

## Electronic Supplementary Information

### Novel Solution-Processable Fluorene-Based Polyimide/TiO<sub>2</sub> Hybrids with Tunable Memory Properties

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## Experimental Section

### Materials

9,9-Bis(4-(4-amino-3-benzyloxyphenoxy)phenyl)fluorene (F-DA) was prepared according to previous literature.<sup>S1</sup> 2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) (**2**) (Chriskev) was purified by vacuum sublimation. 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 stoichiometric mixture of the hydroxyl-containing aromatic diamine F-DA (1.12 g, 2.00 mmol), the dianhydride 6FDA (0.89 g, 2.00 mmol), and a few drops of isoquinoline in *m*-cresol (7 mL) was stirred at ambient temperature under nitrogen for 5 h, then the solution was heated to 170-180 °C and maintained at that temperature for 24 h. The water of imidization was allowed to distill from the reaction mixture along with *m*-cresol, and *m*-cresol was continually replaced so as to keep the total volume of the solution constant. After the solution was cooled to ambient temperature, the viscous solution then was poured slowly into 300 mL of methanol with stirring. The precipitated polymer was collected by filtration, washed thoroughly with hot methanol, and dried under reduced pressure at 150°C for 15 hours. The inherent viscosity of the obtained polyimide **FOH-6FPI** was 0.70 dL/g (measured at a concentration of 0.5 g/dL in DMAc at 30 °C). The IR spectrum of **FOH-6FPI** (film) exhibited broad absorption bands in the region of 3000 to 3700 cm<sup>-1</sup> (O-H stretch) and characteristic imide absorption bands at 1782 (asymmetrical C=O), 1718 (symmetrical C=O), 1388 (C-N), 1356 (C-F), and 748 cm<sup>-1</sup> (imide ring deformation); Yield: 98%.

### Preparation of the Polyimide-TiO<sub>2</sub> Hybrid Films

The preparation of polyimide-TiO<sub>2</sub> hybrid **FTP-50** was used as an example to illustrate the general synthetic route used to produce the hybrid **FTP-X**. Firstly, 0.05 g (0.050 mmole) of **FOH-6FPI** was dissolved in 3 mL of DMAc, and 0.08 g (37 wt%) of HCl was added very slowly to the organic solution and stirred at room temperature for 0.5 h. Then, 0.21 mL (0.62 mmole) of Ti(OBu)<sub>4</sub> dispersed in 0.21 mL of *n*-butanol was added drop-wise to the above solution with a syringe, and the mixture was stirred at room temperature for further 1 hour. The resulting precursor solution was then filtered through a 0.45µm PTFE filter before spin-coated onto an ITO glass plate at 1000-2000 rpm for 60 second. The obtained film was treated by the multi-step heating process of 100, 150, 250 °C for 20 min, and 350 °C for 60 min, respectively.

### Measurement of Basic Properties

Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum 100 Model FT-IR spectrometer with resolution  $1\text{ cm}^{-1}$  and number of scans 4.  $^1\text{H}$  NMR spectrum was measured on a Bruker AC-300 MHz spectrometer in  $\text{DMSO-}d_6$ , using tetramethylsilane as an internal reference, and peak multiplicity was reported as follows: s, singlet; d, doublet; m, multiplet. The inherent viscosity was determined at  $0.5\text{ g/dL}$  concentration using Tamson TV-2000 viscometer at  $30\text{ }^\circ\text{C}$ . Gel permeation chromatographic (GPC) analysis was carried out on a Waters chromatography unit interfaced with a Waters 2410 refractive index detector, calibrating with polystyrene standards. Two Waters  $5\text{ }\mu\text{m}$  Styragel HR-2 and HR-4 columns ( $7.8\text{ mm I. D.} \times 300\text{ mm}$ ) were connected in series with NMP as the eluent at a flow rate of  $0.5\text{ ml/min}$  at  $40\text{ }^\circ\text{C}$ . Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately  $6\text{--}8\text{ mg}$  samples heated in flowing nitrogen or air (flow rate =  $20\text{ cm}^3/\text{min}$ ) at a heating rate of  $20\text{ }^\circ\text{C/min}$ . Coefficient of thermal expansion (CTE) and glass transition temperatures ( $T_g$ ) are measured on a dilatometer (TA instrument TMA Q400EM). The TMA experiments were conducted from  $50\text{ to }450\text{ }^\circ\text{C}$  at a scan rate of  $10\text{ }^\circ\text{C/min}$  with a tensile probe under an applied constant load of  $50\text{ mN}$ .  $T_g$  was taken as the onset temperature of probe displacement on the TMA traces. The CTE data were determined in the range of  $50\text{--}200\text{ }^\circ\text{C}$  by film-fiber probe with expansion mode. 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  $0.5\text{ cm} \times 1.2\text{ cm}$ ) was used as a working electrode and a platinum wire as an auxiliary electrode at a scan rate of  $100\text{ mV/s}$  against a  $\text{Ag/AgCl}$  reference electrode in anhydrous  $\text{CH}_3\text{CN}$ , using  $0.1\text{ M}$  of TBAP as a supporting electrolyte. All cell potentials were taken by using a homemade  $\text{Ag/AgCl}$ ,  $\text{KCl}$  (sat.) reference electrode. The ITO-coated glass slide was used as the working electrode, a platinum wire as the counter electrode, and a  $\text{Ag/AgCl}$  cell as the reference electrode. The microstructure of the prepared films was examined by using a JOEL JEM-1230 transmission electron microscope (TEM). UV-visible absorption was recorded on UV-visible spectrophotometer (Hitachi U-4100).

### Fabrication and Measurement of the Memory Devices

The memory devices were fabricated with the configuration of ITO/thin film/Al. The ITO glass used for memory device was pre-cleaned by ultrasonication with water, acetone, and isopropanol each for  $15\text{ min}$ . The hybrid thin film was prepared according to previous procedure using ITO as substrate. The film thickness was adjusted to be around  $50\text{ nm}$ .

Finally, a 300-nm-thick Al top electrode was thermally evaporated through the shadow mask (recorded device units of  $0.5 \times 0.5 \text{ mm}^2$  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 Keithley 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  $\mu\text{m}$  diameter tungsten wire attached to a tinned copper shaft with a point radius  $<0.1 \mu\text{m}$  (GGB Industries, Inc.).

