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Title: Long range exciton transport in conjugated polymer nanofibers

prepared by seeded growth

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Abstract: Easily processed materials with the ability to transport excitons over length scales of more than 100 nm are highly desirable for a range of light-harvesting and optoelectronic devices. We describe the preparation of organic semiconducting nanofibers comprising a crystalline poly(di-*n*-hexylfluorene) core and a solvated, segmented corona consisting of polyethylene glycol in the center and polythiophene at the ends. These nanofibers exhibit exciton transfer from the core to the lower-energy polythiophene coronas in the end-blocks, which occurs in the direction of the interchain π - π stacking with very long diffusion lengths (> 200 nm) and a large diffusion coefficient ($0.5 \text{ cm}^2/\text{s}$). This is made possible by the uniform exciton energetic landscape created by the well-ordered, crystalline nanofiber core.

One Sentence Summary: Sequential crystallization of copolymers from solution yields nanofibers possessing remarkably long exciton diffusion lengths.

Main Text: The ability to transport excitation energy over length scales comparable to the optical absorption depth (100 nm and beyond) is central to the function of a range of devices, including solar cells. Most thin-film organic semiconductor structures, such as those formed from conjugated polymers, show short exciton diffusion lengths (L_D) of around 10 nm (*1*) that are primarily constrained by energetic disorder. As a result, these are fabricated as blends of electron donor and acceptor materials with length scales for the partly de-mixed materials targeted around 10 nm, so that all excitons can reach the charge-generating heterointerface (*1, 2*). In contrast, diffusion ranges for singlet excitons in purified single crystals are known to be considerably larger (up to 220 nm) (*1, 3–6*). However, in these cases the materials are generally polydisperse in dimensions and problematic to incorporate into useful devices. Device development is thus dependent on the ability to develop uniform nanostructures that are amenable to processing and able to support long range exciton diffusion. Self-assembly of molecular and polymeric amphiphiles in solution has recently emerged as a promising route to core-corona nanoparticles (micelles) that possess many of these attributes. For instance, long range exciton diffusion has been observed in dye molecule H and J fiber-like aggregates by single molecule spectroscopy (*7, 8*), and more detailed investigations performed on single conjugated polymers isolated in matrices or dilute solution (*9, 10*). These latter studies, however, necessarily exclude the role of inter-chain transport on exciton diffusion. Such transport is possible in solution-processed bulk conjugated polymers, which have been reported to show a singlet exciton diffusion length of 70 nm (*11*), but still short of the lengths exhibited in molecular crystals. Herein, we report the formation of uniform nanofibers from the seeded solution self-

assembly of block copolymers with a crystallizable π -conjugated poly(di-*n*-hexylfluorene) (PDHF) block that show exceptional exciton diffusion ranges.

In order to facilitate the study of exciton diffusion within π -conjugated, crystalline poly(di-*n*-hexylfluorene) (PDHF), we prepared segmented nanofibers comprising a continuous PDHF core with a discrete region of energy accepting, quaternized polythiophene (QPT) covalently attached as a corona at each end (Fig. 1B). The central segment contained an electronically insulating poly(ethylene glycol) (PEG) corona, and the length of his region was varied to afford a size series of nanofibers. These segmented nanostructures were prepared using living crystallization-driven self-assembly, a recently developed, seeded growth method to both 1- and 2-D objects of controlled dimensions (12, 13). The resulting structures are generally typified by highly crystalline cores, which can comprise a number of building blocks (14–17). We and Faul have previously demonstrated the use of this method with polythiophene-containing block copolymers to yield fibers with a π -conjugated core, which form ensembles with promising transport properties, but weak fluorescence due to aggregation-induced quenching (18).

Figure 1 near here

PDHF exhibits bright blue fluorescence in the solid state (19), electrospun microfibers (20), and polydisperse nanofibers self-assembled from triblock copolymers in solution (21). The uniform examples employed in the present study, however, were prepared in a multistep approach, so as to achieve the desired segmented coronal structure and varied length of the PEG

component. Initially, ca. 5 - 10 micron long nanofibers, derived from the block copolymer PDHF₁₄-*b*-PEG₂₂₇ (where the numbers refer to the number-average degree of polymerization of each block, see Fig. S1, S3-S5 and S10), were prepared by homogenous nucleation in THF:MeOH (10:8) (Fig. S1). Analysis by TEM, AFM, and wide-angle X-ray scattering (WAXS) revealed the presence of a crystalline PDHF core with a rectangular cross-section (number-average width, $W_n = 12.9$ nm and height = 4.5 nm) surrounded by a PEG corona (Fig. S10-S12). A solution of micelle seeds (number-average length, $L_n = 30$ nm; polydispersity, $L_w/L_n = 1.03$, where L_w is the weight-average length; and height = 4.5 nm) was then prepared by sonication of the multi-micron long fibers (Fig. S13A-B and S14A). Subsequent addition of different volumes of a solution of unimeric (molecularly dissolved) PDHF₁₄-*b*-PEG₂₂₇ copolymer in THF led to the formation of uniform nanofibers of controlled length (Fig. 1A, S14 and S15).

