Supporting information

Novel Porphyrin-containing Polyimide for Memory Devices

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Experiment detail

Materials

Air-sensitive solids were handled in a glove box (MBraun Unilab). A vacuum line and standard Schlenk techniques were employed to process air-sensitive solutions. 3,3',4,4'-Diphenyl sulfonetetracarboxylic dianhydride (DSDA) from TCI was purified by sublimation. Tetrabutylammonium perchlorate (TBAP) (ACROS) was recrystallized twice by ethyl acetate. THF for cross-coupling reactions was purified by a solvent purification system (Asiawong SD-500, Taipei, Taiwan). Other solvents (ACS grade) such as CH_2Cl_2, $CHCl_3$ (Mallinckrodt Baker), hexanes (Haltermann, Hamburg, Germany), acetonitrile (CH_3CN) (ACROS), *N,N*-dimethylacetamide (DMAc) (TEDIA), *N*-methyl-2-pyrrolidinone (NMP) (TEDIA), *o*-dichlorobenzene (TEDIA), and m-cresol (Alfa Aesar) were used without further purification. $Pd(PPh_3)_4$ (Strem) and $Pd(PPh_3)_2Cl_2$ (Aldrich) were used as received. Silica gel 60 (230−400 mesh, Merck) was used for

chromatographic purification.

Compound 1: 2 g of 4-iodoaniline (MW = 219.02 g/mol, 9.13 mmol) was mixed with 7.0 mL of (trimethylsilyl)acetylene (MW =98.22 g/mol, d = 0.69 g/ml, 49.2 mmol, 5.39 equiv) in 15 mL of THF and 15 mL of triethylamine. After 3 cycles of freeze−pump−thaw, 4.4 mol % of $Pd(PPh_3)_2Cl_2$ and CuI were added to the solution under an inert atmosphere in a glove box. The reaction was stirred at 40 °C for 24 h. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using EA/*n*-hexanes = 1/2 as eluent, followed by crystallization from CH_2Cl_2/MeOH to give 1.613 g of **compound 1** (pale yellow solid, MW =189.33 g/mol, yield = 93.3 %).

Compound 2: For the de-protection process, 1 g of **compound 1** (MW =189.33 g/mol, 5.28 mmol) was dissolved in 80 mL THF, and 20 mL of methanol and then 5 mL of 1M $KOH_{(aq)}$ were added. The mixture was stirred in the dark at room temperature for 2 h. Upon completion, the solvent was removed by rotary evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (silica gel) using EA/*n*-hexanes = 1/2 as eluent to give 505 mg of **compound 2** (pale yellow solid, MW = 117.05 g/mol, yield = 81.7 %).

ZnPor-t-diamine: 400 mg of the **Zn(OR)₄Br₂**[1] (MW = 1420.98 g/mol, 0.2815 mmol) was mixed with 98.93 mg of **compound 2** (MW = 117.15 g/mol, 3.0 equiv) in 30 mL of THF and 20 mL of triethylamine. After 3 cycles of freeze−pump−thaw, 15 mol % of $Pd(PPh_3)_4$ and CuI were added to the solution under an inert atmosphere in a glove box. The reaction was stirred at 40 °C for 24 h. The completion of the reaction was monitored by TLC. Upon completion, the solvent was removed by rotary-evaporation. The residue was re-dissolved in CH_2Cl_2 for $NH_4Cl_{(aq)}$ washes. After dried over Na_2SO_4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel) using THF/*n*-hexanes = 1/2 as eluent, followed by crystallization from CH_2Cl_2/MeOH to give 339.4 mg of **ZnPor-t-diamine** (dark green solid, MW: 1493.45 g/mol, yield:

80.7 %). ^{1}H-NMR (CDCl$_3$ at 7.26 ppm, 300MHz, with trace amount of d$_5$-pyridine to increase the solubility): δ_H 9.53 (d, J = 4.5 Hz, 4H), 8.74 (d, J = 4.5 Hz, 4 H), 7.73 (d, J = 8.4 Hz, 4H), 7.66 (t, J = 8.3 Hz, 2H), 6.98 (d, J = 8.4 Hz, 4H), 6.77 (d, J = 8.4 Hz, 4H), 3.92 (s, 4 H), 3.81 (t, J = 6.6 Hz, 8H), 1.40- 1.70 (m, overlapped, 68H), 0.70-0.25 (m, overlapped, 24H). Elemental Anal calcd for C$_{96}$H$_{126}$N$_6$O$_4$Zn．H$_2$O: C 76.29 %, H 8.54 %, N 5.56 %. Found: C 76.52 %, H 8.60 %, N 5.48 %. MALDI-TOF: m/z calcd for C$_{96}$H$_{126}$N$_6$O$_4$Zn 1490.91; found 1491.81 [MH]$^+$.

