

# Excitation Induced Emission Color Change in Conjugated Polymers

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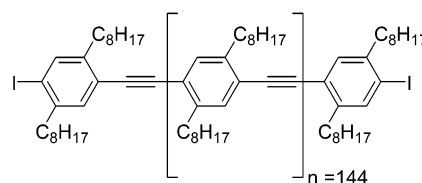
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We report the luminescence color change of poly-(2,5-dioctyl *para*-phenyleneethynylene) (PPE) through variations of the excitation intensity. PPE can exist in one of two phases in a chloroform solution; one is a single molecule phase, and the other is an aggregate phase, where the benzene rings of the adjacent polymer chains stack on top of each other. Only the latter exhibits the intensity dependent color change. The other shows regular photoluminescence; that is, only the emission intensity itself depends on the excitation intensity. The phase change occurs reversibly, and therefore, two ways of changing the emission color are possible. PPE will therefore contribute strongly to future color tuning applications.

Conjugated polymers have received a great deal of attention as candidates for luminescent device applications since the late 1980s, starting with the discovery of electroluminescence in poly-(*para*-phenylene-vinylene) (PPV).<sup>1</sup> Because of their advantages as semiconductors (as opposed to the traditional, inorganic semiconductors), conjugated polymers have been researched extensively over the past two decades. Their feasibility for optoelectronic applications in general and emissive devices in particular has since been determined.<sup>2–4</sup> The advantages of conjugated polymers are ease of deposition at ambient conditions, which leads to possible applications for disposable electronics and cheaper displays, and electronic tunability through chemical changes at the sidegroups or even at the backbone itself. They also exhibit high fluorescence (photoluminescence, PL) quantum yields.

Among the most popular materials for emissive devices made from polymers are the original PPV,<sup>1</sup> polyfluorenes,<sup>5</sup> and ladder-type poly-(*para*-phenylene)s.<sup>6,7</sup> A material close in structure to PPV, poly-(*para*-phenyleneethynylene) (PPE),<sup>8,9</sup> has received considerably less attention, despite its increased thermal, oxidative stability, and superior photophysical properties in solution. Although PPVs are typically green and yellow emitters, PPE emits blue light.

There have been several reports of light emitting devices (LEDs) from PPEs and related materials. Most notably, Bunz et al.<sup>10</sup> and Weder et al.<sup>11</sup> demonstrated blue and green electroluminescence (EL) in PPEs. Additionally, it has been shown<sup>11</sup> that the lowest unoccupied molecular orbital (LUMO) of PPE (3.9 eV) lies beneficially low for electron injection from aluminum cathodes (4.3 eV). The highest occupied molecular orbital (HOMO) of 6.3 eV (ref 12) is very low as well; thus, PPE is a perfect candidate for LEDs as an electron carrying material, owing to its hole-blocking features.



**Figure 1.** Chemical structure of poly-(2,5-dioctyl *para*-phenyleneethynylene).

In this manuscript, we present studies of the photoluminescence of dioctyl-PPE (cf. Figure 1) (ref 13), excited by two-photon absorption. Excitation through two-photon absorption is useful because it distributes a high excitation over a larger, more homogeneous volume than single-photon excitation. The polymer was investigated in its chloroform solution phase in order to analyze the material's intrinsic properties and to exclude all influences from device forming procedures. A Ti-sapphire laser system was used to excite the solution. The laser system delivered 200 fs pulses with 3.2  $\mu$ J per pulse with a repetition rate of 249 kHz. The emission of the laser was centered on 752 nm (1.65 eV). The laser beam was focused onto the solution up to 180 GW cm<sup>-2</sup> mean intensity. The intensity variation was performed with a high-intensity polarizer. The photoluminescence spectra of the material were detected with a fiber optic spectrometer perpendicular to the laser beam path at room temperature.

