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Supporting Information

Electrochromic capacitive windows based on all conjugated polymers for a dual function smart window

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Supporting Information includes:

Supporting Information Figures S1 to S11.

Supporting Information Tables S1 to S5.

Supplementary Video S1, S2.

Supporting Information References S1 to S4.

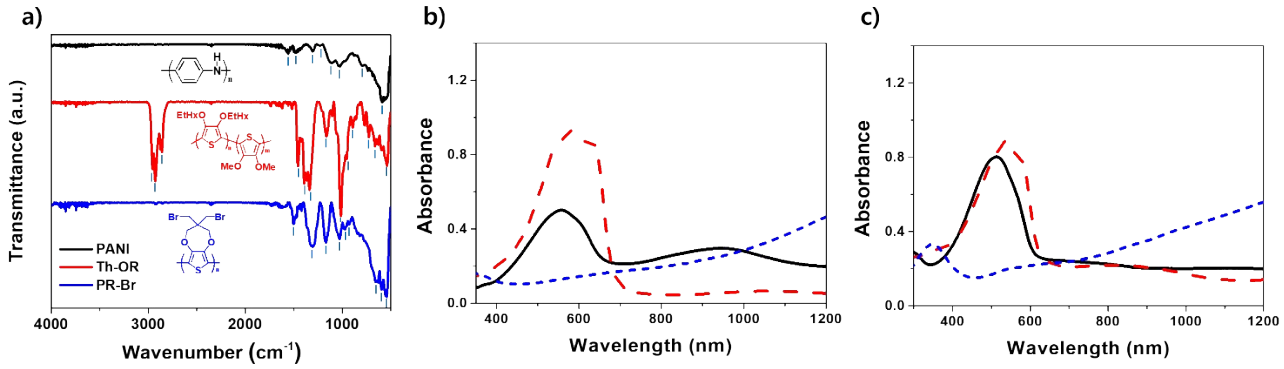

Figure S1. (a) FT-IR spectra of PANI (black), Th-OR (red), and PR-Br (blue), (b-c) UV-Vis spectra of the pristine (black line), fully doped (blue), and fully dedoped (red dashed line) polymeric films, (b) PR-Br, and (c) Th-OR.

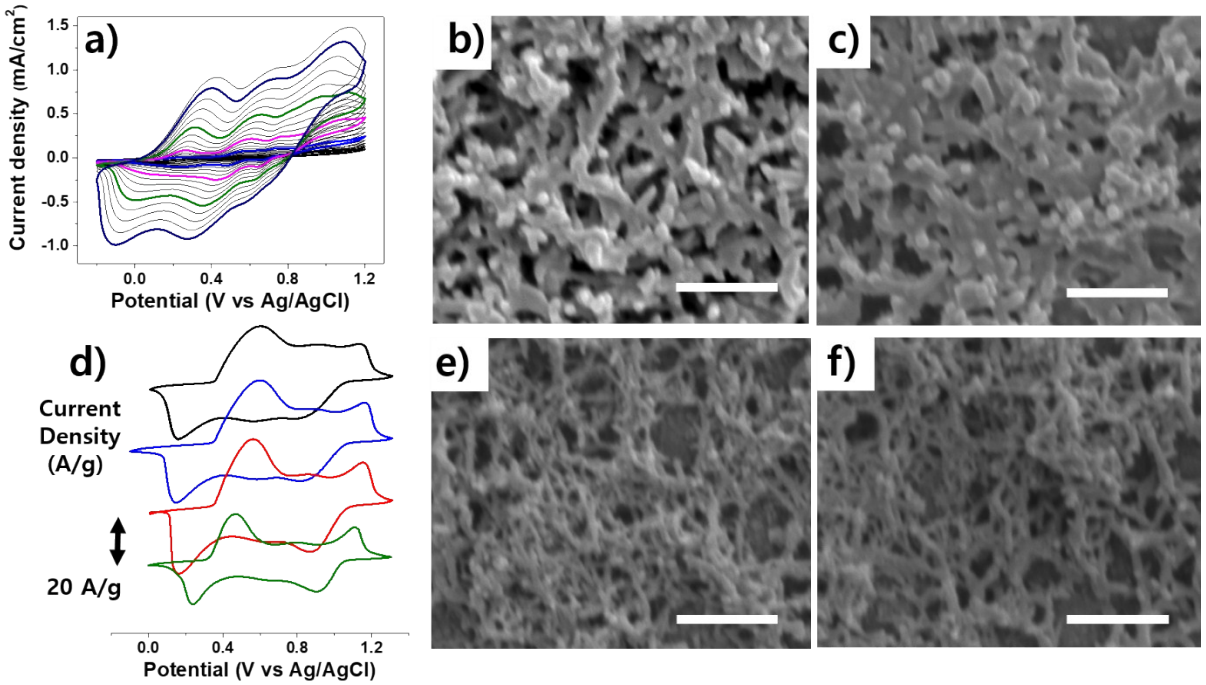

Figure S2. (a) Cyclic Voltammetry for electro-polymerization of aniline in 1 M H_2SO4, 0.05 M aniline aqueous solution. SEM image of PANI film prepared with a scan rate of b) 20 mV/s, c) 50 mV/s, e) 100 mV/s, f) 200 mV/s (scale bar = 1 μm) and (d) CV of monomer free PANI film prepared with a scan rate of 20 mV/s (black), 50 mV/s (blue), 100 mV/s (red), 200 mV/s (green) in SPAn electrolyte, Ag/AgCl electrode and stainless steel were used as a reference electrode, counter electrode, respectively. The CV scan rate was 100 mV/s.

