Thiophene and Selenophene Donor–Acceptor Polyimides as Polymer Electrets for Nonvolatile Transistor Memory Devices

Ying-Hsuan Chou,[†] Nam-Ho You,[‡] Tadanori Kurosawa,[‡] Wen-Ya Lee,[†] Tomoya Higashihara,[‡] Mitsuru Ueda,^{‡,*} and Wen-Chang Chen^{†,*}

[†]Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 10617

[‡]Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo, 152-8552 Japan

Supporting Information

ABSTRACT: We report the nonvolatile memory characteristics of n-type *N*,*N*'-bis(2-phenylethyl)perylene-3,4:9,10tetracarboxylic diimide (BPE-PTCDI) based organic fieldeffect transistors (OFET) using the polyimide electrets of poly[2,5-bis(4-aminophenylenesulfanyl)selenophene-hexafluoroisopropylidenediphthalimide] (PI(APSP-6FDA)), poly-[2,5-bis(4-aminophenylenesulfanyl)thiophene-hexafluoroisopropylidenediphthalimide] (PI(APST-6FDA)), and poly(4,4'oxidianiline-4,4'-hexafluoroisopropylidenediphthalic anhydride) (PI(ODA-6FDA)). Among those polymer electrets,



the OFET memory device based on PI(APSP-6FDA) with a strong electron-rich selenophene moiety exhibited the highest fieldeffect mobility and I_{on}/I_{off} current ratio of 10⁵ due to the formation of the large grain size of the BPE-PTCDI film. Furthermore, the device with PI(APSP-6FDA) exhibited the largest memory window of 63 V because the highest HOMO energy level and largest electric filed facilitated the charges transferring from BPE-PTCDI and trapping in the PI electret. Moreover, the charge transfer from BPE-PTCDI to the PI(APSP-6FDA) or PI(APST-6FDA) electrets was more efficient than that of PI(ODA-6FDA) due to the electron-donating heterocyclic ring. The nanowire device with PI(APSP-6FDA) showed a relatively larger memory window of 82 V, compared to the thin film device. The present study suggested that the donor–acceptor polyimide electrets could enhance the capabilities for transferring and store the charges and have potential applications for advanced OFET memory devices.

INTRODUCTION

Organic memory devices have received extensive research interest recently due to the advantages of the structural flexibility, processabiliy, lightweight and simple manufacturing process compared to those employed in the inorganic silicon technology.^{1–5} The proposed organic or polymeric memory devices include resistor-, capacitor- and transistor-type memories.³ Among these memory devices, organic field effect transistor (OFET) type memories showed the most noticeable application due to easily integrated structure, nondestructive reading, and multiple-bit storage in a single transistor.⁶

The configuration of OFET memory devices is a conventional transistor with an additional polymer electret between a semiconductor layer and dielectric layer. Polymer electrets are dielectric materials with a long-term charge storing ability or electrostatic polarization, including ferroelectric polymers,^{7,8} polymer composites,^{9–13} and nonconjugated polymer.^{6,14,15} The electrical switching of the OFET memory devises arose from charge trapped in chargeable polymer electrets^{12,16,17} or polarization of ferroelectric materials.^{18–20} Naber et al. demonstrated that OFET type nonvolatile memories using an organic ferroelectric electret had an on/off ratio of 10⁴, and the device was stable for more than 1 week.²¹ However, ferroelectric polymers have a low solubility in common solvents and require a high annealing temperature for developing the ferroelectric characteristics, which may degrade the electrical performance of OFETs. Recently, much attention has been attracted on the development of single-component polymer electrets. Kim and co-workers discovered that the pentacenebased OFET memory device using $poly(\alpha$ -methylstyrene) as polymer electret displayed fast writing and erasing speeds around 1 µs.¹⁴ The polymer charge trapping ability of the electret induced memory characteristics and their hydrophilicity and dielectric polarity significantly affected the device performance.²² Recently, our group also found that memory voltage windows of pentacene-based OFET memory devices were significantly affected by the conjugated lengths of polymer electrets.²³ Donor-acceptor polymers can enhance the charge storages through the induced intramolecular charge transfer (ICT) from the donor to acceptor moiety under an applied electric field. However, such class of polymers has not been explored as polymer electret for OFET memory devices.

ACS Publications © 2012 American Chemical Society

Received:
 June 27, 2012

 Revised:
 August 12, 2012

 Published:
 August 29, 2012

Scheme 1. (a) Structure of APSP-6FDA, APST-6FDA, and ODA-6FDA and (b) Synthetic Routes for (I) APSP, (II) APST, (III) PI(APSP-6FDA), and PI(APST-6FDA)



Donor–acceptor polyimides (PIs) have been explored for applications in organic electronics, such as light-emitting diodes,²⁴ photovoltaics,²⁵ and xerography,²⁶ and resistor-type memory,^{16,20,27–32} due to their good electrical properties, thermal stability and chemical resistance.^{16,28,32–36} Most studies on the polyimide-based memory devices were mainly resistortype devices with a simple sandwich structure of metal/ polymer/metal. However, the memory behaviors of resistortype structure are easily affected by filament effects, resulted from the formation of highly conductive metallic filaments induced by the migration of metal atoms from electrodes. Thus, it would be difficult to establish the correlation between polymer structures and memory characteristics. Therefore, we explore the OFET memory devices to minimize the filament effect.

In this study, we report the memory behavior of *n*-type N_iN' bis(2-phenylethyl)perylene-3,4:9,10-tetracarboxylic diimide (BPE-PTCDI) based OFET memory devices using polyimide electrets. The polyimide electrets, PI(APSP-6FDA) and PI(APST-6FDA), are consisted of electron-donating 2,5bis(4-aminophenylenesulfanyl)selenophene (APSP) or 2,5bis(4-aminophenylenesulfanyl)thiophene (APST) and electron-accepting 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), as shown in Scheme 1. For comparison, poly(4,4'-oxidianiline-4,4'-hexafluoroisopropylidenediphthalic anhydride) (PI(ODA-6FDA)) (Scheme 1a) is also used as a polymer electret. The BPE-PTCDI OFET memory device enables the reversible trapping of hole carriers in gate dielectrics. The selenophene and thiophene moieties in PIs are expected to enhance the electron-donating ability. To the best of our knowledge, this is the first study on n-type OFET memory devices using donor-acceptor polymer electrets.

EXPERIMENTAL SECTION

Materials. Selenophene and 2,5-dichlorothiophene were purchased from Sigma-Aldrich Corp. Copper, quinoline, and dehydrated *N*,*N*-dimethylacetamide (DMAc) were used as received. *p*-Aminothiophenol, 1,3-dimethyl-2-imidazolidinone (DMI), oxidianiline (ODA), and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) were purchased from TCI and used as received. All other chemicals were purchased from TCI Japan. BPE-PTCDI was purchased from Luminescence Technology Corp (Taiwan).

