Electronic Supplementary Information (ESI)

Two-dimensional conjugated polymers with weakened interlayer interaction for high-sensitive visible responsiveness to compression stresses

Yui Takeuchi, Hiroaki Imai, Yuya Oaki*

Department of Applied Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan.

E-mail: oakiyuya@applc.keio.ac.jp

Contents

Experimental Methods

Preparation of the layered PDAs. The following monomers were used as purchased without purification: 10,12-pentacosadiynoic acid (PCDA, TCI, 97.0 %), 1-(10,12-pentacosadiynyl)pyridinium bromide ($PCPy^+Br^-$, TCI), 1-bromo-10,12-pentacosadiyne (PCBr, TCI, 96.0 %), and 10,12-Pentacosadiyn-1-ol (PCOH, TCI, 98.0 %). Precursor solution containing 30 mg of these monomers was prepared with 4 cm^3 chloroform (Kanto, 99 %) for PCDA and $PCPy^+Br^-$ and ethanol (Kanto, 99.5 %) for PCBr and PCOH. In the solution, the already polymerized red precipitate was removed by filtration using a filter paper. A piece of filter paper (quantitative grade, 5C, 10 × 20 mm) was dipped for 30 s in the precursor solution and dried at room temperature. The precipitate was obtained by the evaporation of the solvent from the precursor solution and then dried at room temperature. The precipitate and monomer-coated paper were polymerized with the irradiation of UV light (254 nm, 6 W) for ca. 30 s on a temperature-controlled stage set at 20 °C.

Structural characterization. The layered structures were analyzed by Fourier-transform infrared spectroscopy (FT-IR, Jasco FT-IR 4200) and X-ray diffraction (XRD, Bruker D8 Advance) with Cu-Kα radiation. The precipitates were used for these analyses. The polymerization behavior of the monomers was analyzed using the precipitates by Raman spectroscopy (Renishaw, In-via Raman) with the excitation light 785 nm. The precursor solution was dropped on a cleaned silicon substrate. After the evaporation, the precipitate was used for Raman analysis. The morphologies were observed by optical microscopy (Keyence, VHX-970FN) and SEM (Carl Zeiss, MERLIN Compact) operated at 5.0 kV.

Thermoresponsive color-change properties. The PDA-coated papers were heated and cooled using a temperature-controlled stage (As-One, cool plate) and the photographs were taken using a smart phone (iPhone 14). The red-color intensity (x) was calculated from the RGB values of the photographs using a software for image analysis (Image J) by Eqns, S1 and S2. An increment of the x was calculated based on the initial x (x_0) at 20 °C. The thermoresponsive structure change was analyzed by differential scanning calorimetry (DSC, Shimadzu DSC-60 plus) under nitrogen atmosphere. A spectrophotometer (Jasco V-670) was used to measure UV-Vis spectra of the PDA-coated papers. The spectrum was measured on the paper substrate by diffuse-reflectance method using an integrated sphere. The bare filter paper was used as the baseline.

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} 0.4124 & 0.3576 & 0.1805 \\ 0.2126 & 0.7152 & 0.0722 \\ 0.0193 & 0.1192 & 0.9505 \end{bmatrix} \begin{bmatrix} R \\ G \\ B \end{bmatrix} \quad \dots \text{(Eqn. S1)}$$

$$(x, y) = \left(\frac{X}{X+Y+Z}, \frac{Y}{X+Y+Z} \right) \dots \text{(Eqn. S2)}$$

Imaging and measuring the compression stresses. Compression stresses were applied to the PDA-Py$^+$Br$^-$ paper device using a table-top tensile tester (Shimadzu EZ-LX). Compression force (F / N) in the range of 10–500 N was applied to the paper device (10 × 20 mm) via a metal probe. As the tip of the probe as the contact area was 2 × 2 mm (= 4 mm^2), the corresponding compression stresses (P / Pa) applied to the samples were in the range of 2.5 and 125 MPa. After the compression, the photograph was taken using a smart phone (iPhone 14). The compression experiment was carried out on three different paper devices for the reproducibility. An increment of x (Δx) was calculated by the method same as that of the thermoresponsive color changes. Two metallic stamps were attached on the probe for the imaging experiment. The compression was applied to the paper substrate (8 × 8 mm) at 500 N. The image analysis was performed in each divided area 0.25 × 0.25 mm.

