

Supporting Information

Supramolecular Polymeric Micelles as High Performance Electrochemical Materials

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Experimental Section

Materials

All chemicals were purchased from Sigma-Aldrich (USA) at the highest purity grade available. All solvents were purchased from TEDIA (USA) and distilled over calcium hydride prior to use.

Characterizations

Nuclear Magnetic Resonance (NMR) measurement. ¹H-NMR spectra were recorded using a Varian Inova- 400 MHz spectrometer equipped with a 9.395 T Bruker magnet. Samples of ca. 10 mg were analyzed at 25 °C in deuterated solvent. ¹³C-NMR spectra were performed on a Varian Inova- 400 MHz spectrometer operated at 100 MHz. All samples of ca. 30 mg were dissolved in deuterate solvent and analyzed at 25 °C

Fourier Transform Infrared (FT-IR) spectra were obtained from Nicolet Avatar 320 FT-IR spectrometer; 32 scans were collected with a spectral resolution of 1.0 cm⁻¹. The conventional KBr disk method was employed. Sample was dissolved in DMSO and then cast onto a KBr disk and dried in vacuum at 120 °C for 24 h. The variable temperature experiments were scanned from 30 to 150 °C at a rate of 3.0 °C/min.

Gas Chromatography/Mass Spectrometry. GC/MS spectra were obtained with Micromass Trio 2000 mass spectrometer (Micromass, Manchester, UK).

Differential Scanning Calorimetry (DSC). DSC instrument (TA Instruments Q-20) was used to perform thermal analysis. Samples of ca. 5 mg were sealed in an aluminum pan, and then heated from 30 to 200 °C at a rate of 10 °C/min.

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectroscopy (MALDI-TOF MS). MALDI-TOF MS was performed on a Bruker Autoflex II instrument equipped with an ultraviolet-light nitrogen laser ($\lambda = 337$ nm).

UV-Vis and Photoluminescence (PL) Spectra. Ultraviolet-Visible (UV-Vis) and photoluminescence (PL) spectra were measured using a Hewlett Packard Model diode-array spectrophotometer and a Hitachi F-4500 luminescence spectrometer, respectively.

Cyclic voltammetry (CV) measurements were performed using a Bioanalytical Systems (BAS 100 W, USA) electrochemical analyzer operated at a scan rate of 100 mV s^{-1} . The potentials were measured against an Ag/Ag⁺ (0.01 M AgNO₃) reference electrode using ferrocene/ferrocenium (Fc/Fc⁺) as an internal standard.

Elemental Analysis (EA). The carbon, hydrogen, and nitrogen contents of the samples were obtained using a CHN-O-Rapid elemental analyzer (Foss. Heraeus, Germany).

Dynamic Light Scattering (DLS). DLS measurements were conducted using a 90Plus laser particle size analyzer (Brookhaven Instruments Corp., USA), which was calibrated using a 60-nm latex standard. The scattering from a small amount of sample dissolved in DMSO was measured at 90° .

X-ray photoelectron spectra (XPS). XPS results were obtained with a PHI Quantera SXM electron spectrometer from ULVAC-PHI using Al K α x-ray source. The base pressure was about 5×10^{-10} torr.

Raman spectra were acquired using a WITec, Inc. (Ulm, Germany) Model CRM 2000 Confocal Raman Microscope. A spectral range of $220\text{-}3200 \text{ cm}^{-1}$ was employed. The excitation source was an internal He-Ne (632 nm) laser with a power density of ca. $3 \times 10^4 \text{ W/cm}^2$. Sample preparation for Raman test was spin-coated onto a piece ($10 \times 10 \text{ mm}^2$) of Si wafer surface.

Transmission Electron Microscopy (TEM). TEM images were recorded using an FEI T12 transmission electron microscope with a low-energy electron beam (120 keV). Test samples were placed on a carbon-coated copper grid.

Atomic Force Microscopy (AFM). AFM images were scanned in tapping mode (Digital Instrument NS4/D3100CL/MultiMode) using silicon cantilevers in the air at 25°C . AFM images of all samples were spin-coated onto a wafer substrate and then annealed at 120°C .

Device Fabrication and Measurement: Metal-insulator-semiconductor-type memory devices were fabricated in the configuration wafer/silicon dioxide (SiO₂, 200 nm)/ ESTL (PAT/PCBM, 30 nm)/ Zinc oxide (ZnO, 50 nm)/Aluminum (Al, 100 nm). The SiO₂ layer was used as an insulator layer to balance electron transfers. The ZnO layer deposited through a spin-coating process was employed as an active channel layer, then capped with Al metal through thermal evaporation at a rate of 4.0 \AA s^{-1} . The electrical result of current-voltage (I-V) characteristic of metal-insulator-semiconductor device was performed using an Agilent-4156 probe station and an HP-4284 capacitance-voltage (C-V) analyzer, respectively. Note that all of the experiments were performed in air or in a standard fume hood.

