

## Supporting Information

### Supramolecular Assembly-induced Enhanced Emission of Electrospun Nanofibers

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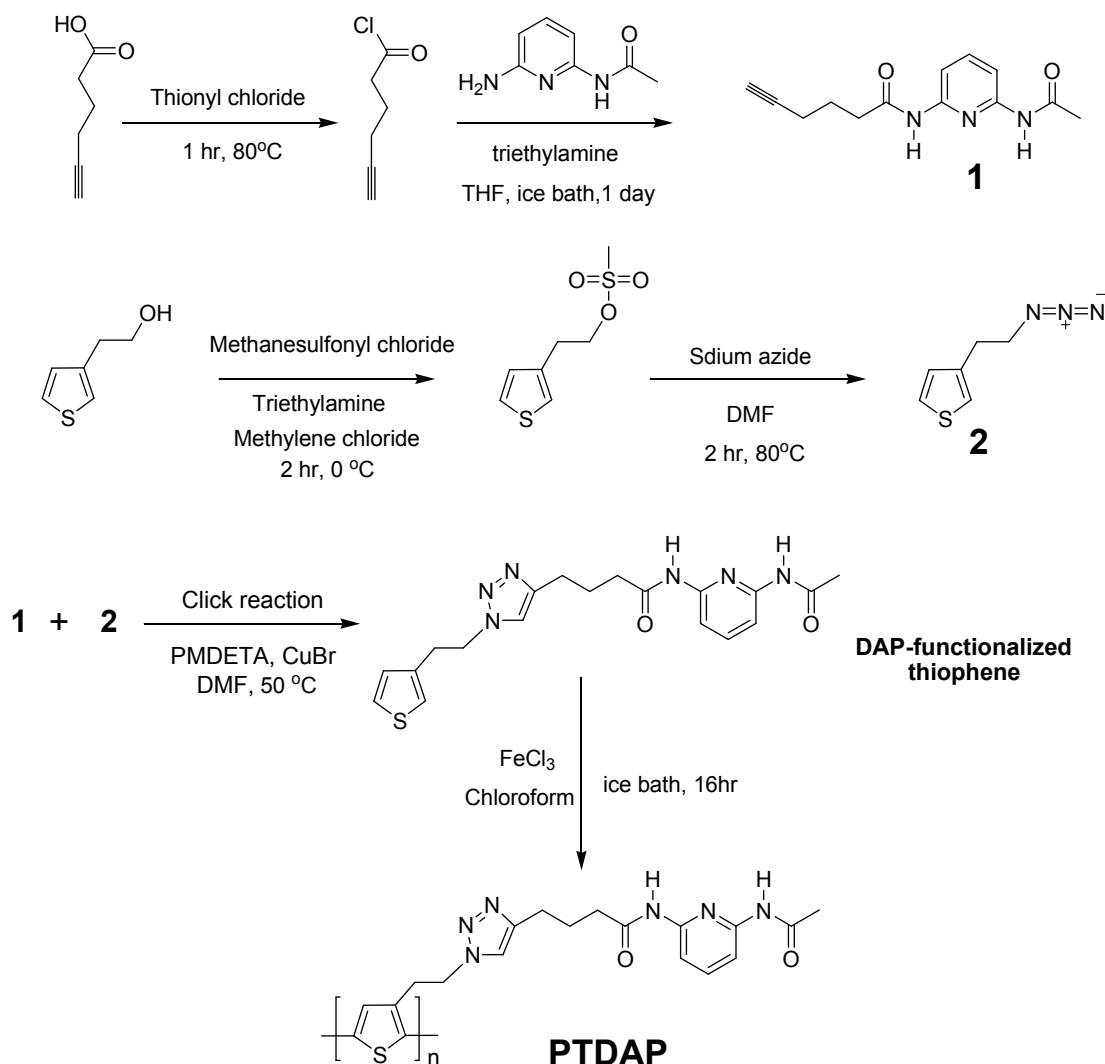
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#### Experimental

**Materials.** *N,N*-dimethylacetamide (DMAc) were purchased from TEDIA and distilled prior to use. Poly1-(4-vinylbenzyl uracil) (PVBU) ( $M_n > 250550$  g/mol, polydispersity index= 2.66) was synthesized according to our previously reported method<sup>42</sup>. Poly(styrene) (PS) were obtained from Aldrich (USA). GPC analysis indicated that the molecular weight of PS was ca. 280,000 g/mol, with a PDI of 2.87. All other chemicals were of reagent grade and used as received without further purification. The syntheses of poly(3-thiophene-triazole-diaminopyridin) (PTDAP) were shown in Scheme 1 and detailed synthetic procedures are provided in the

