

Supporting Information

Highly Transparent Polyhydroxyimide/TiO₂ and ZrO₂ Hybrids Films with High Glass Transition Temperature (*T_g*) and Low Coefficient of Thermal Expansion (CTE) for Optoelectronic Application

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Experimental

Materials

4,4'-diamino-4''-hydroxytriphenylmethane (DHTM) was synthesized according to previous literature.¹ Commercially available 2,2-bis(3,4-dicarboxyphenyl)hexafluoro propane dianhydride (6FDA) (Mp: 246 °C; Chriskev) and alicyclic dianhydride bicyclo[2.2.2]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BCDA) (Mp: 300 °C; from ITRI) were purified by vacuum sublimation. *N,N*-Dimethylacetamide (DMAc) (TEDIA), triethylamine (TEA) (Across) and other reagents were used as received from commercial sources.

Synthesis of 4,4'-diamino-4''-hydroxytriphenylmethane (DHTM)

A mixture of 4-hydroxybenzaldehyde (30.5 g, 0.25 mol), aniline (65.3 g, 0.75 mol), and aniline hydrochloride (3.3 g, 0.025 mol) were added into three-necked 500 mL glass reactor, dissolved at 110 °C under nitrogen atmosphere, and then heated at 150 °C for 1.5 h. The reaction mixture was cooled to room temperature, added 50 mL ethanol and heated to 80°C to dissolve the lumpy material, then cooled and held overnight. Further sublimation in the vacuum condition produced a purple needle crystalline product of DHTM (Scheme 1).

Preparation of the polyhydroxyimides (PHIs)

The synthesis of PHI-6F was used as an example to illustrate the general synthetic route used to produce the PHIs. The DHTM (0.58 g, 2.0 mmol) and 5.8 mL of *m*-cresol were added into two-necked 50 mL glass reactor under nitrogen. Then, 6FDA (0.888g, 2.0 mmol) were added, the polymerization was carried out at room temperature. After the solution was stirred for 6 h, few drops of isoquinoline were added in the mixture and then heated to reflux at 200 °C for 15 hrs. The obtained polymer solution was poured slowly into 300mL methanol and water co-solvent. Finally, dry under reduced pressure at 120°C for 6 hours (Scheme 2). The inherent viscosity, average molecular weight, and solubility behavior of the obtained PHI are summarized in Table 1.

Preparation of the PHIs films

The solution of PHIs in DMAc was casted onto glass substrates and dried at 80 °C for 6 h, and 150 °C for 8 h under vacuum. Finally, PHI film with thicknesses of 20 μm could be obtained and used for solubility tests, optical and thermal measurements.

Preparation of PHIs/titania and PHIs/zirconia hybrid films

The synthesis of PHI-6FTi50 was used as an example to illustrate the general synthesis route used to produce the hybrid films of PHI-6FTiX (Scheme 3). Firstly, 0.05 g of PHI-6F was dissolved in 3 mL of DMAc, and 0.1 mL of HCl was added very slowly into the PI solution and further stirred at room temperature for 30 min. Then, 0.152 mL (0.45 mmole) of Ti(OBu)₄ dissolved in 0.152 mL of butanol was dropwisely added into the above solution by a syringe, and then stirred at room temperature for 2 hours. Finally, the resulting precursor solution was filtered through a 0.45 mm PTFE filter and drop-coated onto glass substrates. The preparation of PHI-6F/zirconia (PHI-6FZrX) hybrids is similar to the PHI-6F/titania mentioned above, and the PHI-6FZr50 was used as an example to illustrate the procedure for producing the hybrid PHI-6FZrX (Scheme 3). Firstly, 0.05 g of PHI-6F was dissolved in 3 mL of DMAc, and then 0.10 mL of acetic acid was added very slowly into the PI solution and further stirred at room

temperature for 30 min. Then, 0.21 mL (0.62 mmole) of $Zr(OBu)_4$ dissolved in 0.21 mL of butanol was added dropwisely into the above solution by a syringe, and then stirred at room temperature for 10 min. Finally, the resulting precursor solution was filtered through a 0.45 mm PTFE filter and drop-coated onto glass substrates.

