Supplementary Information

Light-controlled metal deposition on photochromic polymer films

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1. Photosensitivity and photostationary state

The diarylethene molecule used in our experiment has a very small photosensitivity for ring-opening reaction. The quantum yields of ring-closure (coloring) photoreaction at 365 nm and 410 nm in toluene are 0.6 and 0.8, respectively, whereas that of ring-opening (uncoloring) reaction is around 10^{-5}. No differences of the photostationary state (PSS) were obtained for 365-nm or 410-nm irradiation, as shown in Fig. S1. The fine isomerization patterns shown in Fig. 6 (main text) were, therefore, prepared in high conversion ratio using a GaN-violet laser diode (λ=410 nm).
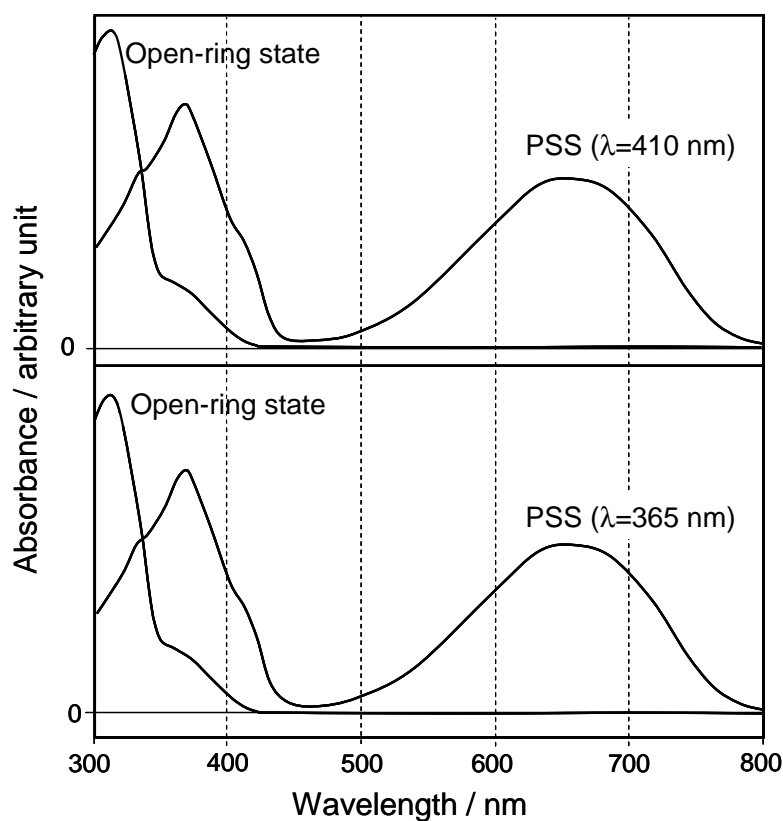

Fig. S1. Photostationary states obtained by violet (λ=410 nm) or UV (λ=365 nm) irradiation.

2. Selective Mg deposition on an amorphous diarylethene (DAE) molecular film

Amorphous DAE molecular films that prepared by vacuum evaporation show selective metal deposition. To investigate the detailed deposition selectivity on the DAE molecular surfaces, Mg was evaporated to the amorphous films with various isomerization ratios. Their absorption spectra are shown by numbers 0-6 in Fig. S2a. The colored film 6 (photostationary state, PSS) contained the colored (closed-ring) isomers of 75%. The colored and uncolored states have T_gs of 85°C and 37°C, respectively. No Mg films were formed on the films in the state of 0, 1 or 2 at a deposition rate of 0.45 nm/s. The half colored state 3, which contains the uncolored (open-ring) isomers of around 50%, shows the threshold for Mg deposition.

The Mg deposition property on the DAE molecular films shows the rate dependency (Fig. S2b). The Mg film were not formed even on the colored film at 0.28 nm/s, and was formed thinly on the uncolored film at a rate of 3.8 nm/s. These results indicate that the density of Mg atoms on the surface influences Mg film formation, and that the Mg film formation is affected by nuclear formation via diffusion and collision of Mg atoms on the surface.