## Supporting Information.



**Scheme S1.** Syntheses of DAP-functionalized thiophene and PTDAP.

### Synthesis of N-(6-acetamidopyridin-2-yl)hex-5-ynamide (**1**)

5-hexynoic acid (1.0 g, 8.9 mmol) was first treated with an excess of thionyl chloride (2.3 mL, 30.0 mmol) and refluxed for 2 h, then 5-hexynoyl chloride was obtained by evaporating the thionyl chloride and dried under vacuum. 2,6-Diaminopyridine (3.3 g, 30.0 mmol) and triethylamine (1.01 g, 10.0 mmol) were dissolved in dry THF (50 mL) cooled to 0 °C in an ice bath. A solution of 5-hexynoyl chloride in anhydrous THF (20 mL) was added dropwise through syringe over a period of 1 h and the reaction mixture was stirred at 0 °C for 1 h and then maintained at room temperature for an additional 6 h. After evaporating the solvent, the residue was recrystallized from toluene to give the pure compound (**1**), yield 0.7 g. (70%), M.p.: 185-190 °C;  $^1\text{H}$

NMR (500 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 7.88 (s, 1H; CH), 7.86 (s, 1H; CH), 7.75 (br, 2H, NH), 7.68 (t, 1H, CH), 2.53 (t, 2H, CH<sub>2</sub>), 2.30 (m, 2H, CH<sub>2</sub>), 2.18 (s, 3H, CH<sub>3</sub>), 2.00 (s, 1H, CH), 1.88 (m, 2H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR(125 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 172.1, 168.9, 149.6, 140.6, 109.7, 109.5, 84.4, 68.3, 37.5, 25.1, 24.8, 22.3 ppm; HRMS (EI): *m/z* 245.1273 [M]<sup>+</sup>

### Synthesis of 3-(2-azidoethyl)thiophene (2)

Methanesulfonyl chloride (2.9 g, 25.0 mmol) was added into 2-(3-thienyl)-ethanol (2 g, 15.6 mmol) in methylene chloride under ice bath for 2 hrs. After extracting with water and removing methylene chloride the product was then reacted with sodium azide in DMF (80 °C, 2 h). After evaporating the DMF, the residue was isolated by flash column chromatography using alumina and ethyl acetate as eluents to give product (2) as a colourless liquid. yield: 2.2 g (93%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 7.30 (m, 1H; CH), 7.05 (br, 1H; CH), 6.97 (d, 1H, CH), 3.50 (t, 2H, CH<sub>2</sub>), 1.64 (t, 2H, CH<sub>2</sub>) ppm; <sup>13</sup>C NMR(125 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 136.4, 127.6, 127.1, 124.0, 49.9, 30.3 ppm; HRMS (EI): *m/z* 153.0458 [M]<sup>+</sup>

### Synthesis of DAP-functionalized thiophene

DAP-functionalized thiophene monomer was synthesized via the direct “click reaction” of (1) and (2) compounds in the presence of CuBr as a catalyst. (1) (0.18 g, 0.75 mmol) and (2) (0.15 g, 0.95 mmol) were dissolved in DMF (3 mL) and then the resulted solution was purged with a dry argon atmosphere for 10 min. N,N',N',N'',N''-pentamethyldiethylenetriamine (PMDETA; 50.7  $\mu$ L, 0.02 mmol) was added via syringe, leading the mixture to becoming homogeneous and then the solution was degassed through three freeze/thaw evacuation cycles. Upon the addition of CuBr (0.003 mg, 0.02 mmol), the color of the solution was gradually changed from light blue to light green. The solution was heated to 50 °C with stirring under an argon atmosphere for 12 h. After cooling to 25 °C, the reaction mixture was passed through an aluminum oxide column to remove the Cu(II) catalyst. Finally, the solvent was evaporated, and the residue was crystallized from toluene; it was then filtrated and dried under vacuum. yield: 0.25 g (83%). M.p.: >250 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/THF-D<sub>8</sub> = 80/20 V%, 25 °C, TMS):  $\delta$  = 7.84 (br, 2H; CH), 7.72 (br, 2H; NH), 7.65 (t, 1H, CH), 7.27 (br, 2H, CH), 6.88 (m, 2H, CH), 4.54 (t, 2H; CH<sub>2</sub>), 3.22 (t, 2H, CH<sub>2</sub>), 2.76 (t, 2H, CH<sub>2</sub>), 2.40 (t, 2H, CH<sub>2</sub>), 2.16 (s, 3H, CH<sub>3</sub>), 2.01 (qui, 2H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR(125 MHz, CDCl<sub>3</sub>/THF-D<sub>8</sub> = 80/20 V%, 25 °C):  $\delta$  = 172.2, 169.1, 149.8, 145.3, 142.3, 140.8, 138.1, 128.3, 127.8, 124.6, 122.6, 110.3, 109.7, 63.4, 37.1, 33.7, 25.3, 24.6, 22.2 ppm; HRMS (EI): *m/z* 398.1535 [M]<sup>+</sup>

