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Optical switching of carrier transport in polymeric transistor with photochromic spiropyran molecules

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1. Atomic force microscope images of the SP-PTAA thin films

The AFM images of the SP-PTAA thin films. Smooth surface morphologies were observed from pristine PTAA and SP-PTAA blended films up to 50 wt. %. Drastic increase in the surface roughness (RMS value) was observed from the blended film with 70 wt% SP as a clear evidence of aggregation. All images were recorded in intermittent contact (tapping) mode under ambient conditions.

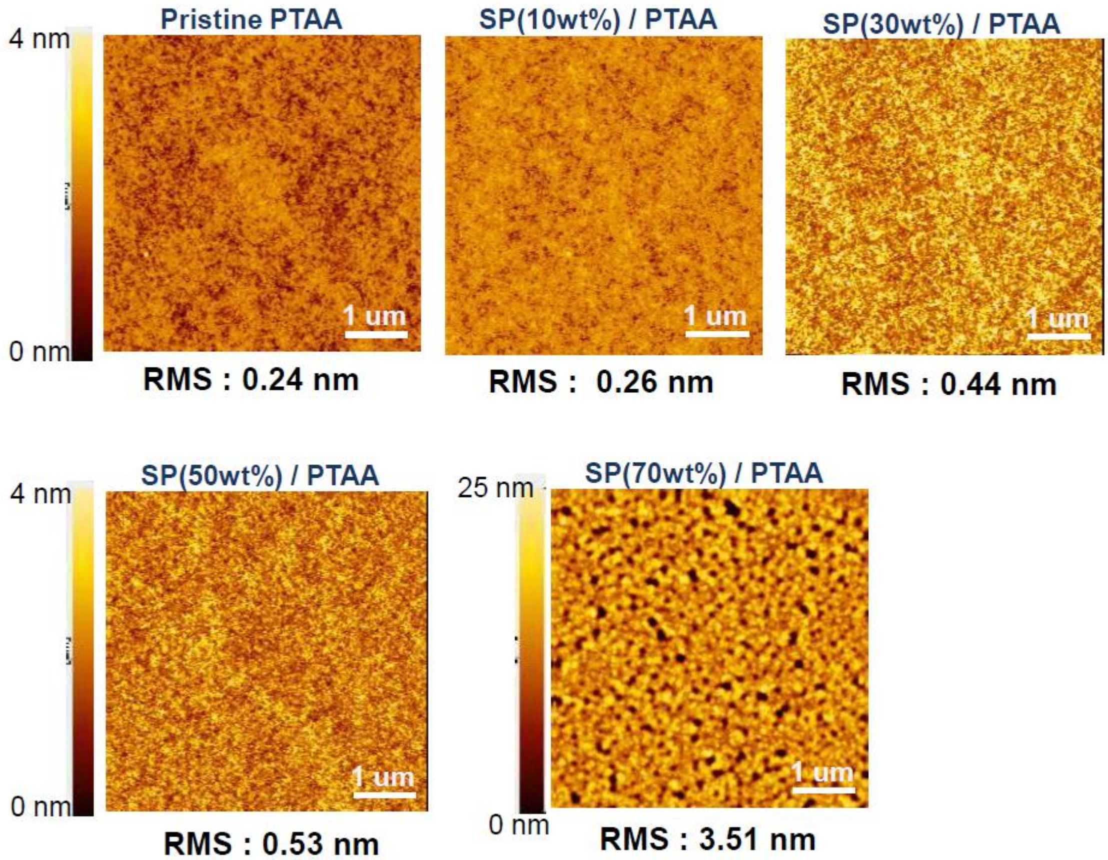

Fig. S1. AFM images of the SP-PTAA thin films containing different compositions of 0, 10, 30, 50, 70 wt% SP.

2. Transistor characteristics of pristine PTAA film

The transistor characteristics of a pristine PTAA film were examined as a reference for the ST-PTAA transistor. The device structure and measurement conditions were the same as those used for the SP-PTAA transistor.