Syntheses:

Synthesis of adenine-functionalized thiophene monomer

3-Bromohexylthiophene was synthesized from commercial PEG 1000 according to the procedures described in previous work.²⁰ 3-Bromohexylthiophene (2.79 g, 20.0 mmol) and anhydrous potassium carbonate (5.58 g, 40.0 mmol) were added to a solution of adenine (5.40 g, 40.0 mmol) in DMF and then the resulting suspension was stirred at 60 °C for 36 h. The insoluble material obtained was filtrated out, washed with water, and recrystallized twice from toluene. Yield: 2.52 g (45%); FAB-MS: m/z (%) = 302; ¹H NMR (400 MHz, CDCl₃): δ = 1.34 (m, 4H), 1.65 (br, 2H), 2.60 (m, 2H), 3.68 (t, 2H), 5.65 (d, 1H), 6.89 (d, 1H), 7.08 (d, 1H), 7.21 (d, 1H), 8.80 (s, 1H). ¹³C NMR (400 MHz, CDCl₃) δ = 26.45, 28.96, 29.19, 30.30, 30.49, 49.06, 102.34, 120.17, 125.45, 128.40, 142.96, 144.65, 151.15, 164.18.

Synthesis of a polythiophene containing pendant adenine groups (PAT)

Adenine-functionalized thiophene (1.73 g, 5.7 mmol) and anhydrous FeCl₃ (9.31 g, 57.4 mmol) was dissolved in dry chloroform (40 mL) and then solution was purged with dry argon for 10 min. The solutions were degassed through three freeze/thaw evacuation cycles. Subsequently, the mixture was reacted for 1 day at room temperature and poured into methanol (200 mL) to precipitate the polymer. The crude polymer was filtered, further purified by extraction in a Soxhlet extractor with refluxing methanol for 48 h, and dried under vacuum, Yield: 1.08 g (63%). ¹H NMR (400 MHz, *d*₆-DMSO): δ = 1.20 (4H), 1.53(2H), 1.71 (2H), 2.65 (2H), 4.05 (2H), 7.07 (1H), 7.20 (2H), 8.08 (2H)

Preparation of PCBM-Loaded Micelles

The PAT was used to encapsulate PCBM via simple solvent blending method. PCBM (ranging from 10 to 40 mg) was mixed with 20 mg of PAT in 5 mL DMSO under stirring at 100 °C for 1 day, and then cooled down to room temperature. Un-encapsulated PCBM was separated by the procedure of filtration through a 0.45 μ m PTFE filter. The amount of the encapsulated PCBM in micelles was analyzed by a UV-visible absorption spectroscopy at 329 nm for PBCM. The PBCM-loading content was determined by using the following expressions:

$$\text{loading content (\%)} = W_t/W_s \times 100\%$$

where, W_t , weight of PBCM that loaded into Micelles; W_s , weight of PCBM-loaded micelle after filtration.

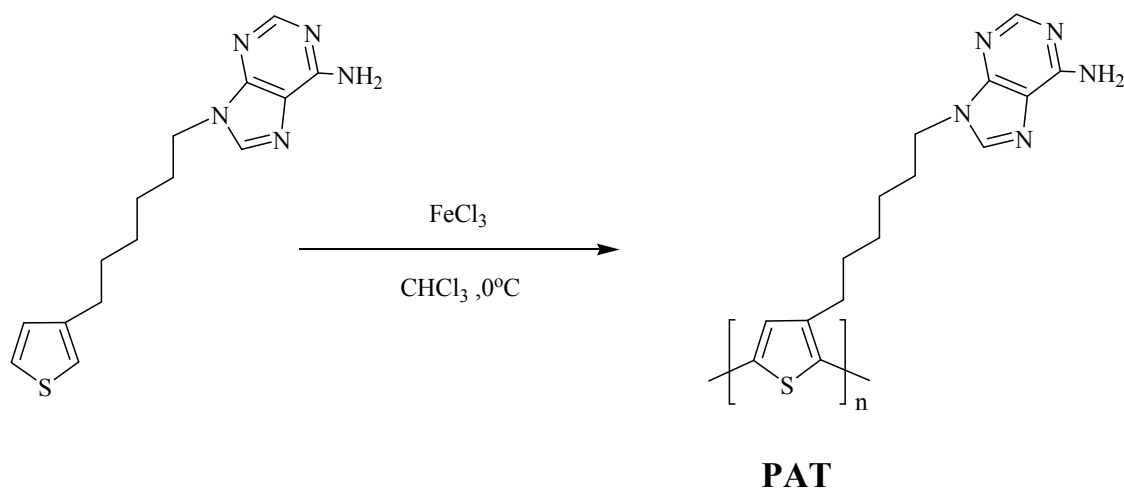
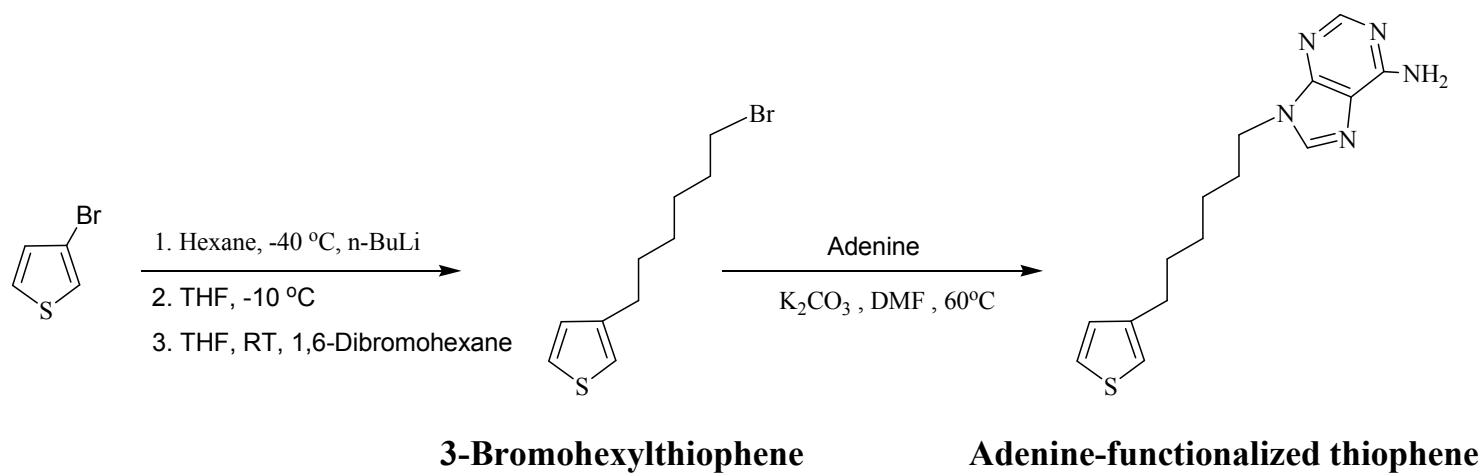
Table S1. PCBM Loading of PCBM Loaded PAT micelles