## Results and Discussion

### Polymer Synthesis and Basic Properties

**FOH-6FPI** was synthesized by the one-step method starting from hydroxyl-containing diamine monomer F-DA and aromatic tetracarboxylic dianhydrides 6FDA in the presence of a catalytic amount of isoquinoline at 170-180 °C as shown in Fig. S1. The formation of **FOH-6FPI** was confirmed by FTIR and NMR. The IR spectrum of **FOH-6FPI** (film) exhibited broad absorption band in the region of 3000 to 3700  $\text{cm}^{-1}$  (O-H stretch) and characteristic imide absorption bands at 1782 (asymmetrical C=O), 1718 (symmetrical C=O), 1388 (C-N), 1356 (C-F), and 748  $\text{cm}^{-1}$  (imide ring deformation) shown in Fig. S2. Furthermore, the IR spectrum of hybrid film **FTP-50** revealed additional absorption bands at 650 to 800  $\text{cm}^{-1}$  (Ti-O-Ti). The  $^1\text{H}$  NMR result of **FOH-6FPI** was also shown in Fig. S3 (DMSO- $d_6$ ,  $\delta$ , ppm): 6.51 (d, 4H), 7.01 (d, 4H), 7.20 (m, 6H), 7.40 (m, 6H), 7.73 (s, 2H), 7.93 (d, 4H), 8.12 (d, 2H), and 10.03 (s, 2H, OH). The inherent viscosity, weight-average molecular weight ( $M_w$ ), and polydispersity index (PDI) of the obtained polyimide were shown in Table S1. The solubility behavior of **FOH-6FPI** was investigated, and the results are also summarized in Table S2. **FOH-6FPI** revealed high solubility in common organic solvents. The thermal properties of the **FOH-6FPI** and **FTP-50** are summarized in Table S3. Typical TGA and TMA curves of **FOH-6FPI** and hybrid materials were depicted in Fig. S4 and Fig. S5, respectively. These hybrid materials both in nitrogen and air revealed excellent thermal stability and higher carbonized residue (char yield) with increasing  $\text{TiO}_2$  content. The titania contents in the hybrid materials could be estimated based on the char yields under air flow, which were in good agreement with the theoretical content and ensured successfully incorporation of the nanocrystalline-titania. Meanwhile, coefficient of thermal expansion (CTE) is one of the important designing parameters for the application of polymer films in microelectronic field, and the CTE values of **FOH-6FPI** and **FTP-50** nanocrystalline-titania hybrid films were measured and summarized in Table S3. **FTP-50** exhibited much higher Tg and lower CTE than those of **FOH-6FPI**.

**Table S1.** Inherent Viscosity and Molecular Weights of **FOH-6FPI**

Polymer	$\eta_{\text{inh}}^a$ (dL/g)	$M_w^b$	$M_n^b$	PDI <sup>c</sup>
<b>FOH-6FPI</b>	0.70	110600	52700	2.10

<sup>a</sup> Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.

<sup>b</sup> Calibrated with polystyrene standards, using NMP as the eluent at a constant flow rate of 0.5 mL/min at 40 °C.

<sup>c</sup> Polydispersity index ( $M_w/M_n$ ).

**Table S2.** Solubility<sup>a</sup> of **FOH-6FPI**.

Polymer	Solvents						
	NMP	DMAc	DMF	DMSO	<i>m</i> -cresol	THF	CHCl <sub>3</sub>
<b>FOH-6FPI</b>	++	++	++	++	++	++	—

<sup>a</sup> The qualitative solubility was tested with 10 mg of a sample in 1 mL of stirred solvent. (++) soluble at room temperature, (+) soluble on heating, (+—) partial soluble on heating, (—) insoluble even on heating.

**Table S3.** Thermal Properties of Hybrid films

Index	Thermal Properties						$R_{w800}$ (%) <sup>d</sup>
	$T_g$ (°C) <sup>a</sup>	CTE (ppm/K) <sup>b</sup>	$T_d^{5\%}$ (°C) <sup>c</sup>		$T_d^{10\%}$ (°C) <sup>c</sup>		
			N <sub>2</sub>	Air	N <sub>2</sub>	Air	
<b>FOH-6FPI</b>	257	87	395	425	440	490	60
<b>FTP-50</b>	375	43	520	510	595	565	82

<sup>a</sup> Glass transition temperature measured by TMA with a constant applied load of 50 mN at a heating rate of 10 °C min<sup>-1</sup> by Tension mode.

<sup>b</sup> The CTE data was determined in the range of 50–200 °C by expansion mode.

<sup>c</sup> 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 30 cm<sup>3</sup>/min.

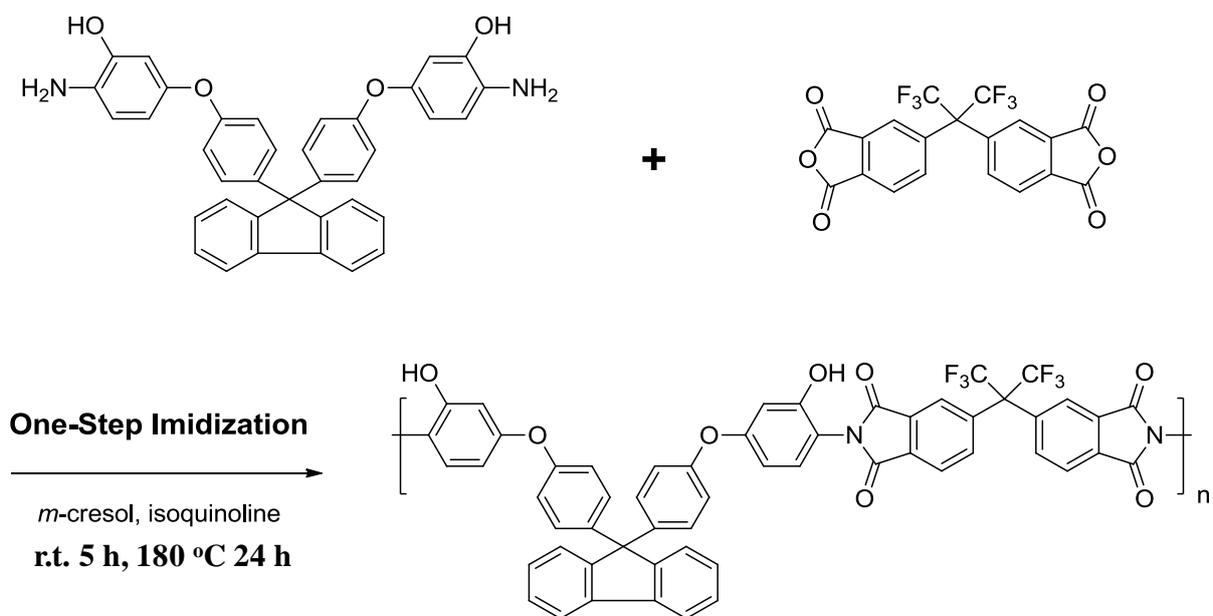
<sup>d</sup> Residual weight percentages at 800 °C under nitrogen flow.

