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Color Combination of Conductive Polymers for Black Electrochromism

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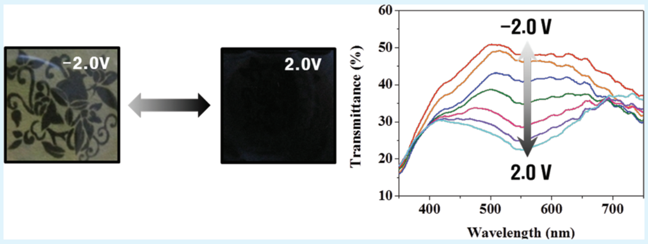
Supporting Information



ABSTRACT: Conducting polymers that absorb three primary colors, red, green, and blue (RGB), were introduced with a yellow electrochromic polymer (Y) for the preparation of black electrochromic devices. Red poly(3-hexylthiophene) (P3HT) and blue poly(3,4-ethylenedioxythiophene) (PEDOT) were coated on one side of the electrode as a cathodically coloring electrochromic (EC) layer, while green poly(aniline-N-butylsulfonate) (PANBS) and yellow EC poly{[1,3-bis(9′,9′-dihexylfluoren-20-yl)azulenyl]-alt-[2″,7″-(9″,9″-dihexylfluorenyl]} (PDHFA) were coated on the opposite electrode to complete a complementary EC device. The yellow PDHFA layer effectively compensated for absorption below 450 nm and above the 600 nm region, which was lacking in the RGB electrode. The resultant RGBY ECD provided a black color near the CIE black with L^*, a^*, and b^* values of 32, −1.1, and 3.7, respectively, covering a broad absorption in the visible range in the colored state. The state of the black EC device was maintained, even after the electricity was turned off for 200 h, showing stable memory effect.

KEYWORDS: *electrochromism, conductive polymer, complementary device, color mixing*

INTRODUCTION

Reversible color change by conjugated polymers through electrochromism has been of increasing interest mainly because of their low operation voltage with memory effect, thin film processability, and simple device structures.[1−9] Among the various conjugated polymers, poly(thiophene) (PTh) and poly(aniline) (PANI)[3,4] have received much attention because of their high coloration efficiency and fine-tuning of color via structure modification.[6] In particular, recent studies have focused on combining the EC materials to realize full or real black color with high contrast.

On the basis of the color mixing theory, all colors can be obtained by mixing the three primary colors, red, green, and blue (RGB), in different ratios, and this constitutes an important step for black EC devices. Further fine-tuning of these EC colors, possibly by adjusting their film thickness and redox states, can generate all possible colors.[10−12] Although most colors can be obtained from these primary colors, the range of colors that can be derived from the primary colors is far from representing the complete color spectrum. Furthermore, the realization of real "black" coloration in an EC system has been delayed due to the difficulty in obtaining the absorptions required in the whole visible region to display a black color. This is attributed to the low absorption of conducting polymers in the high energy region (below 400 nm). A high-cost synthetic route[3,13,14] has been reported; however, it needs improvement in the visible absorption region to produce a real black color. Red, blue, and green cover the 450 to 750 nm wavelength range in the visible region of the electromagnetic spectrum, and the region below 450 nm is covered by yellow. Thus, a yellow EC material has been proposed as the fourth primary color to complete the color spectrum. A few examples of yellow EC materials are triphenylamine-based copolymers with EDOT,[15] phenylanthraquinones,[16] and poly{[1,3-bis(9′,9′-dihexylfluoren-20-yl)-azulenyl]-alt-[2″,7″-(9″,9″-dihexylfluorenyl]} (PDHFA).[17] The choice of EC materials for a full or black EC device is based on the device structure and efficient charge transport for EC reactions in each layer.

For EC device (ECD) fabrication with multicolored layers, it is necessary to find an optimum combination of EC layers with respect to color and also efficient EC reactions since each EC layer has to be integrated in order to match the desired color and obtain a full spectrum. In a device in which multiple EC layers are integrated into one electrode, charge transport and color tuning may be of concern due to the resistance between layers. To this end, we are pursuing a complementary EC device in which the anodically and cathodically coloring EC materials are coated on opposite electrodes as a working and counter electrode, respectively, as previously suggested for a two-color EC system.[18−20] Interlayer resistance can be minimized in this complementary EC structure by using a

