

An Electrochromic Painter's Palette: Color Mixing via Solution Co-Processing

Rayford H. Bulloch,[†] Justin A. Kerszulis,[†] Aubrey L. Dyer,[‡] and John R. Reynolds^{*,†}

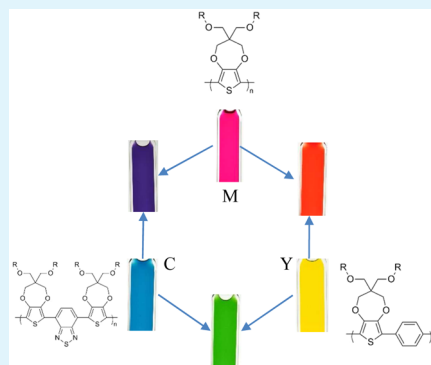
[†]School of Chemistry and Biochemistry and School of Materials Science and Engineering, Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

[‡]Department of Natural Sciences, Clayton State University, Morrow, Georgia 30260, United States

S Supporting Information

ABSTRACT: Electrochromic polymers (ECPs) have been shown to be synthetically tunable, producing a full palette of vibrantly colored to highly transmissive polymers. The development of these colored-to-transmissive ECPs employed synthetic design strategies for broad color targeting; however, due to the subtleties of color perception and the intricacies of polymer structure and color relationships, fine color control is difficult. In contrast, color mixing is a well-established practice in the printing industry. We have identified three colored-to-transmissive switching electrochromic polymers, referred to as ECP-Cyan (ECP-C), ECP-Magenta (ECP-M), and ECP-Yellow (ECP-Y), which, via the co-processing of multicomponent ECP mixtures, follow the CMY color mixing model. The presented work qualitatively assesses the thin film characteristics of solution co-processed ECP mixtures. To quantitatively determine the predictability of the color properties of ECP mixtures, we estimated mass extinction coefficients (ϵ_{mass}) from solution spectra of the CMY ECPs and compared the estimated and experimentally observed color values of blends via a calculated color difference (ΔE_{ab}). The values of ΔE_{ab} range from 8 to 26 across all mixture compositions, with an average value of 15, representing a reasonable degree of agreement between predicted and observed color values. We demonstrate here the ability to co-process ECP mixtures into vibrantly colored, visually continuous films and the ability to estimate the color properties produced in these mixed ECP films.

KEYWORDS: electrochromism, color mixing, organic electronics, colorimetry, conjugated electroactive polymers



INTRODUCTION

When one considers active display technologies, those of the light emitting variety are by far the most dominant. These light emissive technologies span from fluorescent and phosphorescent materials employed in CRTs and plasma displays, as well as variations of LED technologies, including PLED and OLED. Benefits of these displays are largely in the brightness and color purity of the image produced, owed partially to an additive mode of color mixing, as well as the speed with which an image can be changed, while disadvantages are to be found in processing and production costs, energy consumption rates, and the potentially toxic materials used in construction.^{1,2}

On the other hand, nonemissive technologies, such as liquid crystal, electrophoretic, and electrochromic displays produce a visual stimulus in a subtractive fashion, that is, through interactions with transmitted or reflected ambient light. Within this nonemissive family, electrochromic (EC) materials stand out for their ability to switch between distinct color states by a change in charge state, and encompass a wide range of materials from molecular electrochromics, metal oxides, and conjugated polymers.^{3–5} Employing these electrochromic materials as surface coatings leads to devices with a low rate of energy consumption. In electrochromic polymers (ECPs), this low energy use is in part due to a retention of charge state and,

therefore, a retention in color state (color memory), giving an on/off system that requires minimal further power consumption.⁶ ECPs have also been shown to be synthetically tunable, producing a large family of multicolor (colored state to colored state) materials, in addition to a full color palette of vibrant colored polymers that switch to a highly transmissive clear state.⁷ The extent of the colored-to-clear transition is a function of the applied potential across an electrochromic device (ECD), producing a smooth and continuous change through the bleaching and coloring processes, allowing for variable control of a film's color saturation and transmission.

The development of colored-to-clear ECPs employed synthetic design strategies (i.e., modulation of electronic absorption transitions) for broad color targeting to create polymers of a specific hue.⁸ However, due to the subtleties of color perception and the intricacies of polymer structure and material color relationships, fine color control is difficult at best. Held in contrast with the synthetic routes of color control, color mixing is a well-established practice in the printing industry. Color mixing theory asserts that if two color stimuli

Received: October 28, 2014

Accepted: December 18, 2014

Published: January 12, 2015

are mixed, then the resulting color stimulus will lie at some point along a line connecting the two mixed stimuli on a chromaticity diagram.⁹ The practical result of this theory is found in the CMY-K and RYB color mixing systems, which are used as the primary models of subtractive color mixing. As illustrated in Figure 1, we have identified three of the vibrantly

