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Supporting Information

Linkage and donor-acceptor effects on resistive switching memory devices of 4-(*N*-carbazolyl)triphenylamine-based polymers

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Materials

The CzTPA-based diamine monomers, 4,4’-diamino-4”-(3,6-dimethoxycarbazol-9-yl)-triphenylamine [S1] and 4,4’-diamino-4”-(3,6-di-*tert*-butylcarbazol-9-yl)triphenylamine, [S2] were prepared by reported methods. Commercially available 3,3’,4,4’-diphenylsulfone-tetracarboxylic dianhydride (DSDA) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) were heated at 250 °C in vacuo for 3 h before use. The dicarboxylic acid monomers bis(4-carboxyphenyl) sulfone (New Japan Chemicals) and 2,2-bis(4-carboxyphenyl)hexafluoropropane (TCI) were used as received. All other reagents were used as received from commercial sources.

Polymer synthesis

Polyimides[S3]

To a solution of 1.0 mmol of CzTPA-based diamine monomer in 9.5 mL of dried DMAc, 1.0 mmol of dianhydride DSDA or 6FDA was added in one portion. The mixture was stirred at room temperature overnight for about 24 h to yield a highly viscous poly (amic acid) solution. The poly(amic acid) was subsequently converted to polyimide via a chemical imidization process by addition of acetic anhydride 2 mL and pyridine 1 mL, then the mixture was heated at 100 °C for 1 h to effect a complete imidization. The homogenous polymer solution was poured slowly into 200 mL of stirring methanol giving rise to a reddish brown precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried. A polymer solution was made by the dissolution of about 0.5 g of the polyimide sample in 10 mL of hot DMAc. The homogeneous solution was poured into a 9-cm glass Petri dish, which was placed in a 90 °C oven overnight for the slow release of the solvent, and then the film was stripped off from the glass substrate and further dried in vacuum at 160 °C for 6 h. The yields of the polyimides were almost quantitative. The polyimides are coded with ***t*-butyl-6FPI**, ***t*-butyl-DSPI**, **OMe-6FPI**, and **OMe-DSPI** (see **Fig. S1**).

Polyamides[S1, S2]

A mixture of 0.7 mmol of the CzTPA-based diamine monomer, 0.7 mmol of bis(4-

carboxyphenyl) sulfone or 2,2-bis(4-carboxyphenyl)hexafluoropropane, 0.15 g of calcium chloride ($CaCl_2$), 0.7 mL of triphenyl phosphite (TPP), 0.2 mL of pyridine, and 1.5 mL of NMP was heated with stirring at 120 ^{o}C for 3 h. The obtained highly viscous polymer solution was poured slowly into 150 mL of stirring methanol giving rise to a stringy, fiber-like precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried under vacuum at 100^{o}C. Reprecipitation from DMAc into methanol was carried out twice for further purification. The polyamides were obtained in almost quantitative yields. The polyamides are coded with ***t*-butyl-6FPA**, ***t*-butyl-DSPA**, **OMe-6FPA**, and **OMe-DSPA** (see **Fig. S1**).

IR spectra of all the polyamide and polyimide films are shown in **Fig. S2**, and typical ^{1}H NMR and H-H COSY spectra of the representative polyamides and polyimides are illustrated in **Figs. S3**–**S6**.

Instrumentation and measurements

The inherent viscosities were determined with a Cannon-Fenske viscometer at 30^{o}C. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 3–5 mg of samples heated in flowing nitrogen or air (gas flow rate = 40 cm^{3}/min) from 200 to 800^{o}C at a heating rate of 20 ^{o}C/min. DSC analyses were performed on a PerkinElmer Pyris 1 DSC at a scan rate of 20 ^{o}C/min under a nitrogen atmosphere. Electrochemistry was performed with a CH Instruments 750A electrochemical analyzer. Cyclic voltammetry (CV) was conducted with the use of a three-electrode cell in which ITO (polymer film area about 1 cm^{2}, 0.8 cm x 1.25 cm) was used as a working electrode. A platinum wire was used as a counter electrode. All cell potentials were taken with the use of a homemade Ag/AgCl, KCl (sat.) reference electrode. Ferrocene was used as an external reference for calibration (+0.44 V vs. Ag/ AgCl). Measurements were carried out in 0.1 M of TBAP as the supporting electrolyte in acetonitrile. Voltammograms are presented with the positive/negative potential pointing to the right/left with increasing anodic/decreasing cathodic current pointing upward/downward. Ultraviolet-visible (UV-Vis) spectra of the polymer films were measured using an Agilent 8453 UV-Visible diode array spectrophotometer. The optical band gap (E_g) of the aramids was calculated from their low energy absorption edges (λ_{onset}), according to the Planck's equation ($E_g = 1240/\lambda_{onset}$).

Fabrication and measurement of the memory device

The ITO glass used for memory device was precleaned by ultrasonication with water, acetone, and isopropanol each for 15 min. A solution of polyimides or polyamides (5 mg/mL in DMAc) was filtered through 0.45 µm pore size of PTFE membrane syringe filter. Then, 250 µL of the filtered solution was spin-coated onto the ITO glass at a rate of 1000 rpm for 60 s and kept at 70 ^{o}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 mm^2 in size) at a pressure of 10-7torr 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 µm diameter tungsten wire attached to a tinned copper shaft with a point radius < 0.1 µm (GGB Industries, Inc.).

Molecular simulation

The molecular simulation in this study was performed by Gaussian 09 program package. The results of value and distribution of the corresponding energy levels within each basic unit of polymers 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.

