Supporting Information

Novel Electrochemical Devices with High Contrast Ratio and Response Capability of Electrochromic and Electrofluorochromic Behaviours Simultaneously

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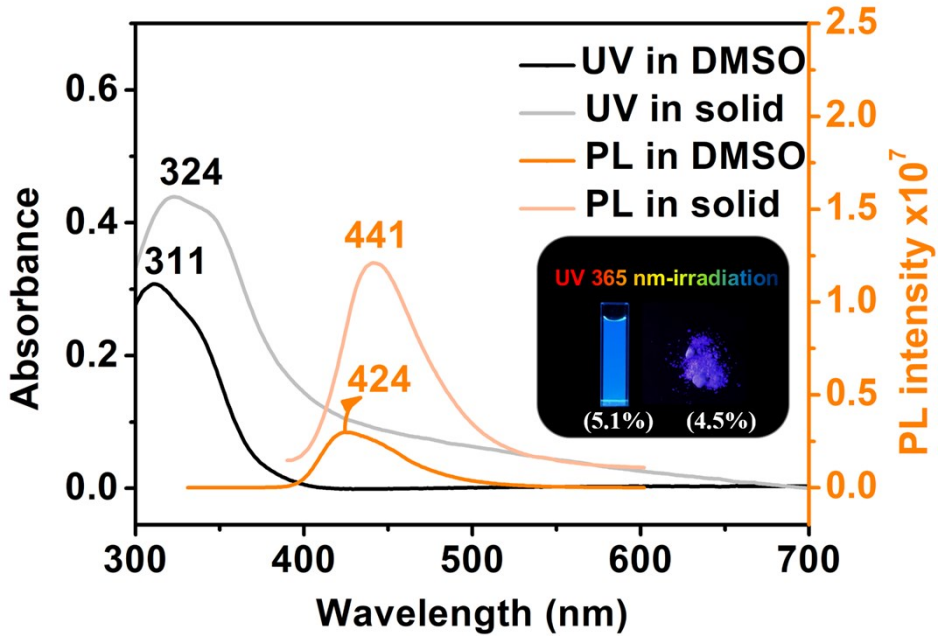


Fig. S1 Absorption and PL spectra of TPPA in DMSO solution and in solid. (Solution concentration: 10 μM)

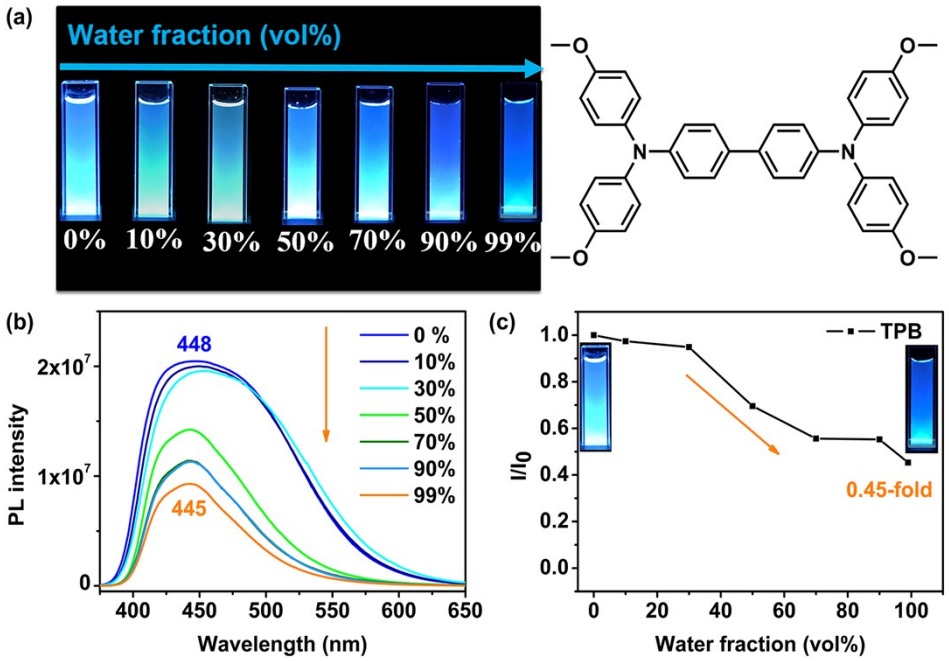


Fig. S2 PL spectra based on **TPB** dissolved in different DMSO-water fraction (Solution concentration: 10 μM)

