Excited State Interaction of Semiconducting Single Walled Carbon Nanotubes with their Wrapping Polymers

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Figure S1. Absorption spectra of P3DDT wrapped CNTs in toluene solution and as a film on quartz. The chirality indices are assigned to the most prominent peaks.
**Figure S2.** Absorption spectrum of a film of neat PF12 and PF12 wrapped CNTs in toluene solution (a). Comparison of the CNT absorbance in the region of $S_{11}$ transitions for PF12-CNT and P3DDT-CNT.

**Figure S3.** Comparison between the steady-state PL (excitation at 400 nm), absorption and PIA (excitation at 532 nm) of P3DDT wrapped CNTs.
**Figure S4.** Photoluminescence spectra of a P3DDT wrapped CNT film cast with and without ultrasonication prior to film casting (excitation at 400 nm).

**Figure S5.** Normalised PIA in the MIR spectral region of neat P3DDT excited at different wavelengths.

**Figure S6.** PIA overview of a P3DDT:PCBM blend excited at different wavelengths. Below polymer band gap excitation also generates a polaron signature which is either due to direct CT absorption or excitation of PCBM with a subsequent hole transfer.
Figure S7. Normalised PIA in the MIR spectral region of P3DDT:PCBM excited at different wavelengths.

Figure S8. Normalised PIA spectra of P3DDT wrapped CNTs excited at different wavelengths.
Figure S9. PIA overview for P3DDT wrapped SWCNTs in presence of excess P3DDT.

Figure S10. Normalised PIA spectra in the MIR spectral region for P3DDT wrapped SWCNTs in presence of excess P3DDT.
**Figure S11.** Normalised PIA spectra in the MIR spectral region for purified P3DDT wrapped SWCNTs and when in presence of excess polymer.

**Figure S12:** PIA spectra for P3DDT-CNT including low energy excitation directly of the S11 manifold. The observed polaron formation also in this case allows to rule out higher-manifold charge transfer as the origin behind the observed polymer polaron.
Figure S13. Overview PIA spectra of neat PF12 films upon above- and below gap excitation. The inset depicts a close-up of the MIR spectral region.

Figure S14. Overview PIA spectra of PF12 blended with PCBM upon different excitation wavelengths. The 780 nm excitation was carried out with a lower energy cut-on filter.
Figure S15. Normalised PIA spectra in the MIR spectral region of PF12:PCBM blends upon excitation with different wavelengths.

Figure S16: PIA overview spectra for FF12 wrapped CNTs upon pumping with different wavelengths.

Discussion of CNT PIA signals:
The position of the trion absorption can be determined using the function \( \Delta E = \frac{A}{d} + \frac{B}{d^2} \)
where \( A \) and \( B \) are empirically found coefficients and \( \Delta E \) the separation of the respective \( S_{11} \) and trion energy.\(^{[1,2]} \) We determine the diameter of the respective tubes from their \((n,m)\) indices using the table given by Qin\(^{[3]} \) and note the determined trion energies in **Table S1**. A careful comparison of positive peaks in the PIA spectrum, e.g. in Figure S3 does not offer an acceptable accordance with trion peaks, even when assuming that some of the peak might be eclipsed by \( S_{11} \) bleaches of larger diameter tubes. We thus turn to an alternative approach, which was similarly used before for the S33 transition.\(^{[4,5]} \) We use the transmission spectrum \( T(E) \) in darkness and calculate a spectrum \( T^*(E) = T(E+dE) \) as an artificial spectrum under illumination. The artificial PIA spectrum can thus be calculated as follows: \( -\Delta T/T = c_1*(T^*-T)/T+c_2 \). We display the result for several \( dE \) (as indicated) in **Figure S17** and find a remarkable consistency between the simulated PIA spectrum and the experimental curve. We thus assume that instead of trion absorption, the small reduction in ground state energy is predominantly responsible for the steady state PIA signal of the CNTs. As outlined in the main text we consider that both a Stark shift and the band gap renormalisation could be the reason behind it.