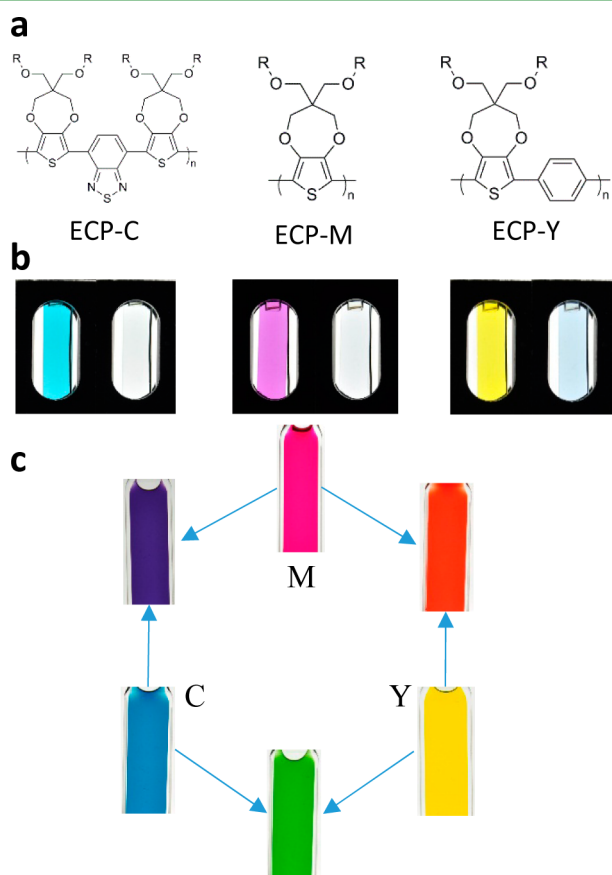


Figure 1. Structures and photography of CMY representative electrochromic polymers in solution and thin films. (a) The repeat unit structures of each of the three ECPs selected, where R = 2-ethylhexyl. (b) Photographs of (left) colored and (right) bleached polymer thin films are shown below their respective repeat unit structures. (c) Solutions of ECPs-C, -M, and -Y at concentrations of 2 mg/mL and 1:1 w/w ratios of these solutions.

colored to highly transmissive switching polymers, referred to as ECP-Cyan (ECP-C), ECP-Magenta (ECP-M), and ECP-Yellow (ECP-Y), which can be mixed to produce a broad gamut of accessible colors.

Previously, this CMY-type color mixing has been facilitated via the use of ECDs possessing multiple, independently addressable ECP layers, allowing for access to a wide gamut of color states.¹⁰ However, for many applications, a multilayer device structure is not the desired route to obtain mixed color states. For applications where a single, particular color state is desirable, though, solution-based color mixing via the co-processing of a multicomponent ECP mixture to produce the targeted color state is a much simpler solution. To demonstrate the color mixing that can be produced in solution, photographs of ECP solutions are shown in Figure 1c, illustrating the vibrant colors of the CMY materials, as well as their ability to produce the secondary green, red, and blue hues.

The intent of the study reported here is both to qualitatively assess the thin film characteristics of the co-processed ECP mixtures, and to quantitatively assess the predictability of color properties in resultant coatings. To assess color predictability in the mixtures created, we estimated mass extinction coefficients (ϵ_{mass}) from solution spectra of each of the CMY-representative ECPs.¹¹ The values of ϵ_{mass} are used as an equalizing factor to control the color contribution from each ECP component, and a comparison between the estimated and experimentally observed color values in each mixed film is made using the color difference term (ΔE_{ab}), as conventionally defined by the CIE 1976 guidelines.¹² The values of ΔE_{ab} range from 8 to 26 across all mixture compositions, with an average value of 15, representing a reasonable degree of agreement between predicted and observed color values. We demonstrate here the ability to co-process ECP mixtures into vibrantly colored, visually continuous films, and the ability to estimate the color properties produced in these mixed ECP films.

MATERIALS AND METHODS

To determine polymer mass extinction coefficients (ϵ_{mass}), we prepared dilute ECP solutions (50 $\mu\text{g/mL}$ in chloroform) and recorded spectra of these solutions with a Varian Cary 5000 UV-vis-NIR spectrophotometer. Following literature precedent and assuming a polymer density of 1 g/cm^3 , we calculated values for ϵ_{mass} .¹¹ Using the value of mass extinction coefficient for each ECP to vary the absorptive contribution of each component to a mixture, we dissolved ECP mixtures in a 1:1 toluene/chloroform solution to a total polymer concentration of 2 mg/mL . Solutions were spray cast onto ITO coated glass slides, purchased from Delta Technologies, Ltd. ($25 \times 75 \times 0.7$ mm, sheet resistance 8–12 Ω/sq) using an Iwata-Eclipse HP-BC airbrush with nitrogen at a pressure of 20 psi. Films were cast until an absorbance of 1 was obtained at the peak wavelength (λ_{max}), monitored with the aforementioned Cary 5000 UV-vis-NIR.

