

Supporting Information

Synthesis and Characterization of Novel Electrochromic Devices Derived from Redox-active Polyamide-TiO₂ Hybrids

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Experimental section

Fabrication of electrochromic device (ECDs)

The ITO-coated glasses used for EC devices washed by three steps, respectively detergent, acetone, and isopropanol each for 15 min by ultra-sonication. The films are prepared by coating onto the anode side ECD ITO-coated glass (25 mm × 30 mm × 1 mm, 5 Ω/ square). In the ECD cathode side ITO-coated glass were laminated with thermosetting plastics by a full-auto dispenser make the active areas of devices to be 20 mm × 20 mm and then covering to the another side. The EC device with gap of 120 μm is transferred to oven for 6 h at 120 °C. Only one tiny hole was left on one side of the devices for the later injection of the highly transparent polymer conductive gel. The gel is consist of poly(methyl methacrylate) (PMMA) (Mw: 120,000), tetrabutylammonium tetrafluoroborate (TBABF₄), and propylene carbonate (PC). PMMA (275 mg) and TBABF₄ (66 mg; 0.1 M) was dissolved in PC (2 ml). The total amount of PC solution was around 0.048 ml inside the device after the injection. Finally, the devices were sealed completely by UV curable adhesive.

Characterization

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 32. The inherent viscosities were determined at 0.5 g/dL concentration using Tamson TV-2000 viscometer at 30 °C. Thermogravimetric analysis (TGA) conducted with a TA Instruments Q50, and experiments were carried out on approximately 3-7 mg film samples heated in flowing nitrogen or air (flow rate = 20 cm³/min) at a heating rate of 20 °C /min. DSC analyses were performed on a PerkinElmer Pyris 1 DSC at a scan rate of 20 °C /min in flowing nitrogen. Ultraviolet-visible (UV-vis) spectra of the obtained films were recorded on Hitachi U-4100 UV-vis-NIR spectrophotometer. The microstructure of the prepared PA hybrid films was inspected 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-coated glass (polymer films area about 25 mm x 6 mm) was used as the working electrode and a platinum wire as the auxiliary electrode at a scan rate of 50 mV s⁻¹ against a Ag/AgCl reference electrode in PC, using 0.1 M of TBABF₄ as the supporting electrolyte. All cell potentials were taken by using a homemade Ag/AgCl, KCl (3 M) reference electrode. The spectroelectrochemical cell was measured by using a two-electrode EC device (active area about 20 mm × 20 mm). Absorption spectra in spectroelectrochemical analysis were measured with a HP 8453 UV-Vis spectrophotometer. Coloration efficiency CE (η) decides the amount of optical density change (δOD) at a specific absorption wavelength induced as a function of the ejected/injected charge (Q; also termed as electro-activity) which is determined from the in situ experiments. CE is given by the equation: $\eta = \delta OD / Q = \log [T_b / T_c] / Q$, where η (cm² /C) is the coloration efficiency at a given wavelength, Q is the injected charge, and T_b and T_c are the bleached and colored transmittance values, respectively.

