

# **Bio-inspired Colour Materials Combining Structural, Dye, and Background Colours**

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## **Author contributions**

Y. T. designed the project. M. S. performed the experiments. All authors discussed the results and contributed to the data interpretation. Y. T. wrote the manuscript.

## **Additional information**

**Supplementary Information** accompanies this paper at <http://www>.

**Abstract:**

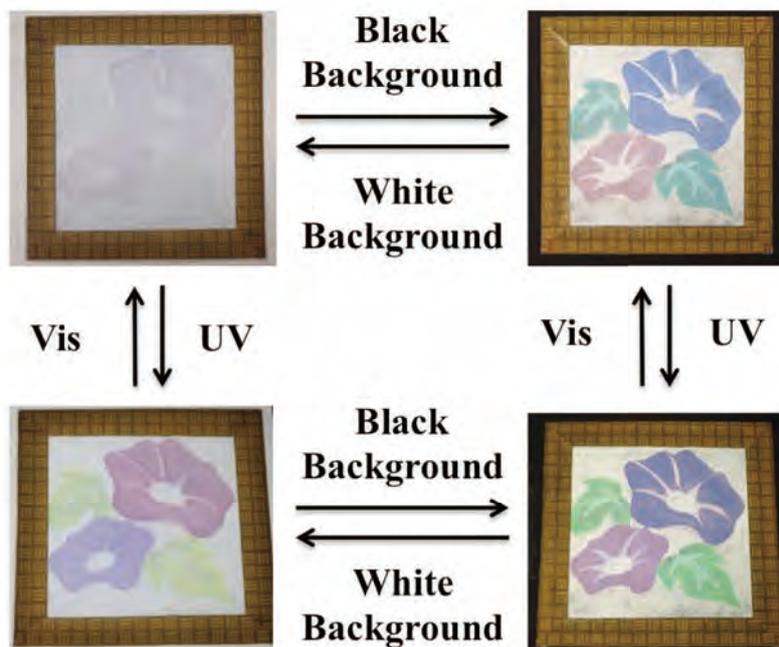
Human beings have developed many dyes and pigments and use them for printed and display materials to share information. Today's information society is not possible without these colour materials. Some living organisms utilize body colour for information exchange and protection by skilfully combining dye, structural and background colours to realize a body colour change based on circumstances. In this study, inspired by the extraordinary body colour changes of living things, we prepared a composite colour material combining photochromic dyes, a black substance, a spherical colloidal crystal exhibiting a structural colour, and a background colour. In addition to combining a dye colour and a structural colour that changes upon light irradiation, the contribution of the different effects of the background colour on each colouring property allowed the construction of a colour material that can reversibly change into various colours under different conditions.

**Keyword:** dye colour, structural colour, background colour, composite colour, bio-inspired colour

TOC

Living organisms skilfully combine various chromatophores to utilize body colour changes for mutual information exchange and protection<sup>[1]</sup>.

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information protection<sup>[1]</sup>. frogs have dermis that plurality of colouring such as iridophore melanophore epidermis, colour can be by the action

chromatophores<sup>[1a]</sup>. Xanthophore contains pigments such as carotenoid and pteridine. The deepest existing melanophore has black melanin granules as pigments. These pigmented cells change their colours depending on the distribution states of the pigments in the cells. Xanthophore absorbs short-wavelength light, i.e., violet and blue light, when the pigments are spread throughout the cell. The light corresponding to green, yellow, and red, i.e., longer-wavelength light, is transmitted via

xanthophore. For melanophores, when melanin granules are spread within a cell, the melanin absorbs all the visible light, and the melanophores become black. However, if these pigments aggregate within the cells, the cells appear colourless and transparent. Iridophore is sandwiched between two pigmented cells. This cell contains many crystal plates of guanine. Based on the arrangement of the crystal plates, iridophore strongly scatters a specific wavelength of visible light. Xanthophore and melanophores are pigmented, whereas iridophore is structurally coloured. Depending on the combination of the states of these three chromatophores, which exhibit different chromogenic properties, frogs can achieve various body colour changes. However, the colouring mechanism of living organisms is still not clearly understood. To accurately understand body colour changes in living organisms, further research is necessary. When artificial materials with dye and structural colours are prepared, creating a combined colour material with colour changes similar to those observed in living organisms is difficult. We have obtained numerous dyes and pigments that reversibly change colour upon exposure to external stimuli. We have also clarified colour development and colour change mechanisms based on stimuli and have developed various applications. Recently, the colouring mechanism of structural coloured materials that can exhibit vivid colours due to fine structures with visible-light wavelengths has been elucidated<sup>[2]</sup>. As a result, stimuli-responsive, structural colour materials can be created<sup>[3]</sup>. Additionally, understanding the colouring mechanisms of these colour materials has clearly shown that the background colour is also important for creating colourful colour materials<sup>[4]</sup>. Generally, additive and subtractive colour mixing reproduce colours. In additive colour mixing, red, green, and blue are mixed to create colours. In the creation process, red, green and blue light are added to the starting black background colour. When all three colours are combined, they produce white. These colours are called the "three primary colours of light", and structural colour materials can also produce various colours by this method. Subtractive colour mixing begins with a white colour as the background, and colours are created by combining cyan, magenta, and yellow dyes on the white background. The obtained colour becomes black when all three colours are mixed. Cyan, magenta and yellow absorb red, green and blue light, respectively, from white light. Because various colours are produced by the three colour pigments, the subtractive colours are called the "colours of the three primary colours". The colouring mechanisms of pigmented and structural colours depend on the background colour, i.e., black or white, and the appearance of those colours is different.

