

Supplementary Information

Thermal-history encoding through ionic-state programming in a monolithic organic thermosynapse

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Other Supplementary Information for this manuscript includes the following:

Supplementary video 1,2,3

Supplementary Notes

Supplementary Note 1. Design of IPN structured thermoresponsive zwitterionic gel

The thermoresponsive zwitterionic gel forms associated polymer domains at low temperatures because of intra- and interchain electrostatic interactions between the zwitterionic side groups. These interactions promoted side-chain association, leading to the formation of ionic aggregates that effectively capture mobile ions, thereby establishing an ion-trapping state. As the temperature increased, the strength of these ionic interactions was reduced, resulting in the dissociation of the aggregates and the corresponding release of the previously trapped ions. Utilizing this UCST behavior, ion transport was efficiently controlled by a trap/release mechanism, allowing for systematic regulation of ionic dynamics and providing high sensitivity at specific temperatures. However, conventional UCST-type polymer solutions often undergo macroscopic phase separation and polymer precipitation at low temperatures, resulting in poor mechanical integrity and limiting their direct use in solid-state synaptic devices. To address this problem, an interpenetrating polymer network (IPN) structure was introduced to enhance the mechanical robustness of zwitterionic gel. In this approach, temperature-inactive PEGDA was incorporated as a second network at various compositions. As the PEGDA content increased, the mechanical strength of the zwitterionic gel improved, and at concentrations above 10 mol%, the storage modulus (G') exceeded the loss modulus (G'') at the overall frequency range, indicating gel-like behavior (Supplementary Fig. N1).

Furthermore, to investigate whether PEGDA affects the temperature-dependent behavior of PDMAPS, we separately analyzed the segmental-relaxation activation energies of PEGDA and the zwitterionic gel without PEGDA. The results showed that PEGDA exhibited constant $E_{a,seg}$ regardless of temperature. In contrast, the zwitterionic gel without the crosslinker showed lower mechanical strength and correspondingly lower $E_{a,seg}$ compared to the crosslinked zwitterionic gel; however, the temperature-dependent behavior remained consistent tendency in both cases (Supplementary Fig. N2). These findings confirmed that the IPN structure enhanced mechanical strength without altering the UCST behavior.

In the absence of the IPN structure, PDMAPS underwent aggregation and gravitational sedimentation at low temperatures, generating concentration gradients and progressively

degrading the ion-confinement/release response during repeated thermal cycling. In contrast, the IPN structure suppressed gravitational redistribution of PDMAPS and maintained a spatially homogeneous polymer network, enabling stable and repeatable ion-confinement/release behavior (Supplementary Fig. N3).

Supplementary Note 2. Room-temperature OECT characteristics and pulse-dependent plasticity of monolithic thermosynapses

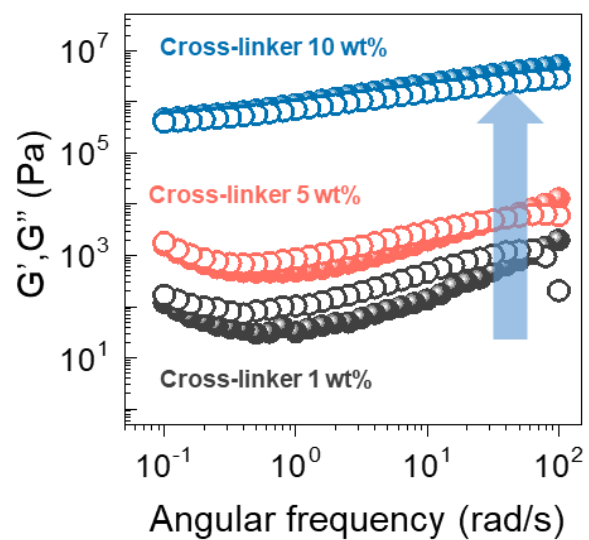
To evaluate the basic device performance of the monolithic thermosynapse, we first measured the output and transfer characteristics at room temperature. As shown in Supplementary Fig. N4a, the drain current exhibited continuous and pronounced modulation with gate voltage, indicating that the mobile ions in zwitterionic gel can effectively regulate the electrochemical doping state of the PEDOT:PSS channel. Based on the output characteristics, a drain voltage of -0.4 V was selected for the subsequent transfer-curve measurements. The transfer curve further confirmed the typical gate-controlled behavior of the OECT. As shown in Supplementary Fig. N4b, when the gate voltage increased to approximately 1.5 V, the drain current decreased markedly, indicating effective dedoping of the PEDOT:PSS channel. These results demonstrate that the monolithic thermosynapse possesses stable transistor characteristics and effective electrolyte gating capability, providing a device basis for subsequent pulse-response measurements.

On this basis, we systematically investigated the effects of pulse number, pulse amplitude and pulse duration on the drain current to evaluate the pulse-dependent dynamic current response and synaptic plasticity of the monolithic thermosynapse. First, as shown in Supplementary Fig. N5a, the number of gate pulses was increased from 1 to 50 under fixed pulse voltage and pulse width. As the pulse number increased, the drain current gradually accumulated and maintained a higher residual current level after stimulation. This result indicates that the monolithic thermosynapse exhibits pulse-number-dependent plasticity, allowing the number of repeated stimuli to be encoded into distinct current output states.