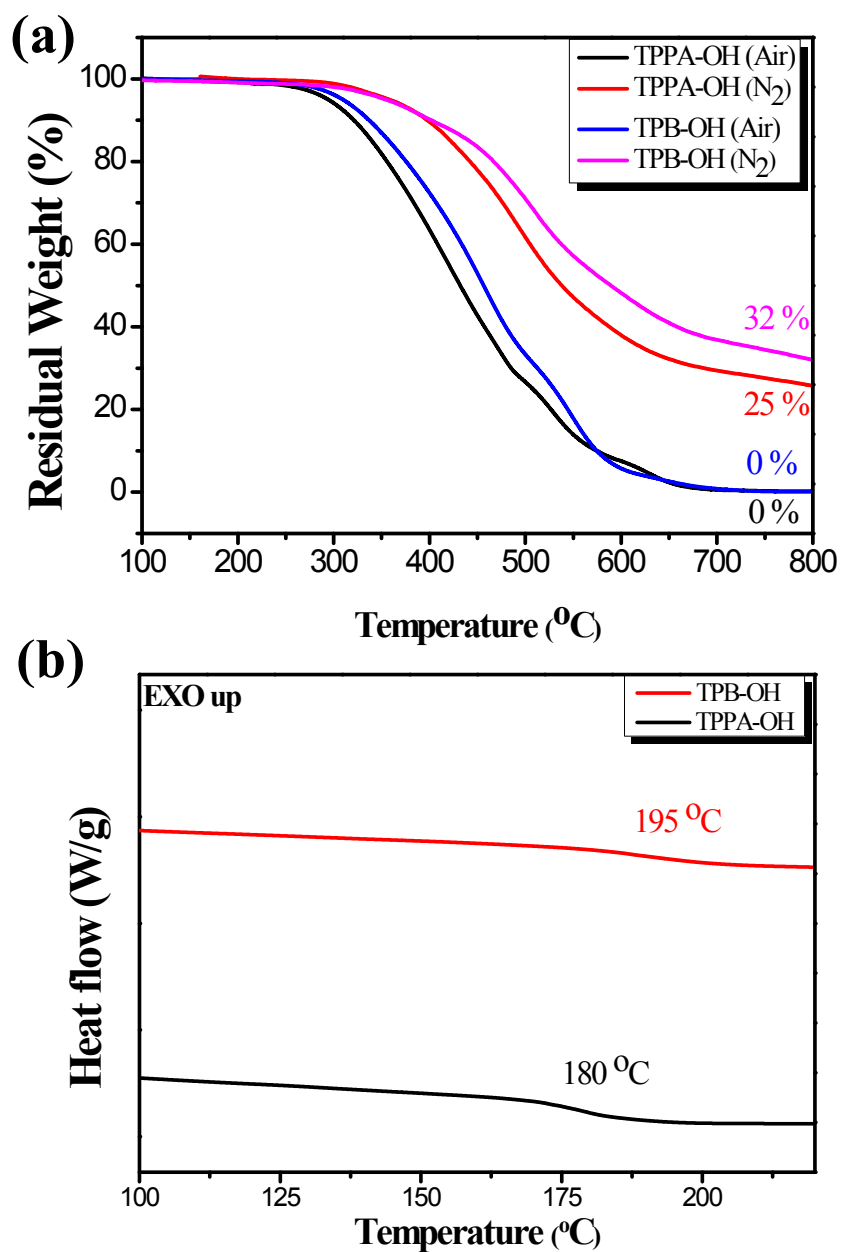


Fig. S1 (a) TGA traces of the polyamides with a heating rate of 20 °C/min under nitrogen and air. (b) DSC trace of polyamides with a heating rate of 20 °C/min in nitrogen.

