

Supporting Information

Mechanochromic Luminescence of Bionanocomposite Hydrogel

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Experimental Procedures

Materials

Gelatin (from bovine skin, type B with bloom value of 220, abbreviated as **GEL**), 1,1'-diethyl-2,2'-cyanine iodide (Pseudoisocyanine, abbreviated as **PIC**) and trisodium citrate dihydrate were purchased from Sigma Aldrich and were used as received. A synthetic Na-hectorite (Laponite RD, abbreviated as **LAP**) was obtained from the Rockwood Industries. A purified sodium bentonite (Bengel Next LU, abbreviated as **BN**) was obtained from Hojun Co., Ltd. The cation exchange capacities of **LAP** and **BN** are 55 and 82 mequiv./100g of clay, respectively. Milli-Q plus water purification system (18 M Ω cm⁻¹, Millipore, USA) was used in all the experiments.

Preparation of clay-PIC suspension

Aqueous suspension of clay-**PIC** was prepared by the method reported previously with some modifications.^[1] Briefly, a stock solution of **PIC** was prepared with a concentration of 4.18 x 10⁻⁴ M by dissolving 1,1'-diethyl-2,2'-cyanine iodide in deionized water. An aqueous suspension of **LAP** and **BN** was prepared in de-ionized water by magnetic stirring for 1 day. An aqueous solution of **PIC** was mixed with an aqueous suspension of clay to obtain stable suspensions of clay-**PIC**. The suspension was sonicated for 15 minutes before use. The samples were denoted as **xClay-PIC**, where x is the **PIC** loading in the unit of mmol/100g clay and clay is **LAP** or **BN**.

Preparation of gelatin/clay-PIC composite hydrogels

The flexible gelatin was prepared by the method reported previously with some modifications.^[2] A stock solution of gelatin was prepared by dispersing gelatin powder in deionized water at room temperature for 30 min, where gelatin swelled, and subsequently heated at 50°C until the solution became homogeneous. The gelatin-**PIC** aqueous solution with the gelatin concentration of 15%wt was prepared by mixing the aqueous solution of gelatin and the aqueous solution of **PIC** at 50°C for 40 min. After removing air bubbles by ultrasonication, the solution was poured into silicone molds and allowed to gel at 4°C for 1h. The gelatin gels thus obtained were soaked in a 20%wt aqueous solution of sodium citrate at room temperature for 3 h to obtain flexible hydrogels. The flexible gelatin/clay-**PIC** hydrogels were prepared in the same way by mixing the clay-**PIC** suspension with the gelatin solution. The concentration of gelatin in all the samples was 15%wt and the concentration of **PIC** in all the samples was 1.39 x 10⁻⁴ M. The samples were denoted as **GEL/xClay-PIC**, where x is the **PIC** loading in the unit of mmol/100g clay, clay is **LAP** or **BN**.

Characterization

Absorption spectra of the clay-**PIC** suspensions and composite hydrogels were recorded using UV-visible spectrophotometer (PerkinElmer Lambda 1050). Fluorescence spectra were recorded on an FLS980 photoluminescence spectrometer (Edinburgh Instruments) using the excitation wavelength of 320 nm. For the photoluminescence under mechanical stimuli, the hydrogels sample were stretched according to definite strain, then fixed on the glass substrate by clip period to be applied for the spectroscopic measurements. The measurement was done at the center of the stretched zone. The appearance of the flexible gelatin and the composite hydrogel was observed under UV irradiation using a UV-LED spotlight (365 nm with 95 mW/cm²) of Ushio SPL-2. The photos were collected during the stretching process by a smartphone (Samsung Galaxy S20, rare-facing camera). To evaluate the colorimetric response, CIE chromaticity coordinates were obtained from the emission spectra of hydrogels at different strains. The coordination was obtained using Origin v.2019 software.

The mechanical properties of the hydrogels were examined on rectangular-shaped gels (L= 40 mm, W= 4 mm and a gauge length of 15 mm) with a thickness of 1.5 mm using a tensile tester (ADMET eXpert 5604, USA). The initial distance, L₀, between the two clamps of the tester was 15 mm and the tensile deformation was performed at the strain rate of 50 mm/min with a 50 lbs load cell. Silicon oil was coated on the hydrogel surface during the tensile test to prevent water evaporation. The measurement was repeated 5 times at room temperature. The tensile strain was calculated by the ratio of the elongation to the initial length ($\epsilon = \Delta L/L_0$). Tensile stress was defined as the load force applied per unit of the original specimen cross-sectional area ($\sigma = F/A_0$).

