Support information

Highly Transparent to Red/Green/Blue Photo-crosslinkable Polymer for Patterned Electrochromic Device

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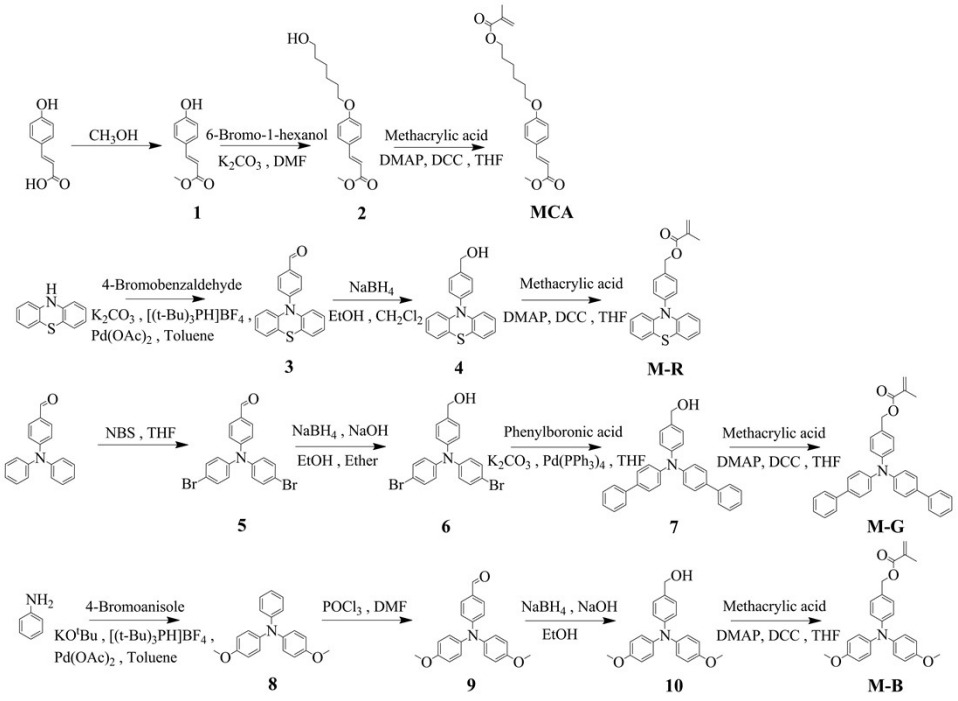

Fig S1. Synthetic routes of the monomers MCA, M-R, M-G and M-B.

Synthesis of monomers

Methyl 4-hydroxycinnamate (1)

Methyl 4-(6-hydroxyhexoxy)cinnamate (2)

Methyl 4-(6-methacryloxyhexoxy)cinnamate (MCA)

4-(10H-Phenothiazin-10-yl)benzaldehyde (3)

(4-(10H-phenothiazin-10-yl)phenyl)methanol (4)

4-(10H-phenothiazin-10-yl)benzyl methacrylate (M-R)

4-(Bis(4-bromophenyl)amino)benzaldehyde (5)

(4-(bis(4-bromophenyl)amino)phenyl)methanol (6)

(4-(di([1,1'-biphenyl]-4-yl)amino)phenyl)methanol (7)

4-(di([1,1'-biphenyl]-4-yl)amino)benzyl methacrylate (M-G)

4-Methoxy-N-(4-methoxyphenyl)-N-phenylaniline (8)

4-(Bis(4-methoxyphenyl)amino)benzaldehyde (9)

(4-(bis(4-methoxyphenyl)amino)phenyl)methanol (10)

4-(bis(4-methoxyphenyl)amino)benzyl methacrylate (M-B)

Methyl 4-hydroxycinnamate (1)

p-Hydroxy-cinnamic acid (2.30 g, 14.0 mmol) was added to anhydrous methanol, a small amount of concentrated hydrochloric acid was added dropwise and heated to reflux for 12 h. After the reaction, product 1 (2.2 g, 12.4 mmol, 88.3%) was obtained after extraction with dichloromethane and purification by column chromatography with dichloromethane as the eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 15.9 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 6.33 (d, *J* = 16.0 Hz, 1H), 5.57 (s, 1H), 3.82 (s, 3H).

