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Photoreversible current ON/OFF switching by photoinduced bending of gold-coated diarylethene crystals

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Gold-coated diarylethene crystals exhibited photoreversible bending upon alternating irradiation with ultraviolet (UV) and visible light. The bending behavior can be well explained by the extended bimetal model which we propose here. Moreover, we have demonstrated that it can be used as an actual electrical circuit photoswitching.

Photomechanical motions of photoresponsive molecular crystals have been attracted much attention because they enable us to convert light energy into mechanical energy in direct without any contact and electric wires. Various compounds which show photomechanical behavior in crystal have been reported for diarylethene,[1-10] furyl fulgide,[11] azobenzene,[12-16] salicylidene-aniline,[17,18] anthracene carboxylates,[19-22] 4-chlorocinnamic acid,[23] 1,2-bis(4-pyridyl)ethylene salt,[24] benzylidenedimethyl-imidazolinone,[25] and so on. Among these compounds, diarylethene derivatives are the most promising compounds functioned as photomechanical actuators because of their rapid response, fatigue resistance, and thermal stability.[26,27] There are various photomechanical motions of diarylethene crystals, such as contraction,[2,5,10] expansion,[8] bending,[2-4,7,8,10] fragmentation,[6] and twisting.[9] Among these photomechanical motions, the bending behavior is the most common motion. The quantitative and theoretical analysis of the photoinduced bending behavior is required. We have reported the crystal thickness dependence of the photoinduced bending behavior of diarylethene crystals.[8,10] It was experimentally clarified that the speed of the bending depends on the thickness of the crystal. When the thickness is thin, the crystal is bent rapidly and largely. In order to discuss the photoinduced bending behavior in the easy-handled model, we have introduced the Timoshenko's equation which is known as the simplified bimetal model.[8,10] The correlation between the initial speed of the curvature change and the crystal thickness can be well explained by Timoshenko's bimetal model in both types of bending behavior caused by expansion and contraction of the photoreacted crystal surface.[8,10] A mixed crystal composed of two diarylethene derivatives exhibited actual photomechanical work to rotate a gearwheel upon controlled irradiation with UV and visible light.[7] The two-component co-crystal composed of a diarylethene and perfluoronaphthalene with 1-5 mm size in length could lift a heavy metal ball which is 200-600 times heavier than the crystal. The crystal can work as a molecular crystal crane in the mesoscopic region.[4] These photomechanical crystals may be used for the photomechanical work by coating other materials to improve strength of the crystals, such as fatigue and fracture. Although the photochromism of diarylethenes in the crystalline phase has been so far reported,[27-29] such coated diarylethene crystals have never been investigated.

Here we report on the photoinduced bending behavior of the gold-coated diarylethene crystals. The crystal of 1,2-bis(5-methyl-2-phenyl-4-thiazolyl)perfluorocyclopentene (**1a**) before and after gold deposition shows the photoreversible crystal bending upon alternating irradiation with UV and visible light. The crystal thickness dependence of the photoinduced bending behavior is also investigated before and after gold deposition. The bending behavior is analyzed by Timoshenko's bimetal model and its extended bimetal model. Moreover, we established the photoreversible current ON/OFF switching using the gold-coated diarylethene crystal. These results provide not only a new useful strategy to design for photomechanical actuators but also a new practical use of photomechanical crystals.

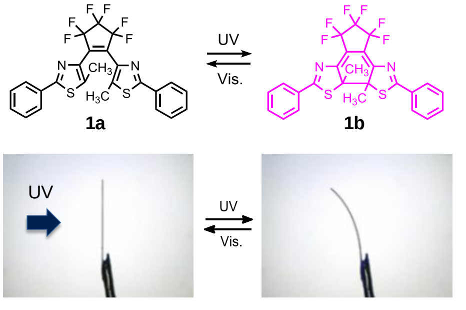

Fig. 1. Molecular structure and the photoinduced crystal bending behavior of diarylethene **1a.**

Rod-like crystals of diarylethene **1a**[2,30] were prepared by recrystallization from *n*-hexane. The crystal shape, face indices, and molecular packing are shown in Fig. S1.[2] Fig. 1 shows the photoinduced bending behavior upon irradiation with UV light to the (0 1 0) face. The crystal of diarylethene **1a** bends toward the incident light. This is ascribed to the contraction of the photoreacted layer in the crystal surface, which is caused by the photochromic reaction from the open-ring isomer to the closed-ring isomer upon irradiation with UV light.[2]