Monomer Synthesis. Synthesis of 2,5-Bis(4aminophenylenesulfanyl)selenophene (APSP). p-Aminothiophenol (2.61 g, 20.4 mmol), quinoline (15 mL), toluene (15 mL), and potassium carbonate (3.47 g, 25.1 mmol) were mixed into a 50 mL round flask. The mixture was heated with stirring at 150 °C for 4 h under a nitrogen atmosphere to remove water with a Dean-Stark apparatus. After complete removal of water, residual toluene was distilled off. Copper powder (0.066 g, 1.04 mmol) and 2,5dibromoselenophene (2.95 g, 10.2 mmol) were added to the mixture, followed by heating at 200 °C for 24 h under a nitrogen atmosphere. Then, the mixture was cooled to room temperature and filtered to remove copper powder. The filtrate was extracted with dichloromethane and water. The solvent was evaporated, and the crude solid was purified by column chromatography using dichloromethane and recrystallized from ethanol to give pale yellow crystals, 1.94 g (51% yield), mp: 104.2 °C (DSC peak temperature). IR (KBr, cm⁻¹), ν (cm⁻¹): 3459, 3351, 3050, 1612, 1492, 1299, 825. ¹H NMR (300 MHz, DMSO-*d*₆, δ, ppm): 7.15 (d, *J* = 8.1 Hz, ArH, 4H), 6.99 (s, ArH, 2H), 6.54 (d, J = 8.1 Hz, ArH, 4H), 5.48 (s, N-H, 4H). ¹³C NMR (75 MHz, DMSO, δ, ppm): 150.8, 146.9, 135.1, 131.5, 119.8, 115.4. Anal. Calcd For C16H14N2: C, 50.92; H, 3.74; N, 7.42. Found: C, 51.31; H, 3.77; N, 7.39.

Synthesis of 2,5-Bis(4-aminophenylenesulfanyl)thiophene (APST). In a 250 mL three-necked flask equipped with a magnetic stirrer, a nitrogen inlet, a Dean–Stark trap, and a condenser were placed *p*-aminothiophenol (9.39 g, 0.075 mol), potassium carbonate (5.39 g, 0.039 mol), DMI (30 mL), and toluene (50 mL). The mixture was heated with stirring at 140 $^{\circ}$ C for 4 h under a nitrogen atmosphere. After complete removal of water, residual toluene was

distilled off. Then, the mixture was cooled to 120 °C, and 2,5dichlorothiophene (4.59 g, 0.030 mol) dissolved in DMI (10 mL) was added dropwise to the mixture. In the following, the reaction mixture was poured into cold water (250 mL) to give a brown oil-like product. The oil solidified several hours later. The upper water layer was decanted and fresh water was added. The solid was crushed, collected and washed thoroughly with water to give a crude product. The crude diamine was recrystallized from ethanol followed by decoloration with activated carbon. White colored crystals (7.92 g) were obtained in 80% yield, mp 128.8 °C (DSC peak temperature). IR (KBr), ν (cm⁻¹): 3451, 3347, 1616, 1592, 1492, 1284, 1176, 829. ¹H NMR (300 MHz, $CDCl_3$, δ , ppm): 7.11 (d, J = 8.1 Hz, ArH, 4H), 6.91 (s, ArH, 2H), 6.55 (d, J = 8.1 Hz, ArH, 4H), 5.36 (s, N-H, 4H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 146.9, 139.8, 133.4, 132.3, 124.3, 116.1. Anal. Calcd For C16H14N2: C, 58.15; H, 4.27; N, 8.48. Found: C, 58.38; H, 4.35: N. 8.29.

Synthesis of Poly[2,5-bis(4-aminophenylenesulfanyl)selenophene-hexafluoroisopropylidenediphthalimide] (PI(APSP-6FDA)). APSP (0.377 g, 1.00 mmol) and dehydrated DMAc (3.49 mL) were charged into a 20 mL flask equipped with a magnetic stirrer under a nitrogen atmosphere (Scheme 1b). After APSP was completely dissolved, 6FDA (0.444 g, 1.00 mmol) was added and the solution was stirred at room temperature for 24 h to afford a viscous poly(amic acid) (PAA) solution. A reaction mixture of acetic anhydride (0.148 g, 1.49 mmol) and pyridine (0.115 g, 1.49 mmol) was added to the above PAA solution. The reaction mixture was stirred at room temperature under a nitrogen atmosphere for 24 h. The resulting solution was poured into methanol, and the precipitate was collected by filtration and washed with methanol. The final product was dried at 200 °C for 10 h under vacuum and the polymer yield was 90%. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) values estimated from size exclusion chromatography (SEC) were 4.91 \times 10⁴ and 9.90 \times 10⁴, respectively, with the polydispersity index (PDI= M_w/M_n) of 2.02. IR (KBr), ν (cm⁻¹): 1786, 1720 (C=O stretching), 1365 (C-N stretching). ¹H NMR (DMSO- d_6 , δ , ppm): 8.13 (d, J = 8.4 Hz, ArH, 2H), 7.93 (d, J =9.0 Hz, ArH, 2H), 7.74 (s, ArH, 2H), 7.52-7.43 (m, ArH, 10H). Anal. Calcd For C35H16N2: C, 53.5; H, 2.05; N, 3.57. Found: C, 53.0; H, 2.00: N. 3.35.

Synthesis of Poly[2,5-bis(4-aminophenylenesulfanyl)thiophenehexafluoroisopropylidenediphthalimide] (Pl(APST-6FDA)). Using APST as a diamine, PI(APST-6FDA) was synthesized by a similar procedure as PI(APSP-6FDA) (Scheme 1(b)). The yield of PI(APST-6FDA) was 92%. $M_{n\nu}$ M_{w} , and PDI values of PI(APST-6FDA) were 4.30 × 10⁴, 7.17 × 10⁴, and 1.66, respectively. IR (KBr), ν (cm⁻¹): 1786, 1720 (C=O stretching), 1377 (C–N stretching). ¹H NMR (DMSO- d_{60} δ , ppm): 8.13 (d, J = 7.8 Hz, ArH, 2H), 7.93 (d, J = 8.7 Hz, ArH, 2H), 7.74 (s, ArH, 2H), 7.49–7.40 (m, ArH, 10H). Anal. Calcd For C₃₅H₁₆N₂: C, 56.9; H, 2.18; N, 3.79. Found: C, 57.2; H, 2.13; N, 3.75.