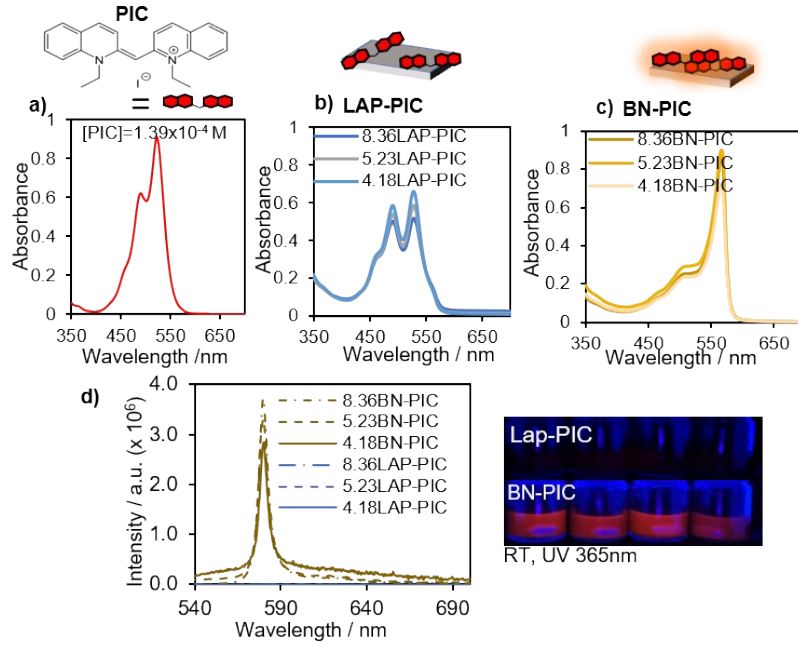


Figure S1. Absorption spectra of a) the 1.39×10^{-4} M **PIC** containing b) **LAP** and c) **BN** at 8.36, 5.23 and 4.18 mmol **PIC**/ 100g clay, respectively. d) Fluorescence spectra, $\lambda_{ex} = 320$ nm of the clays (**LAP** and **BN**)-**PIC** mixtures at different ratios and the photographs of the mixtures under UV light (365 nm) at room temperature.

The contents of gelatin and water in gelatin/clay-**PIC** hydrogels were determined by weighing the original gelatin composite hydrogel samples (before immersion in sodium citrate solution) cut into rectangular shaped specimens (60 mm x 10 mm X 2 mm) (W_1), the gel samples after being immersed in sodium citrate for 3h (W_2) and the gels vacuum-dried at ambient temperature to constant weights (W_3). Water and sodium citrate solution on the surface of hydrogels was wiped off. The weight was measured each hour without changing the sodium citrate solution. The gelatin content (W_{Gel}), sodium citrate content (W_{Cit}) and water content (W_{water}) were calculated using formulas (1), (2) and (3).

$$(1) \quad W_{water} = \frac{W_1 - W_3}{W_2} \times 100$$

$$(2) \quad W_{Gel} = \frac{W_1 \times C_{gel} \times 100}{W_2}$$

$$(3) \quad W_{Cit} = \frac{W_3 - W_1 C_{gel}}{W_2}$$

where C_{gel} is the mass concentration of gelatin in starting hydrogel (15 %wt.)

