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Effects of intercalation rate on structures and temperature-responsive color-change properties of layered polydiacetylene

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XRD patterns and FT-IR spectra of the PCDA-Zn^{2+} samples

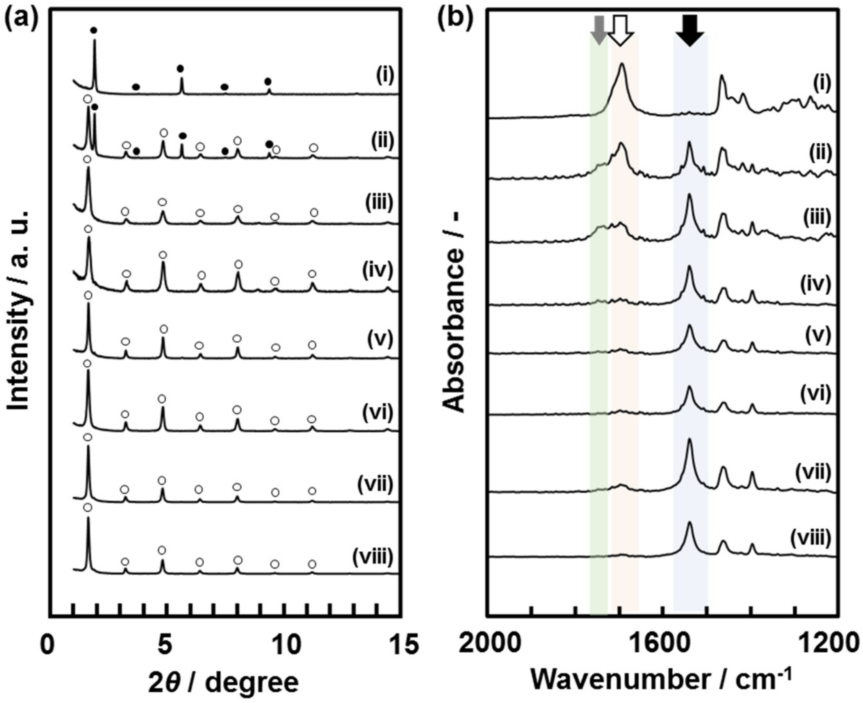

Fig. S1. XRD patterns (a) and FT-IR spectra (b) of all the PCDA and PCDA-Zn^{2+} samples. (a) XRD patterns of the PCDA and PCDA-Zn^{2+} samples prepare at the C_{Zn2+} = 0 (i), 0.5 (ii), 1.0 (iii), 1.5 (iv), 2.0 (v), 2.5 (vi), 5.0 (vii), and 10 (viii) mmol dm^{-3} respectively corresponding to the R = 0, 0.28, 0.60, 0.81, 0.84, 0.82, 0.85, and 1.0. The peak positions of the PCDA and the PCDA-Zn^{2+} were marked with filled and open circles, respectively. (b) FT-IR spectra of the same samples. The white arrow with orange band, the black arrow with blue band, gray arrow with green band indicate the peak positions of the dimerized carboxy group, the carboxylate group, and free monomeric carboxy group, respectively.

The interlayer distance (d_0) of the PCDA on glass substrates was d_0 = 4.63 nm. After the intercalation of Zn^{2+}, the d_0 was expanded to d_0 ' = 5.38 nm. The FT-IR spectra were used for estimation of the intercalation rate (R) by using the calibration curve of the reference samples in Fig. S2.