Preparation of the Polyimide by a Two-step Method via Chemical Imidization Reaction

The polyimide **ZnPor-t-DSDA** was synthesized from 0.224 g (0.15 mmol) of ZnPor-t-diamine in 1.6 mL of DMAc and 0.054 g (0.15 mmol) of dianhydride DSDA was added in one portion. The mixture was stirred at room temperature overnight (ca. 16 h) to afford a viscous poly(amic acid) solution. The poly(amic acid) was subsequently converted to polyimide **ZnPor-t-DSDA** via chemical imidization process by addition of pyridine 0.4 mL and acetic anhydride 0.6 mL, then the mixture was heated at 120 ^{o}C for 4 h to complete imidization. The resulting polymer solution was poured into 300 mL of methanol giving a fibrous precipitate, which was washed thoroughly with methanol, and collected by filtration. The inherent viscosity of polyimide ZnPor-t-DSDA was 0.29 dL/g in DMAc at a concentration of 0.5 g/dL at 30 ^{o}C.

Polymer Properties Measurement

Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer Spectrum 100 Model FTIR spectrometer. The inherent viscosities were determined at 0.5 g/dL concentration using a Tamson TV-2000 viscometer at 30 ^{o}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 μm Styragel HR-2 and HR-4 columns (7.8 mm I. D. x 300 mm) were connected in series with NMP as the eluent at a flow rate of 0.5 mL min^{-1} at 40 ^{o}C and were calibrated with polystyrene standards. Thermo-gravimetric analysis (TGA) was conducted with TA SDT Q600. Experiments were carried out on approximately 6–8 mg film samples heated in owing nitrogen or air (flow rate = 20 cm^3 min^{-1}) at a heating rate of 20 ^{o}C min^{-1}. Thermo-mechanical Analyzer (TMA) was conducted

with TA Q400EM. Experiments were carried out on approximately 4mm x 8mm film samples by extension method, heated in owing nitrogen (flow rate = 20 cm^3 min^{-1}) at a heating rate of 5 ^oC min^{-1}. Electrochemistry was performed with a CH Instruments 611B electrochemical analyzer. Voltammograms were presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards. Cyclic voltammetry (CV) was conducted with a three-electrode cell in which ITO (polymer film with area about 0.5 cm x 1.1 cm) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were measured using a homemade Ag/AgCl, KCl (sat.) reference electrode. UV-visible absorption was recorded on a UV-visible spectrophotometer (Agilent 8453). For ZnPor-t-diamine: NMR spectra (Bruker Avance II 300 MHz NMR spectrometer at National Chi Nan University, elemental analyses (Elementar Vario EL III, Precision Instrumentation Center at National Taiwan University) mass spectra (Microflex MALDI-TOF MS, Bruker Daltonics), electrochemical measurements (CHI Electrochemical Workstation 611A), absorption spectra (Agilent 8453 UV−visible spectrophotometer),and fluorescence spectra (Varian Cary Eclipse fluorescence spectrometer) were recorded with the indicated instruments.

Table S1: Thermal properties of the **ZnPor-t-DSDA**

Polymer[a]	T_g (°C)[b]	CTE (μm/m°C)[c]	T_d^5 (°C)[d] Air	T_d^5 (°C)[d] N_2	T_d^{10} (°C)[d] Air	T_d^{10} (°C)[d] N_2	Char yield (%)[e]
ZnPor-t-DSDA	176	179	370	400	410	415	37

[a] The polymer film samples were heated at 300 °C for 1 h before all the thermal analyses.

[b] Data was recorded by TMA at a heating rate of 20 °C/min and a gas flow rate of 20 cm³/min.

[c] Coefficient of thermal expansion was recorded during 50 -100 °C.

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

[e] Residual weight percentages at 800 °C under nitrogen flow.