Polymer	UV-vis absorption(nm)		Oxidation potential (V) (vs. Ag/AgCl in CH <sub>3</sub> CN)		$E_g^a$ (eV)	HOMO <sup>b</sup> (eV)	LUMO (eV)
	$\lambda_{max}$	$\lambda_{onset}$	$E_{onset}$				
<b>FOH-6FPI</b>	295	385	1.58		3.2	6.02	2.82

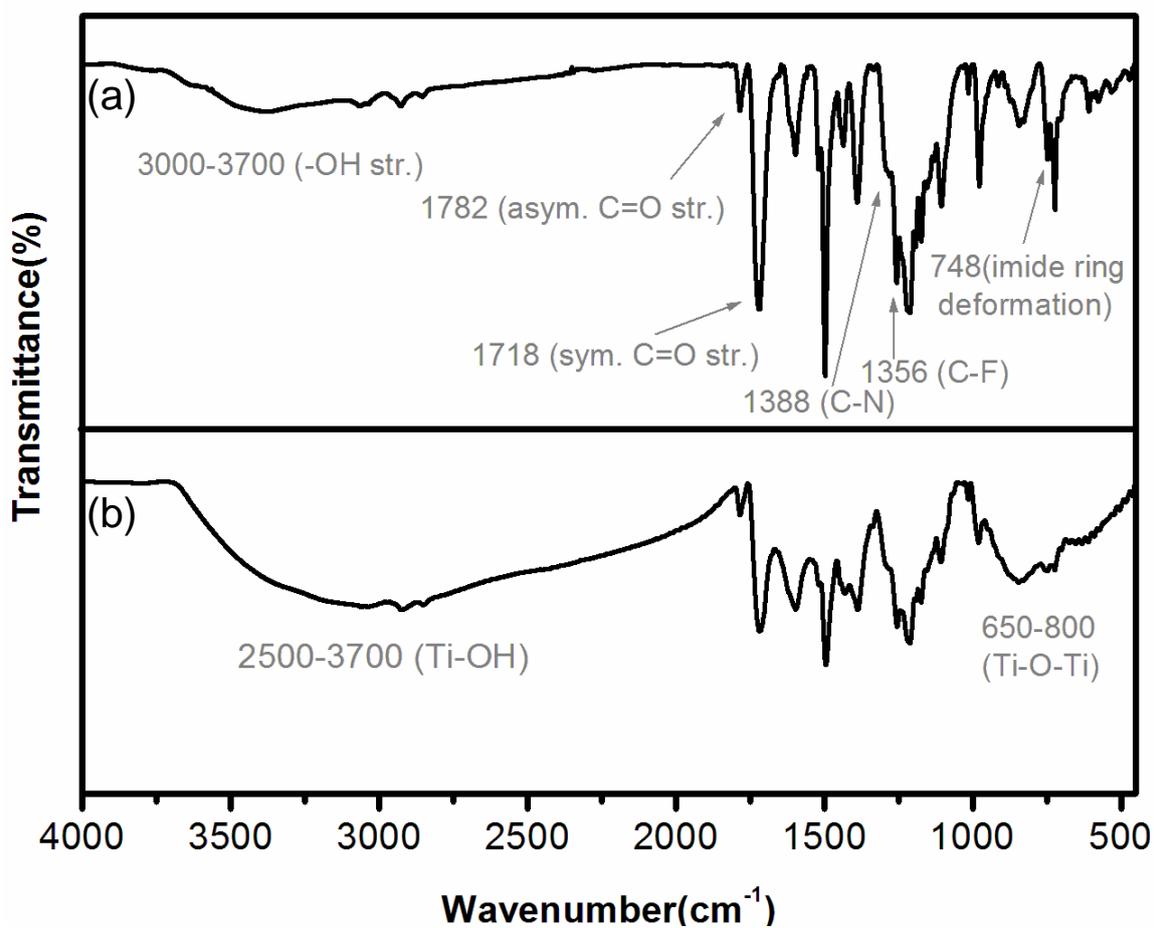
**Table S4.** Electrochemical and Optical Properties of **FOH-6FPI**

<sup>a</sup> The data were calculated from polymer films by the equation:  $E_g = 1240 / \lambda_{onset}$  (energy gap between HOMO and LUMO).

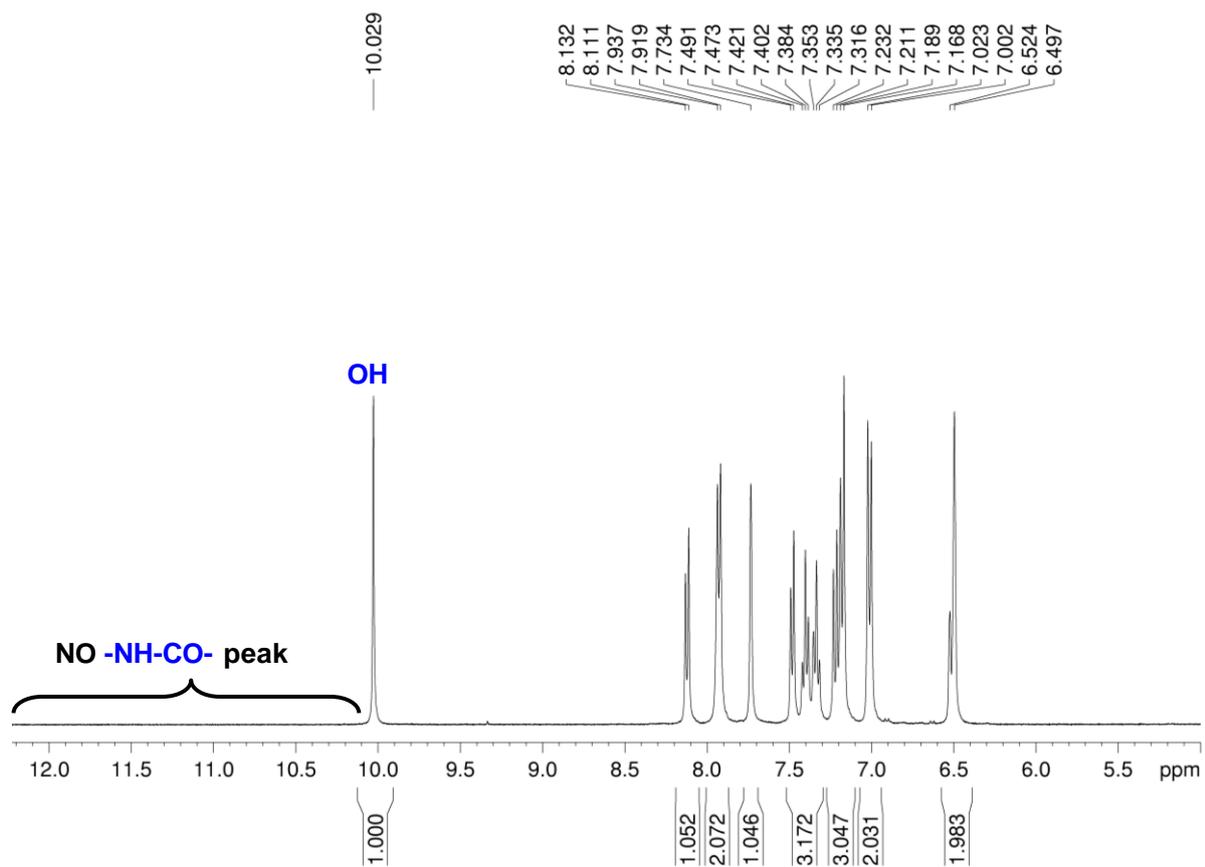
<sup>b</sup> The HOMO energy levels were calculated from CV and were referenced to ferrocene (4.8 eV; onset = 0.36V)



