Direct Measurement of the Triplet Quantum Yield of Poly(3-dodecylthiophene) in Solution

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The photophysics, including radiative and nonradiative quantum yields and decay rates, of regioregular poly-(3-dodecylthiophene) (P3DT) in benzene were studied by means of UV−visible spectroscopy, photoluminescence spectroscopy, photothermal beam deflection (PBD), photoacoustic calorimetry (PAC), and time-resolved photoluminescence spectroscopy. We observe the fluorescence quantum efficiency to be 0.30 ± 0.01 and the internal conversion (from S_1 to S_0) quantum yield of 0.59 ± 0.02 as well as the intersystem crossing (from S_1 to T_1) quantum yield of 0.11 ± 0.01. By measuring the fluorescence lifetime of ca. 490 ps, we estimate a radiative lifetime of 1.64 ns for the singlet excitons and nonradiative decay rate constants of $k_{ic} = 1.21$ ns^{-1} and $k_{isc} = 0.22$ ns^{-1} for internal conversion and intersystem crossing, respectively. The nature and photophysics of triplet states in poly(3-dodecylthiophene) are well characterized using PBD and PAC, and the result suggests that internal conversion plays a major role in energy depletion.

Introduction

Since the discovery of electroluminescence properties associated with conjugated polymers in the 1990s,[1] a wide variety of photonic applications have been developed.[2−6] The photophysical properties of conjugated polymers continue to attract attention due to the complexity in excited-state structures and relaxation pathways. The triplet-state properties play significant roles in a device's quantum efficiency. The emission from the lowest triplet state, T_1, is termed phosphorescence and is red shifted with much a longer lifetime (micro- to milliseconds) relative to fluorescence. As a result of the much smaller rate constant relative to fluorescence, the transition from the T_1 to the S_0 ground state is effectively inhibited through a radiative process. The formation of triplet excitons is believed to reduce the luminescence quantum yield, especially the electroluminescence quantum yield of polymeric light-emitting diodes (PLED). Although most singlet emission species have been studied and well defined, the photophysics of triplet states are less well characterized. Intersystem crossing provides a method to reach the triplet state in optical excitation experiments. Upon photoexcitation, molecules can transfer from the S_1 to the first triplet state T_1 via intersystem crossing.

One of the major concerns at present is the nature and photophysics of triplet excitons in poly(3-alkylthiophene)s.[7−10] Poly(3-alkylthiophene)s is a conjugated polymer that exhibits strong photoluminescence and electroluminescence in the red region.[11−13] Poly(3-alkylthiophene)s also display thermochromic and solventochromic properties.[14−17] More recently, homogeneous polymers have been prepared with adjacent monomers connecting in an alternating head-to-tail regioregular arrange-

ment, and the regioregularity was up to 98%.[18,19] In previous reports, laser flash photolysis, photoinduced absorption, photoacoustic calorimetry (PAC), and thermal lensing measurements were used to study the triplet state of various conjugated polymers.[7−10,20−22] Previous studies of poly(3-octylthiophene) (P3OT), one of the derivatives of poly(3-alkylthiophene)s considered as a conjugated polymer with a relatively high triplet quantum yield in solution, have provided more detailed insights into the triplet state of P3OT, making the nature and photophysics of triplet excitons in poly(3-alkylthiophene)s more complete.[8,10]

In this work, photoacoustic calorimetry and photothermal beam deflection calorimetry (PBD) are utilized to measure the quantum yields of fluorescence (Φ_F), internal conversion (ϕ_{IC}), and triplet state formation (Φ_T) of poly(3-dodecylthiophene) (P3DT) in benzene. The signal generated through heat release from the photoexcited sample is compared with an appropriate reference standard in which all the absorbed photon energy is released as heat. PAC is an excellent experimental technique with which to measure enthalpy changes on a time scale of nanoseconds to microseconds for reactions initiated by the absorption of light. This technique has been previously applied to the study of chemical and biochemical reactions as well as fluorescent polymers.[8,9,23,24] By using a pulsed laser and appropriate deconvolution software, acoustic waves generating photochemical events in the range from nanoseconds to microseconds can be resolved. However, due to frequency bandwidth limitations of piezoelectric detectors and interference from the reflection wave, PAC cannot measure heat release on longer time scales (i.e., tens of microseconds, triplet state). Thus, the heat measured by PAC reveals the energies associated with the relaxation of the S_n to S_1 and S_1 to S_0 transitions as well the S_1 to T_1 transition.