Table S2: The energy levels of **ZnPor-t-DSDA.**

Polymer	Oxidation E_{onset} (V)	λ_{onset} (nm)	E_g (eV)[a]	HOMO (eV)[b]	LUMO (eV)
ZnPor-t-DSDA	0.79	697	1.78	5.23	3.45

[a] The data were calculated from polymer films by the equation: $Eg=1240/\lambda_{onset}$

[b] The energy levels were calculated from CV, energy bandgap, and referenced to ferrocene (4.8 eV; $E_{onset}=0.36V$)

Table S3: Inherent viscosity and solubility behavior of the **ZnPor-t-DSDA.**

Polymer	η_{inh}[a]	Solubility in various solvents[b]					
	(dL/g)	NMP	DMAc	DMF	THF	CHCl$_3$	CH$_2$Cl$_2$
ZnPor-t-DSDA	0.29	++	++	+-	++	+-	+-

[a] Measured at a polymer concentration of 0.5 g/dL in NMP at 30 °C.

[b] The solubility was determined with a 1mg sample in 0.2 ml of a solvent. ++, soluble at room temperature; + soluble at heating; +-, partial soluble even on heating.

Table S4: Inherent viscosity and solubility behavior of the **ZnPor-t-DSDA.**

Polymer	Mw[a]	Mn[a]	PDI[c]
ZnPor-t-DSDA	116600	48100	2.42

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

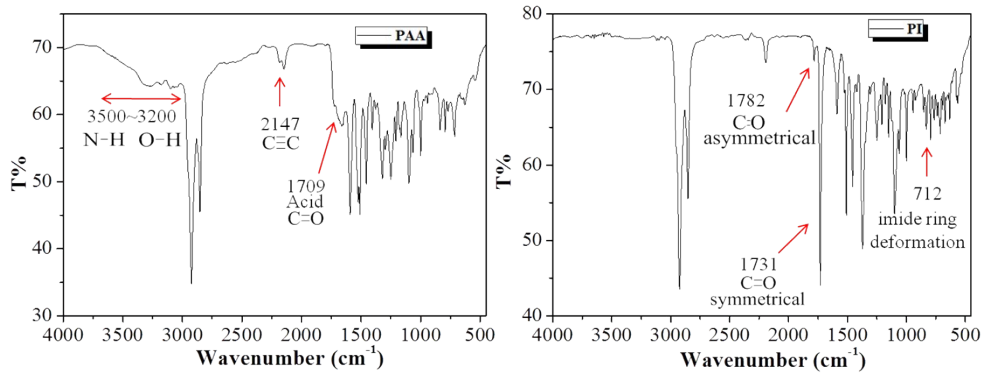[b] Polydispersity index (M_w/M_n).

