

Supplementary Information

Biodegradable, Ionic Thermoelectric Composites via Self-Assembly of Dipeptides and Deep Eutectic Solvents

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Experimental details

General information

Chemicals and solvents were acquired from commercial vendors and were used without further purification. Choline chloride, ethylene glycol, dimethyl sulfoxide (DMSO), Fmoc-Phe-OH, Trizma[®] hydrochloride, calcium chloride, and Proteinase K were purchased from Sigma-Aldrich (St. Louis, MO, USA). H-Phe-Phe-OH, Ac-Phe-Phe-OH, Boc-Phe-Phe-OH, Z-Phe-Phe-OH, and Fmoc-Phe-Phe-OH were acquired from Bachem (Bubendorf, Switzerland). Double distilled water with a resistivity of 18.2 M Ω ·cm was produced using an aquapuri 5 water purification system (Young In Scientific, Seoul, Republic of Korea). AlogP was calculated with Discovery Studio v.17.1.

Preparation of eutectogels

The eutectogels were synthesized by the solvent exchange method. To obtain the deep eutectic solvent, choline chloride (50.0 g, 0.36 mol) and ethylene glycol (44.4 g, 40.0 mL, 0.72 mol) were mixed at 80 °C for 2 h. Dipeptide stock solutions were prepared at a concentration of 1 g·mL⁻¹ in DMSO. Following materials were prepared at a concentration of 100 mg·mL⁻¹ in DMSO due to the solubility issues: H-Phe-Phe-OH, Ac-Phe-Phe-OH, and Fmoc-Phe-OH. The gelation was performed by the addition of stock solutions (50 μ L) into the deep eutectic solvent (450 μ L). The formation of eutectogels was evaluated using the inverted vial method.

Characterization

Fluorescence (FL) spectra were recorded on a FP-8300 spectrofluorometer (Jasco, Tokyo, Japan) in a quartz cell with 10 mm path length at 25 °C. The emission spectra were measured with a 280 nm excitation, 5.0 nm band width, and 1.0 nm data pitch. Three replicate spectra were obtained and averaged.

The Fourier transform infrared spectroscopy (FT-IR) was carried out on a Nicolet 380 FT-IR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) with a real crystal KBr IR card (International Crystal Laboratories, Garfield, NJ, USA) over a range of 400–4000 cm⁻¹ at 25 °C. To prepare the samples for analysis, a 200 μ L portion of the peptide-based gel was carefully spread onto a KBr IR card, ensuring complete coverage. Then, the KBr IR card was dried in a vacuum oven for 4 h and used for spectra measurements.

Circular dichroism (CD) spectra were obtained on a J-1100 Circular Dichroism Spectrophotometer (Jasco, Tokyo, Japan) in a quartz cell with a 0.1 mm path length at 25 °C. The spectra were acquired over a range of 190–350 nm with a 1.0 nm data pitch, 1.0 nm band width, and 500 nm·min⁻¹ scanning speed. The measurement was performed three times and averaged, and the spectra were corrected with a proper solvent baseline.

The optical transmittance (λ =405 nm) of gels was measured on a V-670 UV-VIS-NIR spectrophotometer (Jasco, Tokyo, Japan) in a quartz cell with a 1 cm path length at 25 °C. Baseline correction for each sample was performed with a solvent blank.

The microstructure of the gels was observed using scanning electron microscopy (SEM) on a Sigma 300 (Zeiss, Oberkochen, Germany). The eutectogels for SEM imaging were soaked in deionized water for 3 days, where the water was changed every 12 h to ensure the complete exchange of DES. Then, the samples were freeze-dried to remove the remaining water and sputter-coated with a fine grain platinum before introduced in the microscope.

Powder X-ray diffraction pattern was acquired on a D8 Advance (Bruker, Billerica, MA, USA)

with a Cu anode at 40 kV and 40 mA. The data were collected in the range of $5\text{--}50^\circ 2\theta$ with a step size 0.02° and a $2\text{ deg}\cdot\text{min}^{-1}$ scanning speed. The incident X-ray beam was conditioned with 0.04 rad Soller slits and a 0.5° divergence slit. The XRD samples were prepared by freeze-drying the gels after the water exchange protocol.

