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Supporting Information

High Performance Polymers and their PCBM Hybrids for Memory Device Application

By Hung-Ju Yen,[‡] Chih-Jung Chen,[‡] Jia-Hao Wu, and Guey-Sheng Liou* Functional Polymeric Materials Laboratory, Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan Tel: +886-2-336-5315; Fax: +886-2-336-5237; E-mail: <u>gsliou@ntu.edu.tw</u>

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Experimental Section

Materials

4,4'-Diamino-4"-hydroxytriphenylamine (1) was prepared according to the literature.¹⁷ Tetrabutylammonium perchlorate (TBAP) (ACROS) was recrystallized twice by ethyl acetate under nitrogen atmosphere and then dried *in vacuo* prior to use. All other reagents were used as received from commercial sources.

Polymer Synthesis

The polyimide **OHTPA-6FPI** was synthesized from diamine monomer **1** and dianhydride 4,4'-(hexafluoroisopropylidene)diphthalic anhydride via one-step high-temperature polycondensation. To a solution of 291.4 mg (1.0 mmol) of diamine **1** in 5.0 mL of *m*-cresol, 444.2 g (1.00 mmol) of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride was added in one portion, then 239.0 ul of isoquinoline was added. The mixture was heated at room temperature for 5h, and then at 210 °C for 15hr. The obtained polymer solution was poured slowly into 300 mL of stirred methanol giving rise to a brown fibrous precipitate that was collected by filtration, washed thoroughly with methanol, and dried under vacuum at 100 °C. Reprecipitations of the polymer by NMP/methanol were carried out twice for further purification. Anal. Calcd (%) for $(C_{37}H_{19}F_6N_3O_5)_n$ (699.57)_n: C, 63.53 %; H, 2.74 %; N, 6.01 %. Found: C, 60.48 %; H, 2.71 %; N, 6.13 %.

The synthesis of polyamide **OHTPA-PA** was used as an example to illustrate the lowtemperature polycondensation used to produce the polyamides. A solution of 291.4 mg (1.0 mmol) of diamine **1** in 3.0 mL of *N*-methyl-2-pyrrolidone (NMP) was cooled to -25 to -30 °C on a ice/acetone bath. After 0.32 mL of propylene oxide was added to the mixture, 203.0 mg (1.0 mmol) of terephthaloyl chloride was added in to the mixture. The mixture was then stirred at -10 °C for 1 h then room temperature for 2 h. The solution was poured slowly into 200 mL of methanol. The precipitated polymer was collected by filtration, and dried at 100 °C. Reprecipitations of the polymer by NMP/methanol were carried out twice for further purification. Anal. Calcd (%) for **OHTPA-PA** ($C_{26}H_{19}N_3O_3$)_{*n*} (421.46)_{*n*}: C, 74.10 %; H, 4.54 %; N, 9.97 %. Found: C, 68.38 %; H, 5.10 %; N, 9.49 %; Anal. Calcd (%) for **OHTPA-6FPA** ($C_{35}H_{23}F_6N_3O_3$)_{*n*} (647.58)_{*n*}: C, 64.92 %; H, 3.58 %; N, 6.49 %. Found: C, 59.27 %; H, 3.84 %; N, 6.70 %.