Figure S2c shows the difference of Mg deposition between on the amorphous and crystallized uncolored films. This indicates indirectly that the surface molecular motion influences Mg deposition. The partially crystallized uncolored films before Mg deposition (upper figures) were observed under transmitted white light through crossed polarizer, and therefore, crystallized areas are looked like a white color. The samples after Mg deposition (bottom figures) were observed by transmitted white light and Mg deposited areas are in black color. Mg didn't deposit on the uncolored amorphous film with a low T_g at a deposition rate of 2.2 nm/s or less. However, Mg film was formed easily on the crystal areas than on the amorphous areas despite the same isomerization

state. Because the DAE molecules in the crystal state are in a less-active state than those in the amorphous state, Mg atoms on the crystal are hard to desorb. These results obtained in Fig. S2a-c are consistent with the results reported for another DAE [See ref. 10 in the main text].
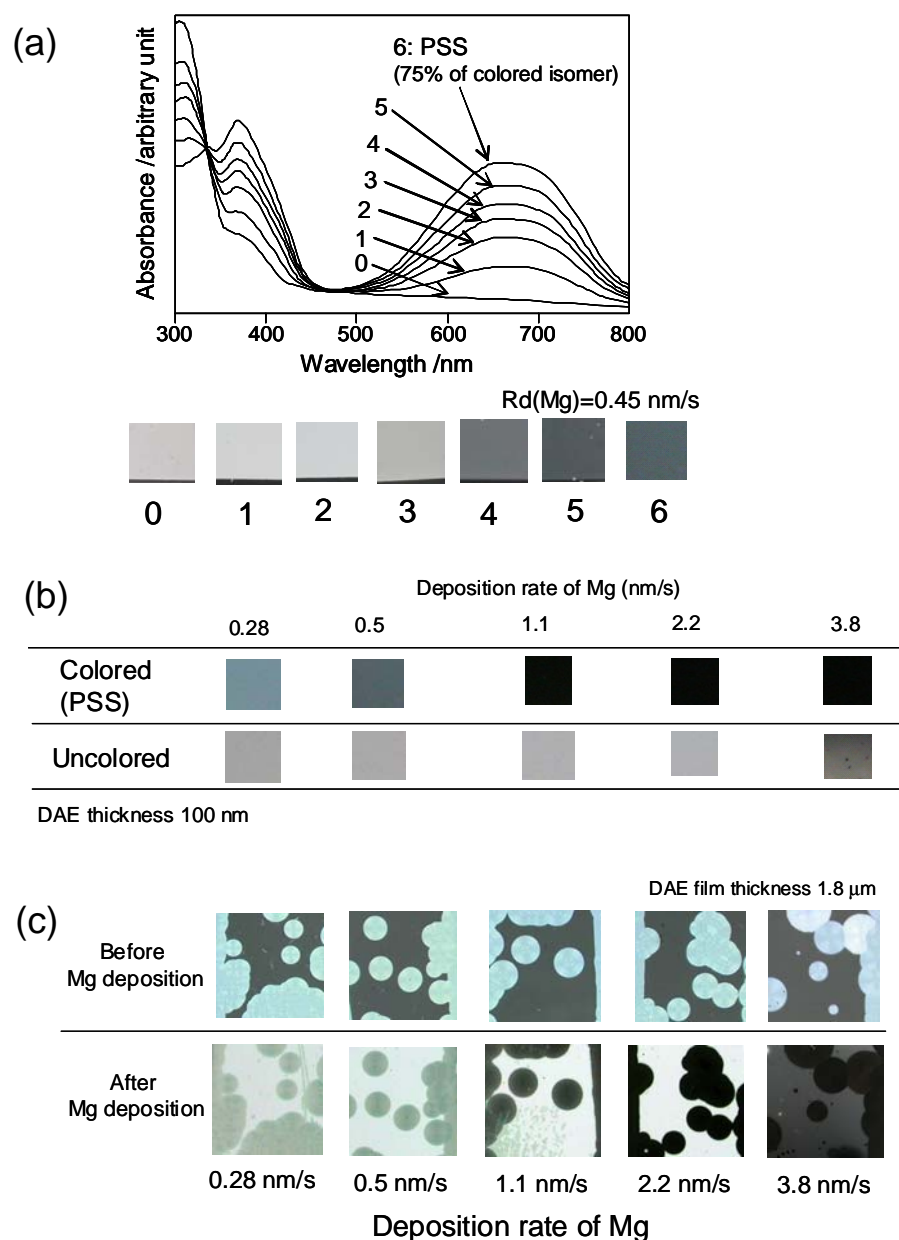

Fig. S2 (a) Absorption spectra of amorphous DAE films with various isomerization ratios and their Mg deposition properties. (b) Deposition rate dependence of selective Mg deposition on the amorphous DAE films. (c) Difference of Mg deposition property between the uncolored amorphous and crystallized DAE surfaces.

