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Supporting Information

Novel Programmable Functional Polyimides: Preparation, Demonstrating Mechanism of CT Induced Memory, and Ambipolar Electrochromic Behavior

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Table S1. Inherent Viscosity and Molecular Weights of Polyimides

polymer	η_{inh} [a] (dL/g)	M_w [c]	M_n [c]	PDI[d]	DP[e]
9Ph-ODPI	0.27	135,400	56,600	2.38	48
9Ph-6FPI	0.43	161,800	83,500	1.94	64
9Ph-DSPI	0.31	148,300	69,700	2.13	57
9Ph-PMPI	0.30[b]	135,400	67,901	1.99	63

[a] Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.
[b] Measured at a polymer concentration of 0.5 g/dL in H_2SO_4 at 30 °C.
[c] Calibrated with polystyrene standards, using NMP as the eluent at a constant flow rate of 0.5 mL/min at 40 °C.
[d] Polydispersity Index (M_w/M_n).
[e] Degree of Polymerization.

Table S2. Solubility Behavior

Code	Solubility in various Solvent[a)]						
	NMP	DMAc	DMF	DMSO	*m*-Cresol	THF	$CHCl_3$
9Ph-ODPI	++	+	+−	+−	+	+	++
9Ph-6FPI	++	++	+	+−	+	++	++
9Ph-DSPI	++	++	+	+−	++	++	++
9Ph-PMPI	+−	+−	+−	+−	+−	+−	+−

[a)] The solubility was determined with a 10 mg sample in 1 mL of a solvent. ++, soluble at room temperature; +, soluble on heating at 70°C-80°C; +−, partially soluble or swelling; −, insoluble even on heating.

Table S3. Thermal Properties of **9Ph-** Series Polyimides

Polymer[a)]	T_g [°C] [b)]	T_d^5 [°C] [c)]		T_d^{10} [°C] [c)]		R_{w800} [%] [d)]	LOI [e)]
		N_2	Air	N_2	Air		
9Ph-ODPI	241	455	435	485	485	63	43
9Ph-6FPI	252	455	455	500	495	59	41
9Ph-DSPI	247	455	450	505	485	61	42
9Ph-PMPI	265	460	460	495	495	66	44

[a)] The polymer film samples were heated at 300 °C for 1 h prior to all the thermal analyses.
[b)] Midpoint temperature of baseline shift on the second DSC heating trace (rate: 20 °C /min) of the sample after quenching from 400 °C to 50 °C (rate: 200 °C /min) in nitrogen.
[c)] 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 cm^3/min.
[d)] Residual weight percentages at 800 °C under nitrogen flow.
[e)] LOI = Limiting Oxygen Index = $17.5+0.4R_{w800}$

