

# Supporting information for: Nano-Engineering Coaxial Carbon Nanotube–Dual Polymer Heterostructures

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## **Solution Binding Competition Absorption and PL**

To quantify the substitution processes in the [F8BT-NT] + P3HT samples, multi-peak fits were carried out on the spectra in Figure S1a and 2c (main text) using OriginPro 8.1 data analysis software. The peaks were fixed at positions corresponding to the [F8BT-NT] and [P3HT-NT] environments for each nanotube species, as ascertained from pure [F8BT-NT] and [P3HT-NT] 100% solutions.

Figure S1b shows the absorption spectra of the [F8BT-NT] chloroform solutions with increasing amounts of excess P3HT from bottom to top. By comparison with the PL spectra (Figure 2c of the main text and Figure S1a), it is evident that the same results are obtained from absorption and photoluminescence measurements (with no Stokes shifts) but the latter enable better resolution of individual tubes.

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Figure S1c displays the evolution of the absorption spectra of a [F8BT-NT] 10% + P3HT solution over time. This demonstrates the dynamic nature of the substitution processes, which continue even after a month. The (6,5) peaks in these spectra were fitted to produce the plot in Figure 2f (main text). The underlying (8,3) and (7,3) peaks were estimated using fits to the spectrum of the [F8BT-NT] 100% sample (containing no P3HT). These peaks were subtracted from the subsequent time-dependent spectra to approximately isolate the (6,5) peaks.

By contrast, Figure S1d shows absorption spectra of [P3HT-NT] nanohybrids over a 2 week period after addition of a large excess of F8BT ([P3HT-NT] 1% + F8BT). No changes in the peak positions are observed, and hence no substitution of bound P3HT by F8BT occurs.