Measurements

Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum 100 Model FT-IR spectrometer with resolution 1 cm^{-1} and number of scans 4. ^1H NMR spectra were measured on a Bruker AV 400 MHz spectrometer in $\text{DMSO-}d_6$, using tetramethylsilane as an internal reference. The inherent viscosity was determined at 0.5 g/dL concentration using Tamson TV-2000 viscometer at $30\text{ }^\circ\text{C}$. Thermogravimetric analysis (TGA) conducted with a TA Instruments Q50, and experiments were carried out on approximately 3-5 mg film samples heated in flowing nitrogen or air (flow rate = $20\text{ cm}^3/\text{min}$) at a heating rate of $20\text{ }^\circ\text{C}/\text{min}$. Coefficient of thermal expansion (CTE) and glass transition temperatures (T_g) were measured by a dilatometer (TA instrument SI-5 TMA Q400EM). The TMA experiments were conducted from 40 to $450\text{ }^\circ\text{C}$ at a scan rate of $10\text{ }^\circ\text{C}/\text{min}$ by a tensile probe under an applied constant load of 50 mN. T_g was taken as the onset temperature of probe displacement on the TMA traces, and the CTE data was determined in the range of 50 – $300\text{ }^\circ\text{C}$. Ultraviolet-visible (UV-vis) spectra of the obtained films were recorded on Hitachi U-4100 UV-vis-NIR spectrophotometer. An ellipsometer (SOPRA, GES-5E) was used to measure the refractive index (n) of the prepared films in the wavelength range of 300 – 800 nm , and the thickness (h) was also determined simultaneously. In-plane (n_{TE}), and out-of plane (n_{TM}) refractive indices of the films formed on the silica substrates were measured using a prism coupler (Metricon, PC-2000) at wavelengths of 632.8 nm at room temperature. The in-plane/out-of-plane birefringence (Δn) was calculated as $\Delta n = n_{TE} - n_{TM}$. The microstructure of the prepared PI hybrid films was examined by using a JOEL JEM-1230 transmission electron microscope (TEM) at an operating voltage of 100 kV . 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 $0.5 * 1.2\text{ cm}^2$) was used as the working electrode and a platinum wire as the auxiliary electrode at a scan rate of 100 mV s^{-1} against a Ag/AgCl reference electrode in anhydrous CH_3CN , using 0.1M of TBAP as the supporting electrolyte. All cell potentials were taken by using a homemade Ag/AgCl, KCl (sat.) as reference electrode.

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 devices was cleaned by ultra-sonication with water, acetone, and isopropanol each for 30 min. The hybrid thin films were casting on ITO substrate, and the film thickness was adjusted to be around 50 nm. Finally, a 300 nm thick Al top electrode was thermally evaporated through the shadow mask (recorded device units of $0.5 * 0.5 \text{ mm}^2$ in size) at pressure of 10^{-7} Torr with a depositing rate of $3\text{--}5 \text{ \AA s}^{-1}$. The electric characterization of the memory device was performed using 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 mm diameter tungsten wire attached to a tinned copper shaft with a point radius <0.1 mm (GGB Industries, Inc.).

Molecular simulation

Molecular simulation in this study was carried out with the Gaussian 09 program package. Equilibrium ground state geometry and electronic properties of basic unit in the polyimide were optimized by means of the 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.