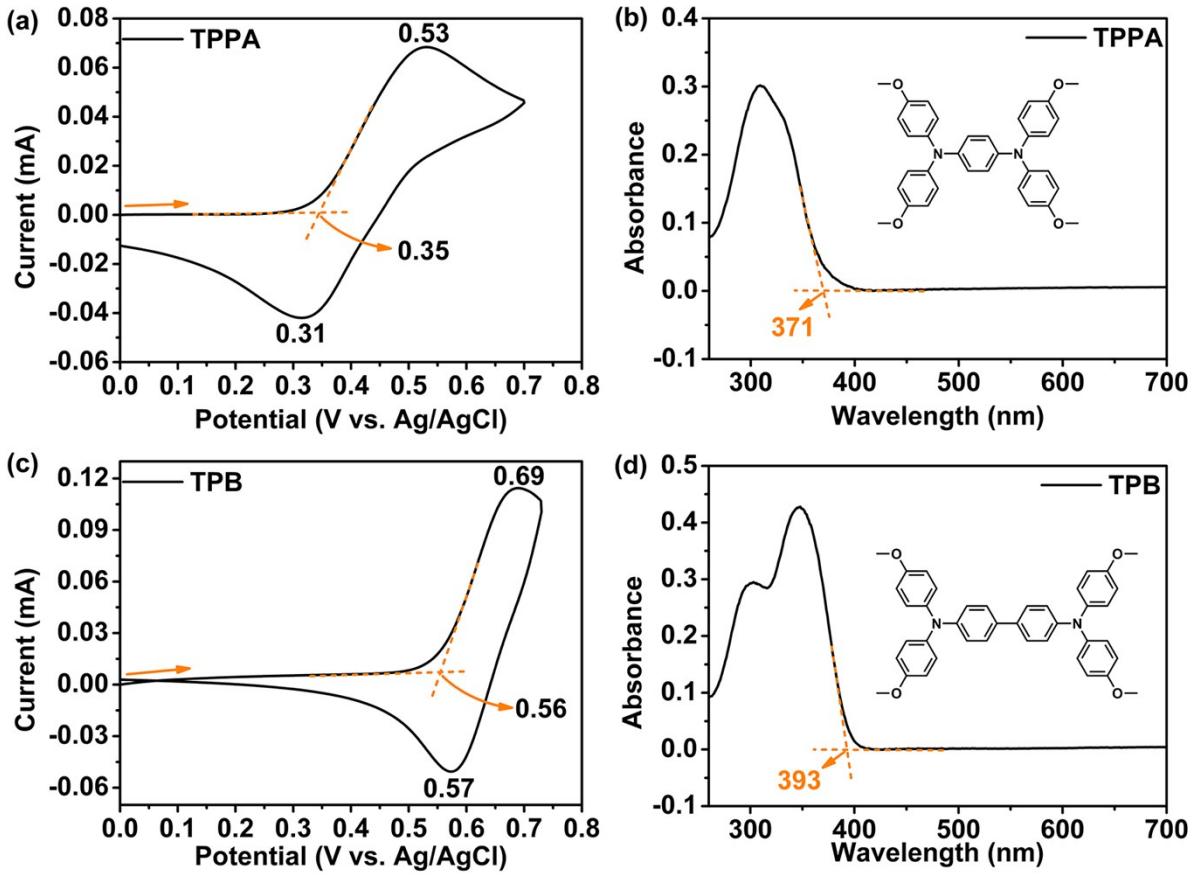
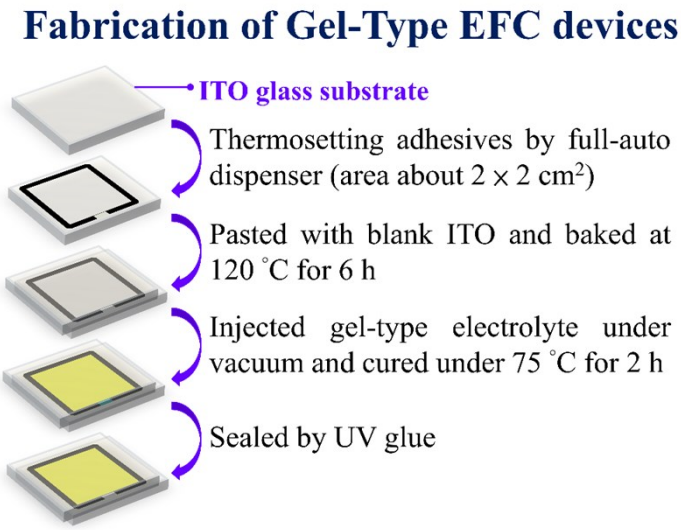


