PHYSICAL REVIEW B **71**, 035204 (2005)

Bandlike transport in pentacene and functionalized pentacene thin films revealed by subpicosecond transient photoconductivity measurements

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(Received 17 August 2004; revised manuscript received 23 September 2004; published 12 January 2005)

We observe bandlike transport in pentacene and functionalized pentacene thin films using time-resolved terahertz pulse spectroscopy. The measured transient photoconductivity exhibits fast (<400 fs) photogeneration of mobile charge carriers and reveals a transient carrier mobility that increases as the temperature decreases from 300 K down to 10 K, indicative of bandlike transport over subpicosecond time scales. A wavelength-independent photoconductive signal is observed. The transient photoconductivity in the thin-film samples exhibits a single-exponential decay, whereas a power-law decay is seen in single-crystal samples.

DOI: 10.1103/PhysRevB.71.035204 PACS number(s): 78.47.+p, 73.50.Gr, 73.50.Pz, 78.20.−e

Organic semiconductors have gained considerable interest due to their potential applications in molecular electronics and photonics.[1,2] Organic thin films are technologically attractive due to their easy processing, low cost, and potentially tunable properties. In order to develop organic electronic devices, it is important to clarify the mechanisms of conductivity in organic materials. However, using thin-film device structures to characterize a material's *intrinsic* electronic properties is complicated due to the effects of metal-organic interfaces at contacts, device geometry, and defects on the overall electronic response of the device. As a result, despite substantial experimental efforts, intrinsic semiconductor bandlike transport characterized by a significant *increase* in carrier mobility as the temperature *decreases* over a wide temperature range[3–5] has not yet been observed in organic thin films,[2] except those containing radical ion salts.[6] In particular, most studies carried out on polyacene thin films reported thermally activated charge transport (mobility increasing with temperature[7,8]) or, in exceptional cases, temperature-independent mobility.[9] On the other hand, bandlike transport has been observed in single crystals of naphthalene, rubrene, anthracene, tetracene, pentacene, and functionalized pentacene by time-of-flight,[3,10] space-charge-limited current,[11] field-effect,[12] and transient photoconductivity measurements.[4,5,13] However, the exact nature of charge carrier transport in organic molecular crystals is still not understood and has been the focus of many theoretical studies.[14–17] Furthermore, the mechanisms responsible for the photogeneration of mobile charge carriers in organic semiconductors remain controversial.[18,19]

Recently, ultrafast techniques that employ terahertz (THz) pulses for assessing the electronic properties of materials have been developed.[20–23] Subpicosecond (sub-ps) gated detection of the amplitude and phase of the electric field of the approximately picosecond-wide THz pulses allows for the real and imaginary components of the conductivity of a material to be determined in the far-infrared region of the spectrum ($\sim$0.1–3 THz) without having to resort to Kramers-Kronig analysis.[20–23] In particular, optical-pump–THz-probe time-resolved techniques allow probing of the transient photoconductivity in materials with sub-ps time resolution and, therefore, represent a sensitive *noncontact* tool for studying the dynamics of mobile charge carriers in materials before they are trapped at defect sites. Optical-pump–THz-probe techniques have been widely utilized in studies of ultrafast carrier dynamics in inorganic semiconductors, quantum dots, superconductors, liquids, insulators[24,25] and, more recently, in organic single crystals[4,5] and polymers.[26]

In this article, we report on the ultrafast photoexcited charge carrier dynamics in low-molecular-weight organic thin films using time-resolved terahertz pulse spectroscopy. We measure the wavelength and temperature dependence of the transient photoconductivity in pentacene and functionalized pentacene thin films which reveal bandlike transport in these polyacene thin films. We also compare the transient photoconductive response in thin films to that observed in single-crystal samples of functionalized pentacene.

For our studies, we chose three systems: (i) regular pentacene (Pc) polycrystalline thin films, (ii) polycrystalline thin films of pentacene derivative functionalized with triisopropylsilylethynyl (TIPS) side groups[4,27] (FPc films), and (iii) FPc single crystals. Pc and FPc films of 150–350 nm thickness were prepared by thermal evaporation of Pc and FPc powder, respectively, heated to 200–250 °C in high vacuum ($\sim 10^{-6}$ Torr) at a deposition rate of 0.3 Å/s on a mica substrate maintained at room temperature. This deposition method resulted in polycrystalline films, as confirmed by transmission electron microscopy, with grain sizes of 0.3–1.2 μm, depending on the film.[28] The FPc single-crystal samples were grown in a saturated tetrahydrofuran (THF) solution at 4 °C and were typically 2 mm $\times$ 4 mm with a thickness of 0.3–0.5 mm. As many as eight single-crystal samples were tested in the experiments presented here and yielded similar results.