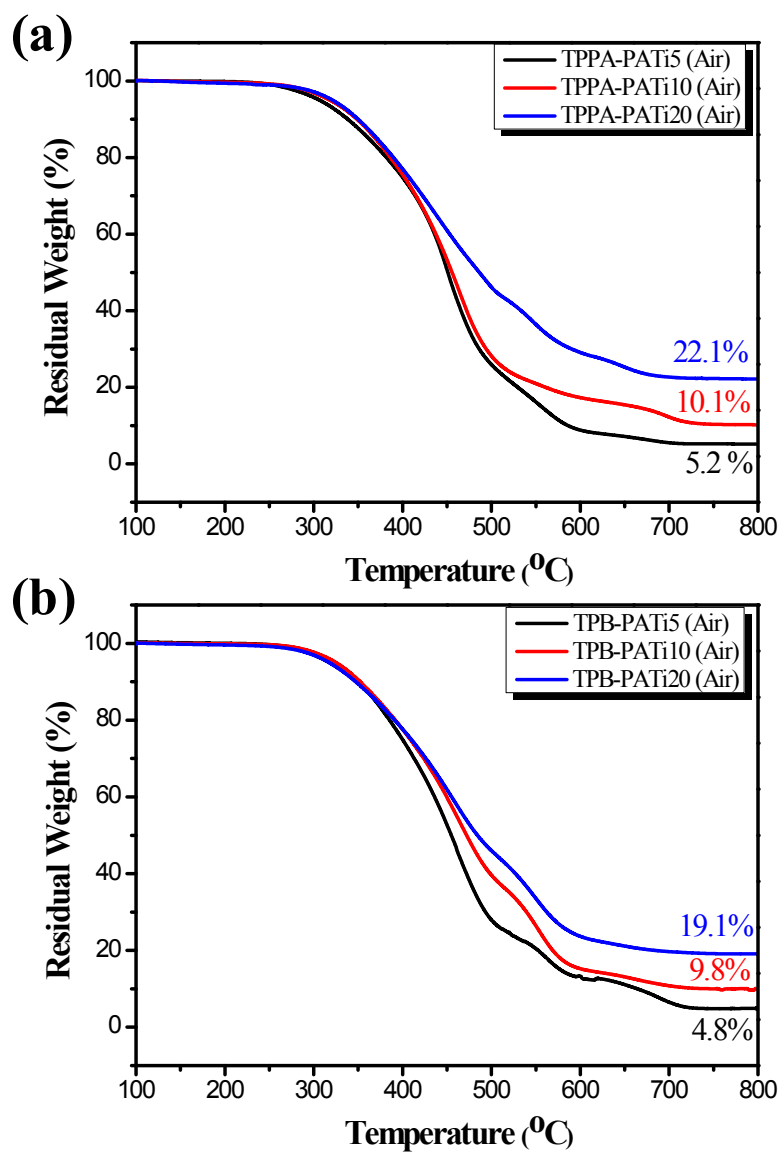


Fig. S2 TGA traces of TPPA-PA/TiO₂ and TPB-PA/TiO₂ hybrid materials in air.

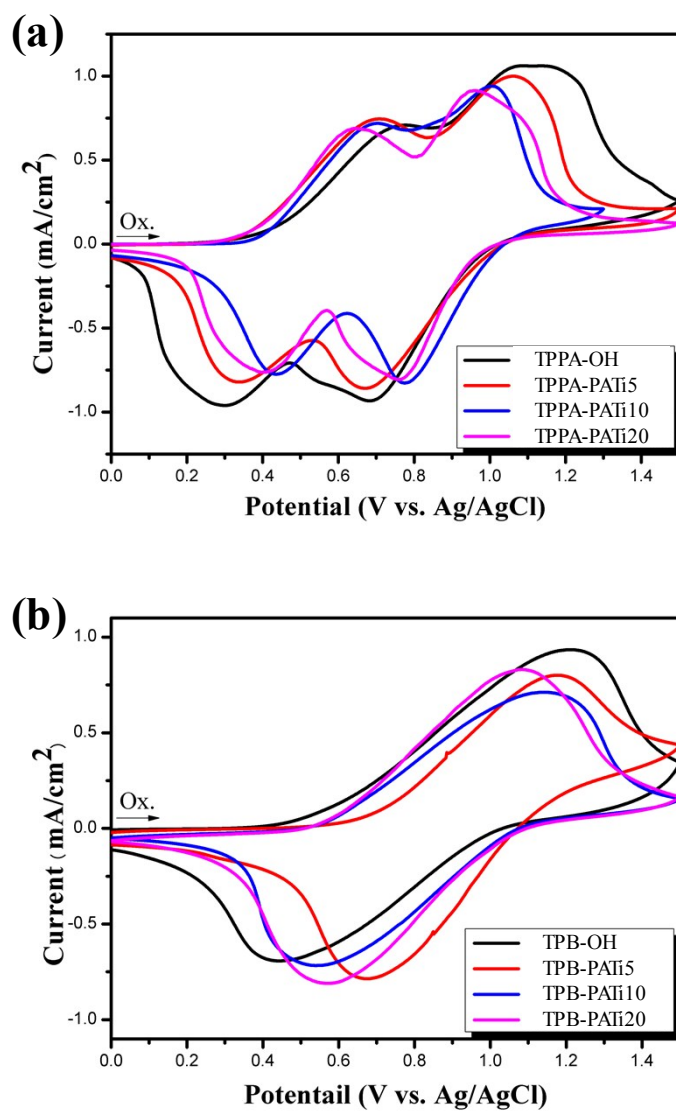


Fig. S3 Cyclic voltammetric diagrams of (a) **TPPA-OH** and **TPPA-PA** hybrid films (b) **TPB-OH** and **TPB-PA** hybrid films on the ITO-coated glass substrate (thickness: 300 ± 50 nm; coated area: $25 \text{ mm} \times 6 \text{ mm}$) in 0.1 M TBABF₄/PC at scan rate of 50 mV s^{-1} .