DSC measurements were performed on a Discovery DSC 25 (TA instruments, New Castle, DE, USA) under a nitrogen atmosphere. A cycle of heating and cooling was carried out over the range of -80 to 80° with a heating rate of $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. The weight of the sample was 10 ± 2 mg.

Gelation kinetics study

Confocal laser scanning microscopy (CLSM) images were obtained using an LSM 700 (Zeiss, Oberkochen, Germany) equipped with a 20x objective lens. The gels were prepared by depositing an aliquot of pre-gel solution ($150\text{ }\mu\text{L}$) onto a slide glass, and then carefully covering it with a cover glass to ensure even spreading without air bubbles. The samples were allowed to equilibrate for the desired time before imaging.

Fluorescence emission of thioflavin T (ThT) was recorded on a Synergy H1 (Biotek, Winooski, VT, USA) with an excitation and emission wavelength at 435 nm and 475 nm, respectively. The samples with varying concentrations of Fmoc-FF were prepared from appropriate stock solutions, and the temperature was controlled using the built-in temperature control system in the instrument. The emission intensity was measured every minute for a total duration of 120 min, and the average of two independent sets was acquired.

Rheological analyses

Rheological measurements were performed using an MCR 302 (Anton Paar, Graz, Austria) equipped with a 25 mm parallel plate geometry and a gap of 0.5 mm. The gels were aged for 24 h before each measurement. Amplitude sweep experiments were carried out at a constant frequency of 10 Hz. Frequency sweeps were performed at a constant strain of 0.1%. The self-healing capability of gels was observed using a repeated two-step shear strain protocol at a constant frequency of 10 Hz. The gels were first subjected to a low shear strain of 0.1% for 5 min, followed by a high shear strain of 50% for 1 min. The shear thinning behavior of gels was investigated by measuring the viscosity depending on a steady shear rate sweep from 0.01 to 100 s^{-1} .

3D printing of the eutectogel was performed based on the direct-ink-writing (DIW) technique using an Imagemaster 350PC Smart system (Musashi Engineering, Tokyo, Japan). Freshly prepared FmocFF stock solution ($100\text{ }\mu\text{L}$) and DES ($900\text{ }\mu\text{L}$) were added into a disposable ink container equipped with a 26G needle, and the mixture was allowed for 50 min at $25\text{ }^\circ\text{C}$. Then, the solution was extruded onto the polymer film or glass under the following conditions: printing speed of $5\text{ mm}\cdot\text{s}^{-1}$, a nozzle height of 0.1 mm, and a pressure of 100 kPa.

Ionic conductivity measurement

The ionic conductivity (σ) of samples was determined by electrochemical impedance spectroscopy (EIS) measurements on an Autolab PGSTAT302N (Metrohm, Herisau, Switzerland) over a frequency range of $10^5\text{--}10^{-1}$ Hz with an AC amplitude of 10 mV. The pre-gel solution or DES were prepared in a Swagelok-type cell with a cross-sectional area (A) of 0.2 cm^2 and a thickness (L) of 1.2 cm. The cell was allowed for 24 h at the desired temperature and relative humidity conditions using a TEMI 1300 (Samwon Technology, Bucheon, Republic

of Korea). The σ was calculated using the equation, $\sigma = L / (R_s \times A)$, where R_s refers to the resistance of the electrolyte, which was measured at the intercept of the real axis in a Nyquist plot.

Biodegradability test

The biodegradability of gels was assessed using a proteolytic enzyme, proteinase K. To prepare the degradation mixture, proteinase K (2.5 or $25 \text{ U} \cdot \text{mL}^{-1}$) was incubated in 50 mM Tris-HCl buffer ($\text{pH } 8.0$) containing 5 mM of CaCl_2 for 4 h in a 15 mL conical tube at 37°C . A disk-shaped hydrogel and eutectogel were used for the assessment, which was prepared by allowing the pre-gel solution ($150 \mu\text{L}$) to undergo gelation in a disposable syringe with a diameter of 10 mm for 24 h . Then, the gels were immersed in the activated degradation mixture, in which the concentration of proteinase K was 0.25 U per 1 mg of FmocFF. The samples were gently shaken for the desired time at 37°C . After shaking, the weight change of the gel was recorded to evaluate its biodegradability.

