

## Observation of triplet exciton dynamics in conjugated polymer films using two-photon photoelectron spectroscopy

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We have utilized two-photon photoelectron spectroscopy to study the dynamics of the long-lived triplet excitons in films of poly[2-methoxy,5-(2'-ethylhexoxy)-1,4-phenylenevinylene]. Our observations indicate that triplet-triplet annihilation is a major deexcitation mechanism for photoexcited triplet excitons. [S0163-1829(97)52024-8]

Conjugated polymers comprise an important material system, combining the structural properties of polymers with electrical properties more commonly associated with semiconductors into a quasi-one-dimensional molecular solid. Poly(*para*-phenylenevinylene) (PPV) and its substituted derivatives, such as poly[2-methoxy,5-(2'-ethylhexoxy)-1,4-phenylenevinylene] (MEH-PPV), have recently attracted particular interest due to their large electroluminescence efficiency,<sup>1</sup> a property of great potential technological interest.

Two-photon photoelectron spectroscopy (2PPES) is a powerful tool for investigating the excited states of a material system,<sup>2</sup> having been used to study ultrafast processes on metal surfaces<sup>3-7</sup> as well as time-resolved relaxation dynamics in various semiconductors.<sup>8-11</sup> In 2PPES, the first photon excites an electron into an intermediate state or states, and the second photon induces the emission of an electron from any or all of the intermediate state or states. This sensitivity to excited-state properties makes 2PPES an excellent tool for studying the excited-state dynamics of conducting polymer films, such as MEH-PPV. Previous photoemission experiments have elucidated many of the ground-state properties of conducting polymers and organic solids,<sup>12-14</sup> and have identified long-lived gap states in polyacetylene films;<sup>15</sup> however, this study is, to our knowledge, the first photoemission-based examination of excitons in an organic solid that has yielded dynamic as well as energetic information.

We have used 2PPES to study the dynamics of long-lived triplet excitons in MEH-PPV films. When an excited-state lifetime is longer than the repetition period of the excitation source, 2PPES indirectly yields dynamical information on the excited state via the intensity dependence of the total photoelectron yield. We have interpreted the observed spectral features and intensity dependence of the photoelectron yield using a rate equation approach<sup>16</sup> which yields insight into the nature of triplet exciton relaxation processes in MEH-PPV.

MEH-PPV in *p*-xylene obtained from UNIAX Corp. was spin coated onto a Au/Si substrate in a dry nitrogen environment. The films were typically 1000 Å thick, as measured by ellipsometry. To minimize uncontrolled oxygen exposure, the films were transferred to ultrahigh vacuum (typically  $2 \times 10^{-10}$  Torr) in N<sub>2</sub>. The excitation source for the two-

photon photoemission experiments was the frequency-doubled output of a titanium-doped sapphire (Ti:Al<sub>2</sub>O<sub>3</sub>) laser.<sup>17</sup> The Ti:Al<sub>2</sub>O<sub>3</sub> laser typically operated with a center wavelength of 825 nm and a pulse repetition period of 12 ns. The fundamental pulses were frequency doubled in a 1.5-mm-thick lithium triborate crystal to generate 3-eV photons. The second harmonic pulsewidth was typically  $\sim 300$  fs, and the average power was 5–50 mW. The second harmonic beam was split from the fundamental and focused onto the sample with an approximate spot diameter of 30 μm, giving a peak intensity of 30–300 MW cm<sup>-2</sup>, or an incident photon flux of  $2-20 \times 10^{13}$  cm<sup>-2</sup> pulse<sup>-1</sup>. We detected no sample degradation due to the high intensity: both the spectrum and total yield at a given laser intensity on a given spot on the film surface were quite reproducible. The photoelectrons were energy analyzed with a double-pass cylindrical mirror analyzer with an energy resolution of approximately 0.05 eV. The sample was held at a constant negative 4-V bias with respect to the analyzer to minimize the noise due to spurious low-energy electrons. The experiment was carried out at room temperature.

