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Letters

Mixing Metallic Luster with Organic Dyes

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Abstract: Both crystal violet and a cyanine dye were incorporated into Nafion sheets by electrostatic co-adsorption method. A dye-mixed Nafion sheet obtained under certain conditions exhibited a deep reddish-purple metallic luster. This color tone was not a simple color mixture of metallic luster by each single dye, suggesting that the aggregate state of each dye was modified by the co-adsorption.

Key words: Metallic luster, Crystal violet, Cyanine dye, Co-adsorption, Color mixing

In recent years, we have focused on metallic luster from solid films of organic dyes that do not contain metallic elements. We have already reported on the properties and mechanism of their metallic lusters from safflower dyes extracted by traditional methods, crystal violet and cyanine dyes. [1,2,3] General reflected light does not include the light of the wavelengths that are absorbed, because the component of the reflected light is the light that the dye did not absorb. However, the above-mentioned dyes and some solid films of dyes reflect the same wavelengths of light that they absorb. The mechanism by which these lusters are generated is commonly explained by interface bronzes.[4] However, some organic dyes and graphite that do not contain metal have a small amount of polarized light components in the reflected light, and it is necessary to investigate the generation mechanism of the reflection.

It is possible to disperse these organic dyes in a transparent polymer film or sheet. Therefore, these dyes can be used not only singly but also mixture. We succeeded in extracting metallic luster with different tones from a single dye by changing the conditions for immobilizing the dye to the transparent polymer sheet. There are cases where the dye exists as a monomer in the solid film, and there are cases where it exists as a dimer or an aggregate. In the two cases, the wavelength of the resonating (absorbing) light is different, so the wavelength of the reflected light is also different.

In the case of color tone due to transmitted light mixing dyes, the light removed from the incident light by their absorptions is simply added to achieve color mixture. In the actual transmitted light, scattered and emission light such as fluorescence are included. When considering only transmitted light, the dye excitation process is important. In dye-sensitized solar cells or a Z-scheme photochemical system, multiple dyes may be used in one system to extend the light absorbing band. In these cases, the excitation process is an important factor, but the subsequent relaxation (deactivation) process is even more important. The concern for their system is whether the different dyes can play their roles independently. In such a dye cocktail system, it is necessary to consider association of dyes, quenching, electron transfer (undesired electron transfer), energy transfer, and the other interactions. [5]

In this research, two dyes were immobilized on a transparent polymer sheet by electrostatic co-adsorption method, and it was confirmed whether the reflected light of these dyes was simply added and mixed individual reflection. It is a goal of the present study to make it possible to design the color tone of metallic luster by mixing dyes with such a technique.

Crystal violet (CV)was dissolved in a good solvent, chloroform, to prepare a 50 mmol/l solution. 3,3'-Dipropylthiadicarbocyanine Iodide (CY)was dissolved in a good solvent ethanol to prepare a 10 mmol/l solution. Mixed solutions were prepared by changing the ratio of these solutions. A Nafion 117 as the transparent basement sheet cut to 13 mm x 30 mm was immersed in this mixed solution for 48 hours to electrostatically co-adsorb the two dyes. After that, the dye on the surface of the sheet was washed off, and the resulting sheet was air-dried.

The reflectance spectrum of the dye-immobilized sheet was measured at the incident angle and detection angle of 30 degrees using a diffuse transmission/reflection measurement system (Ocean Photonics OP-TF/RF-GONIO-MN)and a colorimeter (Konica Minolta Cd-26dG).