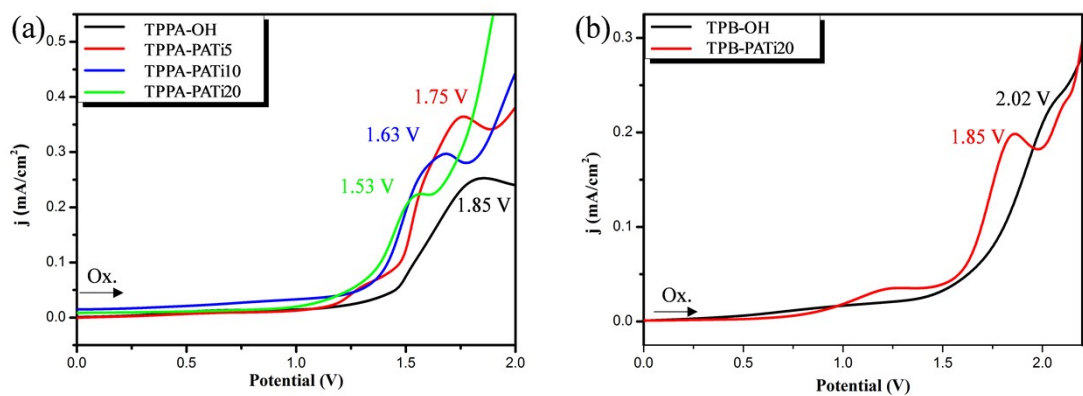


Fig. S4 Partial magnification cyclic voltammetric diagrams of the devices derived from (a) **TPPA-OH** and **TPPA-PA** hybrid films, (b) **TPB-OH** and **TPB-PA** hybrid films on the ITO-coated glass substrate (thickness : 300 ± 50 nm; coated area: 2 cm x 2 cm) in 0.1 M TBABF₄/PC electrolyte.

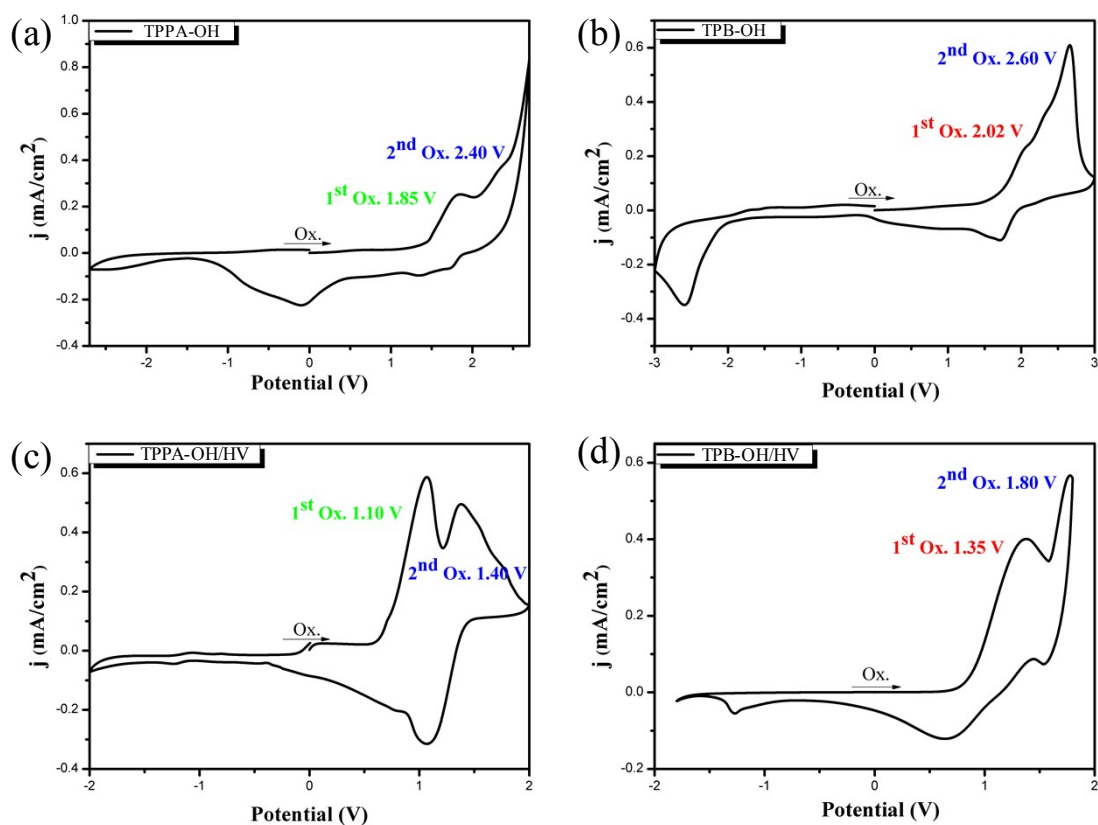


Fig. S5 Cyclic voltammetric diagrams of the ECDs derived from (a) **TPPA-OH** and (b) **TPB-OH** on the ITO-coated glass substrate (thickness: 300 ± 50 nm, coated area: 2 cm x 2 cm) in 0.1 M TBABF₄/PC electrolyte; (c) **TPPA-OH** and (d) **TPB-OH** in 0.1 M TBABF₄/PC electrolyte with 0.015 M HV(BF₄)₂.