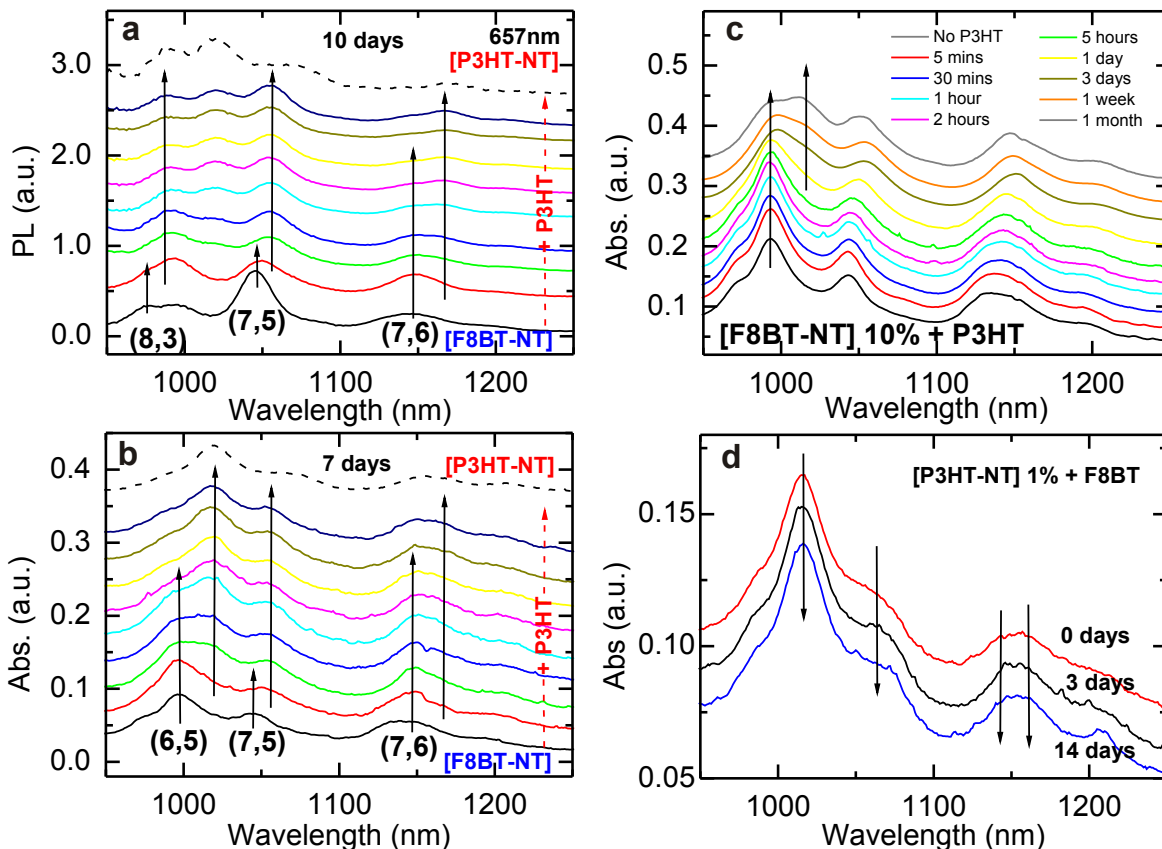


Figure S1: (a) PL spectra corresponding to [F8BT-NT] solutions (Figure 2a, main text) excited at 657 nm and measured 10 days after addition of increasing amounts of excess P3HT. The proportion of the nanohybrids progress (bottom to top) through 100, 50, 20, 15, 10, 5, 2, 1 and 0.5 % with any excess P3HT polymer emission tail subtracted. The dotted line is [P3HT-NT] 100 %. (b) Absorption spectra of [F8BT-NT] nanohybrids in chloroform solutions and excess P3HT taken 7 days after polymer addition, with the same progression of [F8BT-NT] proportions in excess P3HT as in (a). The changes in tube environment from F8BT to P3HT are indicated for the (6,5), (7,5) and (7,6) tubes only. (c) [F8BT-NT] 10% + P3HT nanohybrid absorption spectra taken over a 1 month period to demonstrate the dynamic substitution process, with the F8BT on the (6,5) nanotube becoming increasingly substituted by the excess P3HT. (d) Absorption spectra of the [P3HT-NT] 1% + F8BT nanohybrids taken 0, 3 and 14 days after polymer addition, showing that no change is observed over time. All spectra are offset for clarity.

## Isolating Substituted Nanohybrids

In a similar manner to Schemes A and B in Figure 3a (main text), we isolate the nanohybrids containing one polymer following immersion in an excess of the same polymer (corresponding to a 1% concentration of wrapped polymer out of total polymer). The processes are presented in Schemes C and D in Figure S2a and the absorption spectra of films of the products are shown in Figure S2b. AFM images of the products of Scheme C and D are presented in Figure S2d and e, respectively. In both cases, the structures are  $\sim 2$  nm in height, corresponding to the height of a nanotube bound by 1–2 polymer chains.