Preparation of the PI(ODA-6FDA) Thin Film. The PI(ODA-6FDA),was prepared according to the literature.³⁷ First, the ODA was added into a flask and dissolved in DMAc with stirring. After 20 min, 6FDA was added and reacted at room temperature with stirring under nitrogen. The molar ratio of dianhydried to diamine was 1:1, and the total concentration of the reaction solution was 15 wt %. After 20 h, the reaction solution was spin-coated on a silicon wafer at 3000 rpm for 60 s. The coated film was the cured on a hot plate at 60 °C for 20 min, 100 °C for 20 min, 150 °C for 20 min, and finally at 300 °C in a furnace for 120 min under nitrogen.

Preparation of the BPE-PTCDI Nanowires. To induce the nanowire structure, BPE-PTCDI (1 mg) was dissolved in refluxing *o*-dichlorobenzene (3 mL) in a round-bottom flask with magnetic stirring and heated to 160 °C. After the powder had been completely dissolved in solution at the high temperature of 160 °C, methanol (27 mL) as a nonsolvent was slowly added into the organic solution to induce crystallization. As the solution cooled, its color changed gradually from orange to dark green. After several hours, cotton-like BPE-PTCDI nanowires were observed floating in the solution.³⁸

Device Fabrication and Characterization. The transistor-type memory devices based on a BPE-PTCDI thin film were fabricated on a wafer with a thermally grown 300-nm thick SiO₂ dielectric on highly doped *n*-type Si as a gate electrode. The solution of PI(APSP-6FDA) or PI(APST-6FDA) in chloroform was spin-coated at 1000 rpm for 60 s on a wafer. Thereafter, the polymer thin films were dried under vacuum (10^{-6} Torr) at 100 °C for 1 h to remove residue solvents. The thickness of the prepared thin film was estimated to be 60-65 nm. The thin film of BPE-PTCDI was prepared by thermally deposition with a deposition rate of 0.3–0.4 nm s⁻¹ at 90 °C under vacuum (10^{-7}) Torr) to form a 50-nm-thick film. On the other hand, the nanowires of BPE-PTCDI in solution were spin-coated at 1000 rpm for 60 s onto the PIs electret. The nanowires were dried under vacuum (10^{-6} Torr) at 70 °C for overnight to remove residue solvents. The top-contact source and drain electrodes were defined by 80-nm thick gold through a regular shadow mask, and the channel length (L) and width (W)were 50 and 1000 μ m, respectively. The current-voltage (*I*-*V*) characteristics of the devices were measured by using a Keithley 4200-SCS semiconductor parameter analyzer in a N2-filled glovebox.

Characterization. NMR spectra were recorded on a BRUKER DPX-300S spectrometer at the resonant frequencies at 300 MHz for ¹H and 75 MHz for ¹³C nuclei using CDCl₃ or DMSO-d₆ as the solvent and tetramethylsilane as the reference. FT-IR spectra were measured by a Horiba FT-120 Fourier transform spectrophotometer. M_n and M_w values were evaluated by HITACHI SEC with two polystyrene gel columns (Shodex GPC KD-804, KD-805). N,N-Dimethylformamide (DMF) containing 0.01 M LiBr was used as an eluent at a flow rate of 1.0 mL·min⁻¹ calibrated by polystyrene standard samples. Elemental analyses were performed on a Yanaco MT-6 CHN recorder elemental analysis instrument. Thermal properties were estimated from a Seiko TG/DTA 6300 thermal gravimetric analysis (TGA) system and a thermal analysis instrument of DSC-Q100 differential scanning calorimetry (DSC) under a nitrogen atmosphere at a heating rate of 10 and 6 °C/min, respectively.

Atomic force microscopy (AFM) measurements were obtained with a NanoScope IIIa AFM at room temperature. Commercial silicon cantilevers with typical spring constants of 21-78 N m¹⁻ was used to operate the AFM in tapping mode.

The morphology of the nanowires was determined using a field emission scanning electron microscope (SEM, JEOL JSM-6330F). The FE-SEM images were taken using a microscope operated at an accelerating voltage of 10 kV. Before imaging, the samples were sputtered with Pt.

UV-vis absorption spectrum was recorded on a Hitachi U-4100 spectrophotometer. For the thin film spectra, PIs was first dissolved in chloroform (10 mg/mL), followed with filtering through a 0.45 μ m pore size PTFE membrane syringe filter, and then spin-coated at a speed rate of 1000 rpm for 60 s onto quartz substrate. Cyclic voltammetry (CV) was performed with the use of a three-electrode cell in which ITO (PI films areas were about $0.5 \times 0.7 \text{ cm}^2$) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were taken with the use of a Ag/AgCl, KCl (sat.) reference electrode. The electrochemical properties of the PI films were detected under 0.1 M anhydrous acetonitrile solution containing tetrabutylammonium perchlorate (TBAP) as electrolyte. The thickness of polymer film was measured with a microfigure measuring instrument (Surfcorder ET3000, Kosaka Laboratory Ltd.). The electrical characterization of the memory device was performed by a Keithley 4200-SCS semiconductor parameter analyzer in a glovebox. For the capacitance measurement, metal-insulator-semiconductor (MIS) structure was fabricated by depositing gold electrodes on the polymer-coated n-type Si(300) wafers. The capacitance of the bilayer dielectrics was measured on the MIS structure using Keithley 4200-SCS equipped with a digital capacitance meter (model 4210-CVU).

Computational Methodology. Theoretical molecular simulation of the PIs was calculated through the Gaussion 03 program package. Density functional theory (DFT) method, using Becke's threeparameter functional with the Lee, Yang, and Parr correlation functional method (B3LYP) with 6-31G(d), was exploited for the optimization of ground-state molecular geometry, and electronic properties.

RESULTS AND DISCUSSION

Monomer Synthesis. The synthetic routes for 2,5-bis(4aminophenylenesulfanyl)selenophene (APSP) and 2,5-bis(4aminophenylenesulfanyl)thiophene (APST) are shown in Scheme 1b.

APSP was prepared by a two-step procedure with selenophene as a starting material. Selenophene was then halogenated with N-bromosuccinimide to give 2,5-dibromoselenophene,³⁹ which was further reacted with *p*-aminothiophenol under the Ullman reaction condition to yield APSP. On the other hand, APST was synthesized by aromatic nucleophilic substitution between *p*-aminothiophenol and 2,5-dichlorothiophene. The structure of APSP was characterized by NMR spectroscopy. The ¹H and ¹³C NMR spectra of APSP are shown in Figure S1 of Supporting Information with assignments of all peaks. The signal at 5.48 ppm in Figure S1(a) of the Supporting Information is assigned to the four protons of the amino groups (Ha). The characteristic protons of the selenophene group (Hd) are observed at 6.99 ppm in the spectrum. On the other hand, the protons of the aromatic rings containing an amino moiety (Hb, Hc) are shown at 6.54 and 7.15 ppm, respectively. In the ¹³C NMR spectrum (Figure S1(b) of Supporting Information), the six carbon signals, which are consistent with the expected structure, are observed. Among these peaks, three signals are assigned to quaternary carbons by a nondistored enhancement by polarization transfer-135 (DEPT-135) measurement. In addition, the structure of APSP was confirmed by elemental analysis. The desired structure of APST was also confirmed by ¹H NMR, ¹³C NMR (shown in Figure S2 of Supporting Information), and elemental analysis.