In this study, inspired by the surprising body colour changes of living organisms, we constructed a system with a reversible colour change by combining chromic dyes, a black pigment, a structural colour material, and a background colour. For the chromic dye, diarylethene derivatives, which are photochromic dyes that change colour upon light irradiation, were used. Carbon black (CB) was used as the black pigment. For the structural colour material, spherical colloidal crystals

were used. The colour changes for the colour materials obtained by fusing photochromic dyes, a black pigment, and spherical colloidal crystals were examined while changing the background to black and white.

### **Structure colour properties of spherical colloidal crystals.**

When colloidal crystals composed of fine particles are irradiated with white light, a photonic band gap (PBG) is generated due to a Bragg reflection<sup>[5]</sup>. If the position of the PBG is within the visible-light region, a structural colour is observed from the colloidal crystal. If the size of the fine particles in the colloidal crystal changes, the position of the PBG caused by the Bragg reflection changes, and thus, the hue of the structural colour changes. Because spherical colloidal crystals also produce similar PBGs, they can also exhibit structural colour<sup>[6]</sup>. In this study, we determined that spherical colloidal crystals had different appearances depending on the background colour and their size.

To investigate the effect of the spherical colloidal crystal size and background colour on the colour observed from the spherical colloidal crystals, we prepared a membrane with one layer of different sizes of spherical colloidal crystals on a transparent glass plate (Fig. 1a, Fig. S2). The background colours were white and black. The spherical colloidal crystals were created from monodispersed silica particles with a particle size of 250 nm. When the background was white, the spherical colloidal crystals appeared as a white powder, regardless of their size. However, when the background was black, a green structural colour was observed from the spherical colloidal crystals with an average particle size of 29.0  $\mu\text{m}$ . As the particle size increased, the white in the colour of the spherical colloidal crystals increased, and vivid colours were difficult to observe with the naked eye.

To investigate the effect of the background colour on the structural colour of the spherical colloidal crystals, the reflection spectra of spherical colloidal crystals with an average particle size of 29.0  $\mu\text{m}$  were measured with a white and black background. Spherical colloidal crystals created from monodispersed silica particles with different particle sizes of 220 nm, 250 nm, and 300 nm were used for this measurement. When the background was white, the reflection intensity from the background was high for the entire visible region, and the PBG due to the Bragg reflection from the colloidal crystals could not be observed in the spherical colloidal crystal reflection spectra (Fig. 1b)<sup>[4a]</sup>. As a result, observing the structural colour arising from the spherical colloidal crystals was difficult, and the spherical colloidal crystals appeared as a white powder. For the reflection spectra measured with a black background, the influence of the background light disappeared, and the PBG was clearly observed (Fig. 1c). Using fine silica particles with different particle sizes allowed the

PBGs in different wavelength regions to be observed, and various vivid structure colours were seen. When the background was black, the reflectance of the reflection spectrum increased for the entire visible-light region as the size of the spherical colloidal crystals increased (Fig. 1d). When the crystals present in spherical colloidal crystals are disturbed due to the spherical shape, incoherent multiple scattering occurs in the whole visible-light region. Because spherical colloidal crystals with large sizes are greatly affected by incoherent multiple scattering, the reflectance in the visible-light region is high, even if the background is black<sup>[4a]</sup>. As a result, as shown in Fig. 1a, vivid colours are less likely to be observed from larger spherical colloidal crystals.

The above results revealed that spherical colloidal crystals created from monodispersed silica particles are influenced by their size and background colour, and subsequently, the vividness of the observed colour changes. The vividness of a structural colour of living organisms is determined by the thickness of the material with the fine structure and its background colour. A proper tissue thickness is important for organisms displaying a vivid structural colour because the structural organization is reasonably disordered<sup>[7]</sup>.

#### **Effect of the addition of a black substance into spherical colloidal crystals.**

To alleviate the effect of multiple incoherent scattering of light generated inside colloidal particle aggregates, the introduction of a black substance into the aggregate is advisable<sup>[6d, 8]</sup>. Upon the introduction of a black substance, the PBG becomes prominent, and the structural colour generated from the colloidal particle aggregates becomes brilliant. Here, the effect of the addition of a black substance and the background colour on the structural colour of spherical colloidal crystals was investigated. CB with a particle size of approximately 100 nm was used as the black substance. A required amount of CB was mixed in the aqueous suspension of fine silica particles, and the spherical colloidal crystals containing CB were prepared by a method previously described (see the experimental section).

Photographs of the two different sizes (the average sizes of 29.3  $\mu\text{m}$  and 100.6  $\mu\text{m}$ ) of spherical colloidal crystals composed of 210 nm fine silica particles with different amounts of CB are shown in Fig. 2a. The spherical colloidal crystals were spread on a transparent glass plate with a black background. As described above, when CB was not included, smaller spherical colloidal crystal sizes result in more vivid colour. However, when CB was added, the colour of the spherical colloidal crystals became almost independent of the size. This was evident in the reflection spectrum (Fig. 2b).

The spherical colloidal crystals containing CB exhibited a vivid colour even when the background was white (Fig. 2c). Spherical colloidal crystals displaying structural colours in various

hues were obtained by varying the particle diameter of the monodispersed silica particles constituting the spherical colloidal crystals.