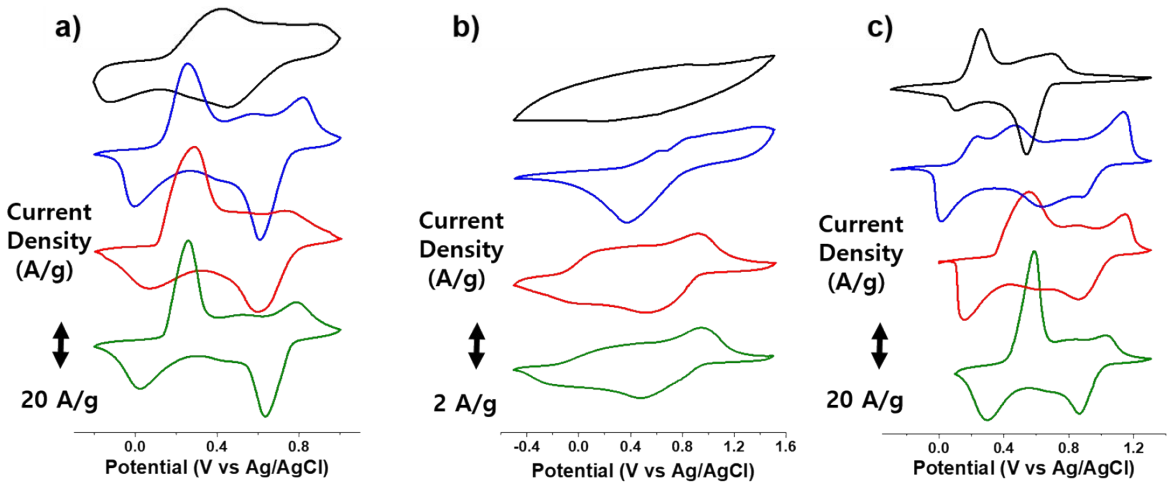

Figure S3. The cyclic voltammetry of the PANI film which was electrochemically polymerized using a potentiodynamic methods sweeping from –0.2 V to 1.2 V at different sweep rate of 20 mV/s (black), 50 mV/s (blue), 100 mV/s (red), 200 mV/s (green) a) in $HClO_4$ 1M, $NaClO_4$ 3 M of aqueous electrolyte, b) in Ionic liquid electrolyte containing 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. (scan rate = 0.1 V/s, PANI film, Ag/AgCl electrode and stainless steel wire was used as a working electrode, reference electrode and counter electrode, respectively) c) The cyclic voltammetry of the PANI film in different acidic organic electrolyte condition of 0.1 M p-toluenesulfonic acid (black), 0.1 M trifluoroacetic acid (blue), 0.1 M dodecylbenzene sulfonic acid (red), d) 0.1M perchloric acid (green), all the electrolyte containing 0.3 M sodium perchlorate for ionic conduction. PANI film for (c) was electrochemically polymerized using a potentiodynamic methods sweeping from –0.2 V to 1.2 V at different sweep rate of 100 mV/s