Figure 1 shows the reflectance spectra of Nafion 117 sheet (Nafion+CV and Nafion+CY) with immobilized CV (100 hours immersion) and CY (100 hours immersion). For the sheet of CV with a golden luster, reflection shoulder and maximum were observed at wavelengths of 550 nm and 615 nm, respectively, based on the absorption of H-aggregates and monomers of CV. [6] For the sheet of CY with a vermilion gloss, reflection maximum was observed at a wavelength of 640 nm due to the absorption of the CY monomer. [7,8]

Next, a mixed solution of CV and CY was prepared by changing

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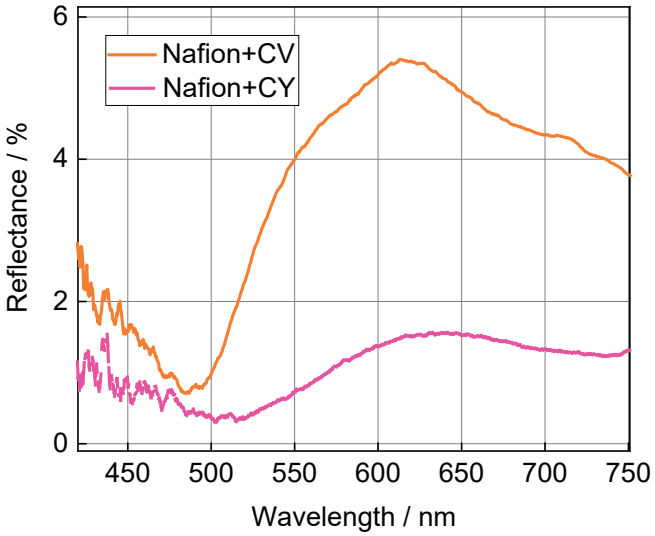

Figure1. Reflectance spectra of the Nafion+CV and the Nafion+CY.

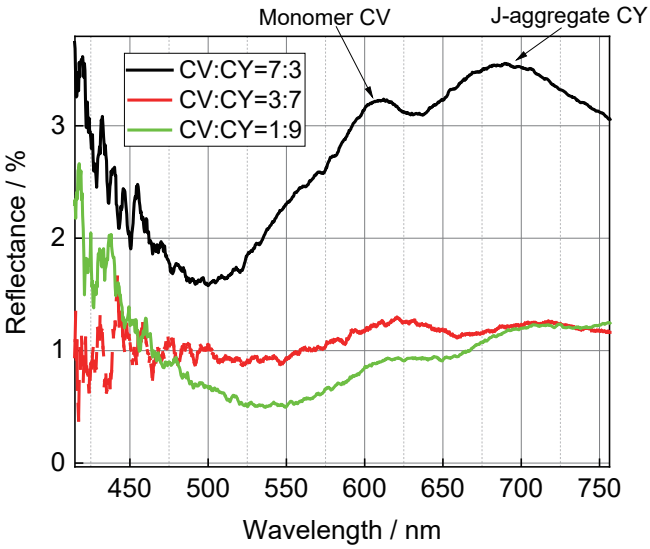

Figure 3. Reflectance spectra of the Nafion+CV+CY.

the ratio in the total volume of 10 ml, and the dyes were introduced into the Nafion sheet by co-adsorption. Metallic luster was observed in all sheets obtained (Nafion+CV+CY). By increasing the ratio of CY in the mixed solution, these color tones changed from a color tone close to that with only crystal violet to a deep reddish purple. (Fig. 2) Figure 3 shows the result of reflectance spectrum measurement of Nafion+CV+CY. In Nafion+CV+CY with the highest CV ratio CV:CY= 7:3, clear reflection maximum of CV was observed at wavelength of 615 nm. However, no CY monomer reflection appeared at wavelength 640 nm, and a new reflection maximum at the wavelength of 690 nm was appeared to be due to the CY J-aggregate absorption.[8] As the CV ratio in the mixed solution decreases, the reflection maximum at 615 nm seems to be gradually weakened and shifted to longer wavelengths. Assuming that the reflection phenomenon occurs only in a very shallow layer on the surface of the material, there is a limit to the number of dyes that can electrostatically bind to the negatively charged sulfonic acid groups present on the surface of the Nafion sheet. Therefore, the number of CVs will decrease when other dyes are incorporated. By using a mixed solution with a high CY ratio, if the reflection maximum of the incorporated CY monomer (λ=640 nm)and the reflection maximum of CV (λ=615 nm)overlap, the reflection maximum in this band will be shifted to longer wavelengths. In order to confirm the aggregation state of CY in the concentrated solution, the transmission spectrum of the mixed solution was carried out. As a result, J-aggregate of CY was not confirmed in the solution of single CY solution and mixed solution with CV. These results suggest that CY in Nafion is unlikely to exist as a monomer state.

