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Electronic Supplementary Information (ESI)

Paper-based measuring device of friction force using stimuli-responsive materials

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Experimental methods

Sparse modeling. The color-transition temperature and its related parameter of the layered PDA samples were extracted from our previous reports.[53,56,60] The training dataset was prepared as shown in Table S1. Multiple regression analysis was performed using a free software R. As values of the explanatory variables (x_i: i = 1–6) have different units and scales, these values were normalized for the multiple regression analysis. The prediction models, such as (eq. 1) and (eq. 2), were obtained. Then, the number of descriptors was reduced on the basis of the chemical relevance to obtain the sparse model.

Synthesis of layered PDA/PEI composites. All the regents were used without purification as purchased. A commercial 10,12-pentacosadiynoic acid (PCDA, TCI, 97.0%), typically 50 mg (0.133 mol), was dissolved in 30 cm^3 of hexane. Then, linear or branched polyethyleneimine (PEI, Aldrich, M_n 60,000, 50 wt% aqueous solution) was added in the hexane solution with the molar ratio of the amine group to PCDA ($R_{PEI/PCDA}$) 0.25, 0.5, 0.75, 1.0, and 2.0. The $R_{PEI/PCDA}$ was calculated on the basis of the ethyleneimine monomer units. The precursor solution containing PCDA and PEI was poured in a petri dish. The precipitate was collected after evaporation of the solvent at room temperature in a fumed chamber. The resultant precipitate was polymerized with irradiation of UV light (254 nm, 6 W) around 5 min on a temperature-controlled stage set at –5 °C.

Preparation of PDA/PEI-coated paper device. A commercial 10,12-pentacosadiynoic acid (PCDA, TCI, 97.0%), typically 10 mg (26.7 mmol), was dissolved in 1 cm^3 of chloroform. Then, branched PEI was added at $R_{PEI/PCDA}$ = 0.25, 0.5, 0.75, 1.0, and 2.0. Then, a filter paper (5C, quantitative grade) 3 cm × 0.5 cm was dipped in the precursor solution. The substrate was rapidly dried using air blower at room temperature. The dried substrate was pressed between polystyrene blocks to obtain the flat surface. The polymerization was achieved by the same method for the powder sample.

Structure characterization. The layered crystal structure was analyzed by powder X-ray diffraction (XRD, Bruker D8-Advance). Fourier-transform infrared (FT-IR, JASCO FT/IR-4200) spectroscopy was measured by KBr method to study the states of the interlayer carboxy groups. The morphology of the powdered sample was observed by field-emission scanning electron microscopy (SEM, Jeol JSM-7100F). The surface morphology of the PDA/PEI paper-based device was observed by field-emission scanning electron microscopy (SEM, Carl-Zeiss MERLIN VP compact) operated at 1.5 kV without conductive coating. The structure changes with heating were studied by differential scanning calorimetry (DSC, Shimadzu DSC-60).

Characterization of the color-change properties with heating. The powdered samples of PDA and PDA/PEI were filled in stainless sample holder with the groove 5 mm × 7.5 mm in size and 1 mm in depth. Then, the samples were heated on a temperature-controlled stage and preserved at the certain temperature to take the photographs. The image analysis was performed on the photograph to estimate the R, G, and B values using Image-J software. The red-color intensity (x) was then calculated using the (eq. S1) as an international standard (ITU-R BT. 709).[68]

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 0.4124 & 0.3576 & 0.1805 \\ 0.2126 & 0.7152 & 0.0722 \\ 0.0193 & 0.1192 & 0.9505 \end{bmatrix} \begin{bmatrix} R \\ G \\ B \end{bmatrix} \quad \ldots \text{(eq. S1)}$$

The relationship between temperature (T) and x values was prepared to estimate the color-transition temperature (T_{trs}). The temperature to achieve $0.5\Delta x$ was defined as T_{trs}, where Δx is the total increment of the x values after the heating (Fig. 2a). UV-Vis spectra were measured for PDA and PDA/PEI ($R_{\mathrm{PEI/PCDA}} = 2.0$) powdered sample by spectrophotometer (JASCO V-670) using an integrating sphere.