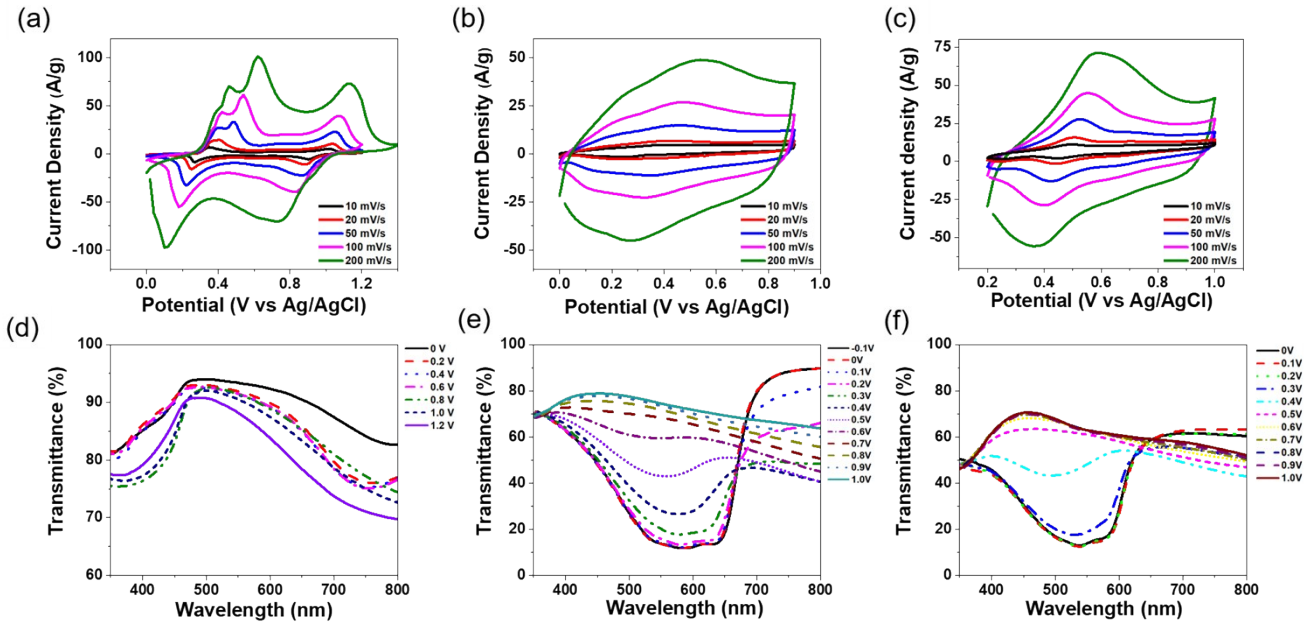

Figure S4. Cyclic voltammetry (a–c) and in-situ spectroelectrochemistry (d–f) of PANI_2 (thickness : 25 nm) (a, d), PR-Br_1 (thickness : 170 nm) (b, e), Th-OR_2 (thickness : 210 nm) (c,f) at given sweep rate and at given voltage. (electrolyte was 0.1 M $HClO_4$, 0.3 M $NaClO_4$ in acetonitrile solution (SPAn), Ag/AgCl reference electrode and stainless steel wire were used as an electrolyte, reference electrode and counter electrode, respectively