Cyclic voltammetry of cast films was performed in a three-electrode cell configuration using an EG&G PAR 273A potentiostat/galvanostat, under CorrWare control. The supporting electrolyte used was a 0.5 M solution of tetrabutylammonium hexafluorophosphate (TBAPF₆, Alfa Aesar, recrystallized from ethanol) dissolved in propylene carbonate (99.5%, Acros Organics), a platinum wire was used as the auxiliary electrode, and a Ag/Ag⁺ electrode was used as the reference. ECP films were cycled prior to spectroscopic measurement until a steady current response was observed, typically within 1–2 cycles. Spectroelectrochemistry of the ECP films was carried out using the same potentiostat/galvanostat described in combination with the Varian Cary 5000 UV-vis-NIR spectrophotometer. All colorimetric values are communicated in the CIE L*a*b* color space. Colorimetric information was generated from the spectra gathered within spectroelectrochemical series, using a simulated D50 light source at the normal/normal (0/0) illuminating/viewing geometry recommended by the CIE for transmittance measurements.¹² Colorimetric values were determined via reconciliation of recorded spectra with functions describing the sensitivities of the color detecting components of the human eye, referred to as standard observer functions, and the spectral power distribution of a standard light source, in this case a D50 standard illuminant.¹³ A full description of the calculation of CIE color coordinates, and a description of technical considerations therein, may be found in a number of publications pertaining to that topic.^{12,14} Photographs were collected in a light booth with a calibrated D50 light source, using the normal/normal (0/0) illuminating/viewing geometry, with a Nikon D90 SLR camera with a Nikon 18–105 mm VR lens, and is reported without further manipulation beyond photograph cropping.

RESULTS AND DISCUSSION

With the goal of prediction and control of the color properties in mixed ECP systems in mind, we performed the necessary

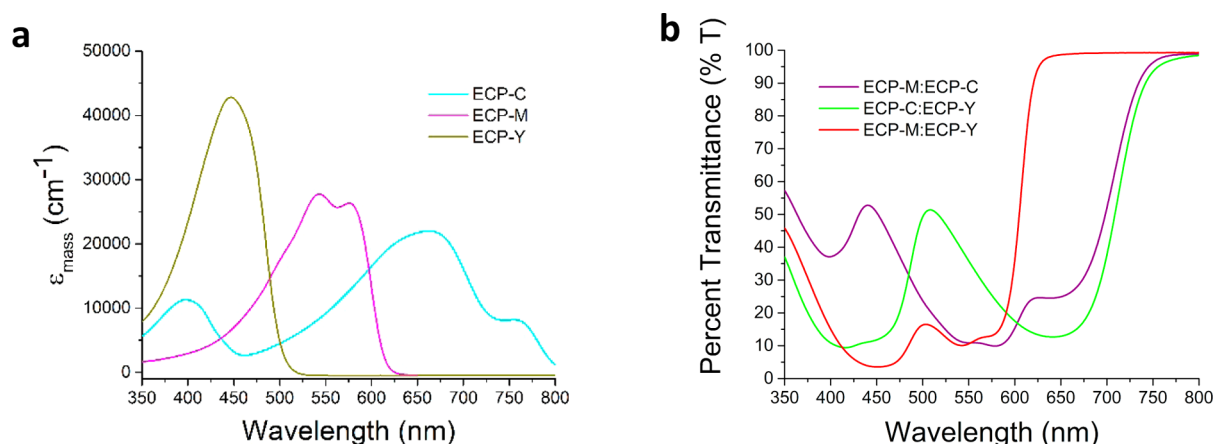


Figure 2. Solution spectroscopy of CMY ECPs and 1:1 (by ϵ_{mass}) mixtures. (a) Mass extinction coefficients in chloroform as a function of wavelength illustrating the increasing relative absorptivity in the order of ECPs-C, -M, and -Y. The extinction coefficients shown were calculated by assuming a polymer density of 1 g/cm^3 .¹¹ (b) Spectroscopy of 1:1 ECP mixtures in chloroform solution. The relative masses of each component ECP in these mixtures was informed by the mass extinction coefficients observed.