Analytical HPLC was performed using a Waters reversed-phase HPLC system (Waters 2489 UV/visible detector, Waters 1525 Binary HPLC pump, Waters 2707 Autosampler, and Waters 5CH column oven) on a C18 column (SunFire C18, $4.6 \times 250 \text{ mm}$, $5 \mu\text{m}$) at 40°C . A binary mobile phase system (A: deionized water + 0.1% TFA, B: CH_3CN + 0.1% TFA) was employed as follows: 5 min at 10% B, a linear gradient to 100% B over 20 min , and hold 100% B for 10 min . The flow rate was $1 \text{ mL} \cdot \text{min}^{-1}$, and the peak was monitored by the absorbance at 220 nm . ESI-MS analysis was conducted on an Agilent 1260 Infinity liquid chromatography system with an Agilent 6120 single quadrupole mass spectrometer.

Thermoelectric application

The ionic Seebeck coefficient was measured in-plane directions by the home-built device using Keithley DAQ6510 instruments in a humidity-controlled chamber. Initially, a glass substrate was treated in a UV-ozone cleaner for 30 min . Subsequently, two lines of Ag electrode were deposited on the glass by silver paste. The T-type thermocouples were placed to the top of the Ag electrode. The dispersion of Fmoc-FF hydrogels and eutectogels was drop-casted on the middle of the Ag electrodes. One Peltier heater and one Peltier cooler were located under the glass substrate, and provided the temperature gradient. The samples were stabilized at certain RH inside the humidity-controlled chamber for 60 min before any measurements were proceeded.

The Ionic thermoelectric capacitor was investigated with same conditions for the ionic Seebeck coefficient measurement. In Figure 3d at stage ii, the temperature difference was applied approximately 1.5 K . In stage iii, the device was connected to an external load with 220Ω while the temperature gradient was maintained. Connecting-disconnecting cycles were performed for 7 times.

Table S1 Eutectogelation of various FF-based gelators.

entry	gelators	[gelators]	solvents	type	assemblies structured in H ₂ O	ref.
1	H-FF	1% (w/v) ^a	ChCl/EG	sol	tube	[1]
2	Ac-FF	1% (w/v) ^a	ChCl/EG	sol	na ^b	[2]
3	Boc-FF	10% (w/v)	ChCl/EG	sol	tube	[2]
4	Z-FF	10% (w/v)	ChCl/EG	sol	fibril	[2]
5	Fmoc-FF	10% (w/v)	ChCl/EG	gel	fibril	[2]
6	Fmoc-F	1% (w/v) ^a	ChCl/EG	gel	fibril ^c	[3]

^a H-FF, Ac-FF, and Fmoc-F were utilized with 100 mg·mL⁻¹ stock solution due to the solubility issues in DMSO. ^b na: not available. ^c under the 0.1 M NaOH conditions.