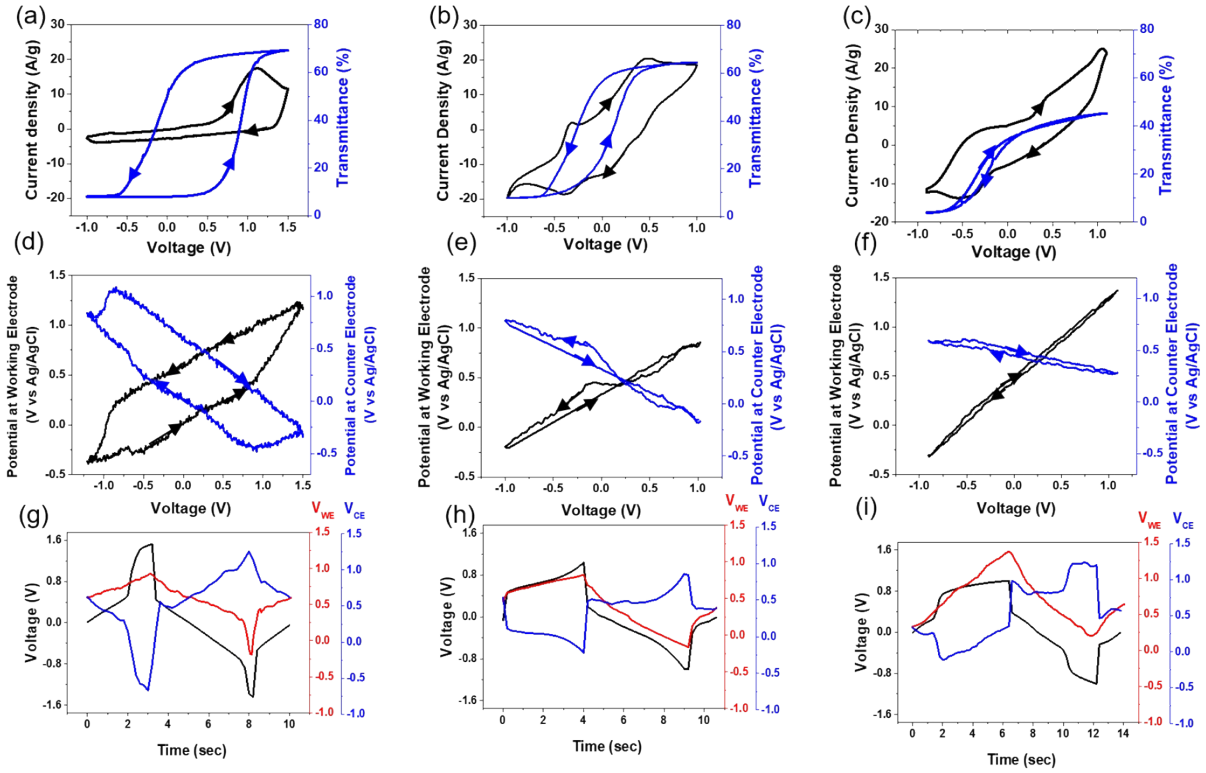

Figure S5. Cyclic voltammetry (black) and corresponding transmittance (blue, λ = 580 nm) of (a) PR-Br (170 nm)//SPAn//PANI(11 nm), (b) PR-Br (170nm)//SPAn//PANI(25 nm) (c) PR-Br (170 nm)//SPAn//PANI (47 nm) and corresponding potential at each electrode (d–f), and charging-discharging graph (g–i) of devices (black) and potential at each electrode (red line : WE (PR-Br), blue line : CE (PANI))

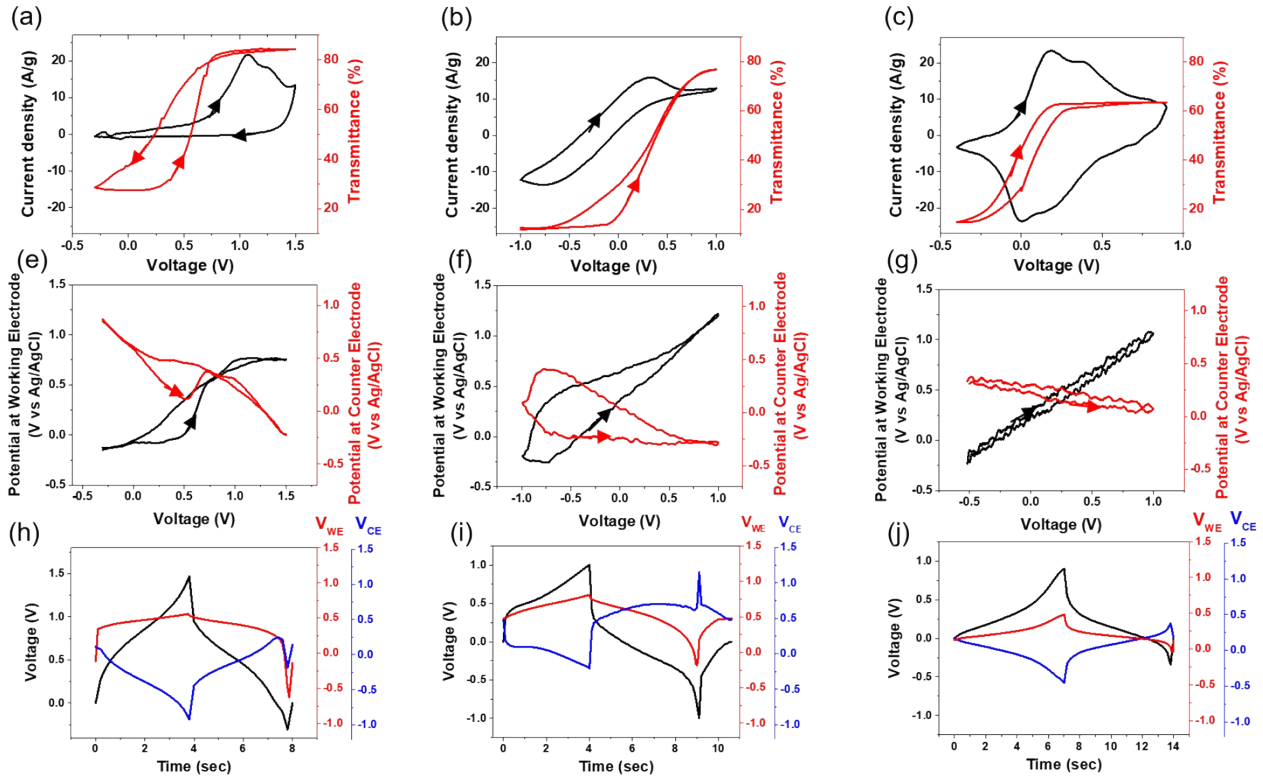

Figure S6. Cyclic voltammetry (black) and corresponding transmittance (red, λ = 532 nm) of (a) Th-OR (210 nm)//SPAn//PANI(11 nm), (b) Th-OR (210nm)//SPAn//PANI(25 nm) (c) Th-OR (210 nm)//SPAn//PANI (47 nm) and corresponding potential at each electrode, and charging-discharging graph of devices (black) and potential at each electrode (red line : WE (Th-OR), blue line : CE (PANI))