PBD is a complimentary probe to PAC for studying molecular dynamics in solutions and in gases on time scales ranging from

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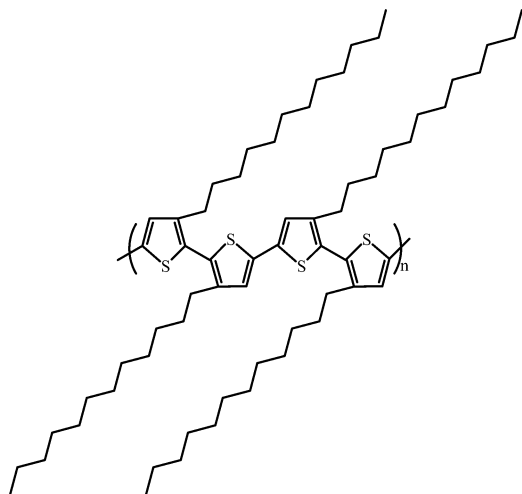§ Yuan-Ze University.
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Figure 1. Chemical structure of P3DT. The regioregularity is 98.5%.

Figure 2. UV−vis absorption and photoluminescence spectra (excited at 355 nm) of P3DT in benzene solution.

Figure 3. One form of simplified Jablonski diagram for our photothermal experiments.

approximately microseconds to tens of milliseconds. Since the PBD technique was reported in 1980,[25,26] a wide range of photophysical, chemical, and biochemical systems have been investigated.[20,27−31] Unlike PAC, the PBD method probes changes in the refractive index of a solution caused by heat release after pulsed laser excitation. Due to the high sensitivity on longer time scales, PBD is a powerful tool to measure triplet-state decay in conjugated polymers. Thus, ϕ_{IC} and Φ_T can be directly obtained from the combination of PAC and PBD, which are sensitive on shorter and longer time scales, respectively. Furthermore, direct measurement of the fluorescence quantum efficiency using a fluorescence spectrometer provides an internal consistent check of the thermal measurements based on the requirements of conservation of energy.

Experiments

Poly(3-dodecylthiophene), one of the derivatives of polythiophenes, contains a 12-carbon alkyl side chain in each thiophene (Figure 1).This material is a commercialized product of Sigma-Aldrich, Inc., with $M_w = 35\,000$ (g/mol) (polystyrene as the standard) and a regioregularity of 98.5%. The material was dissolved in benzene and stirred for 24 h at 50 °C under a nitrogen environment. The solutions were then filtered through a 50 μm filter. Finally, the solutions were adjusted to give an optical density equal to 0.30 at the excitation wavelength (355 nm). The calorimetric reference compound, 2-hydroxybenzophenone (2-HBP), releases heat within the laser pulse width with a quantum efficiency of 1.0.[28] The optical density of both the sample and reference in benzene solutions at 355 nm was carefully matched. Molecular oxygen is known to form a reversible charge-transfer complex with poly(3-alkylthiophene)s which is considered to quench the excited singlet excitons.[32] Thus, samples were prepared in a nitrogen glovebox. Several cycles of vacuum/positive pressure were applied. Samples were then tightly sealed under nitrogen pressure. Optical absorption (UV−vis) and photoluminescence (PL) spectra of the sample solutions were obtained using GBC Cintra-20 and Jobin Yvon FL3-21 instruments, respectively. Time-resolved fluorescence measurements were obtained using a time-correlated single-photon-counting apparatus with time resolution of about 40 ps. The excitation power used was less than 0.5 mW (∼7 pJ per pulse). For the photothermal experiments, photoexcitation was achieved by the 355 nm third harmonic of a Q-switch Nd:YAG laser (New Wave Research). The laser pulse width is ∼5 ns, and the repetition rate was 1 Hz. The laser power is 88 ± 5
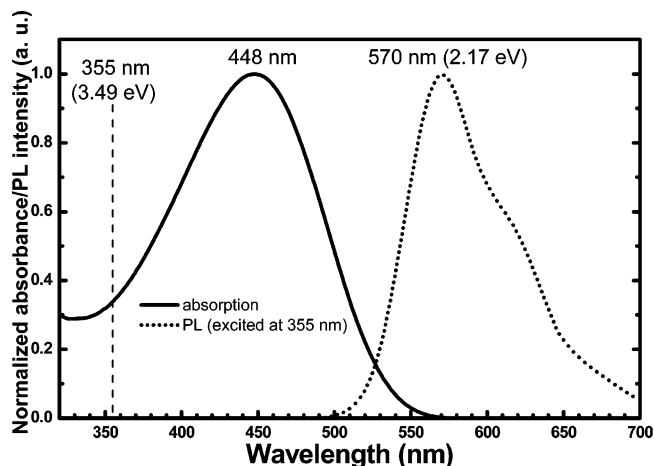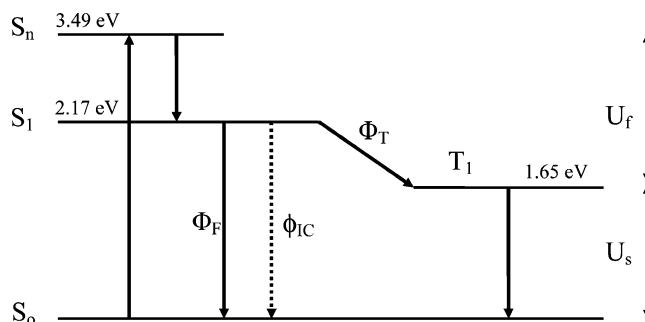
μJ/pulse, and the focused beam diameter is ∼1.7 mm. The sample was housed in a sealed 1-cm quartz cuvette. The cuvette holder (Quantum Northwest) was to hold the temperature at 20 ± 0.5 °C. For PBD experiments, a He−Ne laser of 632.8 nm was used as the probe beam for measuring time-dependent changes in the refractive index of the solution after 355 nm pulse laser excitation. Changes in the refractive index of the solution were detected by a split-photodiode detector. For PAC experiments, the photoacoustic pressure wave generated after laser irradiation was detected by using a microphone (PZT piezoelectric transducer) with 1 MHz bandwidth (GE Panametrics V-103). The microphone was mounted on the sidewall of the cuvette. The signals from the microphone were sent into a preamplifier (GE Panametrics 5670, 40 dB gain). The amplified PBD/PAC signals were recorded using a digital oscilloscope (TDS 784D, TEK). The signals from 50 laser shots were averaged.