## Syntheses of PTDAP

**DAP-functionalized thiophene** monomer (1g, 2.34 mmol) and FeCl<sub>3</sub> (2.5 g, 15.50 mmol) were added into chloroform for oxidative polymerization. The reaction was first under ice bath for 3 h and then reacted in the room temperature for 24 h. The excess of iron ions were removed by methanol and then reduced by hydrazine. The red solid product was collected by filtration with methanol. Yield: 0.75 g (75%). The molecular weight of PTDAP estimated from GPC was 21,000 g/mol (polydispersity index = 1.734) and the  $T_g$  of PTDAP estimated from DSC was 129 °C. The regioregularity of PTDAP was calculated from the <sup>1</sup>H NMR spectrum, and was determined to be 54% (Figure S3). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 10.01 (br, 2H; NH), 7.72 (br, 4H; CH), 7.21 (br, 1H, CH), 4.56 (br, 2H, CH<sub>2</sub>) ppm.

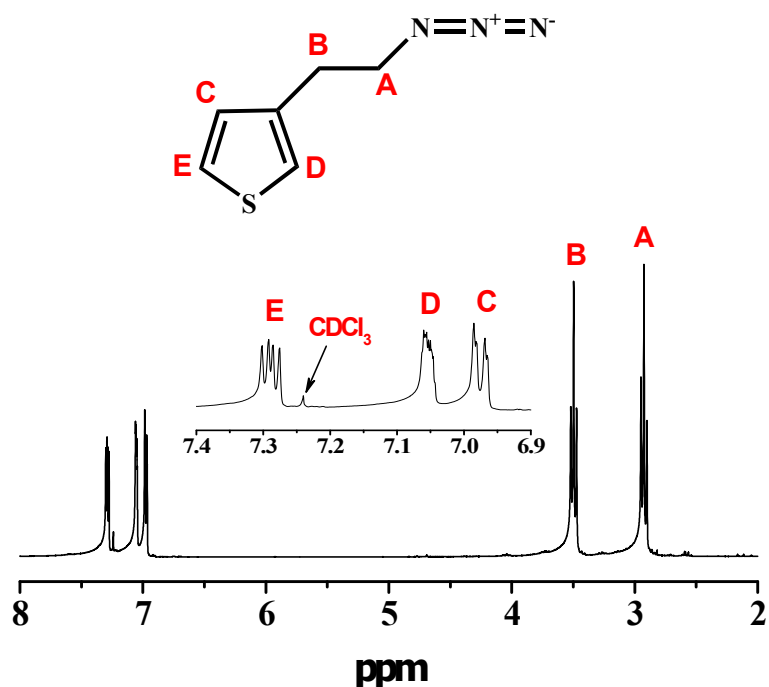
**Preparation of PTDAP / (PVBU and PS) blend nanofibers and thin films.** PVBU / PTDAP blend fiber and PS / PTDAP blend fiber were fabricated by electrospinning technique. The electrospun solution with 10 wt% concentration of PVBU or PS in DMAc was pumped through a metal needle of 0.34 mm inner diameter at a feed rate of 0.2 mL/h by a syringe pump (KD Scientific model 100 series). A distance of 15 cm was maintained between the tip of the syringe and the collector. The high voltage of 20 kV was used to generate the blend fibers which were collected on the surface of a grounded Al plate. The polymer blend compositions of PTDAP with PVBU or PS were various from 1 to 50 wt%.