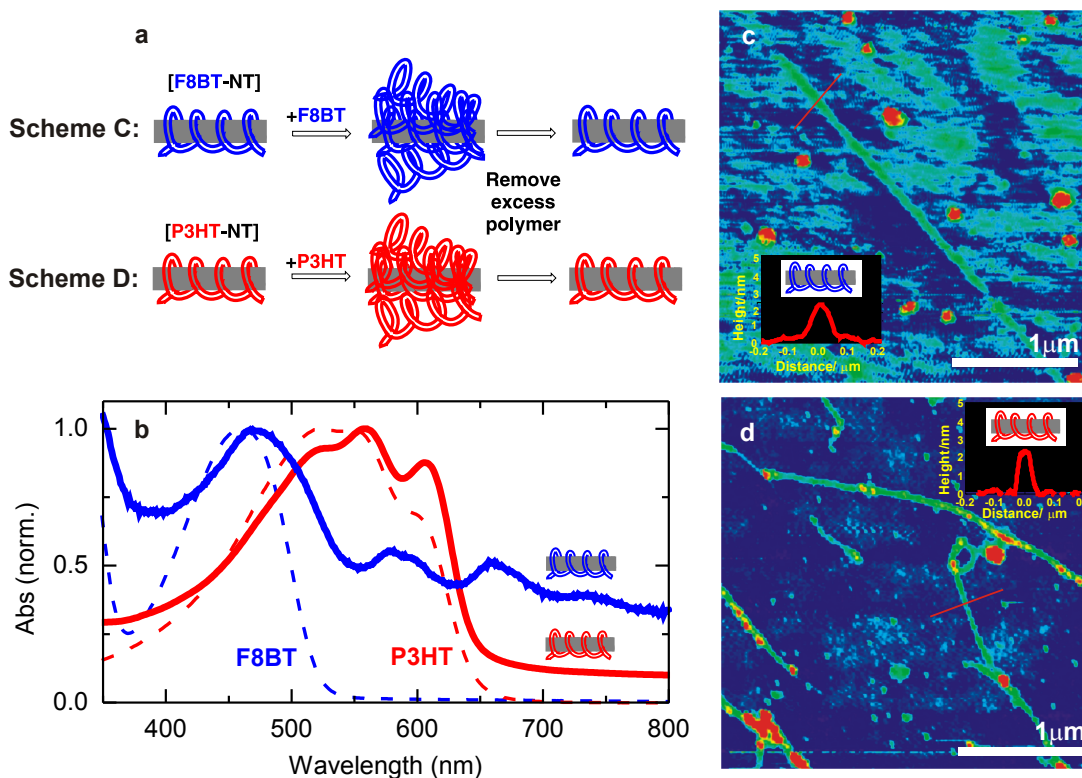


Figure S2: The isolation of nanohybrid species following immersion in an excess of the same polymer. (a) Scheme C shows excess F8BT being added to [F8BT-NT] nanohybrids, such that there is a 1% concentration of wrapped polymer out of total polymer. The solutions are left for 3 days after which any excess unbound polymer is removed. The analogous P3HT control is shown in Scheme D. (b) The absorption spectra of the final products taken from spin-coated films are shown in the blue (Scheme C) and red line (Scheme D). F8BT (dashed blue line) and P3HT (dashed red line) spectra are presented for reference and all spectra are normalized at the polymer peaks. AFM images of the products from (c) Scheme C and (d) Scheme D. The insets show the height analyses across the sections indicated.

## Preparation of Nanohybrid Films

The films were checked to have the correct ratios using absorption spectroscopy (Figure S3) as follows. The ratio of the polymer to E<sub>11</sub> (6,5) nanotube peaks in the absorption spectra of the [F8BT-NT] and [P3HT-NT] films are used to define 100% of each nanohybrid (where it is understood all of the polymer present is wrapped on the tubes). Using this ratio, the absorption magnitude of wrapping polymer in any given sample can be calculated directly from the E<sub>11</sub> (6,5) nanotube peak. The excess polymer component was calculated by subtracting the scaled polymer absorption spectrum of the appropriate wrapped 100% nanohybrid film from the spectrum of the sample under investigation. Finally, for those samples containing both polymers, the relative absorption magnitudes were scaled with the appropriate absorption coefficients at the peak ( $\sim 1.1 \times 10^{-5} \text{ cm}^{-1}$  for F8BT,  $\sim 1.3 \times 10^{-5} \text{ cm}^{-1}$  for P3HT<sup>1</sup>). Therefore, the ratio of the wrapping to excess polymer could be calculated and used to define the percentage of nanohybrids in each excess polymer matrix.