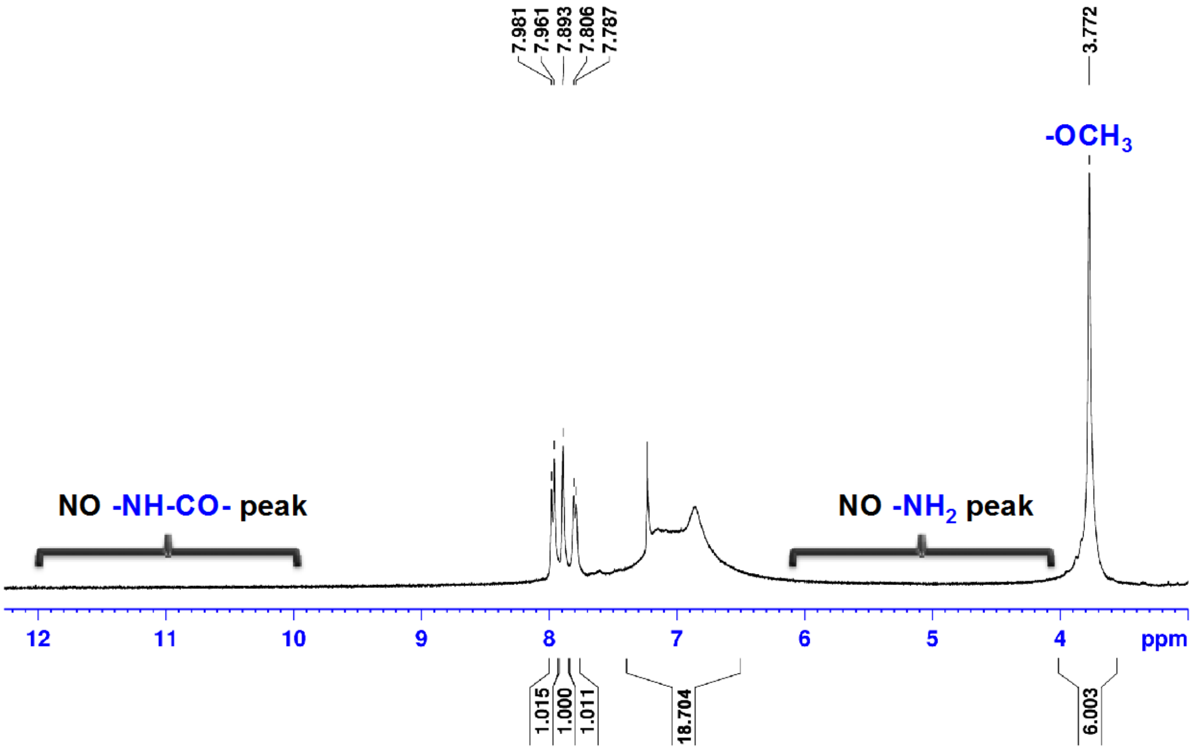

Figure S1. ^{1}H NMR spectrum of polyimide **9Ph-6FDA** in DMSO-d_6.

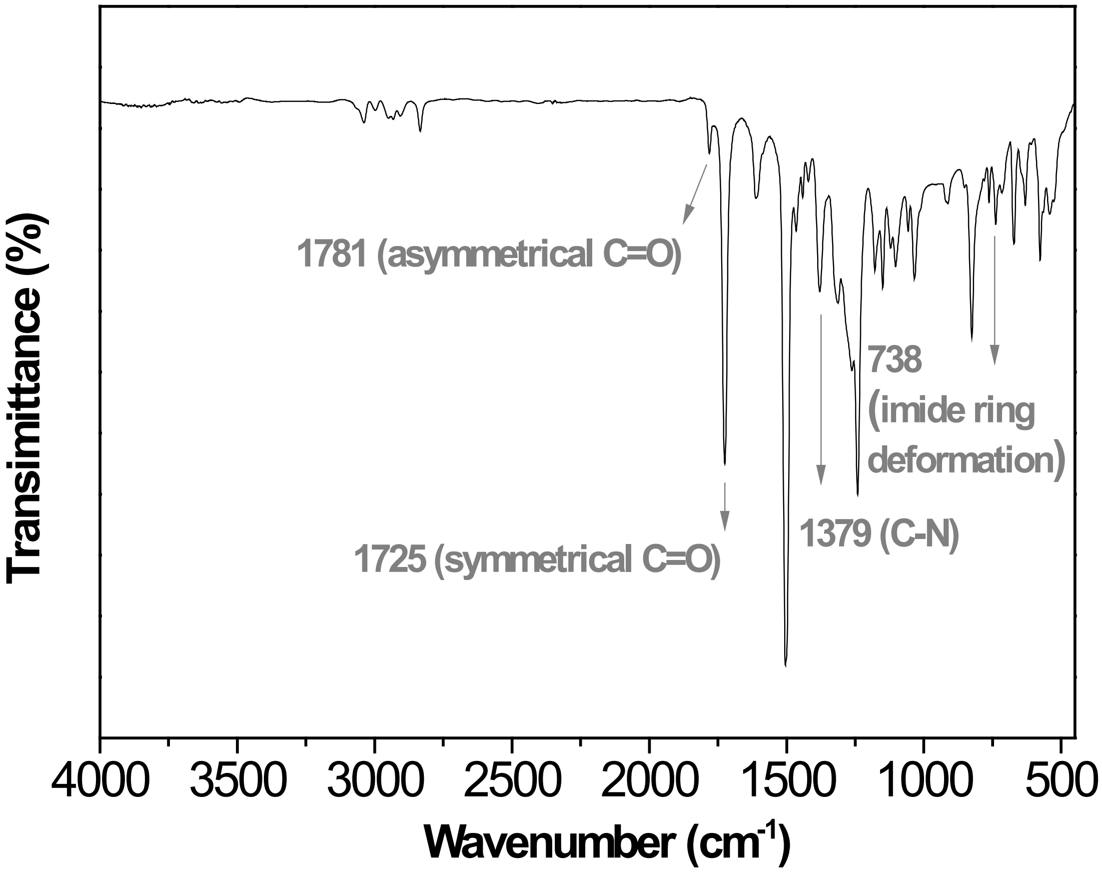

Figure S2. IR spectrum of polyimide **9Ph-DSPI** film.