The crystal thickness dependence of photoinduced bending behavior was investigated. Fig. S2 shows the curvature change of the crystals having different crystal thickness by UV irradiation time. This result indicates that the crystal is bent rapidly and largely when the thickness is thin. In order to discuss the bending speed quantitatively, the initial speed of the bending (V_{init}) was estimated by fitting of the curvature change in a polynomial function, followed by the differential of the function at t = 0. The V_{init} values of the curvature change of the crystal having the thickness of 3.22, 4.82, 6.59, 7.36, 8.53, 9.98, 13.95, and 22.48 μm were determined to be 1.845, 0.918, 0.610, 0.549, 0.467, 0.325, 0.176, and 0.076 $\mathrm{mm^{-1}\ s^{-1}}$, respectively, using the polynomial degree of 6. This result can be theoretically explained by Timoshenko's equation (1) which is well known as a simple bimetal model illustrated in Fig. S3.[31,32]

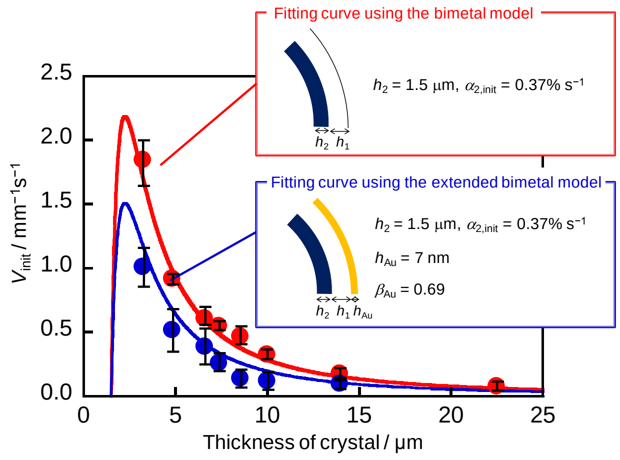

Fig. 2. Initial speed of curvature change relative to the crystal thickness before (red) and after gold deposition (blue). The solid lines show fitting curve using the bimetal model (red) and the extended bimetal model (blue). The value of error bar was obtained from the difference of the polynomial degree to determine the V_{init} in Fig. S2.

$$\mathrm{Curvature} = \frac{1}{R} = \frac{\alpha_2 - \alpha_1}{h_2}\frac{6mn(1+m)}{1+4mn+6m^2n+4m^3n+m^4n^2} \qquad (1)$$

$$= \frac{\alpha_2}{h_2}\frac{6m(1+m)}{1+4m+6m^2+4m^3+m^4} \qquad (2)$$

where R is the curvature radius, α_i (i = 1, 2) are the actuation strains, h_i (i = 1, 2) are the layer thicknesses, $m = h_1/h_2$, $n = E_1/E_2$, and E_i (i = 1, 2) are the Young's moduli. Actuation strain α means the coefficient of expansion or contraction of the layer in the absence of the other layer upon UV irradiation. In the case of diarylethene **1a**, α_2 means the coefficient of contraction because the crystal bends toward the incident UV light. In the non-photoreacted layer, the value of actuation strain α_1 is always zero because the layer cannot expand or contract. Moreover, we considered that the Young's modulus E_1 is the same as E_2 in the initial stage of the bending. As a result, the Timoshenko's equation becomes very simple, as shown in equation (2). The value of h_2 and the initial rate of α_2 ($\alpha_{2,\mathrm{init}}$) can be obtained by the best fitting curve (equation (3)) to the experimental data, as shown in Fig. 2. The values of h_2 and $\alpha_{2,\mathrm{init}}$ were determined to be 1.5 μm and 0.37% $\mathrm{s^{-1}}$, respectively. This result is similar to the other diarylethene crystals.[8,10]