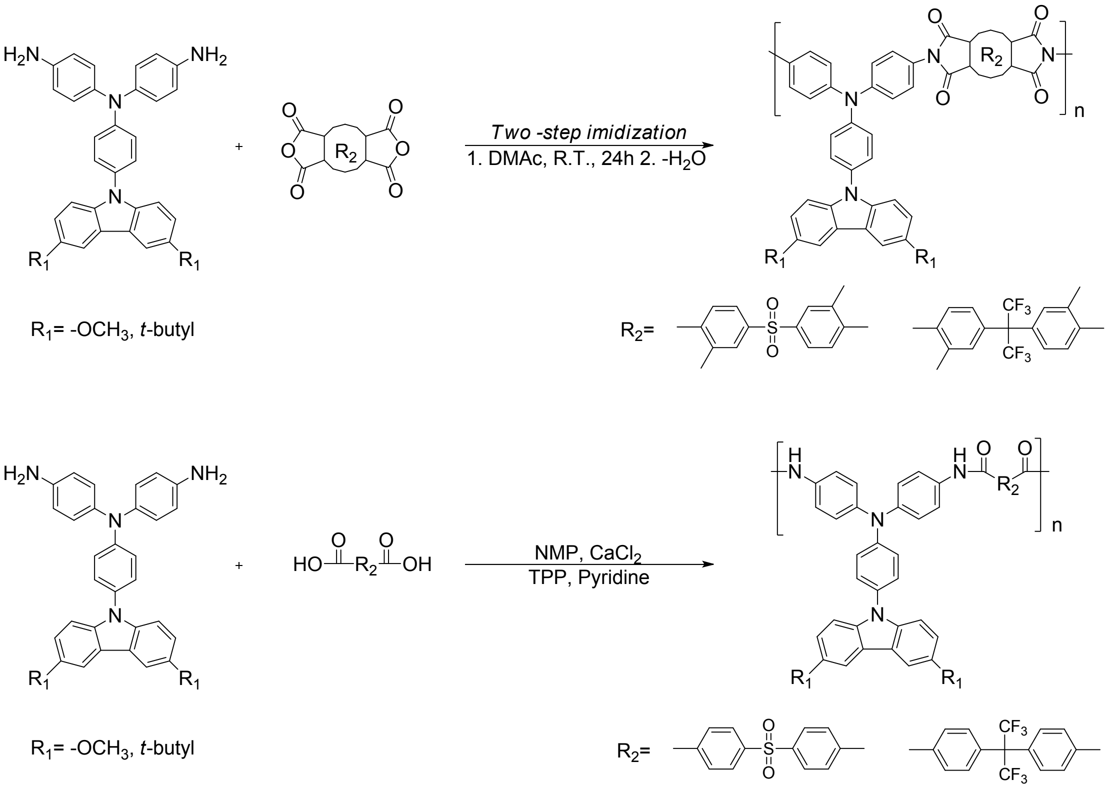

Fig. S1. Synthesis of polyimides[S3] and polyamides[S1, S2].