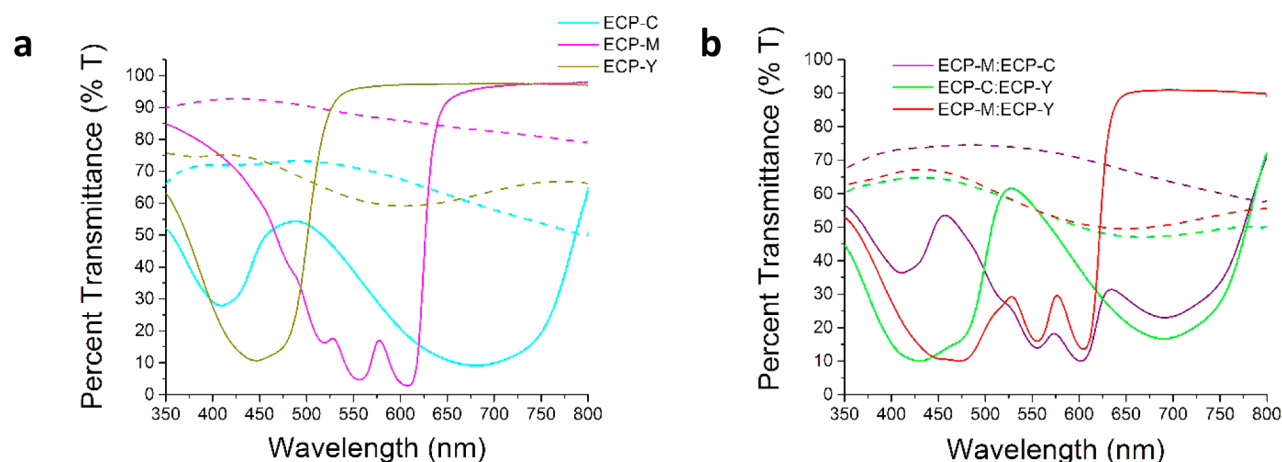


Figure 3. Thin film spectroelectrochemistry of CMY ECPs and 1:1 $\epsilon_{\text{mass}}/\epsilon_{\text{mass}}$ mixtures. Spectra of the fully colored state and most transmissive states attained are shown for films of (a) neat ECPs-C, -M, and -Y, and (b) 50% X/50% Y mixtures. These spectra serve to illustrate both the high contrast available in the neat ECP films, as well as the effect of lower contrast components on the transmissive state of a mixture.

first step of quantifying the ECP-specific absorptivities (and subsequent color properties). Typically, an extinction or absorptivity coefficient would be used to quantify material-specific absorptive properties. In the case of molecular chromophores, the molecular mass of the given species is used as a normalizing factor for the comparison of absorptivity between different species, yielding a molar absorptivity. In the ECP samples, the chromophore unit is not a discrete molecular unit but, in fact, is distributed over some number of heterocycle units along the polymer chain, and an experimental determination of this chromophore “molecular weight” is particularly difficult. Alternatively, the total mass of the polymer in solution can be substituted for the molecular weight normalization (substituting a g/mL term for a mol/L concentration term in the Beer–Lambert law), producing a mass extinction coefficient in units of cm^{-1} , assuming the density of the polymer to be 1 g/cm^3 . The values of ϵ_{mass} for each of the CMY-ECPs was determined spectroscopically (further details in Materials and Methods), and are shown in Figure 2a, showing that relative absorptivity at the peak wavelength decreases in the order of ECP-Y to ECP-M and finally ECP-C. The values of ϵ_{mass} at these peak wavelengths

were used to create 1:1 $\epsilon_{\text{mass}}/\epsilon_{\text{mass}}$ mixtures at a concentration of $50 \mu\text{g}$ total polymer/mL, and spectra for these solutions are shown in Figure 2b. Apparent from these spectra is the inconsistency with a nominally equal contribution from each ECP component, and the differences in absorptive intensity observed in the -M/-Y and -M/-C mixtures. Should specific color matching be desired, for example preparing a specific red, blue, or green hue, then varied ratios would be employed.

Thin films corresponding to the solutions shown in Figure 3 (i.e., ECPs-C, -M, -Y, and the 1:1 $\epsilon_{\text{mass}}/\epsilon_{\text{mass}}$ mixtures), were spray cast onto indium tin oxide (ITO)-coated glass slides in order to monitor the oxidation and reneutralization of the films prepared, referred to as switching. Differences in optical properties are often observed when moving from solution to thin film environments, but particular note should be made of the changes observed upon the initial oxidation–reduction cycling of some ECP films (so-called electrochemical break-in). In general, these observed differences are minor, but in the case of ECP-M, a notable degree of peak sharpening is observed, along with an increase in the absorption maxima at λ_{max} for both observed peaks in that sample. This sharpening is readily apparent in Figure 3a, the transmission spectra of the neutral

(colored) and oxidized (bleached) states of previously switched films. In this instance, all films were cast to yield an optical density of 1.0 ± 0.05 AU at λ_{\max} and, after initial switching, ECPs-C and -Y retain that optical density. This shift in optical properties becomes an important factor when attempting to quantify the color contributions from ECP-M to a given mixture. This effect can be seen in Figure 3b, the spectra of the reduced and oxidized states of 1:1 $\epsilon_{\text{mass}}/\epsilon_{\text{mass}}$ mixtures. As in Figure 3a, films were sprayed until the dominant wavelength reached an optical density of 1.0 ± 0.05 AU, but upon switching, an increase in the ECP-M absorption intensity is again observed, coinciding with the sharpening of the peaks observed in the absorption profile. This shift in optical properties upon electrochemical switching, and its influence on the final color properties of the ECP mixtures will be revisited in the discussion of the prediction of an ECP mixture's color properties.

The spectra shown in Figure 3 also allows for the examination and comparison of the oxidized (bleached, transparent) states in both the neat and mixed ECP films. The electrochromic contrast, measured as the difference in transmittance between the colored and bleached states of a given ECP is highly dependent on the extent to which a material can bleach its color upon oxidation. The CMY ECP materials employed in this study exhibit varying degrees of this ability, shown as the dashed traces in Figure 3a, and from these, it can be seen that ECP-Y retains the highest level of visible light absorption upon bleaching and ECP-M the lowest. This observation becomes especially important in the context of retained absorption in the bleached state of a mixture. Figure 3b illustrates that the bleached state of an ECP mixture is limited by the component with the least transmissive bleached state, leading the mixture lacking ECP-Y entirely to have the most transmissive bleached state, while the mixture containing both ECPs-Y and -C in equal proportion has the least transmissive bleached state. This observation should be qualified with the understanding that even the "least transmissive" bleached state reported in this study still exhibits a comparatively high degree of transmission and color neutrality, but the limiting effect of one of the components in a mixture is an influential factor in further studies to obtain bleached states via ECP co-processing. It should be noted that the data presented in this work, both spectral and colorimetric, was collected under a steady-state regime, meaning a steady current response signifying a stabilization in the extent of oxidation-induced film was observed prior to spectra being recorded. Likely due to the disparity in the onset potentials for oxidation between the CMY polymers, varying degrees of oxidation are observed in each component in a given mixture, producing a number of intermediate color states rather than a smooth, binary colored-to-bleached transition as observed in the neat ECPs.