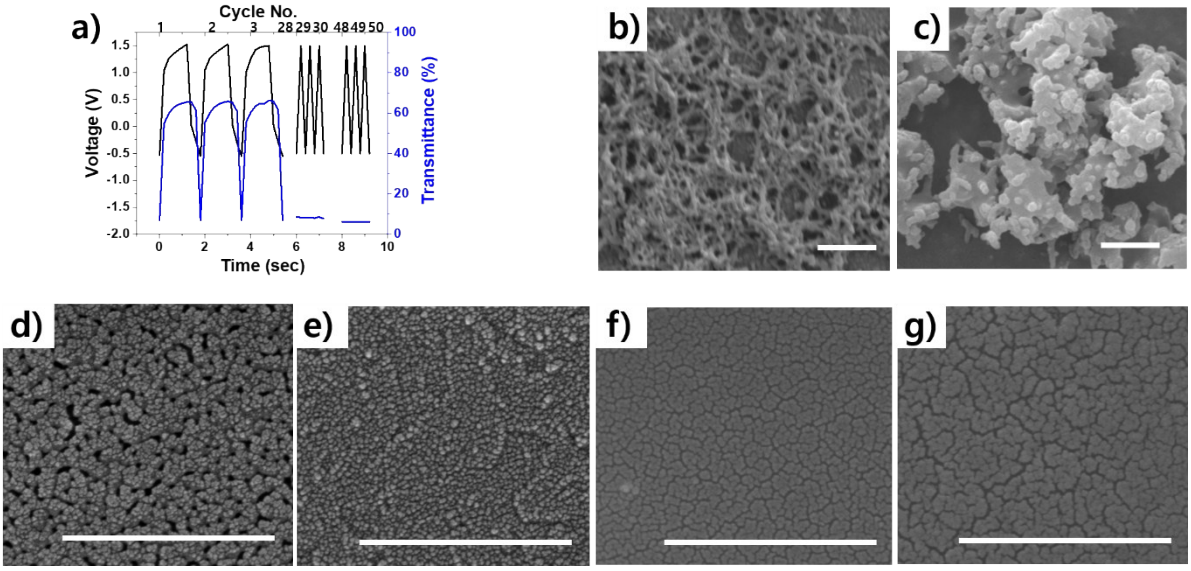

Figure S7. (a) Cycle stability of the BECC with d_{PANI} = 11 nm with SPAn containing 5 wt% PMMA as an electrolyte SEM image of PANI layer of (b) pristine state, and (c) after 120 cycles of operation, PR-Br layer of (d) pristine state, and (e) after 120 cycles of operation, Th-OR layer of (f) pristine state, and (g) after 120 cycles of operation. (scale bar = 1 μm)

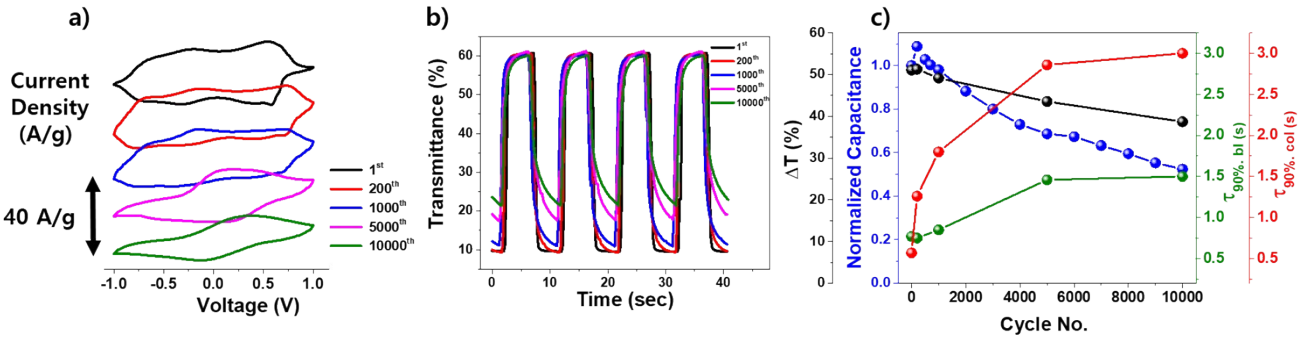

Figure S8. (a) The cyclic voltammetry of the BECCP5 and (b) the optical response time at an applied potential between 1 V~ -1 V: after 1st cycle (black), 200th cycle (red), 1000th cycle (blue), 5000th cycle (magenta), 10000th cycle (green). (c) The change in color contrast (ΔT) at 580 nm (black), normalized capacitance (blue), response time to reach 90 % of the maximum transmittance at bleaching step ($\tau_{90\%.\,bl}$, green), and at coloring step ($\tau_{90\%.\,col}$, red) over time.