Measurement of friction force. The PDA/PEI-coated and PDA-coated paper-based devices (3 cm × 0.5 cm) were used for the quantification of friction force (Fig. S9). In all the experiments, the friction force was applied under 20 °C on temperature-controlled stage to avoid the color change. The cage and weight were used for preparation of the standard curve (Fig. 6a and Fig. S9). The friction force (F) was measured to be 0.20 N using a spring scale for the cage (109 g) without weight (Fig. S9). When the weight of 539 g, 1061 g, and 3000 g was loaded on the cage, the F was measured to be 1.20 N, 2.45 N, and 6.37 N, respectively (Fig. S9). The friction force with the four different F was applied to the PDA/PEI paper-based device with back-and-forth motion (Fig. 6a). The number is defined as $n_{\mathrm{F}} = n$ (n = 0, 2, 4, 6, … , 20). The relationship between n_{F} and Δx was studied four times to ensure the reproducibility (Fig. 6d). Here the Δx was estimated from the differences between the x values before and after application of the friction force at certain n_{F}. Then, the relationship between the accumulated work (W) and Δx as the standard curve was prepared at $n_F = 20$ (Fig. 6e). The optical microscopy (Keyence VHX-1000) images were obtained at certain n_F. Commercial toothbrushes with three different hardness were purchased. Brushing force is set at 50–300 g when brush is pressed to a platform scale. The brushing test was performed by the same experimenter with three different strength, such as weak for 50–100 g, moderate for 150–200 g, and strong for 250–300 g. The Δx at $n_F = 20$ was measured for the nine combinations of the hardness and strength (Table 1). Then, the brushing force as a friction force was estimated using the (eq. 5) as linear approximation in Fig. 6e.

Multiple regression analysis and sparse modeling

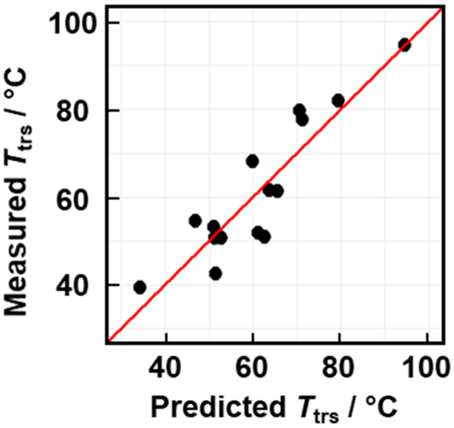

Fig. S1. Relationship between the predicted and measured T_{trs} on the basis of the model using four descriptors, namely d_0 (x_1), L (x_4), m (x_5), and n_{PCDA} / n_{amine}, (x_6).

The four descriptors, namely d_0 (x_1), L (x_4), m (x_5), and n_{PCDA} / n_{amine} (x_6), were used for construction of the prediction model. The prediction accuracy with CVE 24.91 °C was similar to that using the three descriptors, namely d_0 (x_1), m (x_5), and n_{PCDA} / n_{amine} (x_6), with CVE 25.14 °C in Fig. 2d.

Table S1. Dataset for multiple linear regression analysis.

Guest amines	Explanatory variables (x_1–x_6) and objective variables (y)						
	x_1 (d_0 / nm)	x_2 (M_w / g mol^{-1})	x_3 (T_b / C°)	x_4 (L / 10^{-1} nm)	x_5 (m / –)	x_6 (n_{PCDA} n_{amine}^{-1} / –)	y (T_{trs} / C°)
C_1-NH_2	8.14	241.4558	603.2	20.313	1	0.838235	77.6
C_2-NH_2	6.39	31.0571	266.8	1.47	1	2.333333	61.2
C_3-NH_2	5.49	45.0837	291	2.472	1	2.125	50.5
C_4-NH_2	5.69	59.1103	322	3.84	1	2.030303	50.5
C_6-NH_2	5.8	73.1368	351	5.02	1	1.12766	54.4
C_{10}-NH_2	6.22	101.19	403	7.568	1	1.040816	53.2
C_{14}-NH_2	7	157.2963	493.7	12.665	1	1.040816	68.1
C_{16}-NH_2	7.82	213.4026	564.4	17.764	1	1.222222	79.6
C_{18}-NH_2	8.72	269.509	622	22.862	1	1	82
C_4-$(NH_2)_2$	5.23	88.1515	431.7	6.282	2	1.973132	94.7
$(C_6)_2$-NH_2	7.28	185.3495	466.7	15.095	1	0.818182	51.7
$(C_8)_2$-NH_2	7.6	241.4558	570.7	20.198	1	0.694915	50.8
$(C_{10})_2$-NH_2	7.8	297.5621	637.15	25.299	1	0.724138	61.6
C_6C_1-NH_2	6.42	115.2166	415.2	7.54	1	0.724138	42.4
C_4C_3-NH_2	5.14	115.2166	414.15	4.926	1	0.666667	39.2