With the various ECP mixtures all exhibiting highly transmissive and color-neutral states, regardless of composition, we shift our focus to the prediction of the neutral or colored film state, specifically, to the prediction of chromaticity of the ECP mixtures. If the chromaticity coordinates of a mixed color stimulus (a^* and b^* in the CIELAB system) lie along a line connecting the two stimuli being mixed, then it follows that the mixed chromaticity coordinates should follow the trend expressed in the following equations:

$$a_3^* = ((a_1^*x) + (a_2^*y))$$

$$b_3^* = ((b_1^*x) + (b_2^*y))$$

where a_1^* and a_2^* are the a^* coordinates of the materials being mixed, x and y are the fraction contributions weighted by the extinction coefficient of each component, and a_3^* is the a^* coordinate of the mixture produced. Similarly, b_3^* is the b^* coordinate of the mixture produced. Due to the shifts in spectral properties observed upon switching discussed above, this model was first applied to "as cast" mixture films as a basis for comparison, shown in Figure 4. Predicted color values for

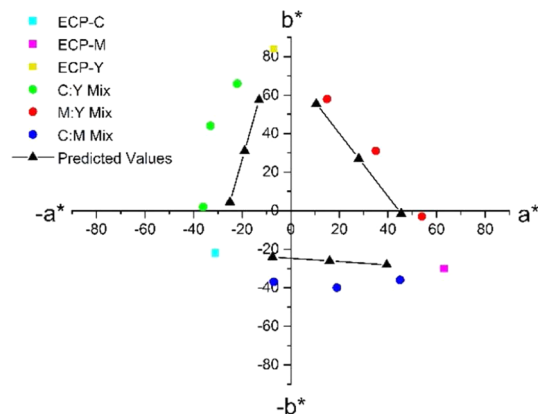


Figure 4. Predicted and observed a^*b^* chromaticity coordinates in as-sprayed ECP films. The a^*b^* values for neat CMY ECP films and varying ratios of each binary ECP mixture. Chromaticity values estimated from the chromaticity coordinates of the neat CMY ECPs are shown as black triangles (\blacktriangle).

mixtures with compositions of 75% X/25% Y, 50% X/50% Y, and 25% X/75% Y for all mixtures (ECP-C/ECP-M, ECP-C/ECP-Y, and ECP-M/ECP-Y) are shown, using the chromaticity coordinates of the neat, "as cast" ECP films (also shown) as the basis for predictions. Qualitatively, an underestimation of mixture chromaticity is a universal feature in the application of this model to "as cast" films, evidenced by all predicted color values lying closer to the origin than the experimentally observed values. Further, the chromaticity differences between predicted and observed values are fairly appreciable (≥ 10 in any one chromaticity coordinate) in the ECP-C/ECP-Y (green) and ECP-C/ECP-M (blue) mixtures shown, but much closer agreement is seen in the ECP-M/ECP-Y (red) mixture. Further, a degree of outward "bowing" in the experimentally observed chromaticity values can be seen for each mixture examined. A number of factors might influence this bowing behavior, such as differences between the optical properties of the solution environments used to estimate mass extinction coefficients and those encountered in the thin film environment. To properly assess the predictability of CMY color mixing using these ECP materials though, we should regard them as the functional, electro-active materials they are.

To do this, we applied a set of spectroelectrochemical series, tracking the shifts in optical properties encountered as an increasing potential across an ECP film, were produced for each mixture produced film. Representative voltage-dependent spectra are shown in Figure 5a, specifically of a 50% ECP-C/50% ECP-M film, illustrating the sequential initial bleaching of the ECP-M component at roughly 0.3 V (peaks ~ 550 nm), followed by bleaching of the ECP-C component (~ 400 and 700 nm), as the potential applied across the film is increased stepwise from -0.3 to 0.9 V. After applying this technique to