3. T_g change of DAE-doped polymer films

When polystyrene (PS) was doped with DAE, the glass transition temperature (T_g) changed depending on the DAE concentration. The original T_g of PS was 100^oC, while the DAE-5%-doped PS films in the colored and uncolored states were 97 and 95^oC, respectively (Fig. S3(a)). The original T_g's of the colored and uncolored states of pure amorphous DAE were 37 and 85^oC, respectively. According to photoisomerization, the T_g change of the DAE-5%-doped PSs was quite insufficient to achieve selective metal deposition. Figure S3(b) shows the concentration dependence of T_g for the uncolored DAE-doped PS. A large T_g change requires a large amount of uncolored DAE doping: more than 50%.

Figure S4 shows the deposition properties of Mg on the PS films with various concentrations of DAE molecules. These PS films were prepared by casting a cyclohexanone-solution containing DAE and PS on the glass substrate and drying at 110^oC for one hour. Only the DAE-50%-doped PS film showed selective Mg deposition. Such a high concentration, however, might cause deterioration in such polymers characteristics as the mechanical, thermal and/or electrical properties.
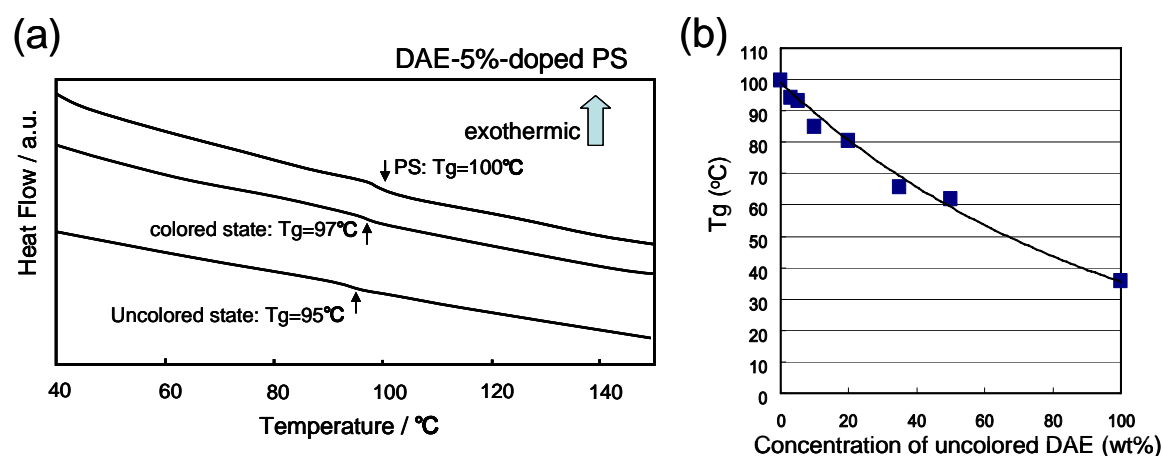

Fig. S3 (a) Differential scanning calorimetry of polystyrene (PS) and DAE-doped PS. (b) Concentration dependence of glass transition temperature for uncolored DAE-doped PS films.
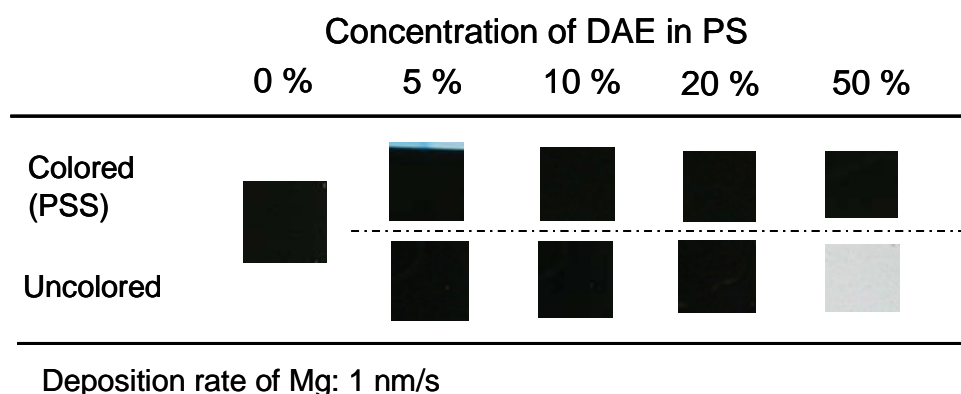
Concentration of DAE in PS

	0 %	5 %	10 %	20 %	50 %
Colored (PSS)					
Uncolored					

Deposition rate of Mg: 1 nm/s

Fig. S4 Mg deposition property of DAE-doped PS. These PS films were dried at 110°C for one hour. Samples were observed by transmitted white light, and the Mg deposited areas look black.

