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 deuterated 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 (λ = 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 Kα 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 220-3200 cm⁻¹ was employed. The excitation source was an internal He-Ne (632 nm) laser with a power density of ca. 3 × 10⁴ W/cm². Sample preparation for Raman test was spin-coated onto a piece (10 × 10 mm²) 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 Å 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.\textsuperscript{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; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): 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). \textsuperscript{13}C NMR (400 MHz, CDCl\textsubscript{3}) 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 FeCl\textsubscript{3} (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%). \textsuperscript{1}H NMR (400 MHz, d\textsubscript{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 μm 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:

\[
\text{loading content (\%) } = \frac{W_r}{W_s} \times 100\%
\]

where, \(W_r\), weight of PBCM that loaded into Micelles; \(W_s\), weight of PCBM-loaded micelle after filtration.

<table>
<thead>
<tr>
<th>Table S1. PCBM Loading of PCBM Loaded PAT micelles</th>
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<tbody>
<tr>
<td>PAT/PCBM ratio (wt/wt)</td>
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<tr>
<td>-------------------------</td>
</tr>
<tr>
<td>1:0.5 (20mg: 10mg)</td>
</tr>
<tr>
<td>1:1.0 (20mg: 20mg)</td>
</tr>
<tr>
<td>1:2.0 (20mg: 40mg)</td>
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Table S2. Electrical properties of PAT/PCBM-based devices.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity (mS cm(^{-1}))(^a)</th>
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<tbody>
<tr>
<td>PCBM</td>
<td>4.95 x 10(^{-6})</td>
</tr>
<tr>
<td>35/65 PAT/PCBM</td>
<td>2.85 x 10(^{-10})</td>
</tr>
<tr>
<td>PAT</td>
<td>NA</td>
</tr>
</tbody>
</table>

\(a\). Electrical conductivity was measured by the four-point probe method at room temperature.
Scheme S1. Syntheses of adenine-functionalized thiophene and PAT.
Fig. S1 $^1$H-NMR and $^{13}$C-NMR spectra of adenine-functionalized thiophene in CDCl$_3$. 
Fig. S2 $^1$H-NMR spectrum of PAT in $d_6$-DMSO.
Fig. S3 GPC traces of PAT using DMF as eluent.

Mn = 2840
Mw = 3522
PDI = 1.24

Fig. S4 MALDI-TOF mass spectrum of PAT.
**Fig. S5** Variable-temperature FT-IR spectra of PAT presented in the range 500–4000 cm\(^{-1}\)

![Variable-temperature FT-IR spectra of PAT](image)

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

![DSC curves of adenine-functionalized thiophene and PAT](image)
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).