PTDAP/PVBU and PTDAP/PS thin films were prepared by spin-coating onto a glass substrate at a spin rate of 1000 rpm for 60 s from the DMAc solvent and then dry in vacuum. The concentration of the spin-coated PTDAP solution was fixed at 20 mg/mL.

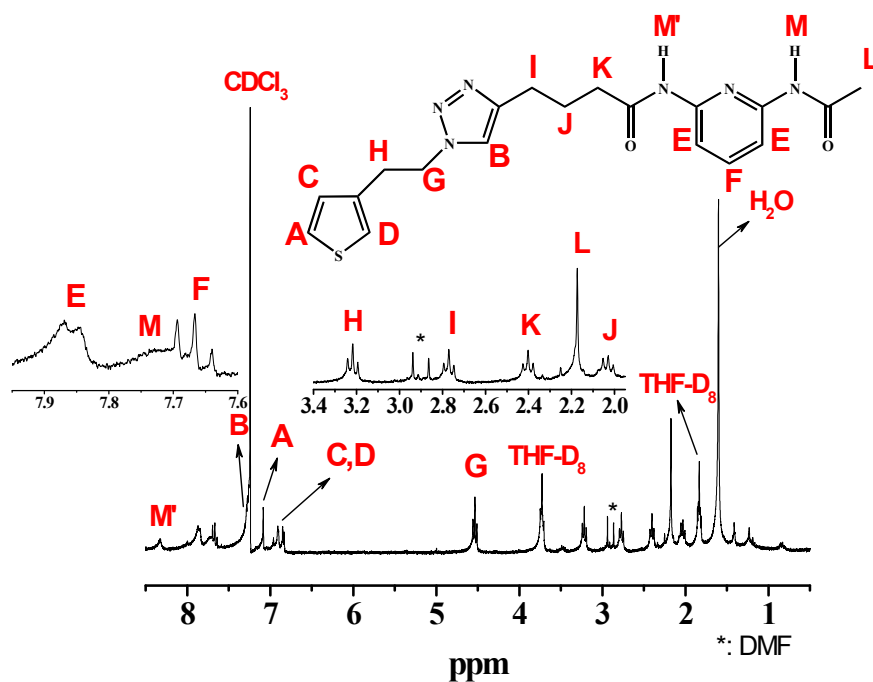
## Characterization

<sup>1</sup>H NMR spectra were recorded using a Varian Inova 500 MHz spectrometer, equipped with a 9.395-T Bruker magnet and operated at 500 MHz. Samples (ca. 5 mg for <sup>1</sup>H NMR) in deuterated solvent were analyzed at room temperature. The weight-average molecular weight (M<sub>w</sub>), number-average molecular weight (M<sub>n</sub>), and polydispersity index (PDI, M<sub>w</sub>/M<sub>n</sub>) were measured using a Waters 410 gel permeation chromatography system equipped with a refractive index detector and three Ultrastaygel columns (100, 500, and 1000 Å) connected in series. N,N-Dimethylformamide was the eluent; the flow rate was 1 mL/min. The system was calibrated using polystyrene standards. Thermal analysis was performed using a differential scanning calorimeter (TA Instruments Q-20) operated under an atmosphere of dry N<sub>2</sub>. Samples were weighed (2–3 mg) and sealed in an Al pan,