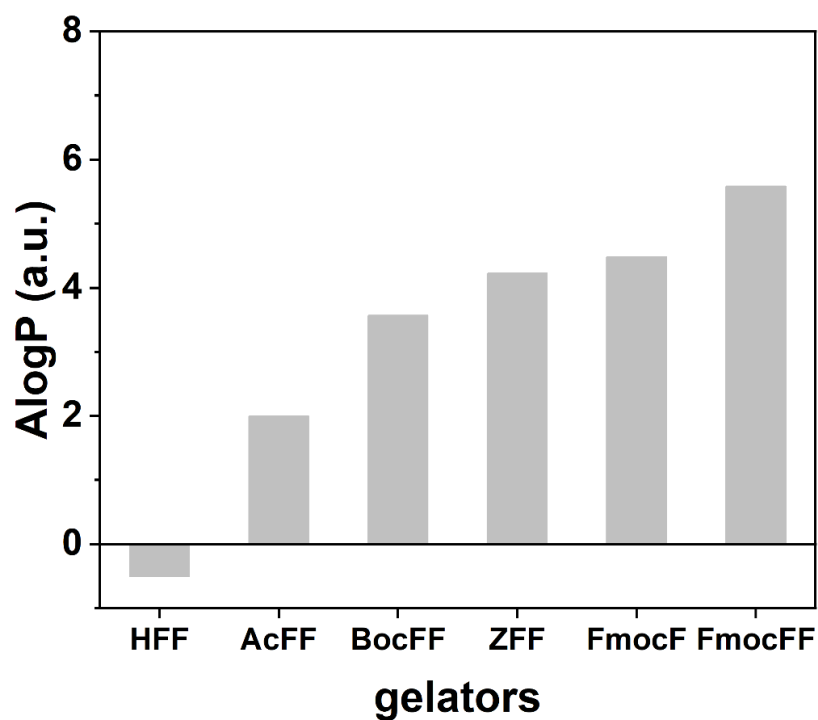


Fig. S1 The Ghose-Crippen-Viswanadhan octanol-water partition coefficient (AlogP) of the FF derivatives calculated by Discovery Studio program v.17.1.

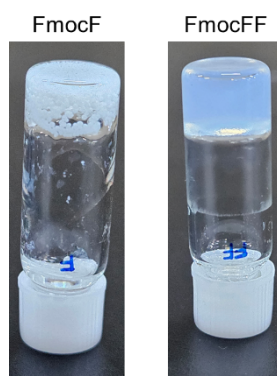


Fig. S2 Photographs of Fmoc-F and Fmoc-FF eutectogels.

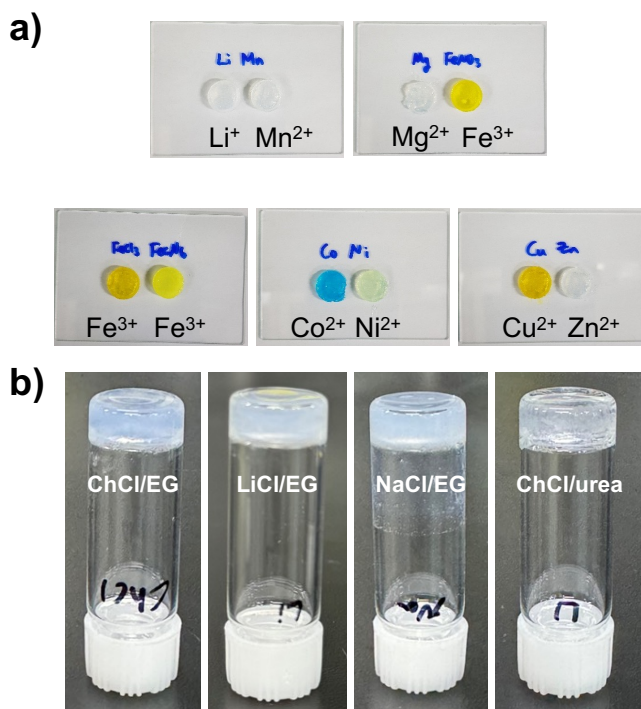


Fig. S3 (a) Photographs of Fmoc-FF eutectogels in ChCl/EG containing various metal salts (0.1 M LiCl, MnCl₂, MgCl₂, FeNO₃, FeCl₃, FeCN₆, CoCl₂, NiCl₂, CuCl₂, and ZnCl₂). (b) Photographs of Fmoc-FF (10% w/v) eutectogels in ChCl/EG, LiCl/EG, NaCl/EG, and ChCl/urea. The molar ratio of LiCl/EG, NaCl/EG, and ChCl/urea is 3:1, 16:3, and 1:2, respectively.