4. AFM images of Mg crystals on polymer films

Surface polymer chains have larger mobility than those inside (refs. 27 and 28 in main text). The large mobility of surface chains can cause active diffusion and enhanced Mg crystal growth. Figure S5 shows atomic force microscopy (AFM) images of Mg crystals on the PS films. The Mg crystals on the 60°C-sample are larger than those on the 110°C-sample, meaning the Mg atoms on the 60°C-sample diffuse more actively than those on the 110°C-sample.
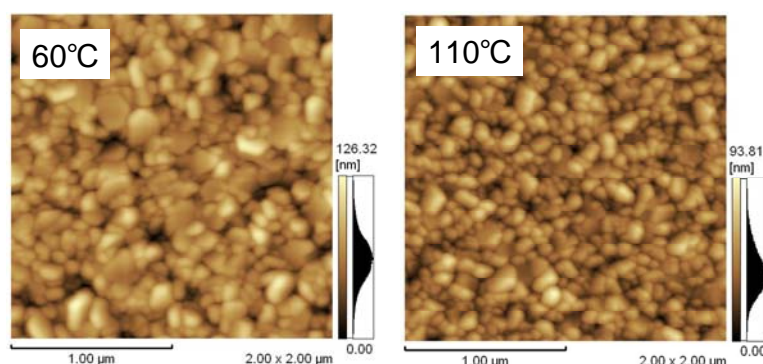
Fig. S5 AFM images of Mg crystals on PS films prepared at 60 and 110°C for one hour.

5. Solvent effect in Mg deposition on polymer films

As mentioned in the main text, the drying temperature dependence of Mg deposition suggests the existence of a critical temperature related to the materials, such as the boiling temperature (T_{bp}) (reflecting vapor pressure) of the solvent or the T_g of the polymer. To test the solvent effect, especially, its T_{bp} effect of the polymer solvent, we investigated Mg deposition on the PS films prepared using the solutions of trichlomethane ($T_{bp}=62^{o}C$), cyclohexanone ($T_{bp}=156^{o}C$), and their mixture. Figure S6 shows the Mg deposition properties on the PS films prepared by casting the solutions on a glass substrate. A thick Mg film was formed on all the PS films prepared at a drying temperature of $120^{o}C$, but it was formed thinly at $60^{o}C$. This result indicates that the Mg deposition property on polymer films does not depend on the solvent and that a variety of solvents can be used to prepare the polymer film. Furthermore, the result also suggests that the thin Mg deposition effect originates in the relation between the drying temperature and the T_g of the polymers.

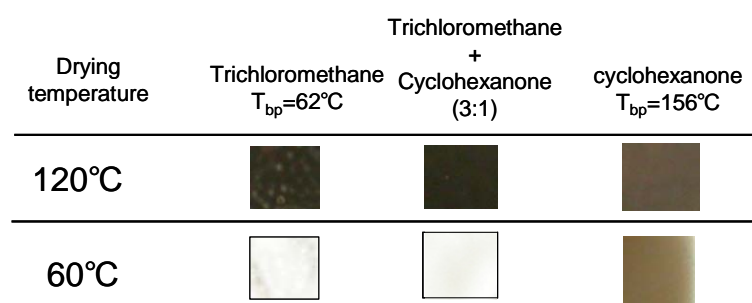| Drying temperature	Trichloromethane $T_{bp}=62°C$	Trichloromethane + Cyclohexanone (3:1)	cyclohexanone $T_{bp}=156°C$
120°C			
60°C			

Fig. S6 Solvent dependence of Mg deposition on pure PS films.

6. Mg deposition property on pure semiconductor polymer films

Figure S7 shows the deposition rate and the drying condition dependences of Mg deposition on pure poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) films, one typical semiconductor polymer. The MEH-PPV films were

prepared by casting the cyclohexanone solution on glass substrates and drying them at various temperatures. Then Mg was evaporated on the films at a variety of the deposition rates. As a result, Mg was deposited on all films at a deposition rate of 5 nm/s, but it was not deposited on the films prepared at temperature below 160°C at a deposition rate below 1 nm/s. The same tendency of Mg deposition on the PS films was observed.