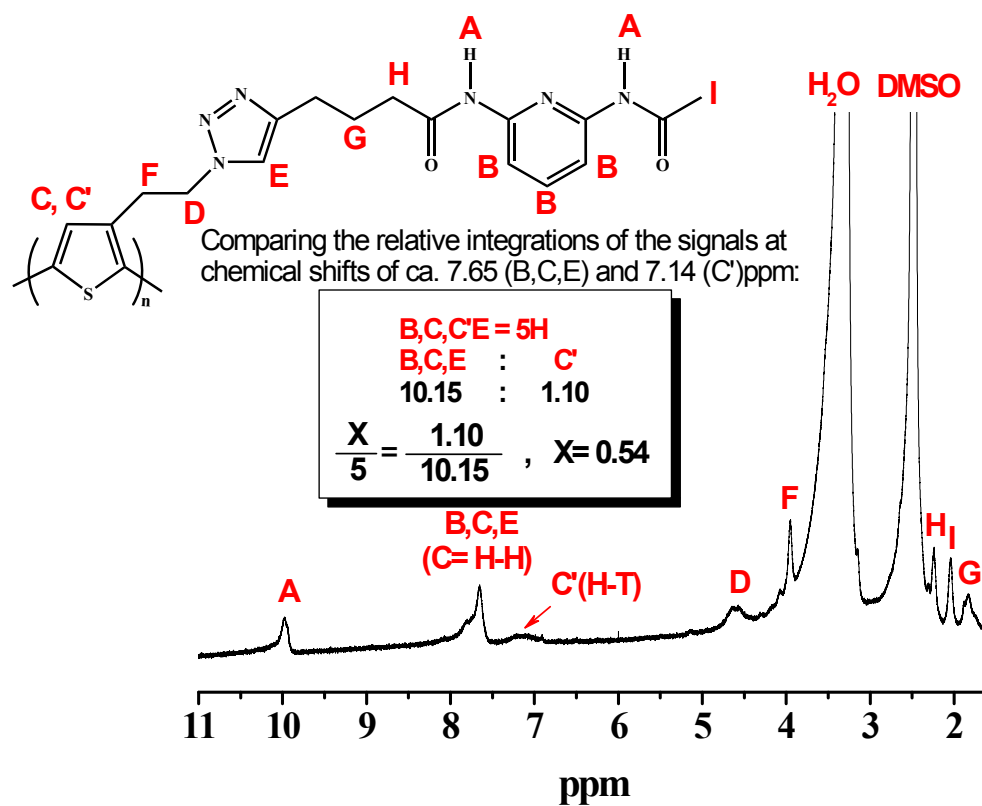
which was scanned from 40 to 220 °C at a scan rate of 10 °C/min. The morphologies of the electrospun fibers were characterized using field-emission scanning electron microscopy (Hitachi S-4700); the samples were sputtered with Pt prior to imaging. Infrared spectra for complex fibers were measured on an attenuated reflectance Fluorescence optical microscope images were taken using a two photon laser confocal microscope (Leica LCS SP5). UV-Vis and photoluminescence (PL) spectra were recorded using an Agilent-8453 spectrometer and a Hitachi F-7000 fluorescence spectrophotometer respectively. Photoluminescence quantum yield was measured by an integrating sphere of HORIBA JOBIN YVON Fluorolog-3 PL spectrometer.