Figure S2 (a) shows the output characteristics under dark conditions. The output curve confirmed that the pristine PTAA film worked as a p-type transistor. Figure S2 (b) shows the transfer characteristics. The on/off ratio, carrier mobility (μ) and threshold voltage (V_{th}) were estimated to be 1.0 $\times 10^4$, 2.8 $\times 10^{-4}$ $cm^2V^{-1}s^{-1}$ and -6 V, respectively. These values are almost the same as those of the SP-PTAA transistor (Fig. 2), revealing that the closed-ring SP molecules had no influence on the transistor properties.

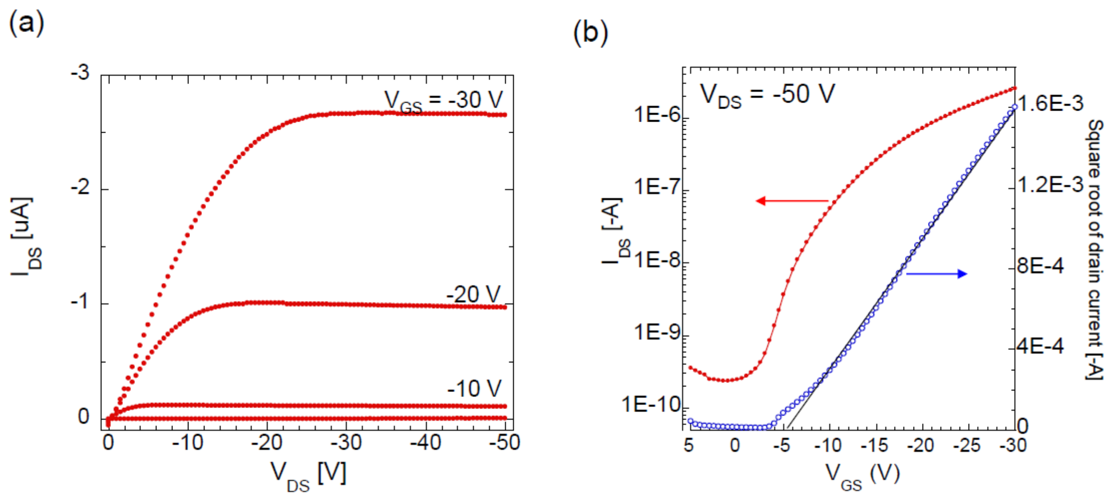

Fig. S2. (a) Output characteristics and (b) transfer characteristics (V_{DS} = -50 V) of a pristine PTAA transistor.

3. Effect of light irradiation on transfer characteristics of pristine PTAA transistor

Figure S3 shows the transfer characteristics at a constant drain bias voltage (V_{DS}=-50V) with UV and VIS irradiation. The irradiation time was fixed at 30 min. No variation in the drain current was observed, indicating that a pristine PTAA transistor experiences no photocurrent or photo-oxidation as a result of light irradiation.

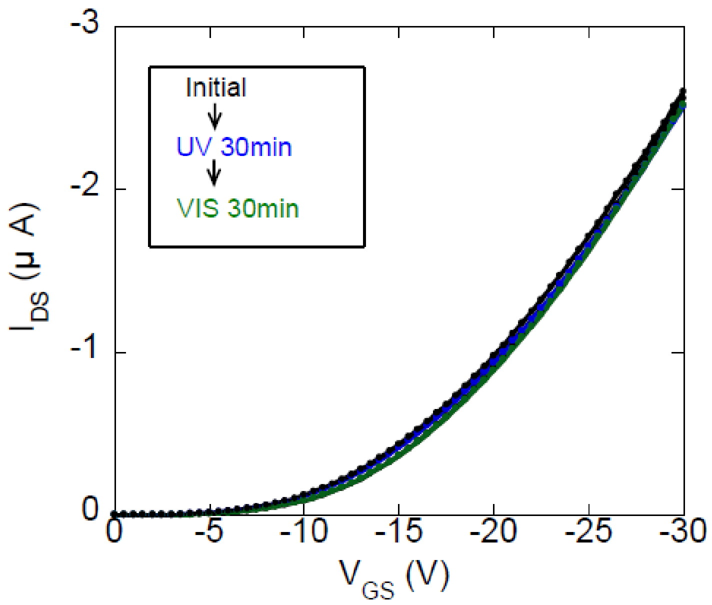

Fig. S3. Persistent transfer characteristics (V_{DS} = -50 V) of a pristine PTAA transistor with alternate UV and VIS light irradiation.