A detailed description of the optical-pump–THz-probe experimental setup used in our studies can be found elsewhere.[25,29,30] Briefly, an amplified Ti:sapphire laser source (800 nm, 100 fs, 1 kHz) was used to generate optical pump pulses in the wavelength region of $\lambda = 400$–800 nm through various wave-mixing schemes as well as THz probe pulses generated via optical rectification in a 0.5-mm-thick ZnTe crystal. The samples were mounted on 1–1.5-mm apertures in an optical cryostat (sample in vapor), and both the THz probe and optical pump pulses were at normal incidence to the surface of the films or the *a*-*b* plane of the FPc crystal samples. The electric field of the THz pulse transmitted through the samples was detected by free-space electro-optic sampling in a 2-mm-thick ZnTe crystal and monitored as a function of delay time with respect to the optical pump pulse.

Figure 1(a) shows the electric field $[T(t)]$ of the THz pulse transmitted through a Pc thin film in the absence of optical excitation at room temperature (solid line, peak value of T_0). The spectrum of this THz pulse peaks at about 1 THz and extends to approximately 2.5 THz [inset of Fig. 1(a)]. Optical excitation of the sample results in a change in the transmitted electric field $[-\Delta T(t)]$, as shown in Fig. 1(a) (dashed line) for the case of the delay time between the optical pump and THz probe pulses of $\Delta t = 0$, which corresponds to temporal overlap between the peak of the optical pump pulse and the positive peak of the THz probe pulse. Figure 1(b) shows the real and imaginary components of the photoinduced conductivity σ in the thin-film sample, as extracted from the THz wave forms in Fig. 1(a).[20–23] The real part of the conductivity (Re σ) is almost constant over the bandwidth of the THz pulse, while the imaginary component (Im σ) of the conductivity is roughly zero. Similar behavior was also observed in recent time-resolved THz pulse studies of transient photoconductivity in pentacene single crystals,[5] and suggests that the conductivity of the mobile photocarriers follows a simple Drude model[31] with $\omega\tau_s \ll 1$, where ω is the THz frequency and τ_s is the carrier scattering time. A simple Drude response was also observed for charge carriers in conducting polypyrrole thin films using terahertz pulse spectroscopy.[21] However, a localization-modified Drude model was needed to describe the nature of charge carriers in conducting poly-3-methylthiophene, where the real part of the conductivity increases with frequency at low frequencies.[22] The real part of the conductivity was also observed to increase with frequency at short time scales in time-resolved THz pulse studies of transient photoconductivity in MEH-PPV polymer thin films.[26]

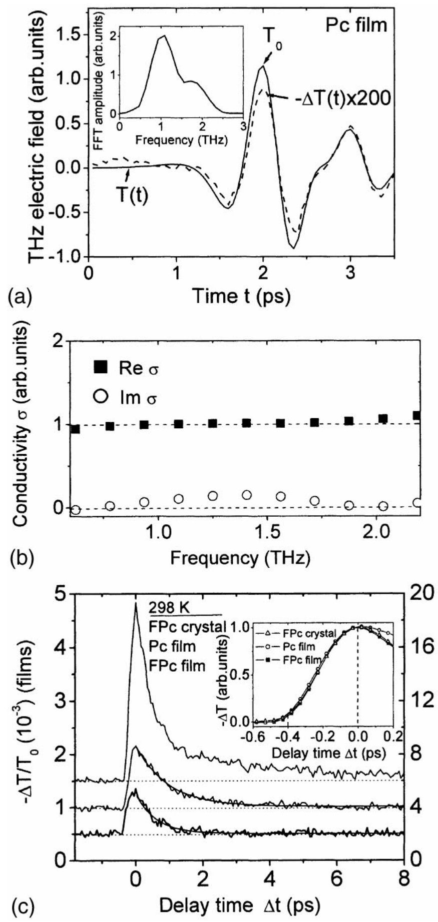

FIG. 1. (a) THz electric field $[T(t)]$ transmitted through an unexcited Pc film (solid line) and the change in THz electric field $[-\Delta T(t)]$ under optical excitation at the optical-pump–THz-probe delay time $\Delta t = 0$. The inset shows the spectrum of the transmitted THz pulse. (b) Frequency dependence of the real and imaginary parts of the photoconductivity (σ) derived from the Pc film data in (a). The dashed lines are guides to the eye for a flat, frequency-independent response. (c) Relative change in the peak of THz transmission $-\Delta T/T_0$ due to transient photoconductivity under optical excitation with $\lambda = 580$ nm and $F \sim 1$ mJ/cm^2, obtained in FPc crystals and FPc and Pc thin films as a function of optical-pump–THz-probe delay time Δt. Single-exponential fits to the thin-film data are also shown. The offset along the *y* axis is for clarity. The inset illustrates the 0.4 ps onset of photoconductivity in these systems, limited by the time resolution of the setup.