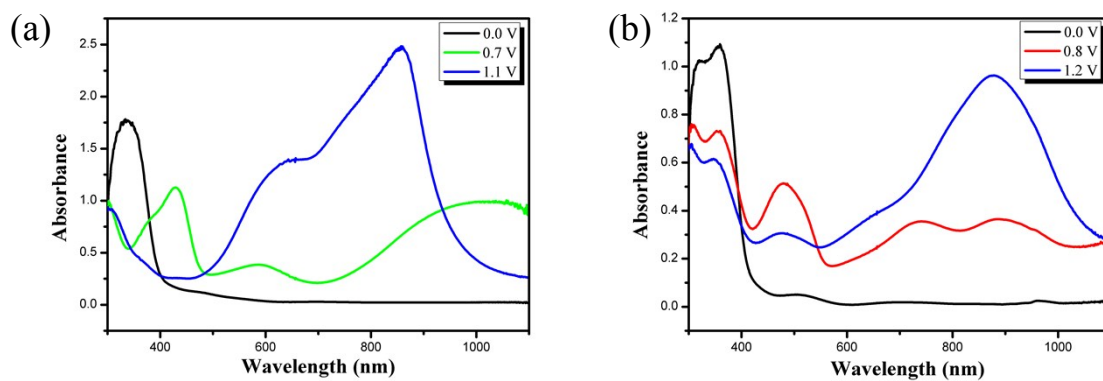


Fig. S6 Spectroelectrochemical behavior of (a) **TPPA-OH** and (b) **TPB-OH** thin films on the ITO-coated glass substrate (coated area: 25 mm × 6 mm, thickness: 300 ± 50 nm) in 0.1 M TBABF₄/PC at the related applied potentials.