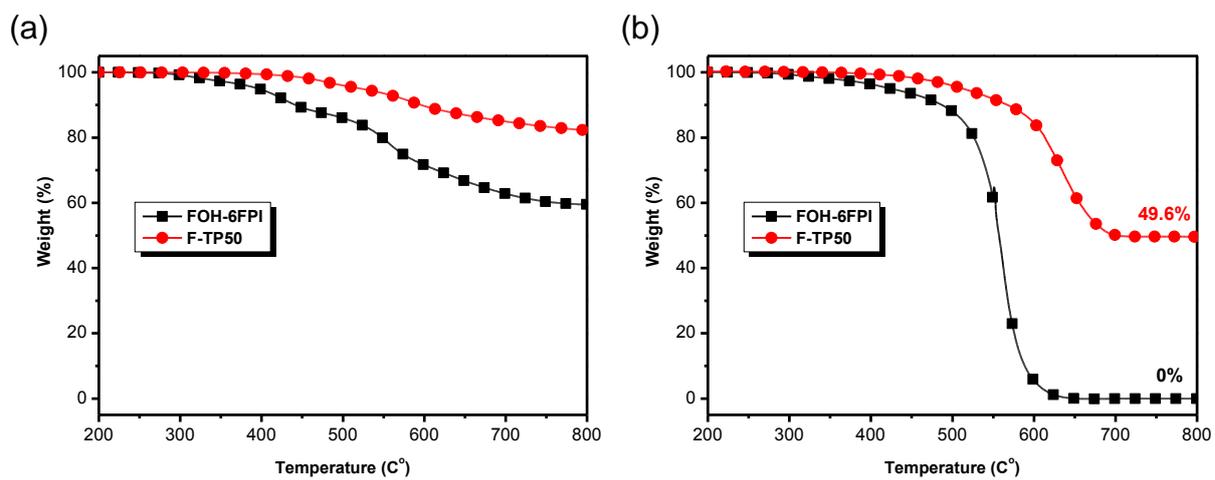
**Figure S1.** Polymer synthesis.



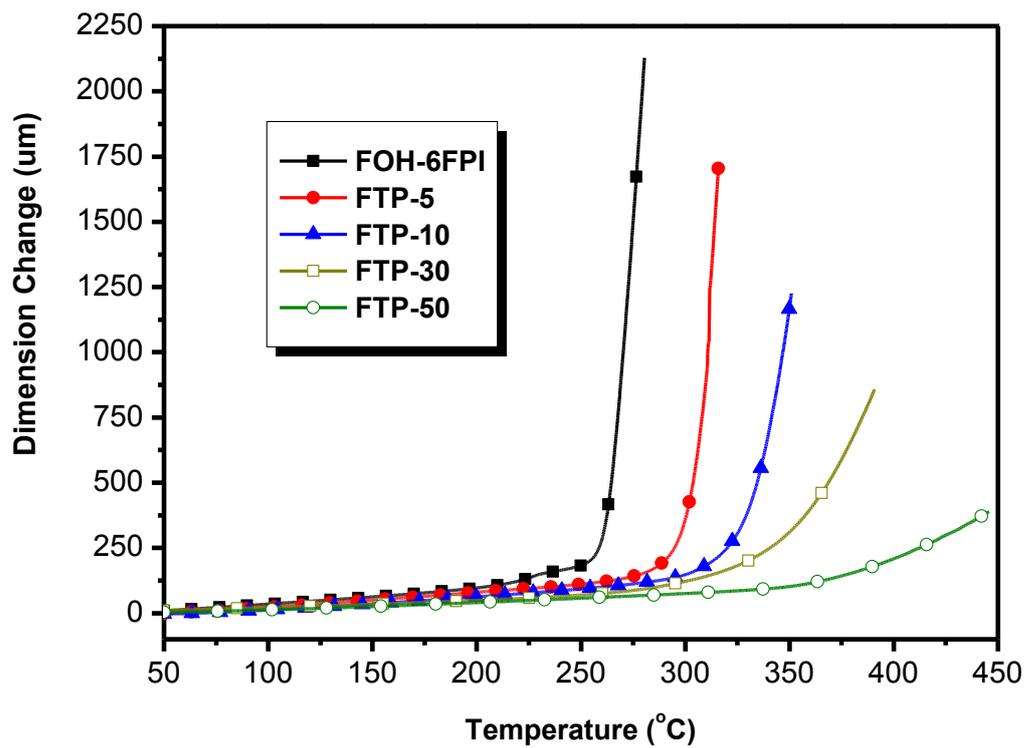
**Figure S2.** FT-IR spectra of the studied films (a) **FOH-6FPI** and (b) **FTP-50**