The PPE was dissolved in chloroform to exhibit a peak optical density of OD = 30 for a light path of 1 cm, which is a very low concentration compared to a solid phase. At this concentration, there are two possible phases.<sup>14,16</sup> One phase is an aggregate phase that is obtained by dissolving of the polymer at 280 K, whereas by extensive magnetic stirring and heating to 320 K, a single molecule phase is obtained. This process is reversible through undisturbed storage at 280 K.<sup>16</sup>

Studying the behavior of the stacked polymer phase with various excitation intensities revealed a new phenomenon, an excitation intensity dependent emission color. Figure 2 shows the beam path of the laser through the two PPE solutions. In

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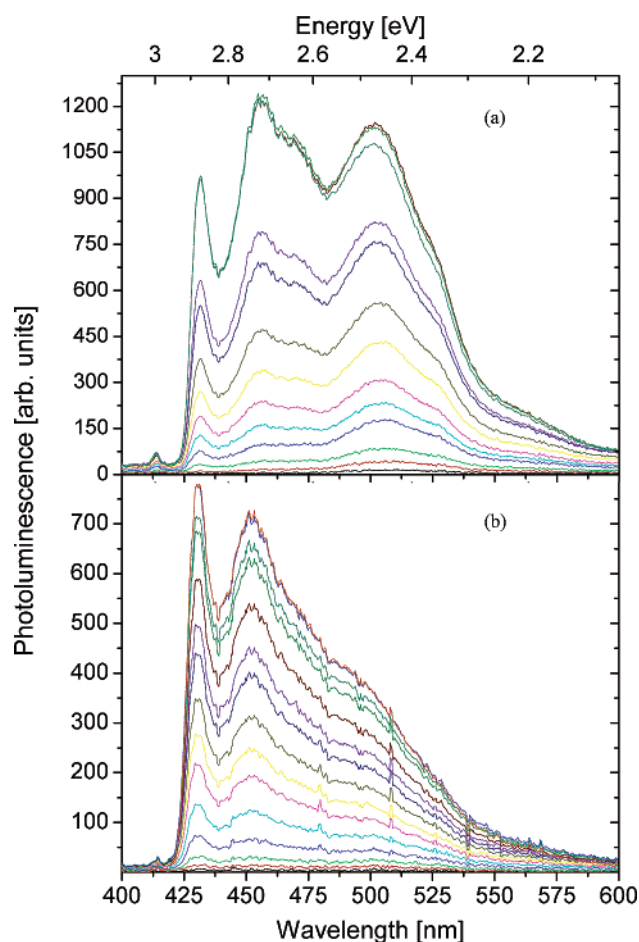
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**Figure 2.** (a) Variation of the emission color of octyl-PPE in an aggregate phase. (b) Constant emission color of octyl-PPE in a separate molecules phase.



**Figure 3.** (a) Emission spectra of octyl-PPE in an aggregate phase: The spectra show the emission when excited with 180 GW cm<sup>-2</sup> (top), 175, 171, 163, 154, 144, 131, 115, 99, 82, 66, 50, 37, and 23 GW cm<sup>-2</sup> (bottom). The relative height of the first two transition peaks, 0–0 and 0–1 is constant, whereas the 0–2 transition becomes more prominent at low excitation intensities (cf. Figure 4). (b) Emission spectra of octyl-PPE in a separate molecules phase. The relative height of the three transition peaks is constant.

both cases, the focal point of the excitation is toward the left side of the glass vessel. At the right side of the picture shown in Figure 2, the intensity had diminished to about one-fourth of the intensity in the focus. Figure 2a shows the color change from blue to turquoise for the aggregate phase polymer solution. The corresponding alteration of the PL spectra is shown in Figure 3a. Figure 2b shows the single molecule PPE solution, with no visible change in the emission color. This observation