Results and Discussion

Figure 2 displays the absorption and emission (normalized with respect to the peak maximum) spectra of P3DT in benzene. The absorption spectrum is characterized by a broad peak with maximum absorption located at 448 nm as well as an absorption edge at ca. 560 nm. The emission spectrum is characterized by a major emission band at ca. 570 nm (2.17 eV) with an excitation wavelength of 355 nm (3.49 eV). The emission range is similar to MEH−PPV in dilute solution, which emits at 560 nm.[8,33,34]

Figure 3 represents a simplified Jablonski diagram which serves as a guide for the photothermal experiments. The P3DT is excited to the S_2 state 3.49 eV above the ground state by a 355 nm laser pulse. The excited molecules in the S_2 state

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subsequently relax to the lowest energy level of S_1 due to vibrational redistribution (picosecond time scale). The typical fluorescence lifetime for the polymer (emission from the S_1 to S_0) occurs on a nanosecond time scale. The excited S_1 state may also decay via nonradiative processes through the release of heat to the solvent. An alternative decay pathway leads to triplet state formation via intersystem crossing (on a nanosecond time scale). Finally, molecules in the T_1 state relax to the ground state by releasing heat on longer time scales (microseconds to milliseconds). The singlet energy gap, 2.17 eV, is determined from the high-energy peak of the fluorescent spectrum of Figure 2. According to Monkman et al., conjugated polymers having the same S_1-S_0 energy should have a similar T_1-S_0 energy.[9] Because of the similar singlet energy gap and chemical structure (small difference in alkyl side-chain length) for P3DT and P3OT, we take the energy gap of triplet state (E_{T1}) of P3OT 1.65 eV to be E_{T1} for P3DT.[8,9,35] There is one similar case for poly-(2,5-hexyloxyphenylenevinylene) (DHO−PPV) and poly(2,5-octyloxyphenylenevinylene) (DOO−PPV). With similar chemical structure and similar absorption and emission spectra, DHOPPV and DOOPPV have the same measured triplet-state energy.[9]