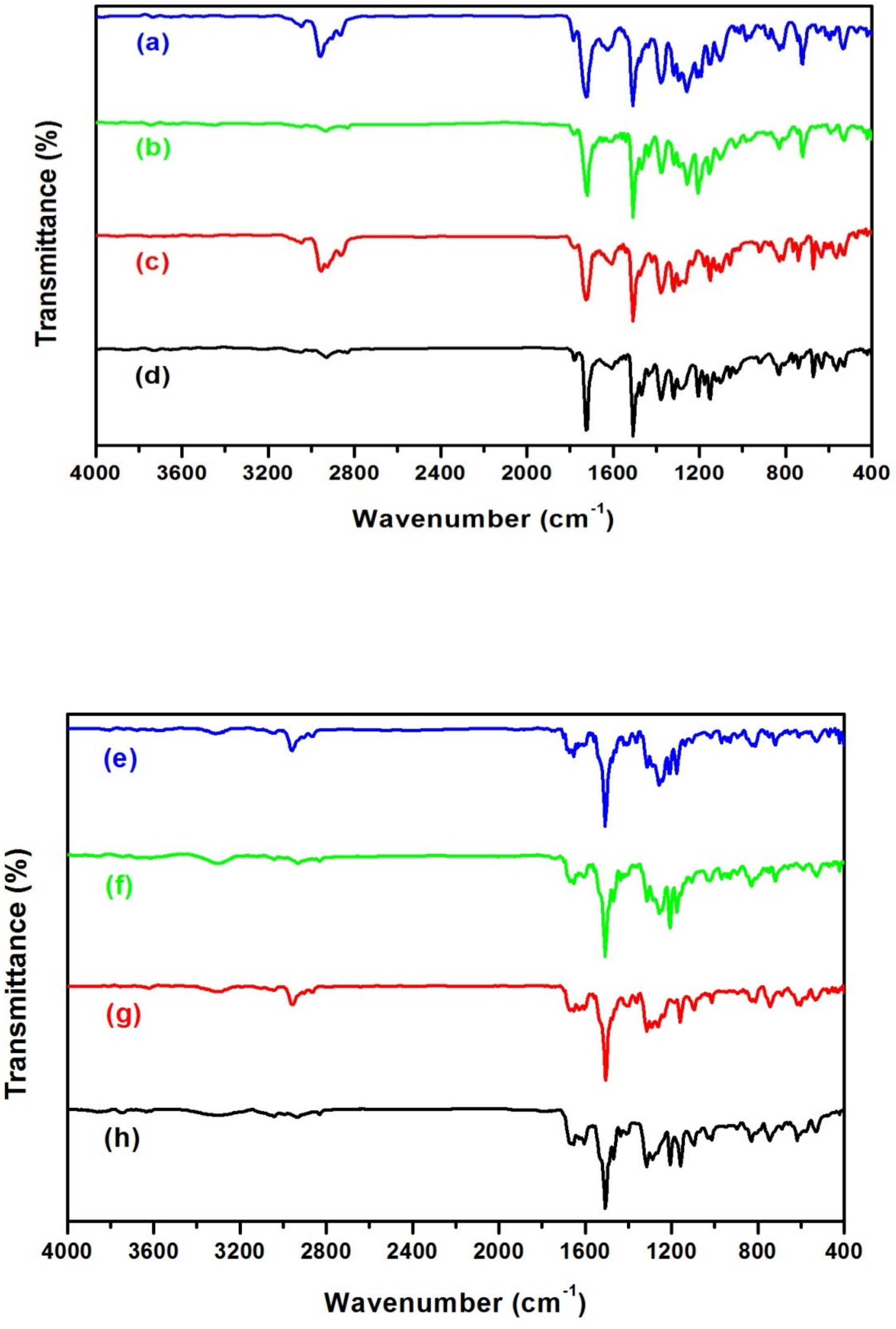

Fig. S2. IR spectra of all the polyimide and polyamide films: (a) ***t*-butyl-6FPI**, (b) **OMe-6FPI**, (c) ***t*-butyl-DSPI**, (d) **OMe-DSPI**, (e) ***t*-butyl-6FPA**, (f) **OMe-6FPA**, (g) ***t*-butyl-DSPA**, and (h) **OMe-DSPA**.

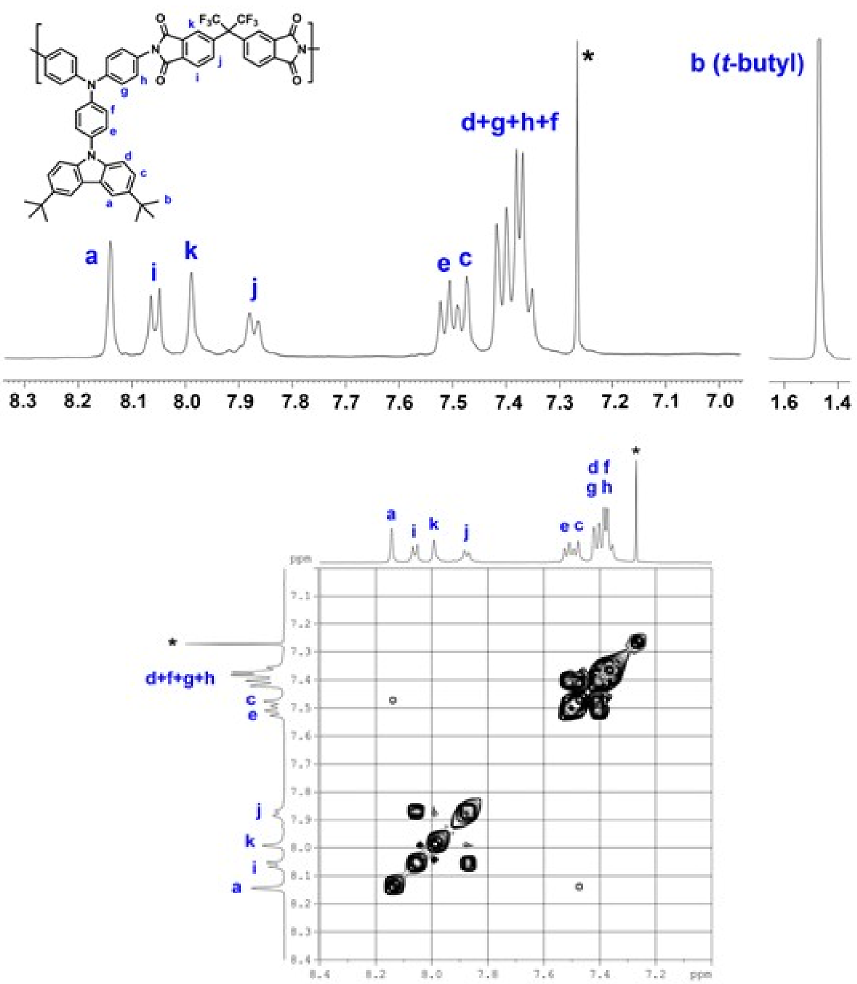

Fig. S3. ^{1}H NMR and H-H COSY spectra of polyimide ***t*-butyl-6FPI** in $CDCl_3$ (* the solvent peak).

