

## Research Article

# Reversible Visualization for Synchrotron Radiation Using Photochromic Dye and Photostimulable Phosphor Composite Film

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The study reported herein is undertaken to visualize reversibly synchrotron radiation by using a composite film comprised of two components: a photochromic SP with the conversion characteristics of UV-to-visible color and PSP BaFCl:Eu<sup>2+</sup> particles with the conversion characteristics of X-rays-to-UV emission.

## 1. Introduction

Almost immediately following their discovery by W. C. Röntgen in 1895, X-rays have been used for medical imaging. In present-day medical radiography, shadow images are made of the internal structures of the human body by placing the patient between an X-ray source and an X-ray detector. Currently, there are two different types of X-ray detectors for direct digital image acquisition: the charge-coupled device (CCD) and the X-ray storage phosphor plate. Most commercially available digital systems are CCD systems, and the image is displayed almost immediately on a computer monitor after exposure of the sensor. However, these systems have several disadvantages, such as a relatively bulky detector, the need for a wire connection between the sensor and the computer, a small active area of photon detection, and a relatively narrow dynamic range. On the other hand, the X-ray storage phosphor plate is an easy structure including its photostimulable phosphor (PSP) particles dispersed in a polymer binder and coated onto a plastic base. X-ray storage phosphors, which can absorb X-rays and convert the absorbed energy efficiently

into ultraviolet (UV) or visible emission, are used in the application of light intensity measurement under continuous X-ray radiation. A high-performance X-ray storage phosphor should be a high-density material or contain heavy elements because the absorption coefficient increases strongly with the atomic number [1]. Europium doped barium fluorohalides BaFX:Eu<sup>2+</sup> (X = Br, Cl) have a number of favorable properties that make them suitable for use as X-ray storage phosphor in detection systems developed for two-dimensional X-ray imaging in the fields of radiography and crystallography [2, 3].

Photochromic spiropyran dyes are currently used in many commercial applications, such as ophthalmic lenses, sunglasses [4], optical memory, and photooptical switching devices [5], due to their reversible colored-decolored reaction under UV/visible light [6–8]. Spiropyran dyes consist of two heterocyclic moieties linked together by a sp<sup>3</sup> spirocarbon atom. Irradiation of UV light and/or temperature increase causes cleavage of the relatively weak spirocarbon–oxygen (C–O) bond followed by conformational rearrangement, leading finally to ring-opened colored isomers, the so-called

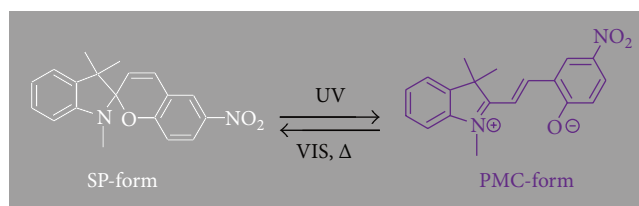


FIGURE 1: Reversible photoisomerization of spiropyran dye 1',3',3'-trimethyl-6-nitrospiro[1(2H)-benzopyran-2,2'-indoline] (SP).

photomerocyanine-form (PMC-form) with a high molar absorption coefficient, as shown in Figure 1. The PMC-form reverts to the closed-ring isomer (spiropyran-form (SP-form)) through a thermally induced ring closure reaction; fading of the colored isomers occurs on a timescale of seconds to minutes at room temperature.

The study reported herein is undertaken to visualize reversibly synchrotron radiation of the superphoton ring-8 GeV (SPring-8) by using a composite film consisting of a photochromic spiropyran dye that has conversion characteristics of UV-to-visible color and PSP BaFCl:Eu<sup>2+</sup> particles that have conversion characteristics of X-rays-to-UV emission.

This present study aims to provide a visual recognition support film capable of allowing SPring-8 operators to recognize visually an irradiated position easily and properly with a simple structure that consists of a spiropyran dye and BaFCl:Eu<sup>2+</sup>.