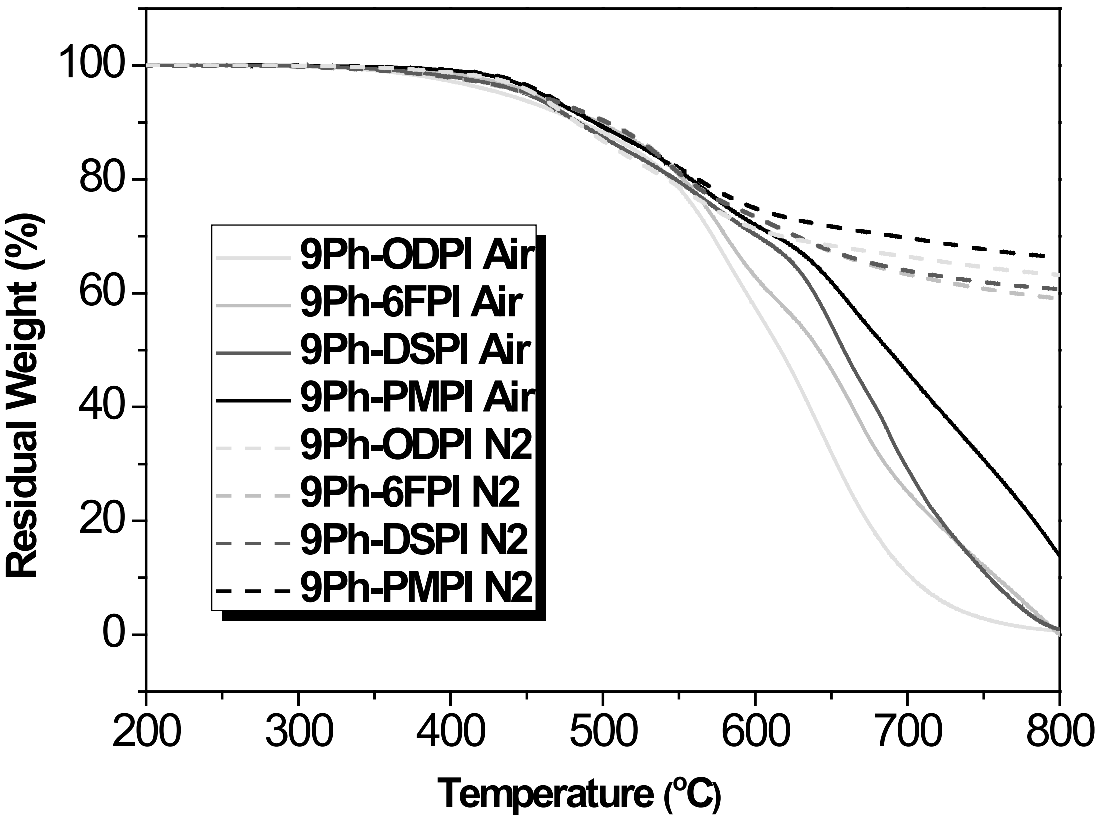

Figure S3. TGA thermograms of **9Ph-** series polyimides.