Calculation of P from Δx.[10] When the tester applies the compression force (F / N) on the contact area (A / m^2) with the coating of PDA-Py$^+$Br$^-$, the applied pressure (P / Pa) is described by the following (Eqn. S3).

$$P = \frac{F}{A} \quad \dots \text{(Eqn. S3)}$$

In the compressed area, the change in Δx has a linear relationship with P as described using (Eqn. S4).

$$\Delta x \propto P \quad \dots \text{(Eqn. S4)}$$

Here the relationship between P and Δx is prepared with the standardizing by unit area to use the standard curve for estimating the unknown P. The relationship between Δx and P is described by (Eqn. S5), *i.e.* the standard curve in Fig. 4a, where a and b are the constants for the device.

$$\Delta x = aP + b \quad \dots \text{(Eqn. S5)}$$

The colorimetrically estimated P can be converted to F with multiplying by area using (Eqn.

S3). If F is not standardized by A, the standard curve is not used to estimate the unknown compression experiment on the different area.

Anion exchange of PCPy⁺Br⁻. Powder of 20 mg PCPy⁺Br⁻ was dissolved in 5 cm³ acetone and then anion-exchange resin (Amberlite IRA-900J Cl) ca. 5 cm³ was added in the solution. After 24 h, the resin was removed with the filtration. The white powder of PCPy⁺Cl⁻ was obtained after evaporation of the solvent at room temperature. The polymerization was carried out with the irradiation of UV light (254 nm, 6 W) for 10 s. Powder of 10 mg PCPy⁺Br⁻ was dispersed in 0.50 cm³ purified water. The dispersion liquid was poured in an aqueous solution (0.50 cm³) containing 4.4 mg of sodium tetrafluoroborate (NaBF₄, TCI, 98.0 %) or 7.4 mg of potassium hexafluoroborate (KPF₆, TCI, 98.0 %). Then, the dispersion liquid was sonicated for 60 min. The precipitates of PCPy⁺BF₄⁻ and PCPy⁺PF₆⁻, were collected after the filtration. UV light (254 nm, 6 W) was irradiated to these samples for 60 s. The molar ratio of these guest anions to the interlayer Br⁻ was set at 2.

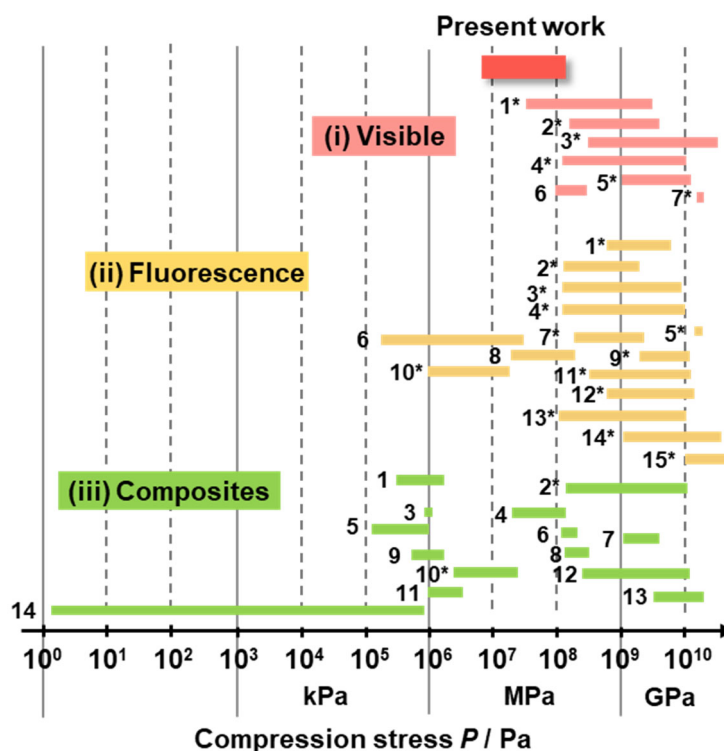**Summary of color-changing materials in response to compression stresses**

Fig. S1. Detection range of compression stresses using stimuli-responsive color-changing materials in previous works.[3–5] (i) Visible detection without UV-light excitation and matrix polymer. (ii) Fluorescent detection without matrix polymer. (iii) Visible and/or fluorescent detections using the composites of chromophore and matrix polymer. The notes (i)-1–7, (ii)-1–15, and (iii) 1–14 corresponds to the references 3a–g, 4a–o, and 5a–g, respectively. The literatures with asterisks used the isotropic compression, such as diamond anvil cell and hydrostatic pressurization. The other literatures without asterisk used uniaxial compression.