Because mixing CB into the spherical colloidal crystals resulted in a vibrant colour, we investigated the angle dependence of the colour. Figure 2d and 2e show the results of the angular dependence of the PBG from different methods. In Fig. 2d, the reflection spectrum was measured by fixing the position of the light source and the detector with respect to the sample at  $10^\circ$  and changing the light irradiation direction,  $\varphi$ , from  $0^\circ$  to  $30^\circ$ . In the method shown in Fig. 2e, light is irradiated from a direction perpendicular to the flat plate upon which the sample is fixed, and a detector is placed at an angle of  $\theta$  relative to the flat plate to measure the reflection spectrum.  $\theta$  was varied from  $10^\circ$  to  $60^\circ$ . The angle dependence of the PBG of spherical colloidal crystals has been reported, but most of the reports used a method similar to the method shown in Fig. 2d. As seen from the reflection spectra in Fig. 2d, no change was observed in the position of the peak even as the angle  $\varphi$  was changed; thus, the position of the PBG arising from the spherical colloidal crystals and its structural colour do not have an angle dependency. The reason for this result is that spherical colloidal crystals have a structure in which crystal planes in the same state are always directed at the surface thereof. However, when the reflection spectra were measured by this method, as shown in Fig. 2e, the position of the PBG shifted to lower wavelengths as the angle  $\theta$  increased. In other words, during this measurement, the position of the PBG and its structural colour has an angle dependency. For a film-like colloidal crystal, the PBG is not observed when the reflection spectra are measured by this method with large  $\theta$  because the PBG is a result of the Bragg reflection. As a result, the structural colour from film-like colloidal crystals also disappears. However, in spherical colloidal crystals, the same crystal planes exist in various directions along the spherical surface, and thus, the PBG is always observed, even at large  $\theta$ , and a structural colour can be seen<sup>[6d]</sup>. Additionally, under natural light conditions, such as sunlight, i.e., multi-directional light, the angle dependency of the hue observed from spherical colloidal crystals decreases compared with that of the film-like colloidal crystals.

These spherical colloidal crystals can also be used as a pigment. Utilizing the background effect, an image can be created in which different pictures appear upon switching the background from white to black. The weevil picture shown in Fig. 2f was drawn using spherical colloidal crystals containing CB (0.2 wt%). For the background of the picture on the left, white paper was used. A pattern using spherical colloidal crystals consisting of only silica fine particles was drawn around the weevil. Because the background was white, the pattern cannot be recognized with the naked eye; only the picture of the weevil is visible. If the background is black, as shown in the picture on the right in Fig. 2f, the pattern drawn with the spherical colloidal crystals displaying different structural colours can be recognized.

As explained in the introduction, frogs utilize a state in which a melanophore is placed on the background of an iridophore. By changing the colour of the melanophore, i.e., the background of the iridophore, the vividness of the structural colour arising from the iridophore changes.

### **Utilization of a photochromic dye.**

Diarylethene is a compound in which two aromatic organic groups are bonded to the 1,2 positions of ethene and a photochromic dye that is reversibly isomerized by light irradiation<sup>[9]</sup>. In many cases, when a solution containing diarylethene is irradiated with ultraviolet light, diarylethene forms a closed-ring structure and exhibits various colours. However, when diarylethene is irradiated with visible light, it becomes colourless and transparent due to the ring opening of the structure. Since both isomers of diarylethene are thermally stable, the compounds have excellent repeated colouration/discolouration durability. We also know that diarylethene exhibits reversible photochromic properties even in the solid state. If diarylethene can be introduced into spherical colloidal crystals in an appropriate state, it can reversibly affect the structural colour property of the spherical colloidal crystals via the colour change accompanying the photoisomerization of diarylethene. When diarylethene is a crystal, its crystal shape slightly changes due to the isomerization accompanying light irradiation<sup>[10]</sup>. In this research, to fuse diarylethene and the spherical colloidal crystals, diarylethene was introduced into the colloidal crystals in a manner to ensure that the isomerization of diarylethene did not affect the structure of the colloidal crystals (described in the supporting information).

When an appropriately coloured diarylethene was added, the mixture became black upon ultraviolet-light irradiation and white upon visible-light irradiation. 1,2-Bis(2-methyl-5-phenyl-3-thienyl) perfluorocyclopentene (1)<sup>[9a]</sup>, 1,2-bis(5-methyl-2-phenyl-4-thiazolyl) perfluorocyclopentene (2), and 1,2-bis(3,5-dimethylthiophen-2-yl) perfluorocyclopentene (3) are white in the ring-opened state, but the ring-closed isomers are blue, red and yellow, respectively (Fig. S4, S5). By combining these three types of diarylethenes in appropriate amounts, a mixture was created that can turn black upon irradiation with ultraviolet light and white upon irradiation with visible light (Fig. S6). Figure 3a shows the colour changes when ultraviolet and visible light are used to irradiate the mixed powder containing these three types of diarylethenes. By fusing this system with spherical colloidal crystals, the vividness of the structural colour property can be changed by light irradiation. Figure 3b shows the observed states when ultraviolet and visible light are used to irradiate the system containing spherical colloidal crystals composed of monodispersed, fine silica particles with a particle size of 290 nm and three types of diarylethenes. When the diarylethene is in a ring-opened state due to

sufficient irradiation with visible light, the fusion is a white powder. When the fusion is irradiated with ultraviolet light, the structural colour derived from the PBG of the spherical colloidal crystals is obvious (Fig. 3c), resulting in a purple powder. This reaction is reversible, and the colour can repeatedly change. Compared with that of the system with added CB, the spherical colloidal crystals with diarylethenes in the closed-ring state had a slightly different hue due to the light scattering influence of the solid diarylethenes (Fig. S7). However, a system that switches structural colour upon light irradiation was obtained.