Calculation method of the intercalation rate *R*

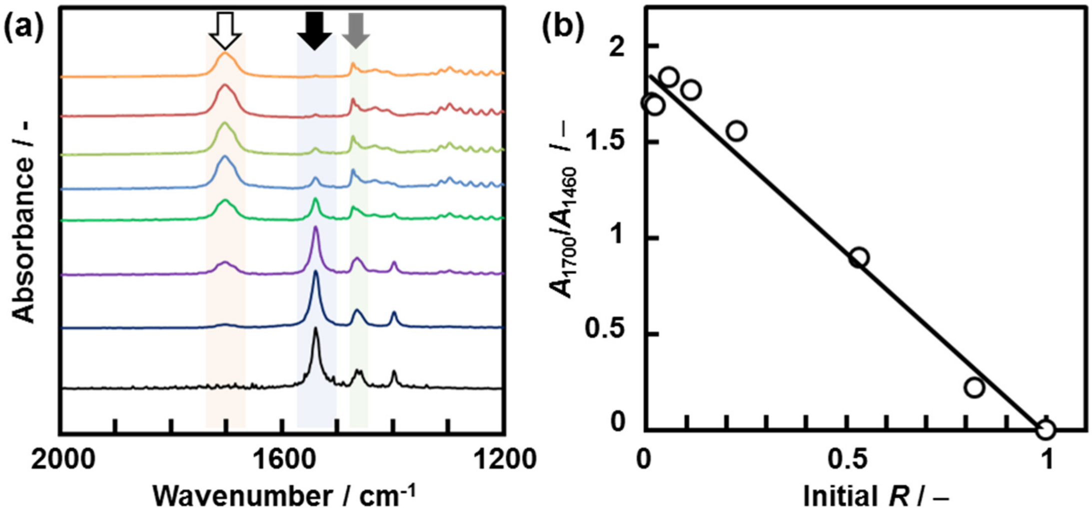

Fig. S2 FT-IR spectra (a) and the calibration curve (b) of the mixture of stearic acid (SA) and stearic acid zinc salt (SA-Zn^{2+}) (a).

The intercalation rate of the Zn^{2+}, namely the *R* value, corresponds to the molar ratio of the carboxylate groups to the total carboxy groups. The molar ratio is estimated from the FT-IR spectra by the following procedure. As the reference, commercial stearic acid (SA) and stearic acid zinc salt (SA-Zn^{2+}) were mixed with certain ratio. FT-IR spectra of the mixtures showed the stretching vibration of the dimerized carboxy group around 1700 cm^{-1} (white arrow with orange band) and the carboxylate group around 1540 cm^{-1} (the black arrow with blue band) respectively originating from the SA and SA-Zn^{2+} (Fig. S2a). In addition, the stretching vibration of the CH_2 groups was observed around 1460 cm^{-1} (the gray arrow with green band) The absorbance of 1700 cm^{-1} (A_{1700}) was divided by that of 1460 cm^{-1} (A_{1460}) to represent the molar ratio of the dimerized groups to the total carboxy groups on the assumption that the excess amount of methylene group was contained in the sample. In this way, the relationship between the initial *R* and the A_{1700} / A_{1540} of the reference samples can be summarized as the calibration curve in Fig. S2b. The R values of the PCDA and PCDA-Zn^{2+} samples were estimated from the A_{1700} / A_{1540} in the FT-IR spectra by using the calibration curve (Figs. S1b and S2b). The C_{Zn2+}, A_{1700} / A_{1540}, and R values are summarized in the Table S1. Since the R lower than 0.28 was not precisely estimated from the FT-IR analysis because the calibration curve to estimate the R had slight inaccuracy at the low concentration range. The R_{calc} was used instead of the R at C_{Zn2+} = 0.1 and 0.2 mmol dm^{-3}.

Table S1. Summarized data of the C_{Zn2+}, A_{1700} / A_{1460}, and R in the present work.

C_{Zn2+} / mmol dm^{-3}	0	0.1	0.2	0.5	1.0	1.5	2.0	2.5	5.0	10
A_{1700} / A_{1460} / –	–	–	–	1.33	0.73	0.34	0.29	0.33	0.27	0.00
R / –	0	–	–	0.28	0.60	0.81	0.84	0.82	0.85	1.0
R_{calc} / –	0	0.074	0.15	0.37	0.74	1.11	1.48	1.85	3.7	7.4

Methods for quantitative analysis of the color-change behavior

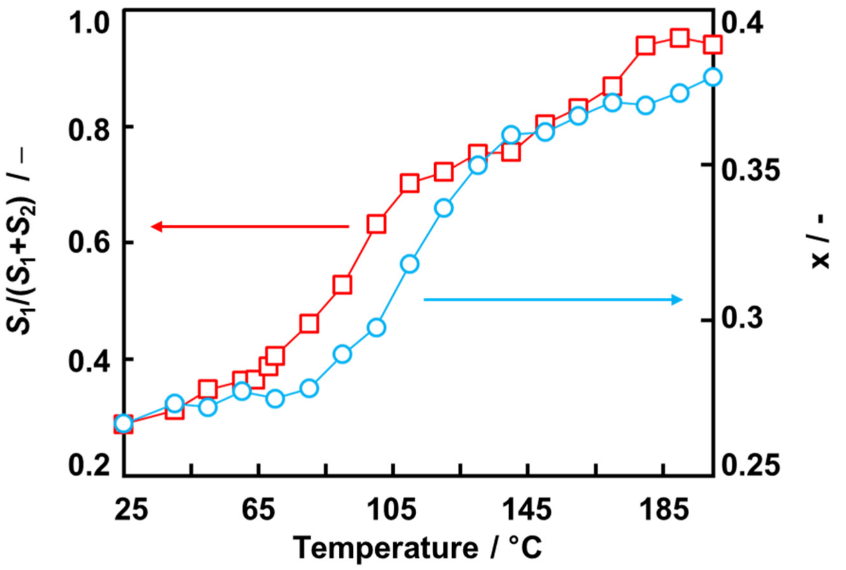

Fig. S3. Two-different methods for estimation of the color-change behavior on the basis of the UV-Vis spectroscopy (squares) and image analysis (circles). The detailed procedure was described in the following explanations.