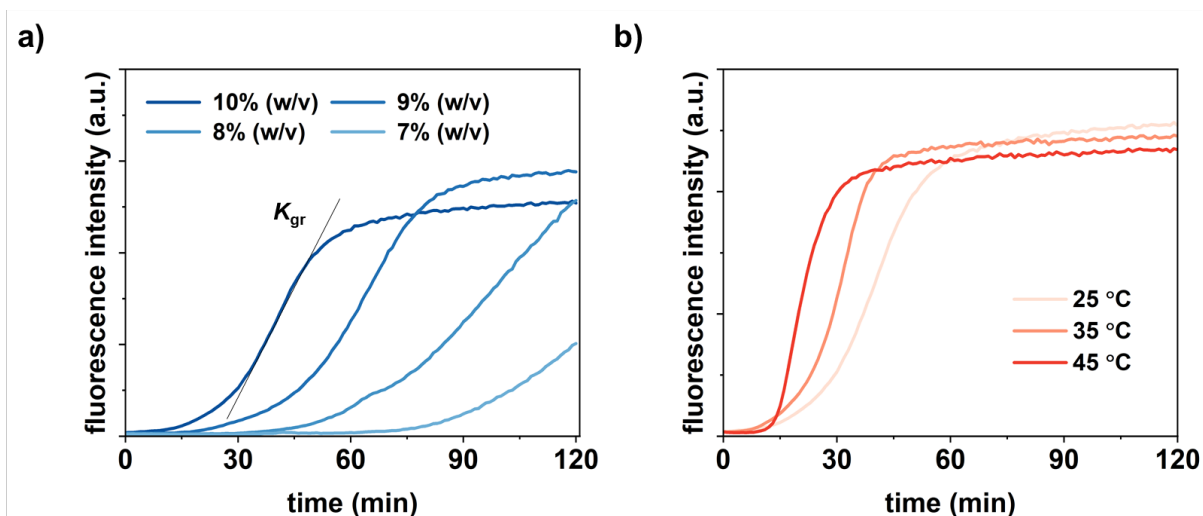


Fig. S4 Time-dependent fluorescence emission profiles depending on (a) Fmoc-FF concentrations at 25 °C and (b) temperatures at [Fmoc-FF]=10% (w/v). The excitation and emission wavelength were 435 nm and 475 nm, respectively.

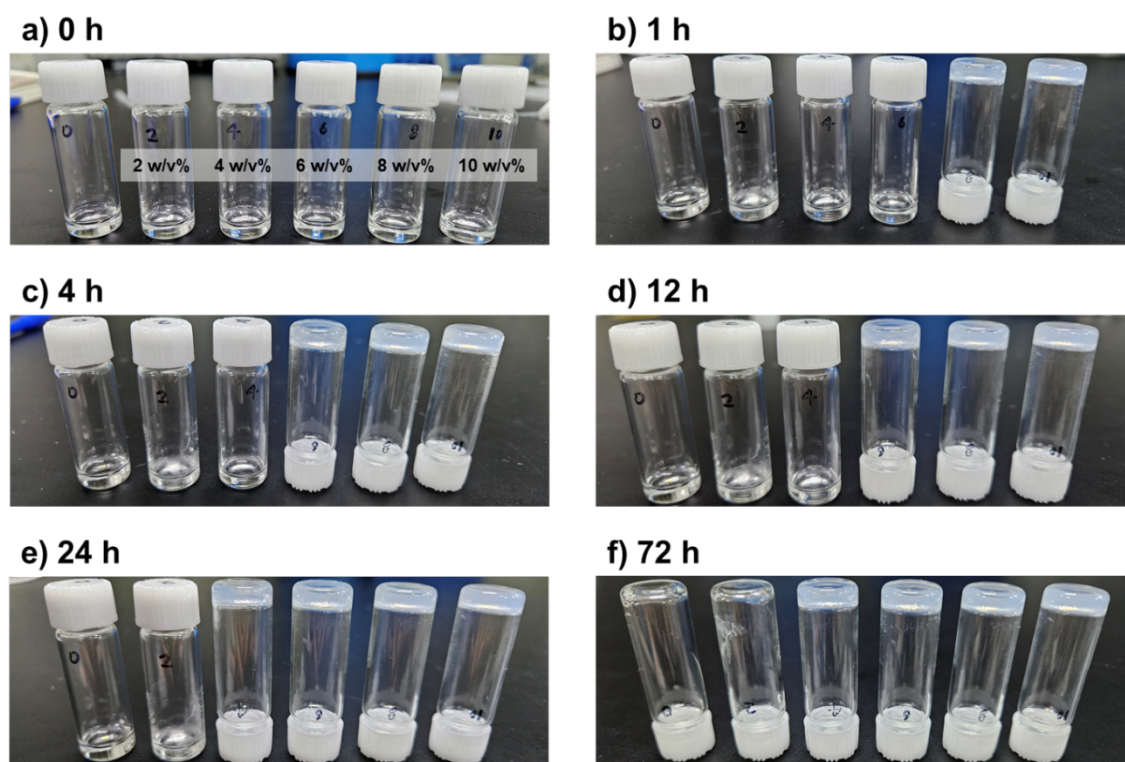


Fig. S5 Time lapse photographs of Fmoc-FF in ChCl/EG. Fmoc-FF concentrations were varied from 2% (w/v) to 10% (w/v). The concentration of DMSO was 10% (v/v). According to the image at 72 hours, the critical eutectogelation concentration of Fmoc-FF was 4% (w/v).

