Optical Pumping of Poly(3-hexylthiophene) Singlet Excitons Induces Charge Carrier Generation

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Ground State Bleaching

Ground state absorbance at 465 nm: $\mathrm{GSA}_{465} = 0.21$

Ground state bleach ΔOD at 465 nm and 25 ps: $\mathrm{GSB}_{465} = -0.0065$

Proportion of excitons produced by pump: $\frac{|\mathrm{GSB}_{465}|}{\mathrm{GSA}_{465}} = 0.031 \equiv 3.1\%$

ΔOD at 1050 nm and 25 ps without push: $\Delta\mathrm{OD}_{1050} = 0.0366$

$\Delta\Delta$OD at 1050 nm and 25 ps with push: $|\Delta\Delta\mathrm{OD}_{1050}| = 0.0102$

Proportion of excitons affected by push: $1 - \frac{\Delta\mathrm{OD}_{1050} - |\Delta\Delta\mathrm{OD}_{1050}|}{\Delta\mathrm{OD}_{1050}} = 0.28 \equiv 28\%$

Fitting parameters for 3-pulse data show some excitons affected by the push are not recovering: $A_3 + A_4 = 0.11 \equiv 11\%$

As a proportion of total ground state absorbance: $0.21 \times 0.031 \times 0.28 \times 0.11 = 0.00022$

Change in ground state bleach signal due to the push pulse is shown in Figure 1, with a $\Delta\Delta$OD of 0.0002 appearing within approximately 5 ps. This indicates that some proportion of excitons that absorb the push pulse are rapidly returning to the ground state but are not relaxing back through the normally excited state.

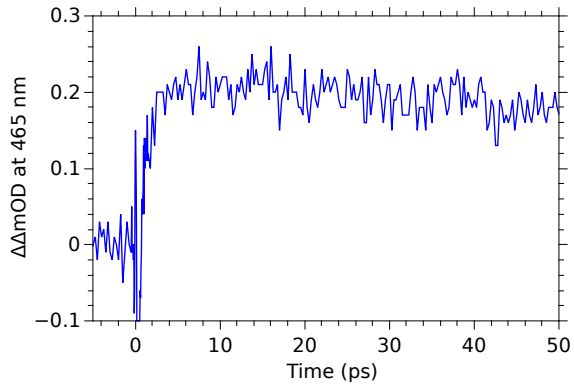

Figure 1: Change in the ground state bleach band at 465 nm due to the push pulse. Despite the low signal to noise level it can be seen that the push is causing an increase in ground state population.

Single Strand Assumption

Volume containing a single polymer strand (V_{strand}):

Molecular weight of P3HT sample: $M_{strand} = 50\,000\,\mathrm{g\,mol^{-1}}$

Molecular weight of monomer unit ($C_{10}H_{14}S$): $M_{monomer} = 166.3\,\mathrm{g\,mol^{-1}}$

Number of monomer units per strand: $n = \frac{M_{strand}}{M_{monomer}} = 300$

Length of single monomer unit: $L_{monomer} = 0.39\,\mathrm{nm}$

Contour length of polymer strand: $L_c = n \times L_{monomer} = 117\,\mathrm{nm}$

Persistence length:[1] $L_p = 2.4\,\mathrm{nm}$

Radius of gyration:

$$\begin{aligned} {R_g}^2 &= \frac{1}{3}L_p L_c - {L_p}^2 + 2\frac{{L_p}^3}{L_c}\left(1 - \frac{L_p}{L_c}\left[1 - e^{-\frac{L_c}{L_p}}\right]\right) \\ &= 8.81 \times 10^{-17}\,\mathrm{m^2} \\ R_g &= 9.38 \times 10^{-9}\,\mathrm{m} \\ &= 9.38\,\mathrm{nm} \end{aligned}$$

Volume of cube containing a strand: $V_{strand} = (2R_g)^3 = 6.6 \times 10^3\,\mathrm{nm^3}$

Volume allowed in solution for a single polymer strand ($V_{allowed}$):

Concentration of polymer solution: $C = 0.1\,\mathrm{g\,L^{-1}} \equiv 2\,\mu\mathrm{M}$