The basic energetics of the 2PPES process are shown in Fig. 1. The first photon  $h\nu$  excites an electron from the

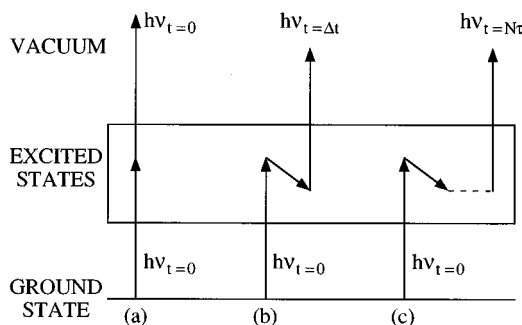


FIG. 1. Three possible two-photon photoelectron processes: (a) The first photon creates an excitation in the material, and the second photon immediately induces photoemission from the excited state. (b) The first photon creates a high-lying excitation which relaxes to a lower energy, and a second photon from the same laser pulse induces photoemission from the lower-energy state. (c) The first photon creates a high-lying excitation which relaxes to a lower energy and a photon from a later laser pulse induces photoemission from the lower-energy state.

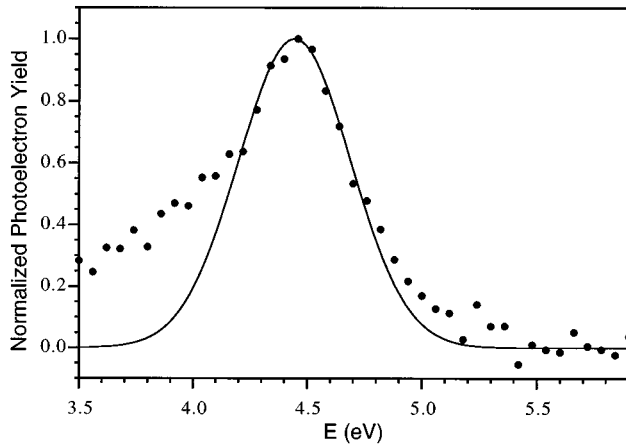


FIG. 2. Two-photon photoelectron spectrum (closed circles) of a pristine MEH-PPV film, showing a Gaussian fit (solid line) to the peak maxima. The spectral feature is attributed to photoemission from the triplet exciton  $T_1$ .

ground state to an intermediate state, and the electron may be emitted from the intermediate state upon absorption of a second photon  $h\nu$ . The excited electron may or may not relax to a lower-energy excited state (e.g., a triplet exciton) between the arrival time of the two photons [Figs. 1(a) and 1(b)]; hence the energy spectrum of the photoelectrons is a sampling of the excited states in the material. If the excited-state lifetime is sufficiently long, photoemission may be induced from the excited state or states by a photon from a subsequent laser pulse [Fig. 1(c)]. If an intermediate state decays in a time shorter than the laser repetition period, photons in the same laser pulse would have to both excite and emit the electron from that state [Figs. 1(a) and 1(b)], leading to a photoelectron yield from that state proportional to the square of the laser intensity. However, if the intermediate state has a lifetime much longer than the pulse repetition period, a large steady-state population builds up in that state, and electrons may be emitted by a photon from a later laser pulse, as illustrated in Fig. 1(c). This leads to a photoelectron yield that is linearly proportional to the laser intensity. If the intermediate-state lifetime is close to the pulse repetition period or if another mechanism exists to limit the steady-state population, the total photoelectron yield will be proportional to (intensity) $^n$ , with  $1 < n < 2$ .