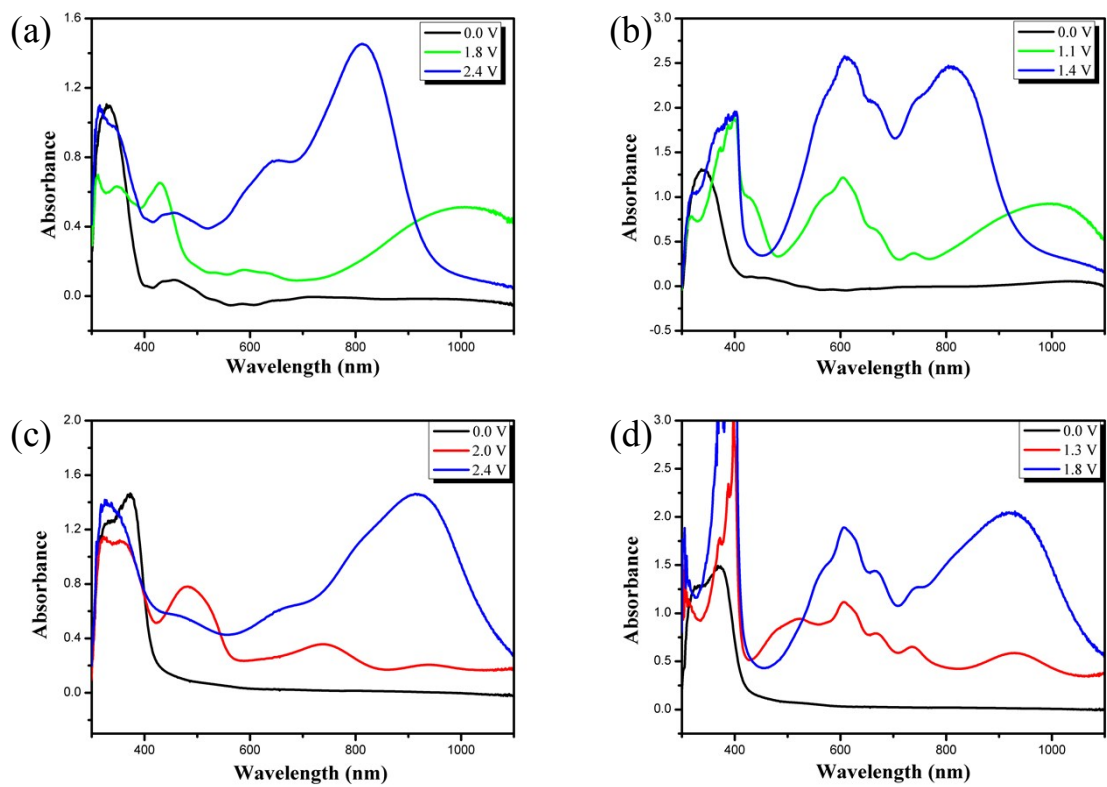


Fig. S7 Electrochromic behavior of the ECDs derived from (a) TPPA-OH, (b) TPPA-OH/HV, (c) TPB-OH, and (d) TPB-OH/HV.

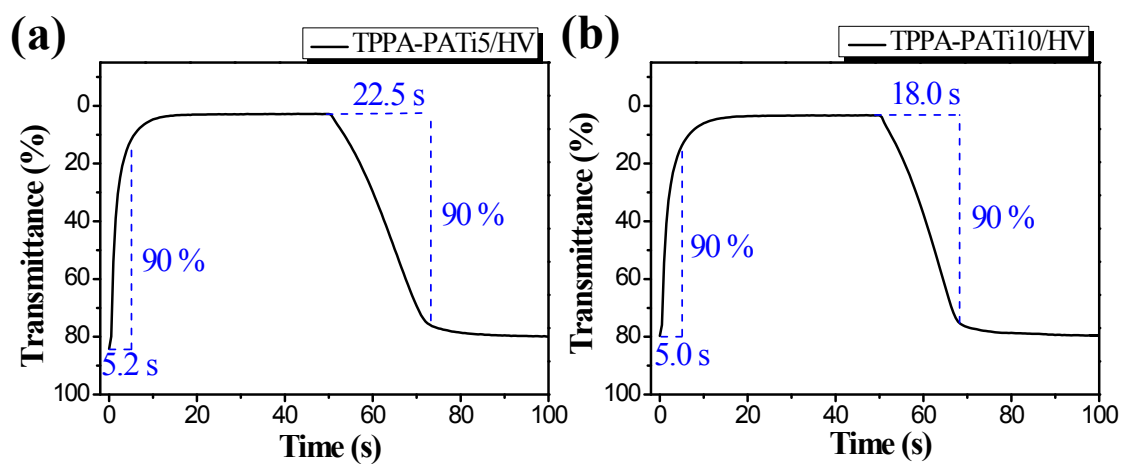


Fig. S8 Electrochromic switching of devices (a) between 1.05 V to -1.1 V for **TPPA-PATi5** and (b) between 1.02 V to -1.1 V for **TPPA-PATi10** monitored at 435 nm (thickness: 300 ± 50 nm) on the ITO-coated glass substrate (coated area: 2 cm x 2 cm) in 0.1 M TBABF₄/PC electrolyte with 0.015 M HV(BF₄)₂.