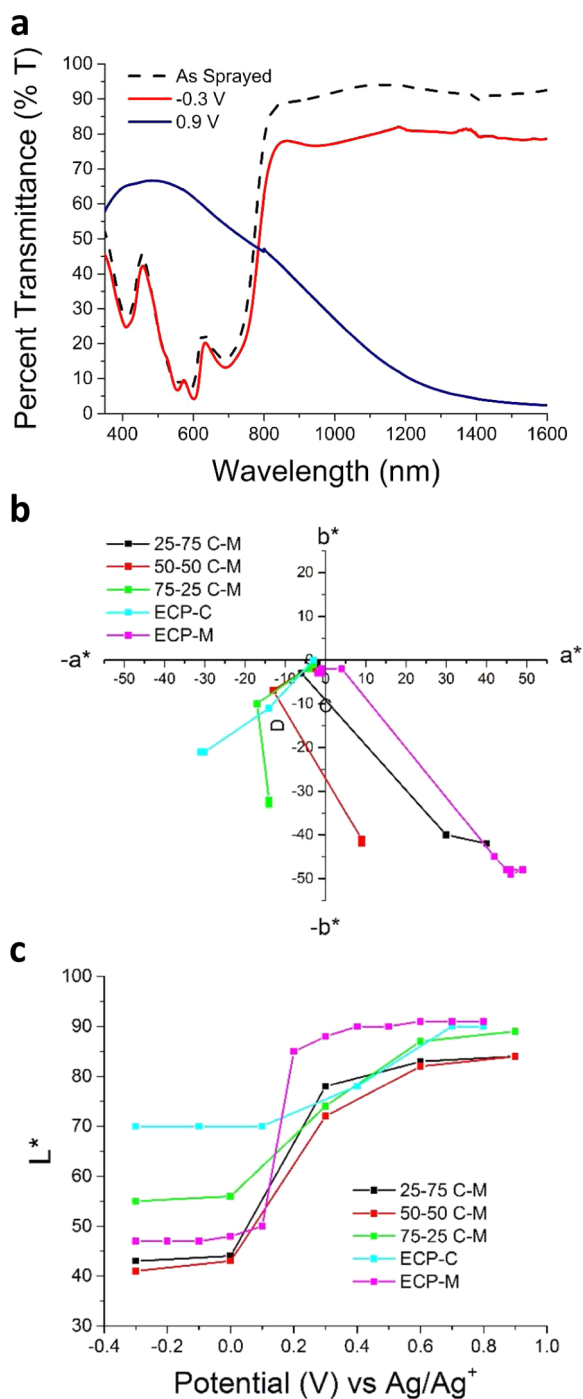


Figure 5. Spectroelectrochemistry and associated colorimetry of ECP-C/ECP-M mixtures of varying composition. (a) Representative spectroelectrochemical series of 1:1 $\epsilon_{\text{mass}}/\epsilon_{\text{mass}}$ ECP-C/ECP-M mixture. (b) Colorimetry of ECPs-C and -M, with the colorimetry of ECP-C/ECP-M mixtures. (c) Luminance vs the applied potential for ECPs-C and -M, and the corresponding mixtures.

both neat CMY films and those of the varying mixture compositions, we calculated colorimetric values, as discussed in Materials and Methods. The colorimetric series produced by this method for the ECP-C/ECP-M mixtures are shown in Figure 5, showing the changes observed in both chromaticity and luminance as a function of increasing applied potential. These changes are characterized by the loss of chromaticity, first by the loss of the ECP-M contribution, producing a series

of color states in the cyan range ($-a^*, -b^*$), followed by a loss of ECP-C color contribution as well, resulting in a final color neutral state, close to the origin. Associated with the loss of color contributions, there is an increase in the luminance, or L^* value, brought about as the various ECP components are induced into highly transmissive bleached states.

The control of chromaticity and luminance in ECPs via the application of a potential is well documented, and the two states relevant to this study are those presented in Figure 3, namely, the fully colored and fully bleached states.⁵ These color states for the ECP mixtures and neat ECP films are shown in Figure 6a, along with the chromaticity values based on the given mixture's composition. Photographs of the mixed ECP films in both the vibrantly colored and highly transmissive bleached states are also shown in Figure 6b to illustrate the continuous and homogeneous film properties obtained and to offer a means to better visualize the colors represented by the plotted a^*b^* chromaticity coordinates. Qualitatively, the chromaticity points in Figure 6a show a lesser degree of divergence from color values predicted, with the lowest degree of divergence seen in the ECP-M/ECP-Y mixtures (red points) and the greatest divergence observed in the ECP-C/ECP-Y mixtures (green points), as was observed with the colorimetry of the "as cast" films. The divergences from the predicted values are quantified by the value of ΔE_{ab}^* , or the color difference. This term, which calculates the Euclidian distance between two sets of chromaticity coordinates, is defined by the CIE 1976 conventions with the following equation:

$$\Delta E_{ab}^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

A lower color difference (small ΔE) signifies a pair of colors that are closer to being identical, and a larger color difference (large ΔE) indicates a pair with a greater difference. The a^*b^* values recorded for the mixed ECP films are shown in Table 1, along with the values predicted using the $L^*a^*b^*$ coordinates of neat ECP films, and the value of ΔE_{ab}^* for these pairs. As mentioned, the generally highest degree of agreement between the predicted and observed values occurs in the ECP-M/ECP-Y mixtures, with values of ΔE_{ab}^* ranging from 12 to 14. To qualify these values, a ΔE_{ab}^* value of less than 2.3 signifies a pair of colors that are perceptually indistinguishable. In essence, the difference between the pair of colors falls below a "just noticeable difference" (JND) threshold, and color pairs with ΔE_{ab}^* values in the range of ~ 10 will therefore be noticeably different from one another, though similar.^{15,14} A poorer agreement between the predicted and observed color values is seen in the ECP-C/ECP-M mixtures, with values ranging from 15 to 19, though a fair degree of consistency is seen in the error in prediction for this mixture. Finally, a remarkable degree of inconsistency is noted in the ECP-C/ECP-Y mixtures, with the two lowest ΔE_{ab}^* values recorded (8 and 11), as well as the highest (25) seen in this family of mixtures.