The normalized two-photon photoelectron spectrum of a pristine MEH-PPV film is shown in Fig. 2 (closed circles). The spectrum is presented here with the 4-V bias offset included. The shape of the photoelectron spectrum is independent of laser intensity and shows only one resolvable peak. The broad low-energy shoulder evident in Fig. 2 is a background signal due to inelastic scattering and detection of spurious low-energy electrons. The width of the observed peak is somewhat dependent on the location of the spot on the film surface; however, at any given point on a sample the shape of the peak is independent of laser intensity.

The total photoelectron yield as a function of laser intensity for a pristine MEH-PPV film is shown in Fig. 3 (closed circles), with the corresponding fit (solid line) showing the total photoelectron yield proportional to (intensity) $^n$ , where  $n = 1.36$ . Since the shape of our experimental photoelectron spectrum of MEH-PPV is independent of laser intensity, the

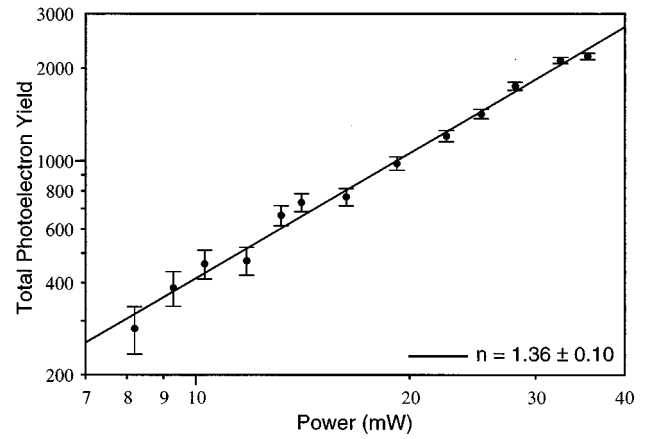


FIG. 3. Intensity dependence of total photoelectron yield for a pristine MEH-PPV film.

primary contribution to the photoelectron yield is either from a single state which has a lifetime close to 12 ns or from a single state with a lifetime much longer than 12 ns, but whose population is limited by other mechanisms. Since the photoelectron spectrum itself is not intensity dependent, we can rule out the possibility of contributions from several states with lifetimes both longer and shorter than the laser repetition period. We therefore conclude that the observed spectral feature is that of the triplet exciton in MEH-PPV.

The excited-state photoelectron spectrum of MEH-PPV can be understood using a rate equation model, similar to that in Ref. 16, illustrated in Fig. 4:

$$\frac{dS_0}{dt} = - \sum_n f(t-nt_o) \times q(1 - e^{-\sigma(S_0 - S_1)}) + \frac{S_1}{\tau_1} + \frac{T_1}{\tau_2} + \frac{\gamma T_1^2}{2},$$

$$\frac{dS_1}{dt} = \sum_n f(t-nt_o) \times \eta q(1 - e^{-\sigma(S_0 - S_1)}) - \frac{S_1}{\tau_1} - \frac{S_1}{(k_{isc})^{-1}} + \frac{\gamma T_1^2}{2},$$

$$\frac{dT_1}{dt} = \frac{S_1}{(k_{isc})^{-1}} - \frac{T_1}{\tau_2} - \gamma T_1^2 + \frac{P^\pm}{\tau_3},$$

$$\frac{dP^\pm}{dt} = \sum_n f(t-nt_o) \times (1 - \eta) q(1 - e^{-\sigma(S_0 - S_1)}) - \frac{P^\pm}{\tau_3},$$

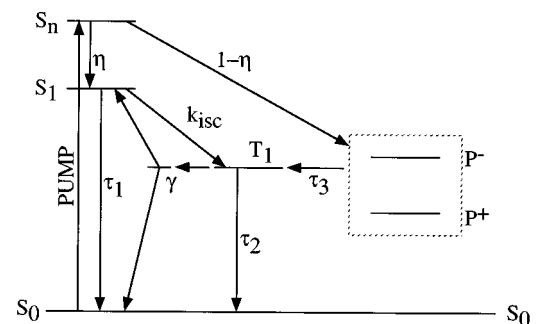


FIG. 4. Diagram of the rate equation model used. The branching ratio, lifetimes, and rates are given in the text.