Measurements

NMR spectra were measured on a Bruker AVIII-500MHz FT-NMR in DMSO- d_6 . The inherent viscosities were determined at 0.5 g/dL concentration using Tamson TV-2000 viscometer at 30 °C. Gel permeation chromatographic (GPC) analysis was carried out on a Waters chromatography unit interfaced with a Waters 2410 refractive index detector. Two Waters 5 μ m Styragel HR-2 and HR-4 columns (7.8 mm I. D. \times 300 mm) were connected in series with NMP as the eluent at a flow rate of 0.5 ml/min at 40 °C and were calibrated with polystyrene standards. Differential scanning calorimetry (DSC) analyses were performed on a TA Instruments Q20 in flowing nitrogen (20 cm³/min). Thermogravimetric analysis (TGA) was conducted with a TA Instruments Q50. Experiments were carried out on approximately 6-8 mg samples heated in flowing nitrogen or air (flow rate = $60 \text{ cm}^3/\text{min}$) at a heating rate of 20 °C/min. Cyclic voltammetry (CV) was performed with a CH Instruments 611B electrochemical analyzer and conducted with the use of a three-electrode cell in which ITO (polymer films area about 0.5 cm x 1.2 cm) was used as a working electrode and a platinum wire as an auxiliary electrode at a scan rate of 100 mV/s against a Ag/AgCl reference electrode in anhydrous CH₃CN, using 0.1 M of TBAP as a supporting electrolyte in nitrogen atmosphere. All cell potentials were taken by using a homemade Ag/AgCl, KCl (sat.) reference electrode. The ITO-coated glass slide was used as the working electrode, a platinum wire as the counter electrode, and a Ag/AgCl cell as the reference electrode. In situ UVvisible spectra experiments were carried out in a transparent device (Figure 4a) using Hewlett-Packard 8453 UV-Visible diode array spectrophotometer.

Fabrication and Measurement of the Memory Device

The memory device was fabricated with the configuration of ITO/thin film/Al as shown in Figure 1. The ITO glass used for memory device was precleaned by ultrasonication with water, acetone, and isopropanol each for 15 min. The hybrid thin film was prepared by the DMAc solution of polymer solutions then filtered through 0.45 μ m pore size of PTFE membrane syringe filter. Then, 250 μ L of the filtered solution was spin-coated onto the ITO glass at a rotation rate of 1000 rpm for 60 s and kept at 70 °C for 10 min under nitrogen. The film thickness was determined to be around 50 nm. Finally, a 300-nm-thick Al top electrode was thermally evaporated through the shadow mask (recorded device units of 0.5 × 0.5 mm² in size) at a pressure of 10⁻⁷ torr with a uniform depositing rate of 3-5 Å/s. The electrical characterization of the memory device was performed by a Keithley 4200-SCS semiconductor

parameter analyzer equipped with a Keithely 4205-PG2 arbitrary waveform pulse generator. ITO was used as common electrode and Al was the electrode for applying voltage during the sweep. The probe tip used 10 μ m diameter tungsten wire attached to a tinned copper shaft with a point radius <0.1 μ m (GGB Industries, Inc.).

Molecular Simulation

The Molecular simulation in this study was performed by Gaussian 09 program package. The results of value and distributions of the corresponding energy levels within each basic unit of **OHTPA-6FPI**, **OHTPA-PA**, and **OHTPA-6FPA** were investigated via density functional theory (DFT) method at the B3LYP level of theory (Beckesstyle three-parameter density functional theory using the Lee-Yang-Parr correlation functional) with the 6-31G(d) basic set.



Figure S1. ¹H (left) and ¹³C (right) NMR spectra of (a) **OHTPA-6FPI**, (b) **OHTPA-PA**, and (c) **OHTPA-6FPA**.



Figure S2. TGA thermograms of polymers at a scan rate of 20 °C/min.



Figure S3. DSC thermograms of polymers at a scan rate of 20 °C/min.



Figure S4. Absorption spectra of polymer thin films.



Figure S5. Cyclic voltammetric diagrams of polymers on an ITO-coated glass substrate over cyclic scans in 0.1 M TBAP/CH₃CN at a scan rate of 100 mV/s.



Figure S6. Current-voltage (*I-V*) characteristics of the ITO/**OHTPA-PA**:PCBM/A1 memory device with various PCBM weight fractions.



Figure S7. Current-voltage (*I-V*) characteristics of the ITO/**OHTPA-6FPA**:PCBM/Al memory device with various PCBM weight fractions.