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minimum number of layers and allowing the charge compensating process at the counter electrode. Herein we report the fabrication of EC layers for color combination, optimizing their thickness and processability, to achieve black color ECD that shows various colors at the intermediate potentials but camouflages to black surrounding in color at the oxidized state. We apply anodically and cathodically coloring conducting polymers in a complementary ECD combining double layered working and counter electrodes using RGBY (red, green, blue, and yellow) coloring EC polymers. A solution-processable, poly(3-hexylthiophene) (P3HT)[20−23] was used as a red material. To avoid dissolution of the EC layers, we deposited PEDOT[24−27] by vapor phase polymerization as a blue EC material. Both P3HT and PEDOT were introduced at the cathode as cathodically coloring EC materials. PANBS[28−30] was coated electrochemically onto a working electrode for a green EC layer, whereas a yellow EC material, PDHFA, was coated onto the PANBS layer by a solution process in order to obtain a complete spectrum yielding a RGBY-combined EC display. Both PANBS (G) and PDHFA (Y) were introduced at the anode as anodically coloring EC materials.

■ EXPERIMENTAL SECTION

Materials. P3HT (M_w = 55 000 g mol^{-1}) was purchased from Rieke Metals, Inc. EDOT (3,4-ethylenedioxythiophene) was obtained from Aldrich and was then polymerized by vapor-phased polymerization (VPP) onto an ITO substrate (Samsung Corning Co., Ltd.). Synthesis of aniline-N-butylsulfonate (ANBUS) and electropolymerization for the PANBS film were performed according to a previously reported procedure.[28] PDHFA[17,31] was synthesized using bromination of azulene to obtain 1,3-dibromoazulene and 2-(4,4,5,5-tetramethyl-1,3,2-dioxaboralan-2-yl)-9,9-dihexylfluorene, followed by boronation with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. A Suzuki coupling reaction was performed between the above-mentioned products to produce 1,3-bis(9,9-dihexylfluoren-2-yl)azulene. The product was brominated followed by a Suzuki coupling reaction with 9,9-dialkylfluorene-2,7-bis(trimethyleneborate) to obtain PDHFA.[32,33] The final product was confirmed by ^{1}H NMR, GPC and elemental analysis (see Figure S1 in the Supporting Information).

Fabrication of Electrochromic Devices (ECDs). P3HT and PDHFA were directly spin-coated onto ITO glass substrates. P3HT was dissolved in chloroform (0.1, 0.25, and 0.5 wt %) and spin-coated at 1600 rpm for 20 s onto ITO-coated glass. PDHFA (1 wt %) was dissolved in chloroform and spin-coated at 1000 rpm for 25 s. For PANBS film fabrication, an electrolyte solution containing 0.1 M of the monomer and $NaClO_4$, perchloric acid, and distilled water in 15 mL of acetonitrile was introduced, and a potential from 0 to 1.5 V was applied with a scan rate of 0.1 V/s.

For the bilayered P3HT- and PEDOT-coated electrode, P3HT was deposited first by a spin-coating method and then PEDOT was deposited by vapor phase polymerization of EDOT onto the oxidant-coated[34] P3HT film. For homogeneous coating of the oxidant, a P3HT film was treated in oxygen plasma for a few seconds. The bilayered film was washed with ethanol after deposition of PEDOT to remove unreacted oxidant, and the film was then dried with N_2 gas. EDOT vapor was generated by heating at 75 °C, and the vapor deposition and polymerization was performed for 10 min in the chamber. The color of the film changed from red to purple after the PEDOT film formed on top of the P3HT film. PANBS and PDHFA layers were introduced to the working electrode as anodically colored green and yellow EC electrodes. EC properties of all EC films are summarized in Table 1.

All ECDs were assembled by placing the electrolyte medium between the two electrodes. The space between the two electrodes was controlled by placing insulating tape (thickness = 60 μm) between them. The liquid electrolyte solution was composed of tertbutylammonium perchlorate (TBAP) and γ-butyrolactone, and the solid electrolyte solution was prepared according to a previously described method.[35]

Table 1. Electrochromic Properties of RGBY Films

ECD	wavelength (nm)	T_c	T_b	CE (cm^2/C)	$\tau_{c0.7}$[a] (s)	$\tau_{b0.7}$[b] (s)
R[c]	515	41	84	300	0.5	0.6
B[d]	600	54	93	250	1.2	1.1
G[e]	470	44	70	30	3.7	1.6
	710	46	92	67	2.4	4.4
Y[f]	350	18	28	468	2.3	1.0
	470	38	46	144	1.4	1.0
	620	92	78	216	3.1	1.1
RB[g]	600	48	86	146	0.7	0.9
RGB[h]	470	22	49	22	2.0	3.4
	530	23	58	45	1.7	3.0
	650	36	62	28	1.1	2.9
RBY[i]	470	11	28	40	20	15
	515	8	39	89	17	11
	600	10	40	178	16	12
	710	33	37	44	10	18
RGBY[j]	470	3	23	60	7.7	7.1
	515	4	31	118	10.4	2.7
	600	5	29	96	13.3	1.9
	710	10	24	56	8.1	2.6