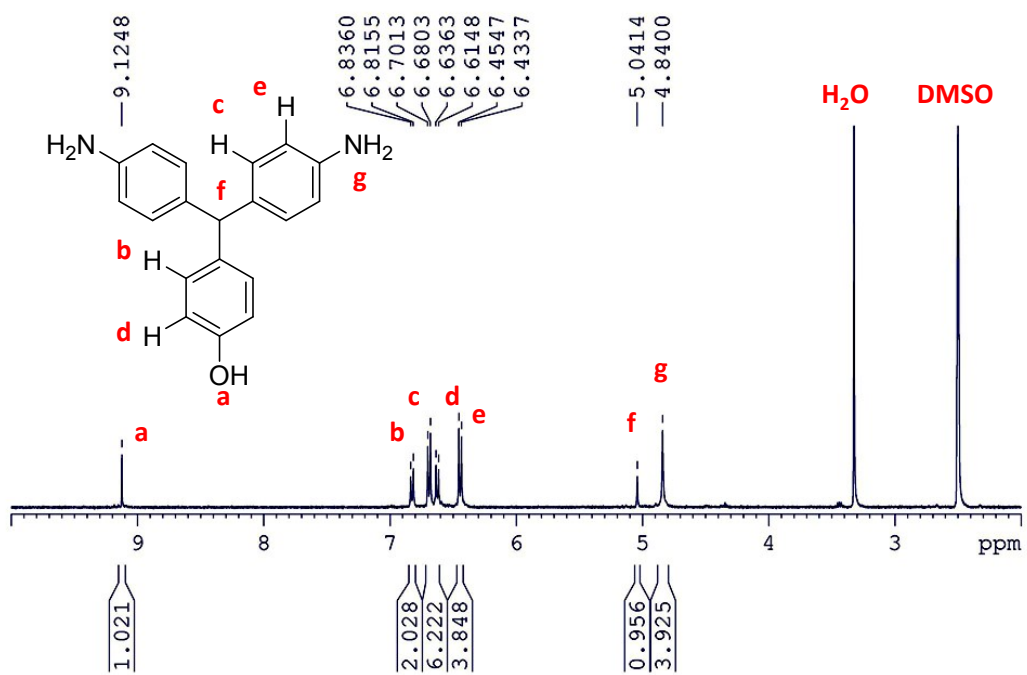


Fig. S1. ¹H NMR spectra of DHTM in DMSO-*d*₆.