Avogadro's number: $N_A = 6.022 \times 10^{23}\,\mathrm{mol^{-1}}$

Number of strands per unit volume: $N_V = C \times N_A = 1.2 \times 10^{18}\,\mathrm{L^{-1}} \equiv 1.2 \times 10^{-6}\,\mathrm{nm^{-3}}$

Volume allowed per strand: $V_{allowed} = \frac{1}{N_V} = 8.3 \times 10^5\,\mathrm{nm^3}$

Probability of multiple strands interacting:

Expected value: $\lambda = \frac{V_{strand}}{V_{allowed}} = 7.95 \times 10^{-3}$

Poisson distribution probability of x strands occupying same space:

$$P_{(x=0)} = \frac{\lambda^0 e^{-\lambda}}{0!} = 0.99$$
$$P_{(x=1)} = \frac{\lambda^1 e^{-\lambda}}{1!} = 7.9 \times 10^{-3}$$
$$P_{(x=2)} = \frac{\lambda^2 e^{-\lambda}}{2!} = 3.1 \times 10^{-5}$$
$$P_{(x=3)} = \frac{\lambda^3 e^{-\lambda}}{3!} = 8.3 \times 10^{-8}$$

Time-Resolved Fluorescence

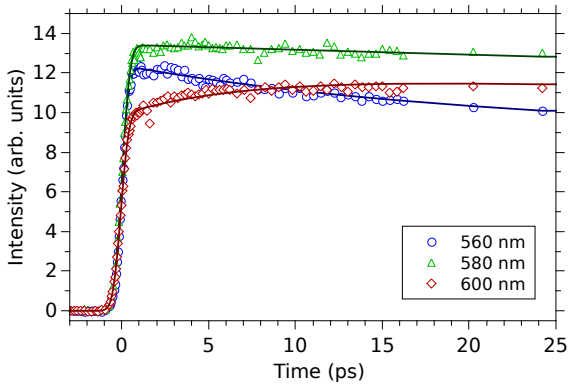

Figure 2: Results of the fluorescence upconversion experiments showing differing dynamics at each wavelength, indicating dynamic red-shifting of the emission is occurring.

Spectral Evolution

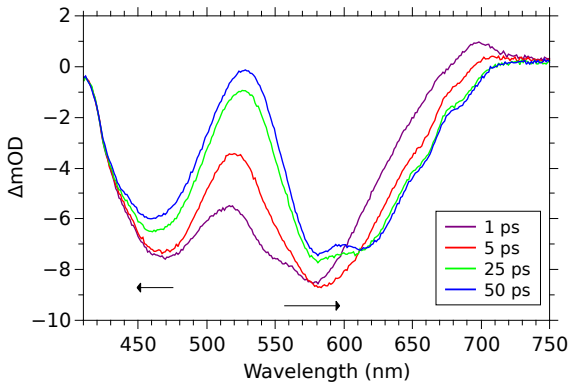

Figure 3: Evolution of the visible spectrum during the pump-probe experiment. The arrows indicate the red-shifting of the SE peak and a slight blue-shifting of the GSB peak.

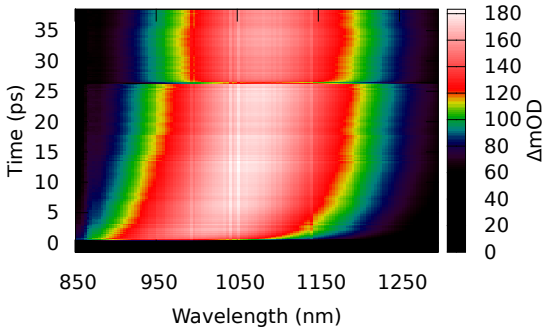

Figure 4: Evolution of the ESA peak during the pump-push-probe ΔOD experiments. Red-shifting of the peak is observed over the course of the experiment. The arrival of the push-pulse can be seen at $t = 25\,\text{ps}$.