Supporting figures
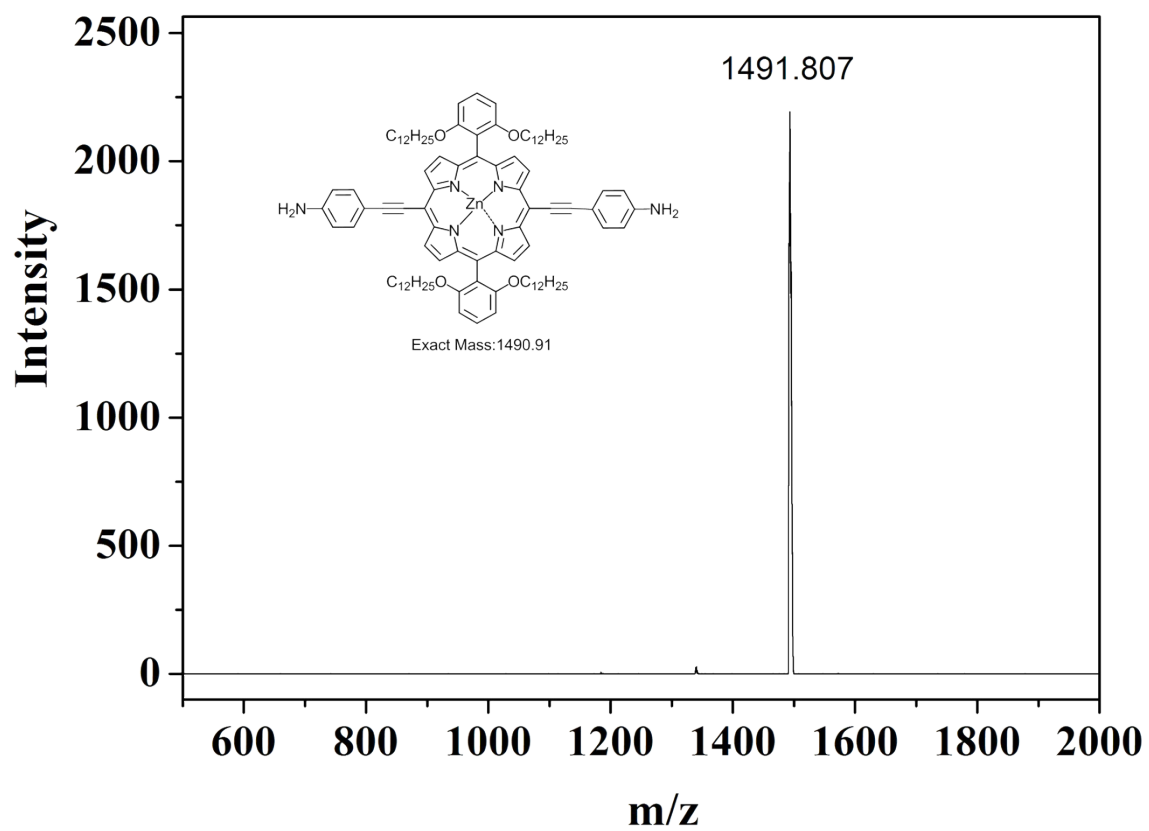
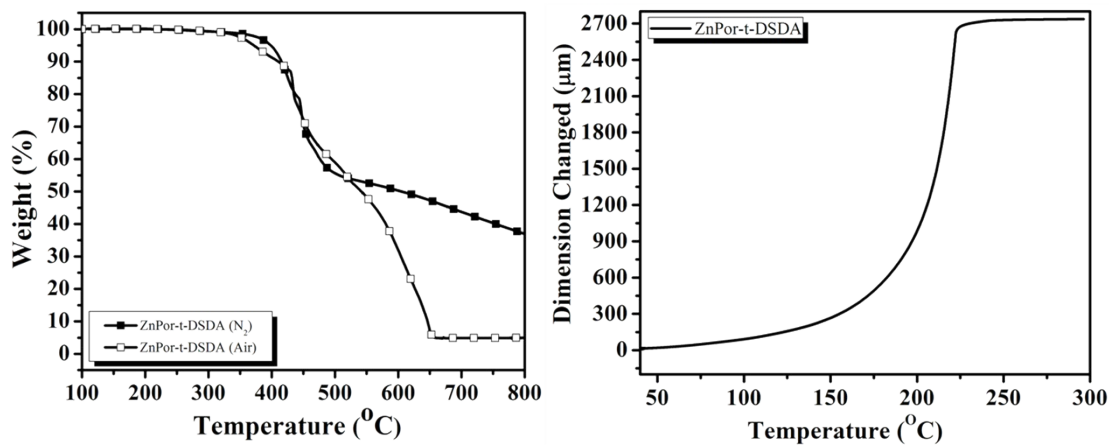**Figure S1**. MALDI-TOF mass spectrum of the **ZnPor-t-diamine.**
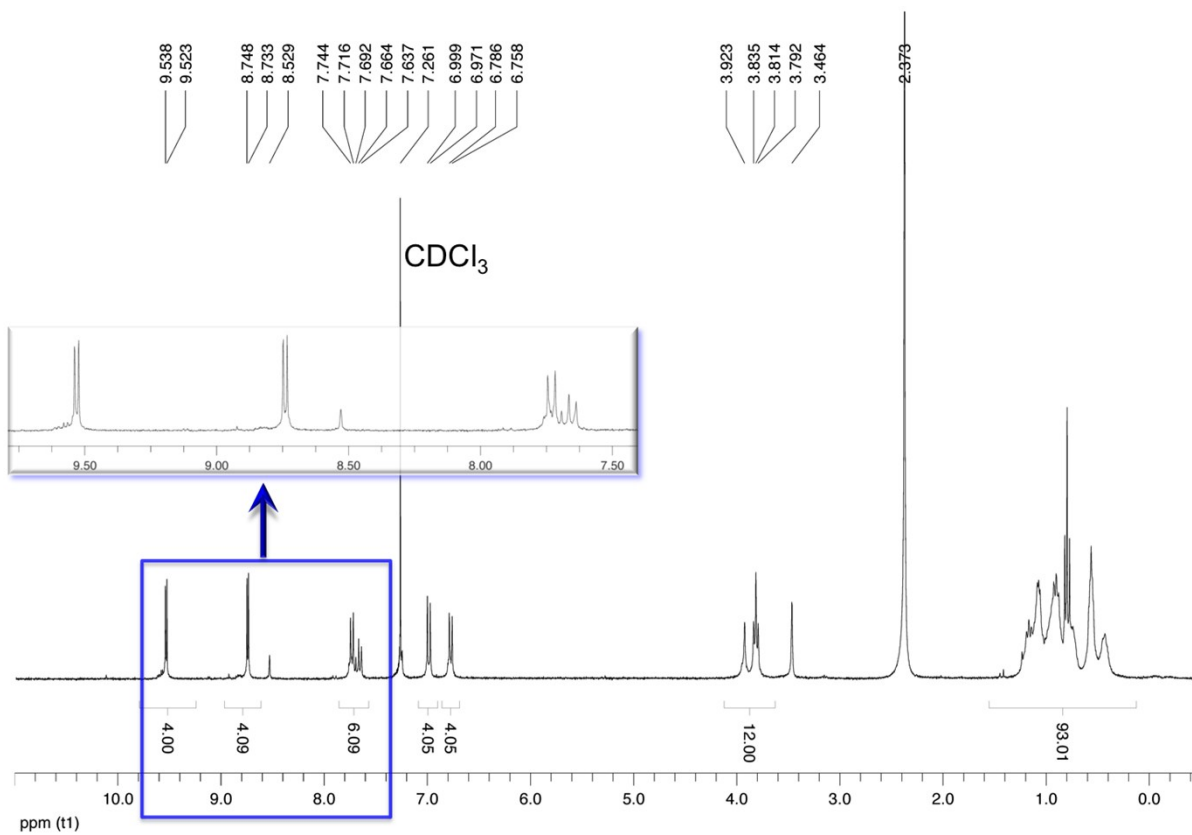
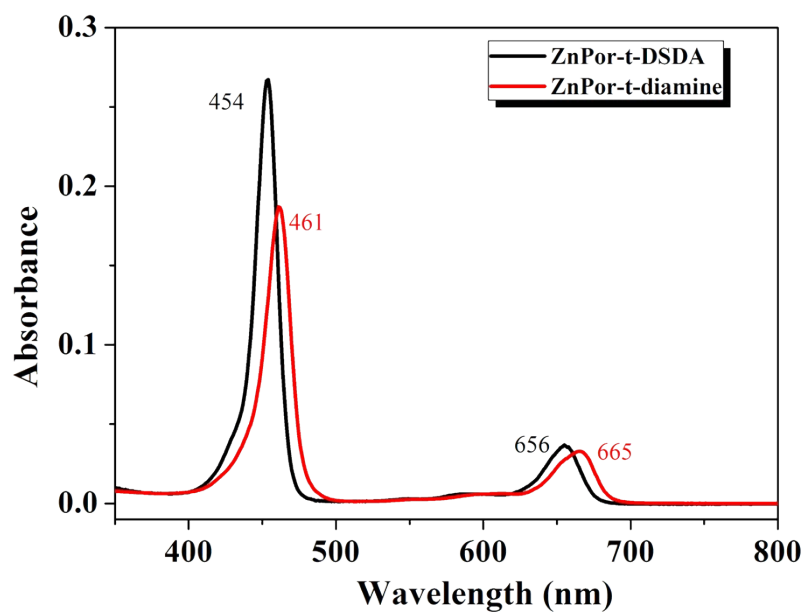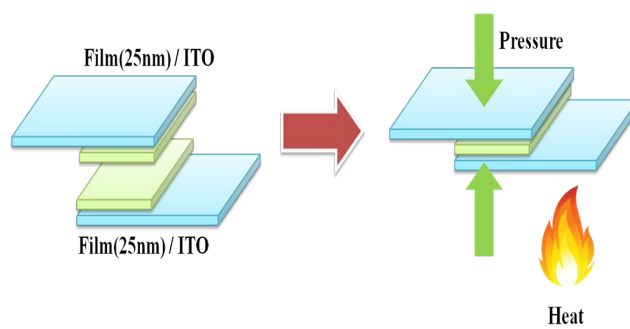**Figure S2.** NMR spectrum of the **ZnPor-t-diamine.**