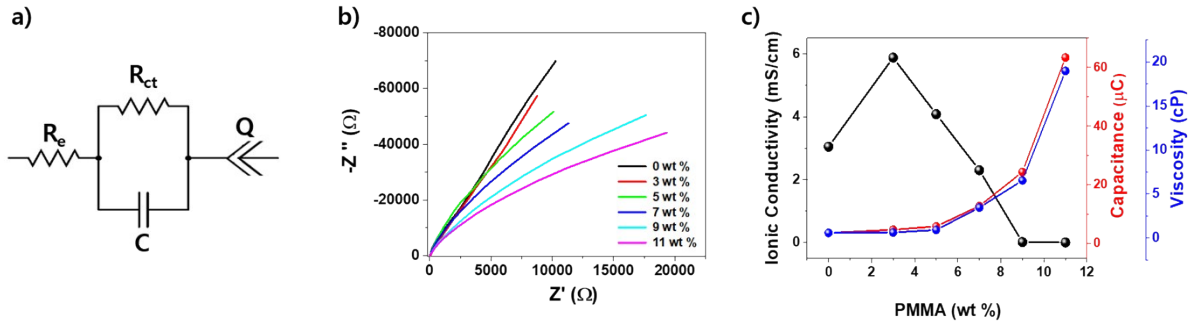

Figure S9. (a) equivalent circuit model consist of bulk electrolyte resistance ($\mathbf{R_e}$), charge transport reistance ($\mathbf{R_{ct}}$), capacitance (**C**), and constant phase element (**Q**) (b)Nyquist EIS spectrum of the device consisted of ITO// electrolyte //ITO, electrolyte was SPAn containing 0 wt% (black), 3 wt% (red), 5 wt% (green), 7 wt% (blue), 9 wt% (cyan), 11 wt% (magenta) of PMMA. (c) resulting ionic conductivity (black), capacitance (red), and viscosity (blue) of the SPAn containing different PMMA concentration.

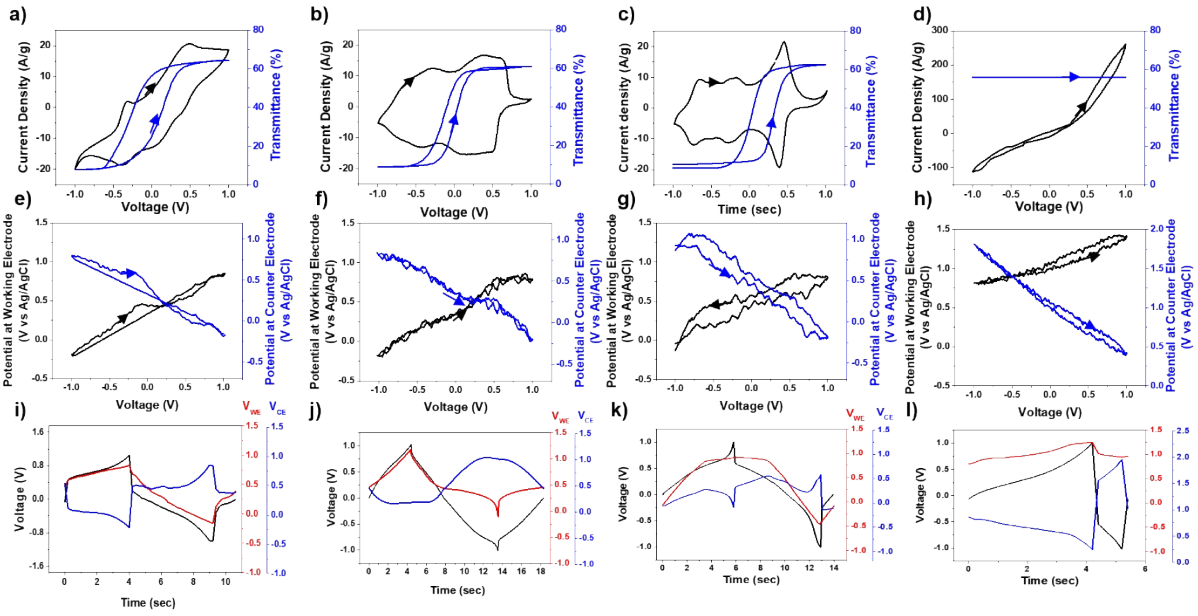

Figure S10. Cyclic voltammetry (black) and corresponding transmittance (blue, λ = 580nm) of PR-Br (170 nm)//PANI(25 nm) with SPAn electrolyte containing (a) 0 wt%, (b) 5 wt% (c) 7 wt% (d) 9 wt% of PMMA and corresponding potential at each electrode (e–h). Charging-discharging graph (i–l) of the devices (black) and potential at each electrode (red line : WE (PR-Br), blue line : CE (PANI)) (charging/discharging current was 0.7 mA)