Push Time and Power Dependency

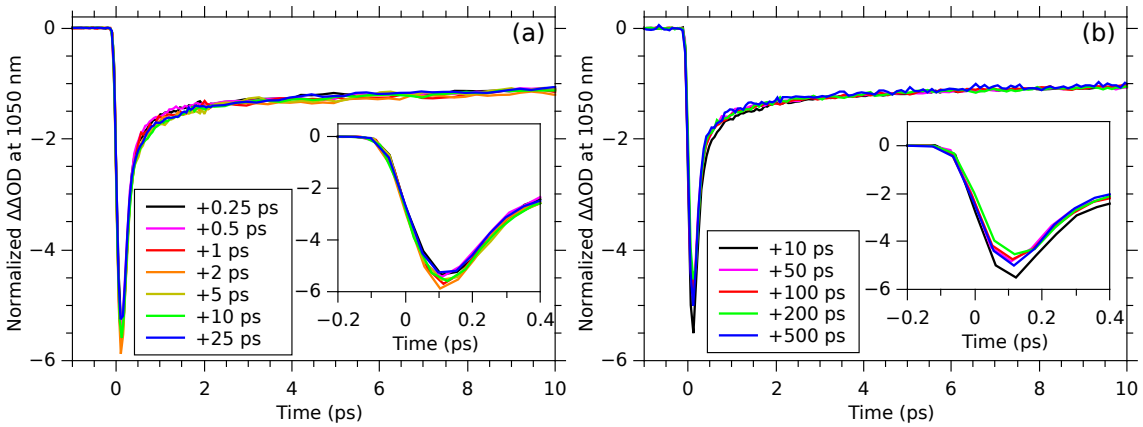

Figure 5: Dependency of the change in excited state absorption on the arrival time of the push pulse after the initial excitation. All curves have been normalised to the change in ΔOD 15 ps after the push pulse. Results from time intervals between 0.25 and 25 ps are shown in (a), with corresponding fitting parameters in Table 2. Additional experiments were conducted with pump-push delays over the entire lifetime of the exciton, (b), confirming the lack of time dependence.

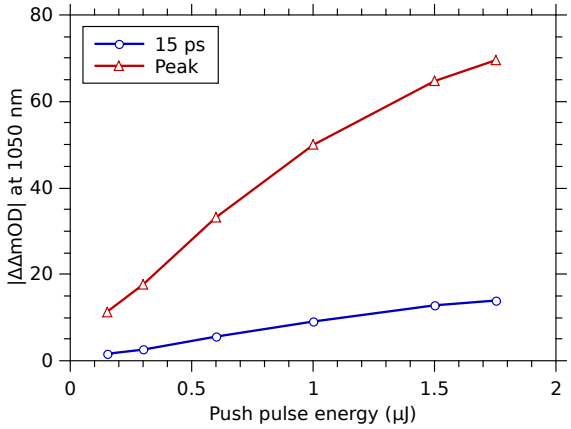

Figure 6: Dependency of the excited state absorption on the power of the push pulse showing the magnitude of the change in ΔOD at 15 ps after the arrival of the push pulse, and at the peak change in ΔOD at approximately 150 fs.

Push-Probe Experiment

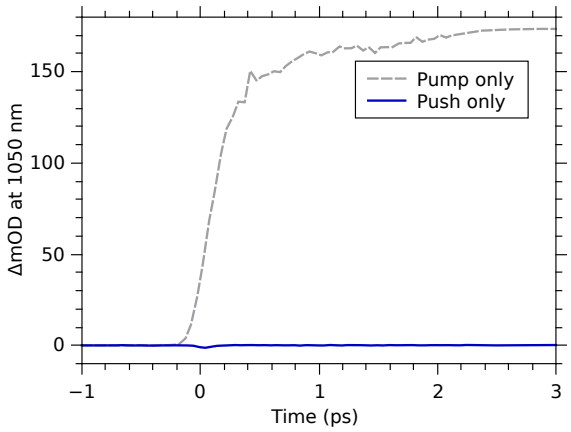

Figure 7: Change in optical density at 1050 nm in the presence of either the 900 nm push pulse (solid line) or the 400 nm pump pulse (dashed line) only. The absence of the induced absorption band from the 900 nm experiment shows that excitons are only produced by the 400 nm pump pulse.