Figure S3 FTIR spectra of the **ZnPor-t-DSDA** polyamic acid (left) and polyimide (right).
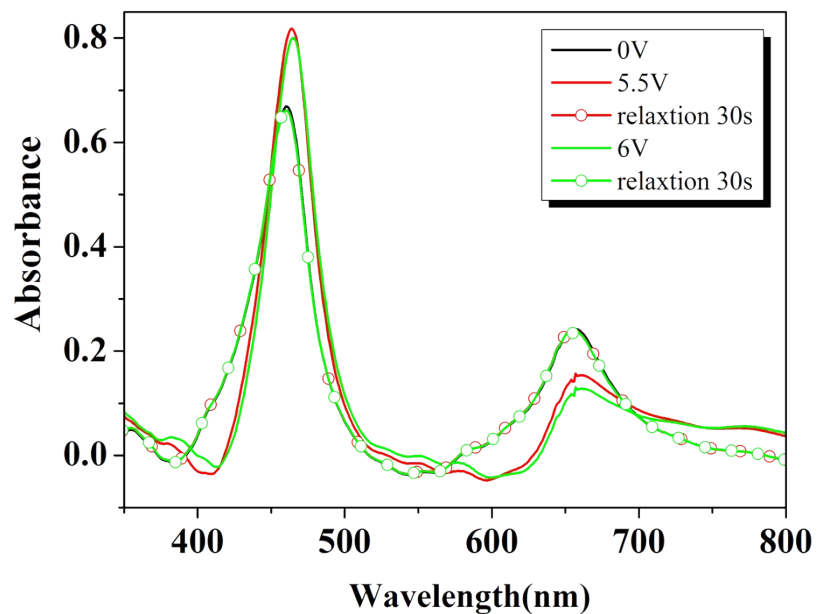