To create nanofibers with a segmented corona an all π -conjugated donor-acceptor diblock copolymer, PDHF₁₄-*b*-QPT₂₂, comprising the same PDHF core-forming block and a quaternized polythiophene (QPT) corona-forming block was prepared (Fig. S2, S6-S9). This material was added in a molecularly dissolved unimeric state (in THF:MeOH 3:1) to the PDHF₁₄-*b*-PEG₂₂₇ nanofibers in THF:MeOH 1:1, leading to growth from the two PDHF core termini. The resulting uniform nanofibers had a B-A-B structure of controlled overall and segment length with a crystalline PDHF core present over the entire length, but with a π -conjugated corona-forming block located only on the terminal (B) segments (Fig. 1A). This was used to produce a size series of near uniform nanofibers with $L_n = 180 \pm 40$, 300 ± 70 , 505 ± 100 , 945 ± 240 , and 1840 ± 540 nm with each QPT segment comprising between 35 and 120 nm of this length, as measured by TEM and supported by AFM (Fig. S13C-D, S16 and S17; Table S1). The dimensional control is illustrated further in Figure 2A (and Fig. S18), which shows a laser scanning confocal

microscopy (LSCM) image of model nanofibers with central A-segments of 1.6 μm and QPT-corona-containing segments of 1.8 μm in length.

Figure 2 near here

The absorption and photoluminescence (PL) spectra of unsegmented PDHF₁₄-*b*-PEG₂₂₇ nanofibers, the absorption spectrum of the QPT homopolymer (see Fig. S19 for emission spectrum), and the energy levels of the two conjugated species are shown in Figure 1C. The significant overlap of absorption and emission in the PDHF indicates a small Stokes shift, while the PL illustrates a high degree of vibronic structure. The good overlap of QPT absorption and PDHF emission gives a PDHF to QPT Förster transfer radius of 4 nm.

We performed further steady state optical measurements on the PDHF₁₄-*b*-PEG₂₂₇ as both nanofiber (of average length 435 nm) and unimer to probe the nature of exciton transport in the PDHF core. The nanofibers show significantly more vibrational structure (Fig. 1C) than the unimer (Fig. S20), and there is no pronounced red or blue shift upon aggregation. This is consistent with a π -stacked polymer possessing a transition dipole along the polymer backbone (22), which would be expected to exhibit both H and J like aggregate characteristics (23, 24). The ratio of the I₀₋₀ to I₀₋₁ PL bands is significantly larger in the nanofiber than in the unimer (Fig. S20), indicating a decreased Huang-Rhys parameter and hence smaller configurational relaxation in the excited state (19).

We studied the energy transfer from PDHF to QPT for the aforementioned size series of segmented nanofibers, and Figure 2B shows the normalised PL when the PDHF is selectively

excited (at 380 nm). We observe significant quenching of the PDHF peak compared to the QPT peak for average A-segment lengths below 775 ± 150 nm. This indicates energy transfer from the A-segment PDHF core to the B-segment QPT corona, although reabsorption of the PDHF PL is expected at this concentration. Further evidence for energy transfer comes from the excitation PL scan (Fig. S21), which maps the absorption (Fig. S22), and the change in PL quantum efficiency with A-segment length (Fig. S23). The latter matches that of pure QPT ($13\pm 5\%$) below the critical length (775 nm), and approaches that for the unsegmented structure ($73\pm 10\%$: a very high value) beyond this length.

Time-resolved PL measurements enable better quantification of energy transfer, as donor quenching kinetics are not affected by reabsorption effects. We used time correlated single photon counting (TCSPC - instrument response time ~ 300 ps) to access low excitation density regimes, and transient grating PL spectroscopy to probe the 1 to 100 ps timescale (see Supplementary Information for details).

From TCSPC, the predominant natural lifetime of the unsegmented PDHF₁₄-*b*-PEG₂₂₇ nanofibers (with average length 435 nm) in solution is 430 ps (Fig. S24), shorter than for the corresponding unimer (700 ps), as expected for a J-aggregate. Figure 3A shows the transient grating PL time slices of the segmented nanofiber with an A-segment core length of 775 nm. We see a reduction of the PDHF emission (~ 480 nm) and a concurrent rise in the broader QPT emission at longer wavelengths (530-630 nm). Figure 3B shows the kinetics of this transfer. We note that the QPT emission must be integrated over a broad wavelength range to account for the slow energy transfer that excitations undergo within the QPT itself (Fig. S25).