Methyl 4-(6-hydroxyhexoxy)cinnamate (2)

The products 1 (2.0 g, 11.2 mmol), 6-bromo-1-hexanol (3.0 g, 16.6 mmol), K_2CO_3 (4.1 g, 29.7 mmol) were added to anhydrous DMF (40 ml) and stirred at room temperature for 24 h. The resulting mixture was poured into 100 mL of distilled water and filtered under reduced pressure. The filter was washed with distilled water to obtain product 2 (2.4 g, 8.6 mmol, 77.0%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 15.9 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.33 (d, *J* = 15.9 Hz, 1H), 4.01 (t, *J* = 6.4 Hz, 2H), 3.81 (s, 3H), 3.69 (t, 3H), 1.88–1.77 (m, 2H), 1.69–1.40 (m, 6H).

Methyl 4-(6-methacryloxyhexoxy)cinnamate (MCA)

The product 2 (2.4 g, 8.6 mmol), methacrylic acid (1.1 g, 12.8 mmol), DMAP (0.11 g, 0.9 mmol) and DCC (2.5 g, 12.1 mmol) were added to THF (50 ml) and stirred at room temperature for 24 h. After the reaction, product MCA (2.2 g, 6.4 mmol, 73.9%) was obtained after extraction with dichloromethane and purification by column chromatography with dichloromethane as the eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 16.0 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.37 (d, *J* = 7.6 Hz, 1H), 5.80 (d, *J* = 1.4 Hz, 1H), 4.02 (t, 2H), 3.83 (s, 3H), 3.71 (t, 2H), 2.09 (s, 3H), 1.98–1.90 (m, 2H), 1.79–1.57 (m, 6H). MS (ESI): 347.2 [$M+H^+$].

4-(10H-Phenothiazin-10-yl)benzaldehyde (3)

A mixture of phenothiazine (1.0 g, 5.0 mmol), 4-bromobenzaldehyde (1.0 g, 5.4 mmol), K_2CO_3 (2.0 g, 14.5 mmol), palladium acetate (0.03 g, 0.15 mmol), and tri-tert-butylphosphonium tetrafluoroborate (0.09 g, 0.3 mmol) in anhydrous toluene (20 ml) was refluxed for 12 h under nitrogen atmosphere. The crude product was purified by extraction with dichloromethane and column chromatography (petroleum ether/dichloromethane, V/V = 1 : 1) to afford product 3 (1.3 g, 4.3 mmol 86.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.84–7.74 (m, 2H), 7.51–7.42 (m, 2H), 7.37–7.27 (m, 4H), 7.25–7.13 (m, 4H).

(4-(10H-phenothiazin-10-yl)phenyl)methanol (4)

The product 5 (1.3 g, 4.3 mmol) and sodium borohydride (0.17 g, 4.5 mmol) was added to a mixture of anhydrous ethanol (5 ml) and dichloromethane (15 ml), stirred at room temperature for 4 h. After the reaction was completed, product 6 (1.3 g, 4.3 mmol, 99.1%) was obtained after extraction with dichloromethane. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.43–7.37 (m, 2H), 7.10–6.99 (m, 2H), 6.85 (m, 4H), 6.30–6.16 (m, 2H), 4.84

(s, 2H).

4-(10H-phenothiazin-10-yl)benzyl methacrylate (M-R)

The product 4 (0.55 g, 1.8 mmol), methacrylic acid (0.31 g, 3.6 mmol), DMAP (0.03 g, 0.25 mmol) and DCC (0.7 g, 3.4 mmol) were added to THF (10 ml) and stirred at room temperature for 24 h. After the reaction, product M-R (0.4 g, 1.1 mmol, 59.6%) was obtained after extraction with dichloromethane and purification by column chromatography with dichloromethane as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.41–7.35 (m, 2H), 7.03 (dd, *J* = 7.3, 1.8 Hz, 2H), 6.90–6.78 (m, 4H), 6.24 (dd, *J* = 9.6, 1.4 Hz, 3H), 5.67–5.61 (m, 1H), 5.30 (s, 2H), 2.02 (s, *J* = 1.1 Hz, 3H). MS (ESI): 374.1 [M+H$^+$].