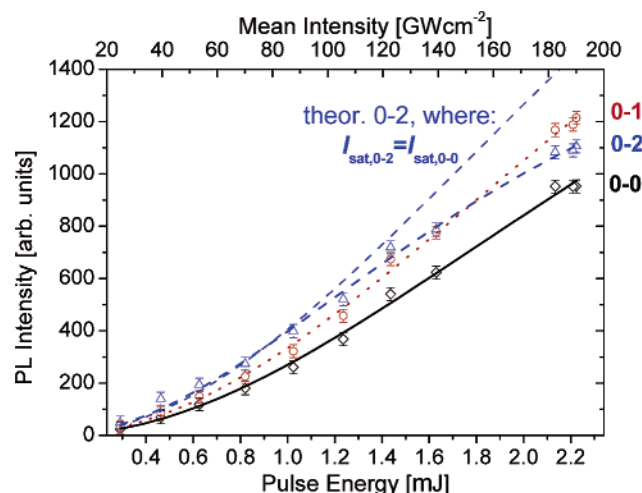
is in agreement with the PL spectra measured for the same solution using intensities from 20 to 180 GW cm<sup>-2</sup>, as shown in Figure 3b. It is important to note that this phenomenon is not due to self-absorption. The spectra in Figure 3a have been measured with constant geometry, only turning the analyzer for the variation of the incident laser intensity. No item of the measurement setup was otherwise moved. Figure 2a has been taken so that the excitation beam is at a constant distance from the side of the glass. The path to the lens of the digital camera through the solution is not perfectly constant, but at an object to image distance of 30 cm with a width of the object of 1 cm, the error is smaller than 3%; not enough to cause the altered emission color on the right side.

This color shift is attributed to the fact that aggregates of PPE in chloroform were observed. The phenyl rings stack on top of each other, which changes the electronic properties. The solution exhibits a yellow color due to an additional absorption peak with an onset wavelength of 450 nm.<sup>15</sup> Furthermore, the formation of aggregates reduces the transition probability for the fundamental and first vibronic transition equally, demonstrated by the data shown as circles in the inset in Figure 4.

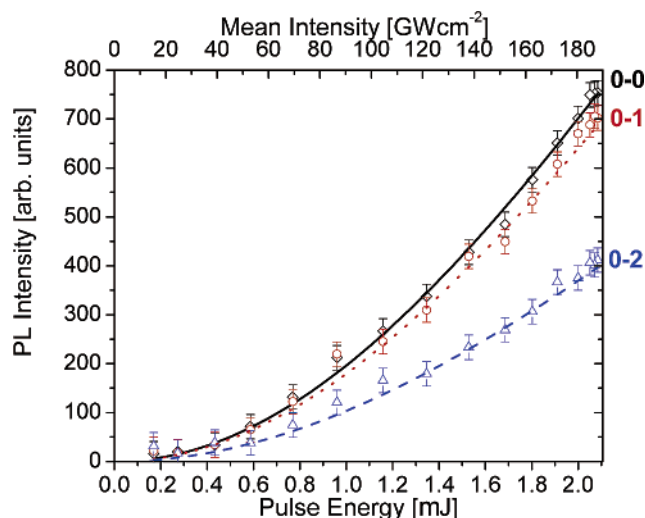
Figure 4 shows the PL emission intensity for the three transitions observed in Figure 3. 0–0 denotes the fundamental  $\pi^*-\pi$  transition; whereas 0–1 and 0–2 are the most visible transitions where vibronic progression occurs, i.e., part of the energy goes into molecular vibration modes (consider simplifying or clarifying). In principle, the emission intensity should depend quadratically on the excitation intensity due to the fact that two photons are needed to lift one exciton into the  $\pi^*$  state. At higher excitation densities, however, ground-state depletion and excited-state accumulation occur,<sup>13</sup> and the following relation describes the PL emission intensity:<sup>17</sup>

$$I_{\text{PL}} \propto \frac{\alpha_2^0}{1 + \frac{I_0^2}{I_{\text{sat}}^2}} I_0^2 \quad (1)$$

where  $I_{\text{PL}}$  is the PL emission intensity,  $I_0$  is the incident intensity,  $I_{\text{sat}}$  is the saturation intensity, and  $\alpha_2^0$  is the constant (or low level excitation) two-photon absorption coefficient. With eq 1, the emission intensity versus excitation intensity of the three transitions is fitted. Because it describes the absorption of a monochromatic light source,  $\alpha_2^0$  is constant. The saturation intensities, however, are found to be dependent on the transition. For the 0–0 and 0–1 transitions,  $I_{\text{sat}} = 265 \text{ GW cm}^{-2}$ , a value similar to the one for the single molecule phase of 285 GW