We note that excitons may also be generated in our samples, but the polarization of photogenerated neutral excitons by the THz electric field would result in a phase shift between the $-\Delta T(t)$ and $T(t)$ wave forms[32] and would produce a nonzero, negative-valued imaginary component of the complex conductivity.[26] Since we do not observe this excitonic signature in our time-resolved THz pulse data and since the extracted conductivity is predominantly real and roughly flat over the frequency bandwidth [Fig. 1(b)], then we can conclude that the origin of the modulation $(-\Delta T)$ of the THz probe pulse must be due to the presence of mobile, Drude-like charge carriers photogenerated by the optical pump pulse in the sample. The absence of the excitonic features in our data (despite the likely presence of photogenerated excitons in our samples[6,14]) could suggest that the polarizability of the excitons at THz frequencies is much smaller than the Drude component due to mobile carriers in these materials. The relative flatness of Re σ and the fact that Im σ is approximately equal to zero up to 2.2 THz, as shown in Fig. 1(b), implies that the scattering rate τ_s for charge carriers is about 10 fs or less, which is similar to the carrier scattering time in conducting polypyrrole of 12.6 fs.[21] Since the width of the main positive peak of the THz pulse [Fig. 1(a)] is greater than 300 fs, it is reasonable to expect that the mobile charge carriers respond in phase with the changing electric field of the THz pulse (i.e., a purely resistive response in the low-frequency limit of the Drude model where $\omega\tau_s \ll 1$). In this case, the optically induced relative change in the THz peak amplitude ($-\Delta T/T_0$) provides a direct measure of the transient photoconductivity. Moreover, for $|\Delta T/T_0| \ll 1$ the photoconductivity (σ) is directly proportional to $-\Delta T/T_0$.[4,5,25,29]

Figure 1(c) illustrates the differential THz transmission ($-\Delta T/T_0$) under optical excitation at room temperature as a function of delay time (Δt) between the optical pump and THz probe pulses, obtained in a FPc crystal and FPc and Pc thin films. The inset of Fig. 1(c) shows the onset of the photoresponse, normalized to its maximum value at $\Delta t=0$, and reveals a fast photogeneration process for mobile carriers with characteristic times below ~400 fs limited by the time resolution of our setup in all our samples. The decay dynamics of the transient photoconductivity yields information about the nature of the charge transport, trapping, and recombination.[33–35] In FPc crystals, the transient photoconductivity exhibited a fast initial decay during the first few picoseconds, followed by a slow decay best described by a power-law function ($\Delta t^{-\beta}$), which has been attributed to dispersive transport.[4,35] In contrast, photoconductivity in both FPc and Pc films exhibited fast single-exponential decay dynamics ($\sim\exp[-\Delta t/\tau]$) with time constants $\tau \sim 0.64$ and 0.97 ps, respectively, most likely due to deep-level traps at the interfaces between crystallites.[8]

In order to better understand the difference in magnitude of the signals [$\Delta T(0)/T_0$] observed in FPc crystals and FPc and Pc films at the same incident fluence, we present the photoconductivity $\sigma = ne\mu$, where e is the electric charge, μ is the charge carrier mobility, and n is the photoinduced carrier density. Such representation of σ is applicable, since σ is real and frequency independent in the studied frequency range in all our samples, as discussed earlier. It can be shown[28] that $-\Delta T(0)/T_0 = \mu\eta F(1-\exp[-\alpha d])A$, where η is the photogeneration efficiency for mobile charge carriers that may include possible partial carrier loss during the first 400 fs after photoexcitation by the pump pulse, α is the absorption coefficient, d is the sample thickness, F is the incident fluence, and A is a constant that incorporates the free space impedance, the optical wavelength, and the refractive index of the unexcited sample. Using this relation, room-temperature values for the product of mobility and photogeneration efficiency ($\mu\eta$) of ~0.19, 0.025, and 0.02 $\mathrm{cm}^2/(\mathrm{V\,s})$ for FPc crystals, FPc thin films, and Pc thin films, respectively, are obtained from the measured peak values of $-\Delta T/T_0$.