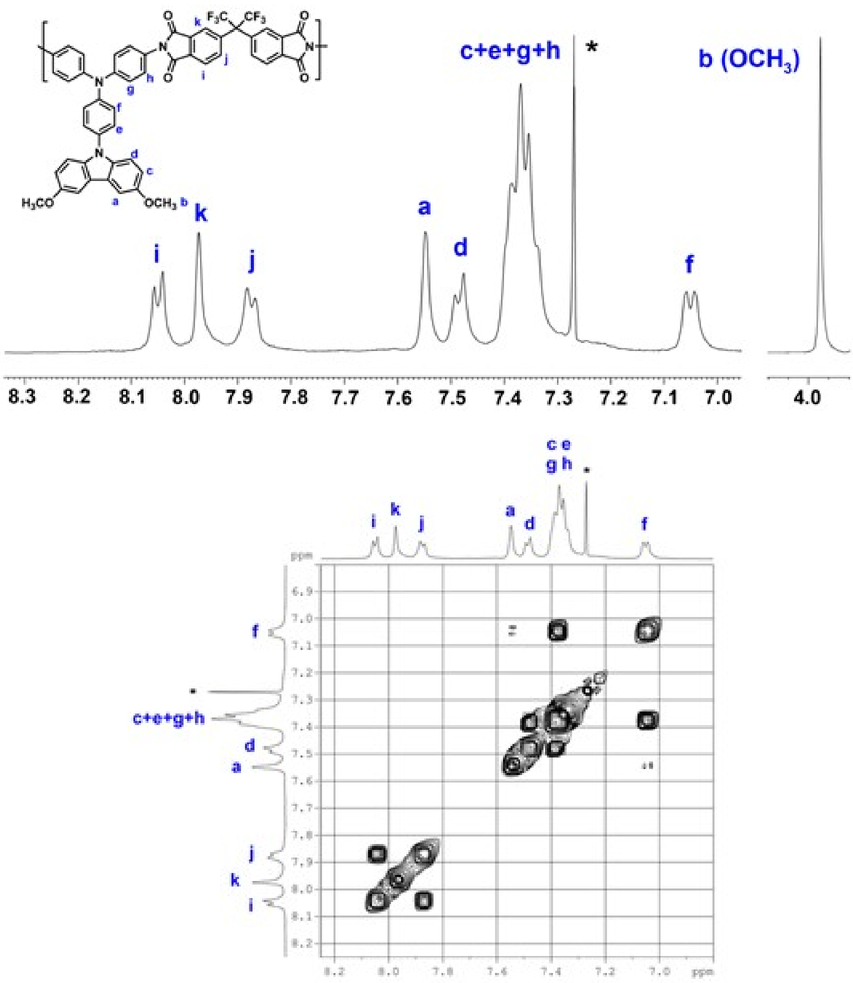

Fig. S4. ^{1}H NMR and H-H COSY spectra of polyimide **MeO-6FPI** in $CDCl_3$ (* the solvent peak).

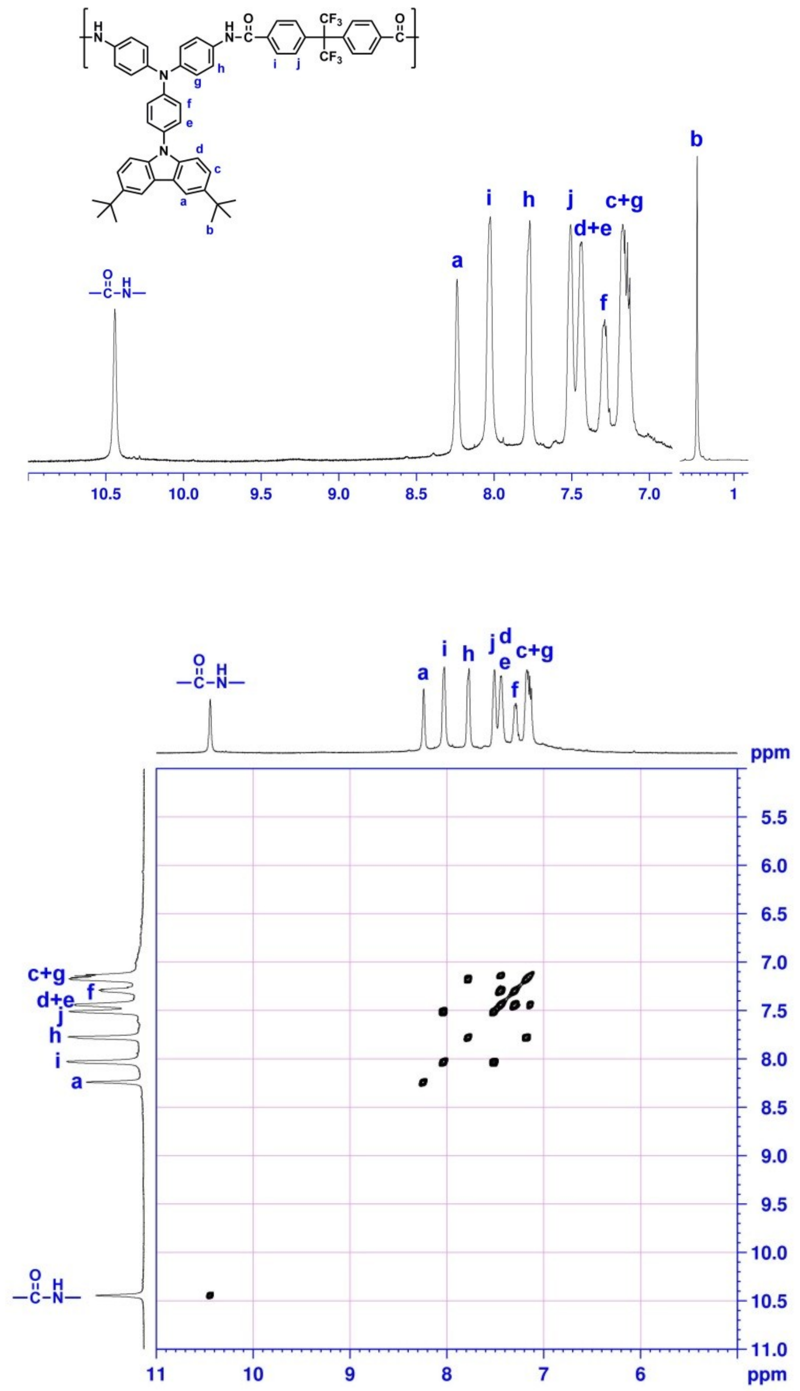

Fig. S5. ^{1}H NMR and H-H COSY spectra of polyamide ***t*-Bu-6FPA** in DMSO-d_6.