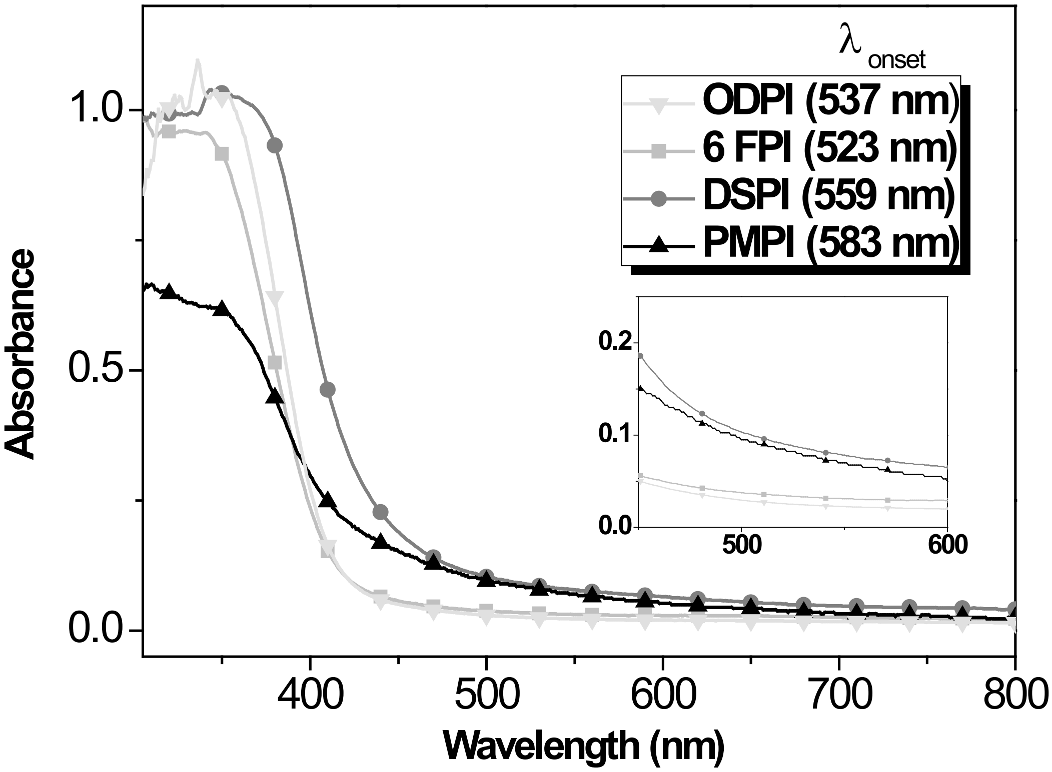

Figure S4. UV-visable absorption spectra of **9Ph-** series polyimides.