Fig. S3 Cyclic voltammetric diagram (left side) of (a) **TPPA** and (c) **TPB** in MeCN by using ITO. The concentration is 10^{-3} M compound and 0.1 M TBAP as the electrolyte in acetonitrile (Scan rate: 50 mV/s). UV absorption spectra (right side) of (b) **TPPA** and (d) **TPB** in acetonitrile (10 μM).

Fabrication of Gel-type Electrofluorochromic Device: (ref.1)

Poly(MMA-HEMA) was obtained by the following process: Methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA) and 2,2'-azobis(2-methylpropionitrile) (AIBN) were dissolved in propylene carbonate and stirred at 75℃ for 24 hours.

The typical procedure to prepare the gel-type electrofluorochromic (EFC) devices is depicted in the **Fig. S4** and **S5**. The ITO glasses utilized in EFC devices were cleaned by ultra-sonication in the order of water, acetone, and isopropanol each for 15 min, respectively. Then, each two ITO (~5 Ω/square) glasses were confined to 120 μm gap by means of curing the thermoset adhesive with a 2 × 2 cm^2 active area under 120 ℃ for six hours, which was routed by a full-auto dispenser. A tiny opening was retained for injecting materials into the device through a vacuum encapsulating method. In this work, the gel-type electrolyte contains 1.5 μmole **TPB** EFC material, the corresponding concentration of $TBABF_4$ and heptyl viologen (HV), 5.6 mg copolymer poly(4MMA-1HEMA) of with mole ratio (4/1) of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA), aliphatic polyisocyanate (0.4 mg Desmodur® N3200), and 0.07 mg dibutyltin diacetate as catalyst dissolving in about 0.05 mL propylene carbonate (PC). After injection, the opening was sealed via a UV-curing adhesive,



and then was cured at 75 °C for 2 h to obtain the crosslinking gel-type EFC device.

Fig. S4 Fabricating procedure of the gel-type EFC devices (Ref.1).

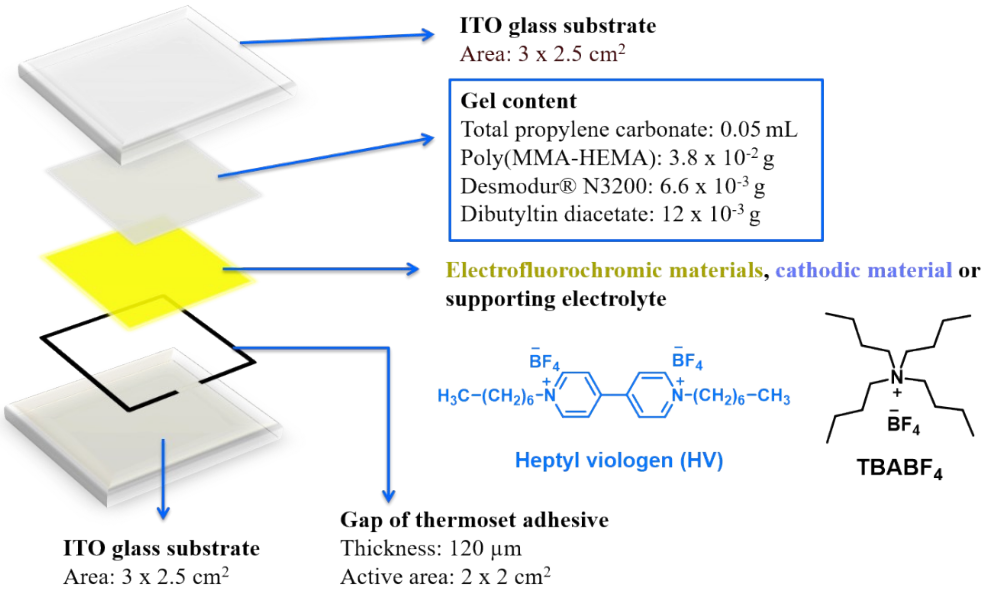


Fig. S5 Scheme of EFC devices (Ref.1).

