Electronic Supplementary Information

Electrically Bistable Memory Devices Based on Poly(triphenylamine)/PCBM Hybrids

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Experimental Section

Materials

4-Methoxytriphenylamine was prepared according to previous literature.^{S1} [6,6]-C₆₁-butyric acid methyl ester (PCBM) and chloroform (ECHO) were used without further purification. 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 polymerization procedure of the studying material **P-TPA** was synthesized via oxidative coupling reaction according to the previous literature.^{S1} To a two-necked 50 mL flask equipped with a magnetic stirrer were placed 4-methoxytriphenylamine (1 mmol) and chloroform (3 mL) under nitrogen atmosphere. A quarter portion of FeCl₃ (1 mmol; total is 4 mmol) was added to the reaction mixture at the interval of 1 h. The solution was stirred at 45 °C for 48 h then poured into a mixture of methanol containing 10% hydrochloric acid to recover the product. Collected powder was washed in dilute ammonia aqueous solution. The resulting polymer was filtrated and dried in vacuo at 120 °C for 12 h (yield: 88.1%). The resulting product exhibited enough molecular weight to afford thin films by spin-coating.

Measurement of Basic Properties

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. × 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. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 6-8 mg samples heated in flowing nitrogen or air (flow rate = 20 cm³/min) at a heating rate of 20 °C/min. Cyclic voltammetry (CV) was performed with a Bioanalytical System Model CV-27 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. 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. The

microstructure of the prepared films was examined by using a JOEL JEM-1230 transmission electron microscope (TEM). Photoluminescence (PL) spectra was measured with Fluorolog-3 spectrofluorometer.

Fabrication and Measurement of the Memory Device

The memory device was fabricated with the configuration of ITO/thin film/Al. 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 chloroform solution of **P-TPA** containing calculated PCBM, which was stirred to form homogeneous solutions then filtrated by 0.45 μ m pore size of PTFE membrane syringe filter and spin-coated at 1000 rpm for 30 seconds onto the ITO substrate and kept at 70 °C for 10 mins 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 the cathode (maintained as common), and Al was set as the anode during the voltage 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.).

Results and Discussion

Polymer Synthesis

P-TPA was synthesized via oxidative coupling reaction using $FeCl_3$ as catalyst. The inherent viscosities, weight-average molecular weights (*M*w), and polydispersity (PDI) of resulting polymer are summarized in Table S1. The solubility behavior of resulting polymer was investigated in some organic solvent qualitatively, and the results are also summarized in Table S1. P-TPA showed well solubility in organic solvent such as *N*-methyl-2-pyrrolidinone (NMP) and CHCl₃.

Thermal Properties

The thermal properties of obtained polymers were recorded by TGA, and the thermal behavior data are summarized in Table S2. Typical TGA curves **P-TPA** are depicted in in Fig. S2. **P-TPA** exhibited good thermal stability with insignificant weight loss up to 500 °C under both nitrogen and air atmosphere. The decomposition temperature at a 10 % weight-loss of these polymers in nitrogen and air were recorded at 500 and 530 °C, respectively. The amount of carbonized residue (char yield) of **P-TPA** in a nitrogen atmosphere was more than 75 % at 800 °C, leading a high limiting oxygen index (LOI) 48.^{S2} The high char yields of **P-TPA** can be ascribed to their high aromatic content.

Electrochemical Properties

The electrochemical behavior of the studied materials were investigated by cyclic voltammetry (CV) conducted for the cast film on an indium-tin oxide (ITO)-coated glass slide as working electrode in anhydrous acetonitrile, using 0.1 M of TBAP as a supporting electrolyte, and the results are summarized in Table S3. The typical CV diagram of **P-TPA** is depicted in Fig. S2, and there is one reversible oxidation redox couple with the lower oxidation potential that could be attributed to the *para*-position substituted electron-donating methoxyl group.

Conducting Mechanism

Fig. S6 shows the I–V curves of 10 wt% PCBM:**P-TPA** device for OFF and the conduction state has well been characterized by ohmic conduction relationship (I ~ V) and trap-limited spacecharge-limited current (SCLC; I ~ Vm+1 (m > 1)) indicating that the carriers overcome the energy barrier and flow through the device by Ohmic conduction and trap-free SCLC process sequentially at the higher bias.^{S3} The inset figure in Fig. S6 shows the obtained slope

in a plot of $\log(I/V)$ vs $V^{1/2}$ of ON state is nearly equal to one. It indicates that the Poole–Frenkel emission dominate in the ON state.^{S3}

Code	yield	η_{inh}^{a} (dL/g)	$M_w{}^b$	$M_n{}^b$	PDI^b	Solvent ^c		с
						DMAc	NMP	CHCl ₃
P-TPA	88.1%	0.40	63000	40000	1.56	—	+	++

Table S1. Inherent	Viscosity an	nd Molecular	Weights of I	P-TPA
	2			

^{*a*} Measured at a polymer concentration of 0.5 g/dL in NMP at 30 °C. ^{*b*} Calibrated with polystyrene standards, using NMP as the eluent at a constant flow rate of 1 ml/min at 40 °C. Polydispersity Index (M_w/M_n) .

^c The solubility was determined with a 5 mg sample in 1 ml of solvent. ++: soluble in room temperature; +: soluble in heating; -: partially soluble even in heating.

Polymer ^a	$T_{\rm d}^{5} (^{\rm o}{\rm C})^{b}$		$T_{\rm d}{}^{10}$	$(^{\mathrm{o}}\mathrm{C})^{b}$	$R_{ m w800}(\%)^{c}$	LOI^d
	N_2	Air	N_2	Air		
P-TPA	440	500	500	530	76	48
0			0			

Table S2. Thermal Properties of P-TPA

^{*a*} The polymer samples were heated at 200 $^{\circ}$ C for 1 h prior to all the thermal analyses. ^{*b*} 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.

^c Residual weight percentages at 800 °C under nitrogen flow.

^{*d*}LOI = Limiting Oxygen Index = $(17.5 + 0.4 \times \text{char yield})$.^{S2}

Polymer	Oxidation $(V)^a$			
	Eonset	$E_{1/2}$	$HOMO^b$	LUMO ^c
P-TPA	0.62	0.85	5.17	2.34

^{*a*} From cyclic votammograms versus Ag/AgCl in CH₃CN. $E_{1/2}$: average potential of the redox couple peaks.

^b The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene ($E_{1/2} = 0.48$ V).

^c The LUMO energy levels were calculated from HOMO – energy gap (2.83) reported before.^{S1}



Figure S1. TGA thermograms of P-TPA at a scan rate of 20 °C/min.



Figure S2. Cyclic voltammetric diagrams of **P-TPA** films on an ITO-coated glass substrate over cyclic scans in 0.1 M TBAP/CH₃CN at a scan rate of 100 mV/s.



Figure S3. Schematic diagram of the memory device consisting of PCBM:**P-TPA** hybrid film sandwiched between an ITO bottom electrode and an Al top electrode.



Figure S4. Current-voltage (I-V) characteristics of the ITO/PCBM:**P-TPA**/Al memory device with 3.5 wt% PCBM weight fraction.



Figure S5. Rewritability test of the ITO/ PCBM:**P-TPA**/Al memory device with 3 wt% PCBM weight fraction.



Figure S6. Experimental and fitted current–voltage (I–V) characteristics of the 10 wt% PCBM:**P-TPA** memory device in the OFF and ON state.

Notes and References:

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