4. Effect of thermal relaxation of open-ring isomer on absorption and transfer characteristics

An open-ring SP (ionic polarized state) is known to change into a closed-ring SP via thermal relaxation. To confirm the effect of the thermal relaxation of SP, we evaluated the absorption and transfer characteristics of the SP-PTAA film.

Figure S4 (a) shows the change in the UV-VIS spectra of SP-PTAA film on a quartz substrate. Initially, an open-ring isomer was formed by 30 min of UV light irradiation. The absorption peak at a wavelength of 550 nm disappeared after 10 hours at room temperature, revealing that the open-ring SP was transformed into a closed-ring SP by thermal relaxation.

Figure S4 (b) shows the change in the transfer characteristics at a constant drain bias voltage (V_{DS}=-50 V). I_{DS} returned spontaneously to its original value after 10 hours at room temperature. This result supports our discussion, namely that the optical switching in the drain current was induced by the photoisomerization of the SP.

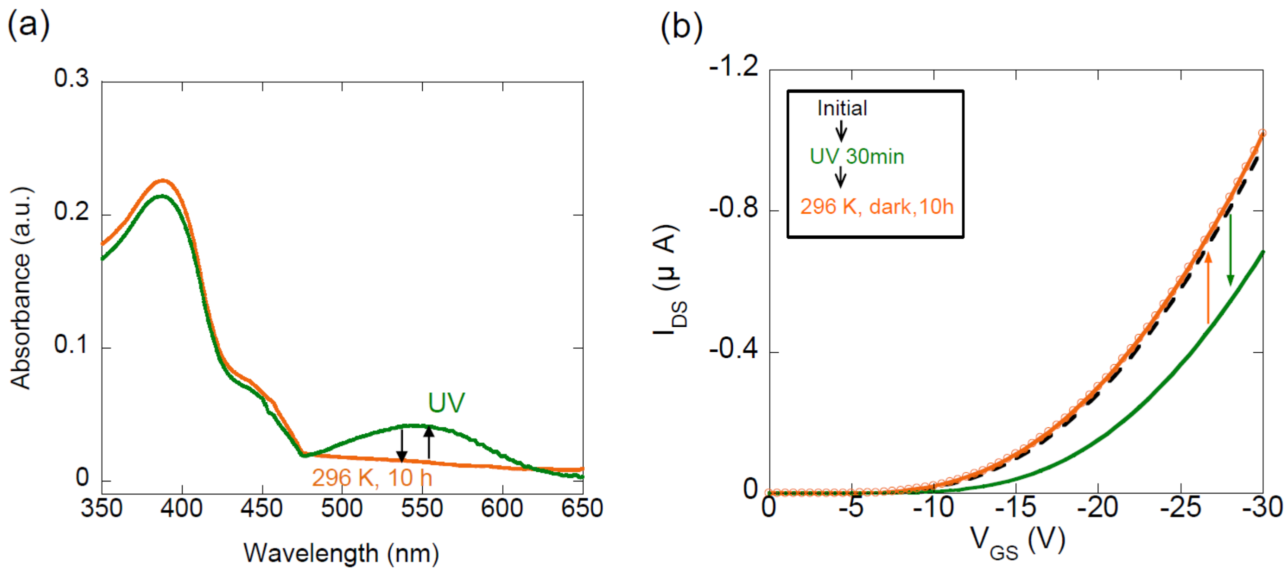

Fig. S4. (a) UV-VIS spectra of the SP-PTAA thin film on a quartz substrate. (b) The change in transfer characteristics (V_{DS} = -50 V) of the SP-PTAA transistor. The transfer characteristic returned to its initial value after 10 hours at room temperature.