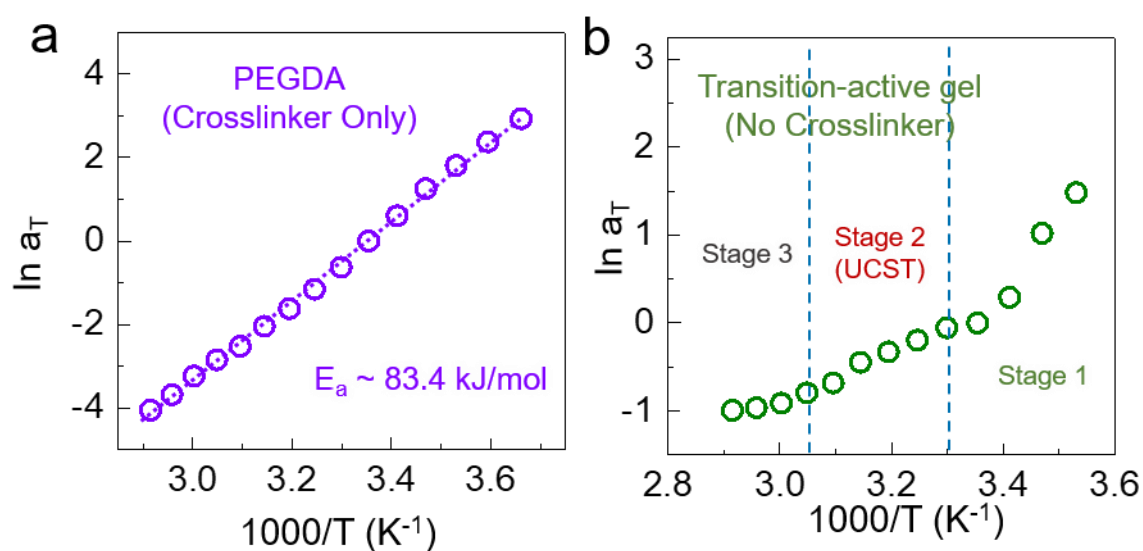
Next, as shown in Supplementary Fig. N5b, the gate-pulse voltage was increased from 0.5 to 4.5 V under the same pulse number and pulse duration. As the pulse voltage increased, both the peak current and the residual current after pulse stimulation gradually increased, indicating

that a stronger gate-driving force induces more pronounced channel conductance modulation. This result demonstrates that the monolithic thermosynapse exhibits pulse-amplitude-dependent plasticity and can encode stimulus intensity into different current output states. Furthermore, as shown in Supplementary Fig. N5c, the duration of each individual pulse was increased from 0.01 to 2 s under fixed pulse number and pulse voltage. As the pulse duration increased, the current response of the device gradually increased, and a higher residual current level was maintained after pulse removal. This result indicates that the monolithic thermosynapse exhibits pulse-duration-dependent plasticity and can electrically encode stimulus duration.

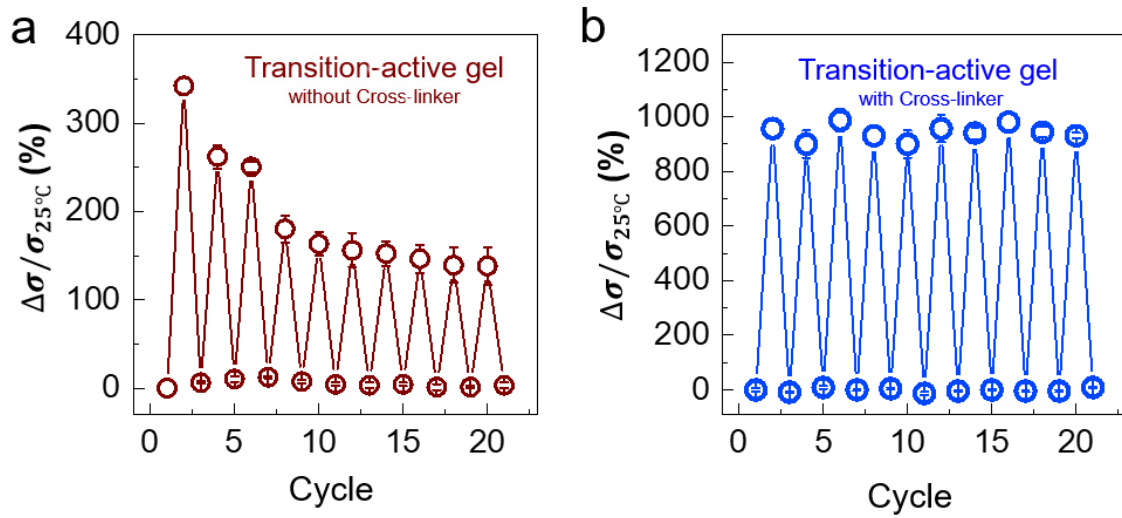
Taken together, the current state of the monolithic thermosynapse can be regulated by pulse number, pulse amplitude and pulse duration. Under stronger or longer stimulation conditions, the device response evolves from a rapidly decaying short-term response to a more stable current-retention state, demonstrating short-term plasticity to long-term plasticity (STP-to-LTP) transition behavior. These room-temperature characteristics provide the baseline device response for the subsequent investigation of thermally enhanced memory behavior.



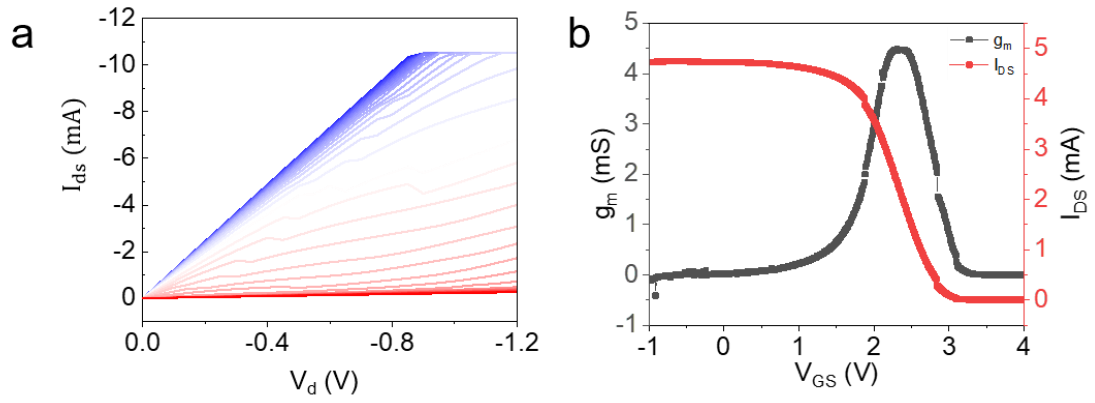
Supplementary Fig. N1. | The rheological properties of zwitterionic gel according to cross-linking density. Frequency sweep of zwitterionic gel with various concentrations of PEGDA.