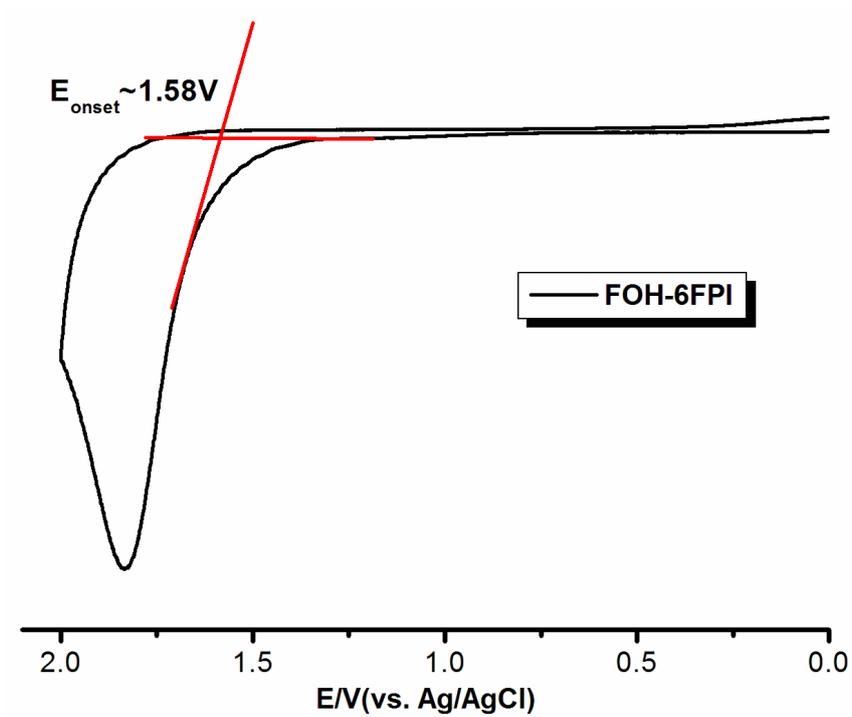
**Figure S3.**  $^1\text{H}$  NMR spectrum of polyimide **FOH-6FPI**.



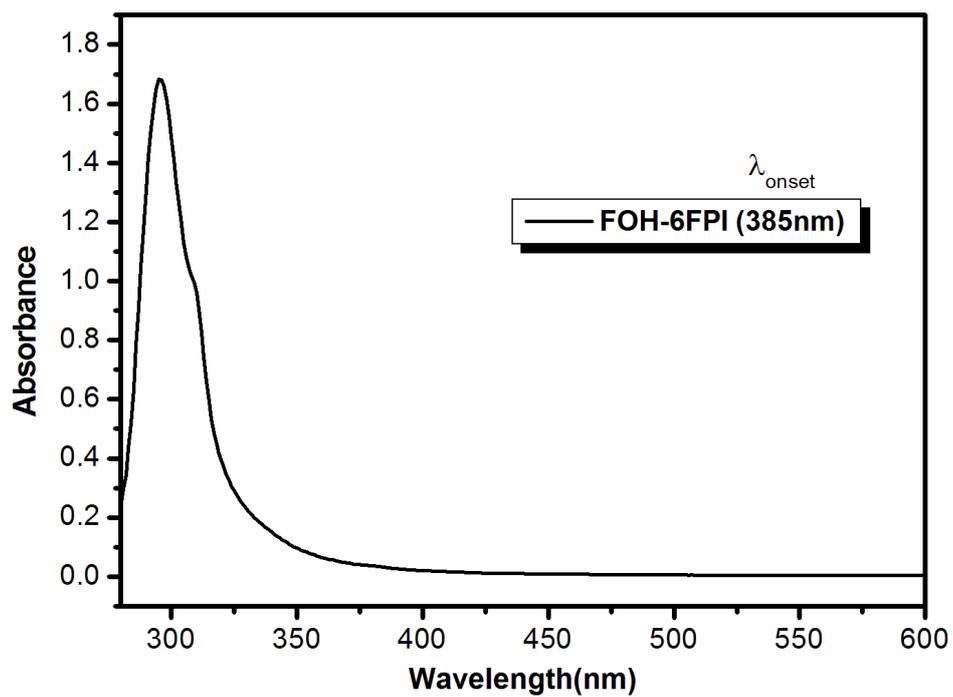
**Figure S4.** TGA thermograms of FOH-6FPI and F-TP50 (a) in N<sub>2</sub> (b) in air.



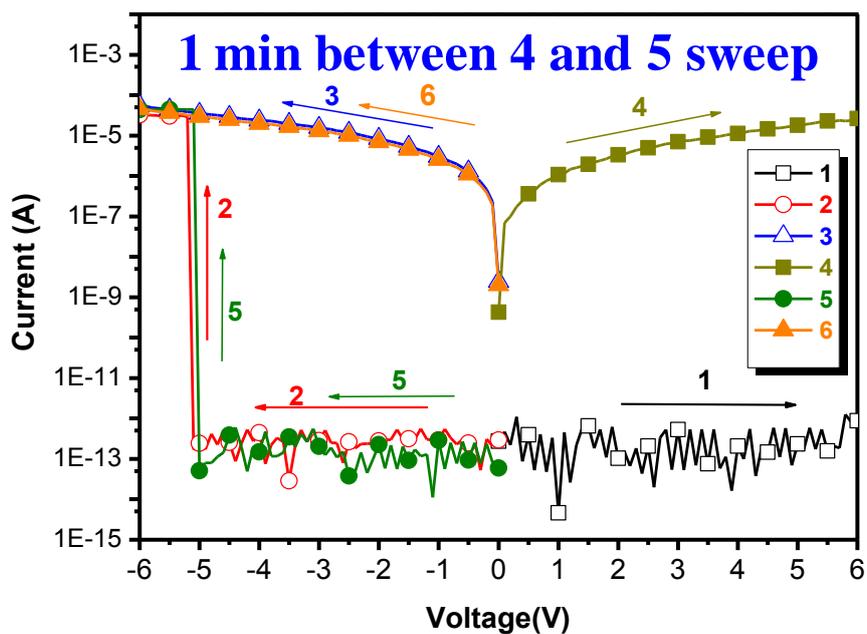
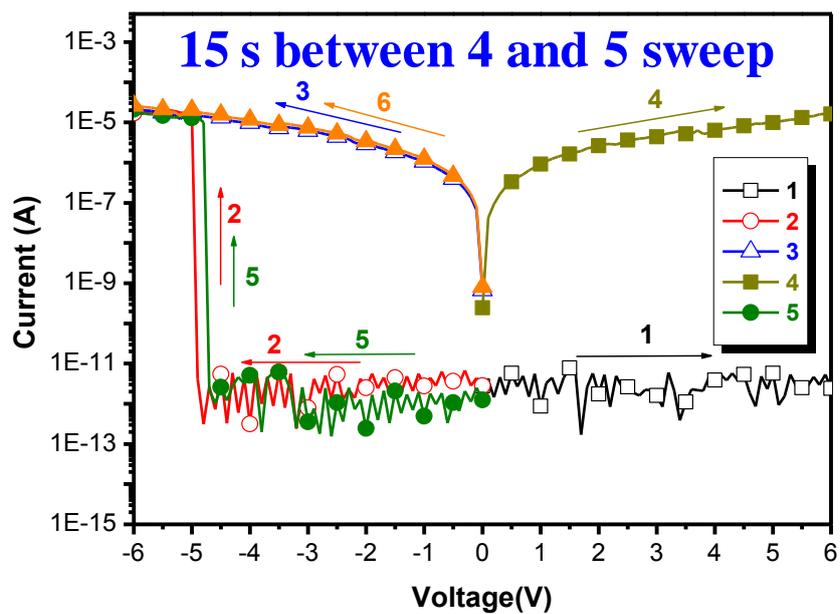
**Figure S5.** TMA thermogram of **FOH-6FPI** and **TiO<sub>2</sub>:FOH-6FPI** hybrid materials.