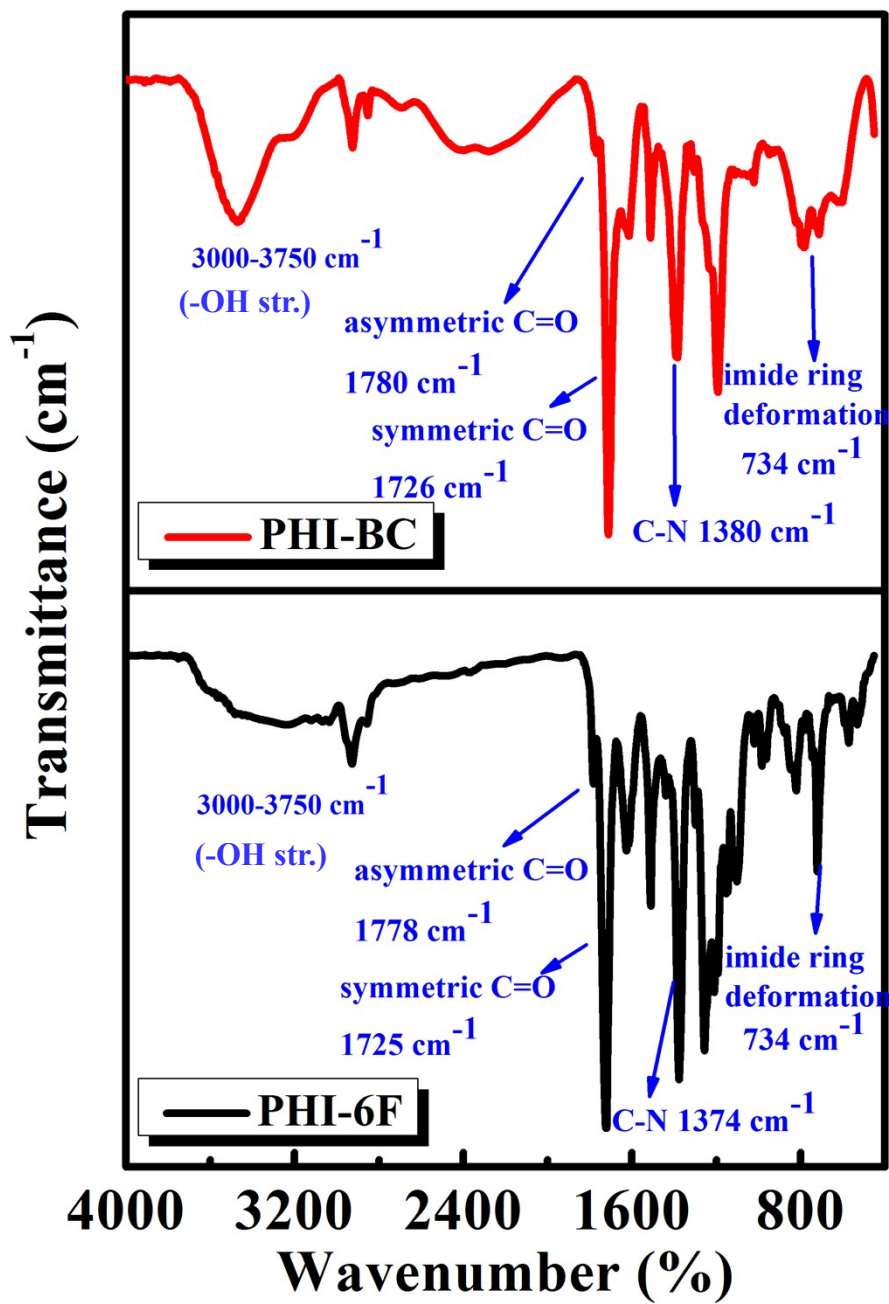


Fig. S2. IR spectra of PHIs.