Figure 3 near here

We modeled the kinetics of the PDHF and QPT PL with a 1-D diffusion model (25) that includes a contribution from Förster resonance energy transfer at the ends of the PDHF nanofiber into the QPT (see Supplementary Materials). For the TCSPC data (Fig. S26) on the 775 nm A-segment length nanofiber solution, the best fit gives a diffusion length of $L_D = 210 \pm 100$ nm and a diffusion constant of $D = L_D^2/2\tau = 0.5 \pm 0.2$ cm²s⁻¹, with errors estimated from the polydispersity of the nanofiber solution and robustness of the fit. Such an exciton diffusion constant is higher than any currently reported for organic semiconductors (1).

Figure 4 near here

Figures 4A and 4B show the transient grating PL kinetics for the PDHF and QPT for a range of shorter segmented nanofibers, as a function of A-segment length. We see significantly faster quenching of PDHF emission and faster rises in the QPT emission as the A-segment length is decreased. To fit the transient grating data, and hence a larger sample of quenching lengths than available to TCSPC measurements, a time-dependent exciton-exciton annihilation term is added to the diffusion model (see Supplementary Materials, and Figs. S27, S28) to account for second-order decay at the higher excitation densities used in this measurement (between $\sim 5 \times 10^{17}$ cm⁻³ and $\sim 10 \times 10^{17}$ cm⁻³). Using a global fit over multiple PDHF_{14-b}-PEG₂₂₇ segment lengths and fluences (Fig S29), we obtain a best fit to our data for an exciton diffusion length of 380 nm. A residual analysis (Fig. S30) confirms the robustness of these values for L_D greater than ~ 150 and less than ~ 600 nm. This agrees within error with the TCSPC result, adding

support to our initial observation of large diffusion coefficients. We consider that the diffusion length most likely falls towards the smaller end of these values, due to the possibility of a small amount of exciton-charge annihilation in the higher fluence measurements, as well as the potential for a small amount of intermolecular energy transfer (Fig. S31). Nonetheless, these results taken together indicate an exceptional diffusion constant for a conjugated polymer structure.

In conjugated polymers efficient exciton diffusion is correlated with an increased degree of structural order (4). Our results are consistent with this, as corroborated by the wide-angle X-ray scattering (WAXS) data (Fig. S12), which shows appreciable structural order in the unsegmented PDHF₁₄-*b*-PEG₂₂₇ nanofibers. This is supported by the pronounced vibronic structure and narrow spectral linewidths in the PL. Ultrafast transient grating PL measurements show evidence of both excitonic movement (during the instrument response time ~200 fs) and some small degree of localization (in the first 700 fs after photoexcitation (Fig. 4C, Fig S32)). We believe that this arises from rapid migration of excitons from the disordered to the ordered regions (evident from the WAXS data), and that exciton diffusion then occurs within these ordered regions in the nanofiber core.

Further understanding can be gained from the self-Förster radius, which is a useful tool for quantifying exciton diffusion lengths (26, 27), although the description has limitations (28, 29). We calculate a self-Förster radius in our PDHF fibers of 2.5 ± 0.2 nm (see Supporting Information). This is large in part because the parallel alignment of polymer chains gives ideal dipolar orientations for energy transfer (we have set κ^2 - our dipole orientation factor - to 1). From this radius we can calculate (27) a diffusion length, $L_D = \frac{R_0^3}{d^2} = 75 \pm 15$ nm, where d is the nearest neighbor distance of 0.46 nm (Fig S.12). Applying a Förster theory beyond the point-

dipole approximation (29) would likely reduce this number slightly, however this gives an estimate of expected exciton diffusion length for an incoherent, nearest neighbor hopping regime. The fact that we measure diffusion lengths beyond this value is clear evidence that excitons are not hindered by the presence of localization sites, or local energy minima (30) in their transport. This provides evidence of a remarkably uniform energy landscape in these materials enabled by their structural order. This uniformity would also benefit transport properties through a narrowing of the excitonic density of states (31).

That we measure a diffusion length greater than our estimate for nearest neighbor Förster transport implies we must look beyond this picture to explain our data. An example of a model that includes some degree of coherence, but reduces to diffusive Förster transport as a limiting case is that proposed by Barford *et al.* (31). This uses a modified Redfield equation to show that a degree of interchain coherence in a polyfluorene film leads to an increase in the mean exciton hopping range, and hence gives a larger diffusion length. This requires inter-chain overlap, and the factor of 2.5 increase we require to account for our measured diffusion range requires a physically reasonable energy transfer integral of around 20 meV. Our measured exciton diffusion rate is high therefore due to a combination of a physical packing structure optimizing the self-Förster radius, a lack of energetic trap sites, and a coherent component to exciton motion.

