

Supporting Information

Supramolecular electrospun nanofibers with high conductivity at ultra-low carbon nanotube content

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Experimental Section

Materials

Poly(styrene) (PS) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Gel permeation chromatography (GPC) analysis indicated that the molecular weight (M_w) of PS was ca. 280,000 g/mol, with a polydispersity index (PDI) of 2.87. Poly(vinylbenzyl uracil) (PVBU; $M_w = 280,000$ g/mol, PDI = 2.87) and diaminopyridine-functionalized polythiophene (PTDAP; $M_w = 21,000$ g/mol, PDI = 1.73) were synthesized according to our previously reported methods.^{8c,d,h} Poly(styrene) (PS) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Gel permeation chromatography (GPC) analysis indicated that the molecular weight of PS was ca. 280,000 g/mol, with a PDI of 2.87. Multi-walled carbon nanotubes (CNTs) were purchased from NanoLab Inc. (Waltham, MA, USA). All other chemicals and solvents were of the highest purity available and were purchased from Sigma-Aldrich. All solvents used for synthetic and chromatographic experiments were high-performance liquid chromatography (HPLC) grade and were acquired from TEDIA (Fairfield, OH, USA) or Fisher Scientific (Fair Lawn, NJ, USA). *N,N*-dimethylacetamide (DMAc) was distilled over calcium hydride prior to use.

Preparation of CNT-incorporated electrospun polymer nanofibers

The 10/90 PTDAP/PVBU (or 10/90 PTDAP/PS) blend composites with different contents (0.3~2.0 wt%) of CNTs were dispersed in DMAc solvent by ultrasonication for 1 h. The sample solutions were pumped through a metal needle with an inner diameter of 0.34 mm at a feed rate of 0.2 ml/h using a syringe pump (model 100; KD Scientific Inc., Boston, MA, USA). The distance between the tip of the syringe and the collector was fixed at 15 cm. A constant voltage of 20 kV was used to produce electrospun fibers and the fibers were collected on aluminum foil in grounded collection plates.

Measurements

Ultraviolet-visible (UV-Vis) and photoluminescence (PL) spectra. UV-Vis and PL spectra were

determined on a Hewlett Packard 8452A diode array spectrophotometer (Hewlett-Packard, Palo Alto, CA, USA) and a Hitachi F-4500 luminescence spectrometer (Hitachi Co., Ltd., Tokyo, Japan), respectively. The PL spectra were measured at 25 °C under an excitation wavelength of 430 nm.

Scanning Electron Microscopy (SEM). Samples were firmly attached onto the silicon substrate, sputtered with platinum and characterized using field-emission SEM (Hitachi S-4700, Tokyo, Japan) at high accelerating voltages of over 10 kV.

Transmission Electron Microscopy (TEM). Ultrathin-section TEM images of electrospun nanofibers were obtained using a FEI T12 TEM (FEI Co. Eindhoven, Netherlands) operating at 120 kV.