where  $S_0$  is the ground-state population,  $S_1$  is the lowest excited singlet exciton population,  $T_1$  is the lowest excited triplet exciton population, and  $P^\pm$  is the population of bound polaron pairs. The photon flux is  $q$ ,  $\sigma$  is the absorption cross section, and  $\eta$  is the branching ratio for singlet/polaron pair formation. The lifetimes of the singlet exciton, triplet exciton, and bound polaron pairs are  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$ , respectively. The rate for intersystem crossing from the singlet exciton to the triplet exciton is  $k_{isc}$ , and  $\gamma$  is the rate for triplet-triplet annihilation. The laser excitation pulse is taken to be a periodic  $\delta$ -function excitation  $\sum_n f(t - nt_o)$ , where  $t_o$  is the laser repetition period.<sup>16</sup> These equations are integrated over many laser pulses, until a steady state is reached.

The initial photon excites a high-lying excited singlet  $S_n$  which either relaxes to the lowest excited singlet  $S_1$  or undergoes fission to form a bound polaron pair  $P^-/P^+$  with a branching ratio  $\eta \sim 0.2$  consistent with previously reported values.<sup>18,19</sup> The bound polaron pair recombines geminately to form a triplet exciton  $T_1$  with lifetime  $\tau_3 \approx 1$  ns. The lowest excited singlet  $S_1$  either undergoes radiative decay with lifetime  $\tau_1 \approx 400$  ps or undergoes intersystem crossing to  $T_1$  with a rate  $k_{isc} \approx (50 \text{ ps})^{-1}$ , consistent with photoluminescence quantum yield measurements.<sup>18-21</sup> Various experiments have arrived at different values for these lifetimes and rates; however, because our focus is on the much longer-lived triplet states, we are insensitive to the variations in these quantities over the entire range of reported values. The triplet exciton  $T_1$  either relaxes nonradiatively to the ground singlet  $S_0$  with lifetime  $\tau_2 \approx 1$  ms,<sup>22-24</sup> or decays via triplet-triplet annihilation with rate  $\gamma$  to a ground singlet and an excited singlet exciton  $S_1$ .<sup>24</sup>

Since the triplet lifetime  $\tau_2$  is on the order of milliseconds, simple monomolecular decay of the triplet excitons is

not sufficient to explain the measured intensity dependence of total photoelectron yield; therefore, another population-limiting mechanism must be active. This mechanism appears to be triplet-triplet annihilation, which has been previously observed in molecular solids such as anthracene,<sup>25</sup> and is believed to occur in MEH-PPV.<sup>24</sup> If triplet-triplet annihilation is neglected in the rate equation model, a large triplet state population is built up, leading to a linear photoelectron yield. However, the fractional exponent of  $n = 1.36$  that we observe is consistent with observed triplet exciton lifetimes in the millisecond range only if triplet-triplet annihilation is an active deexcitation mechanism. This indicates that triplet-triplet annihilation is an important deexcitation pathway in MEH-PPV under steady-state, high-intensity excitation conditions. Including triplet-triplet annihilation as a parameter in our rate equation model, we fit the experimental data well with an annihilation rate  $\gamma \approx 10^{-14} \text{ cm}^3 \text{ s}^{-1}$  and a triplet-triplet interaction distance of 50 Å. Our value of  $\gamma$  is considerably smaller than the measured value for anthracene [ $\gamma_{\text{anthracene}} = 2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  (Ref. 25)]. It is possible that the long alkyl side chains of MEH-PPV restrict interactions between triplet excitons.

In summary, we have used two-photon photoelectron spectroscopy to probe the triplet exciton dynamics of MEH-PPV, and shown that triplet-triplet annihilation is an important relaxation pathway for triplet excitons in MEH-PPV at high excitation intensities.

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