

Supporting information for: Ultrafast charge separation at a polymer–single-walled carbon nanotube molecular junction

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Preparation of P3HT-NT Nanohybrid Solutions

Regioregular P3HT with molecular weight 25000–35000 g mol^{-1} was used as received from Sigma-Aldrich and CoMoCAT nanotubes with small diameter (0.7–0.9 nm) and >90% semiconducting tube purity were purchased from SouthWest Nanotechnologies (SWeNT). All solvents were purchased from Sigma-Aldrich. P3HT was dissolved in chlorobenzene solution to a 0.6 mg/ml concentration and CoMoCAT material was added to 0.3 mg/ml. The dispersion was treated in an ultrasonic disintegrator for 15 mins, followed by centrifugation for 8 mins at $10000 \times g$. The excess P3HT polymer was removed by a solvent extraction where toluene was added to a 2:1 volume ratio. This induced aggregation of the nanostructures and caused precipitation after centrifugation for 4 mins at $16000 \times g$. The unreacted P3HT supernatant was discarded and the residue redissolved in toluene to repeat the purification procedure. Finally, the highly purified nanostructure residue was weighed and redissolved in chloroform to any desired concentration.

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Preparation of P3HT-NT Films

Thin, uniform P3HT-NT films were prepared by spin-coating concentrated chloroform solutions of the P3HT-NT composite onto plasma-etched quartz substrates. Optimal films were obtained with a spin speed of 100 rpm for 120 sec. P3HT-NT composite solutions containing 15 mg/ml excess P3HT (P3HT-NT(1%)) as well as P3HT-only solutions (15 mg/ml) were prepared and treated in the ultrasonic disintegrator for 15 mins and then used to spin-coat on plasma-etched quartz substrates (1000 rpm). A PCBM (American Dye Source)-P3HT composite was also prepared by spin coating at 1000 rpm a 1:0.7 P3HT-PCBM solution with a P3HT concentration of 10 mg/ml. Films were annealed at 120°C for 15 mins. To prevent degradation, all film preparation and storage was conducted in a nitrogen glovebox with an oxygen concentration of <1.5 ppm. Finally, atomic force microscopy (AFM) images were obtained using a ThermoMicroscope M5 after drop casting a diluted solution on a flat silicon wafer in non-contact mode.

Preparation of NT-gelatin films

Sodium dodecylbenzene sulfonate (SDBS)-wrapped nanotubes were prepared by dissolving 15mg CoMoCAT material and 350mg SDBS in 35ml of D₂O. The mixture was treated in an ultrasonic disintegrator for 30 mins, followed by ultracentrifugation at 100,000 ×g for 4hrs. Films were made using gelatin as a matrix by dissolving 0.06 g of gelatin per millilitre of NT-SDBS in D₂O solution. The mixture was deposited on a substrate, desiccated in air and then lifted off to provide free-standing NT-gelatin films.

Photoluminescence and Transient Absorption Measurements

An infrared photoluminescence excitation (PLE) map (Fig. 1, Supporting Information) was recorded on a custom built system detailed elsewhere.¹ Appropriate filters were used to eliminate unwanted higher order wavelengths and reflections. The P3HT film absorption spectrum is overlaid to em-

phasize that the results are consistent with those obtained previously in solution;² namely, the emission from the nanotubes correlates strongly with absorption in the polymer. The PLE and absorption (Fig. 2, main text) spectra show that the (6,5) nanotube species is dominant in the sample.

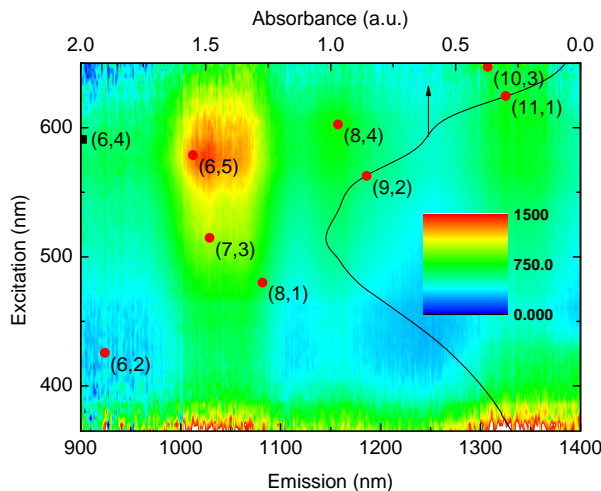


Figure 1: PLE map for the P3HT-NT sample film on a quartz substrate. The resonant nanotube species transitions are labelled in black squares (red circles) for type -1 (type 1) tubes. The black solid line shows the P3HT film absorption spectrum.

The infrared regions of the spectra in Fig. 3 (main text) were recorded using the same setup as for the PLE maps, except with an appropriate grating to allow maximum overlap of the P3HT (visible) and nanotube (IR) emissions. In addition, the excitation source was a 10-mW laser diode with peak wavelength of 405 nm. For the visible region, a Si CCD detector was used and the excitation was from the output of a mode-locked Ti:sapphire laser (Spectra-Physics Tsunami), with pulses of duration 100 fs and at a repetition rate of 80 MHz, frequency-doubled using a barium borate (BBO) crystal. The incident fluence was adjusted using a half-wave plate and polarizer. The spectra measured using the CCD and InGaAs detectors were carefully scaled linearly to overlap over a 30-nm region and displayed using the InGaAs data above 745 nm wavelength and the CCD data below this cutoff. All spectra were corrected for instrumental response using a tungsten filament lamp of known emissivity.

For TCSPC and up-conversion measurements (Fig. 4, main text), the 400-nm frequency-doubled Ti:Sapphire output was again used as the excitation source. For TCSPC, the CCD detector

was replaced by a photomultiplier tube and a fraction of the 800-nm Ti:Sapphire output was directed onto a Si-PIN diode, providing the trigger pulse for a signal period for the measurements. An excitation fluence of 9 nJ/cm^2 was used and the system resolution was 120 ps. The PLUC technique is described elsewhere³ and achieves a much better system resolution of 220 fs. The power dependence was tested (data not shown) and a linear response was observed, indicating that a higher fluence of $0.15 \mu\text{J/cm}^2$ was suitable to use.

The transient absorption experiments (Fig. 5, main text) utilized the output of a Ti:Sapphire regenerative laser amplifier system with a pulse duration of 50 fs. The laser output was split into two beams. The first beam was frequency-doubled to a wavelength of 400 nm and focused onto the sample with a fluence of $50 \mu\text{J/cm}^2$ to act as the pump beam. The second beam was focused onto a sapphire window to generate a white light continuum which was further separated into a probe and reference beam. After passing through the sample, the probe beam and the reference beam were filtered to a wavelength of 730 nm using an interference pass-filter and monitored with two photodiodes coupled to an integrator and a lock-in amplifier. The change in transmission was then determined by chopping the pump beam at half of the regenerative amplifier frequency (at 550 Hz), creating a ‘pump on’ and ‘pump off’ signal, and measuring the difference between the two signals.

References

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