PAT/PCBM ratio (wt/wt)	PCBM loading content (%)
1:0.5 (20mg: 10mg)	23.3
1:1.0 (20mg: 20mg)	31.5
1:2.0 (20mg: 40mg)	33.6

Table S2. Electrical properties of PAT/PCBM-based devices.

Sample	Conductivity (mS cm ⁻¹) ^a
PCBM	4.95 x 10 ⁻⁶
35/65 PAT/PCBM	2.85 x 10 ⁻¹⁰
PAT	NA

a.. Electrical conductivity was measured by the four-point probe method at room temperature.



Scheme S1. Syntheses of adenine-functionalized thiophene and PAT.

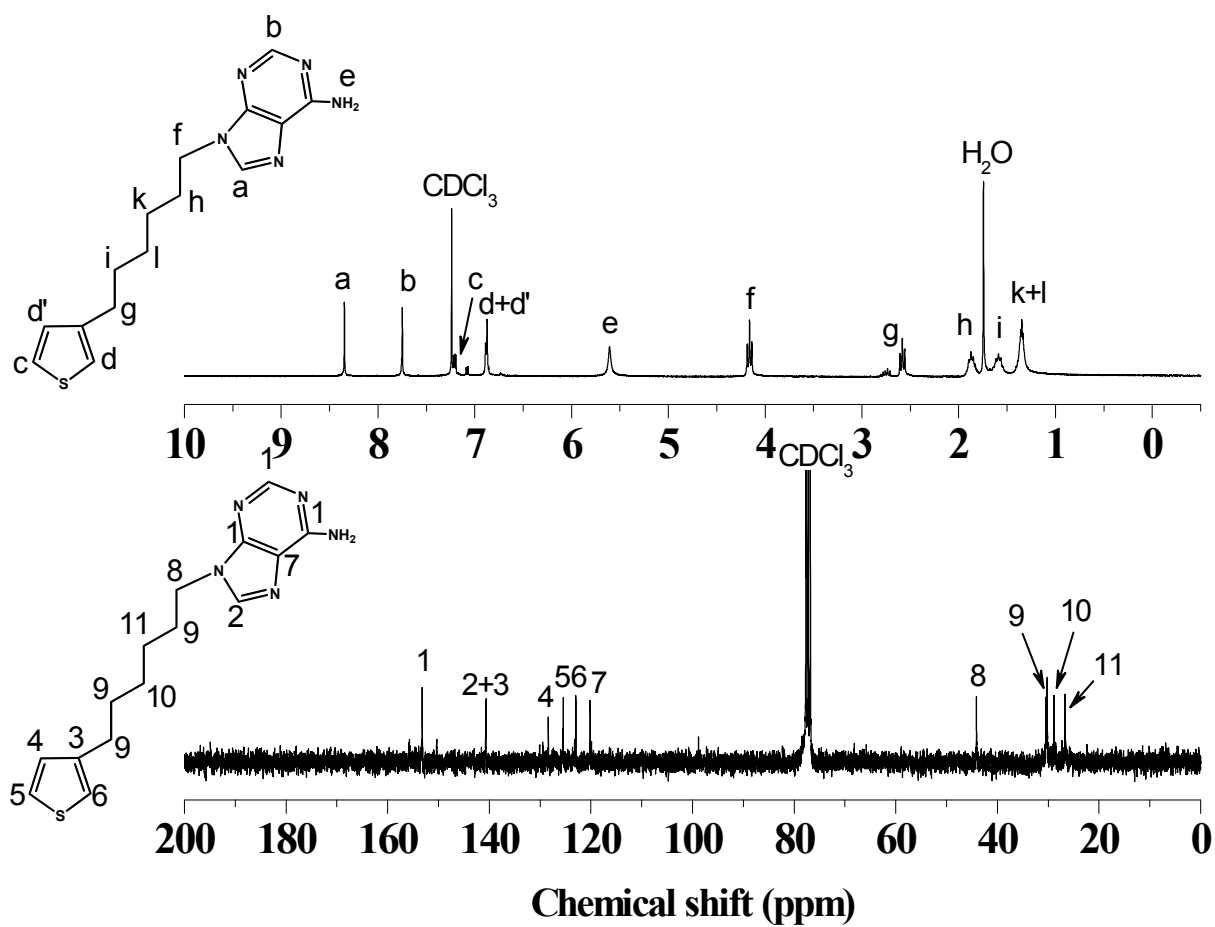


Fig. S1 $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of adenine-functionalized thiophene in CDCl_3 .

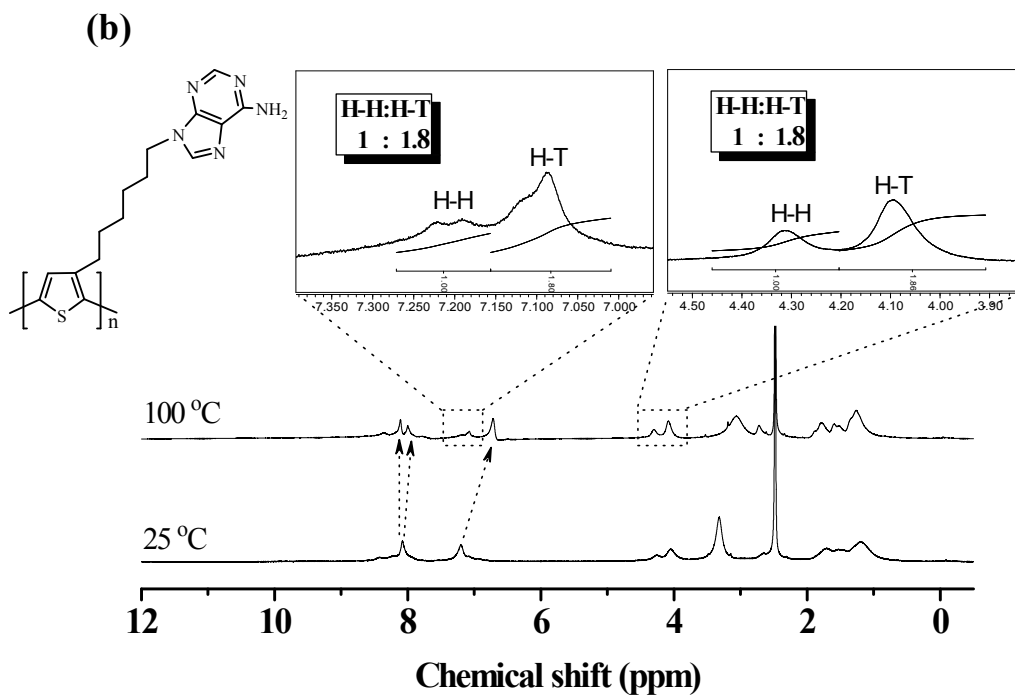
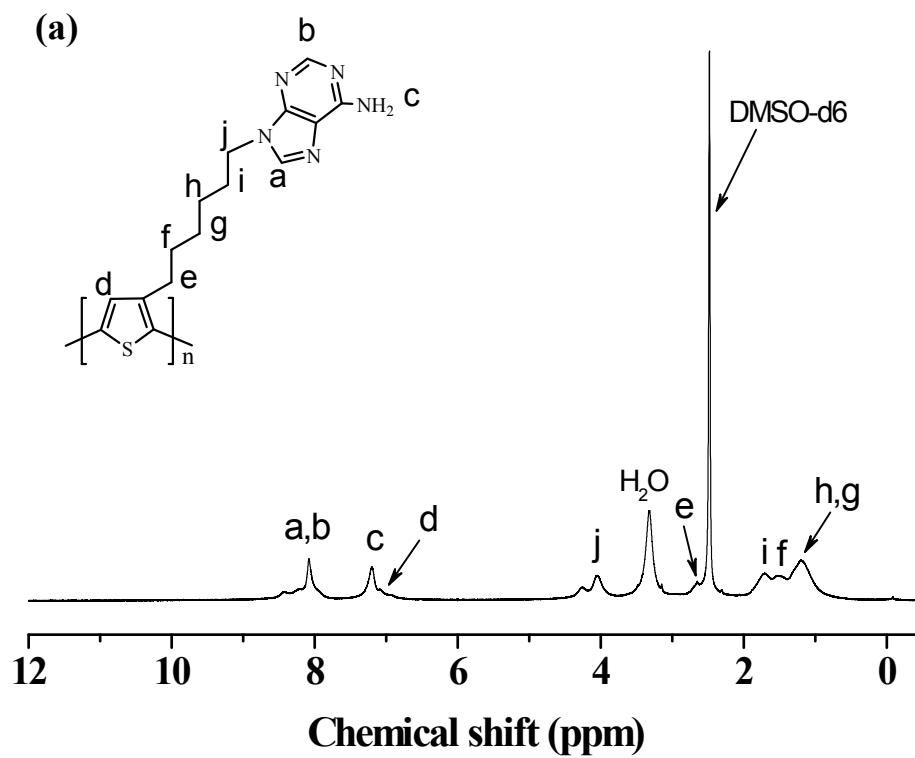