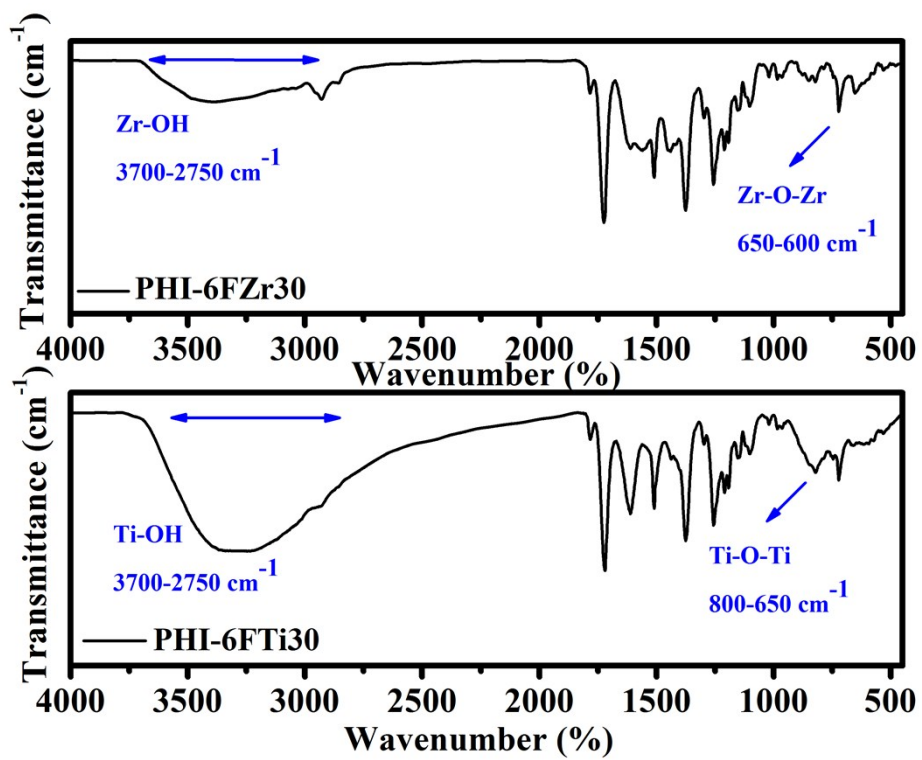


Fig. S3. IR spectra of PHI-6FTi30 and PHI-6FZr30 hybrid materials.