Total 16 layered PDA samples containing the following amines were used for preparation of the dataset; normal alkylamines (C_n-NH_2: $C_nH_{2n+1}NH_2$, n = 1–4, 6, 10, 14, 16, 18), normal alkyldiamines (C_n-$(NH_2)_2$: $H_2NC_nH_{2n}NH_2$, n = 4), normal dialkylamines ($(C_n)_2$-NH: $H_{2n+1}C_nNHC_nH_{2n+1}$, n = 6, 8, 10), and branched alkylamine ($H_{2m+1}C_mCH(NH_2)C_nH_{2n+1}$, m = 1, n = 5 and m, n = 3). The values of the explanatory variables were not completely available for the other amines.

Table S2. Coefficients of the prediction models using the different number of the descriptors.

Descriptors	Number of descriptors for modeling 6	 4	 3
x_1 (d_0 / nm)	11.46	15.76	13.11
x_2 (M_w / g mol^{-1})	–31.37	N. A.	N. A.
x_3 (T_b / C°)	36.17	N. A.	N. A.
x_4 (L / 10^{-1} nm)	–1.835	–3.138	N. A.
x_5 (m / –)	6.081	12.83	12.11
x_6 (n_{PCDA} n_{amine}^{-1} / –)	8.483	4.438	5.390
Intercept / –	61.17	61.17	61.17
CVE / C°	15.75	24.91	25.14

The multiple regression analysis was performed on the dataset in Table S1. The prediction model (eq. 1) was prepared using all the 6 descriptors with the coefficients in Table S2. Then, the number of descriptors were decreased to 4 and 3 for preparation of the more sparse prediction model. The prediction accuracy was not so lowered by change in the number of the descriptors from 4 to 3. Therefore, we used the model (eq. 3) using 3 descriptors to design the layered PDA with stimuli responsivity to weak friction force.

Layered composites with incorporation of linear PEI

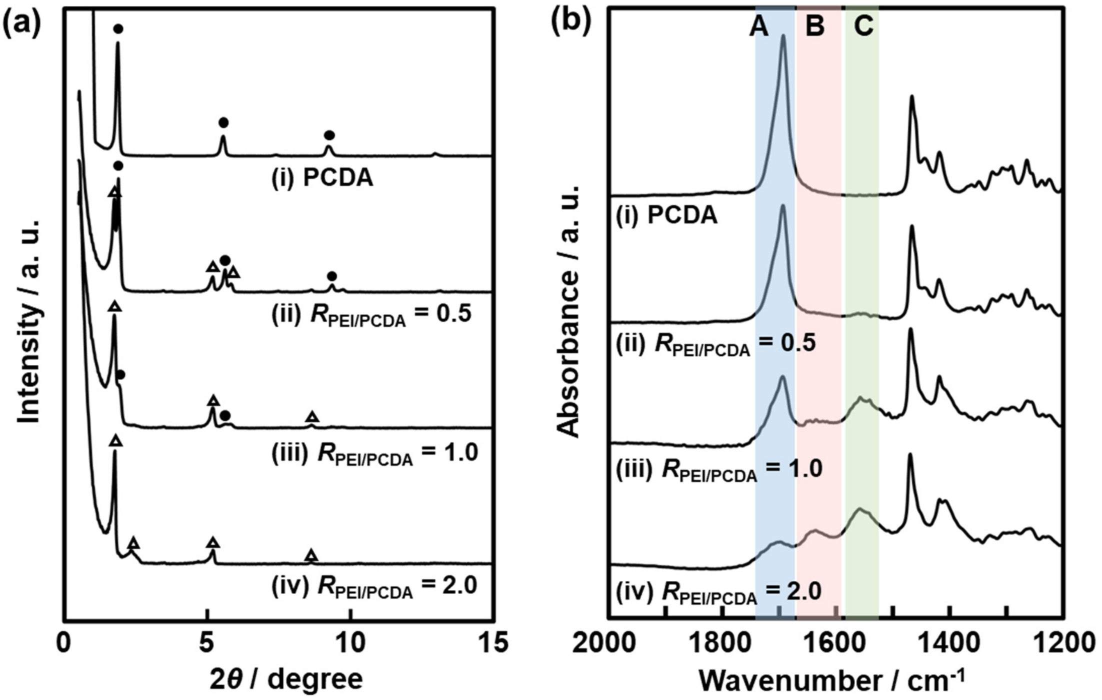

Fig. S2. XRD patterns (a) and FT-IR spectra (b) of the layered PCDA/PEI (linear).