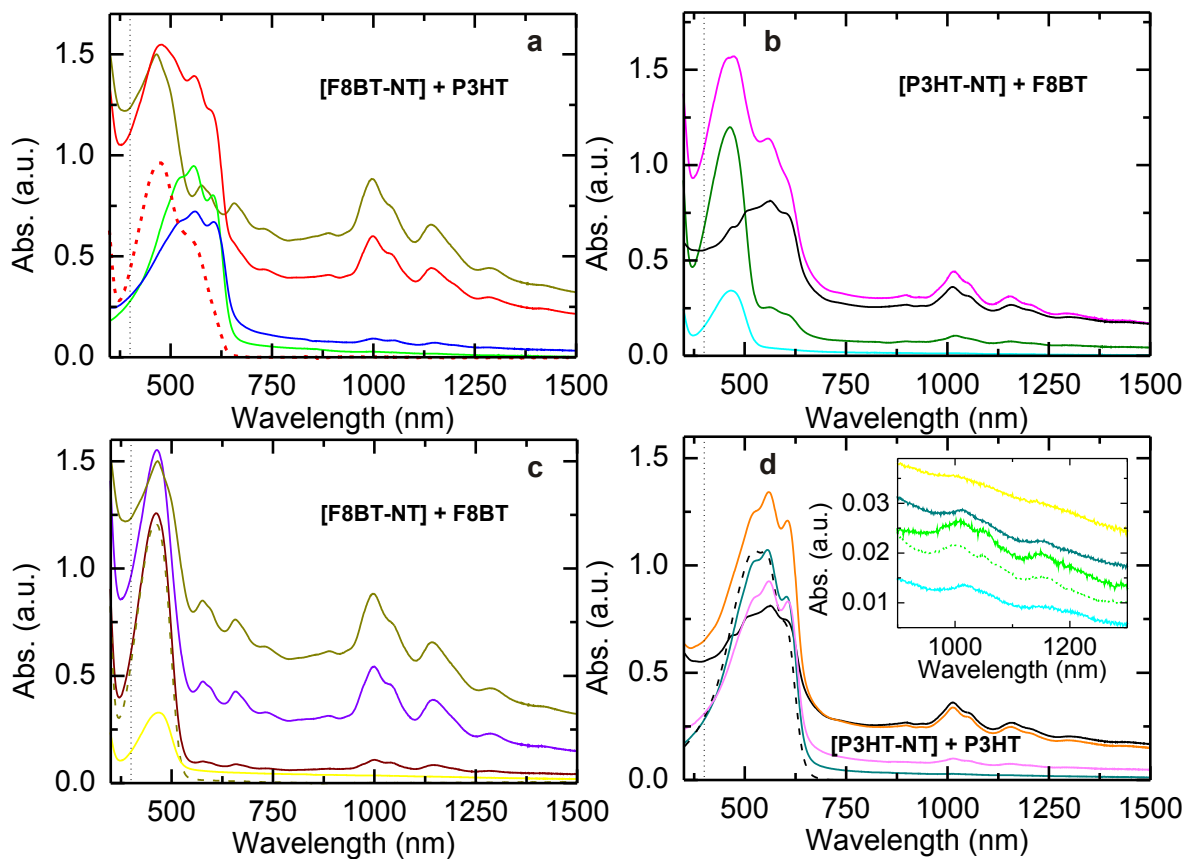


Figure S3: Absorption spectra of films spun-cast within 2 hours of adding various excess polymer to nanohybrid solutions. No scaling or background subtractions were applied. The vertical dotted lines show the excitation wavelength (400 nm) for the steady state and time-resolved polymer PL measurements. (a) [F8BT-NT] X% + P3HT films with X = 100 (dark yellow), 50 (red), 10 (blue) and 1 (green), along with an all-polymer 50:50 F8BT:P3HT blend. (b) [P3HT-NT] X% + F8BT films with X = 100 (black), 50 (magenta), 10 (dark green) and 1 (cyan). (c) F8BT (dark yellow dashed) and [F8BT-NT] X% + F8BT films with X = 100 (dark yellow), 50 (violet), 10 (dark red) and 1 (yellow). (d) P3HT (black dashed) and [P3HT-NT] X% + P3HT films with X = 100 (black), 50 (orange), 10 (pink) and 1 (dark cyan). *Inset*: Enlarged view of the nanotube  $E_{11}$  region of the 1% samples in (a)–(d), along with a [F8BT-NT] 1% + P3HT sample cast within ten minutes (dotted green).

## Molecular Dynamics Simulations

Figure S4 shows single chain molecular dynamics results, where the competitive binding of only one chain of each polymer is studied. We emphasize that the starting chain orientations and positions do not appear to have a significant influence on the final structures (data not shown).