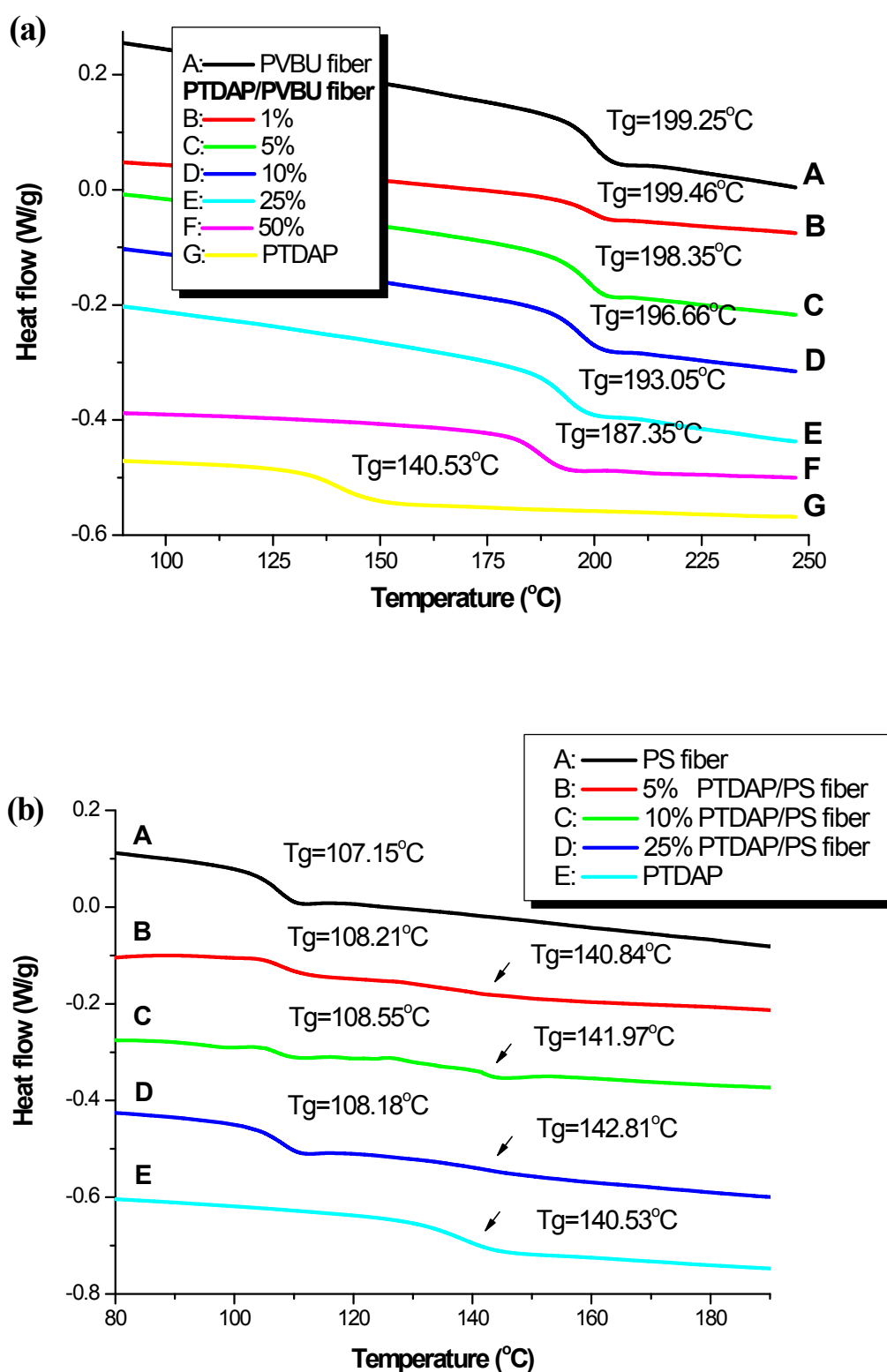
**Figure S1.** <sup>1</sup>H NMR spectrum of compound (2) in CDCl<sub>3</sub>



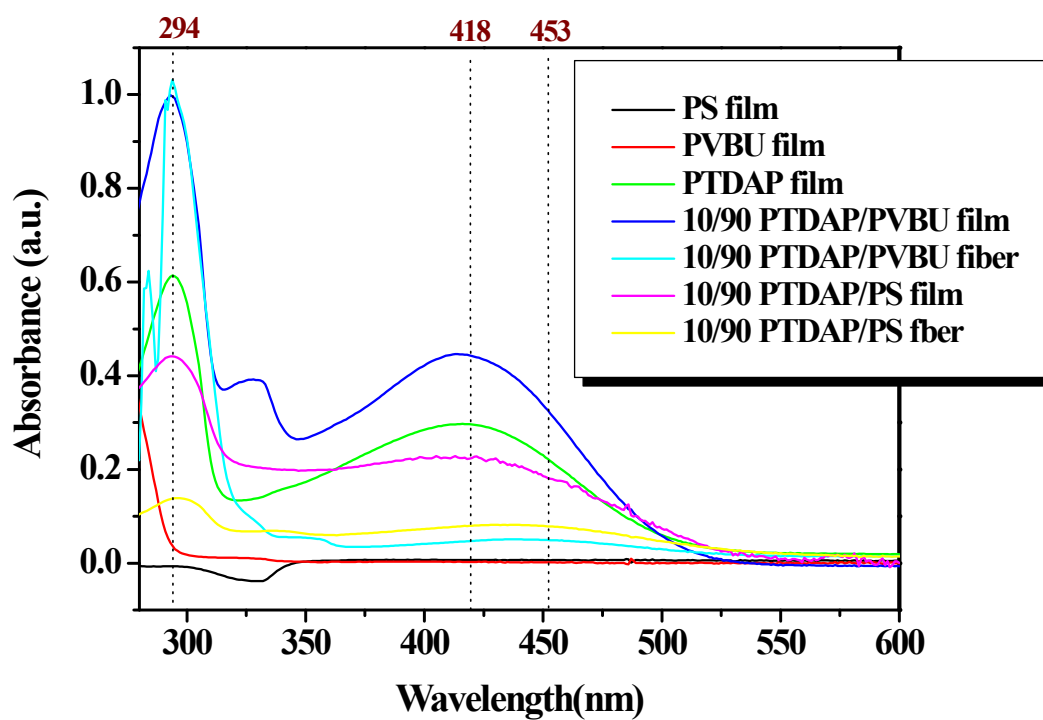
**Figure S2.** <sup>1</sup>H NMR spectrum of DAP-functionalized thiophene in CDCl<sub>3</sub>/THF-D<sub>8</sub> (80/20 V%).