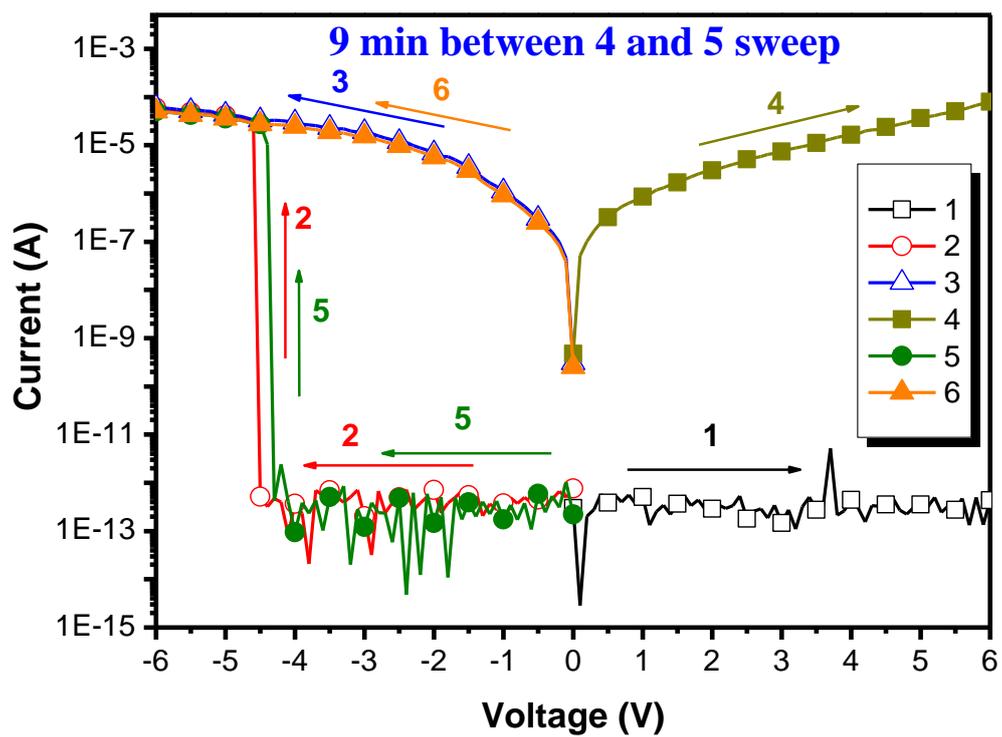
**Figure S6.** Cyclic voltammetric diagram of **FOH-6FPI** film on an ITO-coated glass substrate over cyclic scans.



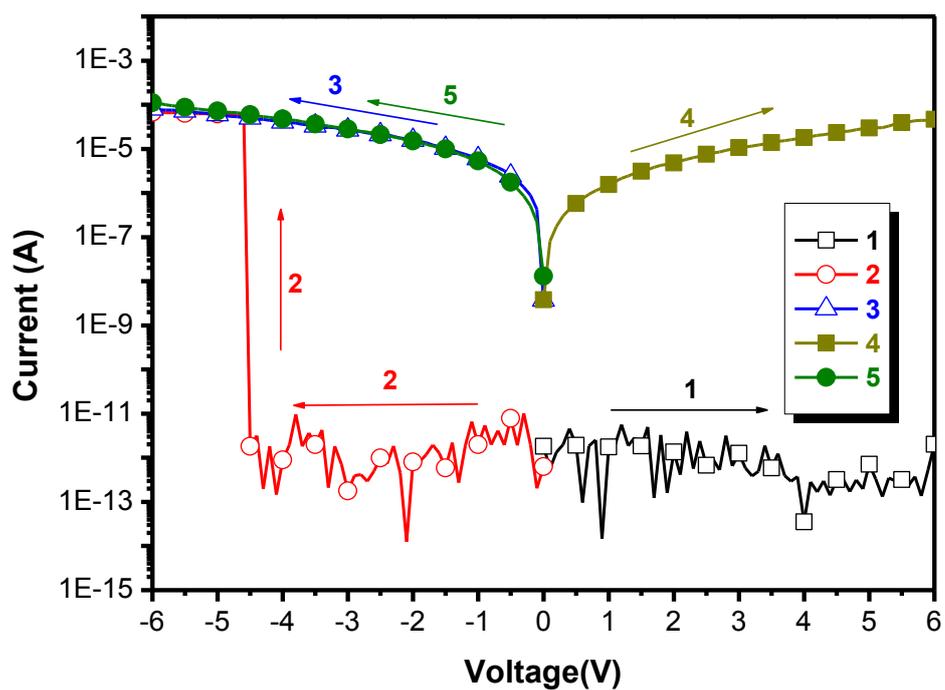
**Figure S7.** UV-visible absorption spectra of **FOH-6FPI**.



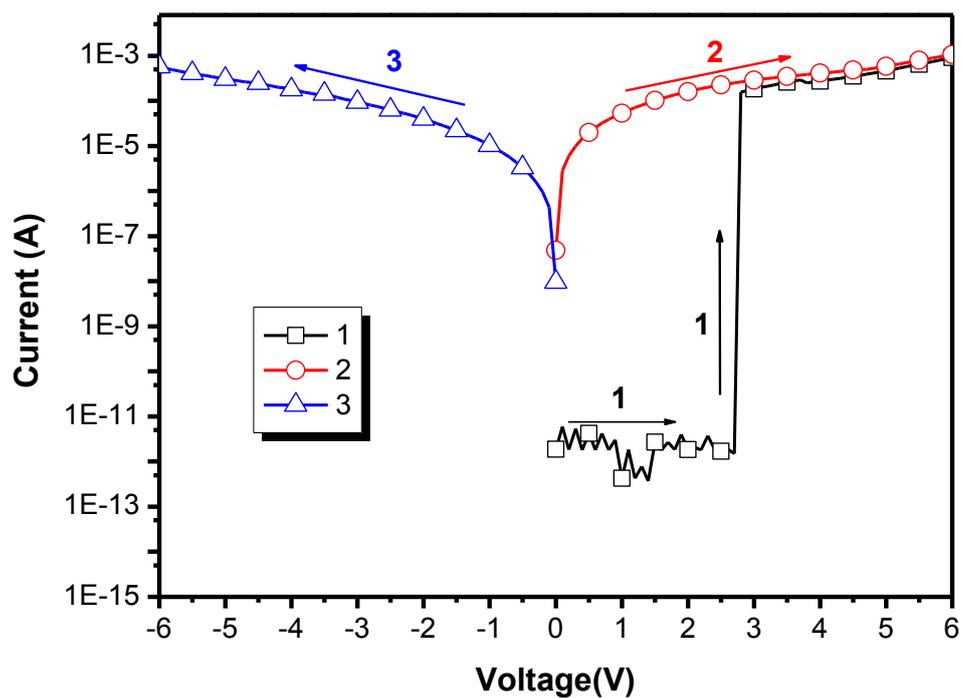
**Figure S8.** Current-voltage (I-V) characteristics of the ITO/FTP-5/Al memory device.