PDA-Py$^+$Br$^-$ exhibited the highest sensitivity to compression stresses in mechanoresponsive materials for visible detection without UV-light excitation and matrix polymer (Group (i) in Fig. S1). The use of matrix polymer is not detrimental as a sensing device. On the other hand, matrix polymer assists to achieve the responsiveness of the mechanophore molecules and/or materials. A fundamental study on the mechano-responsiveness of the material itself is required to understand the structure-property relationship. Mechano-responsive fluorescent materials are

used with the UV-light excitation. The isotropic emission may cause lowering the spatial resolution for the distribution mapping. In addition, the detection of weak stresses is a challenging target because the microscopic molecular motion should be induced by the macroscopic weak force. Therefore, in the present work, we focus on the detection of weak compression stresses without the use of excitation light and matrix polymer.

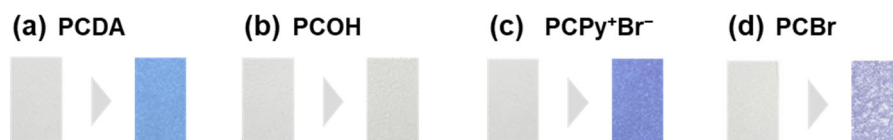**Photographs of the polymerization behavior**

Fig. S2. Photographs of PCDA (a), PCOH (b), PCPy$^+$Br$^-$ (c), and PCBr (d) coatings on a filter paper before (left) and after (right) the UV-light irradiation.

The monomers were deposited on a filter paper with dipping in the precursor solution (See Experimental method in P. S2–S3). The color change to blue was not observed for PCOH even with the UV-light irradiation (254 nm) for 60 s (Fig. S2b), whereas the other DA monomers showed the color change to blue.
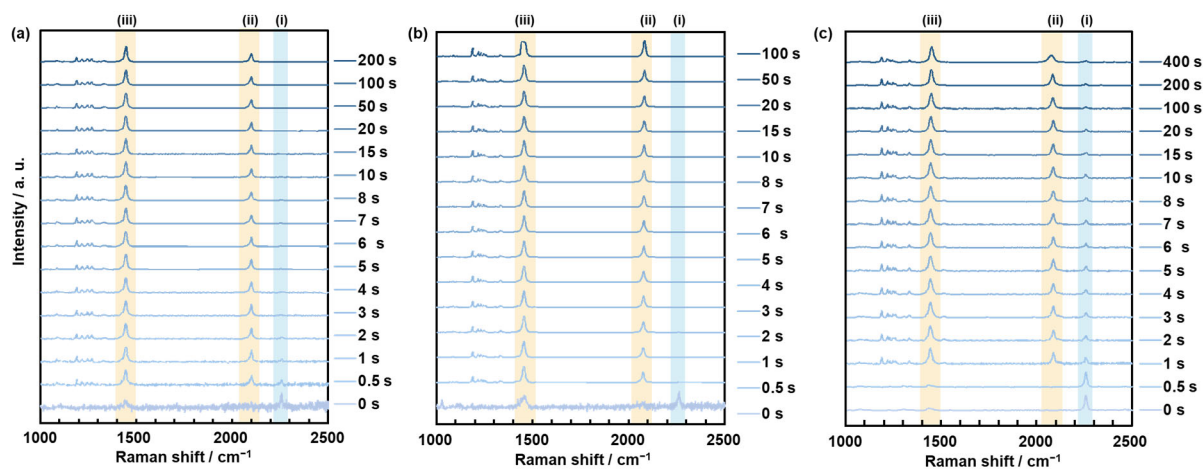
Raman spectra

Fig. S3. Raman spectra of PCDA (a), PCPy$^+$Br$^-$ (b), and PCBr (c) with the irradiation of UV light.