Triplet Exciton Population

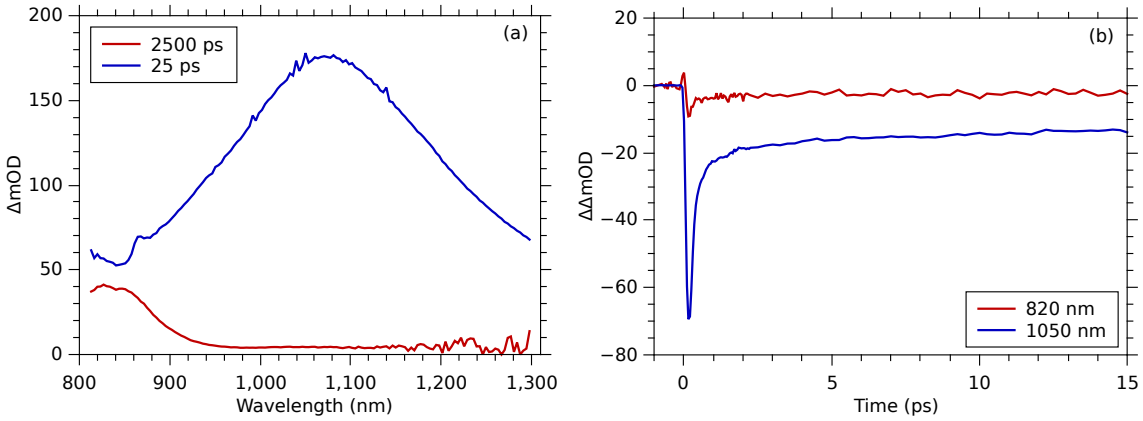

Figure 8: (a) Triplet excitons are observed in the ΔOD data as a long-lived absorption peak centered around 820 nm, most visible at the maximum experimental time window of 2.5 ns after the singlet exciton absorption has decayed. (b) The change in ΔOD at 820 nm does not show evidence of a significant increase in triplet excitons due to the push pulse.

Fitting Parameters

Table 1: Fitting parameters for the pump-probe (ΔOD) data.[a]

expt.	A_1[b]	τ_1 (ps)	A_2	τ_2 (ps)	A_3	τ_3 (ps)
ΔOD_{1050}	−0.19	2.4	0.14	135	0.66	530[c]
ΔOD_{600}	0.18	2.1	−0.22	60	−0.60	530[c]

[a] The ΔOD data was fit to a multi-exponential function $f(t) = \sum_n A_n e^{-t/\tau_n}$. All parameters have a relative error of 15%. [b] $\sum_n |A_n| = 1$. [c] Fixed to value obtained from fluorescence lifetime measurements.

Table 2: Fitting parameters for the pump-push-probe ($\Delta\Delta OD_{1050}$) data with $\lambda_{push} = 900\,nm$.[a]

push (ps)	A_1[b]	τ_1 (ps)	A_2	τ_2 (ps)	A_3	τ_3 (ps)	A_4	τ_4 (ps)
+0.25	−0.83	0.16	−0.06	2.6	−0.09	135[c]	−0.03	530[d]
+0.5	−0.83	0.17	−0.05	4.4	−0.09	135[c]	−0.03	530[d]
+1	−0.83	0.17	−0.06	3.9	−0.09	135[c]	−0.03	530[d]
+2	−0.83	0.17	−0.06	4.5	−0.08	135[c]	−0.03	530[d]
+5	−0.80	0.17	−0.08	2.6	−0.08	135[c]	−0.04	530[d]
+10	−0.80	0.16	−0.08	2.6	−0.08	135[c]	−0.04	530[d]
+25	−0.80	0.16	−0.09	2.4	−0.07	135[c]	−0.04	530[d]

[a] The $\Delta\Delta OD$ data was fit to a multi-exponential function $f(t) = \sum_n A_n e^{-t/\tau_n}$. All parameters have a relative error of 15%. [b] $\sum_n |A_n| = 1$. [c] Fixed to value obtained from pump-probe experiment. [d] Fixed to value obtained from fluorescence lifetime measurements.

