits to the decay dynamics at various temperatures in one FPc and two Pc (Pc 1 and 2) single crystal samples. Dashed lines are guides for the eye.

< 5 ps. Low signal-to-noise ratios obtained with Rub and Tc samples at $\Delta t > 5$ ps did not allow a detailed analysis of the decay dynamics in these crystals. In FPc and Pc crystals, the decay over at least two orders of magnitude in Δt can be fitted with a power law $\sim(\Delta t)^{-\beta}$, with $\beta \sim 0.57 \pm 0.01$ and 0.60 ± 0.01, respectively [inset of Fig. 3(a)].[7,9,10] While the decay dynamics in FPc are weakly temperature dependent [i.e., $\beta \sim 0.5 - 0.7$ from 5–297 K in Fig. 3(c) and in Refs. 7 and 9], which is consistent with multistep tunneling of nearly small molecular polarons (MP),[4,9] those in Pc become faster as the temperature decreases [inset of Fig. 3(b) and Fig. 3(c)], in agreement with Ref. 8. In particular, the power-law exponent β reaches 1.22 ± 0.03 at 5 K [Fig. 3(c)]. Qualitatively, the decay dynamics observed in Rub and Tc crystals at high and low temperatures (e.g., 297 and 10 K) are similar to that of the Pc. Faster decay dynamics at lower temperatures have also been previously observed in conjugated polymers.[21] There, a long-time tail of the photoconductivity was attributed to trap-dominated transport, characterized by reduced charge emission from traps at low temperatures. In our ultrapure Pc crystals, the change in the decay dynamics (for $\Delta t > 2$ ps) occurs at temperatures only below 70 K [Fig.

3(c)], which could indicate that the charge traps are rather shallow. Interestingly, the change in the decay dynamics with temperature is much weaker in FPc [Fig. 3(c)],[7,9] which could indicate the absence of such traps in FPc. The exact nature of the observed difference in the temperature dependence of the decay dynamics of FPc and Pc at $\Delta t > 2$ ps requires further investigation. However, it is possible that the shallow traps observed in the Pc samples are related to structural defects (such as point defects, dislocations, etc.)[17,19,22] specific to a herring-bone-type packing. These defects are apparently absent in FPc, which assumes brick-wall-type packing.[7,11]

In summary, we observed subpicosecond charge photogeneration and bandlike charge carrier mobility in the wide temperature range between 297 and 20 K in Tc, Rub, Pc, and FPc single crystals. At room temperature, similar decay dynamics of the transient photoconductivity are observed in all crystals. The temperature dependence of the decay dynamics for $\Delta t > 2$ ps in FPc is different to those in Pc, Rub, and Tc crystals, which indicates differences in the charge trapping properties of these materials.

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