

ADVANCED MATERIALS

Supporting Information

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Supporting Information for

Poly(9,9-dioctylfluorene) Nanowires with Pronounced
 β -Phase Morphology: Synthesis, Characterization and
Optical Properties

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Nanowire Synthesis.

PFO (poly(9,9-dioctylfluorenyl-2,7-diyl)) source materials with different weight-average molecular weights, M_w , (between 42 000 and 80 000 g/mol) and polydispersities (between 3.0 and 4.3) were purchased from American Dye Source, Inc. Nanowires were fabricated by the method of template synthesis: A porous anodic alumina membrane (alumina template, nominal pore diameters of 200 nm; Anodisc 13, Whatman Ltd.) was placed on a glass coverslip. 50 μ L of a solution (typically 60 mg/mL, dissolved by stirring vigorously at 60 °C) of PFO in tetrahydrofuran (THF) was dropped onto the alumina template. Immediately afterwards, the wetted template was covered by another glass coverslip followed by a microscope slide. A 2.5 kg weight was then applied for 12 h in order to facilitate penetration of the alumina template pores by the PFO solution and to allow for evaporation of the THF solvent. It was noted that templates were initially transparent when wetted by the polymer-THF solution at the outset of the filling process, and were opaque in appearance after 12 hours suggesting that much of the solvent was lost. At the end of the process, a scalpel was used to remove excess PFO material from the surface of the template. To extract the nanowires, a PFO filled template was soaked in 3 M NaOH for at least 20 min. Typically, the resulting wire residue was washed with deionized water followed by acetone and finally suspended in decane, methanol or deionised water by sonication.

Nanowire Stability.

The structural and photophysical characteristics of the nanowires were observed to remain very similar, irrespective of molecular weight or polydispersity of the source material. Films and nanowire mats were typically characterized within 1 hour - 2 days of preparation. In addition, all samples were stored at room temperature, i.e., well below the transition temperature at which β -phase PFO is expected to revert to α or α' forms (> 85 °C).^[S1] Transformation to crystalline forms is expected to be inhibited by the decrease in segmental mobility of β -phase chains following template pore confinement and solvent evaporation.

Concerning the thermal stability of the PFO nanowires, the morphology of nanowire mats deposited on glass coverslips from suspension and dried in air was observed as a function of increasing temperature (heated to 260 °C @ 40°C/min. on Linkman TMS93 heating stage in ambient conditions, and observed under epi-fluorescence illumination). From ambient temperature to 100 °C, the wires were stable and a characteristic blue emission color was maintained. At 120 °C nanowires began to show signs of softening and nanowire emission intensity dropped slightly. At 150 °C nanowires began to melt and the emission color turned slightly green. Emission intensity dropped by a factor of more than 3. Complete loss of structural definition was apparent at 260°C and nanowire emission turned green/yellow.

Concerning the mechanical stability of PFO nanowires, it was observed that the wires were quite flexible. Using manipulation by liquid or air flow, it was possible to align wires without structural damage. However, manipulation by direct probe-nanowire contact caused nanowires to break due to stiction between the wires and the substrate surface. Development of a non-destructive technique for manipulation of single wires using a movable liquid meniscus trapped between a micromanipulator probe is currently in progress.

Concerning the photostability of the wires, nanowires deposited on substrates and exposed to ambient conditions for longer than 1 week exhibited notable signs of spectral and emission intensity degradation. Nanowires embedded in an anodic alumina host template or suspended in a non-solvent

were photostable for much longer periods of time when stored in ambient atmosphere (more than 1 year). Also, luminescence spectra acquired from nanowires deposited on substrates and stored in inert atmosphere conditions were also stable for several months. Finally, during spectroscopic measurements performed either on nanowire mats or on single nanowires, excitation laser powers were kept to a minimum and spectra measured under differing conditions, e.g., laser power, duration of irradiation, spectral acquisition time, etc., were monitored for any changes in spectral characteristics that might suggest conversion from β -phase doped glassy-phase to other phases. No such changes were observed. Under 402 nm CW laser photoexcitation at powers greater than 10 mW/cm^2 , it was necessary to prevent degradation of nanowire emission (i.e., photobleaching of singlet exciton emission and development of a broad, long wavelength ($\sim 550 \text{ nm}$) defect-related emission band due to photo-oxidation) by enclosing nanowire samples in a home built vacuum cell. Under vacuum and 355 nm pulsed laser excitation, melting of PFO nanowires was observed to occur (without development of a defect-related emission band) above excitation energies of 40 mJ/cm^2 (1 ns, 20 kHz).

Structural Characterization.