## 2. Experimental

A spiropyran dye, 1',3',3'-trimethyl-6-nitrospiro[1(2H)-benzopyran-2,2'-indoline] (SP), was used as a UV light-sensitive photoacceptor, and BaFCl:Eu<sup>2+</sup> was used as a UV-radiation source. SP and BaFCl:Eu<sup>2+</sup> were purchased from Tokyo Kasei Co. and Nemoto Lumi-Materials Co., respectively. The SP (45 mg) and BaFCl:Eu<sup>2+</sup> (1500 mg) were mixed, and the mixed powder was dissolved at a rate of 30 wt% to a solution of cyclohexanone and polycarbonate (PC) (0.16 w/w, 50 mL). The suspension was stirred for 10 min. The resulting suspension was applied to a polyethylene terephthalate (PET) substrate using an applicator to produce the SP/BaFCl:Eu<sup>2+</sup> PC composite film. An aluminum deposition film was prepared on the opposite side of the substrate, and its thickness was 60 nm. The deposition rate was 2 nm s<sup>-1</sup>, and the substrate temperature was maintained at an ambient temperature. The practical photograph of the composite/PET/Al three-layered film, its schematic diagram, and an illustration internal of the structure are shown in Figure 2.

The absorption spectrum of the SP toluene solution was measured with a UV-Vis-NIR spectrophotometer (PerkinElmer Co., Lambda 1050UV/Vis/NIR), and the spectral reflectance of the SP/BaFCl:Eu<sup>2+</sup> PC composite film was measured with a spectral colorimeter (Konica Minolta Co., CM-2600d). The powder morphology and particle size of BaFCl:Eu<sup>2+</sup> were characterized using scanning electron microscopy (SEM) (Hitachi S-3000). The Brunauer-Emmett-Teller (BET) specific surface area of BaFCl:Eu<sup>2+</sup>

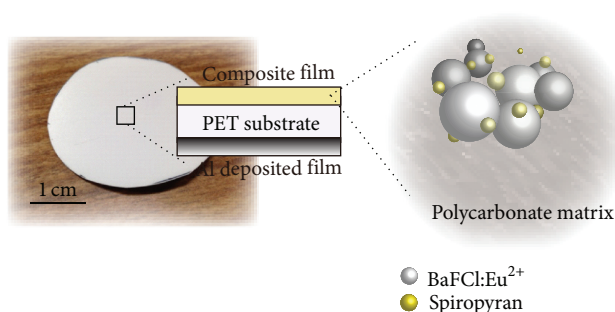


FIGURE 2: Photograph showing the composite (SP/BaFCl:Eu<sup>2+</sup> PC as binder)/PET/Al three-layered film and schematic diagrams of its cross-section and internal structure.

was determined from Kr adsorption at 77°C using a TriStar II 3020 (Shimadzu Co.). The samples were degassed at 500°C for 60 min prior to Kr adsorption measurement. An X-ray diffractometer (Mac Science Co., MX Labo) with Cu K $\alpha$  monochromated X-rays operating at 40 kV and 20 mA was used to produce X-radiation of 0.154 nm. An X-ray excited optical luminescence (XEOL) spectrum of BaFCl:Eu<sup>2+</sup>, which was generated with X-radiation, was guided by a photonic multichannel analyzer (Ocean Optics Co., USB4000) through fused silica fiber (Ocean Optics Co., P400-2-UV-VIS). Synchrotron radiation visualizing was performed at the BL45XU with an undulator at SPring-8. The beam energy and flux were 12.4 keV and  $\sim 10^{11}$  photon s<sup>-1</sup>, and the X-radiation from the SPring-8 was utilized through a chopper at intervals of 100 ms (i.e., 100 ms ON, 100 ms OFF). The beam size of the incident X-rays on the composite film surface was 200  $\mu$ m  $\times$  300  $\mu$ m. All measurements were carried out at room temperature.