In order to gain insight into the photogeneration process, we repeated the experiment at various pump wavelengths. Due to the short temporal width of the optical pulses (~100 fs), the illumination is not monochromatic, as illustrated in Fig. 2(a), which shows the spectra of some of the optical pump pulses utilized in our experiment. Typical optical absorption spectra of the thin-film and single-crystal samples are shown in Fig. 2(b). No transient photoresponse was obtained from FPc and Pc thin films upon excitation at 800 nm—the spectral region in which there is too little absorption [Fig. 2(b)]. At all wavelengths of optical excitation *within* the absorption spectra, we observed a photoinduced change in THz transmission with a fast onset and decay dynamics similar to that shown in Fig. 1(c) in all our samples. Furthermore, $\mu\eta$ calculated from our data is wavelength independent within our experimental error, as shown in Fig. 2(c). Wavelength-independent photocarrier generation has also been observed in other organic semiconductors using ultrafast techniques.[19] However, conventional steady-state photoconductivity measurements typically exhibit wavelength-dependent mobile carrier photogeneration efficiencies,[6,14] as recently reported for pentacene single crystals.[36]

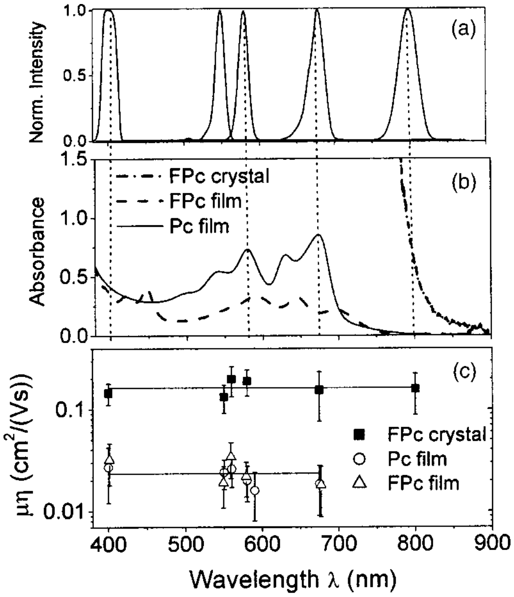

FIG. 2. (a) Normalized intensity spectra of selected optical pump pulses. Spectra of pulses centered at 550 and 590 nm are not included for clarity. (b) Absorption spectra of a FPc crystal and FPc and Pc thin-film samples. (c) Product of mobility and photogeneration efficiency ($\mu\eta$) measured in a FPc crystal and FPc and Pc thin-film samples at room temperature.

The temperature dependence of the photoresponse also provides valuable information about the mechanism of photoconductivity.[3,13] In both single crystals and thin films, the transient photoconductivity *increased* as the temperature *decreased*, as demonstrated in Fig. 3. In particular, Fig. 3(a) shows the photoinduced change in THz transmission ($-\Delta T/T_0$) as a function of pump-probe delay time (Δt) obtained at temperatures of 298, 40, and 10 K upon optical excitation at 400 nm in a FPc crystal sample. Figure 3(b) illustrates $-\Delta T(\Delta t)/T_0$ obtained in a Pc thin film at temperatures of 298, 120, 80, and 20 K using 580-nm excitation. The photoconductivity decay dynamics did not change appreciably with temperature in either the film or single-crystal samples. At all temperatures studied, the transients obtained from the FPc crystals exhibited a fast (<2 ps) initial decay followed by a slow decay, which persisted over time scales from ~2 ps to at least ~600 ps and could be fitted with the power-law function $\Delta t^{-\beta}$, where β ranged between 0.5 and