By combining the diarylethene colour change with the structural and background colours, we attempted to construct a system with various hues. Three systems in which one type of diarylethene was introduced into spherical colloidal crystals created from fine silica particles with different sizes were prepared. The changes in the colours of these systems were accompanied by changes in the colour property of the diarylethenes upon irradiation with light and the background colour (Fig. 4a). The average sizes of the spherical colloidal crystals were all approximately 96.1  $\mu\text{m}$  in size. The upper left (1) is the state after visible-light irradiation with a white background. In this state, all of the diarylethenes in the spherical colloidal crystals are white, and the influence of the background light reflection is large, so all the systems are observed as a white powder. When the background is black (2), the influence of the background light reflection disappears, and all the systems exhibit structural colours derived from the PBG, which is based on the particle diameter of the fine silica particles used. As a result, the systems prepared using fine silica particles 220 nm, 250 nm, and 300 nm in size have slightly blue, green and red structural colours, respectively. In this state, the diarylethenes are in the closed-ring states when irradiated with ultraviolet light, and each colour is shown (3). The colours are mixed with the pigment colours in the structural colours, but if the background is black, the influence of the pigment colours is small, and the hues of these systems do not change much due to the pigmented colours. However, when the background is white (4), the influence of pigment colours increases, and the hues of these systems greatly change. Upon irradiation with visible light, the systems become white again. The reflection spectrum in Fig. 4b shows these colour changes. Based on the above results, systems with reversible hue changes can be created by combining structural, photochromic pigment and background colours. These systems can be used to draw beautiful pictures with various colour changes depending on the conditions (Fig. 4c). As mentioned above, the use of the spherical colloidal crystals of 29.0  $\mu\text{m}$  makes the effect of the background color more pronounced. However, the color change due to light irradiation is more conspicuous in the system using the spherical colloidal crystals with larger particle size because the total amount of the dyes is larger. Since it is difficult to increase the amount of the dyes that can be introduced per unit volume of the spherical colloidal crystals (see **MATERIALS AND METHODS**), the color-changeable portions in the picture shown in Fig. 4c are prepared by the

spherical colloidal crystals with an average particle size of 50.4  $\mu\text{m}$ .

The spherical colloidal crystals formed from only fine silica particles revealed that the vividness of the structural colour development varies depending on the size of the particles and colour of the background. The structural colour is colourful due to the three primary colours of light<sup>[11]</sup>. Therefore, a blacker background results in a more vivid colour. However, because spherical colloidal crystals have a disordered structure, when they are large, the contribution of incoherent multiple light scattering increases, and vivid colours are less likely to occur even with a black background. Therefore, adding a small amount of a black substance, such as CB, to spherical colloidal crystals decreases the contribution of the incoherent multiple light scattering, and the spherical colloidal crystals exhibit a vivid colour. Additionally, if the particle diameter of the fine silica particles changes, the spherical colloidal crystals have various hues. The combination of fine silica particles and CB resulted in a colour material that can be used as various colourful pigments. Next, we showed that when diarylethenes, which are photochromic dyes, are fused with spherical colloidal crystals, a colour material with combined structural and pigmentary colours is created. By combining a plurality of diarylethene derivatives, a mixture that changes between black and white upon light irradiation was obtained. Introducing this mixture into spherical colloidal crystals result in spherical colloidal crystals with a structural colour property, i.e., vividness, that could be changed by light irradiation. Furthermore, because the colour of diarylethene is composed of the three primary colours, its colour is more vivid when the background is white, which is different from the case of a structural colour. Therefore, the colour material shows various colour changes based on the colour change due to the light irradiation of the diarylethene and the background colour. Various colour changes can be realized by frogs using dye, structural, and background colours. The colour change due to a combination of a pigment colour and structural colour as well as the different influences of the background for each colour may effectively contribute to the body colour change.

Although humans use many colour materials in daily life, most of these materials use only pigment colour. Recent studies have developed various structural colour materials, and research on colour materials that combine these various colours in a manner similar to that of living organisms is needed. By examining the properties of artificially constructed composite colour materials, we will be able to understand the colour properties of living organisms. If an artificial colour material with properties that exceed the body colour changes of living organisms is obtained, it will result in a new technology for daily life.<sup>[4a, 8f, 12]</sup>

## **MATERIALS AND METHODS**

### **Method for preparing spherical colloidal crystals.**

Research teams have reported the preparation of spherical colloidal crystals using various microfluidic systems<sup>[6b, 6d, 13]</sup>. If microfluidic systems are used, monodispersed spherical colloidal crystals with sizes ranging from several micrometres to several hundred micrometres can be obtained in principle. However, based on the colouring mechanism, we concluded that a size of several tens of micrometres or more is preferable for obtaining spherical colloidal crystals with vivid structural colour properties. Therefore, spherical colloidal crystals can be prepared by a simpler method<sup>37</sup>.