**Table S1.** \( S_{11} \) transition energy and connected \((n,m)\) indices used to determine the SWCNT diameter and trion energy for \( A = 0.85 \) and \( B = 0.48 \)\(^{[1]} \) and alternatively \( 0.65 \) and \( 0.49 \)\(^{[2]} \)

| \( S_{11} / \text{eV} \) | \( n \) | \( m \) | \( d / \text{nm} \) | \( E_{\text{trion}} / \text{eV} \) | alt. \( E_{\text{trion}} / \text{eV} \) |
|----------------|-----|-----|-------------|----------------|----------------|
| 1.166          | 7   | 5   | 0.818       | 0.990           | 1.006          |
| 1.093          | 7   | 6   | 0.882       | 0.935           | 0.954          |
| 1.028          | 8   | 6   | 0.953       | 0.886           | 0.905          |
| 0.970          | 10  | 5   | 1.036       | 0.843           | 0.862          |
| 0.940          | 8   | 7   | 1.018       | 0.810           | 0.829          |
| 0.908          | 9   | 7   | 1.088       | 0.789           | 0.808          |
| 0.866          | 10  | 3   | 1.096       | 0.748           | 0.767          |
| 0.847          | 12  | 5   | 1.223       | 0.741           | 0.759          |
| 0.814          | 10  | 8   | 1.231       | 0.712           | 0.730          |
Table S2. Excited state energy above the ground state and composition in terms of one-particle excitations with corresponding coefficients for the excited states of P3DDT:CNT. The symbols $H$, $H-i$, $L$ and $L+i$ denote the HOMO, the $i$-th molecular orbital below $H$, LUMO and the $i$-th unoccupied orbital above $L$, respectively.

| Excited state energy | 1.03 eV | 1.07 eV |
|----------------------|---------|---------|
| Excitation (coefficient) | $H-17 \rightarrow L$ (0.17858) | $H-7 \rightarrow L+10$ (0.11186) |
|                      | $H-16 \rightarrow L$ (-0.14579) | $H-6 \rightarrow L$ (0.11536) |
|                      | $H-8 \rightarrow L$ (0.38280) | $H-3 \rightarrow L+1$ (-0.23568) |
|                      | $H-6 \rightarrow L$ (0.28747) | $H-2 \rightarrow L$ (0.10334) |
|                      | $H-3 \rightarrow L$ (-0.16789) | $H-2 \rightarrow L+1$ (-0.19456) |
|                      | $H-3 \rightarrow L+2$ (0.19062) | $H-1 \rightarrow L+1$ (0.41368) |
|                      | $H-2 \rightarrow L$ (0.13341) | $H-1 \rightarrow L+4$ (-0.23726) |
|                      | $H-1 \rightarrow L+1$ (-0.14016) | $H-1 \rightarrow L+4$ (-0.11204) |
|                      | $H-1 \rightarrow L+4$ (0.10149) | $H \rightarrow L+6$ (-0.10018) |

Figure S17. Representative molecular orbitals of the P3DDT:CNT system. Amongst the occupied states, there is an increasing hybridisation of the polymer/nanotube wavefunctions in going from $H-17$ to $H-1$; for $H-7$ it is basically localised on the polymer and corresponds to the HOMO of the unperturbed chain. From $H-6$ to $H$ (not shown) the wavefunctions are localised on the nanotube, similarly to the $L$ state and the subsequent states until $L+9$. $L+10$
is localised on the polymer and is its LUMO state. The different colours indicate opposite signs of the wavefunction.

**Methods:**

**Preparation of semiconducting SWNT dispersions:** Poly(9,9-di-n-dodecylfluorenyl-2,7-diyl) (PF12, Mn=280000 g/mol, Mw=589000 g/mol) was synthesized in a Yamamoto-type homocoupling reaction. Poly(3-dodecylthiophene-2,5-diyl) (P3DDT, Mn=29.200 g/mol, Mw=35.900 g/mol) was synthesised via the GRIM method. HiPCO SWNTs (d=0.8-1.2 nm), purchased from Unidym Inc., were used as received. The polymers were solubilized in toluene using a high power ultrasonicator (Misonix 3000) with cup horn bath (output power 69 W) for 20 min. Subsequently, SWNTs were added to form the SWNT:polymer dispersions with weight ratio of 1:2 (3 mg of SWNTs, 6 mg of polymer, 15 mL of toluene). These solutions were then sonicated for 2 h at 69 W and 16 °C. After ultrasonication, the dispersions were centrifuged at 30000 rpm (109000g) for 1 h in an ultracentrifuge (Beckman Coulter Optima XE-90) to remove all remaining bundles and heavy-weight impurities. During the centrifugation, these components precipitate at the bottom of the centrifugation tube, while the individualised SWNTs wrapped by the polymer, and free polymer chains remain in the upper part as supernatant. One extra step of ultracentrifugation was implemented to decrease the amount of free polymer in solution (enrichment).[6] For this purpose, the supernatant obtained after the first ultracentrifugation, is centrifuged for 5 h, 55000 rpm (367000g), the individualized semiconducting CNTs are then precipitated to form a pellet and the free polymer is kept in the supernatant. Finally, the pellet is re-dispersed by sonication in toluene.
**UV/vis:** Absorption spectra were recorded with a Shimadzu 3600 UV-vis-NIR spectrometer. Films were cast on glass substrates and solutions measured at low concentration in quartz cuvettes.