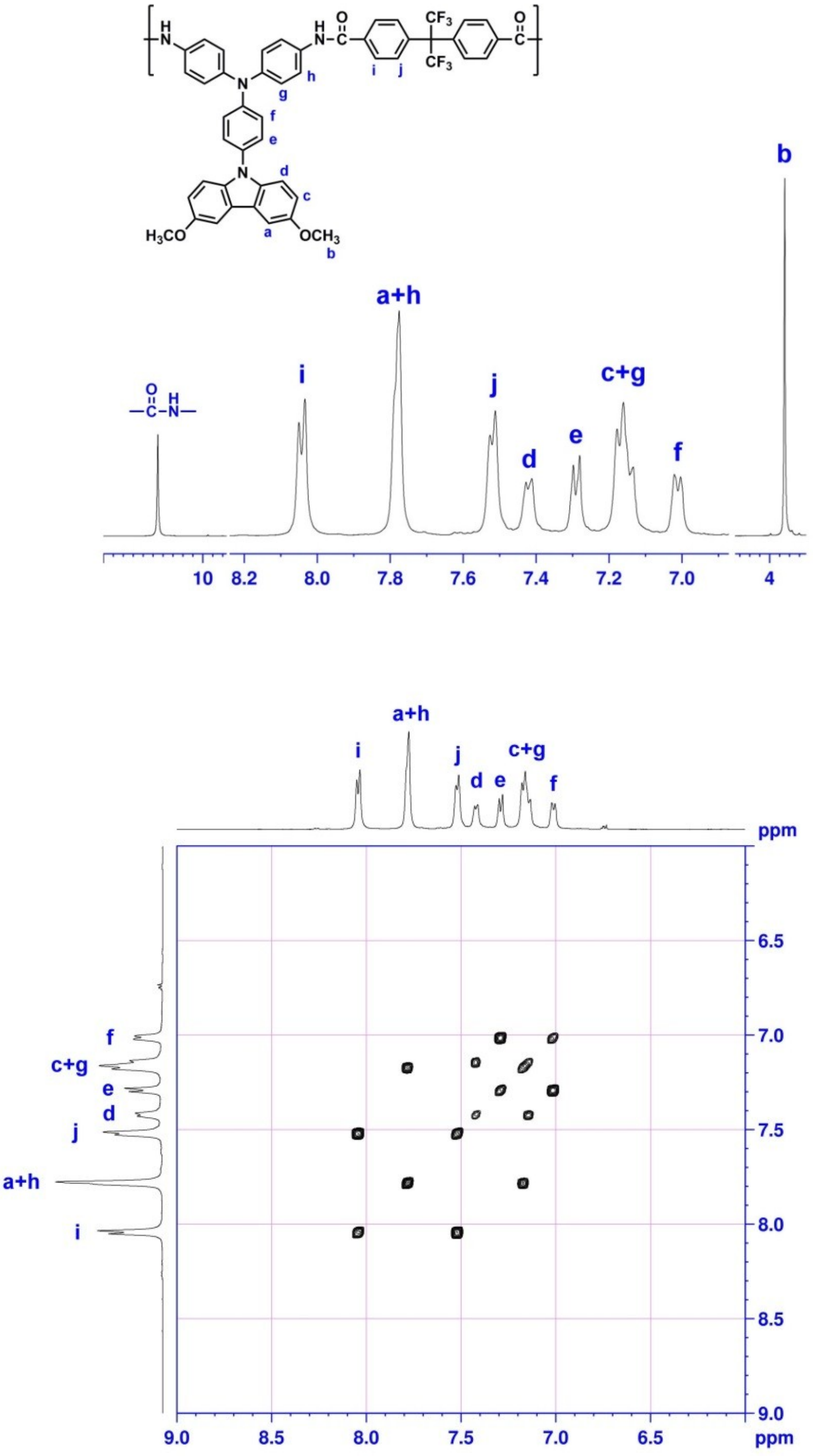

Fig. S6. ^{1}H NMR and H-H COSY spectra of polyamide **MeO-6FPA** in DMSO-d_6.