Figure S4a–c shows the series in which the binding of a single F8BT chain is first simulated and then a P3HT chain is added after 300 ps. After another 300 ps of simulation, equilibrium is again reached and it is apparent that the added P3HT chain binds predominantly to the nanotube and still attempts to ‘wrap’ the tube regardless of the presence of the F8BT. The greater affinity of P3HT for the tube rather than the bound F8BT polymer may give insight into the displacement mechanism occurring over a much longer period of time.

Figure S4d–f shows the reverse situation. The P3HT chain binds to the tube and reaches equilibrium in 100 ps as seen elsewhere,<sup>2</sup> more quickly than for F8BT. The added F8BT chain then binds directly to the P3HT chain only and remains attached. This direct and favorable binding of chains could explain the thick coatings of F8BT forming on the [P3HT-NT] nanohybrids, where the bound P3HT chains act as templates to bind F8BT polymer.

The results for multiple chain studies, including those used to produce the structures in Figure 4 (main text), are shown in Figure S5. The series for P3HT chains binding to [F8BT-NT] structures is shown in Figure S5a–c. Three F8BT chains binding to a (6,5) nanotube are first simulated. After 300 ps, equilibrium is reached and two more chains are added to the system and, after another 150 ps, a sixth chain is added and run for another 200 ps. We note that simulations where all six initial chains were added simultaneously lead to polymer ‘knots’ forming, similar to those observed when using a much longer length of polymer both here (data not shown) and elsewhere.<sup>2</sup> Six chains of P3HT aligned along the tubes axis were then added to the system and equilibrium reached after 200 ps. To create the structure in Figure 4b (main text), which is comprised of 10 P3HT chains and 6 F8BT chains, two more P3HT chains were added and a final two added after another 100 ps, with equilibrium again reached after a further 200 ps.

The reverse case of F8BT chains binding to [P3HT-NT] nanohybrids is shown in Figure S5d–f.

The binding of four P3HT chains to a (6,5) nanotube was first simulated and equilibrium reached after 200 ps. Two more P3HT chains were added to the system and equilibrium again reached after 400 ps. Six F8BT chains aligned along the tube axis were added and simulated until equilibrium (200 ps). To create the structure in Figure 4c (main text), which is comprised of 10 F8BT chains and 6 P3HT chains, two more F8BT chains were added and a final two added after another 100 ps, with equilibrium again reached after a further 200 ps.