Synthesis and Characterization of Pls. Both PIs were prepared by a two-step polycondensation of aromatic dianhydride such as 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) with APSP or APST via soluble poly(amic acid) (PAA) precursors, followed by chemical imidization using acetic anhydride and pyridine as shown in Scheme 1b. The chemical structures of both PIs were confirmed by ¹H NMR, as shown in Figure 1. For the case of PI(APSP-6FDA), the characteristic signals of the three protons of phthalimide moiety



Figure 1. ¹H NMR spectra of PI(APSP-6FDA) and PI(APST-6FDA) in DMSO-*d*₆.

are observed at 8.13, 7.93, and 7.74 ppm while the multiple signals in the range of 7.52-7.43 ppm are assigned to the protons of selenophene group and aromatic rings. Similar to PI(APSP-6FDA), the signals of the three protons of phthalimide moiety of PI(APST-6FDA) are observed at 8.13, 7.93, and 7.74 ppm while the protons signals in the range of 7.49-7.40 ppm are attributed to the thiophene group and aromatic rings. The complete conversion from PAAs to PIs was also confirmed by FT-IR spectra. As shown in Figure S3 of Supporting Information, both PIs exhibit similar IR absorption peaks which originate from the imide moieties located at 1786 cm^{-1} ($\nu_{as,C=0}$), 1720 cm⁻¹ ($\nu_{s,C=0}$), and 1365 cm⁻¹ (ν_{C-N}). In addition, typical absorption peaks due to the aromatic thioether (Ar-S-Ar) are observed at 1257 cm⁻¹. The experimental carbon, hydrogen, and nitrogen contents of the prepared PIs are in a good agreement with the theoretical contents. The number-average molecular weights (M_n) of PI(APSP-6FDA) and PI(APST-6FDA) are 49100 and 43000, respectively, as determined by SEC.

All polymers are readily soluble in common organic solvents such as tetrahydrofuran (THF), DMF, DMAc, NMP, and chloroform. The high solubility may be attributed to the flexible thioether linkages and hexafluoroisopropyl moieties in the polymer structure. The thermal stability of these two PIs was evaluated by TGA and DSC under a nitrogen atmosphere. The 5% weight-loss temperatures ($T_{\rm d5}$) of PI(APSP-6FDA) and PI(APST-6FDA) are 423 and 420 °C, respectively. These PIs not only show high thermal stability but also possess high glass transition temperatures ($T_{\rm g}$) of 250 and 242 °C for PI(APSP-6FDA) and PI(APT-6FDA), respectively. The excellent thermal properties of these PIs are expected to satisfy the requirement of heat resistance in electronic industry.

Optical and Electrochemical Properties. Figure 2a shows the optical absorption spectra of three PIs in solid state films on quartz substrates. The absorption peak maximum wavelengths of PI(APSP-6FDA), PI(APST-6FDA), and PI-(ODA-6FDA) are observed at 288 nm (4.31 eV), 299 nm (4.15 eV) and 224 nm (5.54 eV), respectively. They are attributed to the $\pi - \pi^*$ transition of selenophene (HOMO \rightarrow LUMO4) (4.38 eV), thiophene (HOMO \rightarrow LUMO5) (4.68 eV), and oxidianiline (HOMO \rightarrow LUMO5) (5.55 eV) according to the theoretical analysis shown in Figure 3, Figures S4 (Supporting Information), and Figure S5 (Supporting Information). The band gaps of PI(APSP-6FDA), PI(APST-6FDA) and PI(ODA-6FDA) estimated from the onset of the absorption spectra are 3.26, 3.59, and 3.76 eV, respectively. The order of the band gaps are consistent with the electron-donating ability and the resulted intramolecular charge transfer, APSP > APST > ODA. The electrochemical properties of the PIs were measured by cyclic voltammetry (CV) obtained in anhydrous acetonitile using tetrabutylammonium perchlorate as electrolyte. The highest occupied molecular orbital (HOMO) energy levels of the PIs were calculated from the onset of oxidation waves in CV with reference to ferrocence (4.8 eV) by the following equation: HOMO = $-(E^{\text{onset}} + 4.8 - E_{\text{ferrocene}})$. Besides, the lowest unoccupied molecular orbital (LUMO) energy levels were estimated from the difference between the optical band gap and HOMO level.⁴⁰ The HOMO levels of PI(APSP-6FDA), PI(APST-6FDA) and PI(ODA-6FDA) are -5.48, -5.63, and -5.72 eV, respectively. These results indicate that the selenophene moiety with the highest HOMO (or smallest ionization potential) may result in the larger degree of charge transfer rather than the other two PIs. Besides, PI(APSP-



Figure 2. (a) UV-vis absorption spectra of PIs. (b) Energy diagram of BPE-PTCDI and PIs.

6FDA) and PI(APST-6FDA) apparently exhibit more intense absorption intensity in the wavelength above 360 nm as compared to PI(ODA-6FDA). It indicates that the selenophene and thiophene moieties provide a stronger probability of charge transferring than oxidianiline moieties. Furthermore, due to the heavy atom effect, selenophene is the stronger donor than thiophene, leading to trap the charges deep. Furthermore, the molecular conformation and electronic properties were calculated at the B3LYP/6-31G(d). Figure 3 shows HOMO orbitals are localized at the donor moieties, APSP, while LUMO orbitals are localized at the acceptor moieties, 6FDA. This implies that the charge transfer between donor and acceptor moieties occurs in the excited state of the PIs. However, the charges can be further segregated under an electric field and delocalized to the selenophene, thus stabilizing the charge transfer state.

Surface Structure Characterizations. The water contact angles for PI(APSP-6FDA), PI(APST-6FDA), and PI(ODA-6FDA) surfaces are around 88°, 81°, and 71°, respectively, which exhibit nonpolar and hydrophobic characteristics (see Figure S6 of Supporting Information). This also indicates that PI(APSP-6FDA) possess the smallest surface energy among the three PIs. The morphology of the PIs prepared through spin coating on bare SiO₂ substrates show smooth surface with small root-mean-square value of 0.2–0.5 nm, as shown in the AFM image (Figure S7 of Supporting Information). The surface structure of BPE-PTCDI on the PIs was characterized by AFM, as shown in Figure 4. The BPE-PTCDI OFET memory device can be mainly attributed to the chemical nature of the BPE-

Article



Figure 3. Molecular orbitals of the PI(APSP-6FDA).