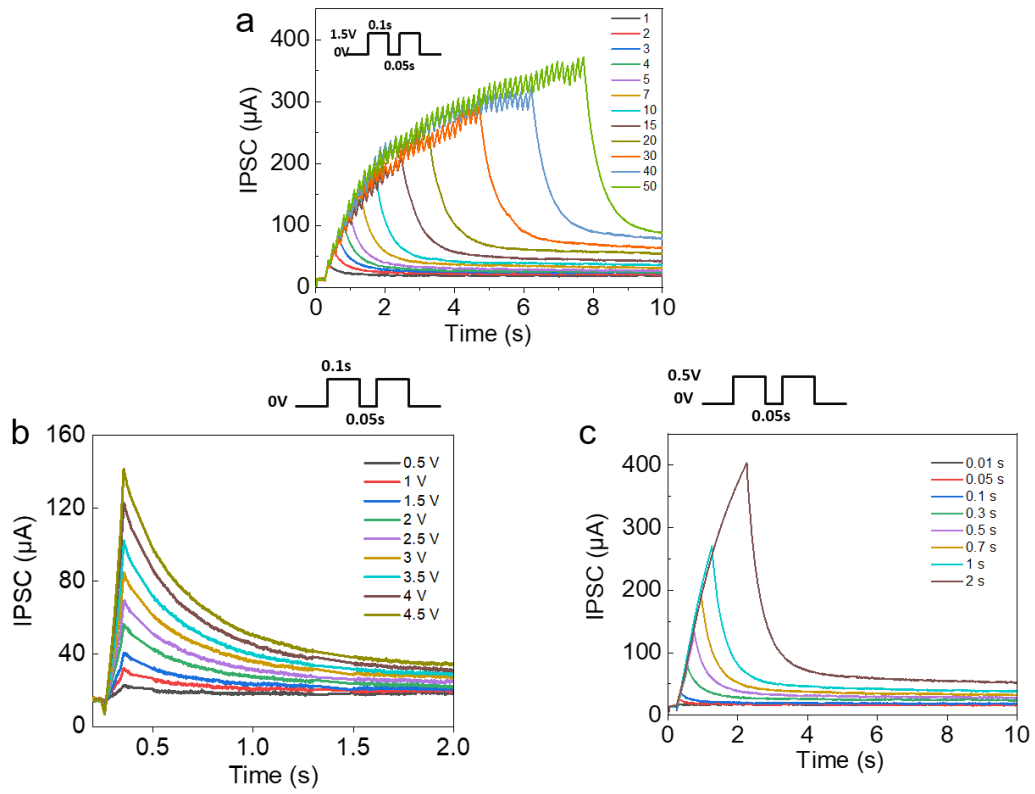
Supplementary Fig. N2. | Decoupling of the rheological properties of PDMAPS and PEGDA in an IPN structured transition-active gel. The plot of horizontal shift factor (a_T) against $1000/T$ for **a**, PEGDA and **b**, transition-active gel without PEGDA



Supplementary Fig. N3. | Stability of ion confinement-release performance in single-network transition-active gel and IPN-structured transition-active gel. Ion confinement-release cycle test between 25 °C and 60 °C of **a**, single-network transition-active gel without crosslinker and **b**, IPN-structured transition-active gel.

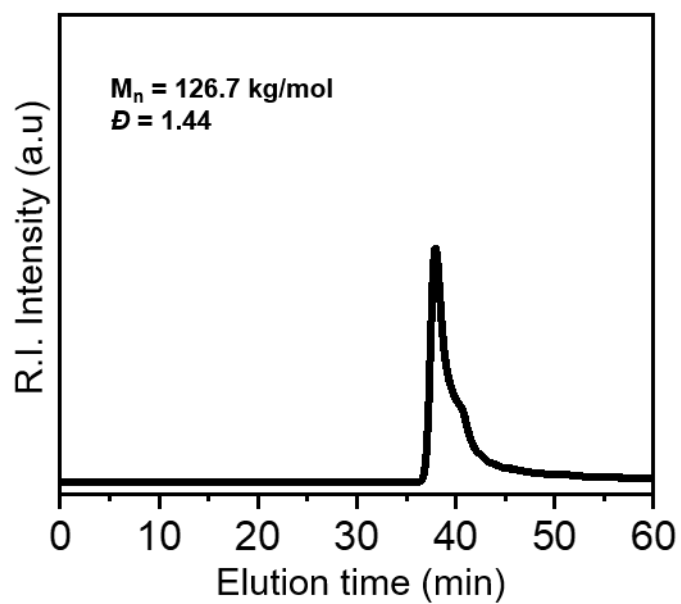


Supplementary Fig. N4. | Basic electrical characteristics of the monolithic thermosynapse.
a, Output characteristics of the monolithic thermosynapse. **b**, Transfer characteristics and corresponding transconductance of the monolithic thermosynapse.

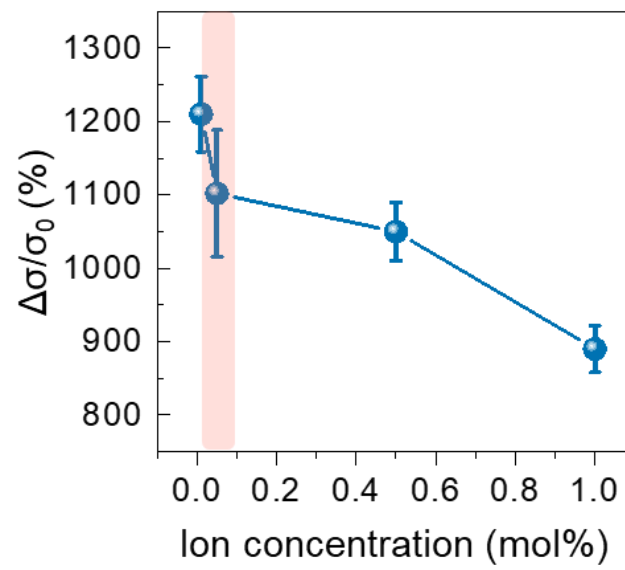


Supplementary Fig. N5. | Dynamic response characteristics of the monolithic thermosynapse under different gate-pulse conditions. a, IPSC responses as a function of the number of consecutive gate pulses. **b,** IPSC responses under different gate-pulse amplitudes. **c,** IPSC responses under different gate-pulse widths.