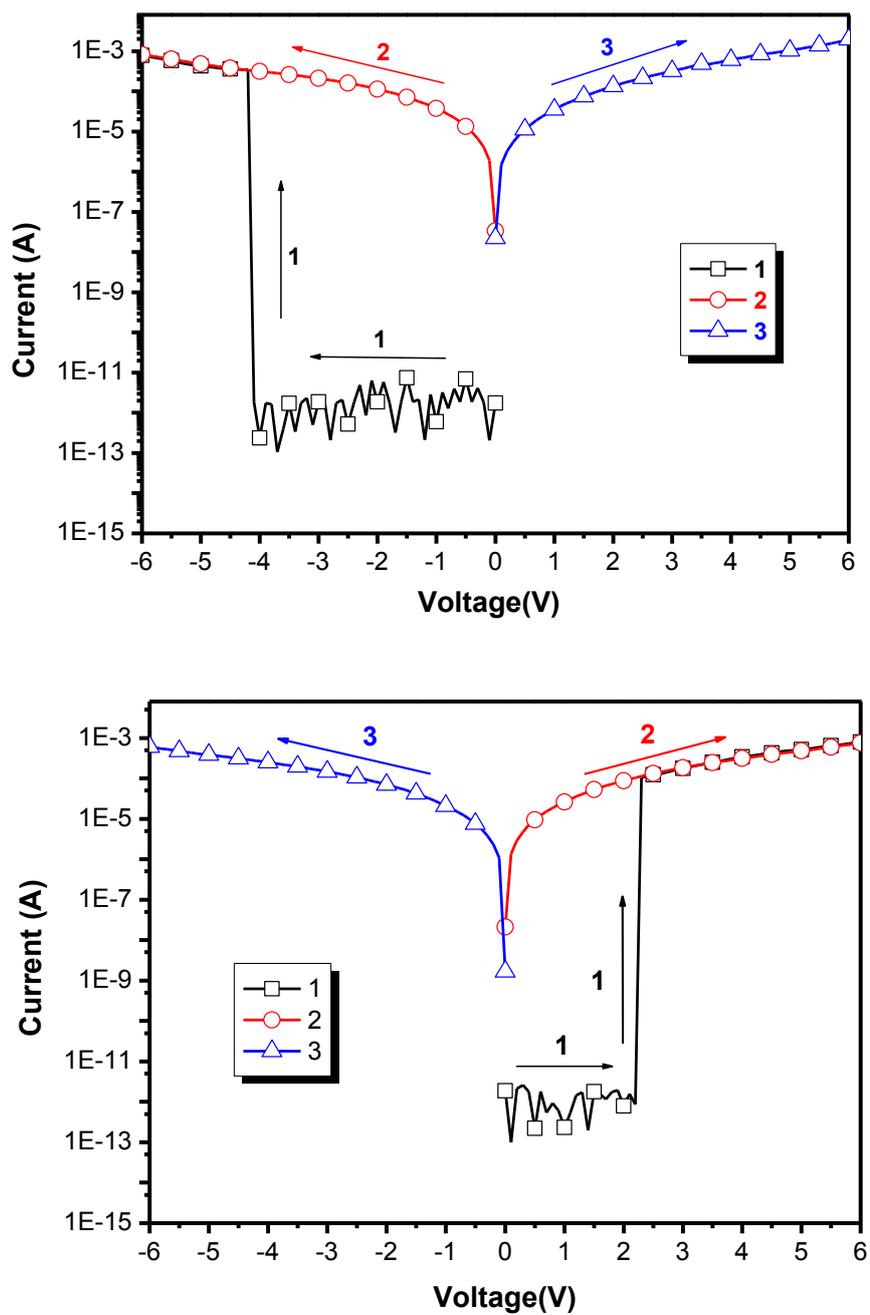
**Figure S9.** Current-voltage (I-V) characteristics of the ITO/FTP-8/Al memory device.



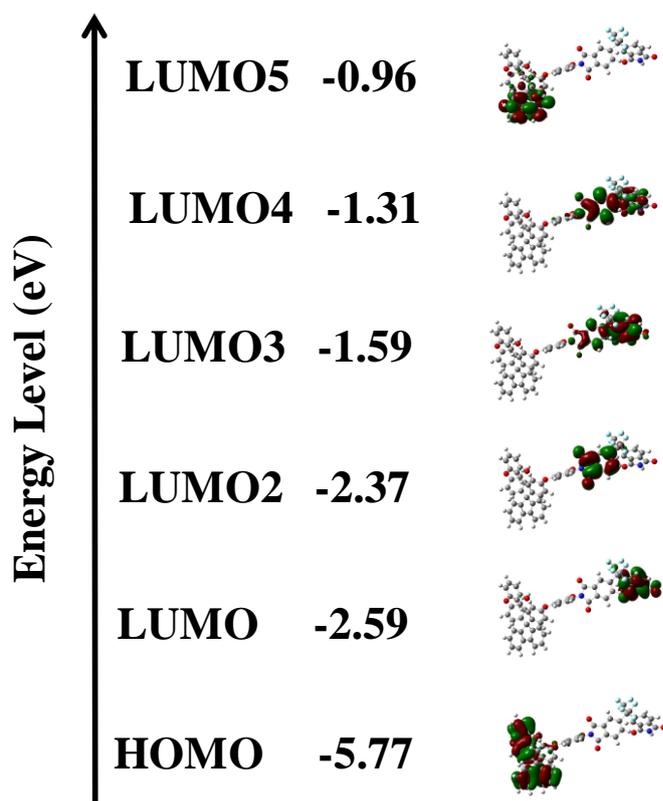
**Figure S10.** Current-voltage (I-V) characteristics of the ITO/FTP-9/Al memory device.