CONCLUSION

By estimating the mass extinction coefficients of electrochromic polymers representative of the CMY color mixing models, we have demonstrated the ability to estimate the colorimetric coordinates of a mixture of these ECPs. This method, in its current form, makes a number of assumptions regarding variables that are likely to influence the accuracy of the predictive model described. The variable mass of solubilizing alkyl chains appended to the ECP backbones are not accounted

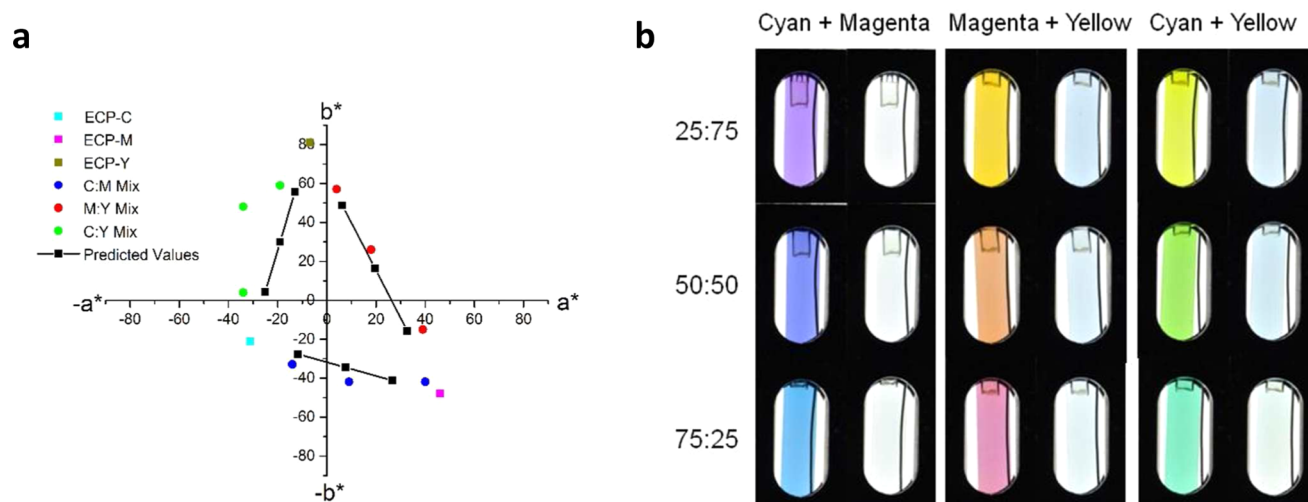


Figure 6. (a) Predicted and observed a^*b^* chromaticity coordinates in electrochemically switched ECP mixtures with colored and neutral state photographs of each mixture. Chromaticity values of neat CMY ECPs and mixtures of varying composition, after electrochemical switching. Predicted values are shown in black squares (■). (b) Photographs of the mixtures in both the (left) colored and (right) bleached states.

Table 1. Chromaticity (L^* , a^* , b^*) Values of Each ECP Mixture Examined, Experimentally Observed and Predicted from Neat CMY-ECP Color Values^a

| mixture composition | predicted | | | observed | | | ΔE_{ab}^* |
|---------------------|-----------|-------|-------|----------|-------|-------|-------------------|
| | L^* | a^* | b^* | L^* | a^* | b^* | |
| 75:25 C/M | 41 | -12 | -28 | 55 | -14 | -33 | 15 |
| 50:50 C/M | 58 | 7 | -34 | 41 | 9 | -42 | 19 |
| 25:75 C/M | 53 | 27 | -41 | 43 | 40 | -42 | 16 |
| 75:25 M/Y | 59 | 33 | -16 | 47 | 39 | -15 | 14 |
| 50:50 M/Y | 71 | 19 | 16 | 61 | 18 | 26 | 14 |
| 25:75 M/Y | 83 | 6 | 49 | 74 | 4 | 57 | 12 |
| 25:75 C/Y | 89 | -13 | 55 | 85 | -19 | 59 | 8 |
| 50:50 C/Y | 82 | -19 | 30 | 73 | -34 | 48 | 25 |
| 75:25 C/Y | 76 | -25 | 4 | 70 | -34 | 4 | 11 |

^aQuantification of agreement between the predicted and observed color values is shown as the value of ΔE_{ab}^* .

for, and an estimation of polymer densities is made by fixing all density values at 1 g/cm^3 , to name a few. Regarding the density approximation in particular, experimental determination of sample densities by flotation measurement determined polymer densities to be 1.06, 1.02, and 1.01 g/mL for ECPs-C, -M, and -Y, respectively.