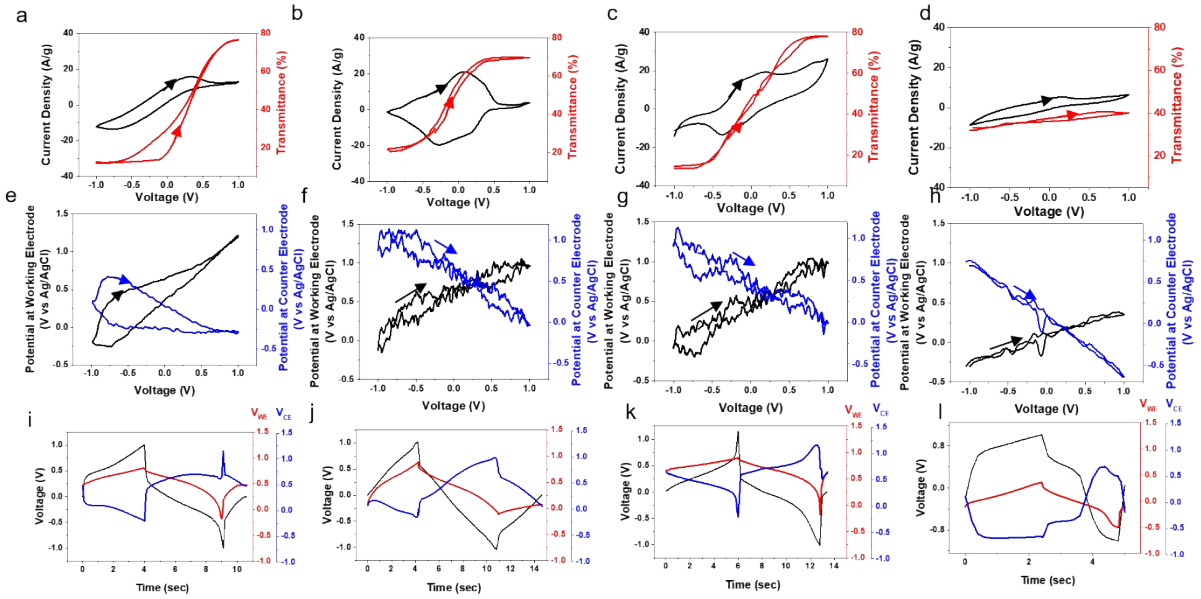

Figure S11. Cyclic voltammetry (black) and corresponding transmittance (blue, λ = 532nm) of Th-OR (210 nm)//PANI (25 nm) with SPAn electrolyte containing (a) 0 wt%, (b) 5 wt% (c) 7 wt% (d) 9 wt% of PMMA and corresponding potential at each electrode (d–f). Charging-discharging graph (i–l) of the devices (black) and potential at each electrode (red line : WE (Th-OR), blue line : CE (PANI)) (charging/discharging current was 0.7 mA)

Table S1 Electrochromic electrode fabrication condition

Sample	Coating rate (rpm)	Spray coating time (sec)	$\Delta T_{\lambda max}$ (%)[a]	$T_{\lambda max.bl}$ (%)	$T_{\lambda max.col}$ (%)	Thickness (nm)[b]
PR-Br_1	1400		61	72	11	170
PR-Br_2	2000		48	81	23	100
PR-Br_3	800		54	61	7.3	250
Th-OR_1		3	43	89	48	130
Th-OR_2		5	56	69	13	210
Th-OR_3		10	51	45	2	270

[a]λ_{max} of blue, red polymeric layer was 580 nm, 532 nm, respectively. [b]determined from alpha-step.

Table S2. The FT-IR band assignments for PANI[S1, 2], Th-OR[S3], and PR-Br[S4]

PANI [S1, S2]		Th-OR [S3]		PR-Br [S4]	
Wavenumber (cm^{-1})	Functional Group	Wavenumber (cm^{-1})	Functional Group	Wavenumber (cm^{-1})	Functional Group
1558	C=N stretching (quinoid form)	2958, 2927, 2856	C-H stretching (CH_2, CH_3)	1500, 1305	Aromatic C=C stretching
1489	C=C stretching (benzoid form)	1456, 1392, 1336	Aromatic C=C stretching	1167	C-H bending
1306, 1232	C-N stretching (benzoid form)	1162	C-H bending	1029	C(ring)-O-C stretching
1113	C-N stretching (quinoid form)	1014	C(ring)-O-C stretching	926, 655, 542	C-S bond in thiophene ring
1024	$C=NH^+$ bending (quinoid form)	727	$-(CH_2)_n-$ bending	597	C-Br stretching
792	C-H out of plane bending	952, 663, 540	C-S bond in thiophene ring		
588	Aromatic ring deformation				

Table S3. The gravitational capacitance of the PANI in different condition. All the measurement was done by sweep rate of 100 mV/s

Specific Capacitance (F/g)		Electrolyte					
		Non-aqueous electrolyte[a]				Aqueous Electrolyte[b]	Ionic Liquid
		0.1 M $HClO_4$	0.1 M CF_3COOH	0.1 M p-TSA	0.1 M DBSA	1 M $HClO_4$	[Bmim]TFSI
Polymerization Scan Rate[c] (mV/s)	20	223				252	14
	50	324				325	12.7
	100	331	322	225	285	355	17.2
	200	118				118	13.9

[a]acetonitrile solution containing 0.3 M $NaClO_4$ for ionic conduction [b]aqueous solution containing 3 M $NaClO_4$ for ionic conduction [c]electro-polymerization scan rate for aniline in 1 M H_2SO_4, 0.05 M aniline.