PTCDI and polymer electrets, since the surface roughness of the polymer electrets are similar.⁴¹ The grain sizes of BPE-PTCDI grown on the PI(APSP-6FDA), PI(APST-6FDA), and PI(ODA-6FDA) surfaces are 205, 136, and 73 nm, respectively. The larger grain size on PI(APSP-6FDA) is probably owing to the lowest surface energy of PI(APSP-6FDA), allowing better interconnection between grains during BPE-PTCDI deposition.⁴²

OFET Performance and Memory Characteristics. The memory characteristics of PI(APSP-6FDA), PI(APST-6FDA), and PI(ODA-6FDA) were examined through OFET memory devices with a bottom-gate/top-contact configuration using *n*-type BPE-PTCDI as a charge transport layer, as shown in Figure 5a. The electric output curves of the devices with PIs as electrets are shown in Figure 5, which exhibit good current modulation, well-defined linear and saturation regions. The transfer characteristics of the BPE-PTCDI OFET devices are shown in Figure 6a–c. These curves exhibit a typical *n*-type accumulation mode. The field-effect mobility is estimated from the plot of the square root of drain-to-source current $(I_{ds})^{1/2}$ versus the gate voltage (V_g) by the following equation in the saturation regime:⁴³



Figure 4. AFM topographic images of BPE-PTCDI on different polymer surface: (a) PI(APSP-6FDA), (b) PI(APST-6FDA), and (c) PI(ODA-6FDA) on 1 μ m × 1 μ m area.

$$I_{\rm ds} = \frac{WC_{\rm poly}\mu}{2L} (V_{\rm g} - V_{\rm Th})^2 \tag{1}$$

where μ is the field-effect mobility, C_{poly} is the gate dielectric capacitance per unit area and V_{Th} denotes the threshold voltage. The capacitances (C_{Tot}) of the different gate dielectrics were measured at 10 kHz. The bare 300-nm-thick SiO₂ wafer has the capacitance of 10.9 nF cm⁻². The capacitances of PI(APSP-6FDA), PI(APST-6FDA), and PI(ODA-6FDA) on the bare SiO₂ are 8.1, 8.63, and 8.7, respectively. The relations between capacitance (C_{Tot}) of the device, SiO₂ layer (C_{SiO_2}), polymer electrets (C_{poly}) and polymer dielectric constant (ε) are defined as the following:

$$\frac{1}{C_{\rm Tot}} = \frac{1}{C_{\rm poly}} + \frac{1}{C_{\rm SiO_2}}$$
(2)

$$C_{\text{poly}} = \frac{\varepsilon_o \varepsilon}{d} \tag{3}$$

Here ε_o and d are the vacuum permittivity and the insulator thickness. The dielectric constants of PI(APSP-6FDA), PI-(APST-6FDA), and PI(ODA-6FDA) estimated from the measured capacitance are 2.16, 2.85, and 3.24, respectively. Note that the dielectric constant of PI(ODA-6FDA) is in a good agreement with that reported in the literature.⁴⁴ The order on the mobility of the BPE-PTCDI devices with different polymer electrets is PI(APSP-6FDA) ($(3.6 \pm 0.07) \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) > PI(APST-6FDA) ($(2.4 \pm 0.06) \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). It is



Figure 5. (a) Schematic structure of the BPE-PTCDI thin film based OFET memory device. (b) Output characteristics of the OFET device with PI(APSP-6FDA) as electret.

consistent with the grain size of BPE-PTCDI on the three PIs. The grain size on the PI(APSP-6FDA), PI(APST-6FDA), and PI(ODA-6FDA) surfaces are 205, 136, and 73 nm, respectively. The larger grain sizes and reduced grain boundaries generally result in higher charge-charier mobilities.^{45–47} Furthermore, the interfacial roughness also affect the OFET mobility. The roughness of the PI spin-coated films on bare SiO₂ substrates



Figure 6. Shifts in transfer curves for BPE-PTCDI OFET memory device with (a)PI(APSP-6FDA), (b) PI(APST-6FDA), and (c) PI(ODA-6FDA) as polymer electrets.

are 0.247, 0.432, and 0.451 nm for PI(APSP-6FDA), PI(APST-6FDA), and PI(ODA-6FDA) respectively. Interfacial roughness may reduce mobility due to charge scattering.⁴⁸ These results reveal that the larger grain size of BPE-PTCDI and the small roughness of polymer electrets surface can produce the high-mobility OFET-type memory devices. The threshold voltages $(V_{\rm Th})$ and the $I_{\rm on}/I_{\rm off}$ current ratios range from 2 to 8 V and 10³ to 10⁴, respectively, as summarized in Table 1. The small

threshold voltage observed from the devices with polymer electrets is probably due to the passivation the silanol groups through the polymer electrets spin-coated on SiO₂ surface.⁴⁹

To investigate the effects of bias voltages, the bias voltages ranged from ± 40 to ± 100 V were applied on the devices, as shown in Figure S9. More negative shifts with increasing writing bias are observed. However, the increase in the negative shift is obtained with the gate bias ranged from -40 to -80 V. The memory windows keep near a constant of about -42 V even though applying a writing bias more than -80 V, indicating that charge trapping is saturated in the writing bias of -80 V. Therefore, we applied the gate voltage of -80 V for controlling memory behaviors of the devices. The drain current of Figure 6a–c was measured with V_d = 100 V. When applied a negative gate bias ($V_{g} = -80$ V, $V_{d} = 0$ V for 1 s), the entire transfer curves of PI(APSP-6FDA), PI(APST-6FDA), and PI(ODA-6FDA) are substantially shifted in the negative direction with threshold voltages $(V_{\rm Th})$ of -42, -21, and -5 V, respectively, served as the "writing" process. This shift leads to a high drain current (ON state) at $V_{\sigma} = 0$ V. When applying a reverse gate bias ($V_g = 80$ V, $V_d = 0$ V for 1s), the transfer curves are shifted in the positive direction with threshold voltages of 21, 18, and 3 V for PI(APSP-6FDA), PI(APST-6FDA), and PI(ODA-6FDA), respectively, served as the "erasing" process. Note that the shifting range of the transfer curves through applying a writing and erasing gate bias is defined as the memory windows. The memory windows between writing and erasing process are 63, 42, and 8 V for PI(APSP-6FDA), PI(APST-6FDA), and PI(ODA-6FDA), respectively, which are probably related to the electrondonating characteristics of the PIs. The strong electrondonating moieties, selenophene and thiophene moieties are able to provide a higher probability to enhance charge transfer than oxidianiline moieties. Furthermore, due to the heavy-atom effect, the selenophene moiety is the stronger donor than thiophene moiety, leading to the more stabilized chargetransferred states in PI(APSP-6FDA). As applying a negative gate pulse (writing process), a large amount of holes are induced through BPE-PTCDI from the source/drain electrode and then tend to transfer to the HOMO levels of the PI electrets. The electrons of BPE-PTCDI are easily accumulated at the interface between BPE-PTCDI and the PI electrets due to a built-in electric field induced from retained holes, even though removing the external gate voltages. Therefore, the negative shifts in the transfer curves are observed. As compared to the other polymer electrets, PI(APSP-6FDA) possesses the highest HOMO energy level may facilitate a large amount of holes transfer from BPE-PTCDI to PI(APSP-6FDA), leading to a larger negative V_{Th} shift. PI(APST-6FDA) and PI(ODA-6FDA) show similar theoretical dipole moment of around 3.00 D, smaller than that of PI(APSP-6FDA) (4.30 D). The larger polarity of PI(APSP-6FDA) may be attributed to heterocyclic selenophene with polarizable selenium atoms. The high dipole moment of polyimide may play important role in the stabilization of trapped charges in the polymer electrets, when applying an external gate voltage. Therefore, both energy levels and molecular polarization may synergistically enhance the charge storage ability in the OFET device with PI(APSP-6FDA) as dielectric layer.