The peak-intensity ratio ($R = I_p / I_m$) of the peak (iii) (intensity I_p) to peak (i) (intensity I_m) was used to study the polymerization behavior in Fig. 2d. The sample was prepared by dropping the solution containing the monomers on a cleaned silicon substrate.
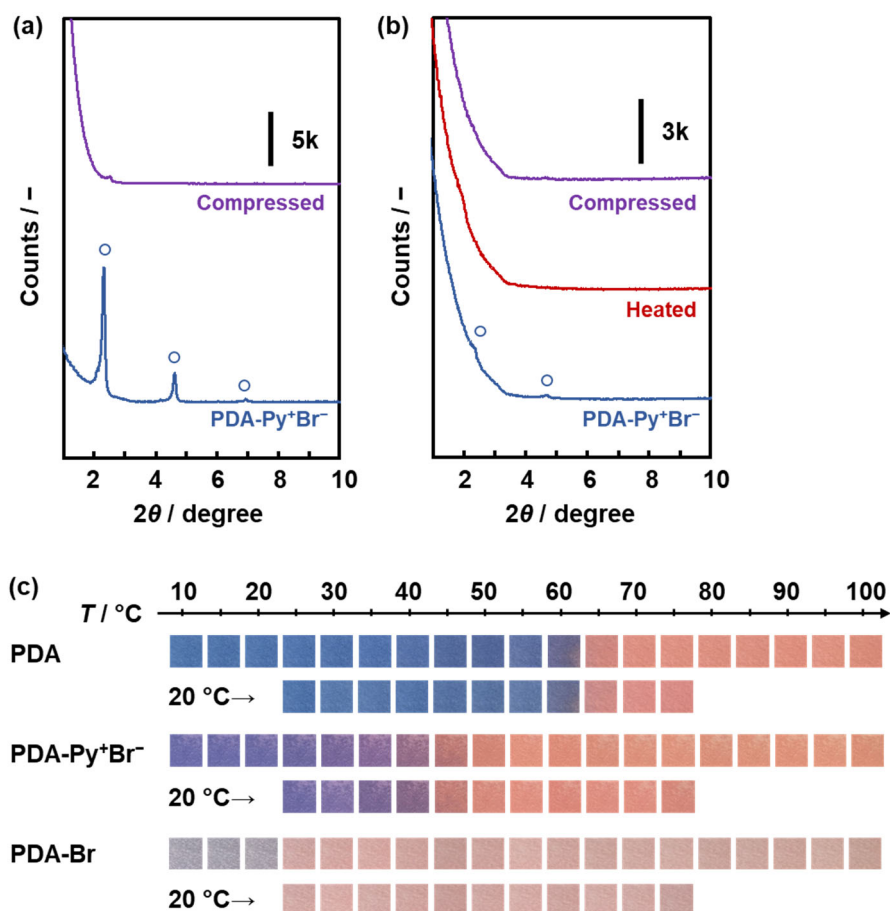
Irreversible color-change properties

Fig. S4.   Additional structural analyses and irreversible color-change properties. (a) XRD patterns of the PDA-Py$^+$Br$^-$ powder samples before and after the application of compression stress. (b) XRD patterns of the PDA-Py$^+$Br$^-$ samples coated on the paper substrate before and after the application of thermal and compression stresses. (c) Thermoresponsive color-change properties with heating at T = 10–100 °C (upper rows) and subsequent cooling at T = 20 °C (lower rows).

The same XRD peaks characteristic of the layered structure were observed for both the powdered and its coated states of PDA-Py$^+$Br$^-$ (the circles in Fig. S4a,b). The peak weakening is caused by the decrease in the sample amount on the paper substrate. In our previous works,[9a,12b] the layered PDA with the intercalation of the guest molecules had the same structures both in the powdered and coated states. In addition, SEM images showed the same sheet-like morphologies of the PDA crystals (Fig. 3). Therefore, we concluded that the same layered PDA-Py$^+$Br$^-$ was formed in both the powdered and coated states.