The layered composites of PCDA/PEI (linear) were obtained by the same method. The XRD patterns and FT-IR spectra of the PCDA/PEI (linear) were similar to those of the PCDA/PEI (branched). The additional interlayer distance (d_0') appeared around 5.1~6.0 nm with an increase in the $R_{PEI/PCDA}$ (the triangles in Fig. S2a). As the $R_{PEI/PCDA}$ increased, the peak of the dimerized carboxy group was broadened and weakened (the band A in Fig. S2b). On the other hand, the absorption bands of the carboxylate and secondary amine groups were observed around 1580–1670 cm^{-1} and 1520–1580 cm^{-1}, respectively (the bands B and C in Fig. S2b).

FT-IR analysis of the precursor solution

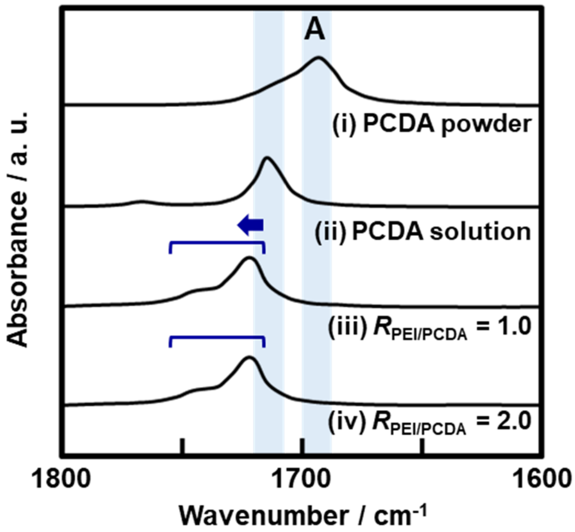

Fig. S3. FT-IR spectra of the PCDA powder (i), hexane solution containing PCDA (ii), and hexane solution containing PCDA and PEI at $R_{PEI/PCDA}$ = 1.0 (iii) and 2.0 (iv).

Powdered state of PCDA showed the absorption band corresponding to the dimerized carboxy group around 1700 cm^{-1}, as represented by the band A (the spectrum (i) in Fig. S3). The peak was slightly shifted to the higher wavenumber region in the hexane solution state (the spectrum (ii) in Fig. S3). This shift is generally caused by the difference in the solid and solution states. The precursor solution containing PCDA and PEI showed the further shift to the higher wavenumber region and broadening of the peak (the blue arrow in Fig. S3). The spectroscopic change implies that PCDA in the precursor hexane solution forms not the dimerized carboxy group but hydrogen bond between the PCDA and PEI.