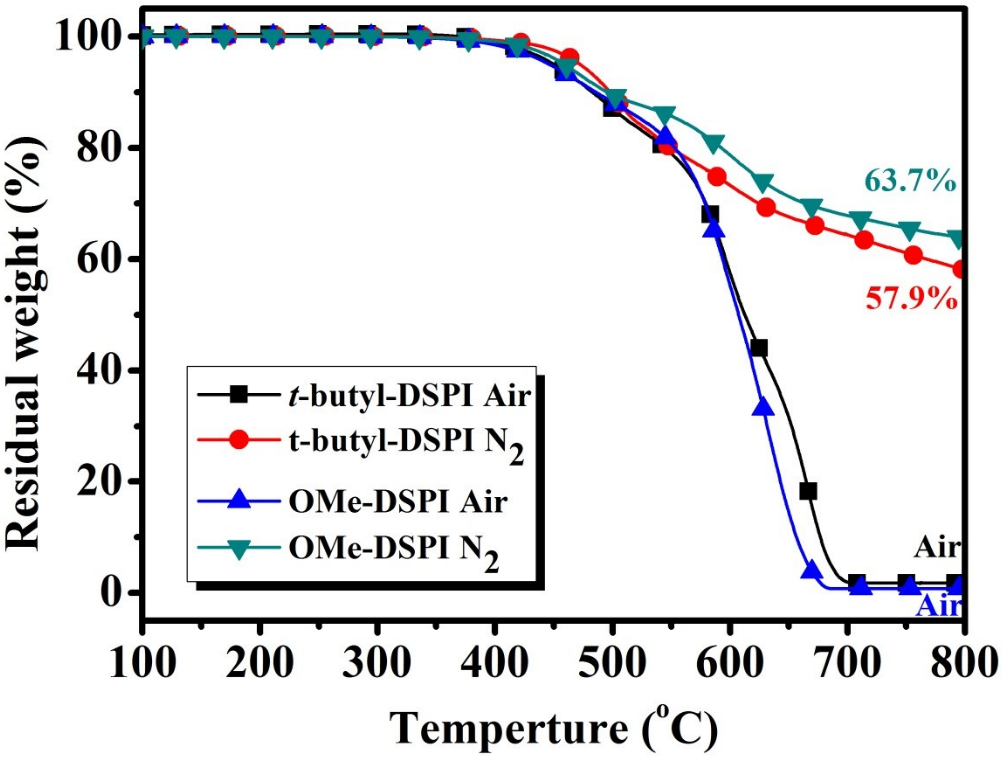

Fig. S7. TGA traces of ***t*-butyl-DSPI** and **OMe-DSPI.**

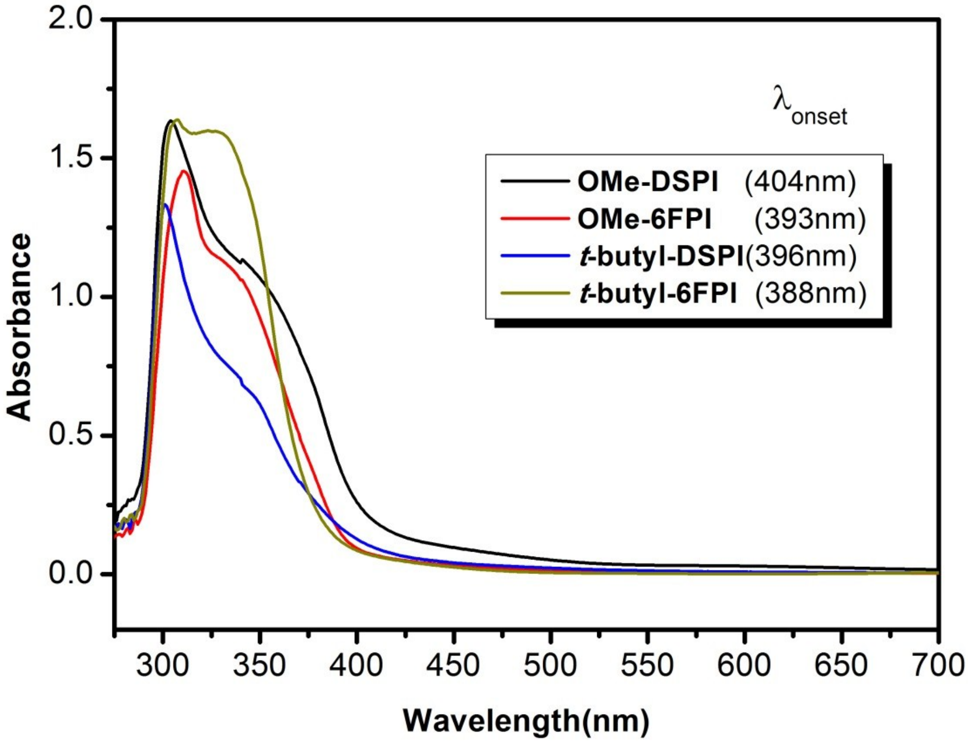

Fig. S8. UV-visible absorption spectra of polyimides films (thickness: 250-350 nm).

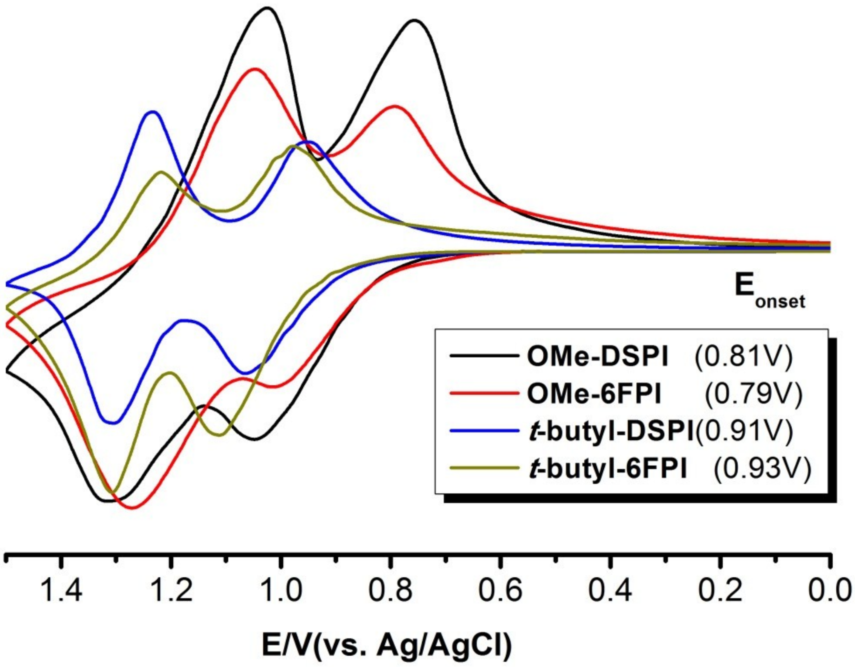

Fig. S9. Cyclic voltammetric diagrams of the polyimide films on an ITO-coated glass substrate.