For photothermal beam deflection measurements, the total heat release after 355 nm pulse laser excitation of P3DT in benzene is described by

$$E_{h\nu} - E_{S1}\Phi_F =$$
$$(E_{Sn} - E_{S1}) + E_{S1}\phi_{IC} + E_{S1}\Phi_T = E_{h\nu} \times \frac{I_{S-PBD}}{I_{R-PBD}} \quad (1)$$

where $E_{h\nu}$ is the excitation energy, 3.49 eV, E_{S1} is the lowest excited state 2.17 eV, Φ_F is the fluorescence quantum efficiency, E_{Sn} is the highest excited state, ϕ_{IC} is the internal conversion quantum efficiency, Φ_T is the triplet-state quantum efficiency, I_{S-PBD} is the signal amplitude of the sample solution, and I_{R-PBD} is the signal amplitude of reference solution. From eq 1 we obtain

$$3.49 - 2.17\phi_F = 3.49 \times \frac{I_{S-PBD}}{I_{R-PBD}} \quad (2)$$

$$(3.49 - 2.17) + 2.17\phi_{IC} + 2.17\Phi_T = 3.49 \times \frac{I_{S-PBD}}{I_{R-PBD}} \quad (3)$$

Shown in Figure 4 is the result of PBD in which the signal amplitudes were normalized by both optical density and laser power. The reference solution will release all absorbed energy on a nanosecond time scale after laser excitation. From the result of PBD for the reference solution, the instrumental response time is several microseconds. This result reveals that PBD can monitor the heat release process in the time range of microseconds to milliseconds. U_F and U_S are the fraction of heat release from a fast (picosecondss to microseconds) and slow process (microseconds to milliseconds), respectively. The ratio of I_{S-PBD} and I_{R-PBD} is equal to 0.81, obtained from Figure 4. As a result, the fluorescence quantum efficiency Φ_F was estimated to be 0.30 ± 0.01 from eq 2. Φ_F was independently measured by a fluorescence spectrometer using MEH−PPV as the reference standard. The fluorescence quantum efficiency obtained by the two methods is comparable, which indicates that PBD can perform quantitative measurements. According to the definition of $\Phi_F + \phi_{IC} + \Phi_T = 1$, we get
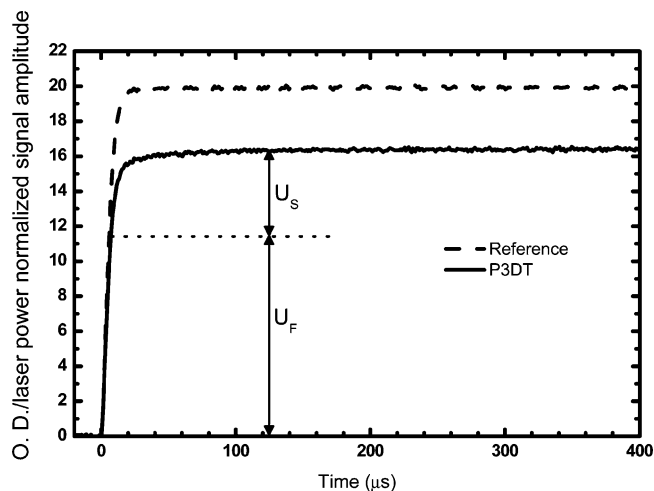
$$\phi_{IC} + \Phi_T = 0.70 \quad (4)$$

Figure 4. PBD waveform of reference 2-hydroxybenzophenone (dashed line) and P3DT (solid line) in benzene solution irradiated at 355 nm. The optical densities of sample and reference solutions were carefully matched.

Figure 5. Photoacoustic waves of reference 2-hydroxybenzophenone (dashed line) and P3DT (solid line) in benzene solutions irradiated at 355 nm. The optical densities of sample and reference solutions were carefully matched.
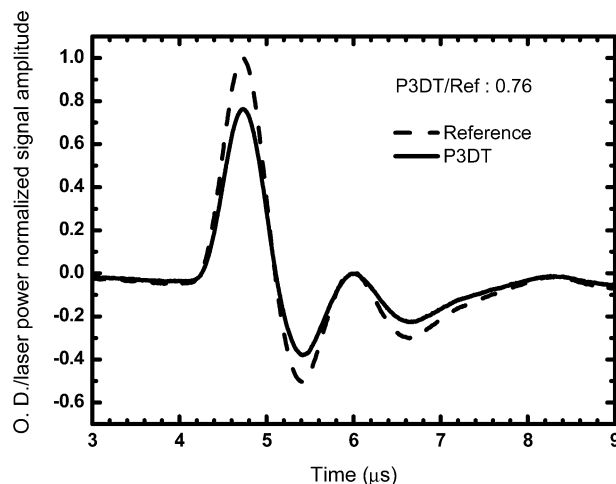
For a slow step

$$\frac{E_{T1}\Phi_T}{3.49 \times 0.81} = U_S \quad (5)$$

If we can resolve the endpoint of the fast step from PBD results, we can get F_{IC} and F_T from eqs 4 and 5. In Figure 4 it is difficult to determine the endpoint of the fast step from our PBD results due to instrumental resolution. Thus, PAC is needed for determining the heat release in the fast step.