The XRD peaks corresponding to the layered structure were weakened and broadened for

the PDA-Py$^+$Br$^-$ powder with the application of compression stress (Fig. S4a). In the coated state, the peaks disappeared after the application of the thermal and compression stresses (Fig. S4b). In these demonstrations, the compression stress with the sufficient strength (5 ton) was applied to both the powdered and coated samples in the area around 2-cm square using an oil hydraulic press. The coated sample was heated at 70 °C for ca. 1 min. The samples were heated $T = 25$–75 °C and then cooled at $T = 20$ °C. The original blue color was not recovered by the cooling (Fig. S4c). The color changes were irreversible for PDA, PDA-Br, and PDA-Py$^+$Br$^-$ samples. The results indicate that the layered structures were deformed with the irreversible color changes. The same structure-property relationship was observed on the different layered PDA in our previous works.[9d]

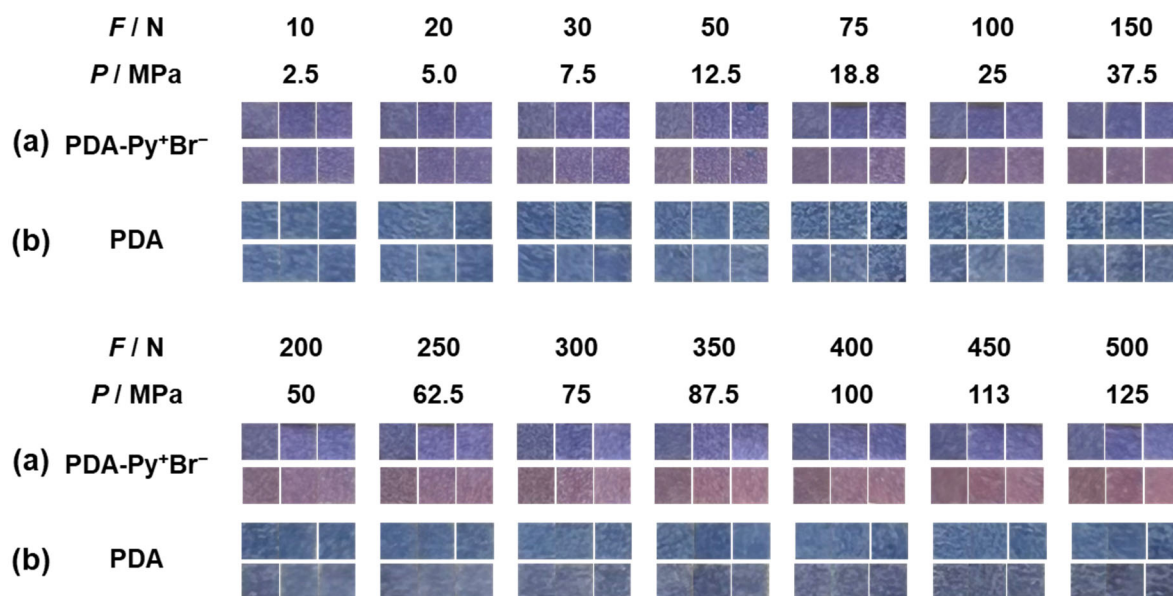**Photographs of PDA and PDA-Py⁺Br⁻ with compression**

Fig. S5. Photographs of PDA-Py⁺Br⁻ (a) and PDA (b) before (upper panels) and after (lower panels) the compression in the range of 2.5–125 MPa.

Three different samples were tested to ensure the reproducibility (the sample number: $N = 3$). The data was used for preparation of the standard curve in Fig. 5b.
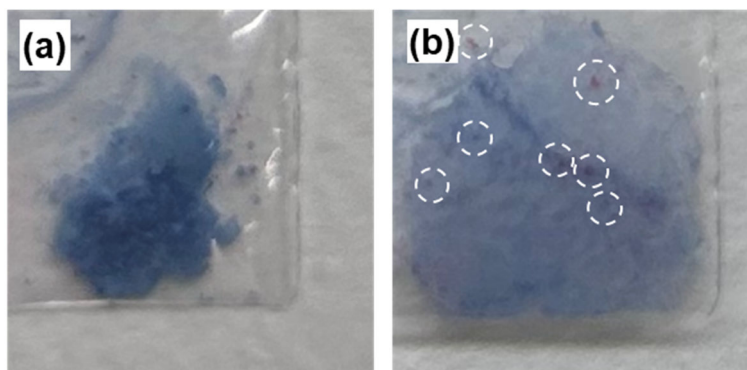
Photographs of PDA-Br with compression

Fig. S6. Photographs of PDA-Br in a plastic bag before (a) and after (b) the compression.