5. Calculation for percent conversion of SP molecules

Photochromism is defined as a reversible change in a chemical species between two forms. To calculate the percent conversion (*x*) of SP molecules from SP-close (A) to SP-open (B), a semiempirical approach is used.[20]

$$A \underset{K_{(vis)} + K_{(dark)}}{\overset{K_{(UV)}}{\rightleftharpoons}} B$$

The change in concentration of SP-open (B) with time can be simply given by the following rate equation: $-dB/dt = K_{(visible)}B - K_{(UV)}A + K_{(dark)}B = K_{(visible)} A_0x - K_{(UV)}A_0(1 - x) + K_{(dark)} A_0x$ where A and B are the concentrations of SP-close and SP-open, $K_{(UV)}$ and $K_{(visible)}$ are the photochemical rate constants, $K_{(dark)}$ is the thermal rate constant for conversion from SP-open to SP-close, and A_0 is the total concentration of all the SP molecules. The percent conversion (*x*) of SP molecules from SP-close to SP-open can be calculated through the following relationship:

$$x = \frac{K_{(vis)}}{K_{(vis)} + K_{(UV)} + K_{(dark)}} \cong \frac{K_{(vis)}}{K_{(vis)} + K_{(UV)}}$$

In polymer matrix, the thermal conversion from SP-open (B) to SP-close (A) is negligible; we can presume the above equation.

In the case of SP in PTAA matrix, the rate constants for each process are calculated to be $K_{(UV)} = \sim 2.25 \times 10^{-4}\ s^{-1}$and $K_{(visible)} = \sim 1.12 \times 10^{-4}\ s^{-1}$ (Figure S5). As a result, the calculated percent conversion (*x*) of SP molecules from SP-close to SP-open is estimated to be about 33.2 %.