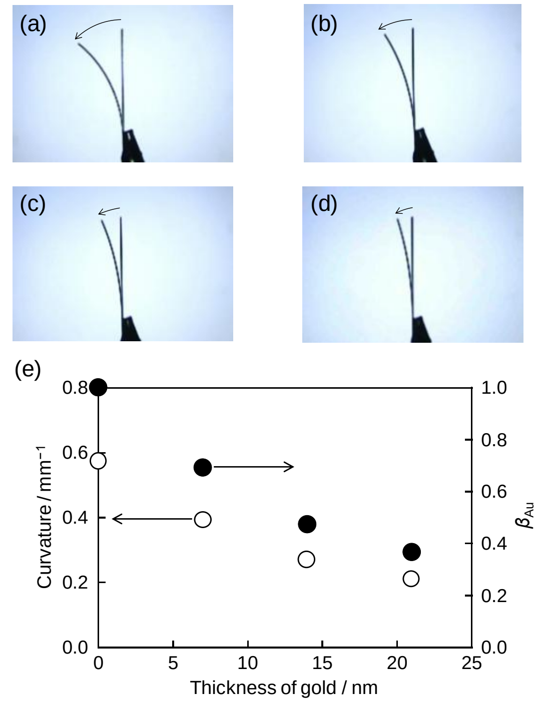

Fig. 3. Optical photograph of the photoinduced bending behavior upon irradiation with UV light for 5 s without (a) and with gold deposition with the gold thickness of 7 (b), 14 (c), and 21 nm (d), respectively. Changes of curvature and β_{Au} value relative to the thickness of gold are shown in (e): The crystal thickness is ca. 14 μm.

$$V_{\mathrm{init}} = \frac{\alpha_{2,\mathrm{init}}}{h_2}\frac{6m(1+m)}{1+4m+6m^2+4m^3+m^4} \qquad (3)$$

Next, we performed the gold deposition to the diarylethene crystals. Fig. S4 shows a gold-coated diarylethene crystal observed under transparent mode. The gold can be cleanly deposited to the crystal surface. Fig. S5 shows the relationship between the thickness of gold and the deposition time. The thickness of gold was observed by AFM. The thickness of gold after the deposition for 15, 30, 45, and 60 s were determined to be 7, 14, 21, and 28 nm, respectively. The thickness of gold increased in proportion to the deposition time. Moreover, we investigated the photoinduced bending behavior of the gold-coated diarylethene crystals. Fig. 3 shows the photoinduced bending behavior before and after the gold deposition to the crystal surface when the crystal thickness is ca. 14 μm. UV light was irradiated to the opposite side of the gold-coated layer. The curvature of the bending crystal without the gold layer was 0.572 $\mathrm{mm^{-1}}$. The curvatures of the bending crystal with the gold thickness of 7, 14, and 21 nm were 0.396, 0.271, and 0.209 $\mathrm{mm^{-1}}$, respectively. The crystal tends not to be bent with increasing the thickness of the gold layer. This is due to the large Young's modulus of the gold (83 GPa)[33] compared with that of the diarylethene crystal (ca. 3.0 GPa) which was determined by means of a manual beam-bending test,[4] as shown in Fig. S6. In order to discuss the delay of the bending due to the gold-coated layer, we introduced the β_{Au} value. The definition of β_{Au} is shown in equation (4).

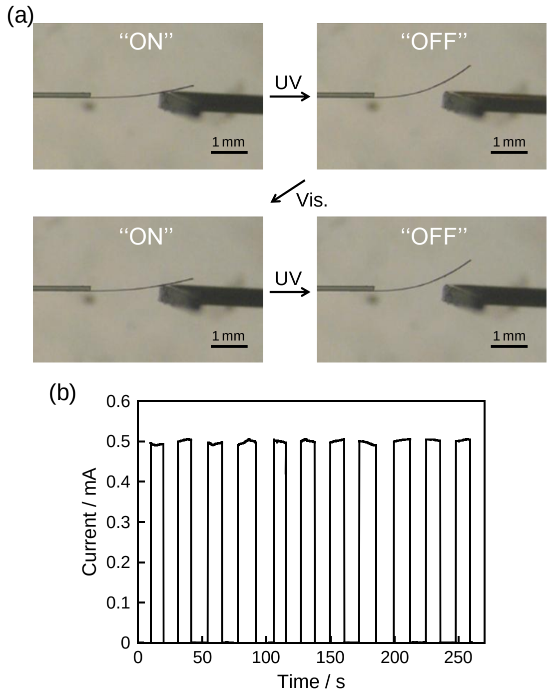

Fig. 4. Photoreversible current switching upon alternating irradiation with UV and visible light. The crystal thickness is 6.2 μm. The gold thickness is 21 nm. The applied voltage is 1.0 V. The external resistance is 2 kΩ.

$$\beta_{Au} = \frac{\text{Curvature in the presence of gold layer}}{\text{Curvature in the absence of gold layer}} \qquad (4)$$

The β_{Au} values for the crystal having the different gold thickness of 7, 14, and 21 nm were determined to be 0.69, 0.47, and 0.36, respectively, as shown in Fig. 3. This result indicates that the gold thickness brings about the delay of the bending speed and it reduces the bending motion by half in the presence of only 14 nm gold layer.