Fig. S2 ¹H-NMR spectrum of PAT in *d*₆-DMSO.

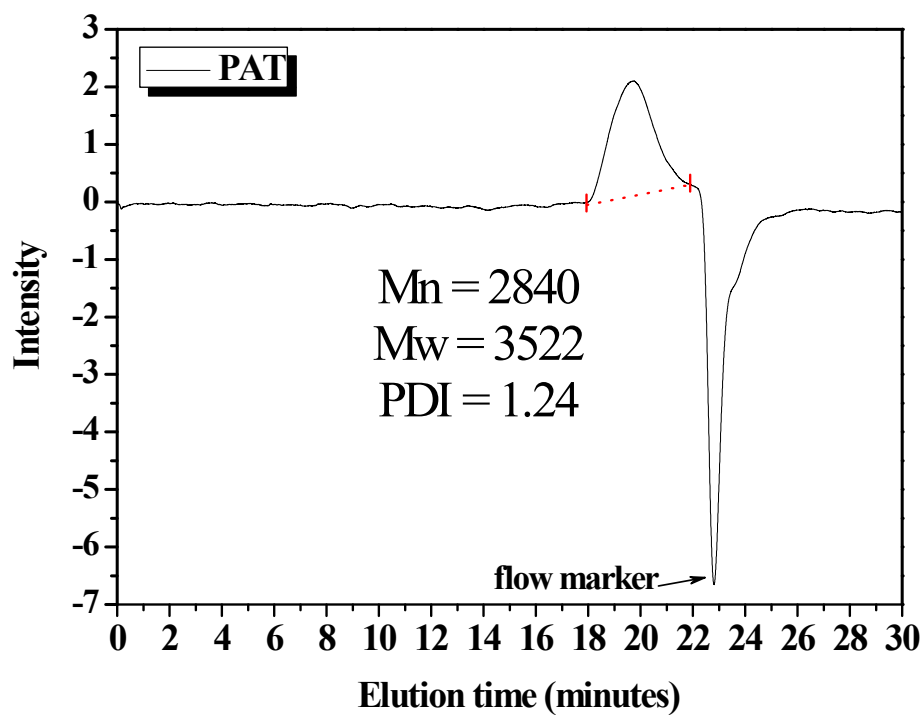


Fig. S3 GPC traces of PAT using DMF as eluent.