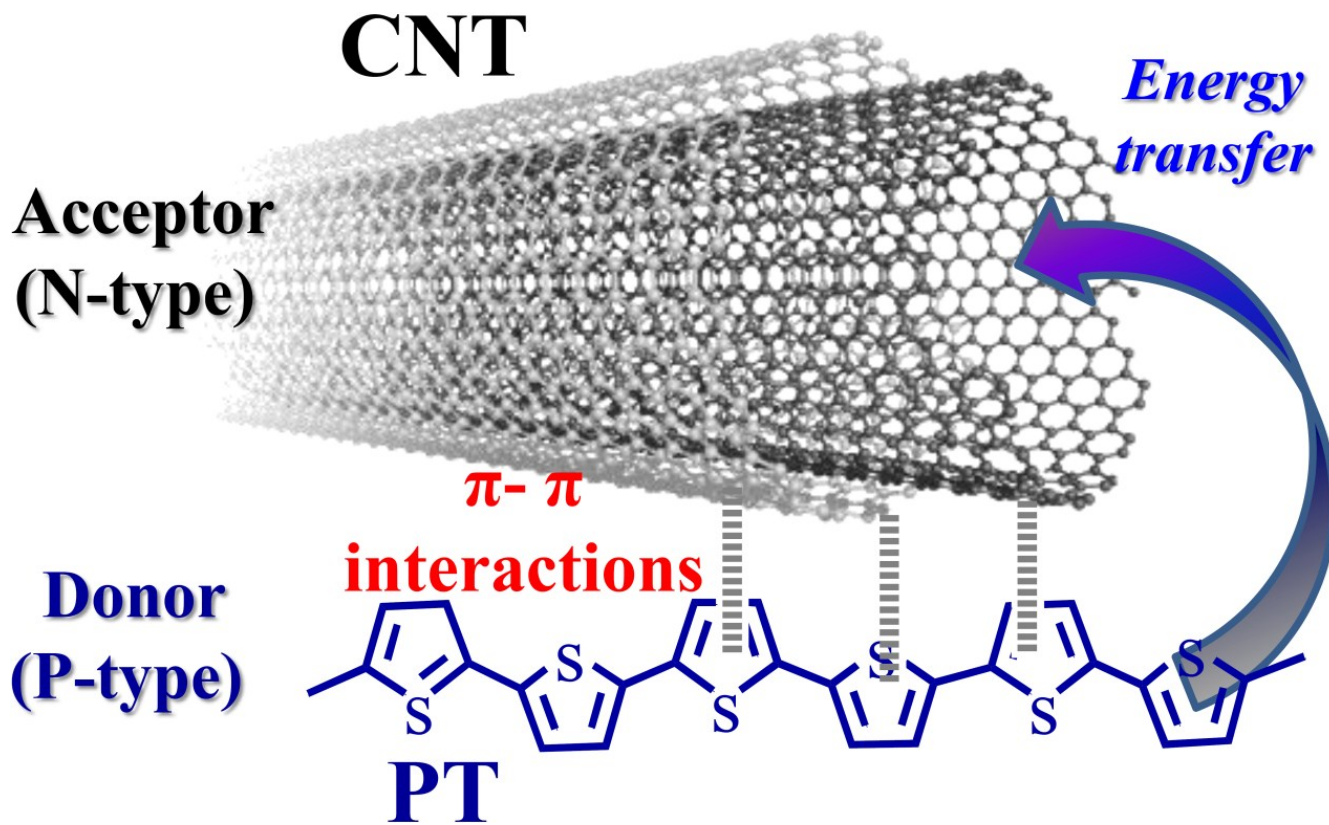
Differential Scanning Calorimetry (DSC). A TA Q-20 thermal analyzer (New Castle, DE, USA) was used to perform DSC experiments. Test samples (ca. 5 mg) sealed in aluminum pans were analyzed over the temperature range of 30-250 °C at a heating/cooling rate of 10 °C/min.

Raman spectra. Samples were placed directly onto the surface of silicon substrate. All spectra were collected using a Witec Confocal Raman (Model CRM 2000, Ulm, Germany). Spectral data were recorded between 500 and 2000 cm⁻¹ at a resolution of 2.0 cm⁻¹ at 25 °C. The excitation source was a helium-neon (He-Ne) laser with a power density of ca. 30 W/cm².

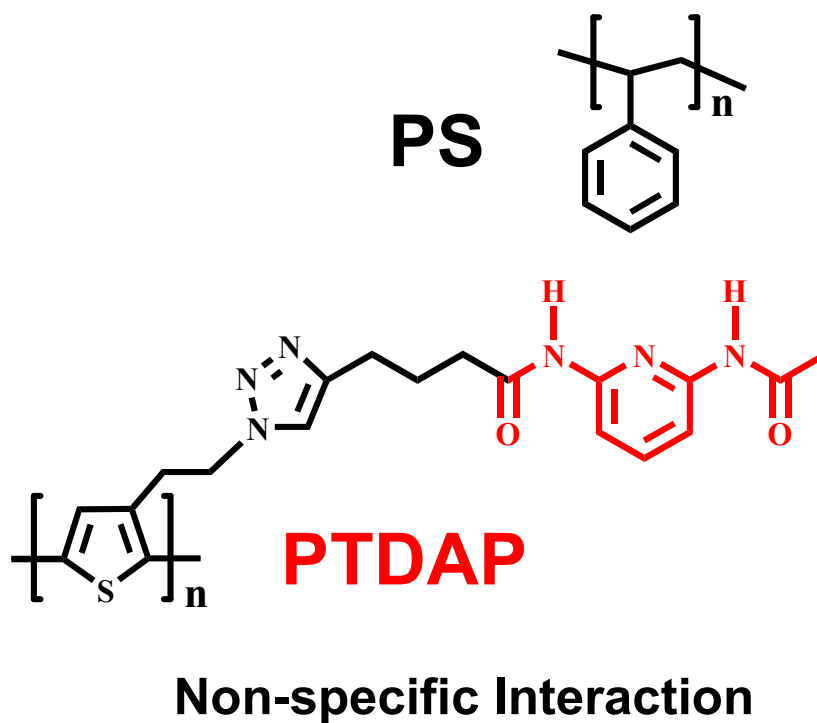
Conductivity Measurements. Electrical conductivity properties of electrospun fibers were measured using a Pico Ammeter (Keithley model 617, Cleveland, OH, USA). For conductivity measurements, each of the samples was placed in a conductivity cell between two gold electrodes at 25 °C and 30% relative humidity. Conductivity was calculated according to the equation:

$$\sigma = \frac{d}{AR}$$

where σ is conductivity, d is sample thickness, A is the surface area of the gold electrode, and R is bulk resistance of the sample measured using an ammeter.



Scheme S1. Structural representation of the energy transfer from polythiophene (PT) to CNTs, indicating the nature of the $\pi-\pi$ interactions between the materials.



Scheme S2. Structural representations of PS and PTDAP.

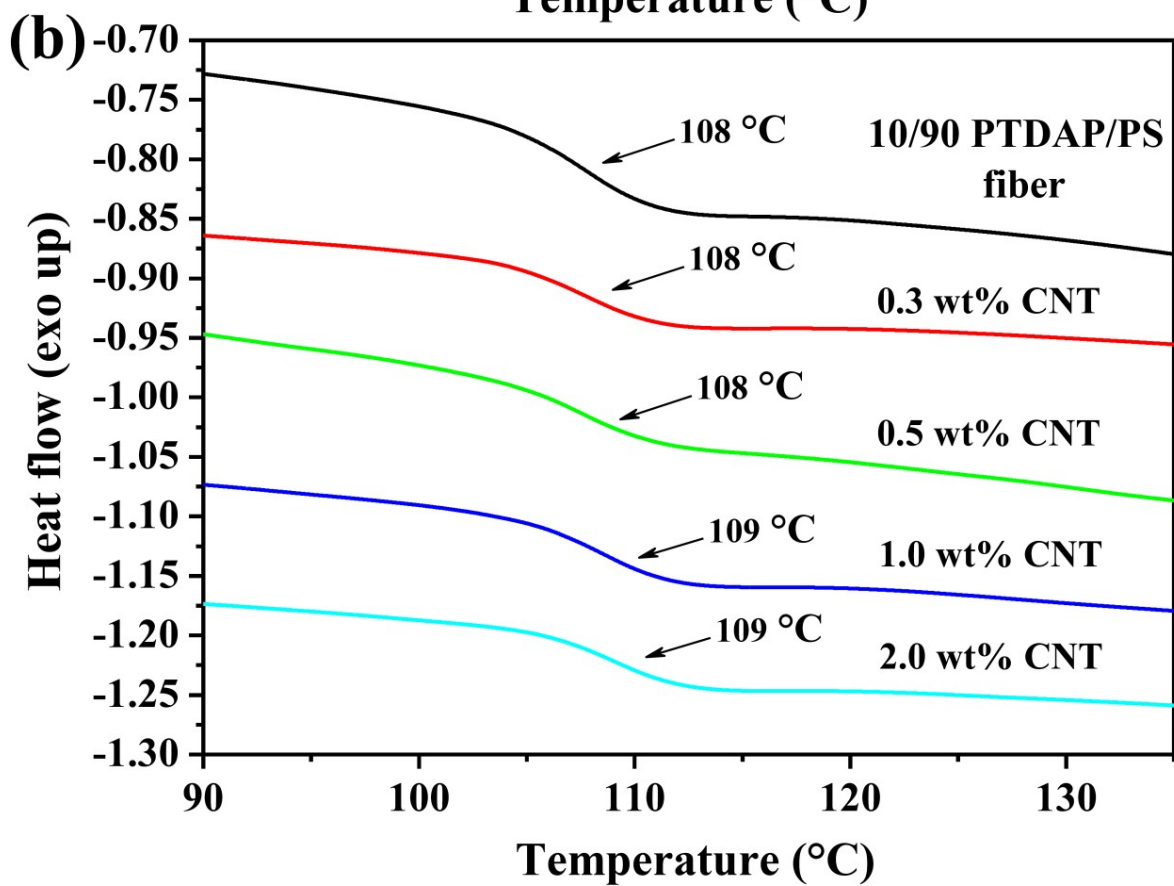
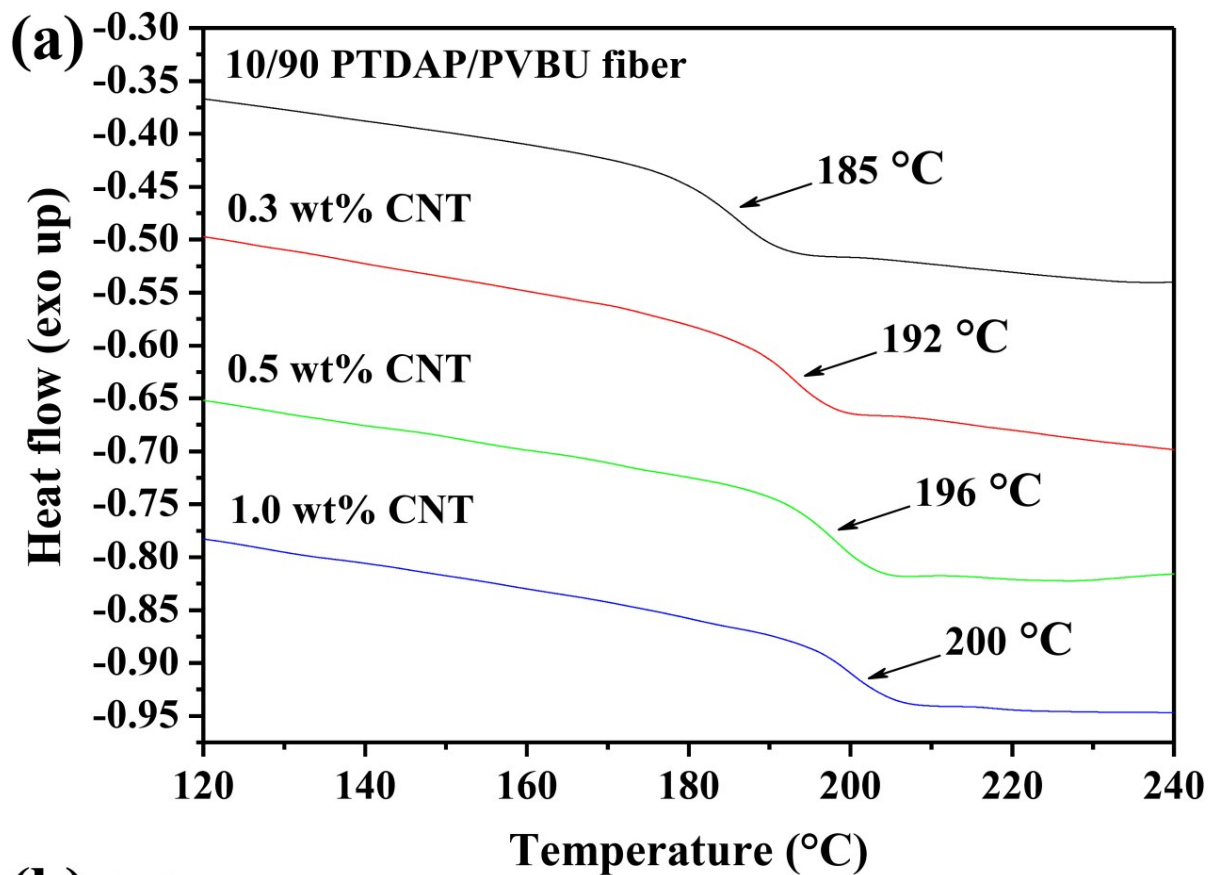


Fig. S1: DSC thermograms of the second heating scans for (a) CNT/PTDAP/PVBU and (b) CNT/PTDAP/PS fibers.