4-(Bis(4-bromophenyl)amino)benzaldehyde (5)

Under light-proof conditions, 4-(N, N-Diphenylamino)benzaldehyde (2.8 g, 10.2 mmol), N-Bromosuccinimide (4.8 g, 27.0 mmol) were added to THF (100 ml), and heated to refluxed for 12 h under nitrogen atmosphere. The crude product was purified by extraction with dichloromethane and column chromatography (petroleum ether/dichloromethane, V/V = 1 : 1) to afford product 5 (3.6 g, 8.4 mmol, 82.3%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.76–7.70 (m, 2H), 7.49–7.43 (m, 4H), 7.08–7.01 (m, 6H).

(4-(bis(4-bromophenyl)amino)phenyl)methanol (6)

The product 5 (2.0 g, 4.7 mmol) was added to a mixture of anhydrous ethanol (15 ml) and anhydrous ether (15 ml), stirred at room temperature, and 10 ml aqueous sodium hydroxide solution (0.1 M in distilled water) containing sodium borohydride (0.17 g) was added and continued to be stirred at room temperature for 4 h. After the reaction was completed, product 6 (2.0 g, 4.6 mmol, 98.2%) was obtained after extraction with dichloromethane. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39–7.34 (m, 4H), 7.31–7.28 (m, 2H), 7.09–7.05 (m, 2H), 6.98–6.91 (m, 4H), 4.67 (s, 2H).

(4-(di([1,1'-biphenyl]-4-yl)amino)phenyl)methanol (7)

The product 6 (2.0 g, 4.6 mmol), phenylboronic acid (1.7 g, 13.9 mmol), 10 ml K_2CO_3 solution (2 M in distilled water), and tetrakis(triphenylphosphine)palladium (0.16 g, 0.14 mmol) were added to anhydrous THF (30 ml) and heated to reflux under nitrogen atmosphere for 12 h. At the end of the reaction, product 7 (0.8 g, 1.9 mmol, 40.7%) was obtained after extraction with dichloromethane and purification by column chromatography (petroleum ether/dichloromethane, V/V = 1 : 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64–7.58 (m, 4H), 7.53 (dd, *J* = 8.9, 2.2 Hz, 4H), 7.48–7.42 (m, 4H), 7.34 (dd, *J* = 12.7, 7.9 Hz, 4H), 7.24–7.15 (m, 6H), 4.70 (s, 2H).

4-(di([1,1'-biphenyl]-4-yl)amino)benzyl methacrylate (M-G)

The product 7 (0.8 g, 1.8 mmol), methacrylic acid (0.2 g, 2.3 mmol), DMAP (0.02 g, 0.16 mmol) and DCC (0.42 g, 2.0 mmol) were added to THF (20 ml) and stirred at room temperature for 24 h. After the reaction, product M-G (0.4 g, 1.1 mmol, 59.6%) was obtained after extraction with dichloromethane and purification by column chromatography with dichloromethane as the eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.2 Hz, 4H), 7.54 (d, *J* = 8.6 Hz, 4H), 7.48–7.43 (m, 4H), 7.38–7.30 (m, 4H), 7.20 (dd, *J* = 22.7, 8.5 Hz, 6H), 6.20 (s, 1H), 5.62 (s, 1H), 5.19 (s, 2H), 2.01 (s, 3H). MS (ESI): 496.2 [M+H$^+$].