The preparation method used in this study is briefly described below. First, 100  $\mu\text{L}$  of an aqueous solution containing suspended silica particles with a uniform particle size (optimum approximately 10-40% by weight) and 900  $\mu\text{L}$  of a hexadecane solution containing 2% by weight of a nonionic surfactant, Span 80, as a stabilizer were placed in a microtube and stirred by a vortex mixer for 5 to 15 seconds to prepare a w/o-type emulsion. Teflon Petri dishes were placed on a hot plate, and we added a hexadecane solution containing 2 wt% Span 80 before heating the mixture to 130 °C. The mixture was heated 5 hours to evaporate the water and cooled overnight. The mixture was then washed with hexane three or four times and dried to obtain the spherical colloidal crystals. The spherical colloidal crystals mixed with CB were prepared in the same manner as described above using a solution containing water-dispersible CB that was previously dispersed in an aqueous suspension of fine silica particles. The CB addition amounts were 0, 0.067, 0.20, and 0.53 wt% with respect to the fine silica particles. For example, the average particle diameter of spherical colloidal particle aggregates prepared under a certain condition is 29.0  $\mu\text{m}$ , and the coefficient of variation obtained in a polydispersed state is 23.4%. An electron micrograph of a spherical colloidal particle aggregate is shown in Fig. S1. In this spherical colloidal particle aggregate, the fine silica particles form colloidal crystals along the spherical surface (Fig. S1a). The Fourier transform image of the electron micrograph shows that the fine silica particles are orderly arranged on the surface of the spherical aggregate (Fig. S1b). The cross-sectional image also shows that colloidal crystals grow along the spherical surface (Fig. S1c). The above results confirmed that "spherical colloidal crystals" in a polydispersed state were obtained by a simple operation.

If the spherical colloidal crystal is mechanically stable, the size of the particles can be classified using stainless-steel mesh sieves. The obtained spherical colloidal crystals were divided using eleven types of stainless-steel sieves with mesh sizes between 38  $\mu\text{m}$  and 250  $\mu\text{m}$ . Monodispersed spherical colloidal crystals were obtained by combining the various mesh sizes (Fig. S1e, S1f).

### **Introduction of diarylethene into the spherical colloidal crystals.**

If the diarylethene concentration in solution is high, diarylethene precipitates as large crystals in the spherical colloidal crystals and on their surface (Fig. S8). When such a crystal is repeatedly irradiated with light, the structure of the colloidal crystal collapses due to the structural changes of the crystal. Because of this, the diarylethene solution was introduced into the spherical colloidal crystals, and after drying, the presence of diarylethene could hardly be confirmed by the electron micrograph. For example, the system with three types of diarylethenes, i.e., 0.22 mM of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (1), 0.27 mM of 1,2-bis(5-methyl-2-phenyl-4-thiazolyl)perfluorocyclopentene (2), and 0.50 mM of 1,2-bis(3,5-dimethylthiophen-2-yl)perfluorocyclopentene (3), was prepared as an ethanol solution to obtain the black and white colour-changing solid. The diarylethenes were contained in the spherical colloidal crystals by sprinkling 240  $\mu\text{L}$  of an ethanol solution on 10 mg of the spherical colloidal crystals and air drying.

Mercury lamps and halogen lamps were used for ultraviolet and visible-light irradiation, respectively.

### **Scanning electron microscope.**

The arrangement of the  $\text{SiO}_2$  colloidal particles in the arrays was investigated using a scanning electron microscope (SEM, Hitachi, Miniscope TM 3000). These samples were coated with a 10-nm Au-Pd layer using a magnetron sputtering apparatus (MSP - 1 S), and the images were acquired using an SEM operated at 15 kV.

### **Optical photographs.**

Photographs of the structural colours of the samples were collected using a digital camera and a digital microscope (KEYENCE VHX-500).

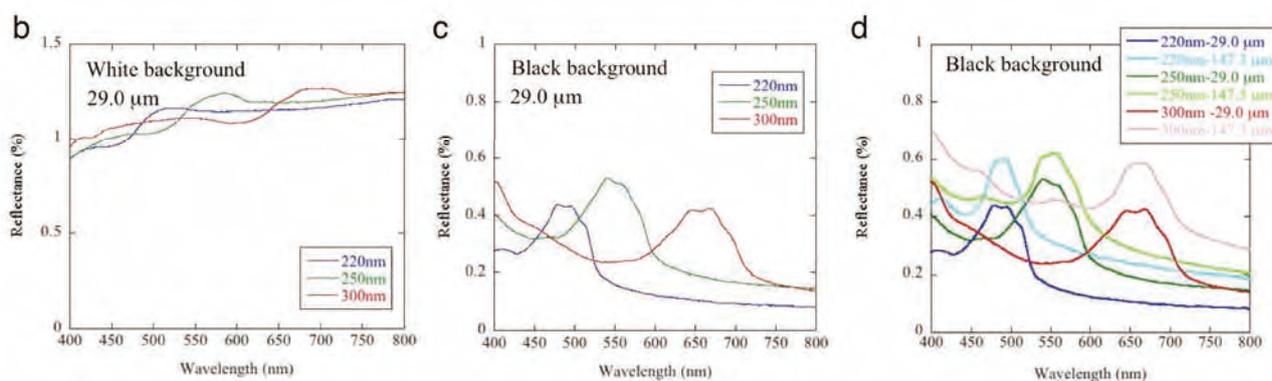
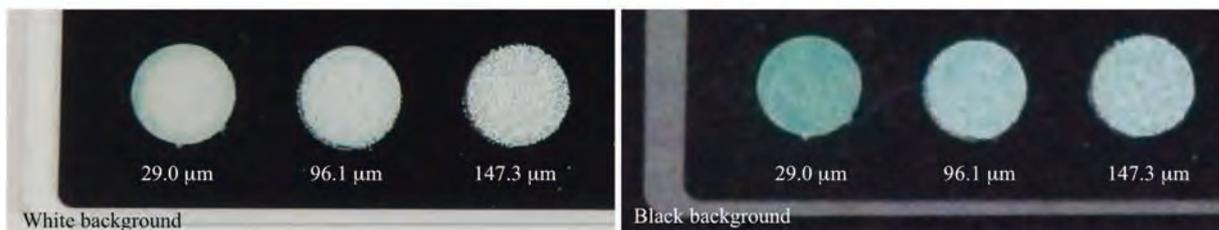
### **Reflection and absorption spectra.**