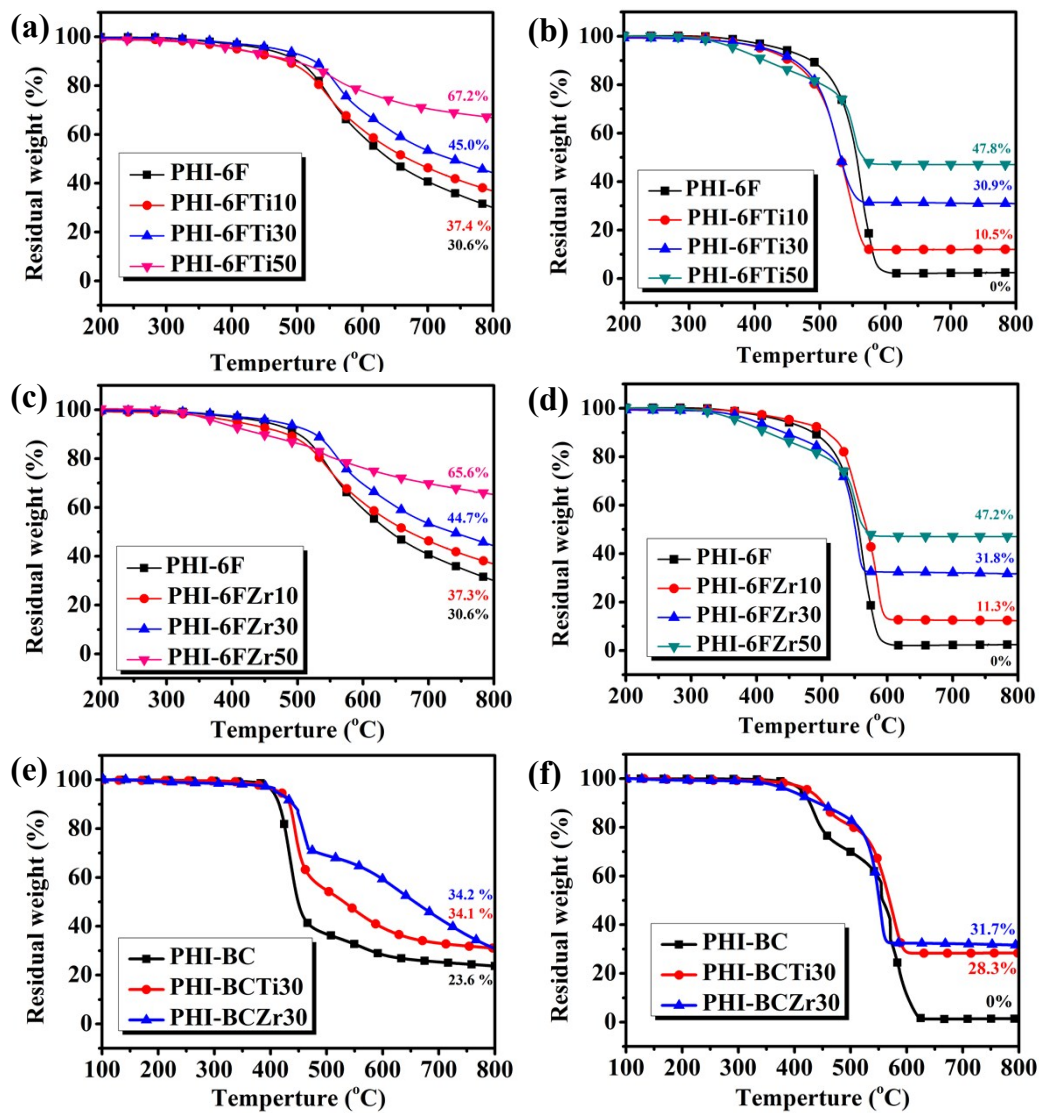


Fig. S4. TGA traces of PHI-6F/TiO₂, PHI-6F/ZrO₂ and PHI-BCM30 hybrid materials (a), (c) and (e) in N₂; (b), (d) and (f) in air.

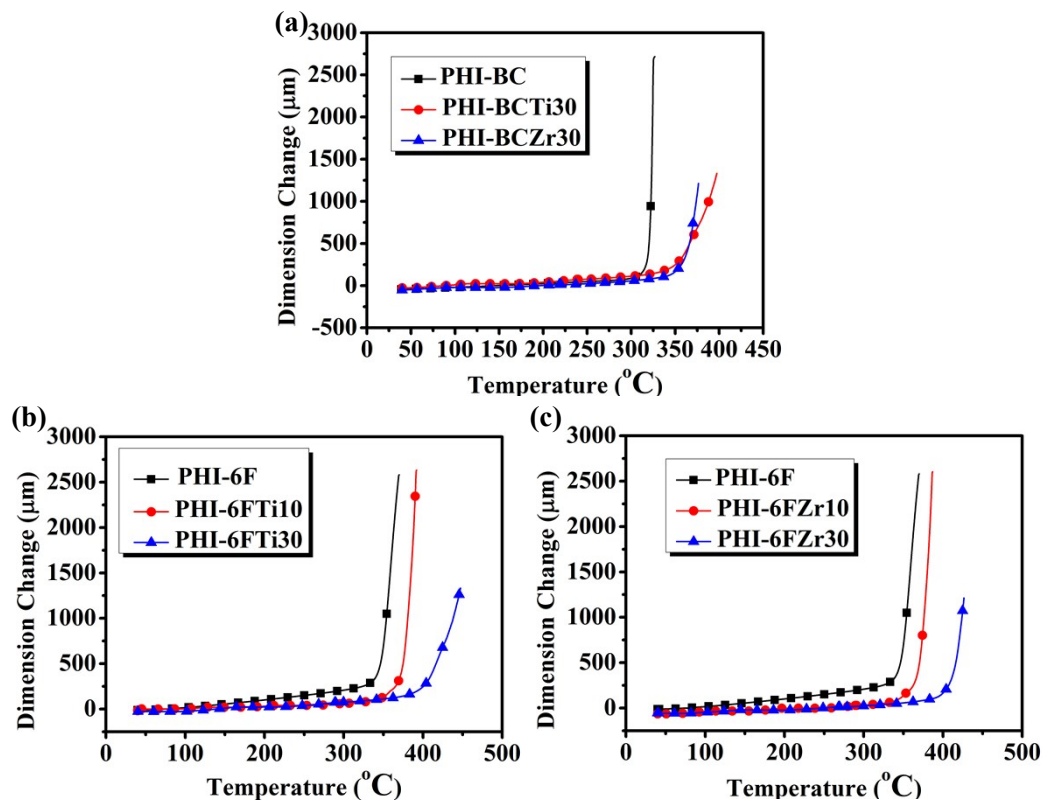


Fig. S5. TMA curves of (a) PHI-BCM30, (b) PHI-6F/ TiO_2 and (c) PHI-6F/ ZrO_2 hybrid films with the heating rate of $10^{\circ}\text{C}/\text{min}$.