Scanning electron microscopy (SEM) images were acquired using a field emission SEM (JSM-6700F, JEOL UK Ltd.) operating at beam voltages between 1 and 10 kV. Empty and PFO filled alumina templates were placed onto adhesive carbon pads mounted on a SEM stub prior to imaging. For imaging of nanowire arrays, a mounted filled template was dissolved in NaOH solution (3M, 20 min) followed by soaking in deionized water leaving freestanding forests of PFO wires. After drying, an ultra-thin layer of gold (~ 5 nm) was sputtered on top of SEM samples to prevent charging during imaging (30 mA, 0.2 torr, 60 s; Scancoat Six Sputter Coater). Transmission electron microscopy (TEM) measurements were acquired for individual nanowires deposited onto FormvarTM/carbon-coated copper TEM grids (JEM-2011 200 kV TEM, JEOL UK Ltd; Gatan DualVision 600 CCD Camera and Digital Micrograph Software, Gatan UK Ltd.). Selected area electron diffraction (SAED) patterns were recorded with a camera length of 35 cm. The TEM was calibrated using standard samples both for magnification and diffraction.

Optical Characterization.

Digital photographs of nanowire arrays on flexible Kapton[®] tape (DuPont Corp.) were taken under white light illumination and in the dark under UV-excitation (312 nm; TFX-20.MC transilluminator, Vilber Lourmat). The sample was prepared by mounting a PFO filled alumina template onto multiple layers of Kapton[®] tape. The template was then dissolved as described previously leaving an array of nanowires on a flexible substrate. Digital photographs of nanowire suspensions in decane were acquired under both diffuse white light illumination and UV excitation at 312 nm on a transilluminator. Epi-fluorescence images of PFO nanowires were acquired using an Axioskop II Plus epi-fluorescence microscope (Carl Zeiss, Inc.) equipped with a 100 W halogen lamp, a 0.9 NA 100x objective (Epiplan-Neofluar, Carl Zeiss, Inc.), a thermoelectrically cooled color CCD camera (DEI-750T, Optronics) and an appropriate filter set (01, Carl Zeiss, Inc.). UV-visible absorption spectra were acquired using a spectrophotometer equipped with an integrating sphere

(barium sulfate as a standard; UV-2401PC, Shimadzu). Photoluminescence (PL) spectra were acquired under UV excitation (355 nm) with a calibrated (Hg(A)) spectrometer (1.4 nm resolution; SP150, Acton Research Corp.). For PFO nanowire spectra, a drop-deposited mat of wires was sandwiched between two fused silica substrates with immersion oil ($n = 1.48$; type FF, Cargille) to minimize light scattering. For the film spectra, a ~ 120 nm thick pristine PFO film was prepared from a 20 mg/ml solution of PFO in chloroform by spin coating onto a quartz substrate (~ 30 μL , 6000 rpm, 60 s) in a controlled atmosphere glove box (MB200, MBRAUN).

Thin film and single nanowire fluorescence lifetime measurements were recorded using a time-resolved scanning confocal fluorescence microscope (MicroTime 200, PicoQuant GmbH) equipped with a XY piezoelectric scanning stage (P-733-2CL, Physik Instrumente GmbH). System operation was controlled by a dedicated software package (MicroTime 200 Version 4.0 software, PicoQuant GmbH). For sample excitation, the output of a 402 nm picosecond pulsed diode laser (40 MHz; 70 ps pulse duration, LDH-P-C-400, PicoQuant GmbH) was coupled into the main confocal unit via a polarization maintaining single mode optical fiber, collimated, and spectrally filtered using a 405 nm band pass filter. The horizontally polarized laser light was and then converted to circularly polarized light using a broadband, achromatic quarter waveplate (Thorlabs, Inc.). The collimated laser beam was then directed into the entrance port of an inverted microscope (IX 71, Olympus Corp.) using a dichroic mirror. A 100x oil immersion objective (1.4 NA, UPlan SAPO, Olympus Corp.) was used both for focusing the excitation light onto the sample (a nanowire mat deposited onto a cleaned glass cover slip at sub-monolayer coverage) which was located on the XY piezoelectric scanning stage of the microscope and for collecting the resulting fluorescence. Sample fluorescence was passed back through the dichroic mirror, spatially filtered by focusing onto a 150 μm diameter pinhole to reject out-of-focus signals, re-collimated, and directed onto an avalanche photodiode (APD; SPCM-AQR-14, Perkin-Elmer, Inc.). Backscattered excitation light was blocked with a 430 nm long-pass filter placed in the collection path. Thin film and single nanowire fluorescence intensity images were recorded by raster scanning the sample through the laser focus spot and recording the resulting fluorescence at the

APD. A pixel integration time of 0.6 ms was typically employed for fluorescence imaging and an incident excitation power <0.06 nW was used to prevent problems associated with sample photobleaching.