Ref.1: *Nanoscale*, **11**, 8597-8603 (2019)

Although, **TPB** demonstrates ACQ property as shown in **Fig. S2**, it displays unique optical phenomenon. It shows high quantum yield (Φ_{PL}) both in solution (34.5%) and solid stated (32.4%). Because of the safety issue, the gel type electrolyte is necessary to be introduced in EFC devices. In general, most of luminphores display aggregation caused quenching effect (ACQ), leading to nearly no-emission in nano-aggregation. It is harmful to apply on gel type EFC devices. Although TPB displays ACQ properties in previous test, it still demonstrates high quantum yield both in solution (Φ_{PL}=34.5%) and in solid (Φ_{PL}=32.4%). This unique optical property is suitable to apply on gel type device.

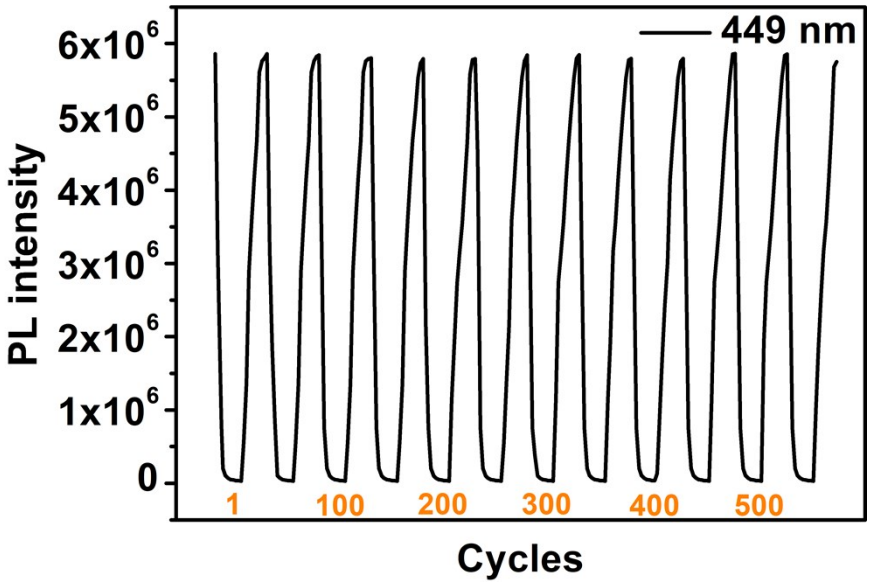
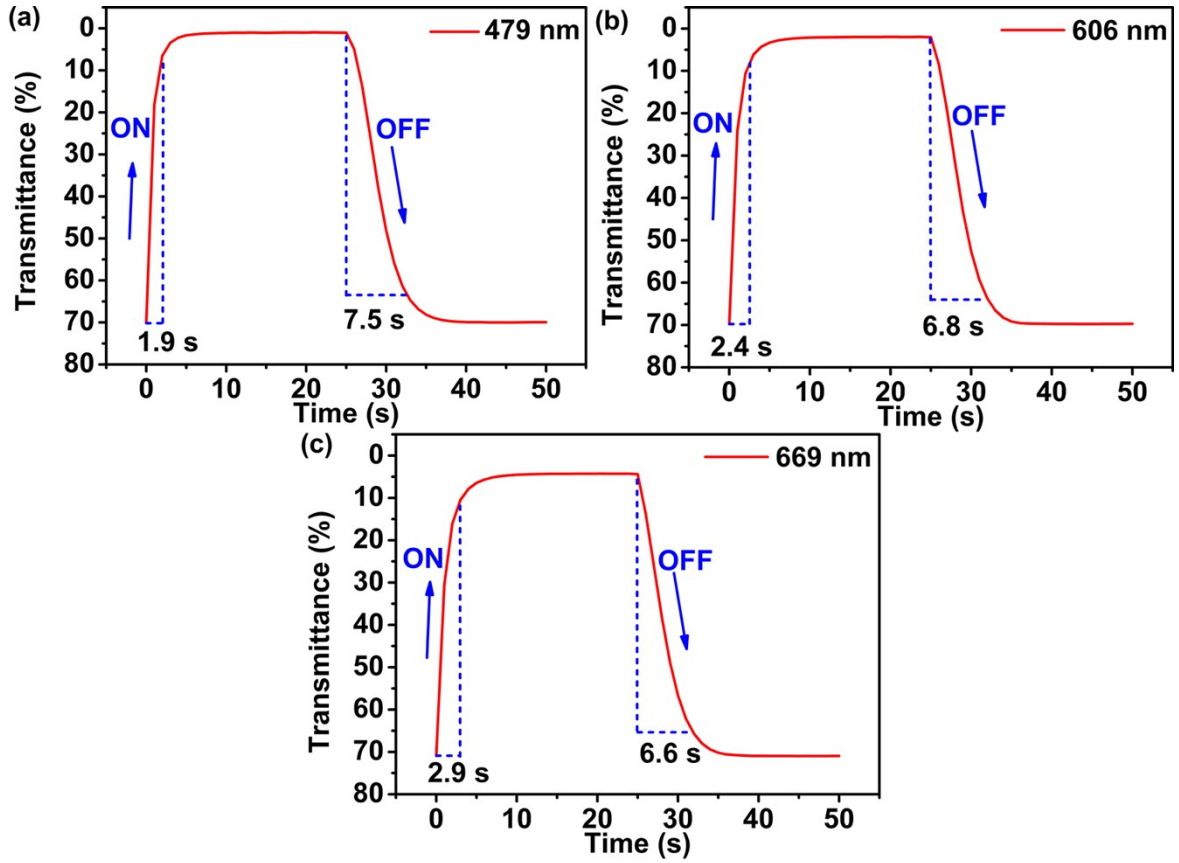