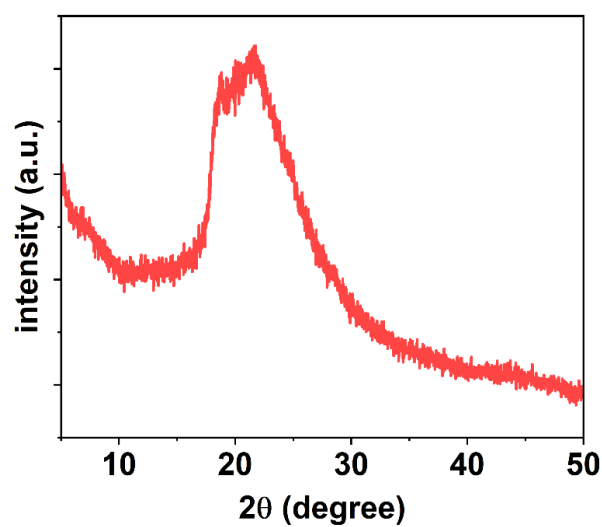


Fig. S6 PXR D pattern recorded for dried Fmoc-FF eutectogel at 25 °C. The concentration of Fmoc-FF for eutectogelation was 10% (w/v).

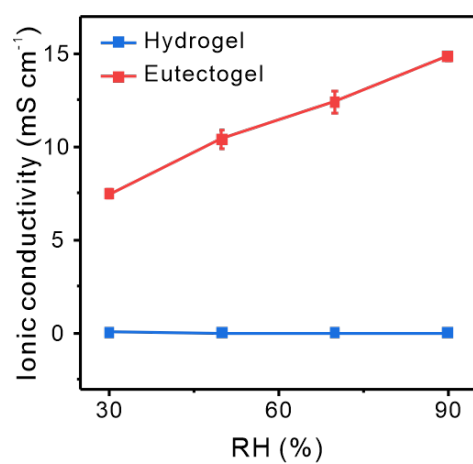


Fig. S7 The ionic conductivity of Fmoc-FF eutectogels and hydrogels including error bars with varying humidity.