The crystal thickness dependence of the photoinduced bending behavior after the gold deposition was also investigated. The thickness of the gold was fixed to 7 nm. Fig. S7 shows photoinduced crystal bending of the gold-coated crystals having different crystal thickness. The bending speed depends on the crystal thickness as well as that of the non-coated crystals. When the crystal is thin, the crystal is bent rapidly and largely. The V_{init} values of the curvature change of the gold-coated crystals having the crystal thickness of 3.22, 4.82, 6.59, 7.36, 8.53, 9.98, and 13.95 μm were determined to be 1.010, 0.515, 0.388, 0.259, 0.139, 0.119, and 0.096 mm^{-1} s^{-1}, respectively. In order to explain the relationship between the V_{init} values and the crystal thickness, we have introduced the extended bimetal model which takes into account the effect of gold by using the β_{Au} value. The extended bimetal model consists of three component materials; the photoreacted layer, the non-photoreacted layer and the gold layer. The equation and illustration of the extended bimetal model are shown in equation (5) and Fig. S8.

$$\text{Curvature} = \frac{1}{R} = \frac{\alpha_2}{h_2}\frac{6m(1+m)}{1+4m+6m^2+4m^3+m^4} \times \beta_{Au} \qquad (5)$$

Fig. 2 shows the experimental data and theoretical calculated line by the extended bimetal model using the β_{Au} value which is obtained by the above mentioned experiment in Fig. 3. It is clarified that the experimental data can be well fitted to the extended bimetal model. This result provides a new useful strategy to design for photomechanical actuators.

Furthermore, we have demonstrated photoreversible current ON/OFF switching of an electric circuit using the gold-coated diarylethene crystal, as shown in Fig. S9. In order to flow current in stable, it is better that the gold thickness on the crystal surface is thicker. However, it was already clarified that the gold-coated diarylethene crystal tends not to bend when the gold thickness increases. Here, we estimated the appropriate gold thickness from the extended bimetal model. Fig. S10 shows the initial speed of the curvature change to the crystal thickness in different gold thickness samples calculated by the extended bimetal model. From this calculation, the gold-coated diarylethene crystal with the crystal thickness of ca. 6 μm can bend with the adequate speed as much as 0.248 mm^{-1} s^{-1} even in the gold thickness of 21 nm. Thus, we use the gold-coated diarylethene crystals with the gold thickness of 21 nm in the following experiments.

Fig. S11 shows the I-V curve of the electric circuit containing external resistance. The current value becomes large in proportion to the applied voltage. When the applied voltage was 0.8 V, the current value for external resistance of 1 and 2 kΩ were ca. 0.8 and 0.4 mA, respectively. The crystal showed no deformation even in the current value over 30 mA. This result indicates that there is no resistance in the gold-coated diarylethene crystal. Fig. S12 shows the current value to the running time. It was clarified that the current value was very stable. Fig. 4 and Video S1 shows the photoreversible current ON/OFF switching using the photoinduced bending behavior of the gold-coated diarylethene crystals upon alternating irradiation with UV and visible light. When the gold-coated diarylethene crystal was irradiated with UV light, the crystal got away from the tip of electric wire and the current cannot flow, which means the switch 'OFF'. Upon irradiation with visible light, the crystal can contact with the tip of electric wire and the current can flow again, which means the switch 'ON'. The crystals can be bent repeatedly without any breaking of the gold layer on the crystal and the current can be switched over 10 cycles only by photoirradiation. This result provides a new practical use of photomechanical crystals as a molecular crystal switch.

Conclusions

In conclusion, we investigated the photoinduced crystal bending behavior of **1a** before and after gold deposition. The crystals of **1a** showed photoreversible crystal bending upon irradiation with alternating UV and visible light before and after gold deposition. It was revealed that the relationship between the initial speed of the curvature change and the crystal thickness was well explained by Timoshenko's bimetal model and the extended bimetal model before and after gold deposition, respectively. Moreover, we have demonstrated the photoreversible ON/OFF switching of the electric circuit using the gold-coated diarylethene crystal. The current could be flowed in the gold layer on the surface of diarylethene crystal without any resistance. Furthermore, the photoreversible current switching by the photoinduced bending of the gold-coated diarylethene crystal could be repeated over 10 cycles upon alternating irradiation with UV and visible light. These findings bring about not only a new strategy to design for photomechanical actuators but also a new practical use of photomechanical crystals.

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Notes and references

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† Electronic Supplementary Information (ESI) available: detailed experimental data (Fig. S1–S12), and movie of current switching (Video S1).]. See DOI: 10.1039/b000000x/

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