The Mg deposition property for a Poly(N-vinylcarbazole) (PVCz, another typical semiconductor polymer) film was also investigated. Figure S8 shows deposition rate and drying condition dependences of Mg deposition on pure Poly(N-vinylcarbazole) (PVCz) films. The samples were prepared by the same manner in the main text. Mg was deposited thinly only on the film dried at 60°C at a rate of 0.35 nm/s. This result is the same tendency but the absolute value of the deposition rate for thin Mg deposition is significantly different from those for PS and MEH-PPV.
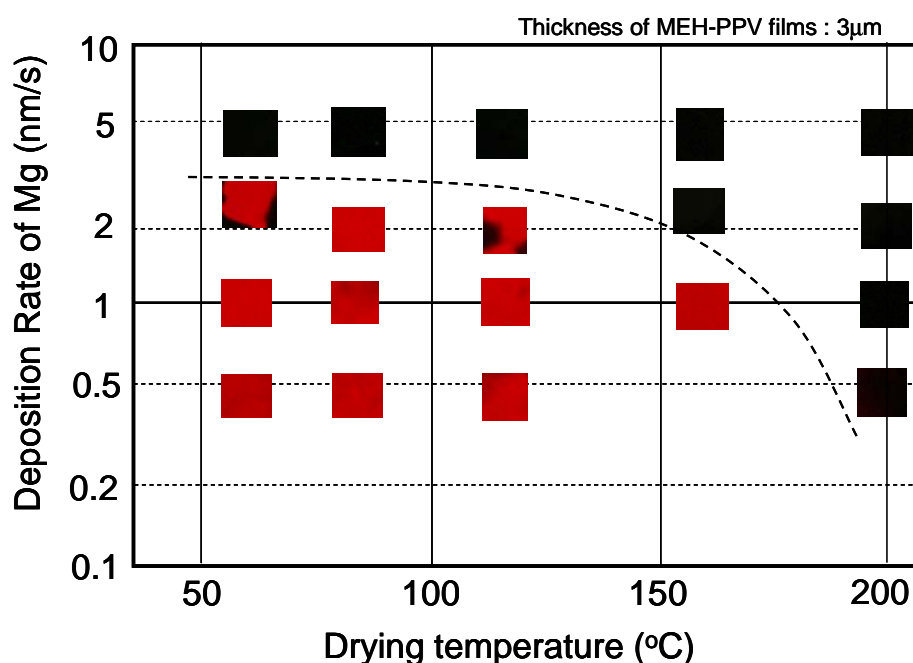

Fig. S7 Deposition rate and drying temperature dependences of Mg deposition properties on pure MEH-PPV films. Black and red areas mean deposition and non-deposition of Mg, respectively.
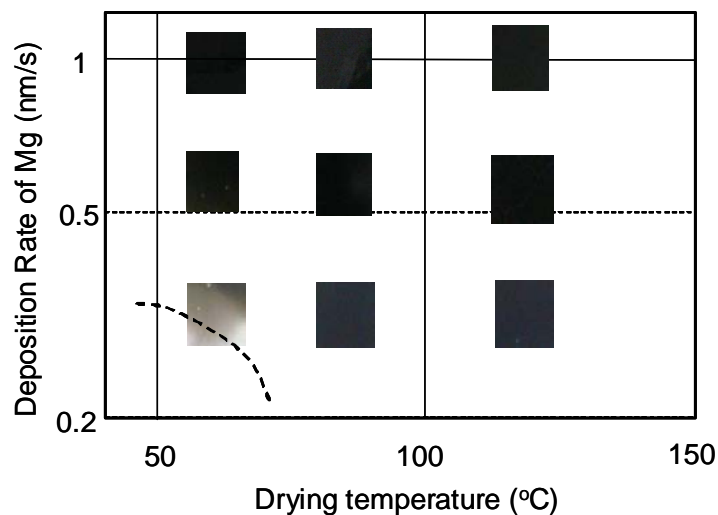
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Fig. S8 Deposition rate and drying temperature dependences of Mg deposition on pure PVCz films.