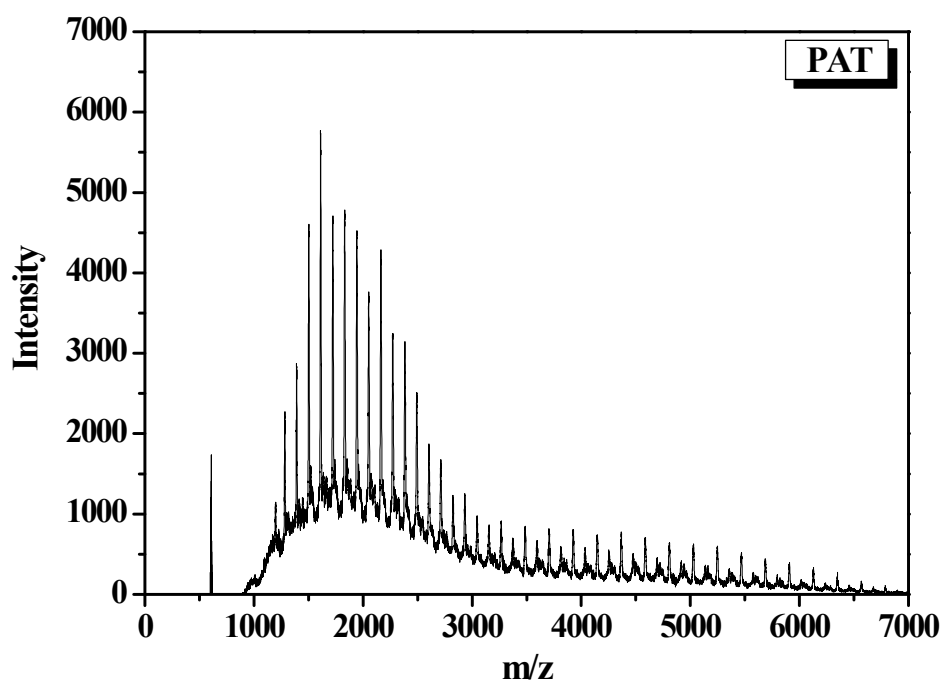


Fig. S4 MALDI-TOF mass spectrum of PAT.

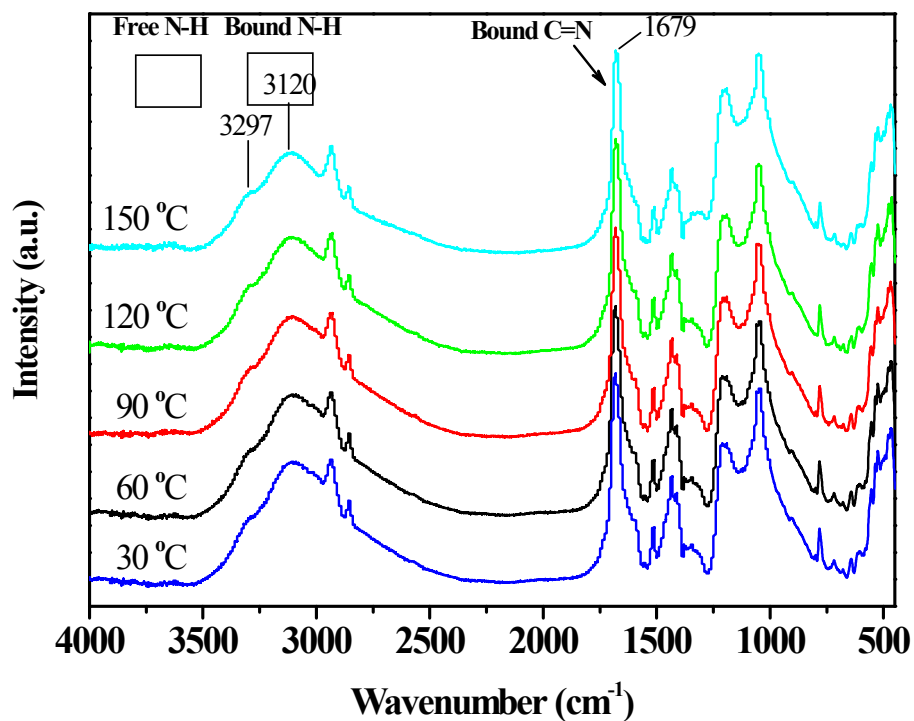


Fig. S5 Variable-temperature FT-IR spectra of PAT presented in the range 500–4000 cm⁻¹

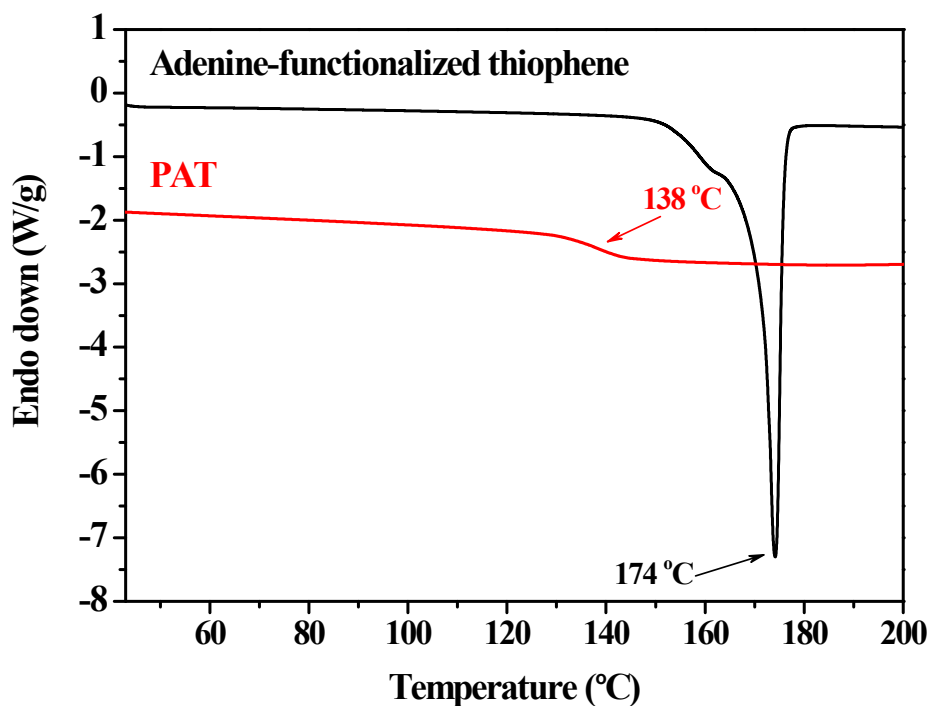


Fig. S6 DSC curves of adenine-functionalized thiophene and PAT.