Fig. S6 Repetitive switching time test of gel-type EFCD based on **TPB/HV** between 1.2 V (on) and -0.1 V (off) with cycle time of 20 s. The 120 μm devices are derived from ITO glass with



2 cm×2 cm active area.

Fig. S7 Electrochromic switching response of liquid-type device based on **TPB/HV** at (a) 479 nm (b) 606 nm and (c) 669 nm between 1.2 V (on) and -0.1 V (off). The 120 μm devices are derived from ITO glass with 2 cm×2 cm active area.

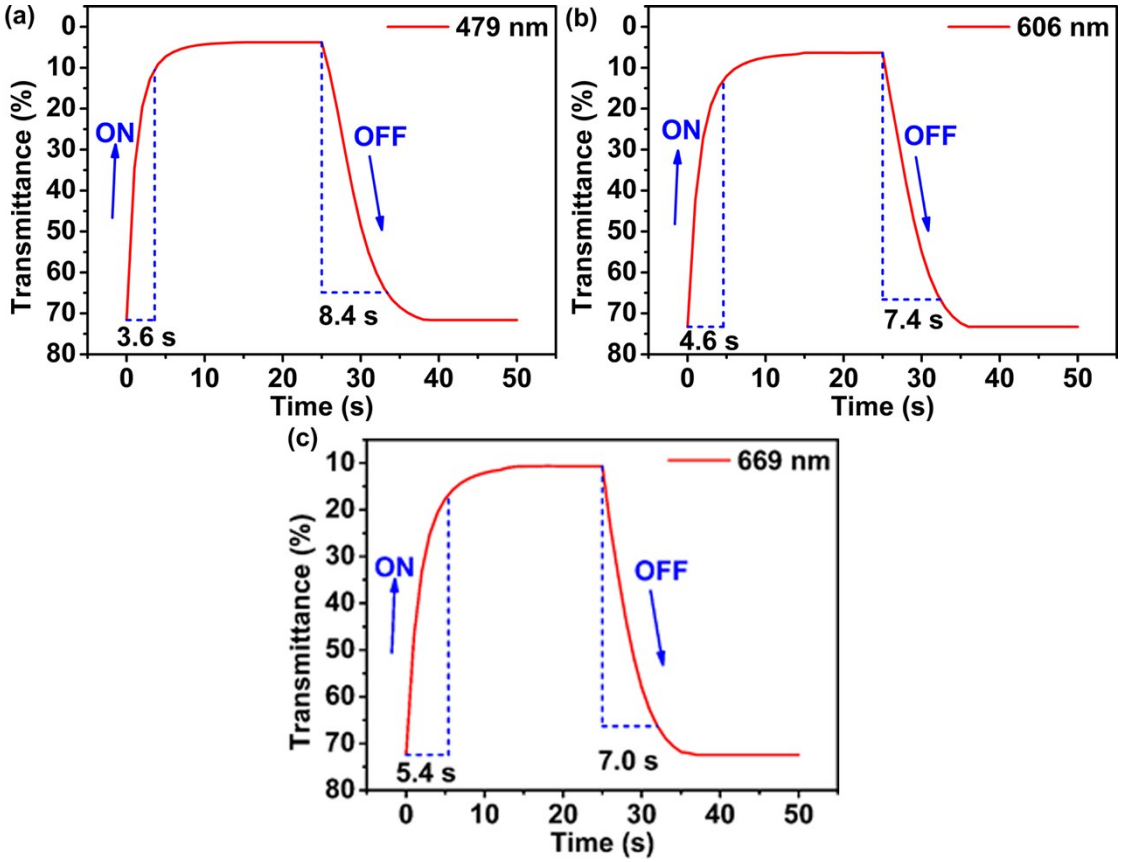


Fig. S8 Electrochromic switching response of gel-type device based on **TPB/HV** at (a) 479 nm (b) 606 nm and (c) 669 nm between 1.2 V (on) and -0.1 V (off). The 120 μm devices are derived from ITO glass with 2 cm×2 cm active area.

Table S1 Optical properties of **TPPA** and **TPB.**
[a] Both λem max of solution and solid state were excited at λabs max.

Sample	DMSO solution			Solid Powder State		
	λabs max [nm]	λem max [nm][ad]	Φ_{PL} [%][b]	λabs max [nm]	λem max [nm][a]	Φ_{PL} [%][c]
TPPA	311	424	5.1	325	441	4.5
TPB	351	448	34.5	362	460	32.4

[b] The quantum yield was measured by using quinine sulfate (dissolved in 1 N H_2SO_4 with a concentration of **10 μM**, assuming photoluminescence quantum efficiency of 0.546) as a standard at 25 ℃.
[c] PL quantum yields of molecules determined using a calibrated integrating sphere.
[d] Solution mixture (good solvent/poor solvent= 1/99 by volume).

Table S2 Single crystal data for **TPB.**

Compound	**TPB**	
Empirical formula	C40 H36 N2 O4	
Formula weight	608.71	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 17.0973(4) Å	a= 90°.
	b = 9.9802(2) Å	b= 90°.
	c = 18.6266(4) Å	g = 90°.
Volume	3178.34(12) $Å^3$	