In the present work, the sample color was represented by the *x* value, namely the intensity of the red color, estimated from the image analysis. The relationship between the temperature and the color was quantitatively characterized by using UV-Vis spectroscopy. These results are consistent with each other (Fig. S3). The color of the sample can be characterized by UV-Vis spectroscopy as follows.[5*b*] The spectroscopic changes, namely the blueshift of the absorption area,[5,*b*,*d*] are characterized by the ratio of the peak area shorter than 570 nm (S_1) and that longer than 570 nm (S_2) [5*b*] The relationship between the temperature (T) and the ratio of S_1 divided by S_1+S_2 ($S_1/(S_1+S_2)$) represents the color-change behavior (the squares in Fig. S3). These two methods show the similar traces about the color-change behavior. Therefore, the image-analysis method is used as the rapid characterization method in the present work.

Color-change properties of the PDA-Zn^{2+} with the lower *R*

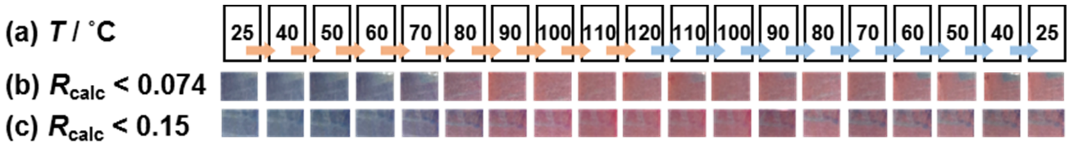

Fig. S4. Temperature-responsive color-change properties of the PDA-Zn^{2+} with $R_{calc} < 0.074$ (b) and $R_{calc} < 0.15$ (c).

We synthesized two PDA-Zn^{2+} samples with the *R* lower than 0.28. The initial Zn^{2+} concentration (C_{Zn2+}) was set at $C_{Zn2+} = 0.2$ and 0.1 mmol dm^{-3}. However, the low *R* value was not precisely estimated from the FT-IR analysis because the calibration curve to estimate the *R* had slight inaccuracy at the low concentration range (Fig. S2b in the ESI). The sample name was defined by using R_{calc} instead of the *R*. These samples showed the irreversible color-transition same as that observed PDA ($R = 0$) without intercalation of Zn^{2+}.

Cycle and long-term stability of the color-change properties

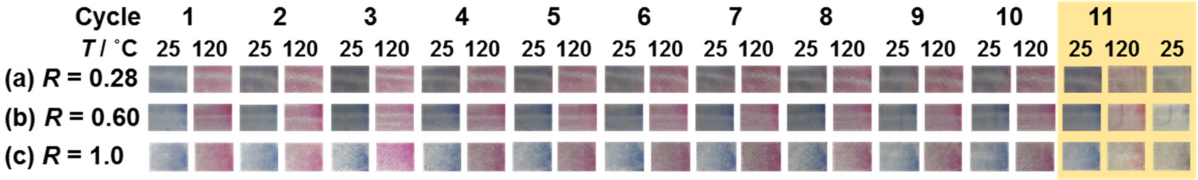

Fig. S5. Cycle and long-term stability of the temperature-responsive reversible color-change properties. (a) $R = 0.28$, (b) $R = 0.60$, (c) $R = 1.0$. The cycle stability and the long-term stability were studied in the 1st–10th cycles and 11th cycle (yellow background), respectively.

The PDA-Zn^{2+} samples on the substrates were put on the heating stage set at 120 °C. The original blue color was changed to the red within 1 sec. Then, the sample was transferred to the cooling stage set at 25 °C. The color returned to the blue within 1 sec. The heating and cooling were performed in the 10 cycles. In the 11th cycle, the heating of the PDA-Zn^{2+} samples was performed at 120 °C for 48 h to study the long-term stability. The reversible color change was observed on the PDA-Zn^{2+} samples in the 10 cycles. The red color reversibly returned to the original blue after the continuous heating, even though the sample color was slightly diluted (the samples at 25 °C in the yellow background). The melting and the recrystallization of the unreacted monomer cause the dilution of the sample color. In addition, the red-color domain slightly remained at $R = 0.28$ after the continuous heating.