To investigate the influence of the size of the spherical colloidal crystals on the optical properties, the reflection spectra were measured by fixing spherical colloidal crystals on a glass plate using transparent double-sided tape or black carbon tape. When the transparent double-sided tape was used, white paper was attached to the back of the glass plate.

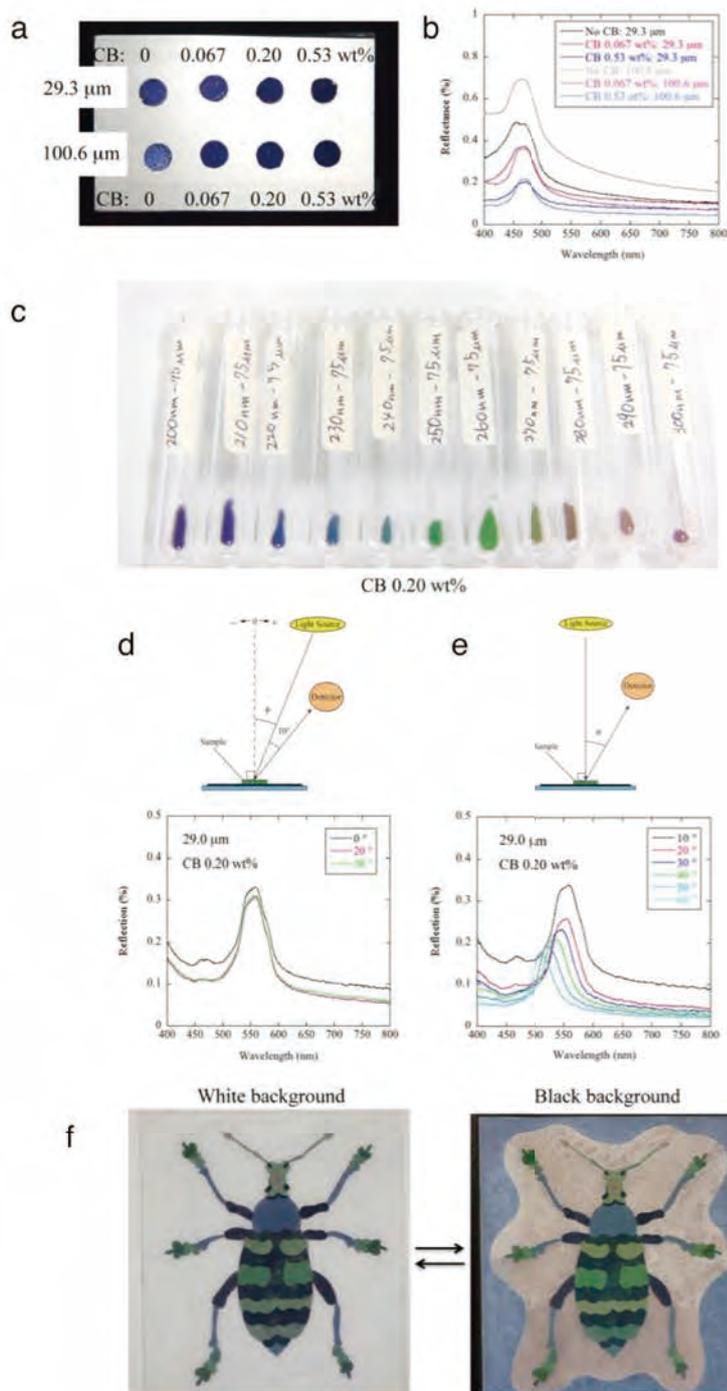
Reflection spectra were measured via two different methods. The light was incident from a

direction perpendicular to the glass surface, and a detector was placed at  $10^\circ$  with respect to the incident direction to measure the reflection spectrum (Fig. 2e). We performed angle-resolved scattering spectrometry to characterize the colours under directional illumination with white light using a UV-vis spectrometer (Nippon Bunko Company, V-670) with an absolute reflectance measurement unit (ARMN-735), an optical fibre spectrometer (QE65000, Ocean Optics), light source (DH-2000-BAL, Ocean Optics), optical fibres (P400-1-SR, Ocean Optics), a reflection/backscattering probe (R400-7-UV-VIS, Ocean Optics), and spectrometer operating software (SpectraSuite, Ocean Optics). The UV-vis spectrometer (Nippon Bunko Company, V-670) was also used to measure the absorption spectra.

a



**Figure 1. Optical properties of the spherical colloidal crystals composed of monodispersed silica particles.** (a) Photographs of the spherical colloidal crystals formed from monodispersed fine silica particles with a particle size of 250 nm. The colour change of the spherical colloidal crystals due to changing the size of the spherical colloidal crystals and the background colour can be observed. The average sizes of the spherical colloidal crystals are 29.0 μm, 96.1 μm, and 147.3 μm. All samples are on transparent glass. The background colour was white on the left side and black on the right side. Because the color of the spherical colloidal crystals is whitish, the surrounding color is black. The size of the circle is 6 mm. (b, c) Reflection spectra of the spherical colloidal crystals formed from monodispersed fine silica particles with particle sizes of 220 nm, 250 nm, and 300 nm. The background colours are white (b) and black (c). The average particle size of the spherical colloidal crystals is 29.0 μm. (d) Reflection spectra of the spherical colloidal crystals with different sizes. The average particle diameters are 29.0 μm and 147.3 μm. The background is black.