Table 3: Fitting parameters for the pump-push-probe ($\Delta\Delta OD_{1050}$) data with $\lambda_{push} = 1200\,nm$.[a]

push (ps)	A_1[b]	τ_1 (ps)	A_2	τ_2 (ps)	A_3	τ_3 (ps)	A_4	τ_4 (ps)
+0.25	−0.78	0.22	−0.09	4.7	−0.11	135[c]	−0.01	530[d]
+0.5	−0.77	0.26	−0.09	8.5	−0.11	135[c]	−0.02	530[d]
+1	−0.74	0.30	−0.11	5.7	−0.13	135[c]	−0.02	530[d]
+2	−0.77	0.26	−0.10	5.2	−0.11	135[c]	−0.02	530[d]
+5	−0.74	0.32	−0.12	4.7	−0.13	135[c]	−0.02	530[d]
+10	−0.78	0.24	−0.10	4.5	−0.10	135[c]	−0.02	530[d]
+25	−0.76	0.29	−0.11	4.2	−0.11	135[c]	−0.03	530[d]

[a] The $\Delta\Delta OD$ data was fit to a multi-exponential function $f(t) = \sum_n A_n e^{-t/\tau_n}$. All parameters have a relative error of 15%. [b] $\sum_n |A_n| = 1$. [c] Fixed to value obtained from pump-probe experiment. [d] Fixed to value obtained from fluorescence lifetime measurements.

Table 4: Fitting parameters for the pump-push-probe ($\Delta\Delta OD_{600}$) data with $\lambda_{push} = 900\,nm$.[a]

push (ps)	A_1[b]	τ_1 (ps)	A_2	τ_2 (ps)	A_3	τ_3 (ps)	A_4	τ_4 (ps)
+0.25	0.86	0.16	0.08	2.8	0.03	109	0.03	530[c]

[a] The $\Delta\Delta OD$ data was fit to a multi-exponential function $f(t) = \sum_n A_n e^{-t/\tau_n}$. All parameters have a relative error of 15%. [b] $\sum_n |A_n| = 1$. [c] Fixed to value obtained from fluorescence lifetime measurements.

Experimental Section

Fluorescence lifetime measurement. Fluorescence lifetimes were measured using a fluorescence upconversion spectrometer (Ultrafast Systems, Halcyone). A continuous wave 532 nm Nd:YVO_4 laser at 8 W (Spectra-Physics, Millenia Prime) pumped a mode-locked Ti:Sapphire oscillator (Spectra-Physics, Tsunami) to produce 800 nm pulses at a rate of 80 MHz. A pulse picker selected pulses at a rate of 40 MHz that were then split into excitation and gate beams. The excitation wavelength of 400 nm was generated by second harmonic frequency doubling of the oscillator output. The gate pulse polarisation was set to the magic angle (54.7°) with respect to the excitation pulse to negate the effects of anisotropy.

Each run of the experiments consisted of the averaging of three scans with each time point sampled for three seconds.

Samples were tested in a quartz cuvette with a 2 mm path length (Starna Cells 21-Q-2) and stirred continuously during the experiments.

Pump-probe and pump-push-probe spectroscopy. A schematic diagram of the apparatus used for the pump-probe and pump-push-probe experiments is shown in Figure 9.

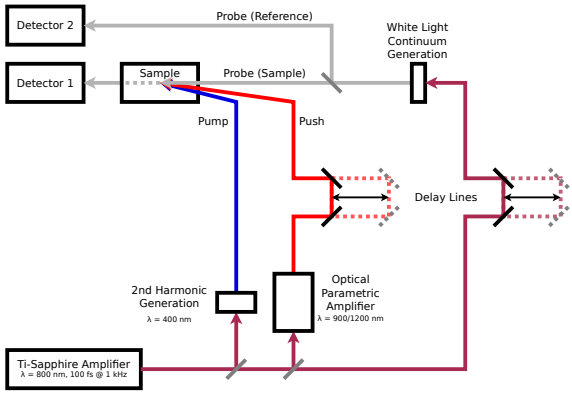

Figure 9: Schematic diagram of the apparatus used for the pump-push-probe experiments.

References

(1) Heffner, G. W.; Pearson, D. S. Molecular Characterization of Poly(3-hexylthiophene). *Macromolecules* **1991**, *24*, 6295–6299.