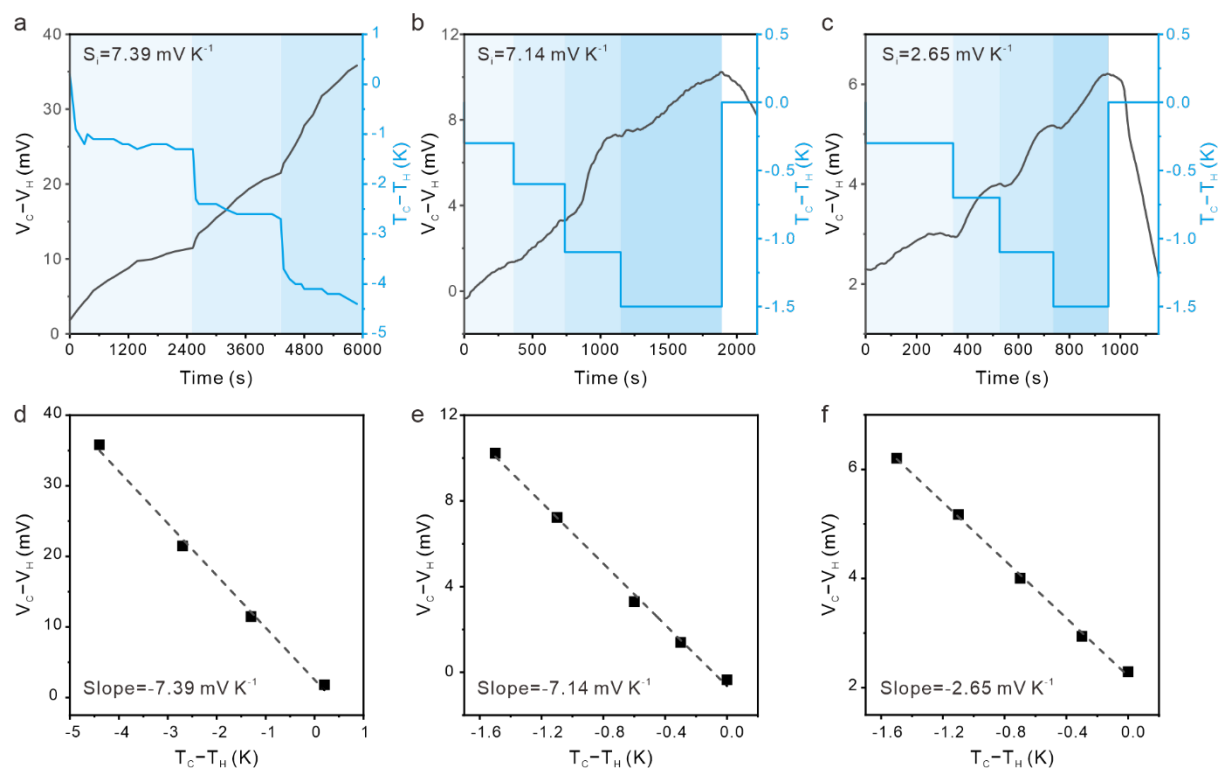


Fig. S8 Thermovoltage measurements for the Fmoc-FF eutectogels. Evolution of voltage difference versus time for various applied ΔT according to the different relative humidity level at (a) 90%, (b) 70%, and (c) 50%. Steady ΔV versus temperature difference at RH of (d) 90%, (e) 70%, and (f) 50%.

Table S2 Ionic thermoelectric parameters of Fmoc-FF eutectogels.

RH (%)	σ_i (mS cm ⁻¹)	S_i (mV K ⁻¹)	κ (W m ⁻¹ K ⁻¹)	zT
50	10.40	2.65	0.087	0.025
70	12.39	7.14	0.087	0.22
90	14.85	7.39	0.087	0.28

Table S3 Quantification of HPLC peak area according to 21.7 min (Proteinase K) and 22.5 min (Tris-HCl).

Degradation time (h)	relative area (a.u.)	
	Proteinase K (21.7 min)	Tris-HCl (22.5 min)
2	3.1	1.0
12	6.9	1.4
48	10.2	1.4

Table S4 Studies on thermoelectric applications utilizing degradable materials.

materials	role	degradability	ref.
Carboxyl functionalized cellulose-based ionogels (CBCIGs)	Ionic TE material	Not specified	[4]
Lignin/PVA	Ionic TE material	Not specified	[5]
Polyhydroxyalkanoates (PHA) /agminated black	e-TE supporter	53.8% weight loss after 9 days (4% NaOH)	[6]
CuI/NC (Nanocellulose)	e-TE supporter	Not specified	[7]
CuI/NC	e-TE supporter	Not specified	[8]
Cellulose/BiSbTe	e-TE supporter	Not specified	[9]
Bacterial cellulose/Bi ₂ Te ₃	e-TE supporter	Not specified	[10]
Dynamic silyl ether bond (BAA) epoxy vitrimer	TEG encapsulation	Completely dissolved for 8 h in 60 °C THF	[11]
PEDOT:PSS/cellulose acetate	e-TE supporter	Completely dissolved for 260 s in acetone	[12]
Poly(l-lactide-co-ε-caprolactone)/PEDOT:PSS	e-TE supporter	Completely dissolved in 35 days in PBS (pH 13) solution	[13]