**Figure 2. Optical properties of spherical colloidal crystals composed of monodispersed silica particles and CB.** (a) A photograph of the spherical colloidal crystals formed from monodispersed silica particles with a particle size of 210 nm and CB. The amounts of CB are 0 wt%, 0.067 wt%, 0.20 wt%, and 0.53 wt% with respect to the amount of fine silica particles. The average sizes of the spherical colloidal crystals are 29.3  $\mu\text{m}$  and 100.6  $\mu\text{m}$ . All samples are on transparent glass. The

background is black. Because the color of spherical colloidal crystals is dark, the surrounding color is white. The size of the circle is 4.5 mm. (b) Reflection spectra of the spherical colloidal crystals containing 0 wt%, 0.067 wt%, and 0.53 wt% CB, as shown in (a). The average particle diameters of the spherical colloidal crystals are 29.3  $\mu\text{m}$  and 100.6  $\mu\text{m}$ . The background is black. (c) A photograph of the spherical colloidal crystals containing 0.20 wt% CB. The size of the fine silica particles ranges from 200 nm to 300 nm, and 11 different sizes were used. (d, e) Angular dependence of the reflection spectra of the spherical colloidal crystals using two different methods. The spherical colloidal crystal contained 0.20 wt% CB, and the average particle diameter is 29.0  $\mu\text{m}$ . (f) Picture of a weevil drawn using spherical colloidal crystals prepared using monodispersed silica particles with various particle sizes and CB. Detailed information on the particles making up this picture is shown in Fig. S3. The picture displays the difference in appearance upon changing the background colour. In this system, the average particle sizes of spherical colloidal crystals of all samples were about 29  $\mu\text{m}$ .