Even under these assumptions, a fair degree of accuracy in the prediction of a given ECP mixture's chromaticity coordinates is demonstrated, and by reducing the number of assumptions applied to the calculations, we are likely to demonstrate a much greater degree of accuracy. The demonstrated ability to generalize the color properties of an ECP mixture, based on percent weight composition, is a great benefit to the ability to color match a target, and tailoring the colorimetric properties of a mixture in general, treating ECPs as electrochromic pigments. Also, importantly demonstrated in this work, is the visual homogeneity of solution co-processed ECP mixtures, with no observations of deleterious effects on either the electrochemical response or film appearance having been observed as a result of the co-processing of multiple ECPs from a common solvent. Additional control of colorimetric properties of co-processed ECP mixtures might be demonstrated by the examination of three component mixtures,

utilizing each of the CMY polymers discussed in this work. Further, while this method allows for direct control of the chromaticity (a^*b^* values) of a mixture, the luminance term is poorly addressed via this model. Incorporation of a fourth color neutral "electrochromic pigment", which demonstrates a black-to-clear color transition, would allow for more direct modulation of the L^* component of a mixture, and would serve to further emulate the CMY-K (K being short for "key", a printing shorthand for black) color mixing model commonly employed in printing.¹⁶

In summation, the co-processing of mixtures of electrochromic polymers has been shown to produce thin films with a high degree of visual homogeneity, which exhibit vibrant colored states and maintain access to the highly transmissive and color neutral states previously observed in the ECPs employed in this work. The ability to predict the color properties of these mixtures, using a solution-derived mass extinction coefficient term as a basis for chromatic contributions from each component, has been demonstrated with an acceptable degree of divergence that has been quantified as the value ΔE_{ab}^* .

■ ASSOCIATED CONTENT

📄 Supporting Information

Spectroelectrochemical series and the associated colorimetric values of ECP-C/ECP-Y and ECP-M/ECP-Y mixtures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

✉ Corresponding Author

*E-mail: reynolds@chemistry.gatech.edu.

📄 Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank BASF for funding.

■ REFERENCES

(1) Mentley, D. E. State of Flat-Panel Display Technology and Future Trends. *Proc. IEEE* **2002**, *90*, 453–459.

- (2) Eden, J. G. Information Display Early in the 21st Century: Overview of Selected Emissive Display Technologies. *Proc. IEEE* **2006**, *94*, 567–574.
- (3) Monk, P. M. S. *The Viologens: Physicochemical Properties, Synthesis, and Applications of the Salts of 4,4'-Bipyridine*. Wiley: New York, 1998.
- (4) Granqvist, C. G. Electrochromic Tungsten Oxide Films: Review of Progress 1993–1998. *Sol. Energy Mater. Sol. Cells* **2000**, *60*, 201–262.
- (5) Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism and Electrochromic Devices*. Cambridge University Press: Cambridge, 2007.
- (6) Beaujuge, P. M.; Reynolds, J. R. Color Control in π -Conjugated Organic Polymers for Use in Electrochromic Devices. *Chem. Rev.* **2010**, *110*, 268–320.
- (7) Dyer, A. L.; Thompson, E. J.; Reynolds, J. R. Completing the Color Palette with Spray-Processable Polymer Electrochromics. *ACS Appl. Mater. Interfaces* **2011**, *3*, 1787–1795.
- (8) Amb, C. M.; Dyer, A. L.; Reynolds, J. R. Navigating the Color Palette of Solution-Processable Electrochromic Polymers. *Chem. Mater.* **2010**, *23*, 397–415.
- (9) Overheim, R. D.; Wagner, D. L. *Light and Color*. Wiley: New York, 1982.
- (10) Bulloch, R. H.; Kerszulis, J. A.; Dyer, A. L.; Reynolds, J. R. Mapping the Broad CMY Subtractive Primary Color Gamut Using a Dual-Active Electrochromic Device. *ACS Appl. Mater. Interfaces* **2014**, *6*, 6623–6630.
- (11) Beaujuge, P. M.; Amb, C. M.; Reynolds, J. R. Spectral Engineering in π -Conjugated Polymers with Intramolecular Donor–Acceptor Interactions. *Acc. Chem. Res.* **2010**, *43*, 1396–1407.
- (12) *CIE Technical Report: Colorimetry*; Commission Internationale De L'Éclairage: Vienna, Austria, 2004.
- (13) Mortimer, R. J.; Varley, T. S. Quantification of Colour Stimuli Through the Calculation of CIE Chromaticity Coordinates and Luminance Data for Application to in Situ Colorimetry Studies of Electrochromic Materials. *Displays* **2011**, *32*, 35–44.
- (14) Schanda, J. *Colorimetry: Understanding the CIE System*. Wiley: New York, 2007.
- (15) Mahy, M.; Van Eycken, L.; Oosterlinck, A. Evaluation of Uniform Color Spaces Developed after the Adoption of CIELAB and CIELUV. *Color Res. Appl.* **1994**, *19*, 105–121.
- (16) Shi, P.; Amb, C. M.; Knott, E. P.; Thompson, E. J.; Liu, D. Y.; Mei, J.; Dyer, A. L.; Reynolds, J. R. Broadly Absorbing Black to Transmissive Switching Electrochromic Polymers. *Adv. Mater.* **2010**, *22*, 4949–4953.