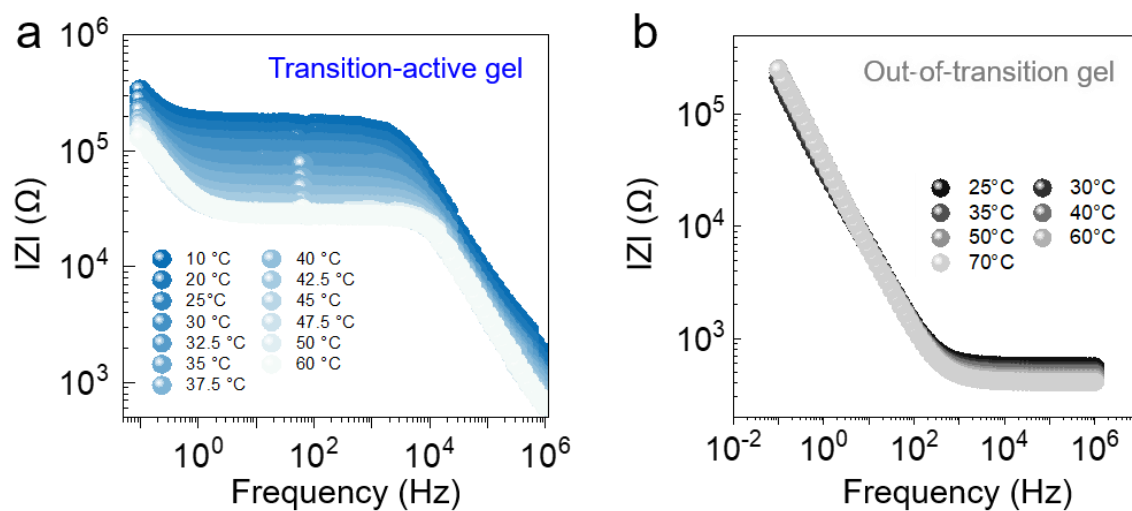
Supplementary Figures



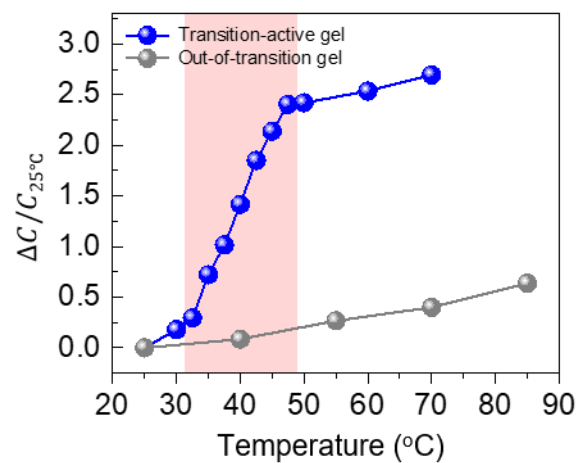
Supplementary Fig. 1 | SEC trace of PDMAPS homopolymer.



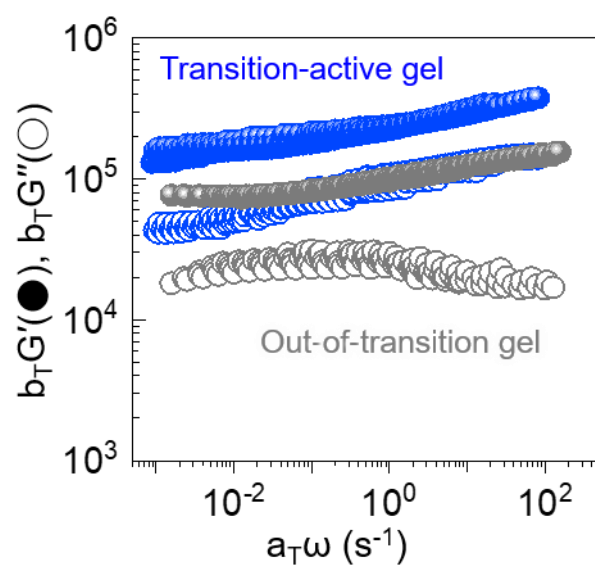
Supplementary Fig. 2 | The ion confinement-release performance of zwitterionic gel according to ion concentration. Relative ionic conductivity of zwitterionic gels as a function of ion concentration between 25 °C and 60 °C.



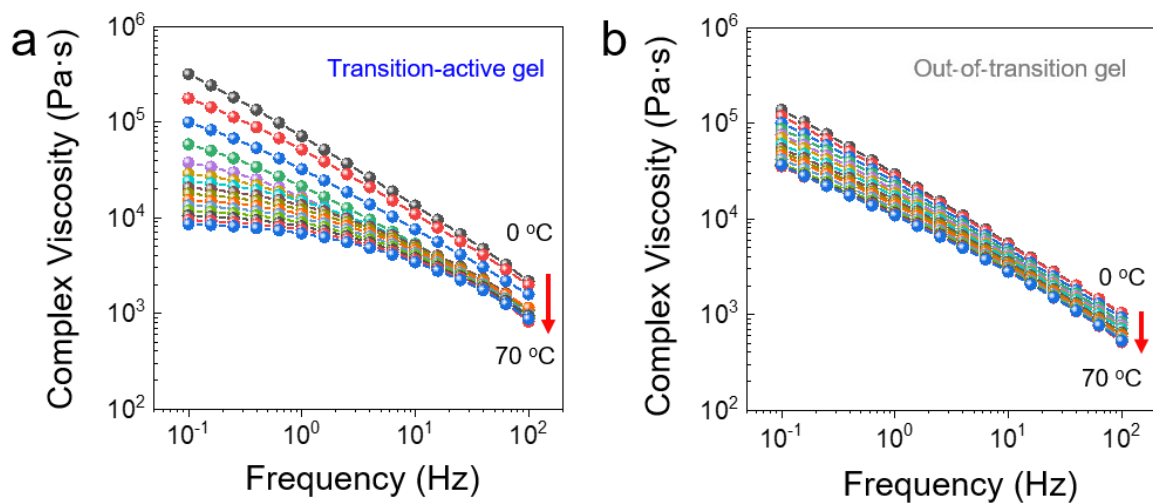
Supplementary Fig. 3 | The ion confinement-release performance of thermoresponsive zwitterionic gel and control gel. Bode plot of **a**, transition-active gel and **b**, out-of-transition gel. To examine the ion confinement-release effect associated with the change in UCST behavior, zwitterionic gels with different ion compositions (0.05 mol% (transition-active gel) and 10 mol% (out-of-transition gel)) were prepared. Accordingly, the comparison focuses on the relative change in ionic conductivity rather than its absolute value.