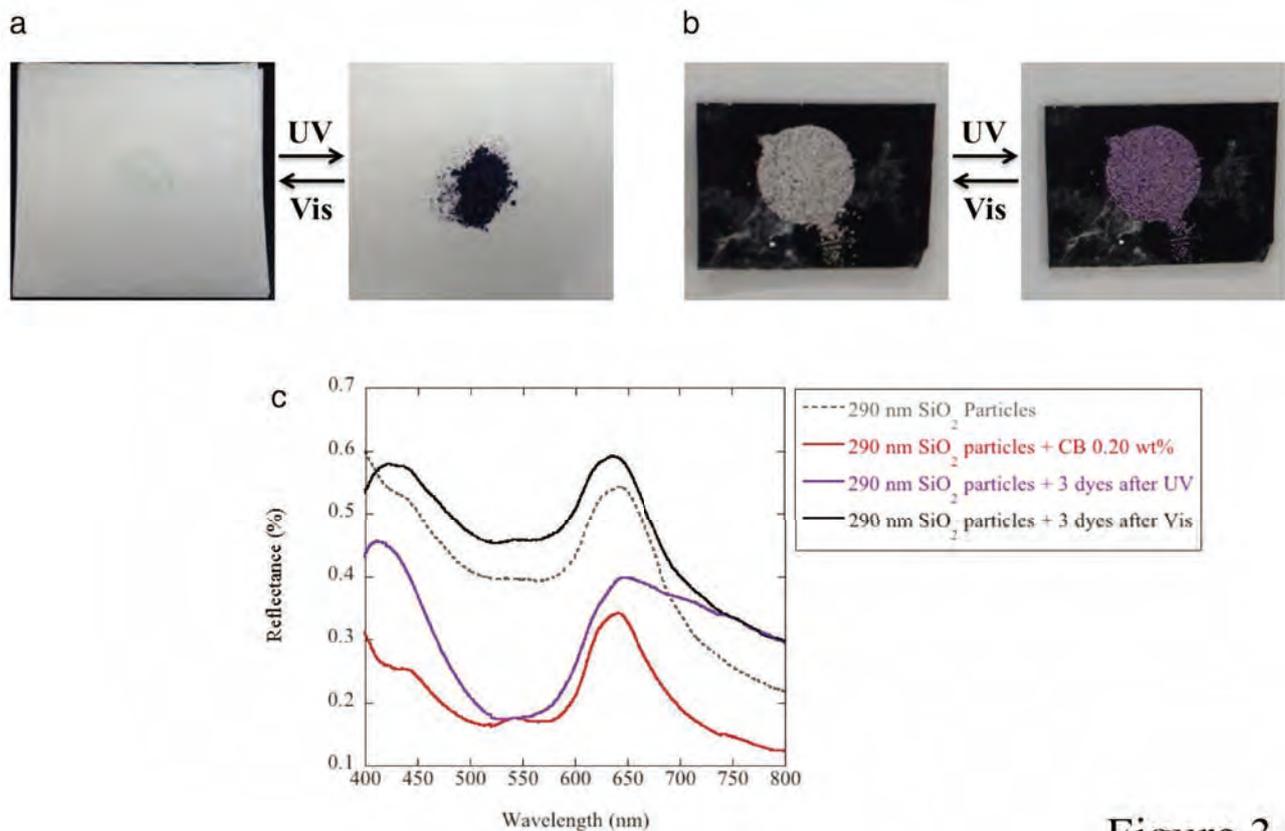
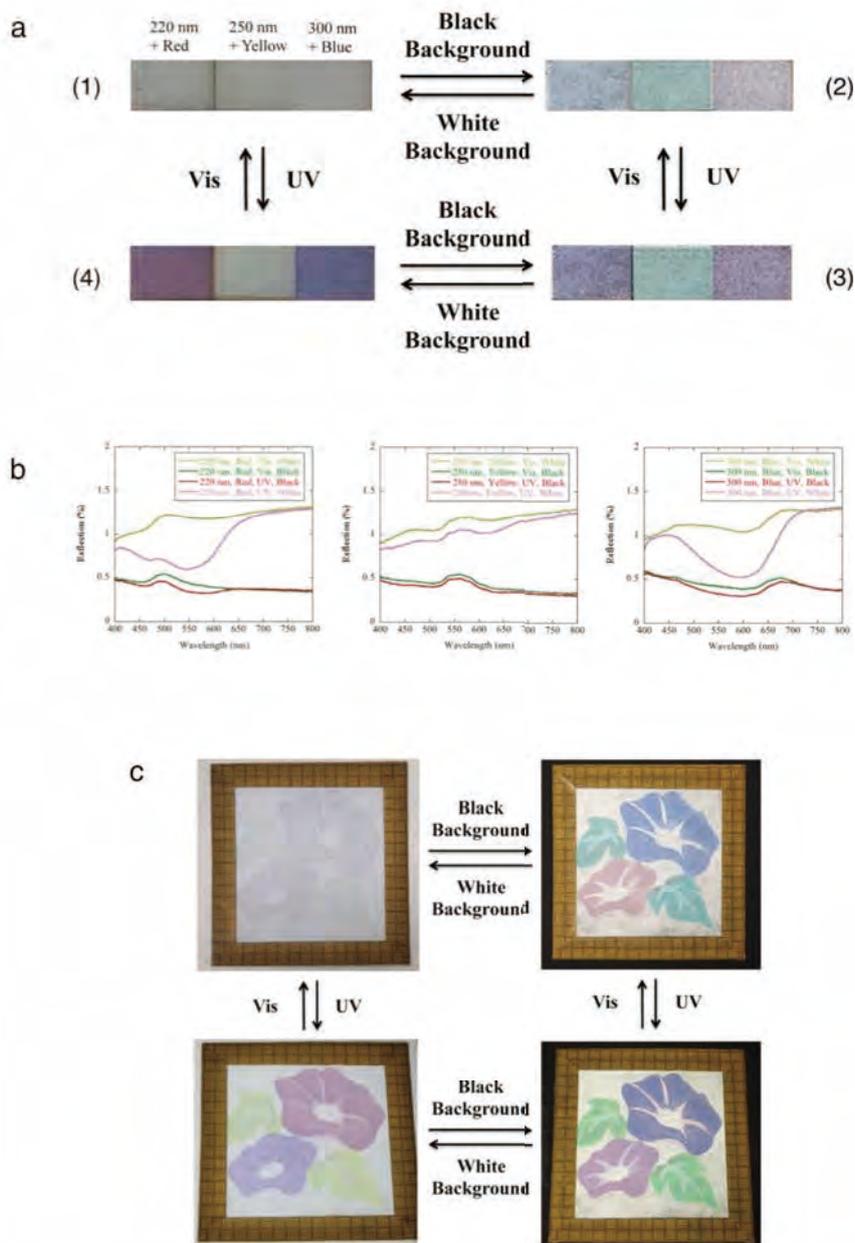


Figure 3

**Figure 3. Optical properties of the composite colour materials with diarylethenes exhibiting different colours in the spherical colloidal crystals: Utilization of a change from white to black in a diarylethene mixture upon light irradiation.** (a) A mixture of diarylethenes of different colours is black upon irradiation with ultraviolet light and white upon irradiation with visible light. (b) A composite colour material was obtained by introducing (a) into a spherical colloidal crystal consisting of monodispersed silica particles with a particle diameter of 290 nm. The background colour is black. When irradiated with ultraviolet light, the structural colour generated by the spherical colloidal crystals increased. (c) Reflectance spectra of the spherical colloidal crystals with/without a small amount of CB compared with the reflectance spectra of (b).



**Figure 4. Optical properties of the composite colour materials with diarylethenes exhibiting different colours in the spherical colloidal crystals: Utilization of the white colour of diarylethene and changes in various dye and background colours upon light irradiation. (a)** Photographs of the colour changes due to light irradiation and changes in the background colour of the spherical colloidal crystals composed of monodispersed silica particles with particle sizes of 220 nm, 250 nm, and 300 nm and including different colour diarylethenes. (b) Reflection spectra corresponding to the change in (a). (c) Colour change in a picture of a morning glory created with the composite colour material due to light irradiation and the background colour. In the system of

Fig. 4c, a sample with an average particle size of spherical colloidal crystals whose color varies with the background color was 50.4  $\mu\text{m}$  was used so that the effect of the background was more remarkable. Detailed information on the particles making up this picture is shown in Fig. S9.



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