Temperature-responsive color-change properties

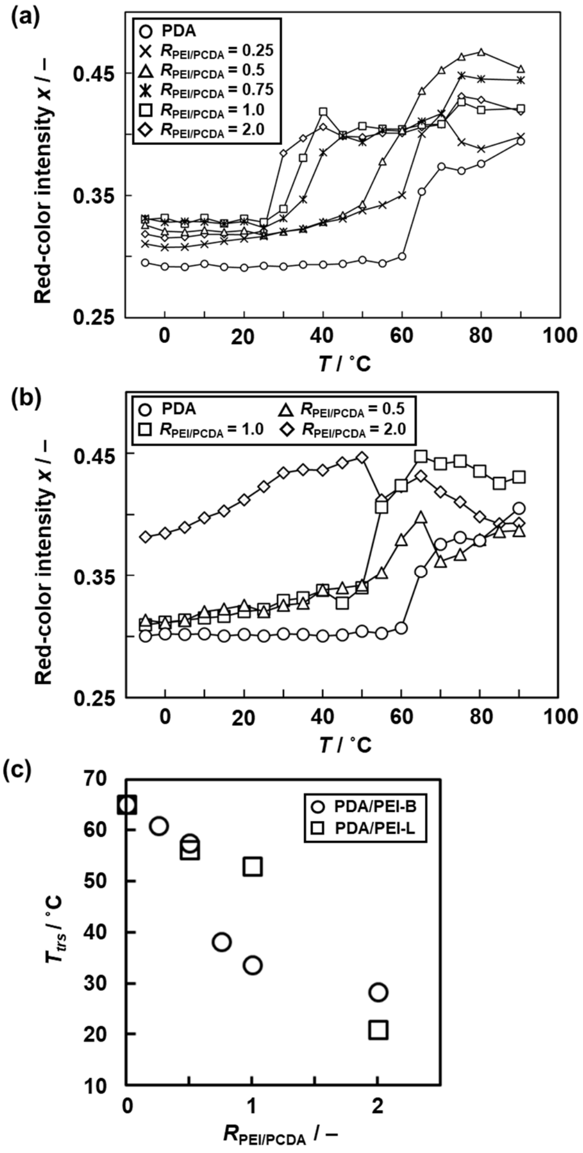

Fig. S4. Summary of temperature-responsive color-change properties. (a) Relationship between T and x for PDA/PEI (branched) at $R_{\mathrm{PEI/PCDA}}$ = 0, 0.25, 0.5, 0.75, 1.0, and 2.0. (b) Relationship between T and x for PDA/PEI (linear) at $R_{\mathrm{PEI/PCDA}}$ = 0, 0.5, 1.0, and 2.0. (c) relationship between $R_{\mathrm{PEI/PCDA}}$ and T_{trs} for PDA/PEI (branched) (PDA/PEI-B) and PDA/PEI (linear) (PDA/PEI-L).

The T_{trs} was lowered with an increase in $R_{\mathrm{PEI/PCDA}}$ for both PDA/PEI-B and PDA/PEI-L.

UV-Vis spectra of the PDA and PDA/PEI

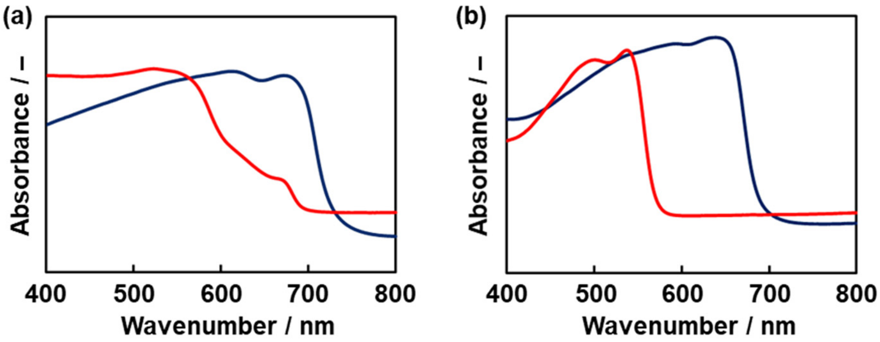

Fig. S5. UV-Vis spectra of PDA (a) and PDA/PEI at RPEI/PCDA = 2.0 (b).

The original states with blue color showed the two broadened absorption peaks centered around 600 nm and 680 nm. The main peak areas were shifted to the region lower than 580 nm after color-changing to red with heating. The spectroscopic changes were similar to those of the other layered PDA-guest composites.[52,53]

DSC thermograms

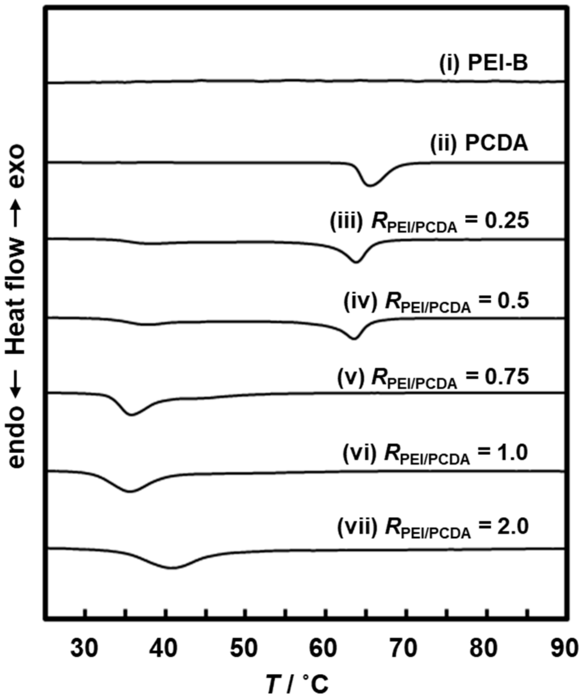

Fig. S6. DSC thermograms of branched PEI (i), layered PDA (ii), and layered PDA/PEI at $R_{PEI/PCDA}$ = 0.25 (iii), 0.5 (iv), 0.75 (v), 1.0 (vi), and 2.0 (vii).