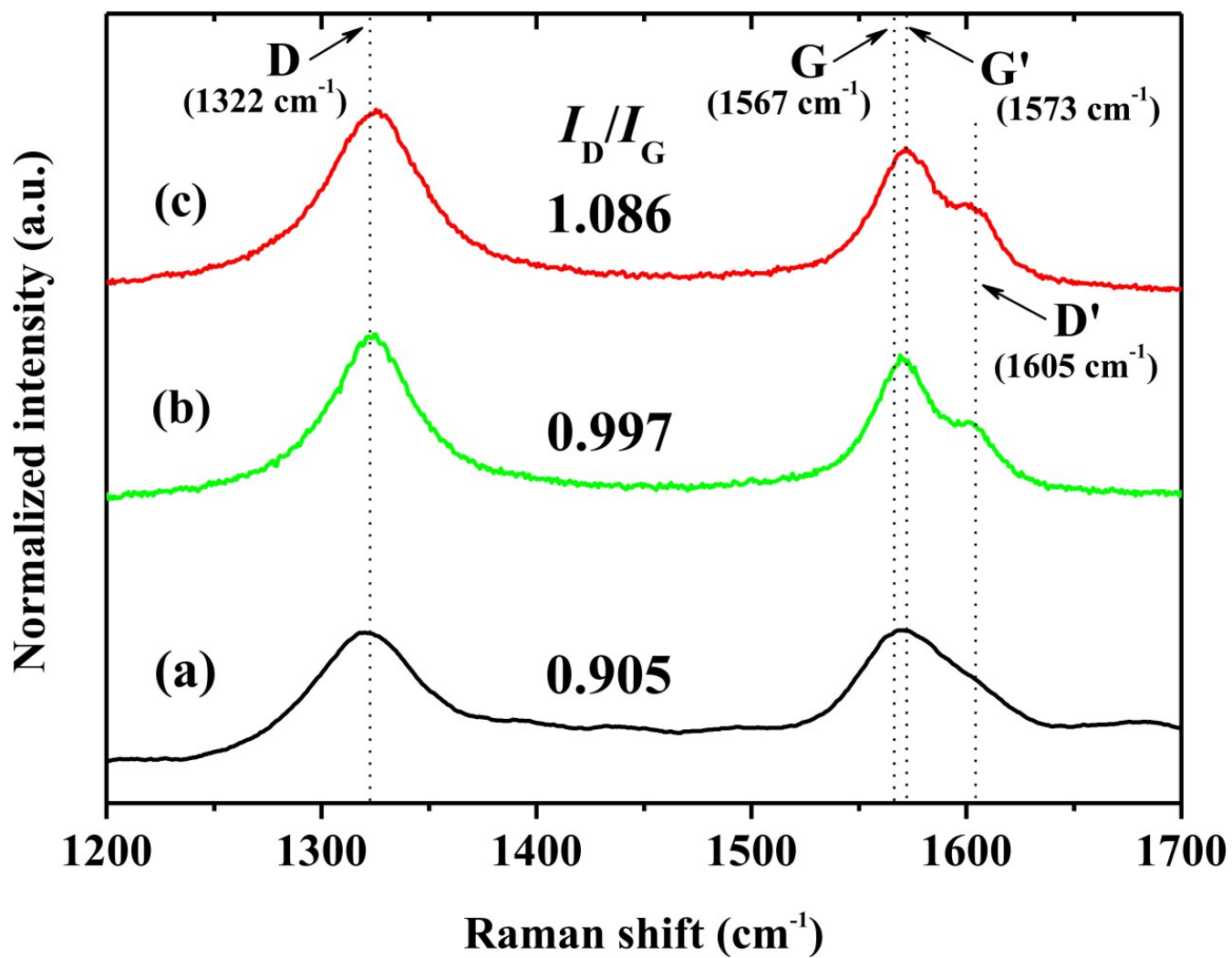


Fig. S2: Raman spectra for (a) CNT, (b) CNT/PTDAP/PS and (c) CNT/PTDAP/PVBU fibers.