[a] Switching time to 70% of the colored state. [b] Switching time to 70% of the bleached state. [c] P3HT (−3 V, +3 V). [d] PEDOT (−4 V, +2 V). [e] PANBS (−4 V, +4 V). [f] PDHFA (−3 V, +2 V). [g] P3HT/PEDOT (−3 V, +3 V). [h] P3HT/PEDOT/PANBS (−4 V, +2 V). [i] P3HT/PEDOT/PDHFA (−4 V, 4 V). [j] P3HT/PEDOT/PANBS/PDHFA (−4 V, +2 V). Step potentials are 15 s/step.

Instrumentation and Measurements. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX 400-MHz NMR spectrometer in $CDCl_3$ at room temperature using tetramethylsilane (TMS) as an internal standard. The operating frequency of the NMR spectrometer was 400.13 MHz (1H). Cyclic voltammetry (CV), UV−vis absorbance, and optical response were measured with an in situ spectro-electrochemical system consisting of a computer-controlled spectrophotometer using an Avaspec-2048 fiber optic spectrometer and an electrochemical subsystem (CHI624B). Coloration efficiency and response time of the ECDs were determined at the absorption max under a square-wave switching potential using chronocoulometry in a solid polymer electrolyte with an EC window size of 2.0 × 2.0 cm^2. The EC response time for coloration and bleaching was determined at a 70% absorption change[36] under the given step potentials. Electrochromic efficiency (EE), including the coloration and bleaching efficiency, was determined by dividing the change in transmittance (ΔT) by the injected/ejected charge per unit area.[36] Colorimetry was measured for ECDs using a color reader CR-10 (Minolta Co., Ltd.). The conductivities of the conducting polymer films were examined using a top-contact four-point probe. Film thickness was measured by an Alpha-Step IQ (Tencor Instruments). The average molecular weight of the polymer was characterized by gel permeation chromatography (GPC) (model Waters R-401 ALC/GPC) with THF as the eluent; a polystyrene standard was used for calibration.

■ RESULTS AND DISCUSSION

Optical Properties of Conjugated Polymers. The cathodically colored P3HT and PEDOT films showed red and blue colors, respectively, upon reduction at 0.39 V and −0.19 V (vs Ag/AgCl), respectively, as expected from the cyclic voltammograms obtained in liquid electrolyte solution containing 0.1 M $LiClO_4$ in acetonitrile (see Figure S2 in the Supporting Information). The anodically colored PANBS and