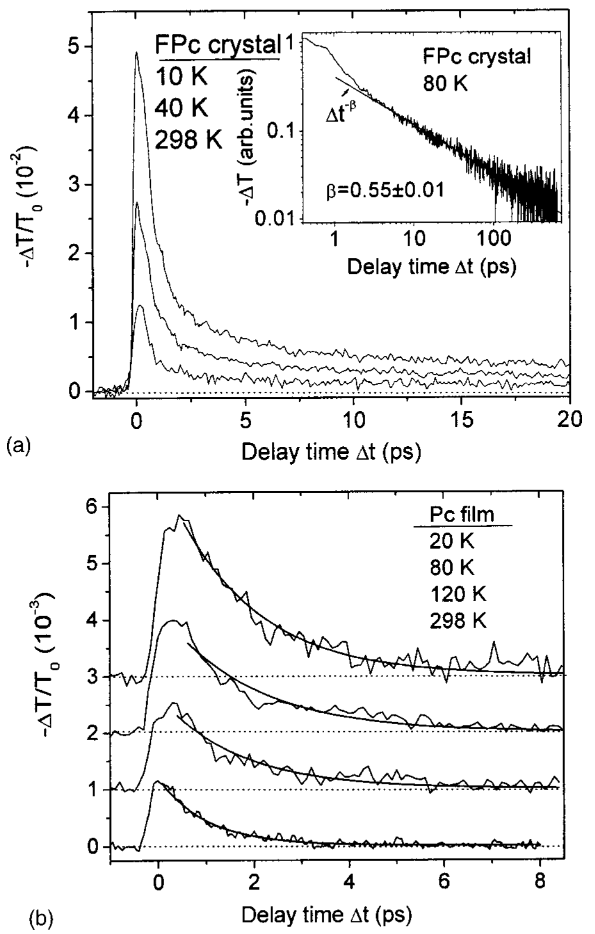

FIG. 3. Differential transmission of the peak of the THz probe pulse as a function of delay time and temperature. (a) FPc crystal under optical excitation at 400 nm with $F \sim 0.4$ mJ/cm^2 at temperatures of 298, 40, and 10 K. The inset shows a power-law fit $\Delta t^{-\beta}$ ($\beta = 0.55$) to the data obtained at 80 K for $\Delta t > 2$ ps. (b) Pc thin film under optical excitation at 580 nm with $F \sim 1$ mJ/cm^2 at temperatures of 298, 120, 80, and 20 K. Single-exponential fits to the data are also shown.

0.7 [e.g., $\beta = 0.55$ at 80 K as illustrated in the inset of Fig. 3(a)].[4] In Pc films, the decay dynamics could be described by a single exponential ($\exp[-\Delta t/\tau]$) throughout the entire temperature range, with a characteristic time constant $\tau \sim 1$–1.7 ps. The temperature (T^o) dependence of $\mu\eta$ calculated from the data for four FPc crystal samples, two Pc thin films, and a FPc thin film is shown in Fig. 4. As the temperature *decreased* from 298 K to 5 or 10 K, $\mu\eta$ *increased* from ~ 0.2 cm^2/(V s) to ~ 2–3 cm^2/(V s) in FPc crystals, and from ~ 0.02 cm^2/(V s) to ~ 0.07 cm^2/(V s) in Pc thin films (with a similar trend seen in FPc films). It should be emphasized that this bandlike mobility which increases as the temperature decreases (Fig. 4) has not been previously observed in polyacene thin films. In addition, even though bandlike mobility has been obtained in several organic crystals,[3–5,11–13] only a few studies reported the bandlike behavior over a wide temperature range,[3–5] as observed in our experiments (Fig. 4). The thin-film data in Fig. 4 can be fitted with the power-law function $\mu\eta \sim (T^o)^{-n}$, with the exponent $n \sim 0.32$, similar to $n \sim 0.27$ reported from transient photoconductivity measurements of Pc single crystals.[5] Recent theoretical studies of intrinsic polaron conductivities in organic molecular crystals have shown that the carrier mobility varies with temperature according to a power law of the form $\mu \sim (T^o)^{-n}$ with $n = 1$ at low temperatures.[17] However, in the FPc crystals studied here, the temperature dependence over the entire temperature range can be better described by a single exponential $\mu\eta \sim \exp[-aT^o]$ (which has been predicted by other theoretical models[15]), as illustrated in the inset of Fig. 4. The physical reason for the difference in temperature dependence of $\mu\eta$ between single crystals and thin films observed in our experiments is currently unknown and requires further investigation. However, assuming η is independent of temperature[33,37,38] or at least does not increase as the temperature decreases, the bandlike temperature dependence of the mobility obtained in thin films (Fig. 4) is especially remarkable since no special purification and/or substrate surface pretreatment that could lead to improved transport properties[39,40] were performed.