For PAC, the heat release in the fast step can be described by

$$\frac{(E_{Sn} - E_{S1}) + E_{S1}\phi_{IC} + (E_{S1} - E_{T1})\Phi_T}{E_{h\nu}} = \frac{I_{s-PAC}}{I_{R-PAC}} \quad (6)$$

In Figure 5 the PAC signal amplitudes of P3DT and reference solutions were normalized by both optical density and laser power. The photoacoustic wave of the reference (dashed line) indicates the time window for PAC is from 20 ns to 3 μs. The PAC result shows that there is no phase difference between P3DT and reference solution. This indicates that there is no other heat release process detected within 3 μs for P3DT solution

after laser excitation. The ratio of the signal amplitude for the sample and reference is 0.76. Equation 6 can be recast as

$$\frac{(3.49 - 2.17) + 2.17\phi_{IC} + (2.17 - 1.65)\Phi_T}{3.49} = 0.76 \quad (7)$$

Thus

$$2.17\phi_{IC} + 0.52\Phi_T = 1.33 \quad (8)$$

From eqs 4 and 8 we get $\phi_{IC} = 0.59$ and $\Phi_T = 0.11$.

Deconvolution for the PBD results was also performed by commercial software (Sound Analysis, Quantum North West). The results were deconvoluted into two parts, fast and slow components. The lifetime of the slow step is calculated as 35 μs, which indicates the decay time of the triplet state. From the two deconvoluted components the slow step ratio U_S is 0.07. From eq 5 the triplet-state quantum efficiency is estimated as 0.12, and the quantum efficiency of internal conversion is 0.58 from eq 4. These procedures show that obtaining the photophysical properties requires superior time resolution in the PBD instrument and reliable deconvolution operation.

The singlet excited-state lifetime, τ_F, measured by time-resolved single-photon-counting photoluminescence for P3DT is 490 ps. A radiative lifetime of 1.64 ns for the singlet excitons and nonradiative decay rate constants of internal conversion $k_{ic} = 1.21$ ns^{-1} and intersystem crossing $k_{isc} = 0.22$ ns^{-1} then can be estimated. The excited lifetime is different from P3OT reported previously.[10] This indicates that although P3OT and P3DT exhibit similar singlet and triplet energy gaps, the kinetic rates for various decay channels can be different.

To use time-resolved photothermal methods to determine triplet yield unambiguously, it is essential to combine PAC, PBD. and PL quantum yield measurements. In general, there are two sources that can contribute to photothermal signal in PAC and PBD: the heat release from the molecules to the solvent and the conformational change of the molecules. For the present experiments, the conformational changes do not contribute to the PAC and PBD signal. Since the fluorescent quantum yield determined by PAC and PBD is identical to the direct PL quantum yield measurements, it is concluded that signals from heat release to solvent dominate the photothermal signal in the present experiments.

Note that time-resolved photothermal calorimetry, PAC and PBD, and the singlet depletion method are complementary in determining the triplet quantum yield. In the singlet depletion technique one needs to know the absolute extinction coefficient in order to obtain the triplet-state quantum yield from the photoinduced absorption measurements. For conjugated polymer, it is difficult to obtain the extinction coefficient because the actual size of absorption excitons cannot be precisely determined. Furthermore, other processes, such as polarons absorption, can contribute to the photoinduced absorption signal in addition to triplet−triplet absorption. On the other hand, if the triplet yield is small (<1%), the singlet depletion method has advantages over the photothermal approach.

Conclusions

In this work heat generating through nonradiative decay processes from picoseconds to microseconds is measured by photothermal beam deflection and photoacoustic calorimetry. The fluorescent quantum yield, internal conversion yield, and triplet-state yield are obtained for P3DT. The decay of the triplet state with a lifetime ≈35 μs is directly observed by PBD. The

internal conversion yield (58%) dominating over the triplet-state yield (12%) indicates that most of the energy is depleted with releasing heat in the transition from the lowest excited state to the ground state. The present work demonstrates that combination of PBD and PAC provides a powerful way to study the photophysics of conjugated polymers in solution.

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