**Photoluminescence:** Films were deposited on quartz substrates, sealed, using epoxy glue, and excited at 400 nm using the second harmonic of a mode-locked Ti:sapphire laser at a repetition rate of 76 MHz. Steady-state spectra were recorded with an InGaAs detector from Andor. Time-resolved traces were taken with a Hamamatsu streak camera working either in the synchroscan or single sweep mode. An optical pulse selector was used to vary the repetition rate of the exciting pulses where necessary.

**Transient absorption:** Transient absorption spectra were recorded using a super continuum laser source (SuperK Extreme, NKT Photonics) that provided both the pump and probe at a MHz repetition rate. The pulse duration was approximately 1 ps and the pump power was always kept below 4µJ cm\(^{-2}\) in order to avoid thermal effects, sample degradation as well as non-linear higher order processes. The signals were measured with an auto-balanced photoreceiver (Nirvana 2017, New Focus) and amplified with a Lock-In amplifier (SR 830 DSP, Stanford Research Systems). All measurements were carried out at room temperature.

**Monochromator based PIA:** Quasi-steady-state PIA studies were performed at RT by exciting the sample with a 532 nm laser, chopped at 141 Hz, and probing with the continuous spectrum of a Xe lamp. The transmitted light is dispersed by a 1200 lines mm\(^{-1}\) grating monochromator (iHR320, Horiba) and detected by a Si detector down to an energy of 1.1 eV.
and an InGaAs detector for lower values. Additional measurements with a blocked Xe lamp account for the sample PL.

**FTIR-PIA:** Thin films were drop-cast from solution onto ZnSe platelets. The samples were then mounted into a cryostat without being exposed to air and positioned in the beam path of a Bruker Vertex 70 FTIR spectrometer. The beam passes two ZnSe windows and is detected using a liquid nitrogen cooled MCT detector. For the MIR, a KBr beamsplitter was employed and exchanged with quartz for the NIR. The samples were cooled down to 77 K and positioned under 45° to allow for sending the pump light through an additional quartz window. To avoid perturbations by the pump light, a filter (GaAs or quartz-based cut-on filters) was furthermore placed in front of the detector. Spectra were acquired with a resolution of 5 cm\(^{-1}\) in the MIR (10 cm\(^{-1}\) in the NIR) and the following cycle was run at least 1024 times: first, the pump was switched on followed by a delay of 1 s to establish equilibrium, which was then followed by a 16-fold averaging of the "light on" spectrum. Next, the light was switched off, followed by another 1 s delay and 16 co-additions for the "light off" spectrum were carried out.

**Computational details:** The geometry of a finite (8,6) nanotube 52 Å length and with edge bonds saturated by hydrogen was optimised by the Density Functional derived method Third order Self-Consistent Charge Density Functional Tight-Binding with empirical dispersion (DFTB3-D3) and 3OB parameter set.\(^{[7,8,9]}\) PF12 and P3DDT were modelled as oligomers containing 8 and 16 units, respectively. These oligomers were arranged in a helical conformation around the nanotube and the geometry of the hybrid systems was optimised within the DFTB3-D3 method, keeping the nanotube conformation frozen in its ground state.
geometry. The optimised geometries of the naked nanotube and the hybrids formed with PF12 and P3DDT wrapping the nanotube were used to calculate the energies, oscillator strengths and wavefunctions of the low lying excited states using the method ZINDO/S-CI.\cite{10}

In the presented calculation, all possible singly excited determinants were used. Calculations were carried out using the softwares DFTB+ and GAUSSIAN 09. Due to finite size effects, the electronic level spacing of these systems is larger than it would be calculated for an infinite nanotube-polymer hybrid. Consequently, the excited states have higher energy. This behaviour has been corrected by a contraction of the electronic spectra, using the $S_{11}$ transition of the air suspended (8,6) nanotube, that peaks at 1.114 eV, to correct the spectrum of the naked finite nanotube. The same contraction factor was used for all spectra.

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