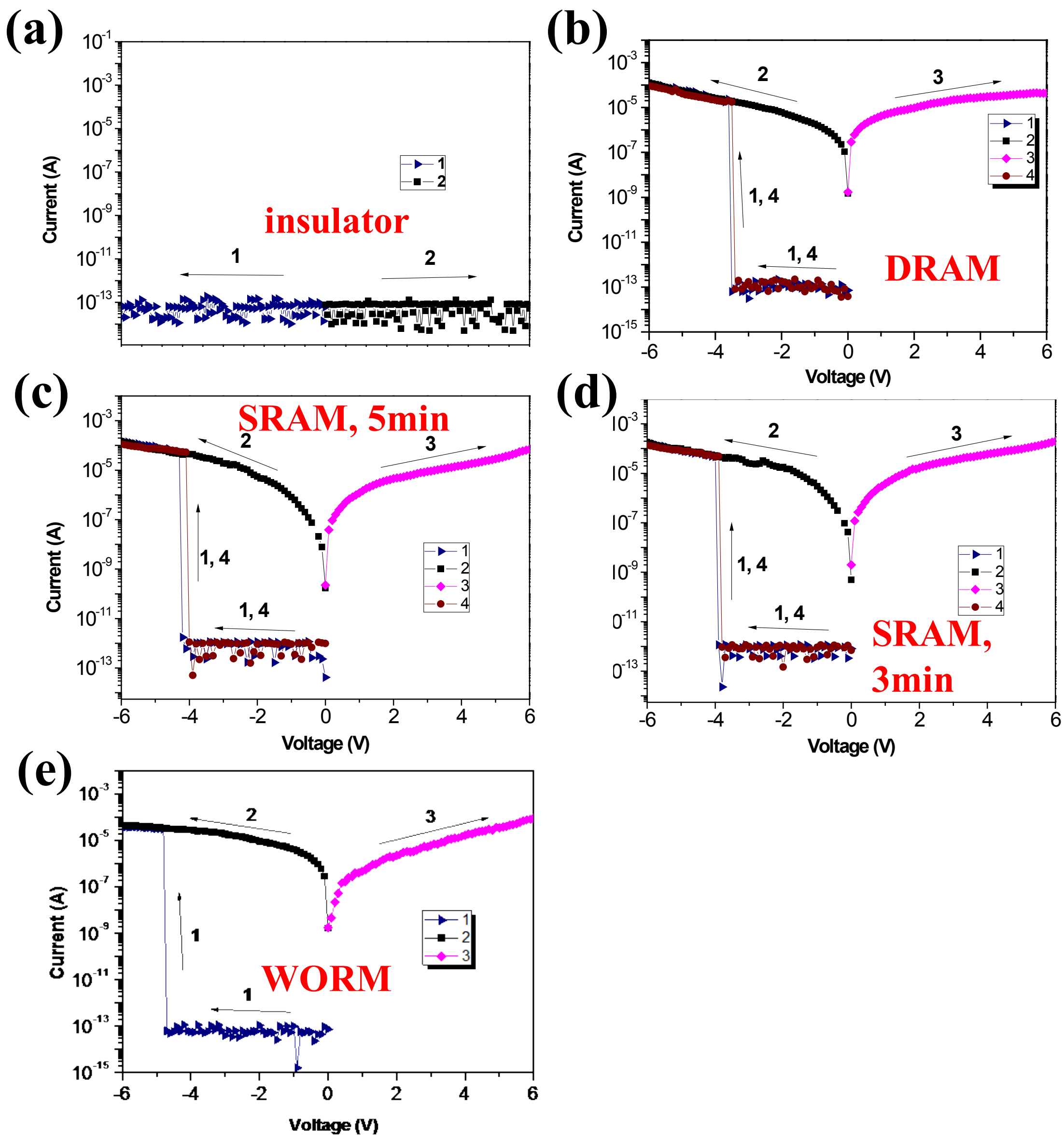

Figure S5. Current-voltage (I-V) characteristics of the ITO/polyimide (50 ± 3 nm)/Al memory devices. (a) **3Ph-ODPI** (b) **3Ph-6FPI** (c) **3Ph-DSPI** (d) **3Ph-PMPI** (e) **3Ph-NPPI**.