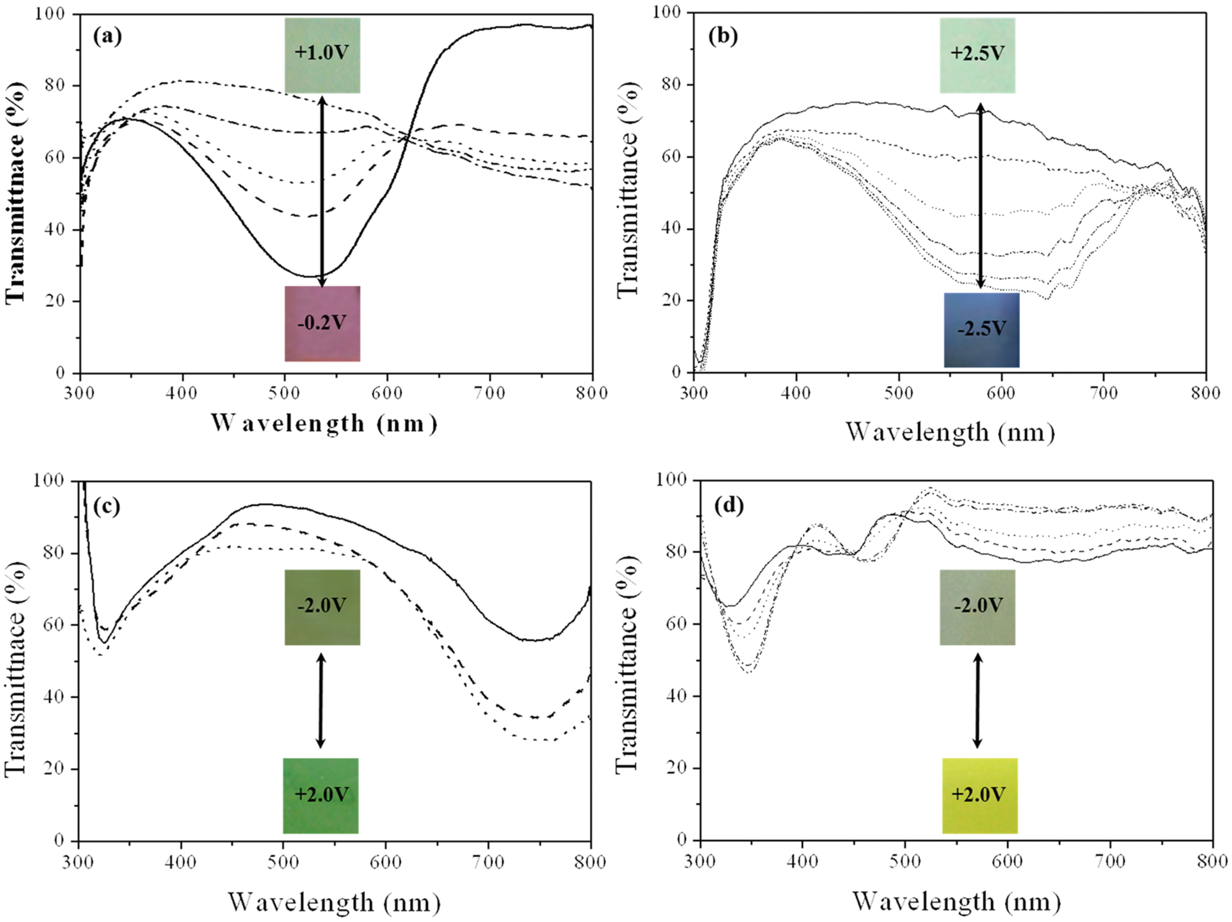

Figure 1. UV−vis transmittance spectral changes of (a) P3HT (+1 V to −0.2 V, vs Ag/AgCl), (b) PEDOT (+2.5 V to −2.5 V), (c) PANBS (−2 V to +2 V), and (d) PDHFA (−2 to 2 V) (top to bottom).

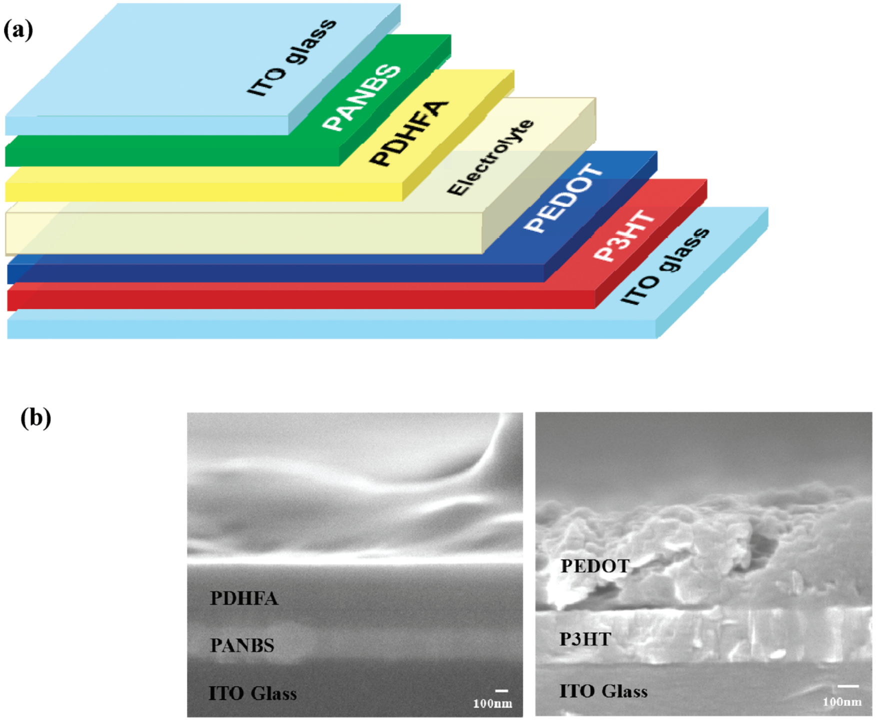

Figure 2. (a) Schematic diagram of the complementary electrochromic device; from top to bottom: ITO glass, PANBS, PDHFA, electrolyte, PEDOT VPP, P3HT, and ITO glass along with the chemical structure of each polymer. (b) FE-SEM image of the EC bilayer.