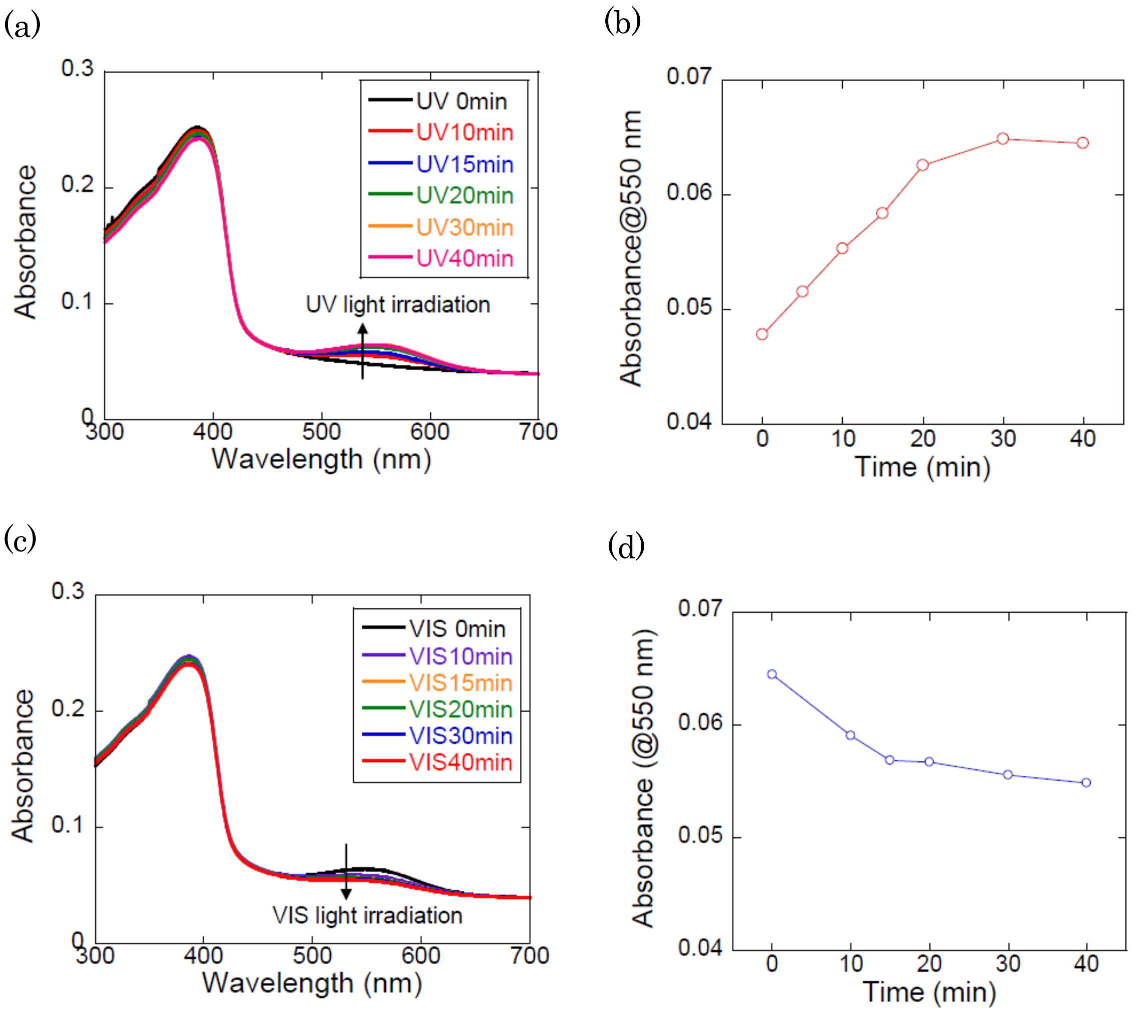

Fig. S5. The gradual transition of the UV-VIS absorption spectra of SP-PTAA thin film on a quartz substrate under UV ((a) and (b)) and VIS ((c) and (d)) irradiation.

6. Transistor characteristics of SPO-PTAA film

The transistor characteristics of SPO-PTAA film were examined as a reference for the SP-PTAA transistor. The device structure and measurement conditions were the same as those for the SP-PTAA transistor.

Figure S6 (a) shows the output characteristics under dark conditions. The output curve confirmed that the SPO-PTAA film worked as a p-type transistor. Figure S6 (b) shows the transfer characteristics. The on/off ratio, carrier mobility (μ) and threshold voltage (V_{th}) were estimated to be 1.0×10^3, 4.0×10^{-4} $cm^2V^{-1}s^{-1}$ and -5 V, respectively. These values are comparable to those of the pristine PTAA transistor (Fig. S2), revealing that the closed-ring SPO molecules had no influence on the transistor properties.

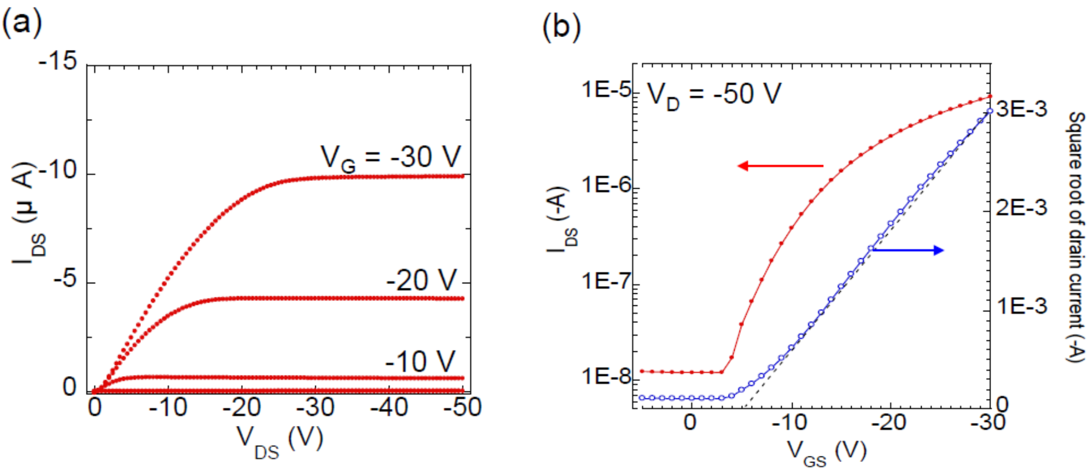

Fig. S6. (a) Output characteristics and (b) transfer characteristics (V_{DS} = -50 V) of the SPO-PTAA PTAA transistor.