4-Methoxy-N-(4-methoxyphenyl)-N-phenylaniline (8)

A mixture of aniline (1.0 g, 10.7 mmol), 4-bromoanisole (4.5 g, 24.1 mmol), potassium t-butoxide (3.6 g, 32.1 mmol), palladium acetate (0.07 g, 0.32 mmol), and tri-tert-butylphosphonium tetrafluoroborate (0.19 g, 0.64 mmol) in anhydrous toluene (40 ml) was refluxed for 12 h under nitrogen atmosphere. The crude product was purified by

extraction with dichloromethane and column chromatography (petroleum ether/dichloromethane, V/V = 1 : 2) to afford product 8 (2.6 g, 8.5 mmol, 79.4%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 11.9, 4.0 Hz, 2H), 7.11 (d, *J* = 8.9 Hz, 4H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.90 (dd, *J* = 19.9, 8.1 Hz, 5H), 3.84 (s, 6H).

4-(Bis(4-methoxyphenyl)amino)benzaldehyde (9)

The product 8 (2 g, 6.6 mmol) was added to anhydrous DMF, a small amount of phosphorus trichloride was add, stirred at room temperature for 1 h, then raise the temperature to 90 ℃ and continue to stirred for 6 h. After the reaction, the product 9 (1.9 g, 5.7 mmol, 86.4%) was obtained after extraction with dichloromethane and purification by column chromatography with dichloromethane as the eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.68–7.61 (m, 2H), 7.19–7.11 (m, 4H), 6.93–6.89 (m, 4H), 6.88–6.85 (m, 2H), 3.84 (s, 6H).

(4-(bis(4-methoxyphenyl)amino)phenyl)methanol (10)

The product 9 (1.8 g, 5.4 mmol) was added to anhydrous ethanol (15 ml), stir at room temperature, and 9 ml aqueous sodium hydroxide solution (0.1 M in distilled water) containing sodium borohydride (0.15 g) was added and continued to be stirred at room temperature for 4 h. After the reaction was completed, product 10 (1.8 g, 5.4 mmol, 99.5%) was obtained after extraction with dichloromethane. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.5 Hz, 2H), 7.08–6.97 (m, 4H), 6.91 (dq, *J* = 7.8, 2.7 Hz, 2H), 6.86–6.75 (m, 4H), 4.57 (s, 2H), 3.78 (s, *J* = 1.8 Hz, 6H).

4-(bis(4-methoxyphenyl)amino)benzyl methacrylate (M-B)

The product 10 (1.8 g, 5.4 mmol), methacrylic acid (0.6 g, 7.0 mmol), DMAP (0.06 g, 0.49 mmol) and DCC (1.5 g, 7.3 mmol) were added to THF (50 ml) and stirred at room temperature for 24 h. After the reaction, product M-B (1.0 g, 2.5 mmol, 45.9%) was obtained after extraction with dichloromethane and purification by column chromatography with dichloromethane as the eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.5 Hz, 2H), 7.08–6.97 (m, 4H), 6.93–6.85 (m, 2H), 6.85–6.75 (m, 4H), 6.13 (s, 1H), 5.55 (s, 1H), 5.09 (s, 2H), 3.78 (s, 6H), 1.95 (s, 3H). MS (ESI): 404.2 [$M+H^+$].

P-R

M-R (0.1 g, 0.27 mmol), MCA (0.18 g, 0.53 mmol) and AIBN (0.04 g, 0.27 mmol) were dissolved in dry THF (10 ml) under nitrogen. The mixture was stirred at 60 °C for 48 h. The polymer was precipitated into methanol three times. After drying, P-R was obtained in 93.0% (0.26 g) yield.

P-G

M-G (0.1 g, 0.20 mmol), MCA (0.14 g, 0.40 mmol) and AIBN (0.03 g, 0.20 mmol) were dissolved in dry THF (10 ml) under nitrogen. The mixture was stirred at 60 °C for 48 h. The polymer was precipitated into methanol three times. After drying, P-G was obtained in 83.0% (0.20 g) yield.