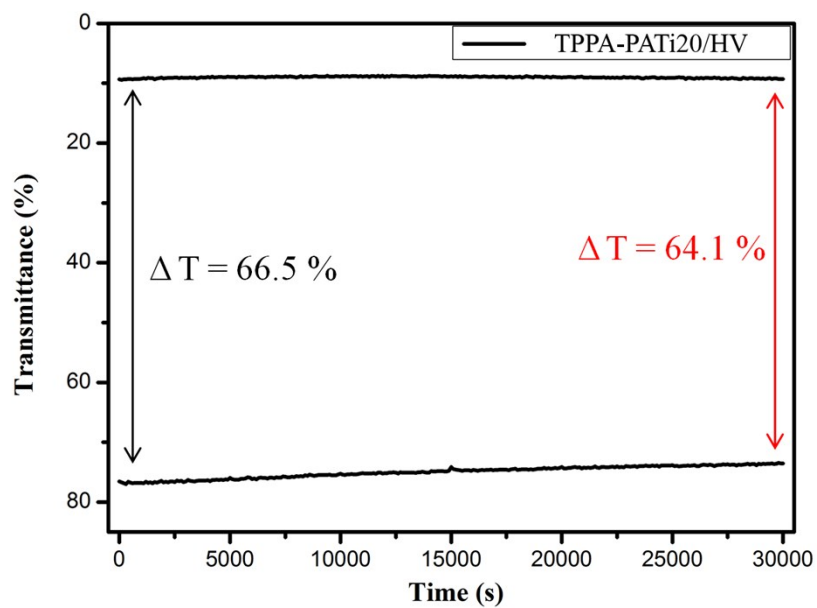


Fig. S9 Electrochromic device of TPPA-PATi20 switching between 1.00 and -1.05 V at 430 nm (thickness: 300 ± 50 nm) on the ITO-coated glass substrate (coated area: 2cm x 2 cm) in 0.1 M TBABF₄/PC electrolyte with 0.015 M HV(BF₄)₂ at a cycle time of 100 s for 300 cycles.

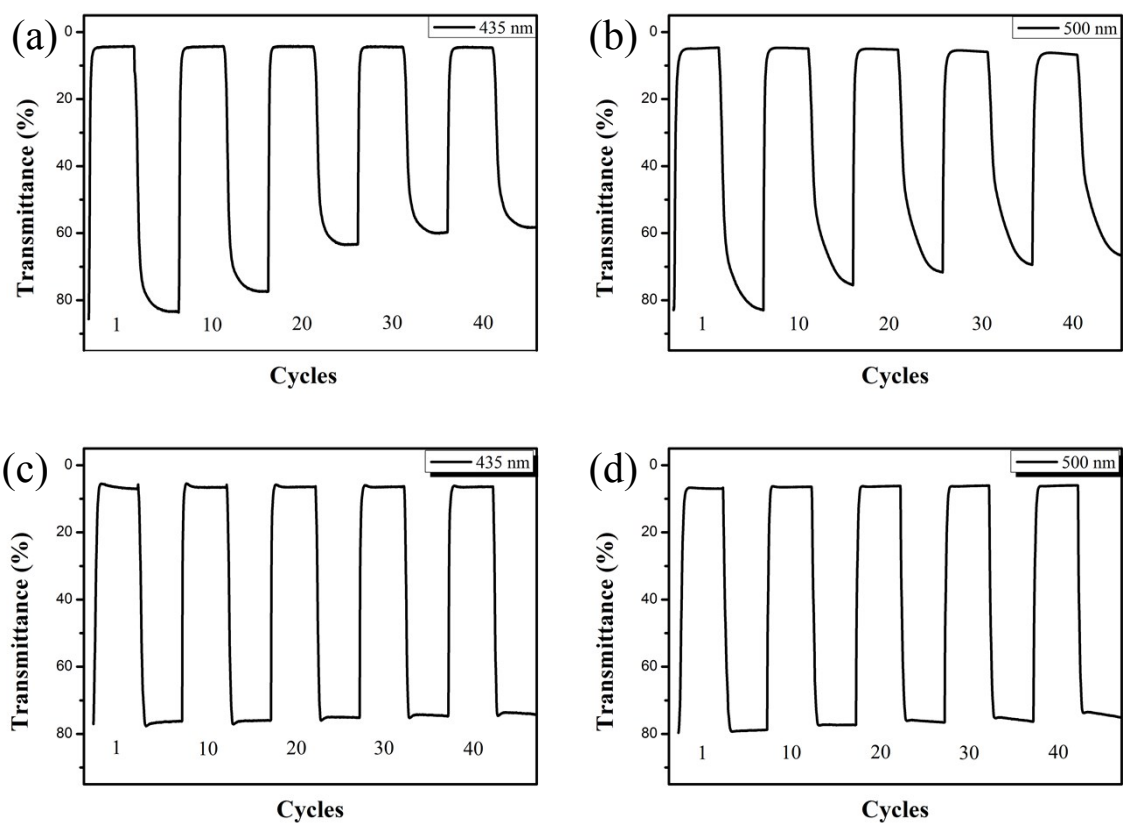


Fig. S10 Electrochromic switch stability of ECDs (a) and (b) derived from blending of **TPPA-OH** and **TPB-OH** switching between 1.5 V to -1.6 V at cycle time 400 s for each cycle; (c) and (d) derived from blending of **TPPA-PA** and **TPB-PA** hybrid (20 wt% TiO_2) switching between 1.4 V to -1.5 V (thickness : 900 ± 100 nm on the ITO-coated glass substrate (coated area: 2 cm x 2 cm) in 0.1 M TBABF₄/PC electrolyte with 0.015 M $\text{HV}(\text{BF}_4)_2$ at cycle time 200 s for each cycle.