## 3. Results and Discussion

The photochromic reaction of the SP was carried out upon irradiation with 365–375 nm light of UV-LED (90 mW/cm<sup>2</sup>). Before UV light irradiation, the main absorption band centered at 336 nm (extinction coefficient  $\epsilon = 9339$  M<sup>-1</sup> cm<sup>-1</sup>) of the SP-form appeared in the near UV range of 250–420 nm. This absorption band is assigned to  $\pi$ - $\pi^*$  transitions of chromene and indoline rings. Upon irradiation with UV light, the toluene solution containing the SP changed from colorless (SP-form) to purple (PMC-form), and a broad absorption band appeared with a maximum at 580 nm. After stopping the UV light irradiation, the absorption band of the PMC-form rapidly decreased for approximately a few seconds at ambient temperature; however, in the case of the SP in the PC composite film, the decay time of the colored PMC-form was prolonged for approximately 5 min at ambient temperature. This result indicates that the decay time of the colored PMC-form in spiropyran can be controlled through matrix selection. In fact, we have reported that matrix polarity, steric hindrance, or acidity can control the thermal stability of the colored PMC-form, and the thermal stability is drastically enhanced by the interaction between an ionic zwitterionic structure of PMC-form and a matrix with

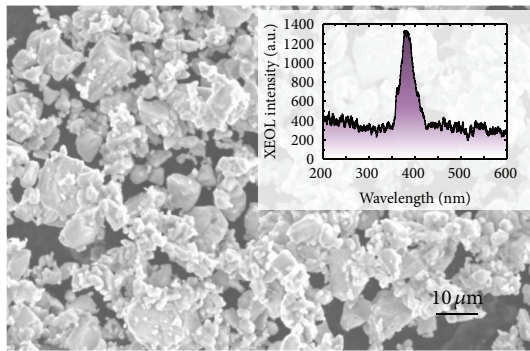


FIGURE 3: SEM image of the BaFCl:Eu<sup>2+</sup> powder and schematic diagrams of the cross-section and internal structure. The inset shows the XEOL spectrum of BaFCl:Eu<sup>2+</sup> powder under the irradiation of a 0.154 nm X-ray (40 kV, 20 mA).

high polarity [9]. Another important property to this study, the PMC-form, is not produced directly with X-radiation; therefore, the photoisomerization of the SP-to-PMC-form can occur only by irradiation with UV.

The morphology of BaFCl:Eu<sup>2+</sup> crystals was characterized by SEM. From the SEM image (Figure 3), it can be seen that the powder was homogeneous polycrystalline particles with diameters ranging from 5  $\mu\text{m}$  to 30  $\mu\text{m}$  and an average particle diameter of 13  $\mu\text{m}$ . To analyze further the BaFCl:Eu<sup>2+</sup>, the BET specific surface area was measured. The BET specific surface area of the BaFCl:Eu<sup>2+</sup> shows 0.4 m<sup>2</sup> g<sup>-1</sup>, which indicates that the BaFCl:Eu<sup>2+</sup> particles with a spherical shape that are not porous compare well with the calculated value of 0.1 m<sup>2</sup> g<sup>-1</sup> assuming spherical particles. The BaFCl:Eu<sup>2+</sup> powder can emit near-ultraviolet light when exposed to X-rays, and it has been well known as a photostimulable phosphor (PSP) [10]. The inset in Figure 3 shows that the BaFCl:Eu<sup>2+</sup> powder shows a strong photoluminescence centered at 381 nm when excited with X-radiation of 0.154 nm at room temperature. A very small and narrow photoluminescence at 360 nm is also observed. The Eu<sup>2+</sup> ion shows a photoluminescence that strongly depends on its valence state and the nature of the host lattice. The 381 nm peak is due to the electronic transition from the 4f<sup>6</sup>5d<sup>1</sup> (<sup>2</sup>e<sub>g</sub>) state of Eu<sup>2+</sup> to the 4f<sup>7</sup> (<sup>8</sup>S<sub>7/2</sub>) ground state, and the narrow peak of 360 nm is attributed to the intraband transition from 4f<sup>7</sup> (<sup>6</sup>P<sub>7/2</sub>) to 4f<sup>7</sup> (<sup>8</sup>S<sub>7/2</sub>) [11]. Accordingly, the strong photoluminescence of 381 nm overlaps with the region in which SP can be photoisomerized; thus, the BaFCl:Eu<sup>2+</sup> powder is an appropriate combination with the SP for its photoisomerization.