P-B

M-R (0.1 g, 0.25 mmol), MCA (0.09 g, 0.25 mmol) and AIBN (0.04 mg, 0.25 mmol) were dissolved in dry THF (10 ml) under nitrogen. The mixture was stirred at 60 °C for 48 h. The polymer was precipitated into methanol three times. After drying, P-R was obtained in 94.7% (0.18 g) yield.

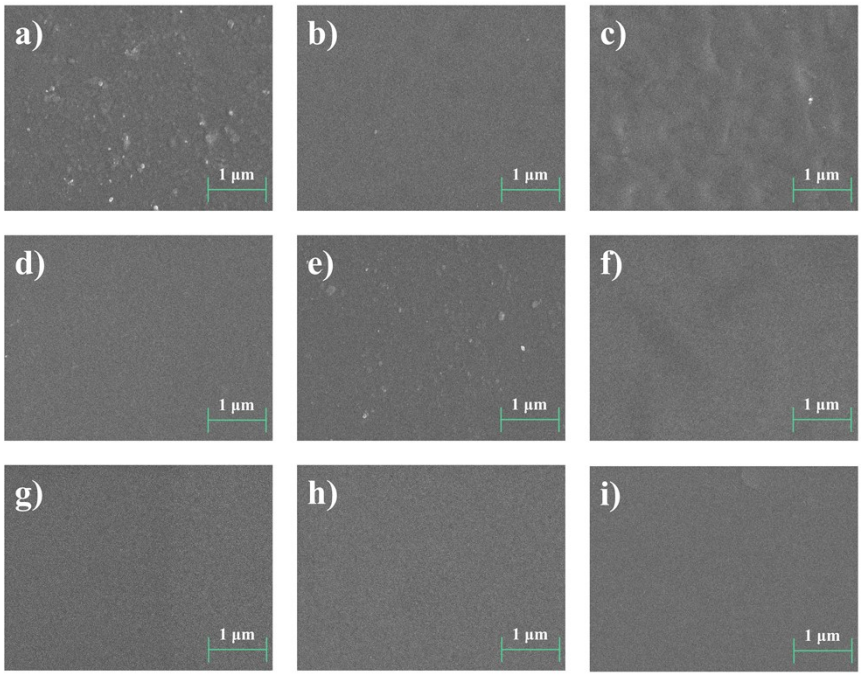

Fig S2. SEM images of spin-coated (a) P-R, (d) P-G, (g) P-B films; cross-linked (b) P-R, (e) P-G, (h) P-B films; cross-linked and washed (c) P-R, (f) P-G, (i) P-B films on ITO glass substrate.

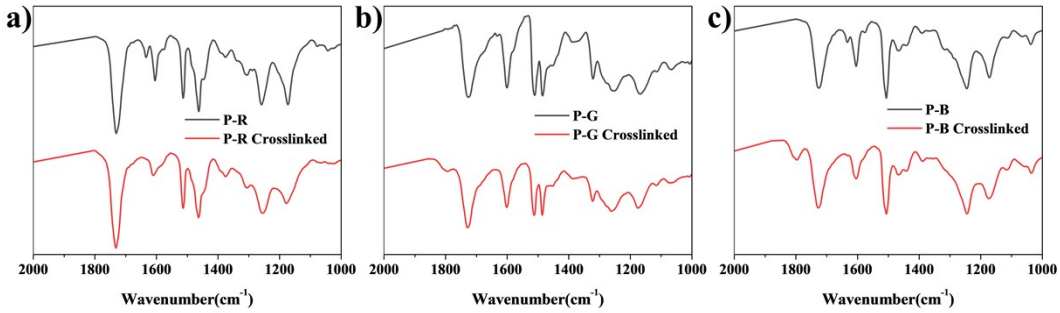

Fig S3. FTIR spectra of spin-coated film (black), cross-linked by UV light (red). (a) P-R, (b) P-G, (c) P-B on ITO electrodes.