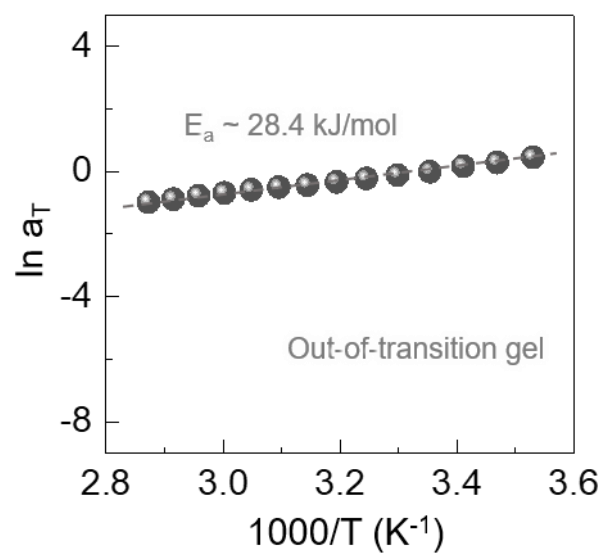
Supplementary Fig. 4 | Effect of UCST characteristics on free-ion availability of zwitterionic gels. Relative EDL capacitance changes of transition-active gel and out-of-transition gel.



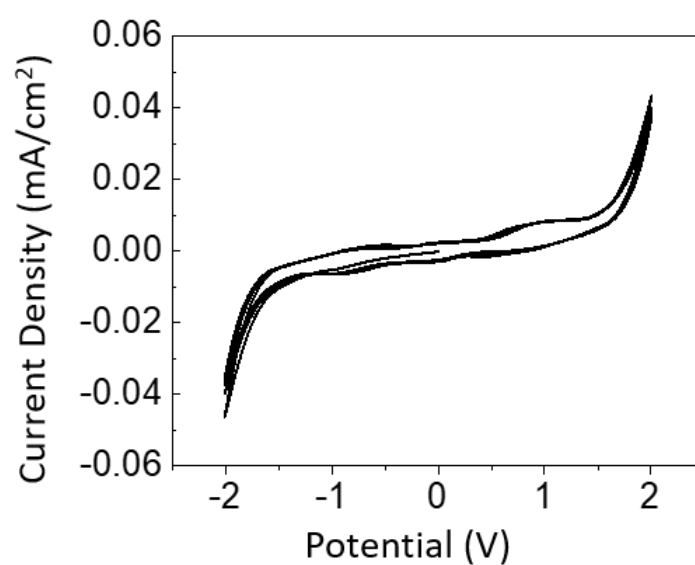
Supplementary Fig. 5 | Rheological behavior of zwitterionic gels with different UCST conditions. TTS master curves of the transition-active and out-of-transition gels.



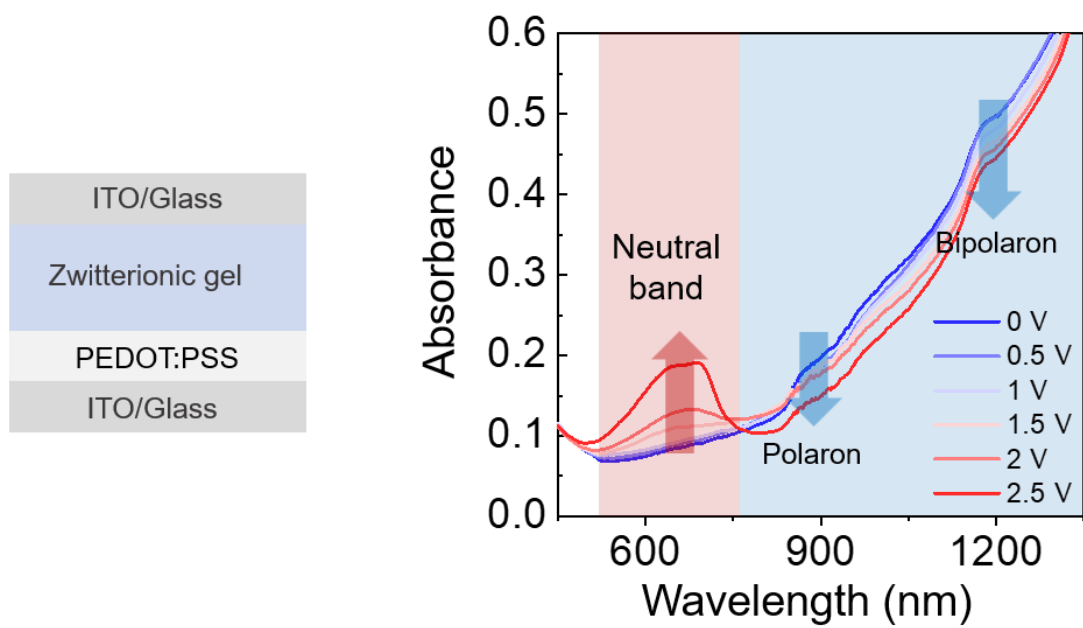
Supplementary Fig. 6 | The rheological properties of thermoresponsive zwitterionic gel and control gel according to temperature. Complex viscosity of **a**, transition-active gel and **b**, out-of-transition gel at various temperatures. The horizontal shift factor was calculated as following: $\log(a_T) = \log \eta^*(\omega, T) / \eta^*(\omega, T_0)$, where a_T is horizontal shift factor, $\eta^*(\omega, T)$ is complex viscosity at ω (frequency, 5Hz) under T , and $\eta^*(\omega, T_0)$ is complex viscosity at ω (5Hz) under reference temperature (20 °C).