On the other hand, Kim et al.¹⁸ proposed a model, the electric field in the insulator layer (E_i) can be expressed by the following equation:

Table 1. Characteristics of BPE-PTCI based	OFET Memory	Devices with Pol	ymer Electrets
--	-------------	------------------	----------------

	electrets	mobility $[cm^2 V^{-1} s^{-1}]$	on/off ^a	memory window ^b [V]
thin film	PI(APSP-6FDA)	$(3.6 \pm 0.07) \times 10^{-3}$	8.7×10^{3}	63
	PI(APST-6FDA)	$(2.4 \pm 0.06) \times 10^{-3}$	1.4×10^{3}	41
	PI(ODA-6FDA)	$(1.8 \pm 0.11) \times 10^{-3}$	-	8
nanowires	PI(APSP-6FDA)	$(7.5 \pm 0.05) \times 10^{-2}$	6.2×10^{3}	82
	PI(APST-6FDA)	$(5.6 \pm 0.12) \times 10^{-2}$	3.7×10^{3}	64
	PI(ODA-6FDA)	$(2.1 \pm 0.09) \times 10^{-2}$	1.3×10^{3}	43
¹ On /off ducin summent up	tion of reading at $V = 0 V^{b}$	AV is defined as V V		

"On/off drain current ratios of reading at $V_{\rm g}$ = 0 V. " $\Delta V_{\rm Th}$ is defined as $V_{\rm Th}$ (erasing) – $V_{\rm Th}$ (writing).

$$E_i = \frac{V_g}{d_i + d_j \left(\frac{\varepsilon_i}{\varepsilon_j}\right)} \tag{4}$$

Here V_{g} is the applied gate voltage and $d_{ij} \varepsilon_{i}$ and $d_{ij} \varepsilon_{i}$ are the thickness and dielectric constant of the polymer electret layer and SiO_{2} , respectively. The estimation of E_i for the various 60 nm thick polymer electret layers after the application of V_g = 100 V is as follows: 4.24 \dot{MV} cm⁻¹ (PI(APSP-6FDA)); 3.43 MV cm⁻¹ (PI(APST-6FDA)); 3.09 MV cm⁻¹ (PI(ODA-6FDA)). The electric field was inversely proportional to the dielectric constant. Moreover, the higher electric fields in polymer electrets may affect the $V_{\rm Th}$ shifts in the transfer curves. After the charges are transferred to the polymer electrets, most holes would become trapped deep within the electret, and remain as space charges in the polymer electrets. Furthermore, the shift on the threshold voltage is enhanced with the electric filed. PI(APSP-6FDA) reveals the largest negative shift of the threshold voltages, since PI(APSP-6FDA) has the smallest dielectric constant, resulting in the highest electric field. The above result clearly indicates that the PI(APSP-6FDA) with the smallest ionization potential and largest electric field lead to more holes transferred from BPE-PTCDI to PI(APSP-6FDA) among the studied donoracceptor PIs.

We prepared the BPE-PTCDI thin film device on a bare substrate. The OFET mobility of the BPE-PTCDI thin film device was 1.8×10^{-3} cm² V⁻¹ s⁻¹. The BPE-PTCDI device on the bare substrates showed slightly lower charge mobilities, compared to that on the D–A PIs, probably because the hydroxyl groups on the bare SiO₂, acted as charge traps to reduce charge transport. Besides, the BPE-PTCDI morphology on bare SiO₂ substrates without PI film showed abundant gain boundaries (Figure S10 in Supporting Information), which also acted as charge traps, led to the inferior OFET performance. The thin-film devices without polymer electrets only exhibited a memory window of 5 V, much smaller than the devices with PI(APSP-6FDA) or PI(APST-6FDA). This indicates that the donor–acceptor PI layer significantly improved charge storing ability of the devices.

The time during which the stored charge is retained in the dielectric layer is defined as the retention time. Figure 7 is the retention time of the BPE-PTCDI thin film with PI(APSP-6FDA) or PI(APST-6FDA) as electrets. The retention time of the ON and OFF states of the device at a gate voltage of 0 V are maintained for 10^4 s with a high on/off current ratio of around 10^3 . This long retention time indicates that the OFET memory device based on donor–acceptor PIs as polymer electrets is a promising candidate for organic nonvolatile memories. The multiple switching stability of the device using PI(APSP-6FDA) and PI(APST-6FDA) as electrets were evaluated through write–read–erase–read (WRER) cycles, as



Figure 7. Retention time testing of the OFET memory devices based on BPE-PTCDI thin film with (a) PI(APSP-6FDA) and (b) PI(APST-6FDA) as electrets.

shown in Figure 8. The operation conditions of WRER cycles are summarized as follows. The drain current was measured at $V_{\rm d}$ =100 V. The writing, reading and erasing were at the gate voltages of -80, 0, and +80 V, respectively. The ON/OFF current ratios more than 10³ can be achieved in WRER cycles. The device can be operated over 100 cycles. The good stability and reversibility reveal that the OFET memories with polyimide electrets have potential for the applications of nonvolatile flash-type memories.