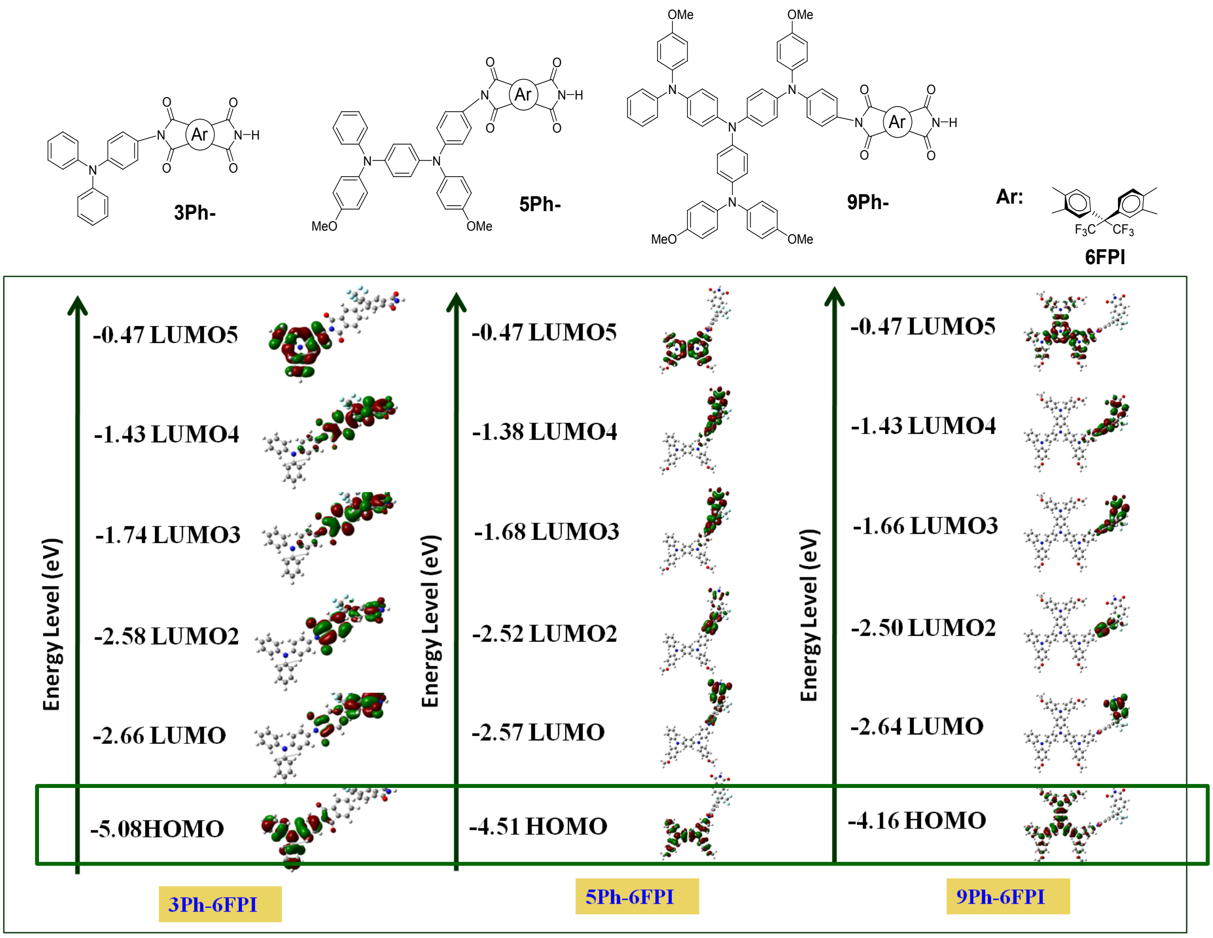

Figure S6. Calculated molecular orbitals and corresponding energy levels of the basic units for **3Ph-6FPI**, **6Ph-6FPI**, and **9Ph-6FPI**.

Polymer	HOMO (eV)	LUMO (eV)	E_g (eV)
3Ph-ODPI	5.02	2.48	2.54
3Ph-6FPI	5.08	2.66	2.42
3Ph-DSPI	5.15	3.02	2.13
3Ph-PMPI	5.22	3.21	2.01
3Ph-NPPI	5.12	3.41	1.71
5Ph-ODPI	4.48	2.48	2.00
5Ph-6FPI	4.51	2.57	1.94
5Ph-DSPI	4.57	2.97	1.60
5Ph-PMPI	4.54	3.14	1.40
5Ph-NPPI	4.53	3.36	1.17
9Ph-ODPI	4.15	2.44	1.71
9Ph-6FPI	4.16	2.64	1.52
9Ph-DSPI	4.22	2.98	1.24
9Ph-PMPI	4.22	3.15	1.07

Figure S7. Energy levels of polyimides from gaussian simulation.