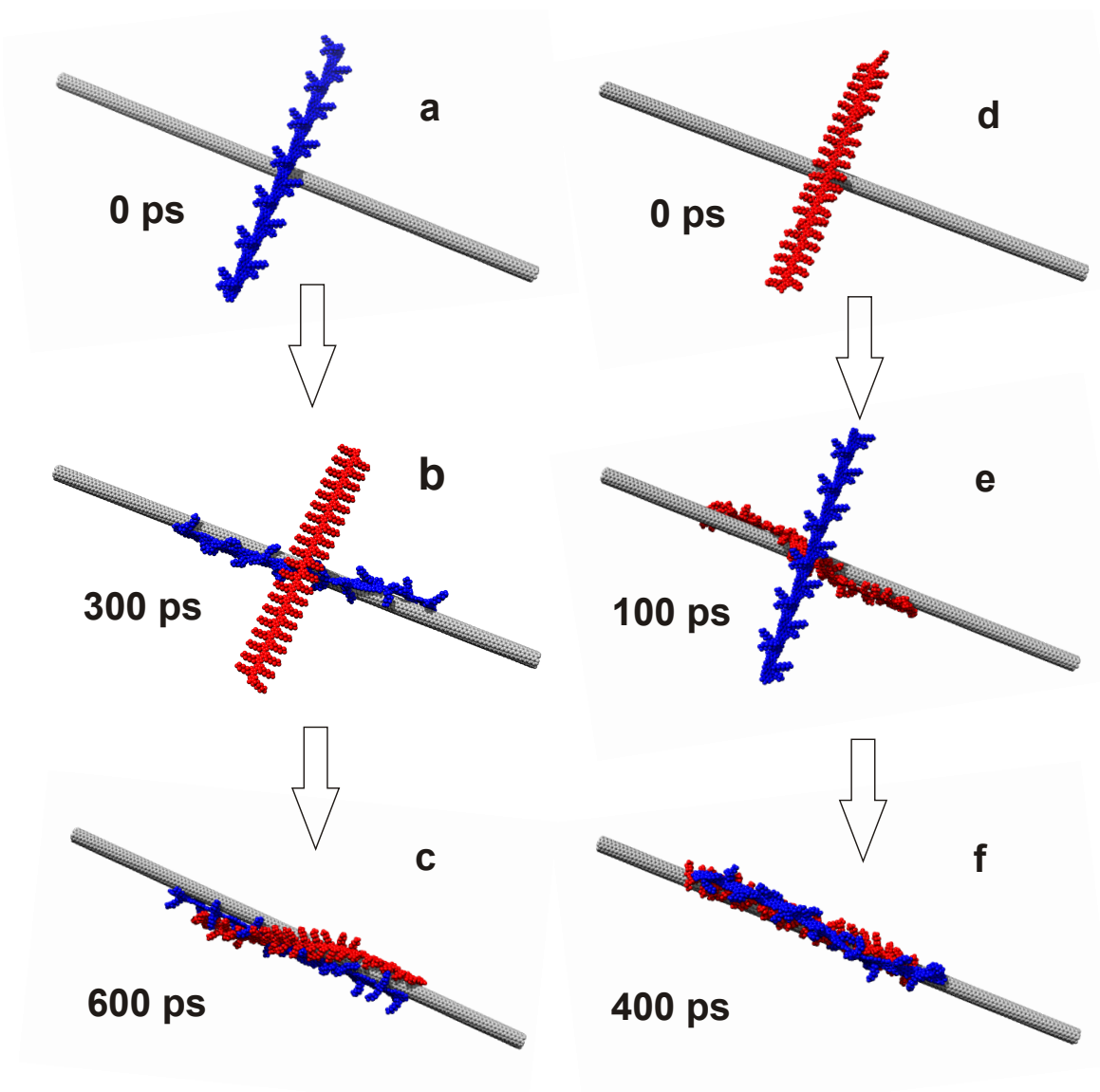


Figure S4: Single chain molecular dynamics results. (a) An F8BT chain binding to a (6,5) nanotube. After 300 ps, a P3HT chain is added in (b) and the result after a further 300 ps of simulation is shown in (c). (d)–(f), The same results but with the chains reversed, except the F8BT chain is added after only 100 ps because the [P3HT-NT] system reaches equilibrium more quickly than [F8BT-NT].