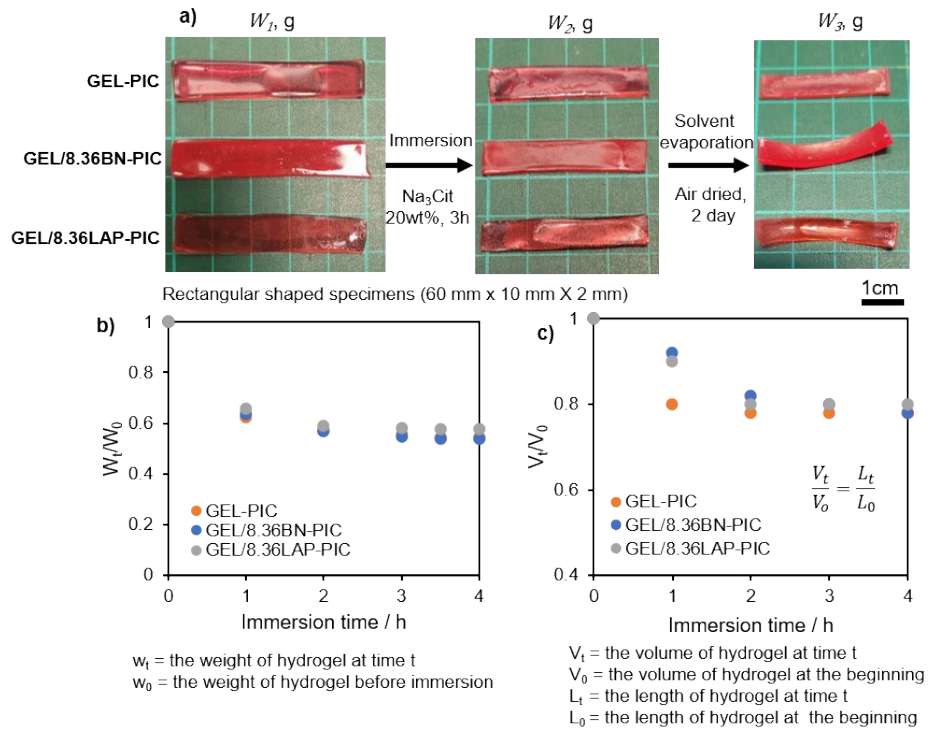


Figure S2. a) The photos of composites hydrogel before and after the immersion in sodium citrate solution. b) The weight ratio of composite hydrogels as a function of soaking time in 20%wt sodium citrate solution. c) volume change ratio of composite hydrogel in 20%wt sodium citrate solution.