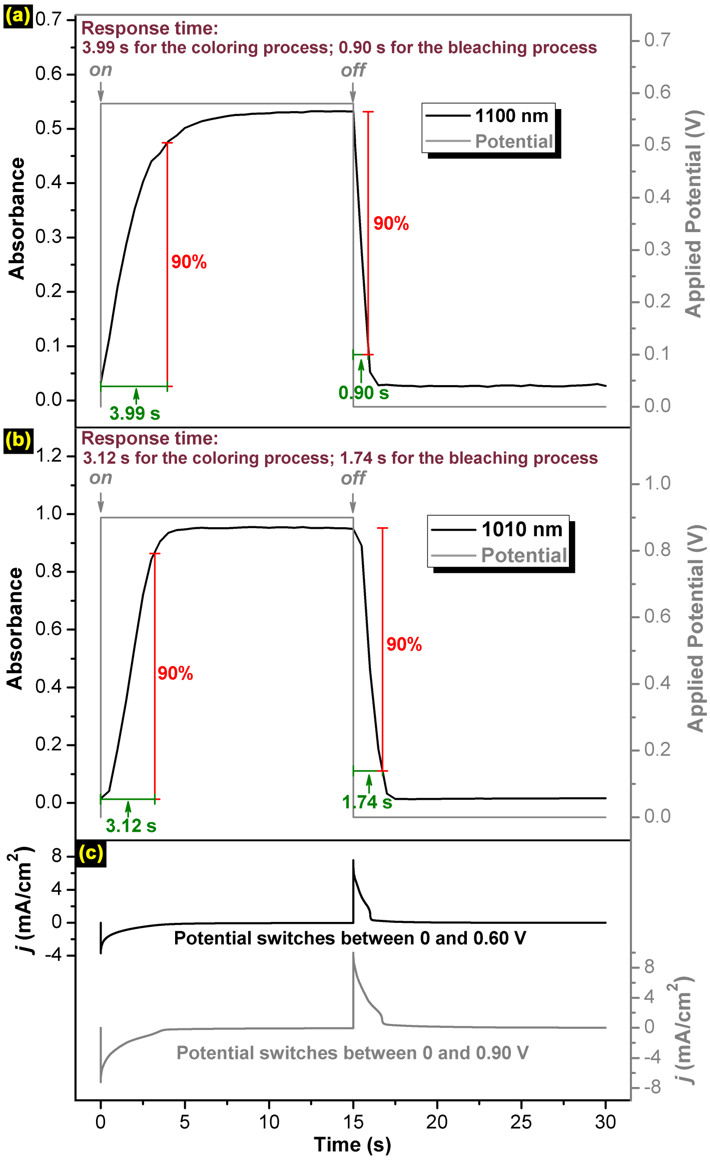

Figure S8. Calculation of optical switching time at (a) 1100 nm, (b) 1010 nm at the applied potential, and (c) current-time curves of polyimide **9Ph-PMPI** thin film (130±10 nm in thickness) on the ITO-coated glass substrate.

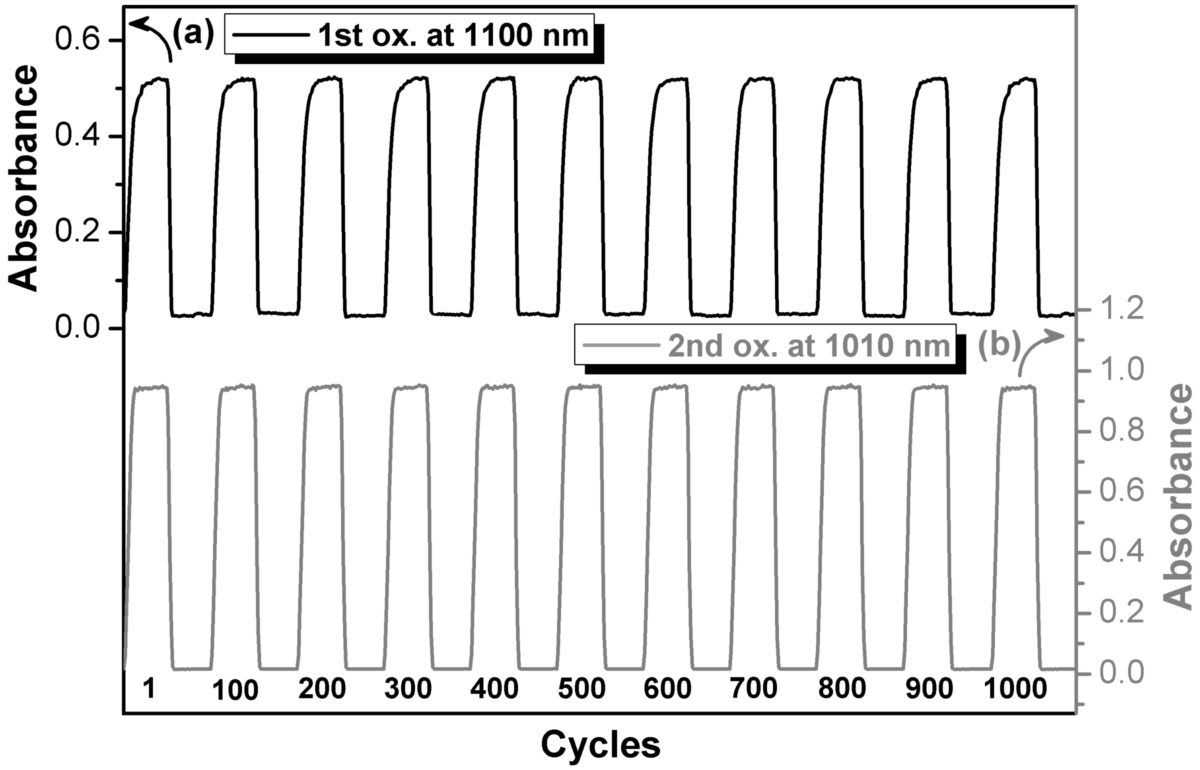

Figure S9. Absorbance change between (a) 0 and 0.60 V and (b) 0 and 0.90 V (vs. Ag/AgCl) of polyimide **9Ph-PMPI** thin film (130±10 nm in thickness) on the ITO-coated glass substrate (coated area: 1.2 cm × 0.5 cm) in 0.1 M TBAP/CH_3CN with a cycle time of 30 s monitored at the given wavelength.

