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Electrochromism of 2,2′-Azinobis(3-ethylbenzothiazoline-6-sulfonate) Incorporated into Conducting Polymer as a Dopant

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We report on multicolor electrochromism achieved by doping a molecular electrochromogen into a conducting polymer (polymeric electrochromogen). Polypyrrole was used as the polymeric electrochromogen, which is cathodically colored from gray to yellow at −0.4 V (vs. Ag/AgCl). 2,2′-Azinobis(3-ethylbenzothiazoline-6-sulfonate) {abbreviated as ABTS} was used as the molecular electrochromogen. ABTS is oxidized to its radical form around +0.45 V with a color change from colorless to greenish blue,[1,2] as shown in Figure 1a. The redox reaction of ABTS/its radical is reversible with one electron transfer.

Pyrrole is anodically electropolymerized to generate polarons and then bipolarons with one positive charge for three to four monomeric units.[3,4] Counteranions are required during polymerization to keep the electro-neutrality. Since ABTS is a dianion containing two sulfonate groups, it can be incorporated electrostatically into a polypyrrole backbone. Polypyrrole was electrodeposited on indium tin oxide/poly(ethylene terephthalate) (ITO/PET) substrate in an aqueous solution of pyrrole monomer and ABTS by imposing anodic potential at 0.6 V or by sweeping between 0.0 and 1.0 V repeatedly. An increase in current was observed as time passed or the number of cycles increased, indicative of the formation of conductive film and incorporation of ABTS into the conducting polymer. Energy-dispersive spectroscopy revealed the existence of sulfur that originates only from ABTS. The ratio of pyrrole to ABTS in the films was estimated at 10:1 (5 pyrrole units per one negative charge) by using elemental analysis.

Polypyrroles have been doped with various molecules, some of which have electrochromic properties. However, a very limited number of studies was devoted to the electrochromism of dopants in the conducting polymer. As far as we know, only three kinds of electrochromogens doped in polypyrrole were spectro-electrochemically studied: indigo carmine, phthalocyanines, and porphyrines. In the indigo carmine doped polypyrrole,[5] the dopant enhanced the contrast of color change of polypyrrole from blue at +0.4 V to yellow at −0.6 V since the dopant has the same color transition at −0.2 V, pH 4.0.[6] The change in UV/Vis spectra of phthalocyanines[7,8] and porphyrines[9] doped in polypyrroles with applied potential were reported but their electrochromism was not investigated in detail.

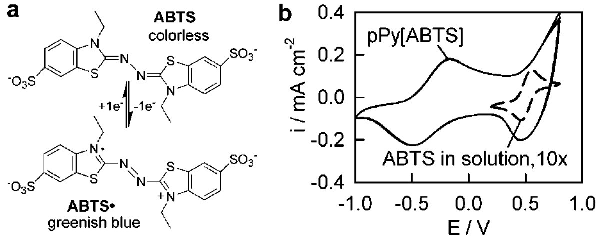

Figure 1. (a) Reversible one-electron reaction between ABTS (colorless) and ABTS• (greenish blue). (a) Cyclic voltammogram for ABTS-doped polypyrrole (pPy[ABTS]) in 200 mM KCl. pPy[ABTS] was electrodeposited on ITO/PET by potential sweeping between 0.0 and 1.0 V for 90 cycles. 200 mM pyrrole and 2.5 mM ABTS in aqueous solution was used for polymerization. Cyclic voltammogram for 0.25 mM ABTS was also shown for comparison. Its current was magnified 10 times. Scan rate was 20 mV s^{-1}.

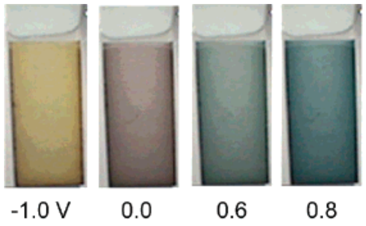

Figure 2. Digital photographs of coloration of pPy[ABTS] according to the indicated potentials. The width of strip of ITO/PET substrate was 1 cm.

The ABTS-doped polypyrrole (abbreviated as pPy[ABTS]) shows two electrochemical processes. Figure 1b shows the cyclic voltammogram of pPy[ABTS]. The first process (cathodic peak at −0.5 V and anodic peak at −0.15 V) is associated with the reduction/oxidation of polypyrrole backbone. The second process is due to the electrochemistry of ABTS incorporated in a polypyrrole matrix. Shown in Figure 1b, for comparison, is the cyclic voltammogram of ABTS in solution. The cathodic peak potential of pPy[ABTS] at +0.45 V corresponds exactly to that of ABTS in solution. The anodic peak is not obvious for the film used for the figure. However, more apparent anodic peak was observed with thinner films.

Figure 2 shows the multicolor electrochromism of pPy[ABTS]: the anodic coloration from brown (at 0.0 V) to greenish blue (at 0.6 and 0.8 V) is attributed to the oxidation of ABTS to its radical and the cathodic coloration to yellow (−1.0 V) is based on the reduction of polypyrrole itself.

The transmission spectra were obtained with the anodic and cathodic coloration of pPy[ABTS] in the visible region.

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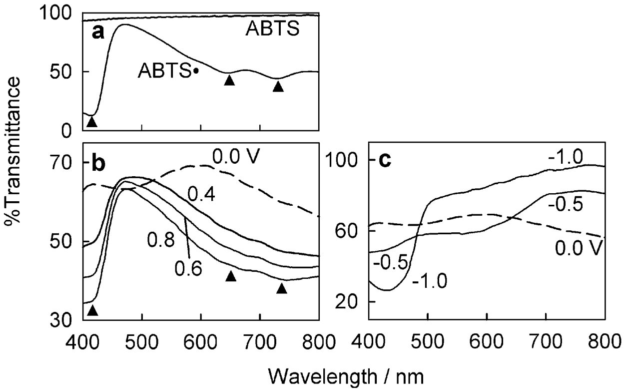

Figure 3. Visible transmission spectra of (a) ABTS and its oxidized radical (ABTS) and (b and c) pPy[ABTS] at indicated potentials. 25 μM ABTS and 25 μM ABTS in solution were used in (a). The peaks associated with ABTS radical were indicated by triangular symbols.