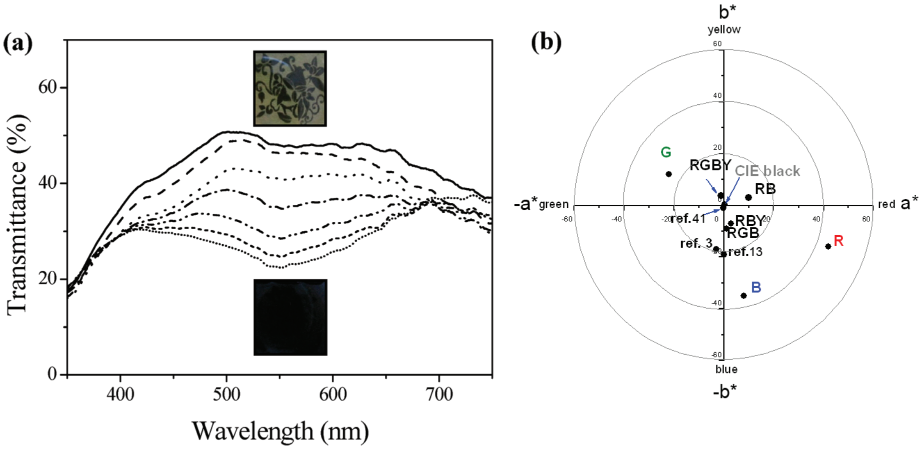

Figure 3. (a) Transmittance spectra of the complementary RGBY device and a photograph of the device in the colored state and the bleached state (inset). (b) CIE diagram of the electrochromic devices.

PDHFA exhibited green and yellow colors, respectively, by oxidation at 0.6 and 0.44 V (vs Ag/AgCl), respectively (see Figure S2a in the Supporting Information). In the two-electrode system where liquid electrolyte was sandwiched between an EC electrode and a bare ITO electrode, coloration occurred over a wide range. Figure 1 shows the UV−vis transmission spectral changes and photographs of the colored state (inset) of the four polymer films after thickness optimization on each film at voltages from −2 to 2 V in a two electrode system. The redox states of each polymer were easily controlled by the electrical potential, which yielded different tones and transmissions of color.

The P3HT film (thickness: 200 nm) showed a color change from red to transparent sky blue after oxidation, affording a high transmittance at ∼500 nm (Figure 1a). PEDOT (thickness: 410 nm) was deposited onto ITO glass by VPP of EDOT because it afforded a smooth surface with high conductivity, as previously reported.[37] The PEDOT film prepared by evaporating EDOT for 10 min in a VPP chamber showed a color change from dark blue to transparent sky blue upon oxidation, with a maximum intensity change at 600 nm (Figure 1b). The PANBS film was deposited by electrochemical polymerization of ANBUS (monomer), and its thickness was controlled by the number of voltage scan cycles (see Figure S4 in the Supporting Information). As shown in Figure S4b in the Supporting Information, the transmittance spectra of PANBS films in the colored and bleached states were dependent on the thickness of the film. In Figure 1c, the PANBS film of 430 nm thickness showed a color change from dark green to pale green upon reduction, with ∼40% transmittance change at ∼750 nm. The coloration efficiency of the PANBS film with a thickness of 150 nm was 83 cm^2/C with an EC response time of 2.5 s, as determined by the absorbance change at 750 nm. PDHFA and PANBS are quite less effective, compared to PEDOT and P3HT upon potential application. The spin-coated PDHFA film (thickness: 340 nm) showed a transmittance change in response to the applied potential between dark yellow and pale-blue in the colored and bleached states, respectively (Figure 1d). This film displayed a yellow color with a maximum absorption at 350 nm, and changed to pale green with an absorption band greater than 550 nm. The absorption maxima at colored states for P3HT, PEDOT, PANBS, and PDHFA were 515, 600, 710, and 350 nm, respectively, which would cover the whole visible range when combined.

Combination of EC Colors in a Bilayered ECD.