Table S4. The resistances, capacitances, and viscosity of SPAn electrolyte containing different PMMA concentration.

PMMA conc. (wt%)	R_e [Ω]	R_{ct} [Ω]	σ [S/cm]	C [μF]	Q [μF]	χ^2	Viscosity (cP)
0	38.98	1.31	3.05×10^{-3}	3.63	20.4	0.010	0.578 (±0.06)
3	55.32	0.68	5.88×10^{-3}	4.73	26.5	0.005	0.625 (±0.07)
5	35.96	0.98	4.08×10^{-3}	5.86	26.5	0.007	0.92 (±0.1)
7	39.74	1.74	2.30×10^{-3}	12.8	29.8	0.017	3.46 (±0.6)
9	58.72	264	1.52×10^{-5}	24.4	28.4	0.003	6.54 (±0.7)
11	42.75	1344	2.98×10^{-6}	63.4	41.2	0.001	18.98

Table S5. Electrochromic capacitive window properties in this study.

Sample Name	PR-Br (nm)	Th-OR (nm)	PANI (nm)	PMMA (wt%)[a]	Cap (mF)[b]	Cap (mF)[c]	Energy Density (Wh/kg)	Power density (kW/kg)	CoulE (%)	ΔT (%)[d]	E_{WE} (V)[e]	E_{CE} (V)[e]	Conductivity (S/m)[f]	Viscosity (cP)
BECC1	170		11	0	1.15	0.72 0.9	5.3 (bl) 6.3 (col)	37.2 (bl) 19.2 (col)	56.3 55.3	61	0.56 0.8	-0.44 -0.2	0.305	0.58
BECC2	170		25	0	2.48	0.6 0.84	1.0 (bl) 1.2 (col)	14.1 (bl) 12.0 (col)	25 33.3	57	0.86 0.83	-0.14 -0.17	0.305	0.58
BECC3	170		47	0	2.01	1.2 0.96	2.3 (bl) 1.5 (col)	13.7 (bl) 2.75 (col)	31.3 42.1	41	1.28 1.37	0.28 -0.37	0.305	0.58
BECCP5	170		25	5	3.80	2.04 2.88	9.7 (bl) 13.5 (col)	75.3 (bl) 58.8 (col)	77.2 84.2	51	0.86 1.17	-0.14 0.17	0.408	0.92
BECCP7	170		25	7	3.00	2.58 0.6	9.6 (bl) 1.1 (col)	29.3 (bl) 15.6 (col)	74.1 35.7	54	0.82 0.91	-0.18 -0.09	0.230	3.5
BECCP9	170		25	9	3.66	0.06 0.12	1.04 (bl) 2.44 (col)	29.3 (bl) 15.6 (col)	2.4 25	0	1.42 1.25	0.42 0.25	0.002	6.5
RECC1		210	11	0	1.44	1.36 0.4	5.2 (bl) 0.33 (col)	19.2 (bl) 5.83 (col)	89.5 50	57	0.66 0.49	-0.34 -0.51	0.305	0.58
RECC2		210	25	0	1.53	0.9 0.4	1.92 (bl) 2.08 (col)	21.1 (bl) 21.8 (col)	37.5 50	64	1.22 0.80	0.22 -0.20	0.305	0.58
RECC3		210	47	0	4.01	4.67 0.3	5.25 (bl) 0.17 (col)	24.8 (bl) 2.66 (col)	74.3 12.5	49	1.07 1.00	0.07 0	0.305	0.58
RECCP5		210	25	5	3.25	1.44 2.28	5.33 (bl) 10.5 (col)	27.8 (bl) 51.6 (col)	57.1 86.3	60	1.05 0.89	0.05 -0.11	0.408	0.92
RECCP7		210	25	7	2.41	1.26 0.36	2.5 (bl) 0.8 (col)	16.2 (bl) 13.2 (col)	35 12.8	64.5	1.04 0.90	0.04 -0.10	0.230	3.5
RECCP9		210	25	9	0.69	0.78 0.12	1.8 (bl) 3.2 (col)	3.99 (bl) 0.64 (col)	54.2 18.2	7.1	0.3 0.34	-0.7 -0.66	0.002	6.5

[a]the concentration of the PMMA (wt%) in the SPAn electrolyte, [b]determined from CV graph in Fig. S5a–c, S6a–c, S10a–d, S11a–d, [c]determined from CD graph in Fig S5g–i, S6g–i, S10i–l, S11i–l, [d]Transmittance change at 580 nm for BECC, at 532 nm for RECC, [e]potential at each electrode upon V_{ap} of 1 V, determined from CV graph (up), and CD graph (down), [f]Ionic conductivity was determined from the electrochemical impedance spectroscopy (EIS).

Supplementary Video S1. The movie of energy transfer from BECCs to a RECC.

Supplementary Video S2. The movie of energy transfer from BECCs to a red LED.

Supporting Information references

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