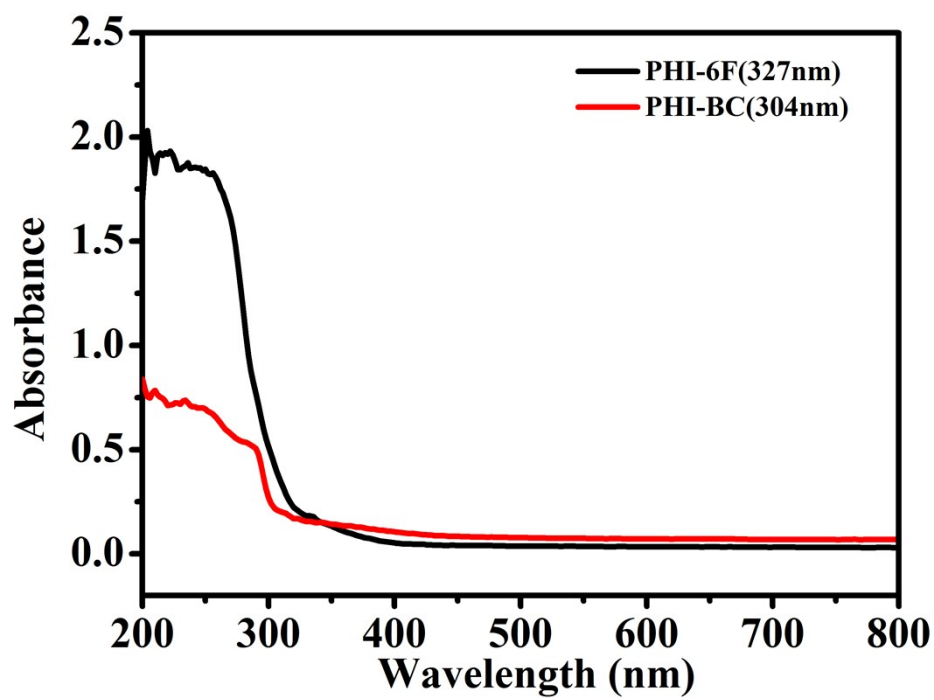


Fig. S6. UV-vis absorption spectra of PHIs films.

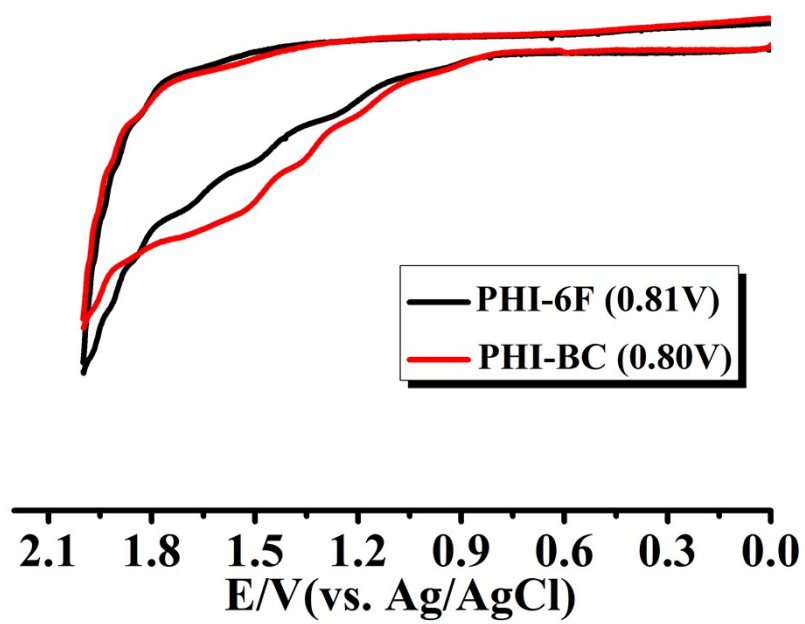


Fig. S7. Cyclic voltammetric diagrams of the **PHIs** films on an ITO-coated glass substrate.