**Figure 4.** Plot of the PL emission intensity versus the excitation intensity for the three different transitions in the aggregate phase of PPE. The experimental data for the 0–0 fundamental is depicted with the symbol  $\diamond$ , whereas the transitions with vibronic progressions are shown as  $\circ$  for 0–1 and  $\Delta$  for 0–2. The associated curves depict theoretical fits with eq 1. Demonstrating the strong dependence of the fits on the saturation intensity in eq 1, a second fit for the 0–2 transition is shown, where the saturation intensity is identical for the 0–0 and 0–1 fits, it describes the data well at low intensities, but fails at higher intensities.



**Figure 5.** Plot of the PL emission intensity versus the excitation intensity for the three different transitions in the nonaggregate phase of PPE. The fit of all three transitions leads to the same saturation intensity.

$\text{cm}^{-2}$ , shown in Figure 5. The 0–2 transition, on the other hand, has a saturation intensity of  $170 \text{ GW cm}^{-2}$ . It can be immediately seen from Figure 4 that the difference in saturation intensity is definitely possible to discern, within the measurement accuracy, when looking at the graph for the 0–2 transition (dashed). One, which follows the experimental data, is fitted with the saturation intensity of  $170 \text{ GW cm}^{-2}$ . The other one, which only follows the data for low intensities, is plotted for a saturation intensity of  $265 \text{ GW cm}^{-2}$ , equal to those of the 0–0 and 0–1 transition. This underlines the high significance of the measured data and the applied analysis.

Therefore, at higher excitation intensities, there is a smaller contribution of the 0–2 peak to the overall PL spectrum, and the emission color shifts toward the blue as observed in Figures 2 and 3.

The saturation intensity can be described as a function of several material constants, as well as experimental influences:<sup>13</sup>

$$I_{\text{sat}} = \sqrt{\frac{N\hbar\omega(8\ln(2))^{1/2}}{2\alpha_2^0\tau}} \quad (2)$$

where  $N$  is the number of excitonic states contributing to the absorption and emission process,  $\tau$  is the temporal width of the laser beam profile, and  $\hbar\omega$  is the energy per two photons (3.3 eV). The parameters  $\tau$  and  $\hbar\omega$  of the laser system do not vary throughout these measurements. Thus

$$\frac{N_{0-0}}{N_{0-2}} = \frac{I_{\text{sat},0-0}^2}{I_{\text{sat},0-2}^2} = 2.43 \quad (3)$$

which means that only about 40% of all excitonic states can contribute to the 0–2 transition in the aggregate phase.

It follows that two types of excitons exist in the aggregate solution. One is identical to the exciton in the nonaggregate solution, and its emission spectrum shows contributions of all vibronic paths, 0–0, 0–1, and 0–2. The other one, however, shows only two vibronic peaks in its emission spectrum, 0–0 and 0–1. It is likely that the alteration of the electronic bandstructure due to stacking influences the decay paths and, thus, chains that overlap due to aggregation will exhibit excitons of the second species, whereas isolated chains exhibit only excitons of the first species, identical to those in the nonaggregate solution (Figure 5).

In summary, we report the first demonstration of color tuning by means of excitation variation in a semiconducting material. In addition to the chemical stability and remarkable electronic characteristics, the reported phenomenon makes PPE extremely appealing for optoelectronic applications. Furthermore, owing to the feasibility to switch back and forth between the aggregated and nonaggregated phase, PPE has the potential to create dynamic color switching devices beyond standard LED applications. Through theoretical analysis of the PL emission process and its saturation, the mechanism of the color change was found. In the aggregate solution, the excitonic states behave differently than in a single molecule solution, and it is seen in particular that only 40% of all possible excitons can contribute to the 0–2 vibronic transition.

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