Z	4	
Density (calculated)	1.272 Mg/m^3	
Absorption coefficient	0.652 mm^{-1}	
F(000)	1288	
Crystal size	0.25 x 0.15 x 0.15 mm^3	
Theta range for data collection	5.13 to 67.98°.	
Index ranges	-20<=h<=14, -12<=k<=11, -9<=l<=22	
Reflections collected	6983	
Independent reflections	2880 [R(int) = 0.0271]	
Completeness to theta = 67.98°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.95176	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2880 / 0 / 208	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R1 = 0.0455, wR2 = 0.1236	
R indices (all data)	R1 = 0.0578, wR2 = 0.1354	
Largest diff. peak and hole	0.214 and -0.216 $e.Å^{-3}$	

Table S3 Energy level of **TPPA** and **TPB.**

Sample	**Oxidation potential (V)** (Vs Ag/AgCl in MeCN)	**U-vis absorption**			
	$\mathbf{E_{onset,ox}}$	$\boldsymbol{\lambda}_{\mathbf{onset}}$ (nm)	E_g[c] (eV)	HOMO[a] (eV)	LUMO[b] (eV)
TPPA	0.35	371	3.35	-4.79	-1.44
TPB	0.56	393	3.16	-5.01	-1.85

[a]The HOMO energy levels were calculated from CV and were referenced to ferrocene in **TBAP/MeCN** (4.8 eV; onset= 0.36 V).

[b]The LUMO were calculated from sample by the equation: E_g = LUMO-HOMO.

[c]The data were calculated from sample by the equation: $E_g = 1242/\boldsymbol{\lambda}_{onset}$ (energy gap between HOMO and LUMO).

Table S4 Electrochromic switching response at the relative wavelength of **different type** devices based on **TPB/HV** between 1.2 V (on) and -0.1 V.

Sample	**479 nm**			**606 nm**			**669 nm**		
	t_c (s)	t_b (s)	ΔT (%)	t_c (s)	t_b (s)	ΔT (%)	t_c (s)	t_b (s)	ΔT (%)
Liquid-type	1.9	7.5	69.0	2.4	6.8	67.9	2.9	6.6	66.2
Gel-tpye	3.6	8.4	67.8	4.6	7.4	67.0	5.4	7.0	61.7