Figure 4 shows the reflectance spectra of the SP/BaFCl:Eu<sup>2+</sup> PC composite film before and after synchrotron radiation at room temperature. Before synchrotron radiation, the color of the composite film is white, derived from the colorless SP-form and the white BaFCl:Eu<sup>2+</sup>. Upon synchrotron radiation for 3 s, the composite film changed from white to deep purple, and a broad reflectance band appeared with a maximum at 580 nm, which is assigned to the  $\pi$ - $\pi^*$  transitions of the PMC-form. The result implies that

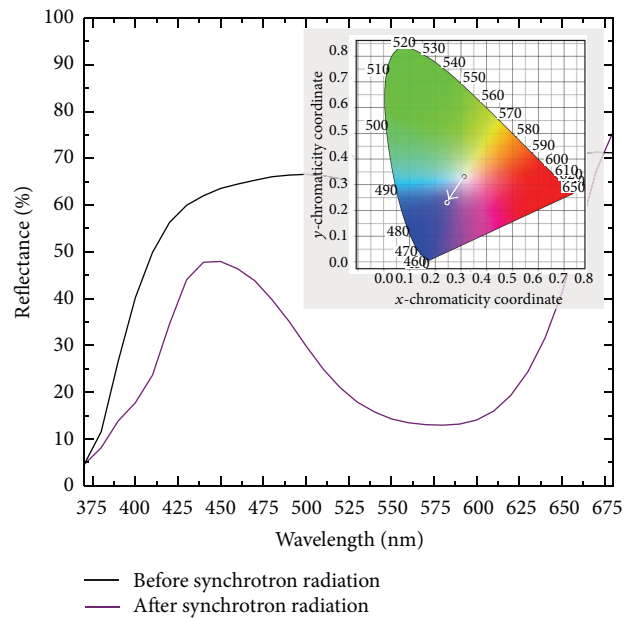


FIGURE 4: Reflectance spectra of the SP/BaFCl:Eu<sup>2+</sup> PC composite film before and after synchrotron radiation for 2 s. The inset shows color shift in the CIE1931 chromaticity diagram at the maximum brightness. Color coordinates of the composite film are shown as open circles.

the photoisomerization of the SP/BaFCl:Eu<sup>2+</sup> PC composite film is accomplished indirectly by absorbing the XEOL derived from BaFCl:Eu<sup>2+</sup> in the composite film. The SP/BaFCl:Eu<sup>2+</sup> PC composite film shows a high visualization property to the synchrotron radiation of SPring-8, which is also suggested from the color difference Commission Internationale de l'Eclairage (CIE) chromaticity diagram of the SP/BaFCl:Eu<sup>2+</sup> PC composite film before and after synchrotron radiation. For this color change, the CIE chromaticity coordinates ( $x$ ,  $y$ ) are found to be from (0.31, 0.33) to (0.24, 0.22), corresponding to white and deep purple, respectively (the inset in Figure 4). Furthermore, the color change is also expressed using the color space CIE  $L^*a^*b^*$ , which was calculated from the spectral reflectance that the spectral colorimeter measured. The color changes in terms of the CIE  $L^*a^*b^*$  are as follows:  $L^*$  is 83.76 to 52.12;  $a^*$  is -1.43 to 12.39; and  $b^*$  is 0.92 to 33.51; thus, the magnitude of total color difference  $\Delta E^*_{ab}$  is calculated to be +48.76.  $\Delta E^*_{ab}$  is defined by the equation  $\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ , where  $\Delta L^*$  is the lightness difference,  $\Delta a^*$  is the red/green difference, and  $\Delta b^*$  is the yellow/blue difference. Consequently, the total color difference  $\Delta E^*_{ab}$  of the SP/BaFCl:Eu<sup>2+</sup> PC composite film can be easily recognized. More-over, the colored area disappeared for approximately a few hours, so the color change can be used many times repeatedly.