No peak was observed on the DSC thermogram of branched PEI (the chart (i) in Fig. S6). Pure PDA showed the endothermic peak around 65 °C because of the deformation of the layered structure (the chart (ii) in Fig. S6). As the $R_{PEI/PCDA}$ increased, the endothermic peak appeared around 40 ˚C. On the other hand, the endothermic peak around 65 °C disappeared. An increase in $R_{PEI/PCDA}$ leads to decrease in the layered PDA domain and increase in PDA/PEI domain, as shown in Fig. 3c. Moreover, the layered PDA/PEI has the structure transition around 40 °C lower than 65 °C for pure PDA. The results support that the PDA/PEI has lower T_{trs} compared with PDA.

SEM image of the PDA/PEI in the powdered state

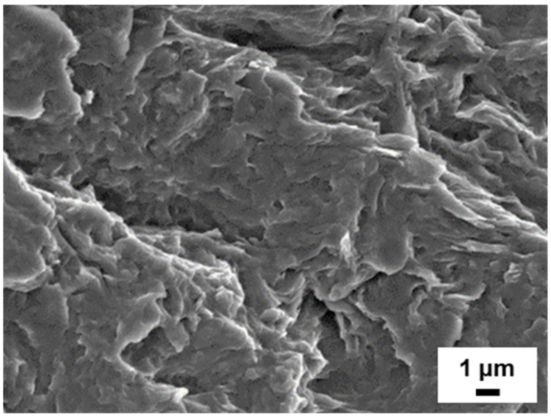

Fig. S7. SEM image of the PDA/PEI precipitates formed at $R_{\mathrm{PEI/PCDA}} = 1.0$.

The layered PDA showed the sheet-like morphologies around 1 μm in lateral size.

Temperature-responsive color-change properties of the paper-based device

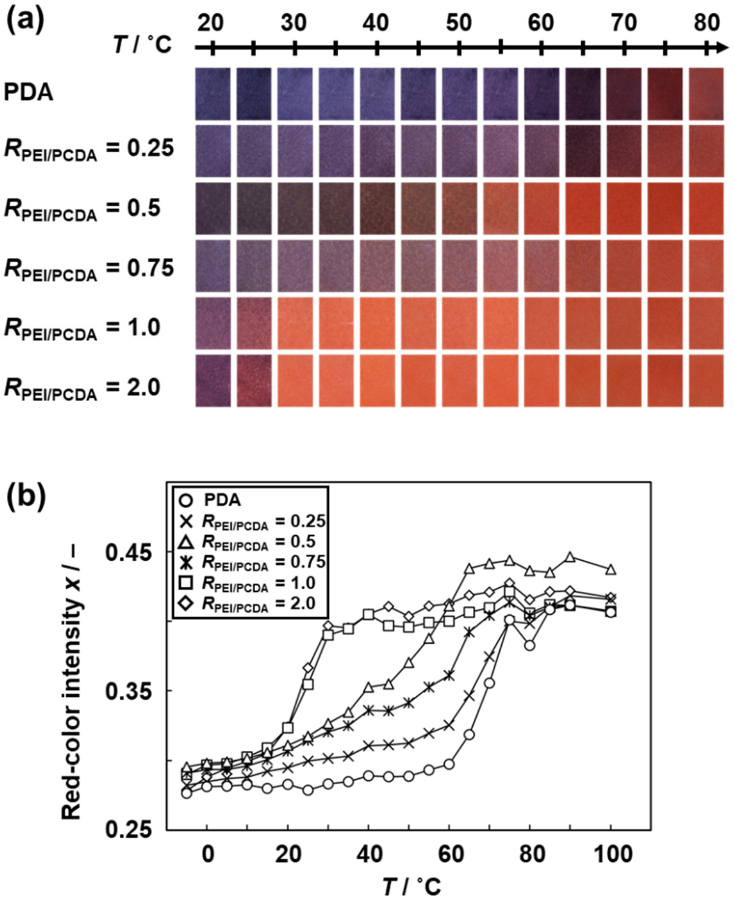

Fig. S8. Temperature-responsive color-change properties of PDA/PEI coated on a filter paper. (a) Photographs of the paper-based devices with heating. (b) Relationship between T and x.