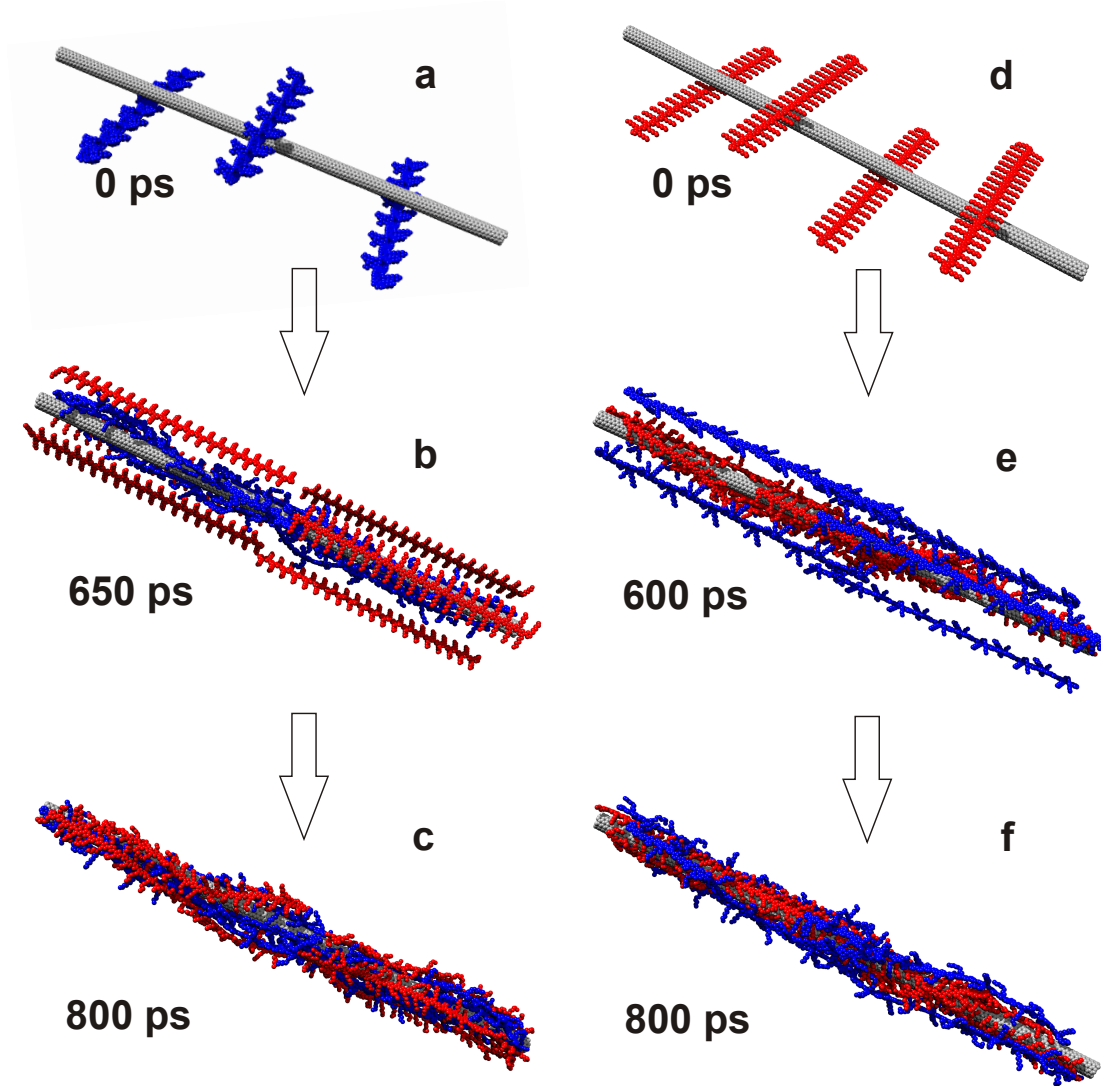


Figure S5: Multiple chain molecular dynamics results. (a) The binding of three F8BT chains to a (6,5) nanotube is first simulated. Another two F8BT chains are added after 300ps and a sixth chain is added after another 150ps. (b) After another 200ps, six P3HT chains are added to the system. (c) The result of the simulation after 150ps. (d) Four P3HT chains binding to a (6,5) nanotube are simulated. After 200ps, two more chains are added to the system. (e) After another 400ps, six F8BT chains are added to the system. (f) The result of the simulation after another 200ps.

## Polymer Photoluminescence Measurements

Figure S6a and b show the TCSPC results for F8BT emission (550 nm) from the samples. The [F8BT-NT] + P3HT samples in Figure S6a show a response on the order of the system resolution ( $\sim 120$  ps) because the emission from wrapped F8BT is significantly quenched by the tubes and/or P3HT. The decay curves for the [P3HT-NT] + F8BT samples in Figure S6b become increasingly faster as the [P3HT-NT] nanohybrid proportions and hence density of quenching centers increase, reaching the instrument resolution for the 50 % samples.

The TCSPC results for P3HT emission (640 nm) from the samples are shown in Figure S6c and d. As the [F8BT-NT] proportion increases in Figure S6c, the P3HT emission shows an increasingly faster decay that cannot be resolved for the [F8BT-NT] 50% + P3HT sample. For the [P3HT-NT] + F8BT samples, shown in Figure S6d, the [P3HT-NT] 10% and 1% in excess F8BT samples show long-lived decays that are attributed to probing the tail of the dominant long-lived F8BT emission. The emission from the pure [P3HT-NT] nanohybrids shows a system-limited response.