**Figure S11.** Current-voltage (I-V) characteristics of the ITO/FTP-30/Al memory device.

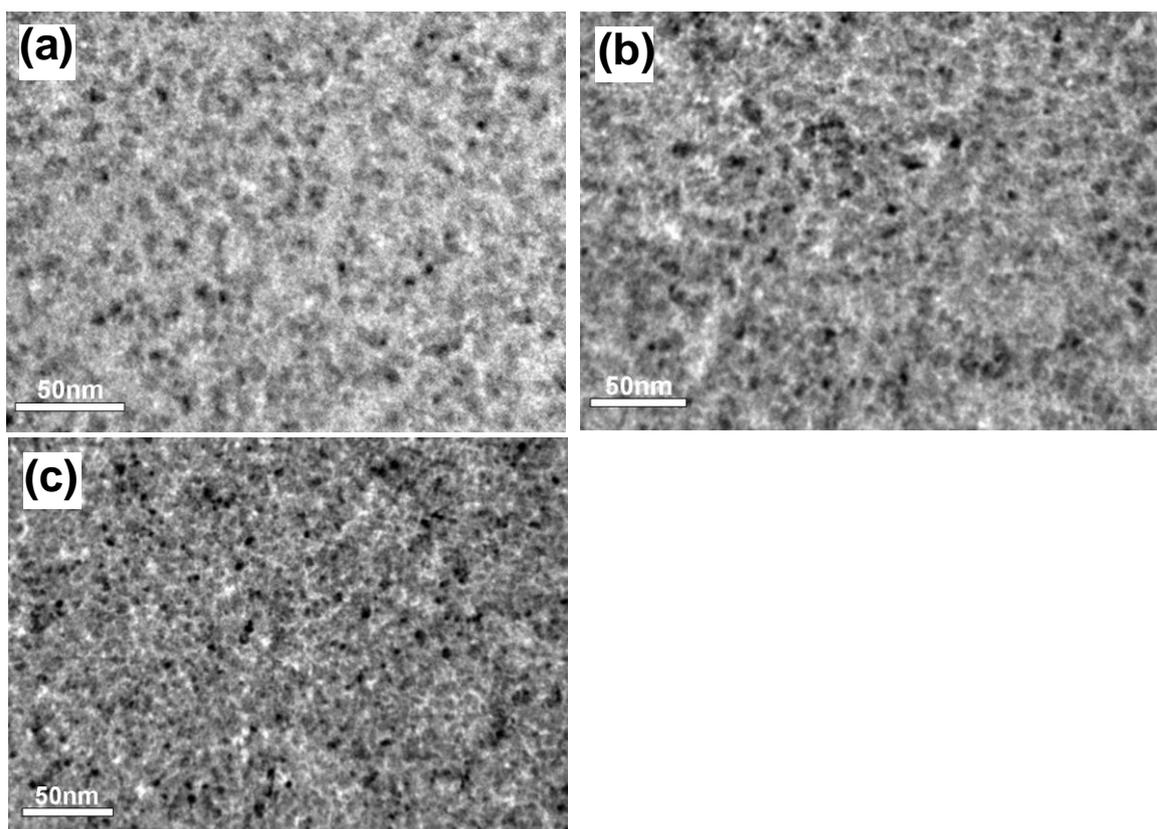


**Figure S12.** Current-voltage (I-V) characteristics of the ITO/FTP-50/Al memory device.

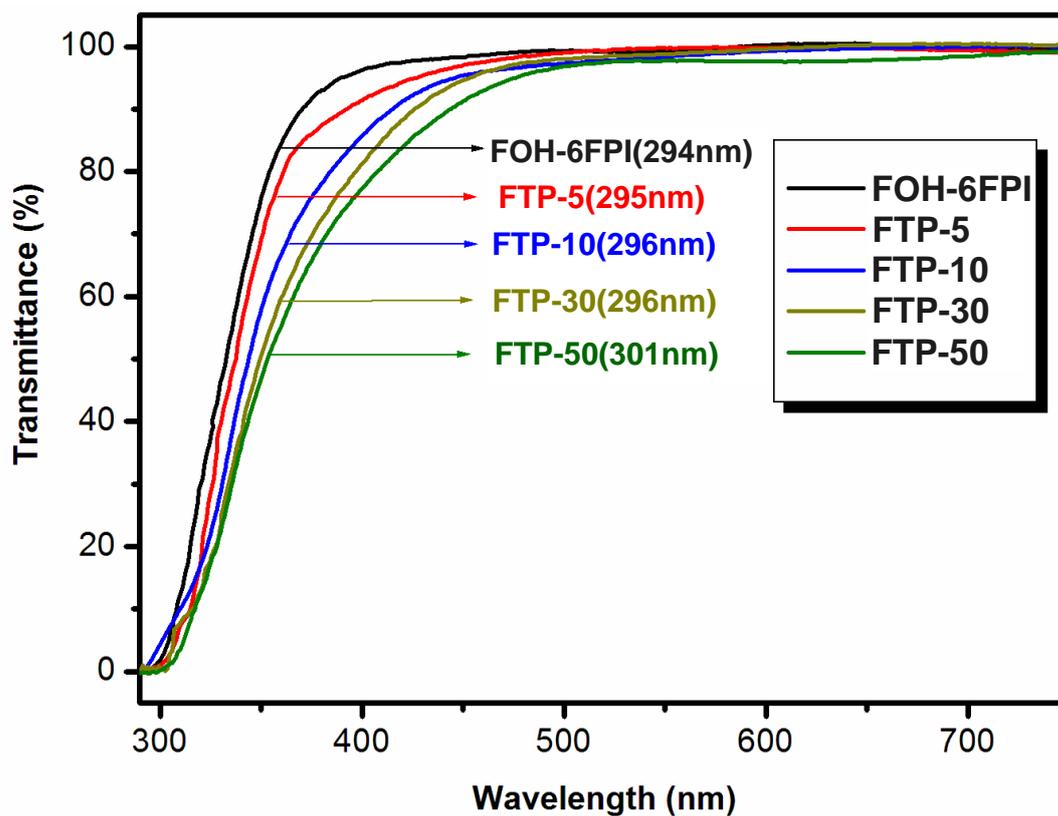


**Dipole Moment: 2.03D**

**Figure S13.** Calculated molecular orbitals and corresponding energy levels of the basic units (BU) for FOH-6FPI.



**Figure S14.** TEM image of the hybrid material (a) **FTP-5**, (b) **FTP-10**, (c) **FTP-30**.



**Figure S15.** Transmittance UV-visible spectra of **FOH-6FPI** hybrid thin films (450~550nm).

## Notes and References:

S1. Y. T. Chern, U.S. Patent 20060241187, 2006.