The color-change behavior of the paper-based device is similar to that of the powdered state in Fig. 4a.

Reference experiment for measurement of friction force 1

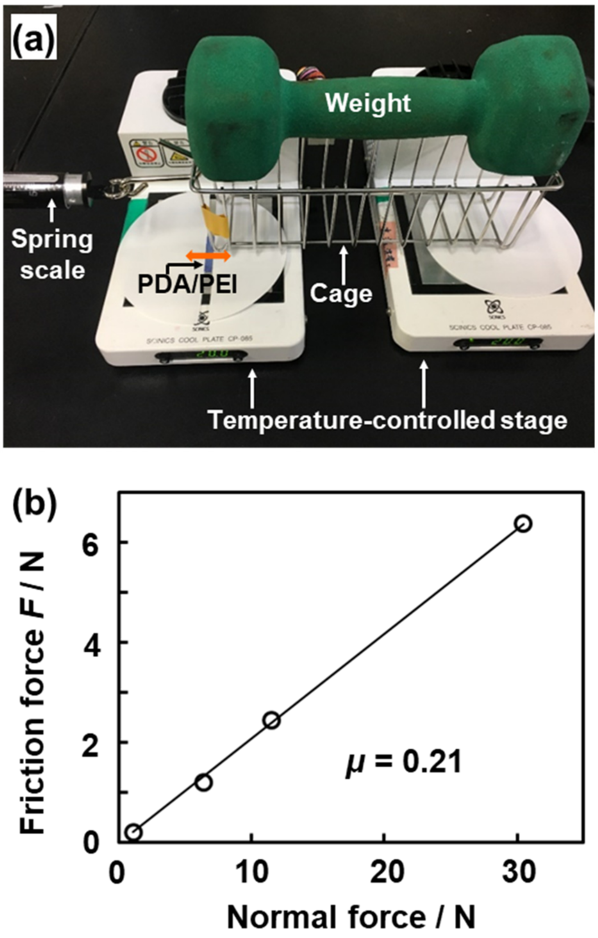

Fig. S9. Photograph of the experimental setup (a) and relationship between normal force and friction force (*F*) (b).

The friction force was measured by using a commercial spring scale (Fig. S9a). The normal force was changed by the weights on the cage. The relationship between normal force and *F* was obtained (Fig. S9b).

Reference experiment for measurement of friction force 2

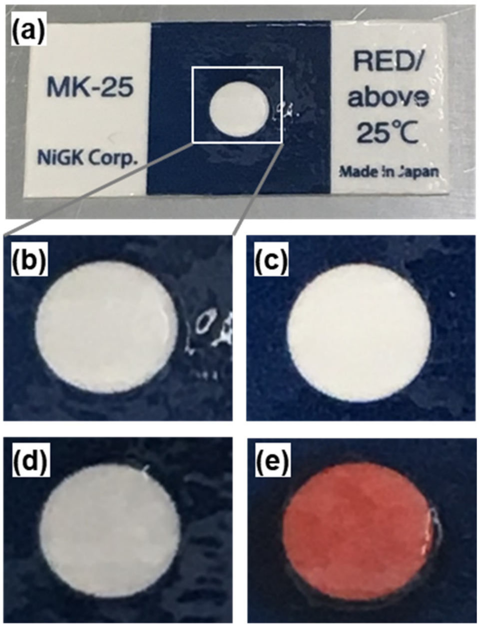

Fig. S10. Photographs of a commercial thermo-label (a), its magnified image (b), after application of friction force at 6.37 N (c), after strong brushing with hard brush (d), and after heating at 25 °C (e).

This commercial thermo-label shows the color change from white to red above 25 °C (Fig. S10a,e). This thermo-label was set on a temperature-controlled stage kept at 20 °C (Fig. S10b). The color change was not observed by application of friction force at 6.37 N under n_F = 20 and strong brushing force using hard brush (Fig. S10c,d). As reference, the color of the thermo-label was actually changed to red at 25 °C (Fig. S10e). These results indicate that the color changes of the PDA/PEI were not caused by friction heat but friction force itself.