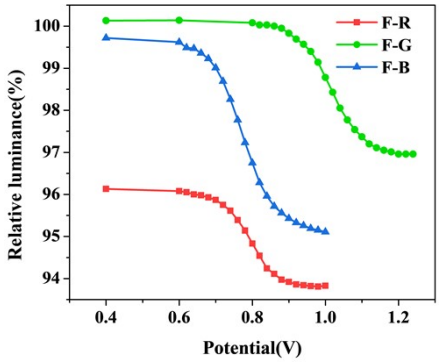

Fig S4. Relative luminance (L*) as a function of increasing applied potential for F-R, F-G, F-B.

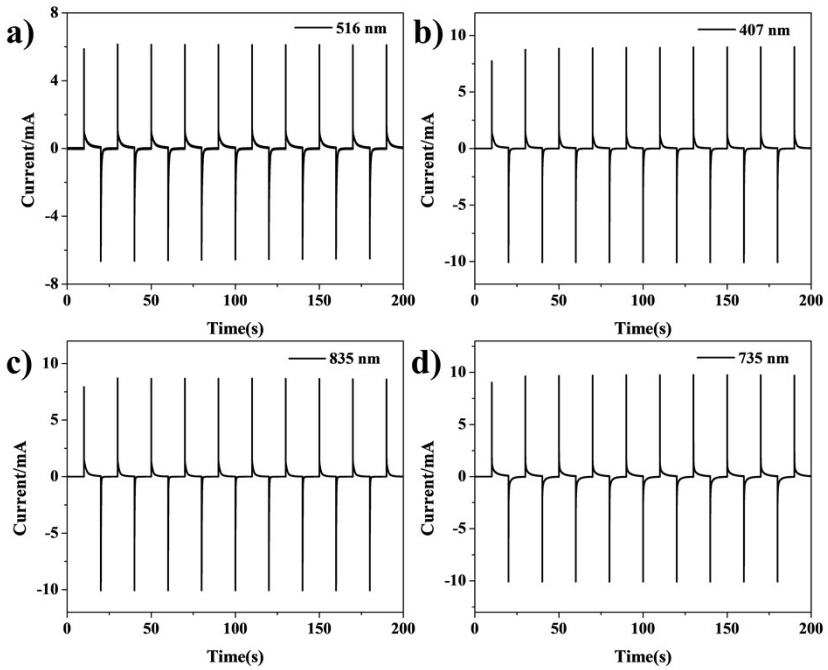

Fig S5. Chronoamperometry date of (a) F-R, (b, c) F-G, (d) F-B.

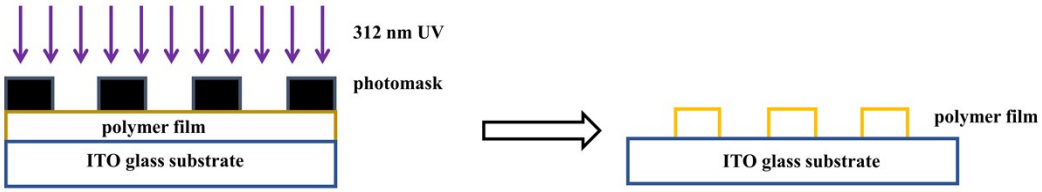

Fig S6. Schematic of the direct photopatterning procedure.

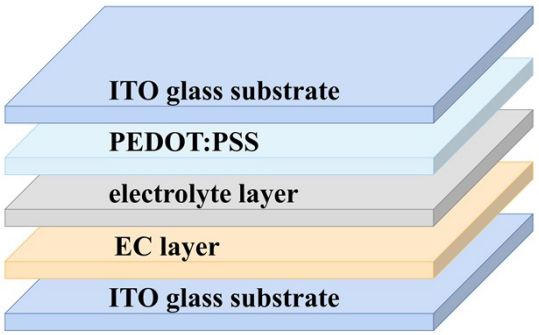

Fig S7. Schematic diagram of the electrochromic device.