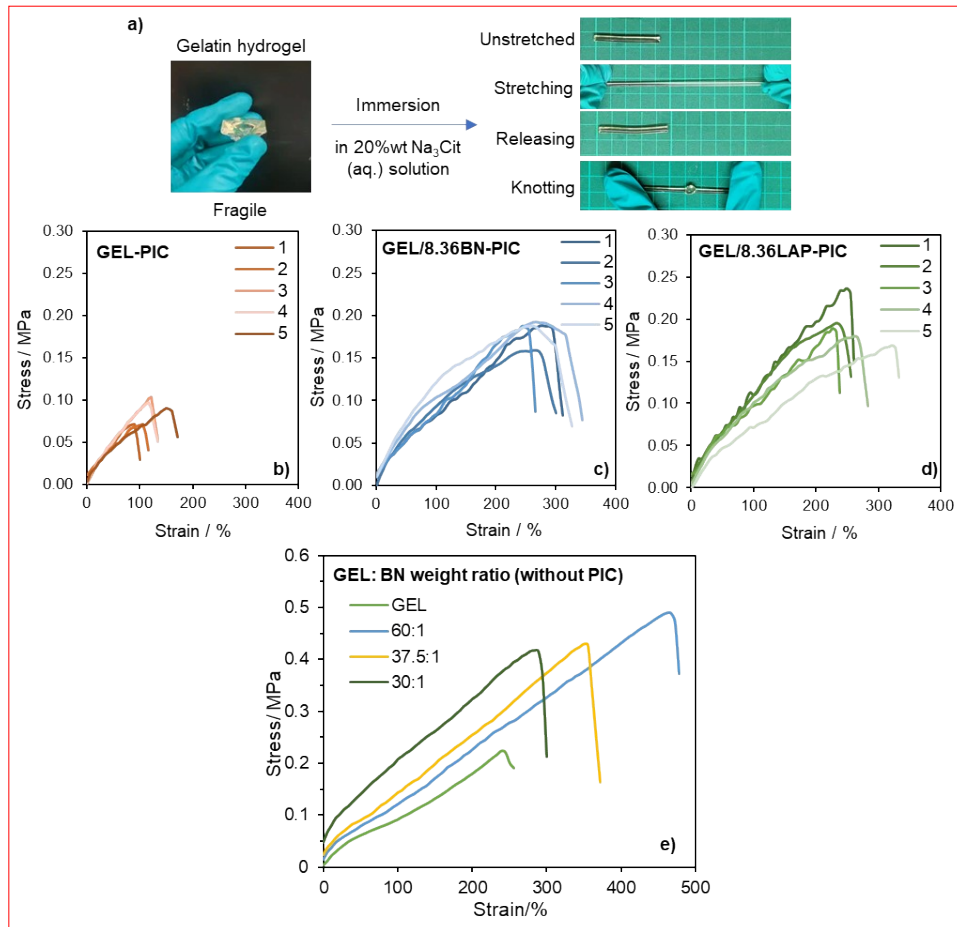


Figure S3. a) Photographs of the GEL before and after the immersion in sodium citrate solution. Tensile stress-strain curves of the a) GEL-PIC, b) GEL/8.36BN-PIC, c) GEL/8.36LAP-PIC and e) GEL-BN composite hydrogel at different gelatin:BN weight ratios (without the addition of PIC).

Table S1 Physical properties of the composite hydrogels.

	Gelatin content (w/w%)	Water content (w/w%)	Clay content (w/w%)	Na ₃ Cit Content (w/w%)	Tensile strength (MPa)	Strain (%)	Modulus (MPa)
GEL-PIC	26.2	58.5	-	15.3	0.087 ± 0.02	116.7 ± 22.6 ^a	0.07 ± 0.01
GEL/8.36BN-PIC	26.3	60.4	0.44	12.8	0.183 ± 0.01	266.7 ± 12.2	0.10 ± 0.02
GEL/8.36LAP-PIC	25.4	60.0	0.42	14.2	0.194 ± 0.03	257.8 ± 35.5	0.10 ± 0.01

[a] Data reported as the average ± S.D.

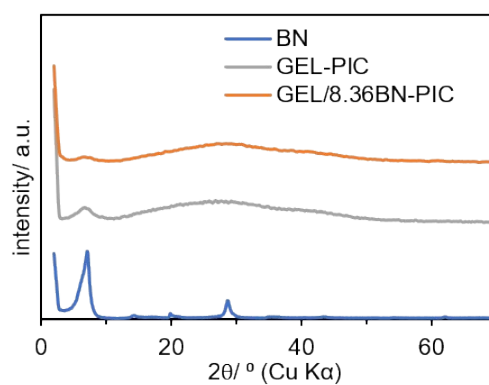


Figure S4. The X-ray diffraction patterns of BN, gelatin hydrogel (GEL) and GEL-BN hydrogel.