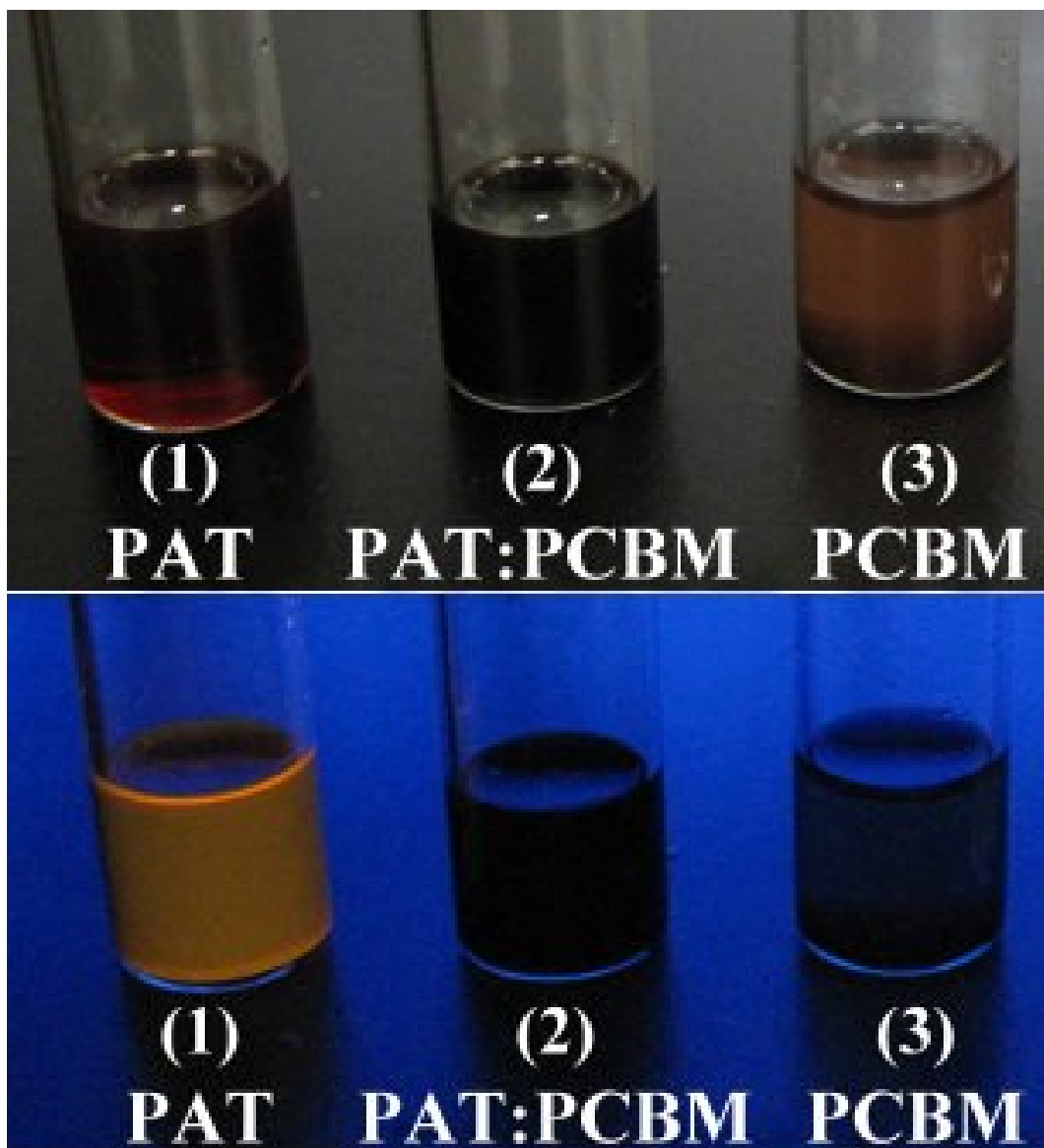


Fig. S7 Enlarged image of **Figure 1(c)**: Comparison of solubility characteristics by the digital photographs between PAT, PAT/PCBM and PCBM in DMSO, simultaneously exposed under natural light (upper panel) and UV lamp illumination (lower panel).