Before the compression, the PDA-Br was in the solid powder at room temperature under ambient pressure (Fig. S6a). The sample melted without the color change after the compression (Fig. S6b). After the compression, the powdered state was changed to liquid-like viscous state. The sample was spread over the wider area compared with the original state (Fig. S6b). The observation implies the melting of the sample. The red color was partially observed in the sample (the circles in Fig. S6b). However, the color change was not observed in the most of the compressed area.
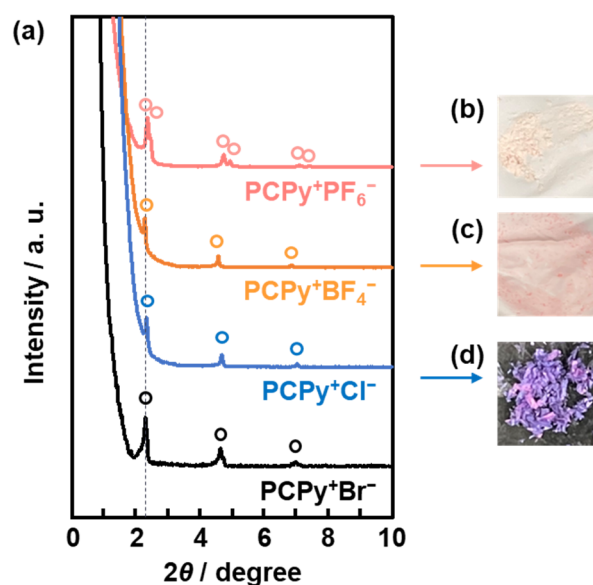
Ion-exchange to the other anions

Fig. S7. XRD patterns (a) and photographs (b–d) of PCPy$^+$PF$_6^-$ (b), PCPy$^+$BF$_4^-$ (c), and PCPy$^+$Cl$^-$ (d) after the UV-light irradiation (254 nm, 6 W) for 30 s.

Table S1.   Quantitative analysis of the halogens in the samples.

Samples	Measured Br / wt % (Calculated / wt %)	Measured Cl / wt % (Calculated / wt %)	Measured F / wt % (Calculated / wt %)
PCPy$^+$Br$^-$	17.54 (15.90)	–	–
PCPy$^+$Cl$^-$	1.79 (0)	6.47 (7.75)	–
PCPy$^+$BF$_4^-$	0.81 (0)	–	15.2 (15.0)
PCPy$^+$PF$_6^-$	0.39 (0)	–	20.9 (20.1)

The method for the ion exchange was described in the experimental method (P. S2–S3). The original PCPy$^+$Br$^-$ had d_0 = 3.80 nm. After the ion-exchange, d_0 was changed to 3.70 nm for PCPy$^+$PF$_6^-$, 3.85 nm for PCPy$^+$BF$_4^-$, 3.75 nm for PCPy$^+$Cl$^-$ (Fig. S7). The shifts imply the ion exchange in the interlayer space.

Table S1 summarizes the measured and theoretically calculated weight percentage of the halogens before and after the ion exchange. Whereas the content of Br$^-$ decreased after the ion exchange to Cl$^-$, BF$_4^-$, and PF$_6^-$, the content of the corresponding halogens (Cl and F) increased

(Table S1). These analyses support that the ion-exchange from Br^- to Cl^-, BF_4^-, and PF_6^- was achieved.