Electrochromic layers were coated at the anode and cathode and then assembled into the structure shown in Figure 2 using the same coating method used for the preparation of the individual EC films described above. The layering of each ECP is based on the consideration of their interfacial interactions. First, an electrode was coated with cathodically coloring P3HT (R) and then with PEDOT (B). Then, the opposite electrode was coated with anodically coloring PANBS (G), and then with PDHFA (Y) in order to complete a complementary RBGY-ECD. When the anode undergoes an oxidation (doping) process, the opposite (counter) electrode of the complementary ECD undergoes reduction,[18] leading to bleaching. Full coloration can be reversibly achieved from the complementary ECD when an opposite potential is applied to the anode. The interfacial contact was improved by coating P3HT first and then coating PEDOT layer on it. The formation of rough PEDOT surface by electrochemical deposition was already reported,[37] and it resulted in inhomogeneous layer formation of P3HT on PEDOT layer with poor contact at the interface. Thus PEDOT was coated on top of P3HT layer by vapor phase polymerization method, which is known to give more homogeneous film than electrochemical deposition.[37] This resulted in improved adhesion between P3HT and PEDOT layer. Moreover, by having PEDOT layer as a front layer in contact to the electrolyte layer, the charge transport in the cell would be more favorable because of the high conductivity of PEDOT of 44.4 S/cm compared to that of P3HT of 0.10 S/cm. The transport of electrons and ions is directly related to EC properties such as coloration efficiency and response time.[18,38,39] For the opposite bilayer, PANBS was coated first as the water-soluble PANBS form more homogeneous film on ITO film than on an organic film. Then PDHFA was coated on the top of PANBS layer to give good interfacial contact with the PANBS layer. The cross-cut images from a field-emission scanning electron microscope (FE-SEM) showed that the bilayered EC electrode was coated uniformly and held together between the polymers without much gap at the interface (Figure 2 b).

The color of the bilayered cathodically colored electrode, consisting of P3HT and PEDOT, was optimized by controlling the thickness of the P3HT while the PEDOT film thickness was held constant (410 nm) in order to achieve high absorption from 500 to 650 nm. P3HT layer thickness was varied by

Figure 4. Photographs of electrochromic switching in one cell (RGBY) taken after placing the ECD on a white paper background with black bouquet, at different potentials in two electrodes with liquid electrolyte.

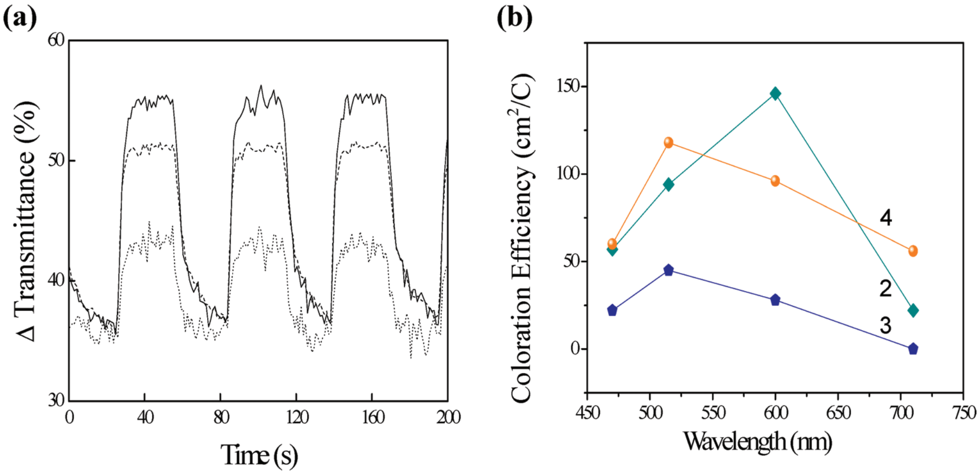

Figure 5. (a) Optical response of the RGBY ECD to the application of potential between 1.5 V and −2 V for 30 s. Solid, dashed, and dotted lines represent 515, 600, and 710 nm, respectively. (b) Coloration efficiencies of RB (2), RBG (3), and RBGY (4) layered ECDs at different wavelengths.

controlling the solution concentration using 0.1, 0.25, and 0.5 wt % P3HT, respectively. The color of each cell consisting of P3HT (R) and PEDOT (B) prepared from different P3HT thicknesses varied according to the applied potential, as expected from the different redox states of P3HT and PEDOT (see Figure S2a in the Supporting Information). A maximum color contrast was obtained from the combination of 200 nm thick P3HT and 410 nm thick PEDOT in a bilayered structure (RB) that showed a broad absorbance in the range of 500−650 nm with an accompanying color transition from transparent sky blue to dark purple (see Figure S5a in the Supporting Information). The transmittance of the trilayered device (RGB, Figure S5b), consisting of the cathode coated with P3HT (R), PEDOT (B) and the anode with PANBS (G) showed broad absorbance in the 500 to 700 nm wavelength region at −2 to 2 V. This absorption region of the RGB device was broader than that of the RB device (see Figure S5a in the Supporting Information); however, there was a spectral window at 400−500 nm, which remained transparent between the potential range of −2 to 2 V.