BPE-PTCDI Nanowires OFET Memory Performance. For comparison, we prepared the nanowires of BPE-PTCDI with a diameter of 200 nm through a solvent-exchanged method, as shown in Figure 9a. Parts b–d of Figure 9 exhibit



Figure 8. (a) Gate voltage applied to the WRER cycles. Reversible current response to the WRER cycles of memory device with (b) PI(APSP-6FDA) and (c) PI(APST-6FDA) as electrets. The drain current was measured at $V_d = 100$ V. The writing, reading, and erasing were at the gate voltages of -80, 0, and +80 V, respectively.

the transfer curves of the OFET memory devices based on the BPE-PTCDI nanowires. However, the width (W) and length (L) of the individual nanowires crossing the source and drain electrodes were used to estimate the active channel area based on the SEM images for estimating charge mobility. The OFET mobility of the BPE-PTCDI nanowires device with PI(APSP-6FDA) is 7.5×10^{-2} cm² V⁻¹ s⁻¹, which is an order of magnitude higher than the thin film device. Because of the thin film contains abundant gain boundaries as charge traps, reducing charge transport, and leading to the inferior OFET performance compared to nanowires. Furthermore, the



Figure 9. (a) SEM images of the BPE-PTCDI nanowires induced by methanol nonsolvent into *o*-dichlorobenzene on the PI(APSP-6FDA) substrate; (b) Shifts in transfer curves of the BPE-PTCDI OFET memory device with PI(APSP-6FDA), (c) PI(APST-6FDA), and (d) PI(ODA-6FDA) as polymer electrets.

memory windows of the nanowires devices using the electret of PI(APSP-6FDA), PI(APST-6FDA), and PI(ODA-6FDA) are 82, 64, and 43 V, respectively. This is probably due to the enhanced electrical field of the nanowires in the interface. The electric field of nanowires was shown to be much higher than that of thin film because the electric field was inverse proportional to the diameter.⁵⁰ Consequently, the high electric field of nanowires led to the OFET memory device with better performances compared to the thin film device.

CONCLUSIONS

We have successfully synthesized two new donor-acceptor PIs, PI(APSP-6FDA) and PI(APST-6FDA), as polymer electrets for BPE-PTCDI-based OFET memory devices. The theoretical and experimental results showed the order of the electrondonating ability selenophene > thiophene> oxidianiline and resulted in the degree of intramolecular charge transfer in PIs, APSP > APST > ODA. The grain sizes of BPE-PTCDI grown on the PI(APSP-6FDA), PI(APST-6FDA), and PI(ODA-6FDA) surfaces are 205, 136, and 73 nm, respectively, attributed to the hydrophobicity of the PIs. The BPE-PTCDI OFET memory device based on the PI(APSP-6FDA) electret exhibited the highest field-effect mobility and the largest memory window compared to the others because the strong electron-donating led to the efficient charge transfer form BPE-PTCDI to PI(APSP-6FDA), and resulted in largest shifts of threshold voltages. Moreover, PI(APSP-6FDA) or PI (APST-6FDA) transferred the charges from BPE-PTCDI to electrets easier than the oxidianiline moiety of PI(ODA-6FDA). Furthermore, due to the heavy-atom effect, the selenophene moiety is the stronger donor than thiophene moiety, leading to the more stabilized charge-transferred states in PI(APSP-6FDA). Besides, the BPE-PTCDI nanowires based OFET memory device exhibited higher OFET mobility and memory window compared to the thin film device. The present study suggested that the donor-acceptor polyimide electrets could have potential applications for high performance nonvolatile OFET memory devices.

ASSOCIATED CONTENT

S Supporting Information

NMR spectra of the monomers, APSP and APST, FTIR spectra of PI(APSP-6FDA) and PI(APST-6FDA), molecular orbitals of the PI(APST-6FDA) and PI(ODA-6FDA), contact angles of PI(APSP-6FDA), PI(APST-6FDA), and PI(ODA-6FDA), atomic force microscopy (AFM) topographies of PI(APSP-6FDA), PI(APST-6FDA), and PI(ODA-6FDA) spin-coated on bare SiO₂ substrates, output characteristics of the OFET device, and the shifted I-V curves. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mial: (W.-C.C.) chenwc@ntu.edu.tw; (M.U.) ueda.m.ad@ m.titech.ac.jp.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support from National Science Council of Taiwan is highly appreciated.

REFERENCES

- (1) Yang, Y.; Ouyang, J.; Ma, L. P.; Tseng, R. J. H.; Chu, C. W. Adv. Funct. Mater. 2006, 16, 1001.
- (2) Cho, B.; Song, S.; Ji, Y.; Kim, T.-W.; Lee, T. Adv. Funct. Mater. 2011, 21, 2806.
- (3) Ling, Q.-D.; Liaw, D.-J.; Zhu, C.; Chan, D. S.-H.; Kang, E.-T.; Neoh, K.-G. Prog. Polym. Sci. 2008, 33, 917.
- (4) Guo, Y.; Yu, G.; Liu, Y. Adv. Mater. 2010, 22, 4427.
- (5) Sekitani, T.; Yokota, T.; Zschieschang, U.; Klauk, H.; Bauer, S.; Takeuchi, K.; Takamiya, M.; Sakurai, T.; Someya, T. *Science* **2009**, *326*, 1516.
- (6) Guo, Y.; Di, C.-a.; Ye, S.; Sun, X.; Zheng, J.; Wen, Y.; Wu, W.; Yu, G.; Liu, Y. *Adv. Mater.* **2009**, *21*, 1954.
- (7) Schroeder, R.; Majewski, L. A.; Grell, M. Adv. Mater. 2004, 16, 633.
- (8) Singh, T. B.; Marjanovic, N.; Matt, G. J.; Sariciftci, N. S.; Schwodiauer, R.; Bauer, S. Appl. Phys. Lett. 2004, 85, 5409.
- (9) Leong, W. L.; Lee, P. S.; Lohani, A.; Lam, Y. M.; Chen, T.; Zhang, S.; Dodabalapur, A.; G. Mhaisalkar, S. *Adv. Mater.* **2008**, *20*, 2325.
- (10) Leong, W. L.; Mathews, N.; Mhaisalkar, S.; Lam, Y. M.; Chen, T.; Lee, P. S. J. Mater. Chem. 2009, 19, 7354.
- (11) Leong, W. L.; Mathews, N.; Tan, B.; Vaidyanathan, S.; Dotz, F.; Mhaisalkar, S. J. Mater. Chem. 2011, 21, 8971.
- (12) Baeg, K.-J.; Noh, Y.-Y.; Sirringhaus, H.; Kim, D.-Y. Adv. Funct. Mater. 2010, 20, 224.
- (13) Liu, B.; McCarthy, M. A.; Rinzler, A. G. Adv. Funct. Mater. 2010, 20, 3440.
- (14) Baeg, K. J.; Noh, Y. Y.; Ghim, J.; Kang, S. J.; Lee, H.; Kim, D. Y. *Adv. Mater.* **2006**, *18*, 3179.
- (15) Baeg, K.-J.; Noh, Y.-Y.; Ghim, J.; Lim, B.; Kim, D.-Y. Adv. Funct. Mater. 2008, 18, 3678.
- (16) Ling, Q.-D.; Chang, F.-C.; Song, Y.; Zhu, C.-X.; Liaw, D.-J.; Chan, D. S.-H.; Kang, E.-T.; Neoh, K.-G. J. Am. Chem. Soc. **2006**, 128, 8732.
- (17) Ouyang, J.; Chu, C.-W.; Szmanda, C. R.; Ma, L.; Yang, Y. Nat. Mater. 2004, 3, 918.
- (18) Wei, D.; Baral, J. K.; Osterbacka, R.; Ivaska, A. J. Mater. Chem. 2008, 18, 1853.
- (19) Fang, Y.-K.; Liu, C.-L.; Li, C.; Lin, C.-J.; Mezzenga, R.; Chen, W.-C. Adv. Funct. Mater. 2010, 20, 3012.
- (20) Kuorosawa, T.; Chueh, C.-C.; Liu, C.-L.; Higashihara, T.; Ueda, M.; Chen, W.-C. *Macromolecules* **2010**, *43*, 1236.
- (21) Naber, R. C. G.; Tanase, C.; Blom, P. W. M.; Gelinck, G. H.; Marsman, A. W.; Touwslager, F. J.; Setayesh, S.; de Leeuw, D. M. Nat. Mater. 2005, 4, 243.
- (22) Leong, W. L.; Mathews, N.; Tan, B.; Vaidyanathan, S.; Dotz, F.; Mhaisalkar, S. J. Mater. Chem. 2011, 21, 5203.
- (23) Hsu, J.-C.; Lee, W.-Y.; Wu, H.-C.; Sugiyama, K.; Hirao, A.; Chen, W.-C. J. Mater. Chem. 2012, 22, 5820.
- (24) Mal'tsev, E. I.; Brusentseva, M. A.; Lypenko, D. A.; Berendyaev, V. I.; Kolesnikov, V. A.; Kotov, B. V.; Vannikov, A. V. *Polym. Adv. Technol.* **2000**, *11*, 325.
- (25) Mühlbacher, D.; Brabec, C. J.; Sariciftci, N. S.; Kotov, B. V.; Berendyaev, V. I.; Rumyantsev, B. M.; Hummelen, J. C. *Synth. Met.* **2001**, *121*, 1609.
- (26) Wang, Z. Y.; Qi, Y.; Gao, J. P.; Sacripante, G. G.; Sundararajan, P. R.; Duff, J. D. *Macromolecules* **1998**, *31*, 2075.
- (27) Tian, G.; Wu, D.; Qi, S.; Wu, Z.; Wang, X. Macromol. Rapid Commun. 2011, 32, 384.
- (28) Liu, Y.-L.; Wang, K.-L.; Huang, G.-S.; Zhu, C.-X.; Tok, E.-S.; Neoh, K.-G.; Kang, E.-T. *Chem. Mater.* **2009**, *21*, 3391.
- (29) Wang, K.-L.; Liu, Y.-L.; Shih, I. H.; Neoh, K.-G.; Kang, E.-T. J. Polym. Sci., Part A: Polym. Chem. 2010, 48, 5790.
- (30) Liu, C.-L.; Kurosawa, T.; Yu, A.-D.; Higashihara, T.; Ueda, M.; Chen, W.-C. J. Phys. Chem. C **2011**, 115, 5930.
- (31) Lee, W.-Y.; Kurosawa, T.; Lin, S.-T.; Higashihara, T.; Ueda, M.; Chen, W.-C. *Chem. Mater.* **2011**, *23*, 4487.