Figure S4 TGA (left) and TMA (right) thermograms of the **ZnPor-t-DSDA.**
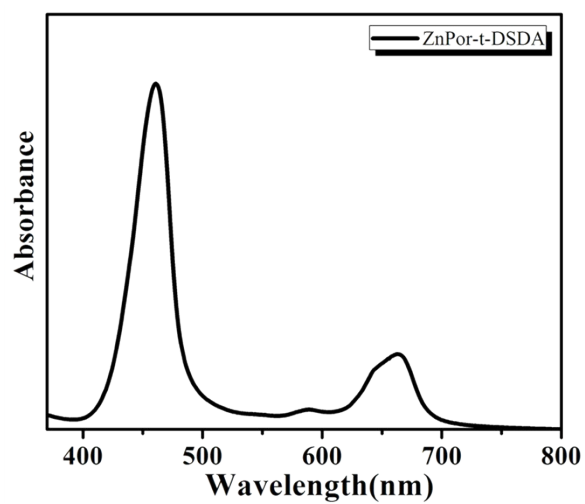
Figure S5. UV-visible absorption spectra of ZnPor-diamine and **ZnPor-t-DSDA** in THF solution, the concentration of ZnPor-diamine and **ZnPor-t-DSDA** is about 5×10^{-7} mol/L.
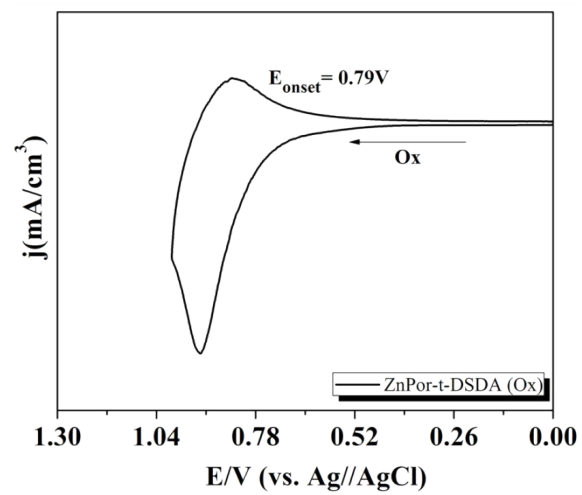

Figure S6. Transparent memory device fabrication process.

Figure S7. In situ UV-visible spectra of the transparent polymer memory device of ITO/polyimide thin film/ITO during switch process.

Figure S8. UV-vis absorption spectrum of **ZnPor-t-DSDA** film.

Figure S9. Cyclic voltammetric diagram of **ZnPor-t-DSDA** film on an ITO-coated glass substrate.

Reference

1. Lee, C. Y.; Hupp, J. T., *Langmuir* **2010,** *26*, 3760-3765.