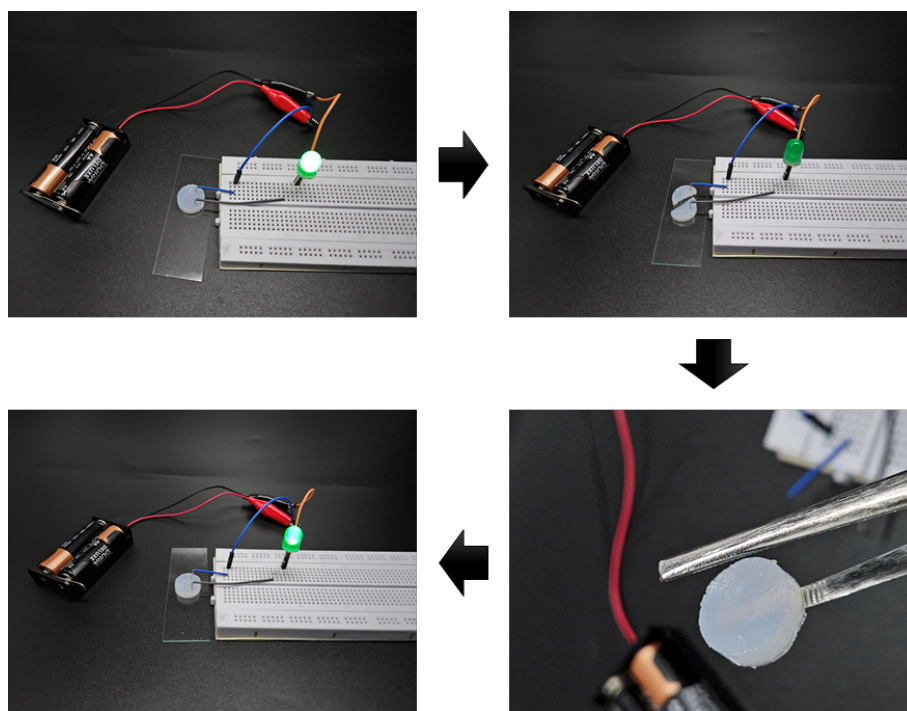


Fig. S9 LED bulb tests with ion-conductive and self-healable Fmoc-FF eutectogel.

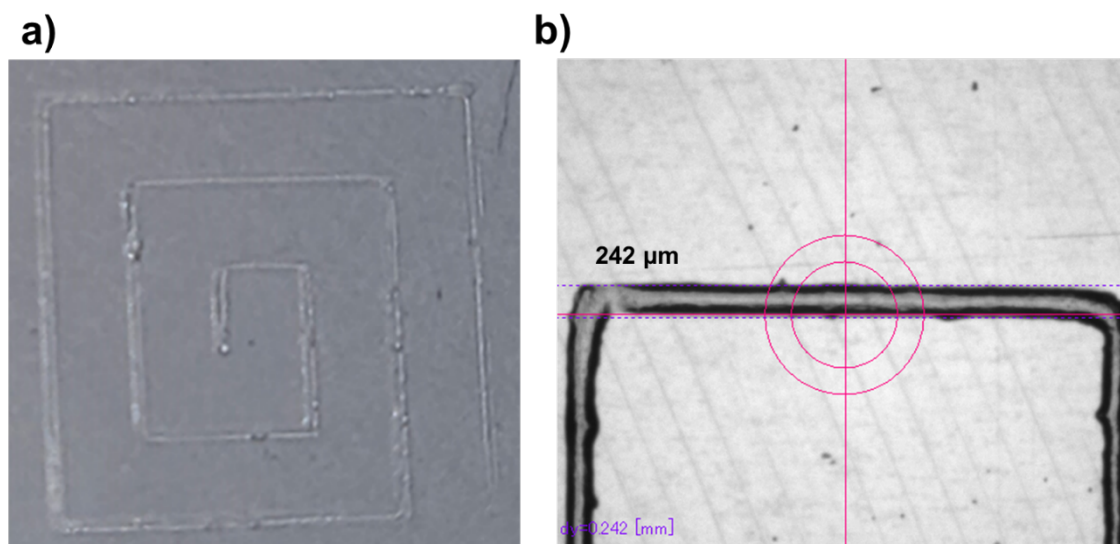


Fig. S10 Photographs of extruded Fmoc-FF eutectogel from a 3D printer (a) Photograph of 3D printed Fmoc-FF eutectogels taken by Samsung Galaxy S23. (b) Magnified optical image of 3D printed Fmoc-FF eutectogels by built-in camera in Musashi 350 PC smart.

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