Table 1. Electrochromic Parameters for Anodic Coloration of PPy[ABTS] at 730 nm (413 nm) and Color Difference[a]

		response time, τ (s)		efficiency, η (C^{-1} cm^2)		color difference, ΔE^* (0.6 V)	
	$\Delta\%T$	coloration	bleaching	coloration	bleaching	vs 0.0 V	vs −1.0 V
A (thin film)	5.4 (4.5)	2.2 (4.7)	1.7 (0.5)	55 (33)	46 (77)	3.8	11
B (thick film)	16 (23)	8.0 (12)	5.2 (1.2)	63 (82)	63 (150)	11	44

[a] Coloration was achieved by a potential step from 0.0 V (gray) to 0.6 V (greenish blue), and bleaching vice versa. Samples A and B were electropolymerized potentiostatically at 0.6 V for 10 min and by potential sweep between 0.0 and 1.0 V for 90 cycles, respectively.

ABTS itself is colorless without any absorption in the visible region, but its radical counterpart is greenish blue with the characteristic absorption peaks at 415, 645, and 730 nm as indicated with triangles in Figure 3a. For anodic coloration of pPy[ABTS] (Figure 3b), the transmission decreases in the range of 400−450 nm and 550−800 nm with increasing positive potential up to +0.8 V. A small change in transmission is observed around 475 nm that accounts for the greenish blue coloration shown in Figure 2. Also, the characteristic absorption peaks of ABTS radical at 415, 645, and 730 nm ascertain that the coloration is driven by oxidation of ABTS. Cathodic coloration to yellow (Figure 3c) is due to the reduction of polypyrrole backbone: absorptive between 400 and 480 nm and transmittive between 480 and 800 nm.

The electrochromic parameters for the anodic coloration of pPy[ABTS] were summarized in Table 1. The change in transmittance at 730 and 415 nm was traced as a function of applied potential. Thick film (sample B) showed a higher contrast with slower response than thin film (sample A). According to morphological investigation on the pPy[ABTS] using scanning electron microscope (SEM), spherical particles were deposited on the substrate at the initial stage of electropolymerization (less than 5 min at 0.6 V). The particles were sphere-shaped and monodispersed with 50 nm in diameter. As the polymerization proceeded, a multilayer of the particles was built and significant portion of particles was interconnected (10 min, sample A). After 20 min, a dense and smooth film was obtained. pPy[ABTS] made by potential sweep for 90 cycles (sample B) also showed the same morphology.

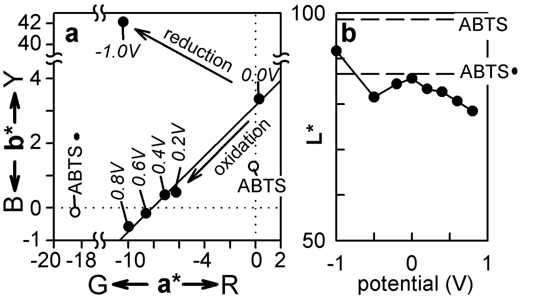

Figure 4. CIE L*a*b* coordinates of colors of pPy[ABTS] (sample B; thick film, solid circles). ABTS and its radical form (ABTS) were also included for comparison (open circles in (a); dashed horizontal lines in (b)). 1931 2° observer and illuminant D65 proposed by CIE were used. L* = lightness, a* = red(+)/green(−) and b* = yellow(+)/blue(−).

Repeated switching stability for pPy[ABTS] was measured by 10 s double potential step: bleached to brown or gray at 0.0 V and colored to greenish blue at 0.6 or 0.8 V. The films of pPy[ABTS] made by potential sweep were more stable than the potentiostatically electrodeposited ones. For potential steps between 0.0 and 0.6 V, the sample B was electrochemically and chromically stable at least up to 1500 cycles, whereas the charge capacity of sample A decreased by half at 500 cycles. For 0.0−0.8 V steps, all films of pPy[ABTS] were unstable irrespective of the synthetic methods. The other important electrochromic property is the optical memory. The potential of sample B decreased down to 0.4 V at 30 min after the applied potential at 0.6 V was turned off. Transmittance at 730 nm changed about 4% (from 44% to 48%), which indicates 25% variation with respect to the total chromic change ($\Delta\%T = 16\%$ as shown in Table 1).

From the spectra, CIE color coordinates and differences (ΔE^*) were calculated to identify color corresponding to applied potentials (Figure 4 and Table 1).[10,11] The components of green and blue became stronger during the anodic coloration while yellow color was developed during the cathodic process. All colors were fairly bright, giving $L^* = 80-90$.

We believe that the concept presented here, the combination of molecular electrochromogen and polymeric electrochromogen, can broaden the choice of colors. We are currently investigating the electrochromism of various dopants incorporated in polypyrrole as well as other conducting polymers. Our ultimate goal is to make a palette of electrocolorants. Some colors would come from mono-dopants like presented here and the other group of colors could be obtained by codoping multiple electrochromogens providing different colors.

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Supporting Information Available: Temporal profiles of current and cyclic voltammograms for electrodeposition and scanning electron micrographs of pPy[ABTS] (PDF); a movie (MPG) showing the electrochromism of pPy[ABTS]. This material is available free of charge via the Internet at http://pubs.acs.org.

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