In summary, we have synthesised segmented nanofibers of controlled length with a PDHF core and containing a QPT corona at each terminus. Spectroscopic measurements in solution show that these nanostructures exhibit long-range exciton transport on the critical length scale comparable to the optical absorption length in conjugated polymers, and that this is enabled by the high degree of structural order in the PDHF core. In context, a 200 nm thick film (the

depth of our diffusion length) of conjugated polymer of average absorption coefficient (32) would absorb 98% of incoming photons. Such diffusion lengths could enable light harvesting devices that use these polymer structures as antennae coupled to photodetector materials of limited absorption (such as monolayer transition metal dichalcogenides (33)), as well as enabling much simpler bilayer design of organic photovoltaics compared to those based on the bulk heterojunction.

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Supplementary Materials:

Materials and Methods

Figs. S1 to S32

Table S1

References (33 – 52)

Figure Captions

Fig. 1. Formation of segmented PDHF nanofibers by multi-step self-assembly. (A) Schematic diagram illustrating the seeded growth process and the structures of PDHF₁₄-*b*-PEG₂₂₇ and PDHF₁₄-*b*-QPT₂₂. (B) Illustration of the segmented B-A-B nanofiber structure with separate donor and acceptor domains. (C) Normalized absorption of QPT aggregates in THF:MeOH (orange dashes), and unsegmented PDHF nanofibers ($L_n = 1605$ nm), Photoluminescence (PL) emission of unsegmented PDHF nanofibers ($L_n = 1605$ nm) in the same solution (blue line). The I_{0-0} peak in the PL is at 425 nm and I_{0-1} at 455 nm. The inset shows the energy levels of the PDHF and QPT.

Fig. 2. Photoluminescence of segmented PDHF B-A-B nanofibers in solution. (A) Laser scanning confocal microscopy (LSCM) image of the uniform segmented PDHF nanofibers with a crystalline PDHF core (blue emission) and two terminal segments with QPT coronas (orange emission). L_n for the central and terminal segments were 1.6 μm and 1.8 μm , respectively. (B) PL spectra of segmented PDHF nanofibers with different A-segment lengths, normalized to peak maxima. In each case, the solutions of segmented nanofibers ($\sim 0.5\text{mg/mL}$) in THF:MeOH (1:1) were excited at the PDHF absorption peak of 380 nm. Emission arising from direct excitation of the QPT in the 1605 nm sample was unresolved.

Fig. 3. Transient grating PL spectra and kinetics of segmented PDHF B-A-B nanofibers. (A) Transient grating PL timeslices of a segmented nanofiber solution (0.5 mg/mL) with an

average A-segment length of 775 nm, showing energy transfer from the PDHF to the QPT acceptor corona. There is a decay of the core PDHF I_{0-1} peak (which appears at 480 nm due to a filter cutting off the blue edge of the spectrum), due to exciton annihilation and quenching to the acceptor. There is a concurrent rise in the broad QPT PL peak from 550-630 nm in the first 10s of picoseconds (materials are excited with a 200 fs laser pulse at 400 nm with an equivalent excitation density of $\sim 5 \times 10^{17} \text{ cm}^{-3}$) (B) Normalized PL kinetics of PDHF decay and rise of QPT signal for the spectra shown in Figure 3A. The green line shows the PDHF signal (integrated from 430 – 460 nm) and the blue line shows the QPT PL (integrated from 530 nm to 630 nm).

Fig. 4. Size dependent transient PL kinetics and corresponding diffusion length model fits.

(A) Transient grating photoluminescence kinetics (squares) of PDHF PL signal (integrated from 430-460 nm) in segmented PDHF B-A-B nanofibers of different A-segment lengths. The PL decay time decreases with decreasing segment length, showing efficient transfer. Solid lines are example fits of a 1-D diffusion model with a diffusion length of $L_D = 340 \text{ nm}$. The system was excited with a 400 nm, 200 fs laser pulse, at $\sim 1 \times 10^{18} \text{ cm}^{-3}$ equivalent excitation densities for the samples in solution. (B) The corresponding PL kinetics (squares) of the rise in the QPT signal in the segmented PDHF B-A-B nanofibers, fitted with the same 1-D exciton diffusion model (solid lines) and diffusion length in the PDHF of $L_D = 340 \text{ nm}$. (C) Transient grating spectra of PDHF-*b*-PEG nanofibers in solution. Timeslices show spectra at early times after excitation with excitation density $\sim 5 \times 10^{17} \text{ cm}^{-3}$. Spectral red-shifting is present until $\sim 200 \text{ fs}$, and the ratio of the first and second vibronic peaks continues to reduce until $\sim 700 \text{ fs}$ (Fig. S32).