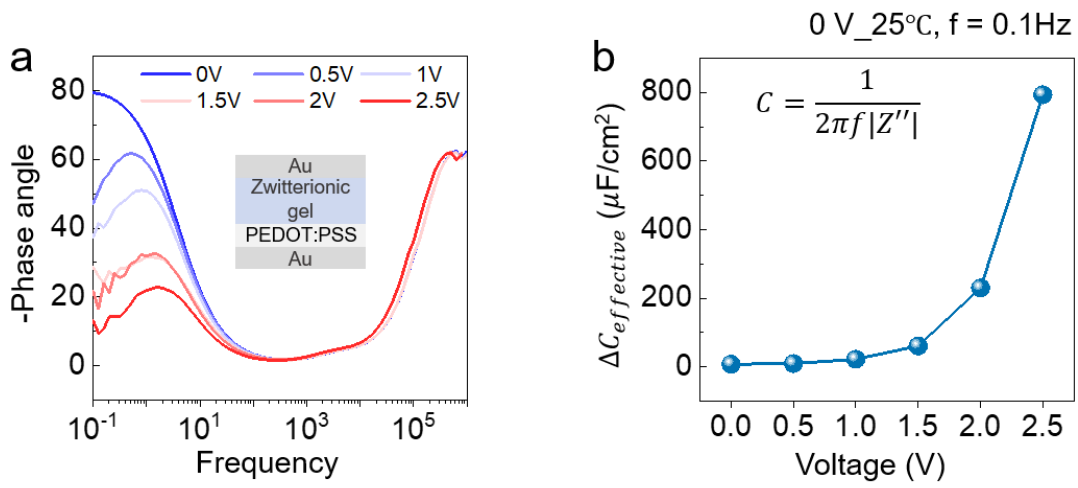
Supplementary Fig. 7 | Structural dynamics of out-of-transition gel. The plot of a_T against $1000/T$ for out-of-transition gel.



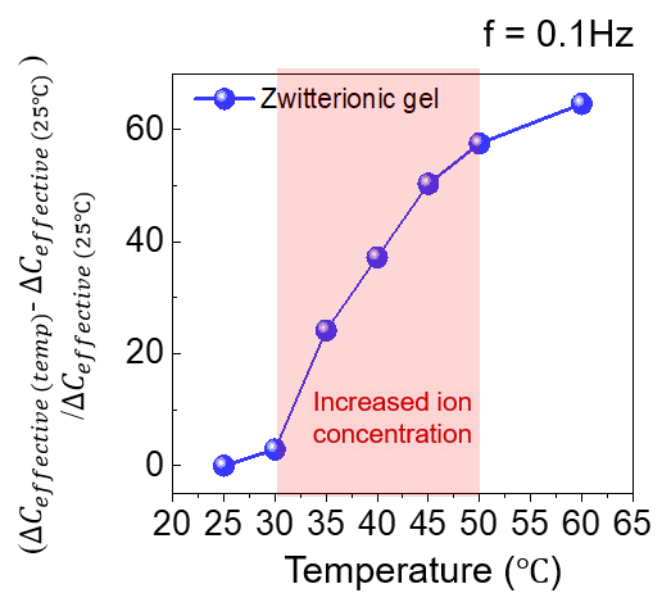
Supplementary Fig. 8 | Cyclic voltammetry characterization of zwitterionic gel. Cyclic voltammogram of zwitterionic gel measured over a potential window from -2 to 2 V.



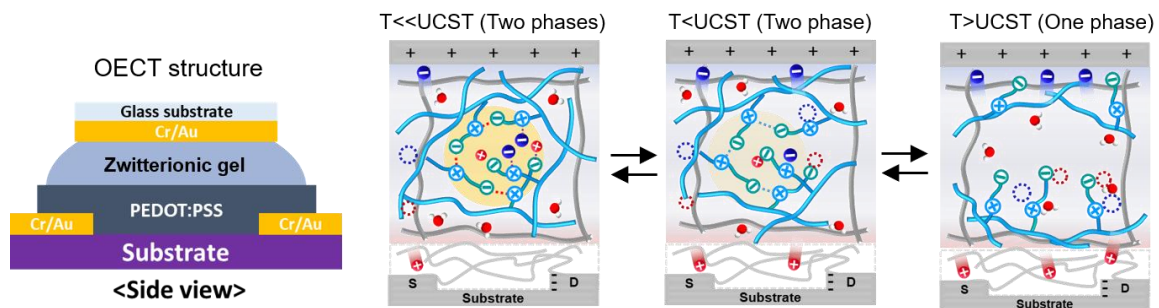
Supplementary Fig. 9 | UV-vis absorption spectra of PEDOT:PSS with LiTFSI. The variation of the absorption spectra was obtained under applied voltage ranging from 0 V to 2.5 V.



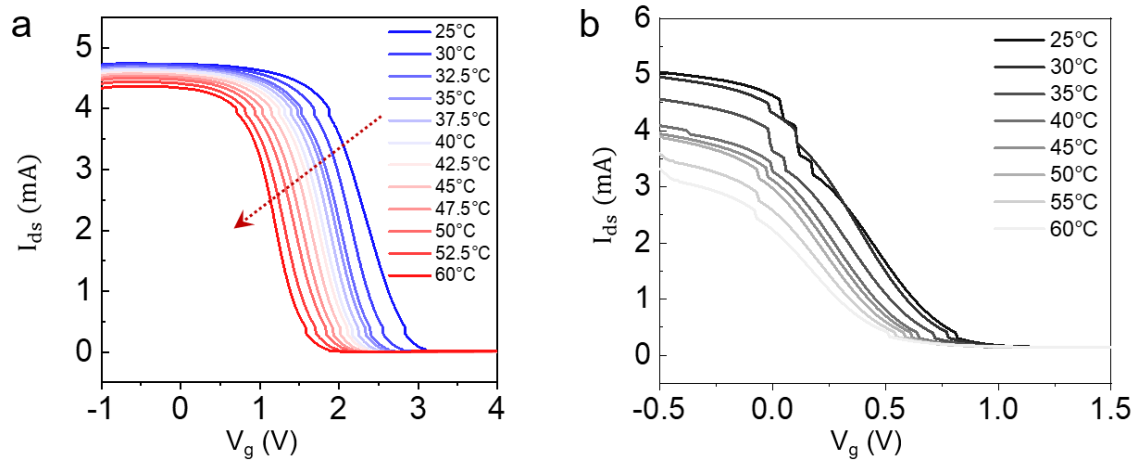
Supplementary Fig. 10 | Voltage-dependent impedance characteristics of the zwitterionic gel /PEDOT:PSS capacitor. **a**, Phase angle as a function of frequency and **b**, extracted capacitance as a function of applied voltage for the transition-active gel/PEDOT:PSS capacitor. The impedance spectra were measured under different DC voltages from 0 to 2.5 V. The inset shows the capacitor structure.