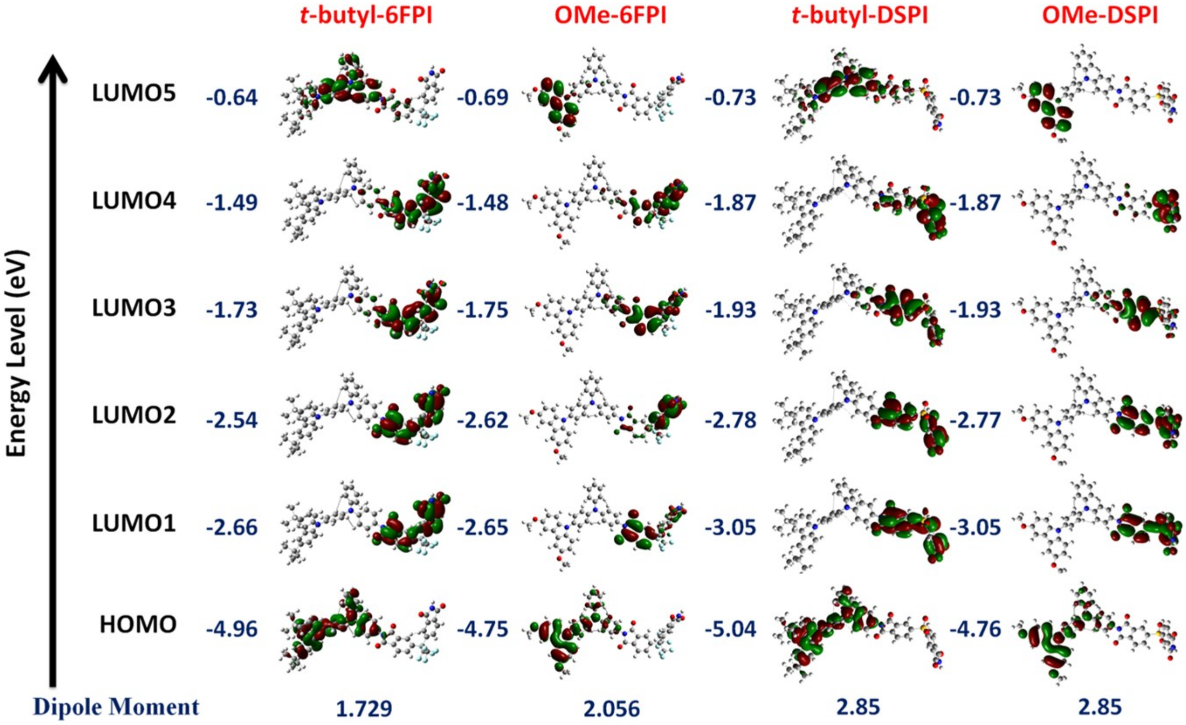

Fig. S10. Calculated molecular orbitals and corresponding energy levels of the repeating units for the polyimides.

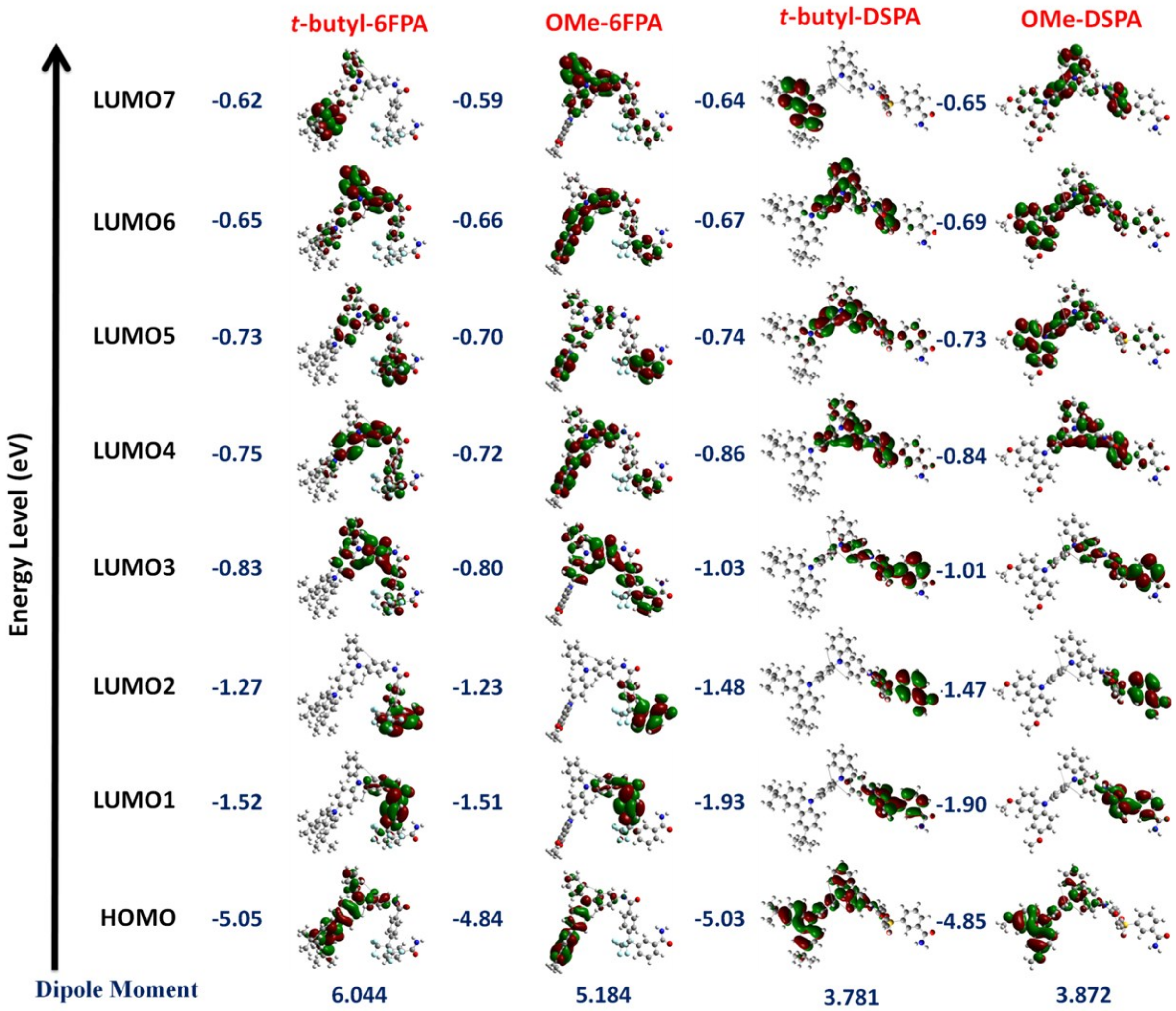

Fig. S11. Calculated molecular orbitals and corresponding energy levels of the repeating units for the polyamides.