Figure 4 schematically shows the result of color mixture of reflected light in this study. As a result, it was not a simple summation of the reflected light of the single dyes. For CV alone, green and orange light with wavelengths of 550 nm and 615 nm, respectively, are reflected to incident white light. With CY alone, reddish-orange

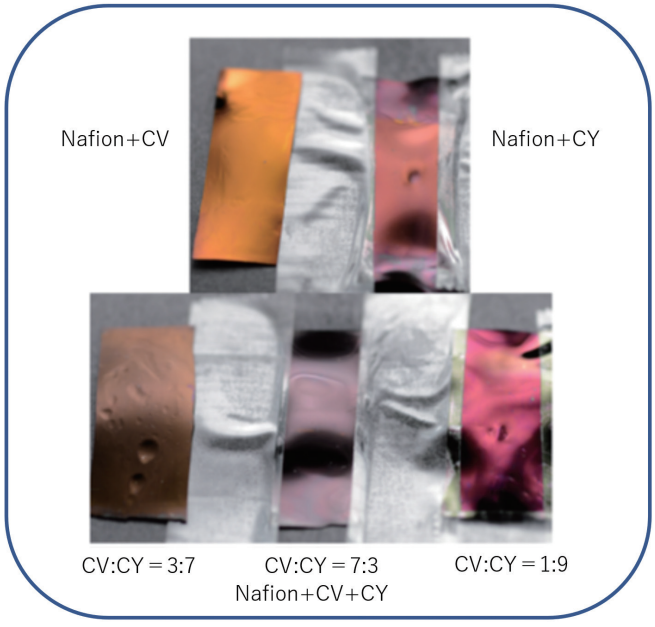

Figure 2. Photographs of the obtained Nafion sheets.

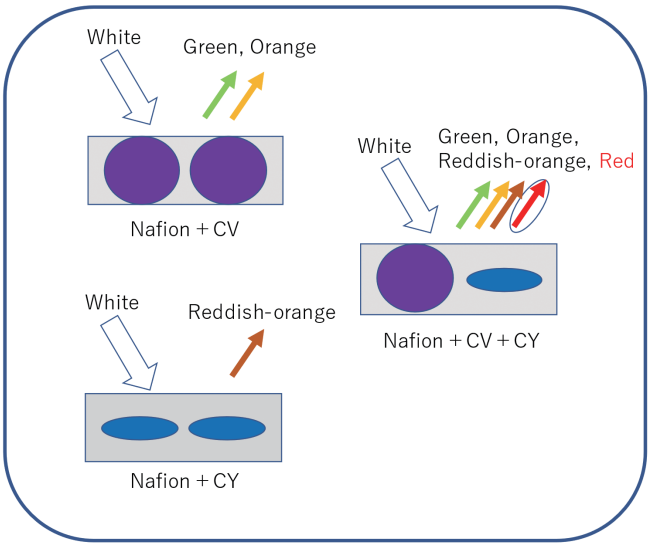

Figure 4. Schematic diagrams for differences in reflection between Nafion+CV, Nafion+CY, and Nafion+CV+CY.

light with a wavelength of 640 nm is reflected. Due to the mixing of the dyes, the reflected light with a wavelength of 640 nm by the CY monomer is present but weakened. On the other hand, light with a wavelength of 690 nm from the J-aggregate of CY was newly appeared, besides the reflection of CV. Finally, the color tone of the Nafion+CV+CY (CV:CY=1:9)was deep reddish purple.

In this study, we succeeded in mixing colors with a metallic luster through the co-adsorption of multiple dyes. Although the color tone was not obtained by simply adding the reflected light of the individual dyes, it is considered that this is because the state of the immobilized dye (monomer or aggregate) is different from that of the single dye. In the presence of CV and CY, the reason why CY does not remain monomeric in Nafion should also be investigated in detail from the viewpoint of the charging state of the dye.

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