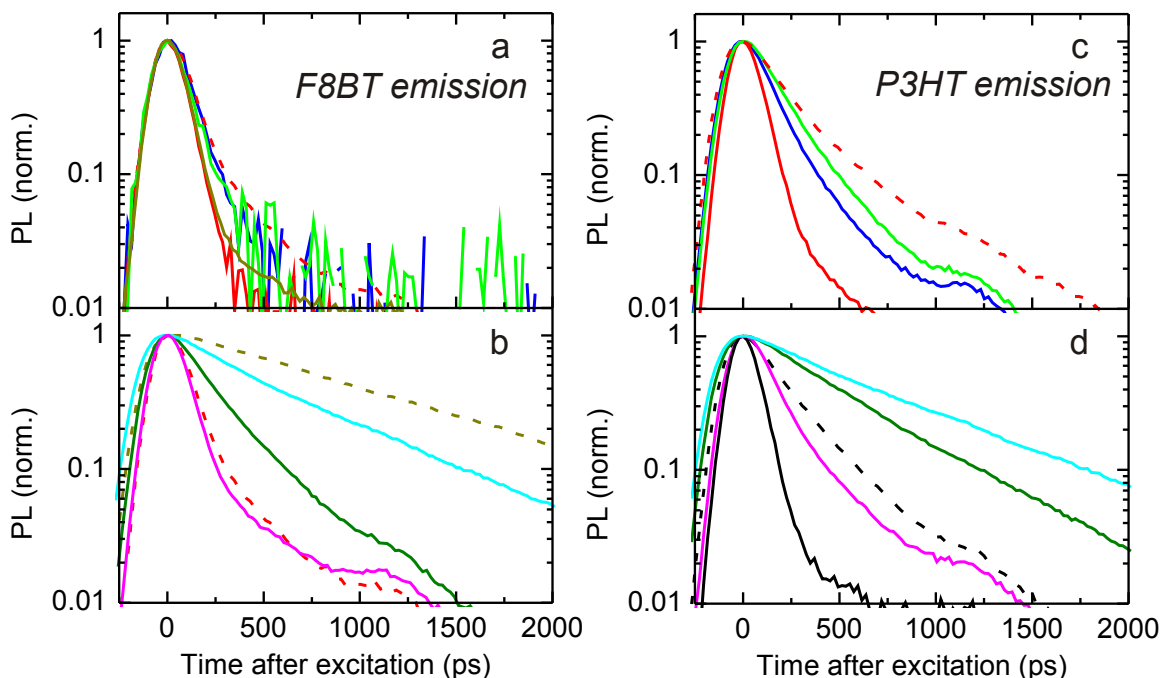


Figure S6: TCSPC measurements following photoexcitation at 400 nm to time-resolve the (a) and (b) F8BT emission at 550 nm and (c) and (d) P3HT emission at 640 nm from film samples. Results for the [F8BT-NT] + P3HT series, namely 50:50 F8BT:P3HT (red dashed), [F8BT-NT] 1% (green), 10% (blue) and 50% (red) in excess P3HT, and [F8BT-NT] 100% (dark yellow) are shown in (a) and (c). (b) and (d) show the same results but taken from the [P3HT-NT] + F8BT series, namely F8BT (dark yellow dashed), 50:50 F8BT:P3HT (red dashed), [P3HT-NT] 1% (cyan), [P3HT-NT] 10% (dark green) and 50% (magenta) in excess F8BT, along with [P3HT-NT] 100% (black) and P3HT (black dashed).

## References

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2. Bernardi, M.; Giulianini, M.; Grossman, J. C. Self-Assembly and its Impact on Interfacial Charge Transfer in Carbon Nanotube/P3HT Solar Cells. *ACS Nano* **2010**, *4*, 6599–6606.