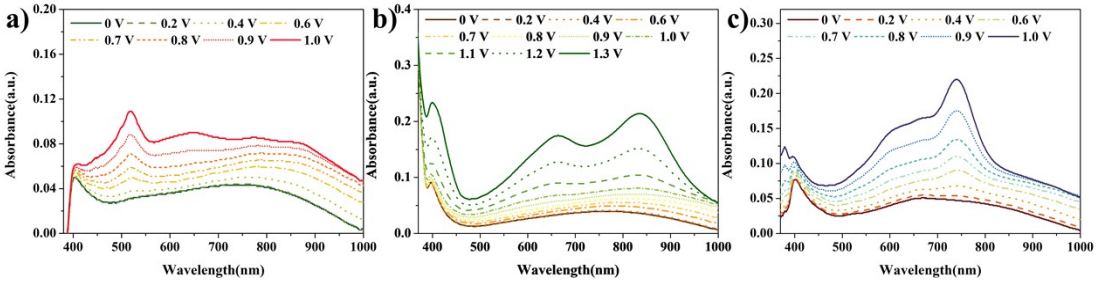

Fig S8. Spectroelectrochemistry of EC devices (a) F-R and PEDOT:PSS; (b) F-G and PEDOT:PSS; (c) F-B and PEDOT:PSS.

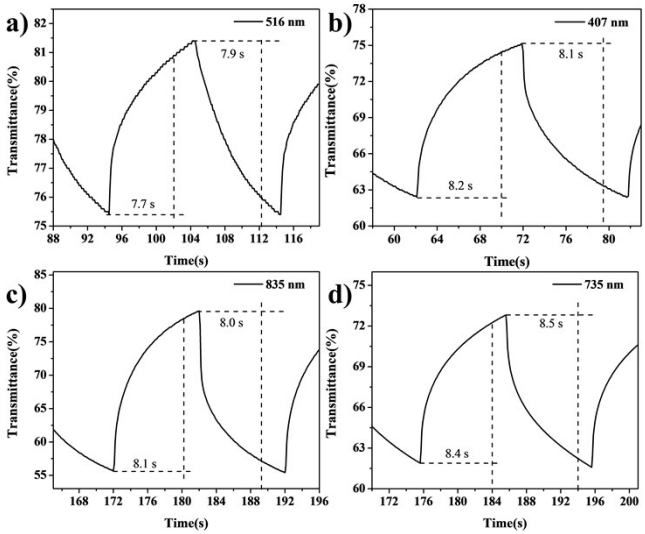

Fig S9. Switching time of EC devices (a) F-R and PEDOT:PSS at 516 nm between -0.5 V and 1.0 V, (b, c) F-G and PEDOT:PSS at 407 nm and 835 nm between -0.5 V and 1.3 V (d) F-B and PEDOT:PSS at 735 nm between -0.5 V and 1.0 V with a residence time of 10 s.

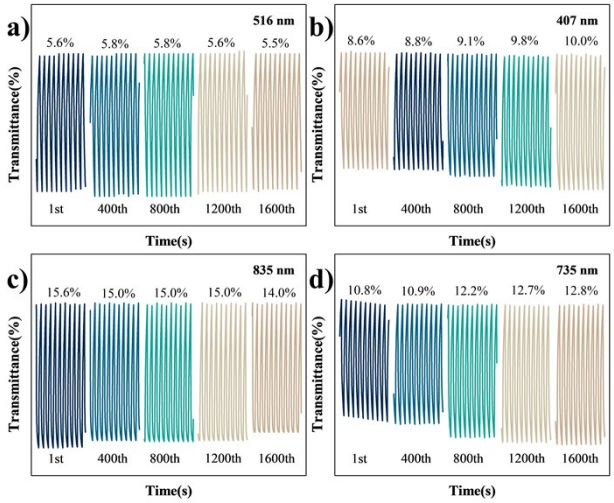

Fig S10. Cyclic stability of EC devices (a) F-R and PEDOT:PSS at 516 nm between -0.5 V and 1.0 V, (b, c) F-G and PEDOT:PSS at 407 nm and 835 nm between -0.5 V and 1.3 V (d) F-B and PEDOT:PSS at 735 nm between -0.5 V and 1.0 V with a residence time of 10 s.