(32) You, N.-H.; Chueh, C.-C.; Liu, C.-L.; Ueda, M.; Chen, W.-C. *Macromolecules* **2009**, *42*, 4456.

(33) Liu, Y.-L.; Ling, Q.-D.; Kang, E.-T.; Neoh, K.-G.; Liaw, D.-J.; Wang, K.-L.; Liou, W.-T.; Zhu, C.-X.; Chan, D. S.-H. *J. Appl. Phys.* **2009**, *105*, 044501.

(34) Hahm, S. G.; Choi, S.; Hong, S.-H.; Lee, T. J.; Park, S.; Kim, D. M.; Kwon, W.-S.; Kim, K.; Kim, O.; Ree, M. *Adv. Funct. Mater.* **2008**, *18*, 3276.

(35) Hahm, S. G.; Choi, S.; Hong, S.-H.; Lee, T. J.; Park, S.; Kim, D. M.; Kim, J. C.; Kwon, W.; Kim, K.; Kim, M.-J.; Kim, O.; Ree, M. J. Mater. Chem. 2009, 19, 2207.

(36) Kim, K.; Park, S.; Hahm, S. G.; Lee, T. J.; Kim, D. M.; Kim, J. C.; Kwon, W.; Ko, Y.-G.; Ree, M. J. Phys. Chem. B **2009**, *113*, 9143.

(37) Chang, C.-C.; Chen, W.-C. Chen. Mater. 2002, 14, 4242.
(38) Oh, J. H.; Lee, H. W.; Mannsfeld, S.; Stoltenberg, R. M.; Jung,

E.; Jin, Y. W.; Kim, J. M.; Yoo, J.-B.; Bao, Z. Proc. Natl. Acad. Sci. U.S.A. 2009, 106, 6065.

(39) Kim, Y. M.; Lim, E.; Kang, I.-N.; Jung, B.-J.; Lee, J.; Koo, B. W.; Do, L.-M.; Shim, H.-K. *Macromolecules* **2006**, *39*, 4081.

(40) Liu, C.-L.; Hsu, J.-C.; Chen, W.-C.; Sugiyama, K.; Hirao, A. ACS Appl. Mater. Interfaces **2009**, *1*, 1974.

(41) Yoon, M.-H.; Kim, C.; Facchetti, A.; Marks, T. J. J. Am. Chem. Soc. 2006, 128, 12851.

(42) Ma, H.; Yip, H.-L.; Huang, F.; Jen, A. K. Y. Adv. Funct. Mater. 2010, 20, 1371.

(43) Zaumseil, J.; Sirringhaus, H. Chem. Rev. 2007, 107, 1296.

(44) Lee, C.; Shul, Y.; Han, H. J. Polym. Sci., Part B: Polym. Phys. 2002, 40, 2190.

(45) Verlaak, S.; Arkhipov, V.; Heremans, P. Appl. Phys. Lett. 2003, 82, 745.

(46) Bao, Z.; Lovinger, A. J.; Dodabalapur, A. Appl. Phys. Lett. 1996, 69, 3066.

(47) Torsi, L.; Dodabalapur, A.; Rothberg, L. J.; Fung, A. W. P.; Katz, H. E. Science **1996**, 272, 1462.

(48) Kingon, A. I.; Maria, J.-P.; Streiffer, S. K. Nature 2000, 406, 1032.

(49) Chua, L.-L.; Zaumseil, J.; Chang, J.-F.; Ou, E. C. W.; Ho, P. K. H.; Sirringhaus, H.; Friend, R. H. *Nature* **2005**, *434*, 194.

(50) Fuhrer, M. S.; Kim, B. M.; Durkop, T.; Brintlinger, T. Nano Lett. 2002, 2, 755.