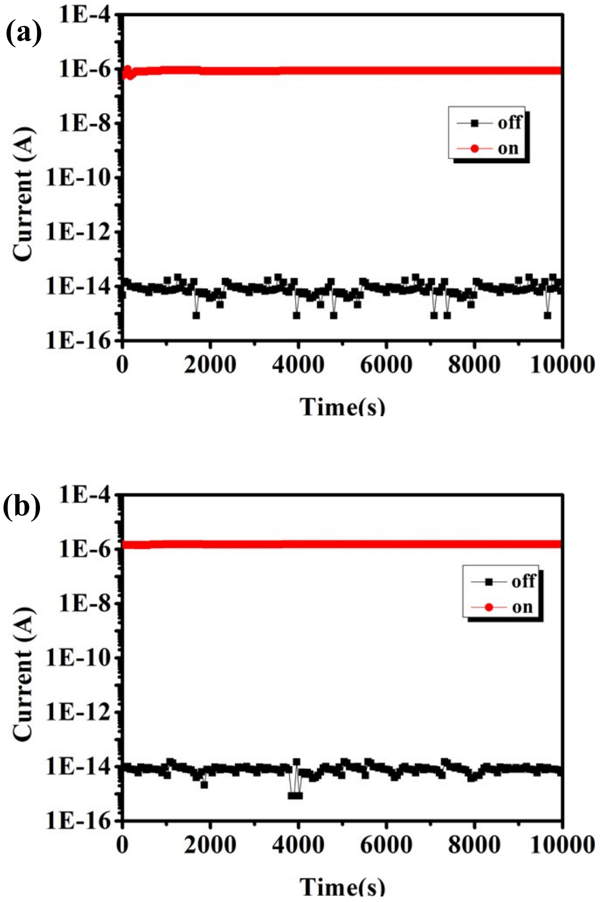

Fig. S12. Retention times on the ON-, and OFF- states of the ITO/Polymer (50nm thick)/Al devices (a) **OMe-DSPI** and (b) **OMe-DSPA.**

Table S1 Inherent viscosity and solubility behaviors of polymers[S1–S3]

Code	η_{inh} (dL/g)	GPC Data[c]			Solubility in various solvents[e]					
		M_n	M_w	PDI[d]	NMP	DMAc	DMF	DMSO	*m*-cresol	THF
***t*-butyl-6FPI**	2.64 [a]	69500	129200	1.86	＋＋	＋＋	＋＋	＋	＋＋	＋＋
***t*-butyl-DSPI**	1.75 [a]	69650	121900	1.75	＋＋	＋＋	＋＋	＋	＋＋	＋＋
OMe-6FPI	1.80 [a]	59750	113500	1.90	＋＋	＋＋	＋＋	＋	＋＋	＋＋
OMe-DSPI	2.48 [a]	63200	123300	1.95	＋＋	＋	＋－	＋－	－	＋
***t*-butyl-6FPA**	0.39[b]	16250	33100	2.04	＋＋	＋＋	＋＋	＋＋	＋＋	＋＋
***t*-butyl-DSPA**	0.39[b]	18200	35100	1.93	＋＋	＋＋	＋＋	＋	＋＋	＋＋
OMe-6FPA	0.56[b]	20500	50500	2.46	＋＋	＋＋	＋＋	＋＋	＋	＋＋
OMe-DSPA	0.54[b]	23000	57000	2.48	＋＋	＋＋	＋＋	＋＋	＋	＋－

[a] Inherent viscosity of the poly(amic acid) precursors measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

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

[c] Calibrated with polystyrene standards, using NMP as the eluent at a constant flow rate of 0.5 mL min^{-1} at 40 ℃.

[d] Polydispersity Index (M_w / M_n)

[e] Qualitative solubility was tested with 5 mg of a sample in 1 mL of solvent. ＋＋, soluble at room temperature; ＋, soluble on heating; ＋－, partially soluble or swelling; －, insoluble even on heating.

Table S2 Thermal properties of polymers[S1–S3]

Polymer[a]	T_g (°C)[b]	T_d at 10 % weight loss (°C)[c]		Char yield (wt%)[d]
		N_2	Air	
***t*-butyl-6FPI**	333	564	565	63
***t*-butyl-DSPI**	364	495	482	58
OMe-6FPI	324	529	492	59
OMe-DSPI	377	497	485	64
***t*-butyl-6FPA**	310	522	524	64
***t*-butyl-DSPA**	321	487	479	62
OMe-6FPA	296	508	507	72
OMe-DSPA	308	492	480	66

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

[b] Glass transition temperature measured by TMA with a constant applied load of 5 mN at a heating rate of 10 °C/min by film/fiber probe in nitrogen.

[c] Decomposition temperature at which 10% weight loss recorded by TGA at a heating rate of 20 °C/min and a gas-flow rate of 20 cm^3/min.

[d] Residual weight percentage at 800 °C in nitrogen.

References:

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S3. H. M. Wang and S. H. Hsiao, *J. Polym. Sci. Part A: Polym. Chem.,* 2014, **52**, 1172.