Table S1 Inherent Viscosities and Molecular Weights of the Polyamides

Code	η_{inh} (dL/g) ^a	M_w ^b	M_n ^b	PDI ^c
TPPA-OH	0.31	18600	9800	1.90
TPB-OH	0.26	16100	8100	1.99

^a Measured at a polymer concentration of 0.5 g dL⁻¹ in DMAc at 30 °C.

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

^c Polydispersity Index (M_w/M_n).

Table S2 Solubility behaviors of the polyamides^a

Index	Solubility in various Solvents						
	NMP	DMAc	DMF	DMSO	<i>m</i> -cresol	THF	CHCl ₃
TPPA-OH	++	++	++	++	+-	-	-
TPB-OH	++	++	++	++	+-	-	-

^a 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 S3 Thermal properties of the polyamides^a

Polymer	T_g (°C) ^b	T_d at 5 % weight loss (°C) ^c		T_d at 10 % weight loss (°C) ^d		char yield (wt%) ^e
		N ₂	Air	N ₂	Air	
TPPA-OH	180	350	300	400	320	32
TPB-OH	195	350	320	400	340	25

^a The polymer film samples were heated at 200 °C for 1h 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 300 °C to 50 °C (rate: 200 °C /min) in nitrogen.

^c Temperature at which 5% weight loss recorded by TGA at a heating rate of 20 °C /min and a gas-flow rate of 20 cm³/min.

^d Temperature at which 10% weight loss occurred.

^e Residual weight percentage at 800 °C in nitrogen.

Table S4 Reaction composition of the **TPPA-PA** and **TPB-PA** hybrid films

index	Reactant composition/wt%		Hybrid film inorganic content/wt%	
	polymer	Ti(OBu) ₄	Theoretical	Experimental ^a
TPPA-OH	100	0	0	0
TPPA-PATi5	82.0	18.0	5	5.2
TPPA-PATi10	67.8	32.2	10	10.1
TPPA-PATi20	48.8	51.2	20	22.1
TPB-OH	100	0	0	0
TPB-PATi5	82.0	18.0	5	4.8
TPB-PATi10	67.8	32.2	10	9.8
TPB-PATi20	48.8	51.2	20	19.1

^a Experimental titania contents were estimated from TGA in air atmosphere.

Table S5 Electrochemical response behavior of polyamide **TPPA-OH** and their hybrids at the first oxidation redox couples

	ΔE (V) ^a				
	1 cycle	100 cycle	300 cycle	500 cycle	1000 cycle
TPPA-OH	0.40	0.38	0.38	0.38	0.38
TPPA-PATi5	- ^b	0.27	0.30	0.27	0.27
TPPA-PATi10	- ^b	0.21	0.23	0.20	0.20
TPPA-PATi20	- ^b	0.21	0.20	0.19	0.17

^a $\Delta E = |E_{pa} - E_{pc}|$; ^b - : Not available.

Table S6 Optical and electrochemical data collected for coloration efficiency measurements of TPPA-PATi20/HV ECD

Cycling times ^a	ΔT^b	δOD^c	Q (mC/cm ²) ^d	η (cm ² /C) ^e	η decay (%) ^f	ΔT decay (%) ^g
1	66.5	0.931	6.65	140.0	0	0
100	66.4	0.916	6.58	139.2	0.57	0.02
200	65.3	0.910	6.55	138.9	0.78	1.80
300	64.1	0.892	6.49	137.4	1.85	3.61

^a Switching between 1.0 and -1.05 V

^b Transmittance change at 435 nm.

^c Optical density (δOD) = $\log[T_{\text{bleached}}/T_{\text{colored}}]$, where T_{colored} and T_{bleached} are the maximum transmittance in the oxidized and neutral states, respectively.

^d Ejected charge, determined from the in situ experiments.

^e Coloration efficiency is derived from the equation $\eta = \delta OD/Q$.

^f Decay of coloration efficiency after cyclic scans = $(\eta_0 - \eta)/\eta_0 \times 100\%$.

^g Decay of transmittance after cyclic scans = $(\Delta T_0 - \Delta T)/\Delta T_0 \times 100\%$.