After the ion exchange, the polymerization was carried out with the irradiation of UV light. The polymerization with the coloration was not observed for $PCPy^+PF_6^-$ (Fig. S7b). The topochemically polymerizable structure was not obtained with the ion exchange to the large cations. The red-color PDA was obtained for $PCPy^+BF_4^-$ (Fig. S7c). The layered structure is disordered by the large cations. $PCPy^+Cl^-$ showed the color change to purple after the polymerization (Fig. S7d).
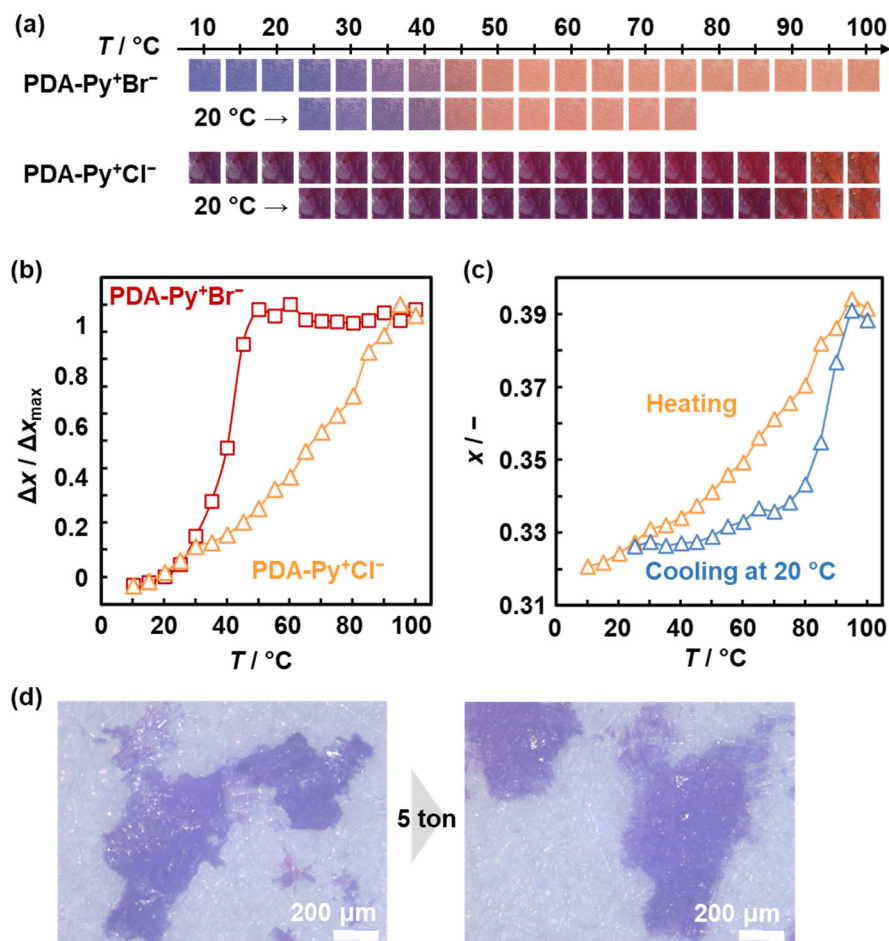
Responsivity of PDA-Py+Cl−

Fig. S8. Color-change properties of PDA-Py+Cl− compared with those of PDA-Py+Br−. (a) Photographs of PDA-Py+Br− and PDA-Py+Cl− in the range of T = 10–100 °C with heating at T (upper) and subsequent cooling at 20 °C (lower). (b) Relationship between T and $\Delta x / \Delta x_{max}$ for PDA-Py+Br− (square) and PDA-Py+Cl− (triangle). (c) Relationship between T and x of PDA-Py+Cl− with heating at T (orange) and subsequent cooling at 20 °C (blue). (d) Photographs of PDA-Py+Cl− powder on a filter paper before (left) and after (right) the application of compression 5 ton.

The sample was heated to T = 25 °C and then cooled at 20 °C. This heating and cooling operations were repeated in the range of T = 25–75 °C (Fig. S8a). Whereas the color change from blue to red was observed around 40 °C for PDA-Py+Br−, PDA-Py+Cl− showed the thermoresponsive gradual color change from dark purple to red in the wider temperature range

(Fig. S8a,b). In addition, PDA-Py$^+$Cl$^-$ exhibited the reversibility with cooling at 20 °C (Fig. S8a,c).

Compression force (5 ton = 49 kN) was applied to the PDA-Py$^+$Cl$^-$ powder on a filter paper (Fig. S8d). Based on the area of the filter paper (4 cm^2), the compression stress was calculated to be 122.5 MPa. The color change of PDA-Py$^+$Cl$^-$ was not induced by the compression stress, whereas the color change of PDA-Py$^+$Br$^-$ was observed with the application of the smaller compression stresses (Fig. 5a). The results indicate PDA-Py$^+$Cl$^-$ has no responsiveness to compression stresses.