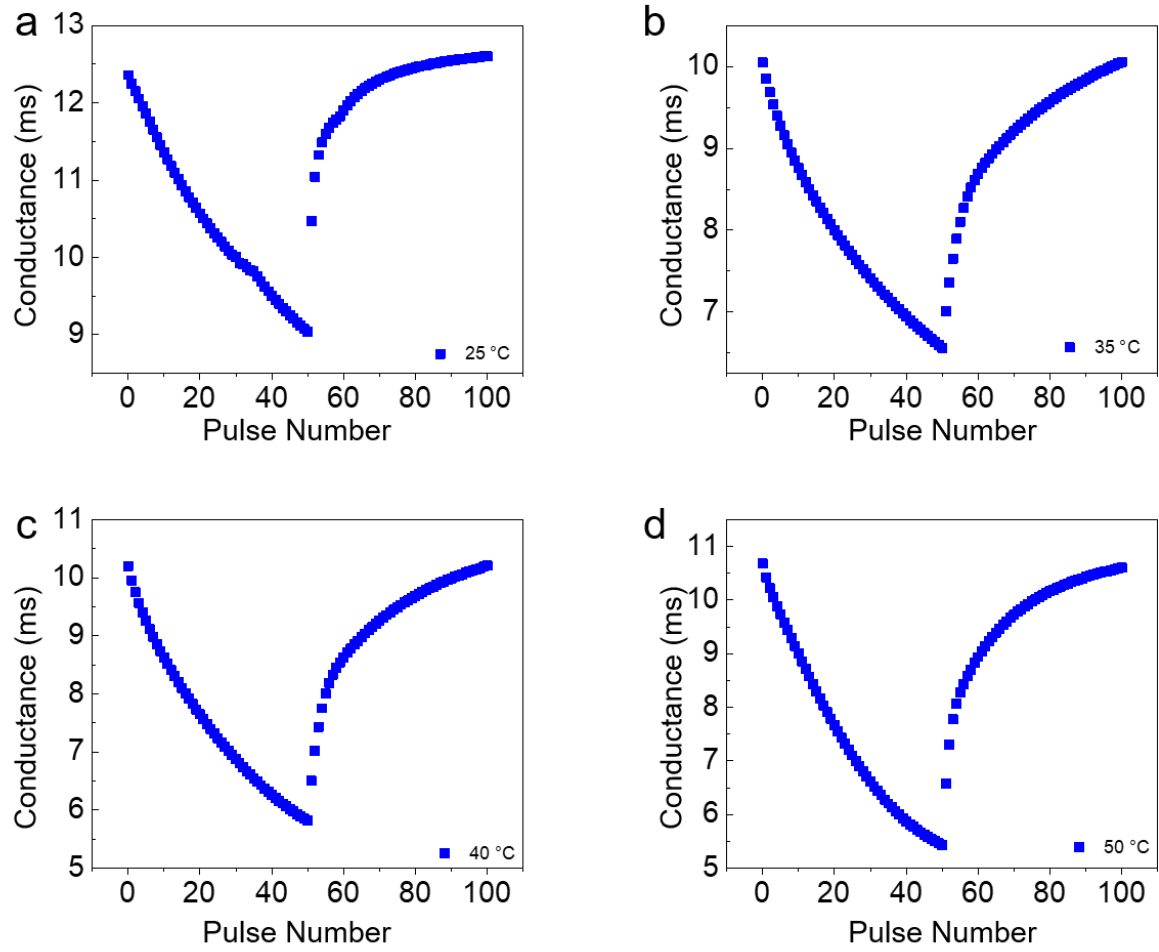
Supplementary Fig. 11 | Temperature-dependent capacitance of the thermoresponsive zwitterionic gel/PEDOT:PSS capacitor. Extracted capacitance measured at -1.5 V as a function of temperature



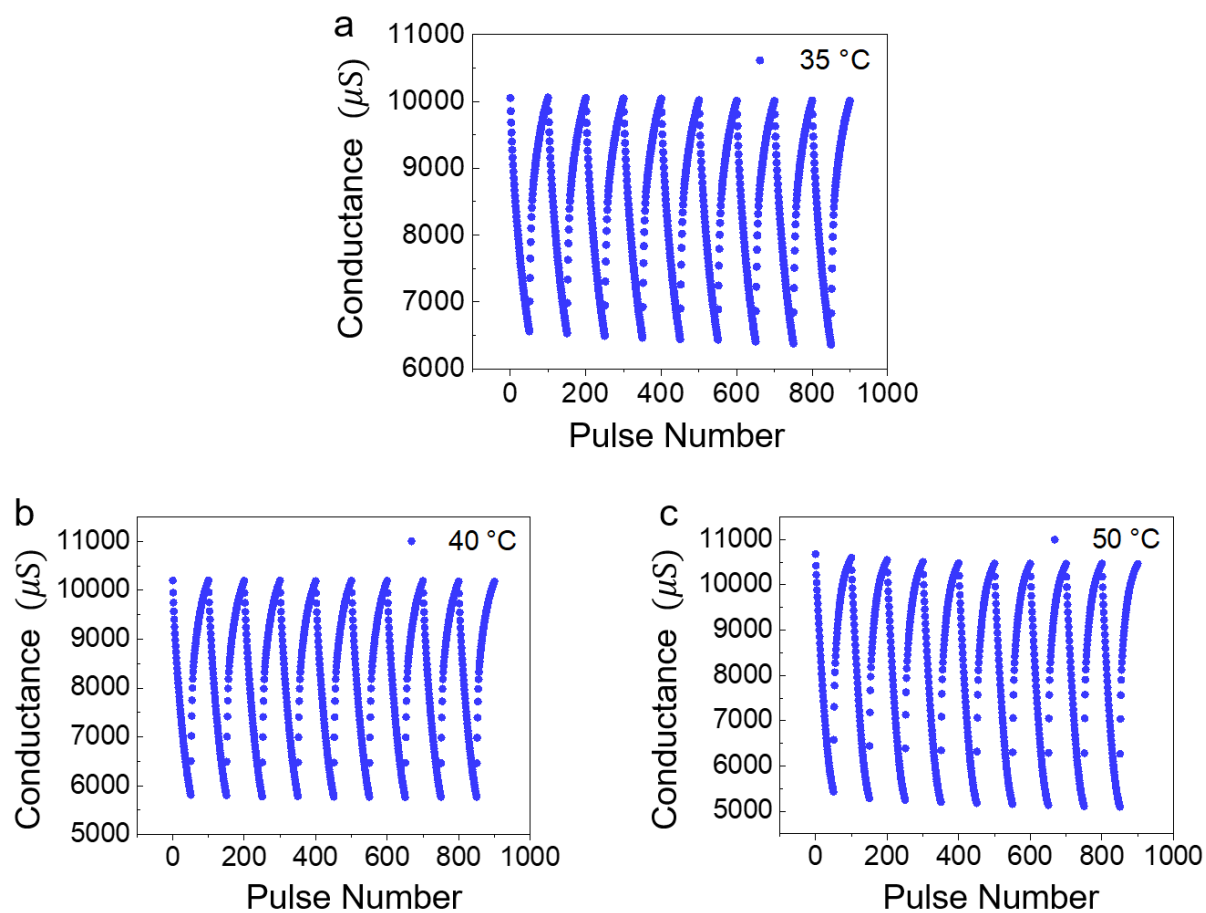
Supplementary Fig. 12 | Schematic illustration of the monolithic thermosynapse structure and temperature-dependent ionic modulation mechanism.