Following image acquisition, fluorescence lifetime transients were recorded using a time correlated single photon counting (TCSPC) technique with a TimeHarp 200 board (PicoQuant GmbH). Briefly, a selected point on the film or nanowire was positioned at the focus spot of the excitation laser beam. Subsequently, the emission from the excited region (~ 500 nm diameter excitation spot) was recorded over a period of 60 s with the APD. The excitation power was adjusted to maintain a fluorescence emission count rate of $< 10^4$ counts/s at the APD in order to preserve single photon counting statistics. The instrumental response function (IRF; 0.46 ns full-width-at-half-maximum) of the entire system was measured on a cleaned glass cover slip in place of the active sample. All emission lifetimes were fitted with a reconvolution multi-exponential model using FluoFit 4.0 software (PicoQuant GmbH). All lifetimes were fitted to a χ^2 value of less than 1.4.

Raman spectra of PFO nanowires and pristine PFO thin films were acquired using a Renishaw Raman microscope equipped with a 100x objective (0.9 NA; Epiplan-Neofluar, Carl Zeiss, Inc.). Excitation was with the 514.5 nm line of an Ar⁺ ion laser. Measurements were carried out in micro-Raman mode at room temperature in a backscattering geometry. The pristine thin film sample was prepared by spin coating a 15 mg/mL PFO in THF solution onto a thermally oxidized Si substrate (~ 30 μ L, 3500 rpm, 60 s) resulting in a film thickness of ~ 100 nm (measured using AFM). For nanowire spectra, wires were drop deposited onto a thermally oxidized Si substrate from a decane suspension. Excitation at 514 nm caused the Raman signals for both samples to be superimposed on a fluorescent background from the polymer. Hence, a baseline was subtracted from the raw data for comparison of the spectra from the PFO nanowires and the as spun thin film. For calibration an undoped Si wafer was used.

Electrochemical Characterization.

Tetra-n-butylammonium hexafluorophosphate (TBAPF₆; Sigma-Aldrich Ireland Ltd.) was dried under vacuum (100 °C, 12 hours) prior to use. Hexane and acetonitrile (non aqueous grade; Sigma-Aldrich Ireland Ltd.) were used as received after being transported unopened into a controlled atmosphere glovebox (< 0.1 ppm O₂ and H₂O). Electrochemical and electrochemical luminescence (ECL) samples were prepared in the glove box, sealed in airtight vials and removed from the box for measurements. Cyclic voltammograms (CV) were recorded on a computer controlled potentiostat (Model CH660A, CH Instruments, Inc.). Electrochemical cells consisted of an indium tin oxide (ITO) working electrode (0.07 cm²), a Pt wire counter electrode and a Pt wire quasi-reference electrode. Electrochemical cells were prepared by cleaning with nitric acid (Analar grade, Sigma-Aldrich Ireland Ltd.) and DI water (> 18MΩcm, Millipore Q) followed by annealing in vacuum (50 °C, 2 hours). To perform electrochemical analysis, PFO nanowires, suspended in hexane, were dispensed onto ITO working electrodes and the supporting solvent allowed to evaporate. To perform CV measurements, a 0.75 mL aliquot of 0.1 M TBAPF₆ in acetonitrile was added to the electrochemical cell and CV scans recorded at 0.2 V/s scan rate with a scan range between -2.5 and +2 V (first step negative potential).

Electrochemiluminescence Characterization.

For ECL experiments, a 0.75 mL aliquot of 0.1 M TBAPF₆ in acetonitrile was added to an electrochemical cell and a triple-potential step sequence was repetitively applied to the cell. After an initial waiting time of 200 ms a negative potential step of -2.5 V was applied to the ITO versus Pt counter electrode for 150 ms, whereupon the potential was stepped positive to 2.0 V for 150 ms. This voltage cycling was repeated for 10 min. A home-built inverted microscope (Aurora II NSOM system, Veeco Instruments Ltd.) was employed for acquisition of far-field luminescence spectra of the PFO nanowire mats. For PL spectral acquisition, the electrochemical cell was placed on the motorized X-Y stage (ca. 1 μm resolution) of the microscope. PFO nanowires were optically excited using a 405 nm CW laser (Blue Photon, LG-Laser Technologies GmbH). The laser light was directed and focused

onto the sample using a UV mirror (model 5100, New Focus, Inc.), and a 100x objective lens (NA 0.8; LMPlanFL, Olympus UK Ltd.). The same objective lens was also used to collect the luminescence from the nanowires, which was then directed, using an optical train of mirrors (including a 390 nm dichroic mirror (390DRLP, Glen Spectra) to reject backscattered laser light) into an imaging spectrometer (SP-150, Acton Research Corp.) equipped with a liquid nitrogen cooled charge-coupled device (CCD; VersArray LN-512B, Princeton Instruments, Inc.). Images and spectra were acquired using Winspec/32 spectroscopy software (Princeton Instruments, Roper Scientific, Inc.). Electrochemically generated luminescence spectra were acquired using the same optical setup with a 10 min. spectral integration time.