Figure S5c in the Supporting Information illustrates the UV−vis absorbance spectra in the colored state for the experimentally obtained single and trilayered (RGB) films. Experimentally obtained spectra for the RGB device reasonably matched those of simulated spectra for the RGB-layered film generated by combining each R, G, B layer spectra, revealing broad absorptions along the visible wavelength from 500 to 800 nm, which demonstrates the feasibility of obtaining a black color by combining the EC films.

Combination of EC Colors with Yellow EC for a Black ECD. As the combination of RGB in the trilayer lacked absorption in the high-energy region (350−500 nm), an anodically yellow coloring PDHFA layer was coated on the PANBS film, yielding a complementary device with RGBY layers (Figure 2). In this RGBY device, yellow coloration at 350−430 nm broadened spectral absorption to the whole visible range, and absorption contrast between the dark and bleached state at various potentials was increased (Figure 3a). The black coloration was vivid in the RGBY device when the anode was oxidized at +2 V, which resulted in reduction at the cathode, leading to coloration both at the anode and cathode, as illustrated by the photograph in Figure 3a (inset). The black color was bleached when the reverse potential was applied at the anode (−2 V), leading to a reduction at the anode and oxidation at the cathode, as illustrated by the photograph in Figure 3a (inset). The doped P3HT and PEDOT was transparent sky blue, and when combined with the undoped pale green PANBS and colorless PDHFA layers, the device appeared transparent in the bleached state.

A quantitative measure of the color of the ECDs was examined colorimetrically using the 1976 CIE Lab (of $L^*a^*b^*$), where the L^* represents light versus dark, a^* represents red versus green, and b^* represents yellow versus blue in the sample.[13,40] The CIE diagram for each device is compared in Figure 3b, and values obtained from CIE Lab measurements are summarized in Table S2 in the Supporting Information. In a colored state, the RGB device showed an L^* value of 29, which is comparable to that reported in the literature,[3] i.e., an L^* value of 26, with enhanced a* and b* values. This indicates that the black coloration of the RGB device in this study was enhanced compared to previous reports. Specifically, the blue hue (b^*) improved compared to the black color in previous reports.[3,34] Importantly, the RGBY device showed black color near CIE black with L^*, a^*, and b^* values of 32, −1.1, and 3.7, respectively. Such black coloration in the RGBY device is comparable to that from the ECD based on one material reported in the literature,[41] which showed similar $L^*a^*b^*$ values to the CIE black.

Figure 4 shows photographs of RGBY devices, which were placed above a paper printed with a black and white bouquet. At a negative potential between −2.0 and −1.2 V, the anodic EC materials were in the neutral state and thus the anode remained bleached as transparent yellow. Moreover, the cathode EC materials (R, B) were in a doped state and thus also remained bleached. Thus, the combined color of RBGY appeared bleached and showed the background print. The RBGY device became darker as more positive potential was applied, showing first a reddish color for the dedoping of P3HT (R), then blue purple because of dedoping of PEDOT (B) at a more positive potential, and dark upon doping of PDHFA (Y) and PANBS (G) at applied potentials higher than 0.4 V. It was noteworthy that various color tones of RGBY were obtained at potentials between ±2 V, which does not occur in one-material based black electrochromic devices.[14,41,42] Thus this black color ECD shows various colors at the intermediate potentials but camouflages to black surrounding in color at the oxidized state. The coloration was reversible by doping/dedoping potentials. Furthermore under an alternative step potential of +1.5 V and −2 V, it switched between transparent yellow and black color.

The optical response of the black four-layered ECD was determined from the transmittance change of the colored to bleached states in response to an alternative step potential of +1.5 V and −2 V.As shown in Figure 5a, the transmittance of the RGBY device changed within 3 s, as determined at the three major wavelengths, 515, 600, and 710 nm, representing red, blue and green coloration, respectively, in response to the applied step potentials.