A practical application of visualization for synchrotron radiation using the composite film is shown in Figure 4. Each picture in Figure 5 shows the visualization appearance for synchrotron radiation at an interval of 100 ms

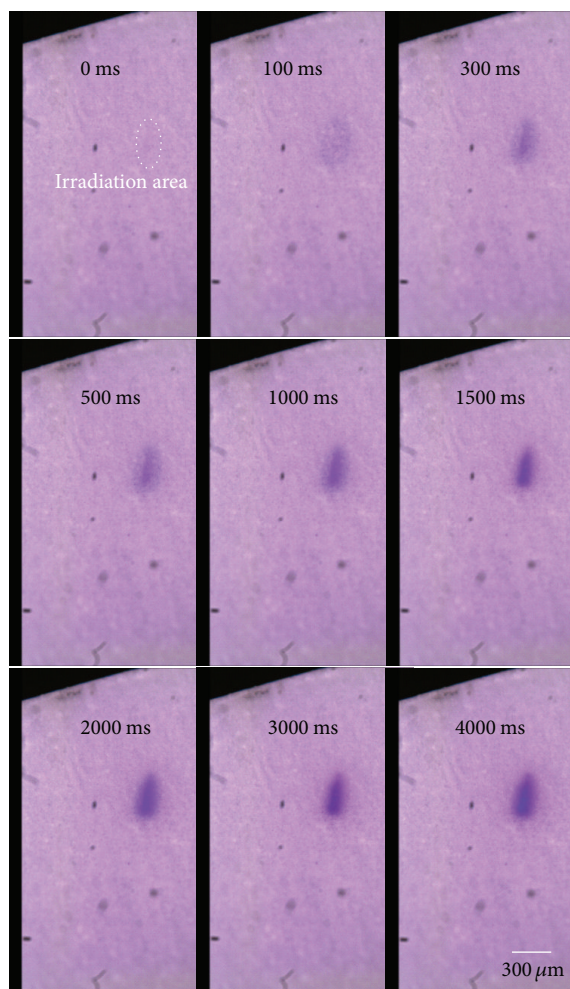


FIGURE 5: Photographs showing visualization for the synchrotron radiation of SPring-8 using the SP/BaFCl:Eu<sup>2+</sup> PC composite film. Deep purple areas indicate the spot that is irradiated with the synchrotron radiation of SPring-8.

(see Movie S1 of the Supplementary Material available online at <http://dx.doi.org/10.1155/2014/236382>). The deep purple area indicates the synchrotron radiation area, which is in good agreement with the beam size of the synchrotron radiation, and the pale pink area (the actual color is white, and the visual change is due to room lighting) is the unirradiated area. The color intensity of the deep purple area visualized by synchrotron radiation is saturated within 3000 ms; thus, the photostationary state is reached within 2000 ms. In addition, bleaching of the composite film was confirmed for a few minutes in an ambient temperature; the visible absorption band of the PMC-form had completely disappeared. The visualization for synchrotron radiation was repeated a few dozen times with depression of the absorption intensity of the PMC-form to less than 30%. The visualization synchrotron radiation using the composite film shows very similar characteristics to the GAFCHROMIC EBT2 dosimetry film which has been designed specifically as a time-and-cost-saving tool that addresses the needs of medical physicists and dosimetrists

working in radiotherapy environments; however, the reusable visualizing characteristics of the SP/BaFCl:Eu<sup>2+</sup> PC composite film is significantly different from the commercially available dosimetry films. Furthermore, the visualization property of the SP/BaFCl:Eu<sup>2+</sup> PC composite film is one possible way to the detection of radiation rays of radioactive materials and will provide efficient color change in accordance with the intensity of the absorbed dose.

#### 4. Conclusions

We successfully demonstrated the reversible visualization of synchrotron radiation by using the composite film comprised of a photochromic SP with the conversion characteristics of UV-to-visible color and PSP BaFCl:Eu<sup>2+</sup> particles with the conversion characteristics of X-rays-to-UV emission.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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