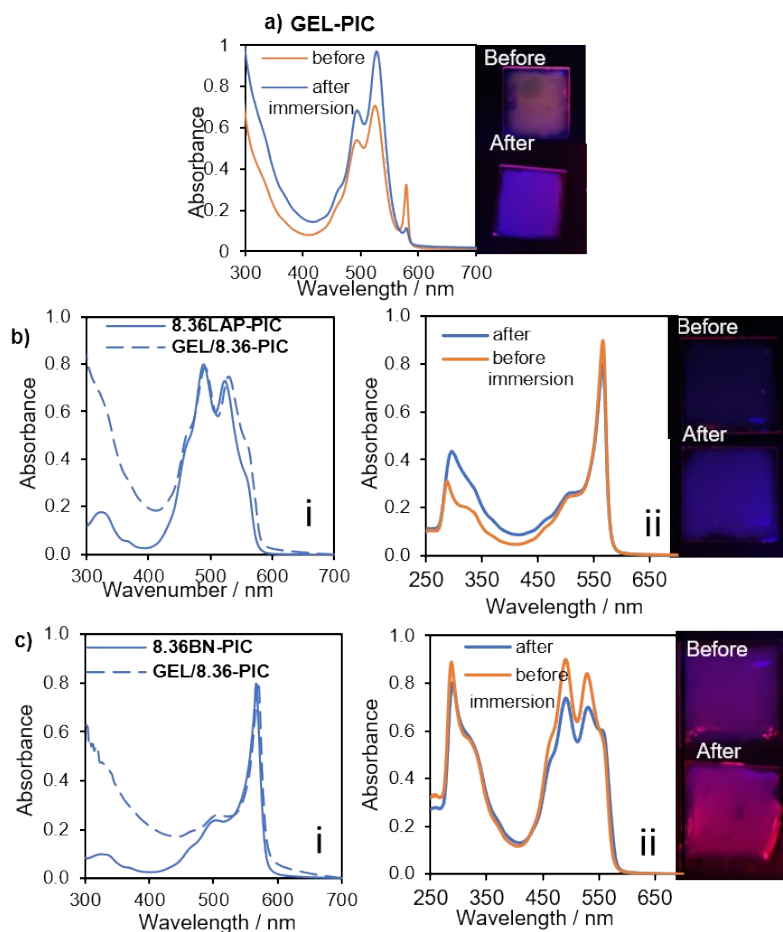


Figure S5. a) Absorption spectra of **GEL-PIC** before and after the immersion in sodium citrate solution. Absorption spectra of b) **8.36LAP-PIC** and c) **8.36BN-PIC** in gelatin hydrogel(i); Absorption spectra of **GEL/8.36Clay-PIC** before and after the immersion in sodium citrate solution (ii)

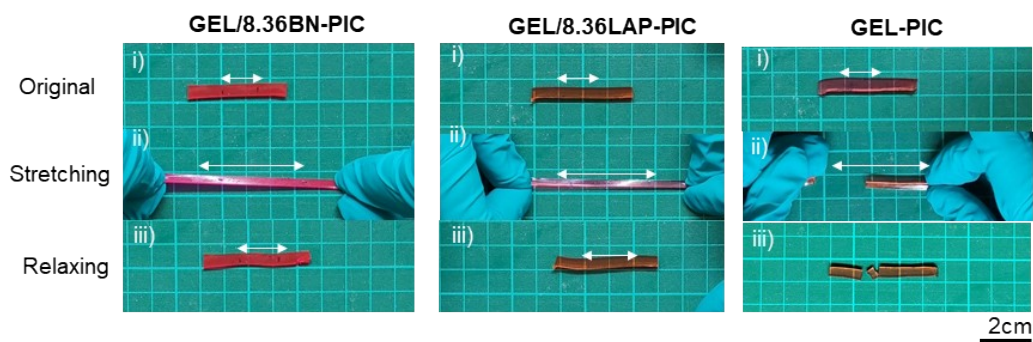


Figure S6. Photos showing the shrinkage behavior of **GEL/8.36BN-PIC**, **GEL/8.36LAP-PIC** and **GEL-PIC**: A gel strip in the original (i), elongated (ii), and recovered (iii) shapes.

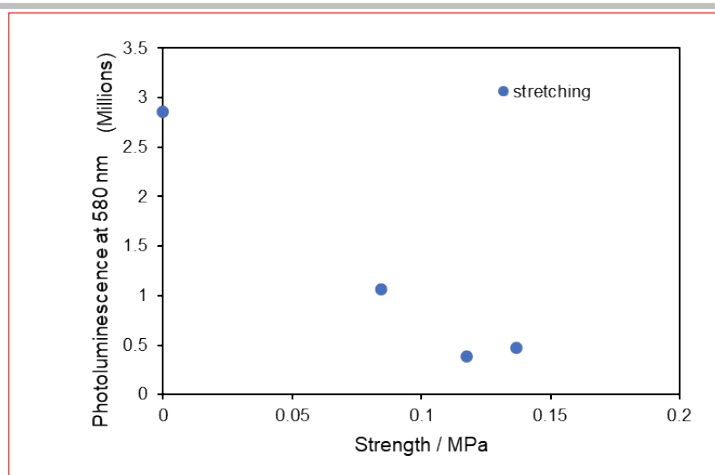


Figure S7. Photoluminescence intensity as a function of the strength of the GEL/8.36BN-PIC.

References

- [1] M. Ogawa, R. Kawai and K. Kuroda, *J. Phys. Chem.*, **1996**, 100, 16218-16221.
- [2] X. Wang, C. Qiao, S. Jiang, L. Liu and J. Yao, *Soft Matter*, **2021**, 17, 1558-1565.