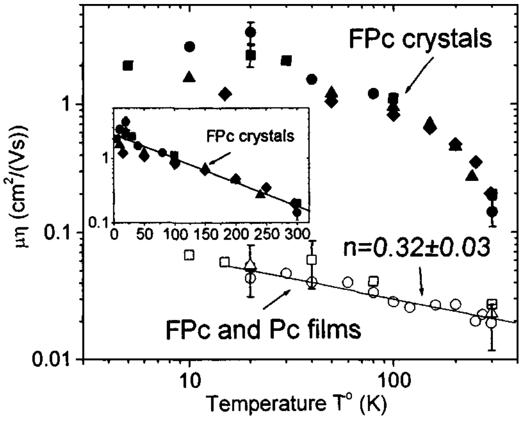

FIG. 4. Temperature dependence of the product of charge carrier mobility μ and photogeneration efficiency η for several FPc crystal samples (solid symbols: squares and diamonds, samples 1 and 2 at 800-nm excitation; triangles and circles, samples 3 and 4 at 400-nm excitation), Pc thin films (open symbols: circles, sample 1 at 580-nm excitation; squares, sample 2 at 400-nm excitation), and a FPc thin film (open triangles at 580-nm excitation). A power-law fit $\mu\eta \sim (T^o)^{-n}$ ($n = 0.32$) to the data obtained in the Pc thin film (sample 1) at 580-nm excitation is also shown. The inset shows the same data obtained in FPc crystals replotted on a semilogarithmic scale, where the solid line is a guide for the eye.

It is conventional to describe charge photogeneration in organic solids by electric-field-assisted[41] and temperature-assisted exciton dissociation as described by the Onsager model.[6,14] However, the sub-ps, wavelength-independent photogeneration in the absence of an external electric field bias (the electric field amplitude of the THz probe pulse is less than 10^3 V/cm and does not affect the measured transient photoconductivity in the samples[30]) and the *increase* in photoconductivity as the temperature *decreases*, as observed in our experiments, are not consistent with a carrier generation mechanism due to the dissociation of excitons[6,14] and indicate that one of the primary photoexcitations in FPc and Pc thin films and FPc single crystals is mobile charge carriers[4,5,33,38] and not only excitons.[6,42] On our time scales, the observed temperature dependence of the photoconductivity in both crystals and thin films is consistent with both a temperature-independent charge photogeneration efficiency and the nearly small molecular polaron (MP) transport model, which treats the motion of a charge carrier as a heavy quasiparticle (formed as a result of interaction of a charge carrier with vibrational modes) with a temperature-dependent effective mass (m^*) described by an exponential $[m^* \sim \exp(aT^o)]$ or power-law $[m^* \sim (T^o)^b]$ behavior.[14,15] Furthermore, the propagation of the MP through a crystal is described as a multistep tunneling process via isoenergetic sites,[14,15] which agrees with the temperature-independent power-law decay[35] of the transient photoconductivity over at least three orders of magnitude in time, as observed in FPc crystals [inset of Fig. 3(a)]. In thin films, fast carrier capture due to deep traps at the grain boundaries[8] results in a single-exponential decay and prevents the observation of MP transport on time scales >3–6 ps after excitation at all temperatures.

The room-temperature mobility values $[\mu \sim 0.2\ \mathrm{cm}^2/(\mathrm{V\,s})$ and $\sim 0.02\ \mathrm{cm}^2/(\mathrm{V\,s})$ for the crystals and thin films, respectively], estimated from the peak values of the transient photoconductivity and under the assumption that $\eta = 1$, are within the range of those obtained in similar systems using other experimental techniques.[7,39,43] However, most studies reported thermally activated charge transport and, therefore, the "effective" trap-limited mobility values, whereas our measurements assess "intrinsic" transport, characterized by higher mobility over time scales shorter than typical carrier trapping times. Furthermore, since it is more likely that $\eta < 1$ due to a significant exciton population density (which the THz probe is not sensitive to in our case) and a partial carrier loss due to recombination and trapping occurring at times <400 fs after the photoexcitation (shorter than the time resolution of our experiment), then the intrinsic mobilities are higher than those listed above.

In summary, sub-ps wavelength-independent charge photogeneration in FPc single crystals and FPc and Pc thin films suggests that mobile charge carriers are one of the primary photoexcitations in these materials. A substantial increase in mobility as the temperature decreased was observed in all samples, indicative of bandlike charge transport. Charge carrier decay dynamics were temperature independent and best described for thin films by a fast single-exponential decay due to deep trapping and in FPc crystals by a fast initial decay (<2 ps) followed by slow power-law decay (>2 ps) due to dispersive charge transport via multistep tunneling consistent with the nearly small molecular polaron model.

This work was supported by NSERC, CFI, CIPI, ONR, and iCORE. O.O. thanks the Killam Trust.

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