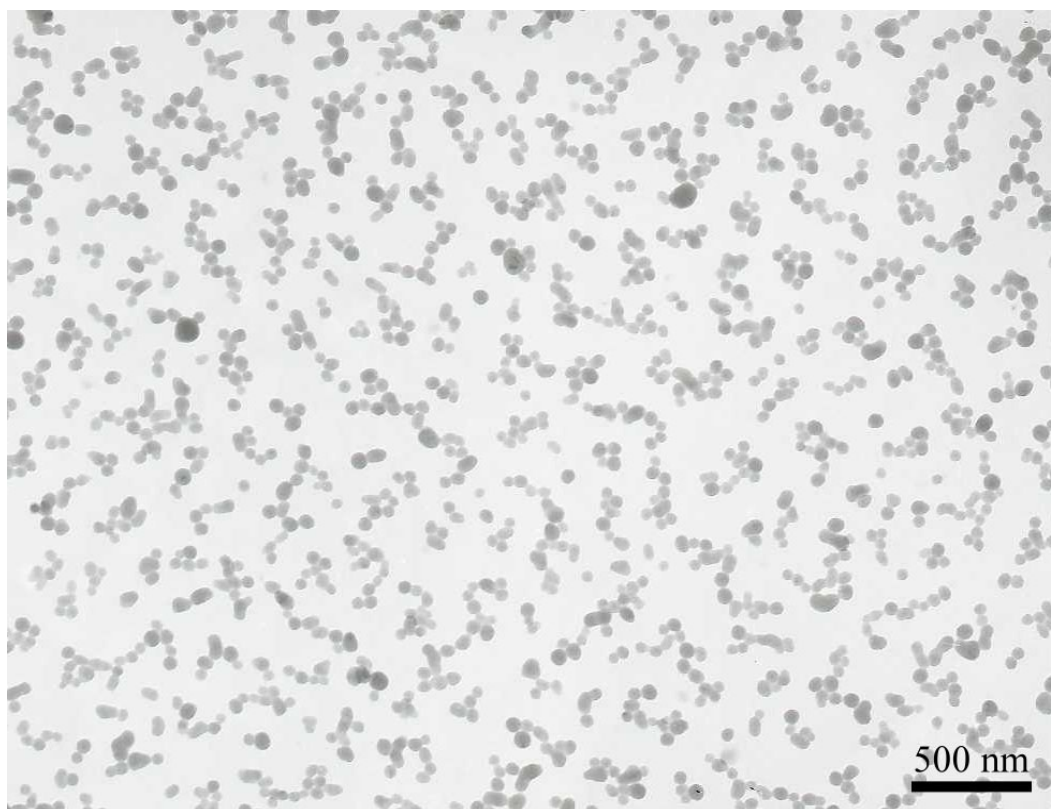


Fig. S8 TEM image of PAT on carbon coated copper grid. The sample was drop-cast from a DMSO solution onto the TEM grid.

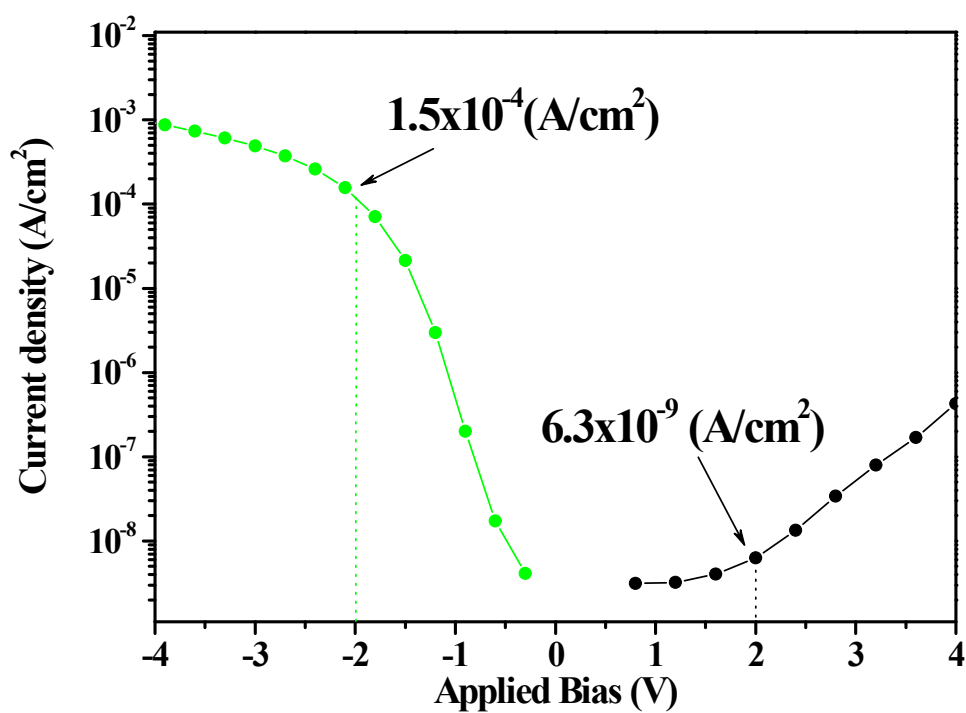


Fig. S9 Enlarged part of the low-voltage region in **Figure 4(c)**.