Electroluminescence Characterization.

Poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS; Baytron P, VP AI 4083, H. C. Stark GmbH) was prepared by filtering through 0.45 μm nylon filters. OLED substrates comprised of indium tin oxide (ITO) ($10 \Omega/\square$) electrodes lithographically patterned on glass and electrically contacted using aluminum interconnection tracks. A patterned polyimide over-layer, deposited in a manner so as to surround each electrode, was used to define a 1 mm^2 device area and to prevent spurious electrical connection between ITO anode and the subsequently evaporated cathode. Prior to device fabrication, substrates were prepared by cleaning with a solvent wash (50 °C; acetone, 1 min; TCE, 5 min; acetone, 1 min; IPA, 5 min) and oxygen-plasma (50 W, 105 Pa, 5 min), followed by deposition of a typically 100 nm thick PEDOT:PSS layer by spin-casting. Nanowires dispersed in decane were drop deposited onto the PEDOT layer and allowed to dry in a controlled atmosphere glovebox ($<0.1 \text{ ppm O}_2$ and H_2O). To complete device fabrication, aluminum (200 nm) was thermally evaporated at $3 \times 10^{-5} \text{ Pa}$ at a rate of 0.2 nm/s. Current-voltage-EL intensity characteristics of fabricated devices were measured under inert atmosphere conditions using a DC power supply (2400 source meter, Keithley Instruments, Inc.), a calibrated silicon photodiode (818 SL, Newport Corp.) and an optical power meter (1835-C, Newport Corp.), all under LabVIEW™ control. Voltage was

increased at 0.25 V intervals and the emitted light was detected using the Si detector placed directly in contact with the backside of the device. EL spectra of light emitted from devices were measured under ambient atmosphere conditions using a calibrated Spectralon[®] integrating sphere (Labsphere, Inc.) coupled to a monochromator and photomultiplier tube (Ocean Optics, Inc.). To prevent device degradation in ambient conditions, devices were encapsulated in protective epoxy prior to their removal from the glovebox.

Estimating the β -Phase Fraction in PFO Nanowires.

The fraction of β -phase present within the nanowires was estimated by fitting three Gaussian curves to the absorption spectrum of the nanowire mat shown in Figure 3a using a non-linear least squares algorithm (Fig. S1).^[S2] An additional Gaussian was fit to the data to account for the background signal - mainly arising due to optical scattering from the nanowire mat. The amount of β -phase was taken to be the sum of the area under the fitted Gaussians at 412 and 438 nm divided by the total area under all Gaussians (neglecting the background). In this way, a value of $21 \pm 0.5 \%$ for the fraction of β -phase present in the nanowires was extracted. According to Chunwaschirasiri *et al.* the larger oscillator strength of the β -phase in comparison to the other PFO conformers should be considered when estimating β -phase fraction from absorption spectra.^[S3] Therefore, the fraction of β -phase estimated from the nanowire absorption spectrum in this work is considered to be an upper limit.

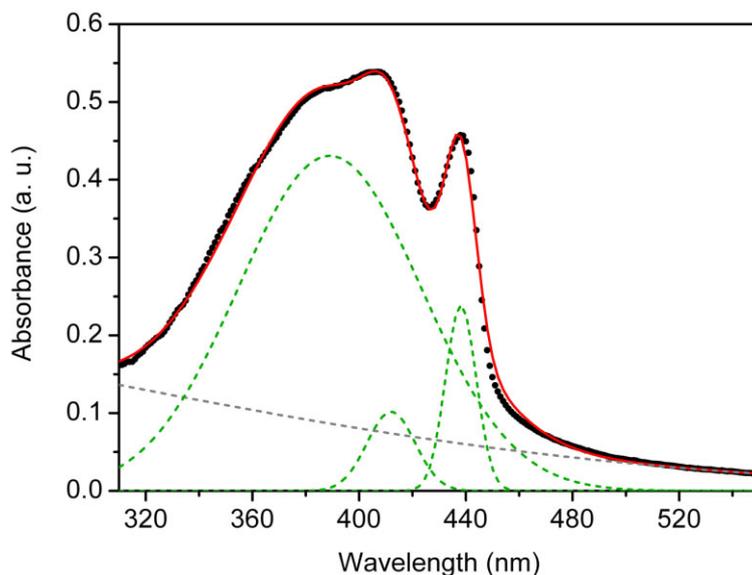


Figure S1. Plot of three Gaussian functions (green dashed lines) and a background Gaussian function (grey dashed line) which were fit to the nanowire mat absorption spectrum (solid black circles). The sum of all four Gaussians is also included (solid red line).

References.

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