Figure S8. Retention test on the ON and OFF states of the ITO/polymer with 2% PCBM/Al devices under a constant stress of -1 V. Polymer: (a) **OHTPA-6FPI**, (b) **OHTPA-PA**, and (c) **OHTPA-6FPA**.



Figure S9. TEM images of **OHTPA-6FPI**:PCBM spin-coating films with (a) 1 %, (b) 2 %, (c) 5 %, and (d) 10 % of PCBM weight fractions.



Figure S10. PL spectra of OHTPA-6FPI:PCBM hybrid thin films (λ_{ex} =346 nm).

Table S1. Inherent Viscosity^a and Molecular Weights^b of Polymers

Polymer	$\eta_{inh}(dL/g)$	$M_{ m w}$	$M_{\rm n}$	PDI ^c	\mathbf{DP}^d
OHTPA-6FPI	0.58	189,300	98,600	1.92	141
OHTPA-PA	0.48	74,700	28,600	2.61	68
OHTPA-6FPA	0.98	219,400	94,900	2.31	147

^{*a*} Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C. ^{*b*} Calibrated with polystyrene standards, using NMP as the eluent at a constant flow rate of 0.5 mL/min at 40 °C.

^{*c*} Polydispersity Index (M_w/M_n) . ^{*d*} Degree of Polymerization.

Code	Solubility in various solvent ^a							
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF	CHCl ₃	
OHTPA-6FPI	++	++	++	++	+	++	+-	
ОНТРА-РА	++	++	++	++	+-	+-	_	
OHTPA-6FPA	++	++	++	++	+	++	_	

Table S2. Solubility Behavior of Polymers

^{*a*} The solubility was determined with a 10 mg sample in 1 mL of a solvent. ++, soluble at room temperature; +, soluble on heating at 70°C-80°C; +-, partially soluble or swelling; -, insoluble even on heating.

Polymer ^a	$T_{g} (^{o}C)^{b}$	$T_{\rm d}^{5} (^{\rm o}{\rm C})^c$		$T_{\rm d}{}^{10}$ (°C) ^c		$R_{ m w800}(\%)^d$	LOI ^e
	_	N_2	Air	N_2	Air		
OHTPA-6FPI	324	550	530	590	580	59	41.1
OHTPA-PA	275	490	475	545	525	70	45.5
OHTPA-6FPA	314	500	480	545	520	62	42.3

Table S3. Thermal Properties of Polymers

^{*a*} The polymer film samples were heated at 300 °C for 1 h prior to all the thermal analyses.

^b Midpoint temperature of baseline shift on the second DSC heating trace (rate: 20 °C /min) of the sample after quenching from 400 °C to 50 °C (rate: 200 °C /min) in nitrogen

^c Temperature at which 5 % and 10% weight loss occurred, respectively, recorded by TGA at a heating rate of 20 °C/min and a gas flow rate of 20 cm³/min.

^dResidual weight percentages at 800 °C under nitrogen flow.

^{*e*}LOI = Limiting Oxygen Index = $(17.5 + 0.4 \times \text{char yield})$.

Polymer	UV-vis absorption of the polymer films (nm)		Oxidation (vs. Ag/Ag0	E_{g}^{b}	HOMO ^c	LUMO	
	λ_{max}	λ_{onset} -	$\frac{E_{1/2}^a}{1 \text{st}}$	- E _{onset}	(eV)	(eV)	(eV)
OHTPA-6FPI	302, 346	557	0.96	0.85	2.23	5.29	3.06
OHTPA-PA	303, 362	466	0.61	0.52	2.66	4.96	2.30
OHTPA-6FPA	300, 352	425	0.62	0.55	2.92	4.99	2.07

Table S4. Redox Potentials and Energy Levels of Polymers

^{*a*} $E_{1/2}$ (Average potential of the redox couple peaks). ^{*b*} The data were calculated from polymer films by the equation: $E_{\rm g} = 1240/\lambda_{\rm onset}$ (energy gap between HOMO and LUMO).

^c The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV; onset = 0.36V).