The EC response of the RGBY ECD was slower than the single (R or B) or bilayered RB device, possibly due to the introduction of the green EC (PANBS) and yellow EC (PDHFA), which showed slow response in the visible light absorbing range (Table 1). Such a slow response could be attributed mainly to low electrical conductivity as the conductivities of PANBS and PDHFA were 0.7×10^{-2} and 4.9×10^{-3} S/cm, respectively, whereas that of PEDOT and P3HT were 44.4 and 0.10 S/cm, respectively.

The slow EC response in G and Y resulted in low coloration efficiency in this region, as it consumed more charge for the optical density change compared to that in R and B coloration. Thus, CE was highest for the bilayered RB device at 600 nm. However, the CE for the RB device for different colors, determined at different wavelengths, was low as there was not much absorption in the RB device (Figure 5b). On the other hand, the RGBY device showed high CE in all important color regions, as the absorption of the RGBY device covered the whole spectral region. The maximum CE for RGBY was observed to be 118 cm^2/C in the red region, which is larger than that of the trilayered RBG and RBY devices, despite the presence of identical PANBS (G) and PDHFA (Y) layers. Such a result could be attributed to the effective charge balancing between the anode and cathode by both bilayered structures in the complementary structure.

The unique advantage of ECDs over other displays such as LCDs and OLEDs is its memory effect, which maintains the colored or bleached state even after the applied electrical voltage is turned off. This memory effect originates from the stable electrochemical doping/dedoping process and is an important property of ECD for energy saving displays, as it allows the display of static information without applying electricity. Figure 6 shows the memory effect of the tetra-layered ECD at different wavelengths for 420 h. The device was applied at −2 V for 30 s to produce a color, and then the electrical supply was disconnected. The colored state was maintained, and the absorbance at three different wavelengths was maintained at nearly the same intensity as the initial absorption for a long period of time. The absorbance loss after 208 h of electrical disconnection was less than 10%, indicating that the black EC state was sustainable.

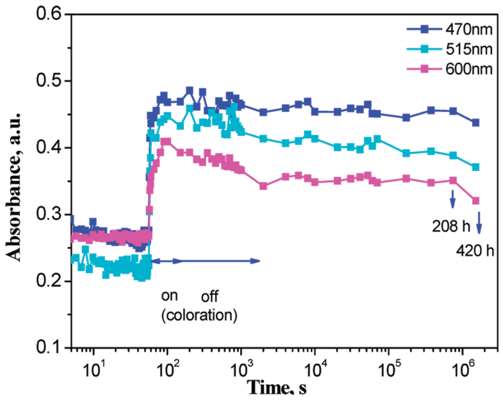

Figure 6. Memory effect for the RGBY device without electricity at three different wavelengths.

■ CONCLUSION

A black EC device was prepared by color combination of conducting polymers in a charge balancing complementary structure. Cathodically coloring red P3HT (R) and blue PEDOT (B) layers resulted in a dark purple color absorbing between 500 and 650 nm, and an anodically coloring green PANBS (G) layer with a yellow PDHFA (Y) layer on the opposite electrode complemented the absorption regions less than 500 nm and greater than 650 nm. The CIE measurement revealed that the broadly absorbing RGBY film conferred a black near CIE black with L^*, a^*, and b^* values of 32, −1.1, and 3.7, respectively. The coloration efficiency of the black ECD was determined to be 118 cm^2/C with a response time of 2.7 s. The colored state of the tetra-layered (RGBY) device was maintained longer than 200 h after the electricity was disconnected, providing a stable memory effect.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR spectrum of PDHFA in $CDCl_3$. Asterisks indicate TMS, $CDCl_3$, and residual solvent; CV of R, G, B, and Y single layers in liquid electrolyte; CV of complementary device with GY in the anode and RB in the cathode in a SPE-based two-electrode; transmittance spectra change of the P3HT and PEDOT film after applying a potential; optical response of the P3HT and PEDOT bilayer after applying potential between 0.8 V and −0.2 V for 10 s; film thickness and transmittance spectra change of PANBS by number of scan cycles; transmittance spectra change of PANBS as a function of the number of scan cycles; transmittance spectra of bilayered and trilayered; UV−vis absorbance of P3HT (R), PEDOT (B), PANBS (G), and their trilayered films in a colored state; CIE-Lab coordinates of all polymers characterized in both the colored and bleached states. This material is available free of charge via the Internet at http://pubs.acs.org/.

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