**Figure S3.** <sup>1</sup>H NMR spectrum of PTDAP in D<sub>6</sub>-DMSO

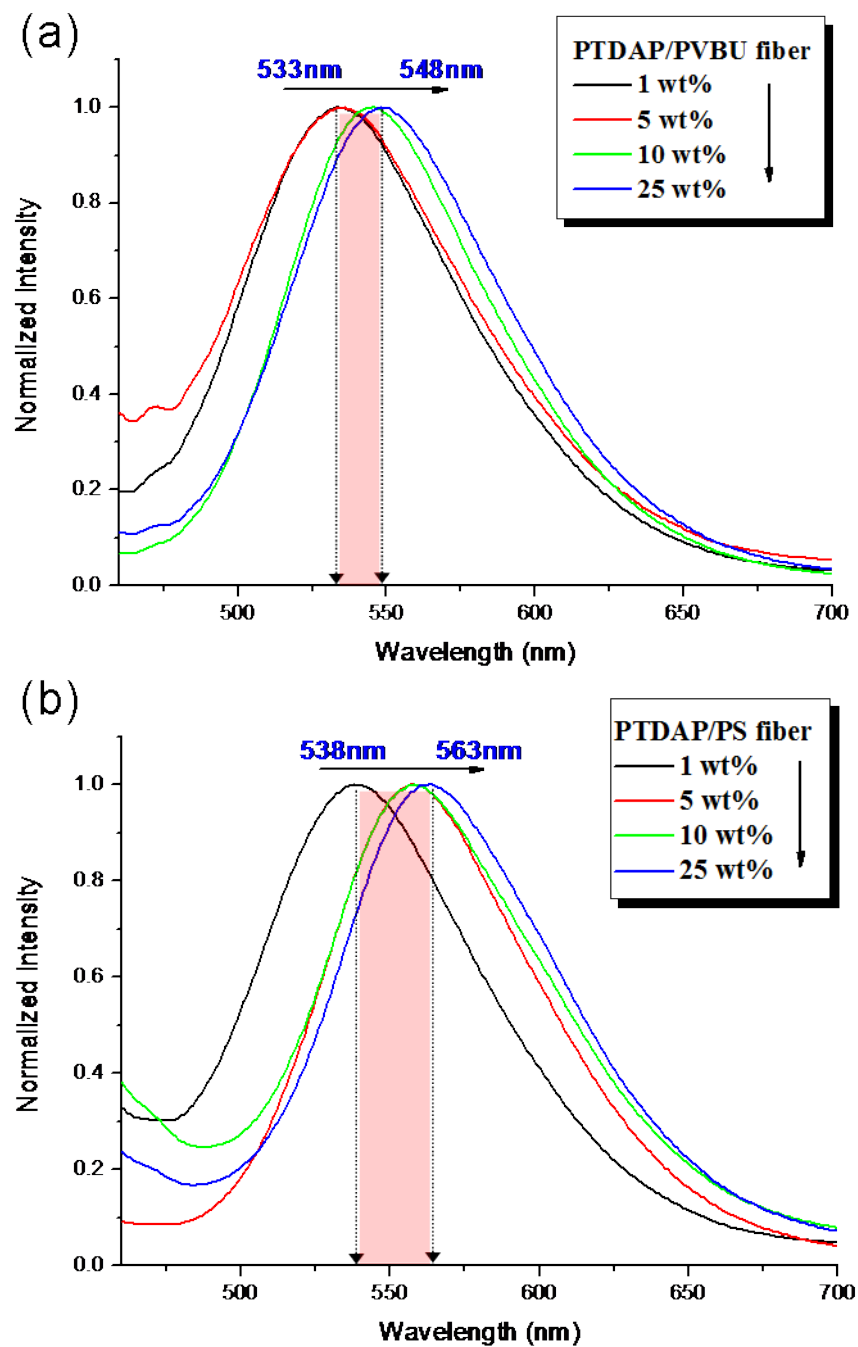


**Figure S4.** DSC data of (a) PTDAP/PVBU blend fibers and (b) PTDAP/PS blend fibers

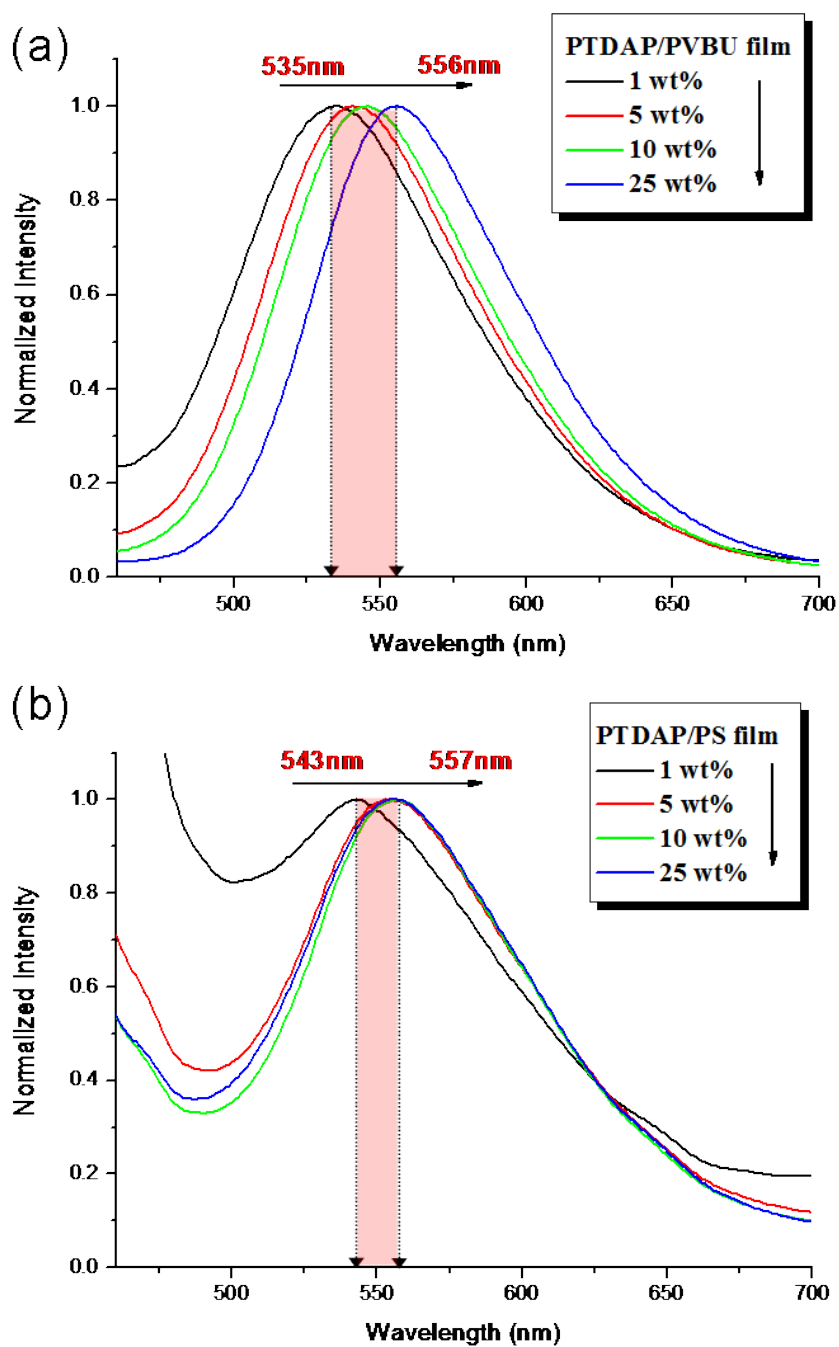


**Figure S5.** Absorption spectra of PTDAP/PVBU and PTDAP/PS composites in thin film and fiber states.





**Figure S6.** Photoluminescence emission spectra of (a) PTDAP/PVBU blend fibers and (b) PTDAP/PS blend fibers with 1 to 25 wt % PTDAP



**Figure S7.** Photoluminescence emission spectra of (a) PTDAP/PVBU spin-coated films and (b) PTDAP/PS spin-coated films with 1 to 25 wt % PTDAP