7. Mg deposition on the DAE-doped polymer films

Figure S9 shows detailed data of the deposition rate and the DAE concentration dependences of Mg deposition on the DAE-doped PS films. All DAE-doped PS films were dried at 60°C for one hour. Black color indicates Mg deposited area and white undeposited. Selective deposition was achieved for all samples at deposition rates of 0.4nm/s and 1.0 nm/s. However, the Mg films were formed on the both isomerization states even for the DAE-50%-doped sample at a deposition rate of 6.0 nm/s. This indicates that the Mg deposition property is depending on many parameters including the DAE concentration, the isomerization state, the drying condition and the deposition rate of Mg.
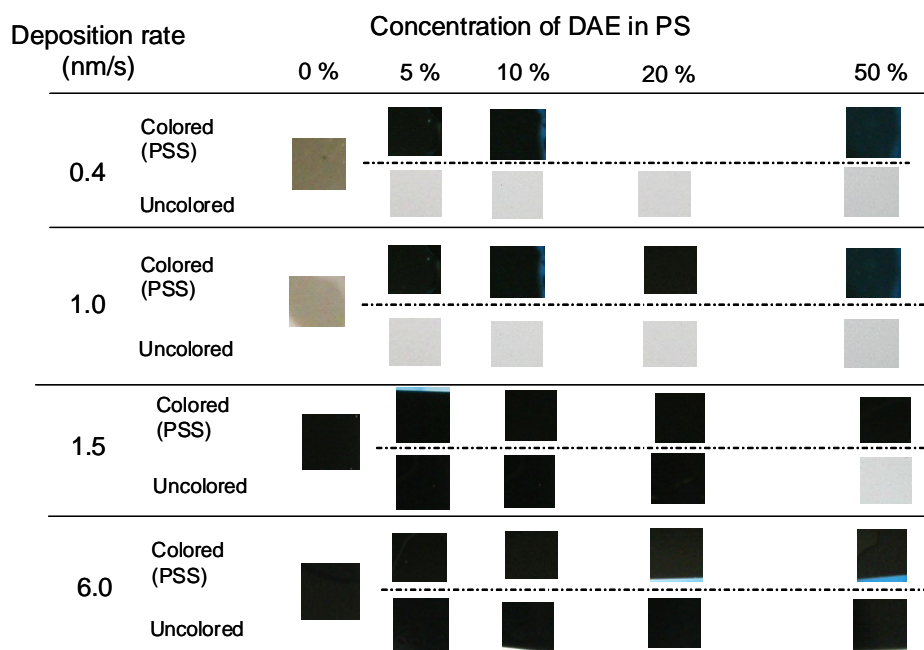
Fig. S9 Detailed Mg deposition properties of DAE-doped PS films.

8. Contact angle of a water droplet on the photochromic surfaces

Figure S10 shows contact angles of a water droplet on the amorphous DAE molecular films (top) and on the DAE-5%-doped PS films dried at 60°C for one hour (bottom). No significant differences of the angle were observed, meaning that the deposition selectivity is not related to the surface energy.

DAE molecular surface

Uncolored surface: 91°   Colored surface: 90°

DAE-5%-doped PS surface
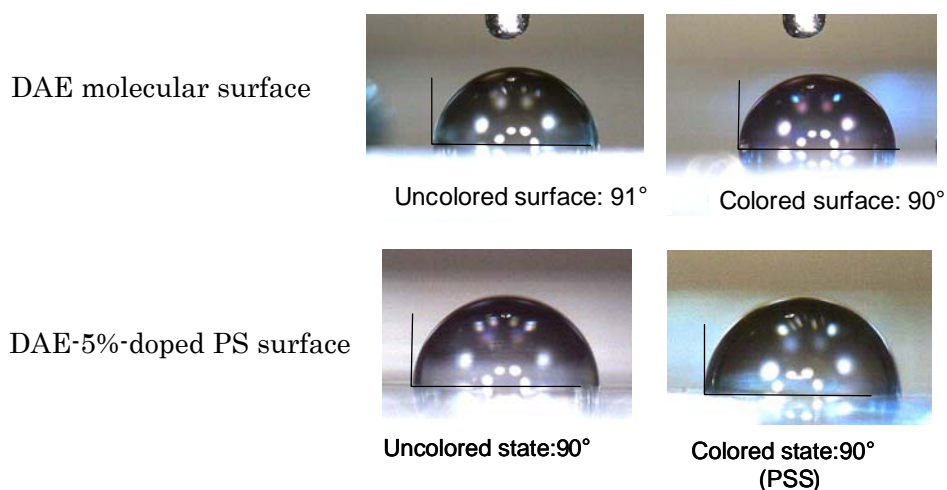
Uncolored state:90°   Colored state:90°
(PSS)

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Fig. S10 Contact angles of a water droplet on photochromic surfaces.