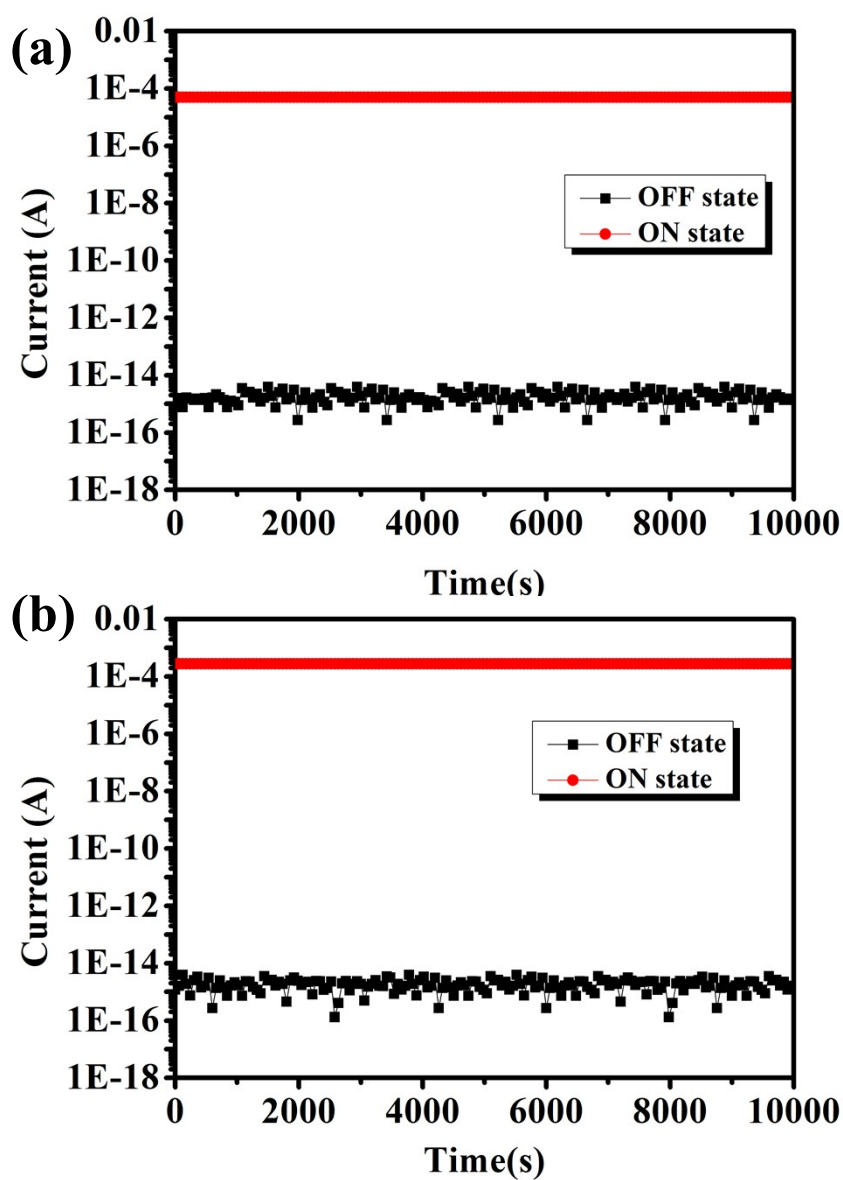


Fig. S8. The stability of memory devices at the ON and OFF states of the ITO/ PHI-6F hybrid materials (50 ± 3 nm)/Al devices (a) PHI-6FTi30 and (b) PHI-6FZr30.

References

T. Nakayama, A. Mochizuki and M. Ueda, *React. Funct. Polym.*, 1996, **30**, 109.