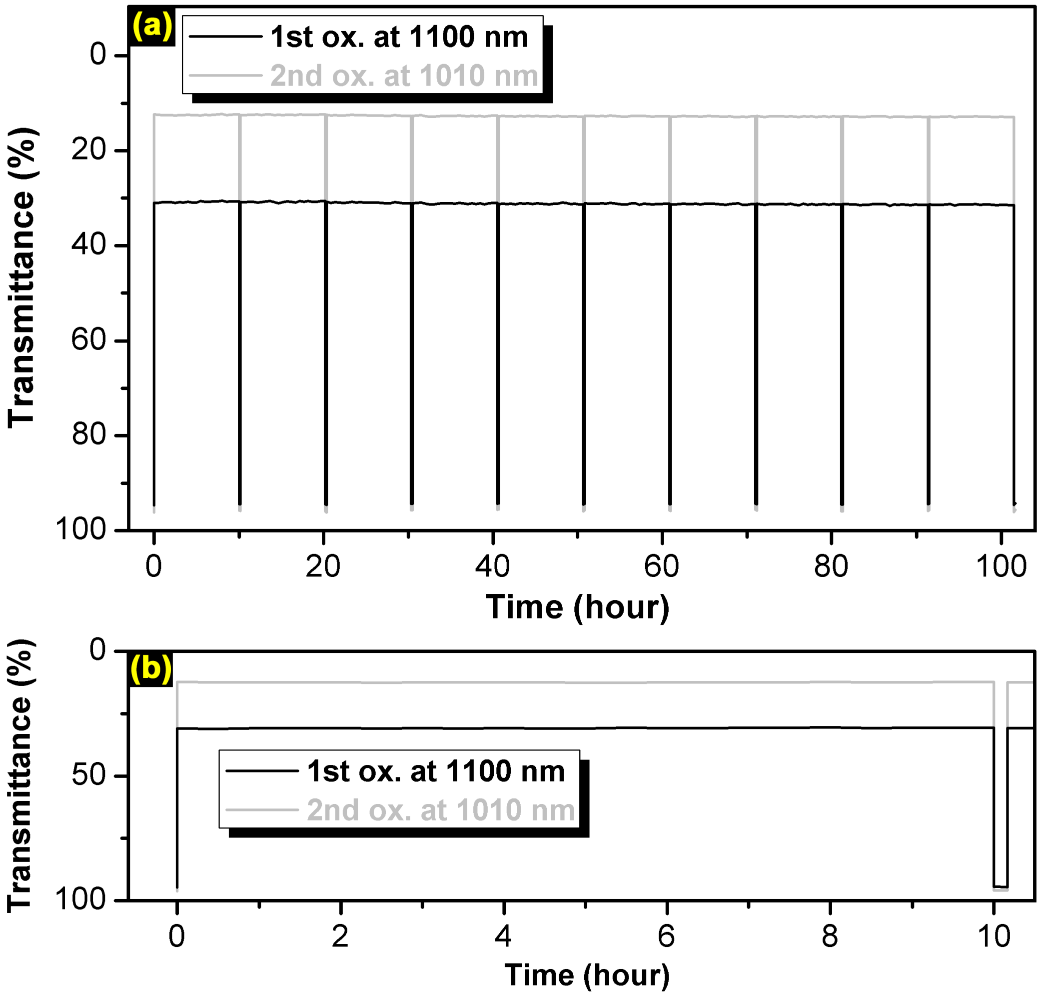

Figure S10. Potential step transmittance change at 1st and 2nd oxidized states for (a) continuous 10 cycling test and (b) 1 switching cycle of a single-layer flexible ITO-coated PEN EC device, using polyimide **9Ph-PMPI** (130±10 nm in thickness) as active layer with a cycle time of 10 hour and 10 min for coloring and bleaching processes, respectively.