Supplementary Fig. 13 | Temperature-dependent transfer characteristics. a,b, Transfer curves of the **a**, monolithic thermosynapse and **b**, conventional OECT measured at different temperatures from 25 to 60 °C.

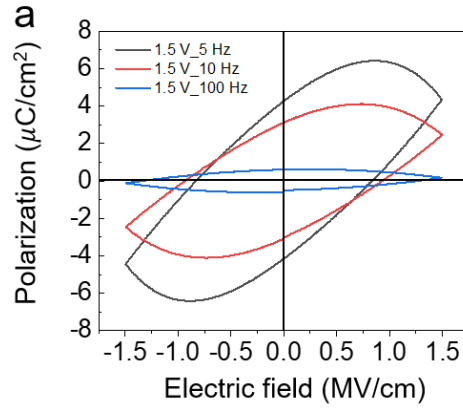


Supplementary Fig. 14 | Temperature-dependent synaptic conductance modulation of monolithic thermosynapses. a-d, Conductance evolution during consecutive LTD and LTP pulse stimulation at **a**, 25 °C, **b**, 35 °C, **c**, 40 °C, and **d**, 50 °C.

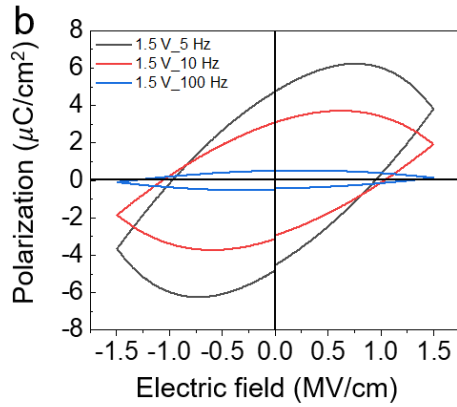


Supplementary Fig. 15 | Long-term reversible synaptic modulation of monolithic thermosynapses. **a-c**, Conductance evolution under repeated alternating LTD and LTP pulse stimulation at **a**, 35 °C, **b**, 40 °C, and **c**, 50 °C, showing stable reversible conductance modulation over 900 pulses.

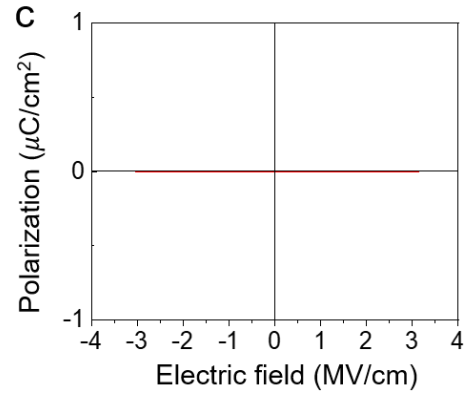
- Zwitterionic gel_w/ UCST (0 mol% LiTFSI)



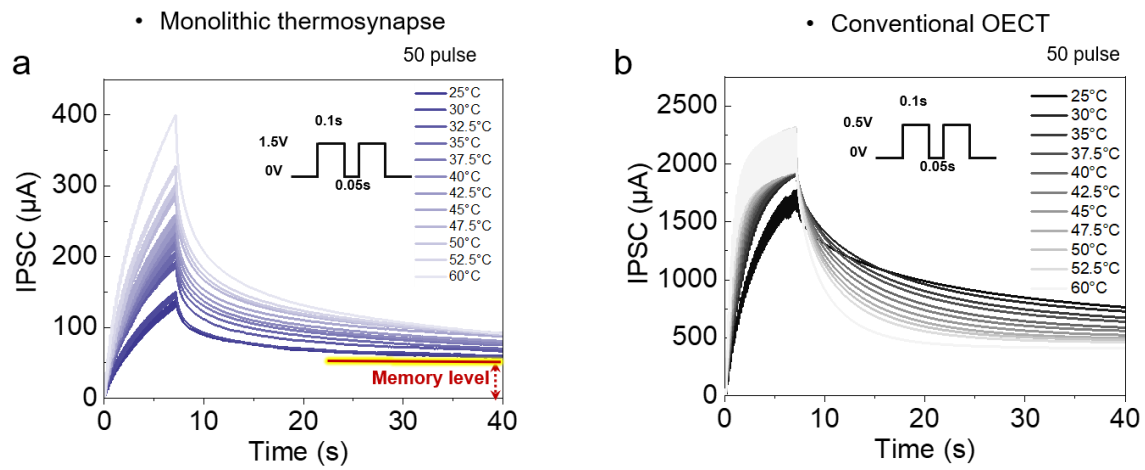
- Zwitterionic gel_w/ UCST (0.05 mol% LiTFSI)



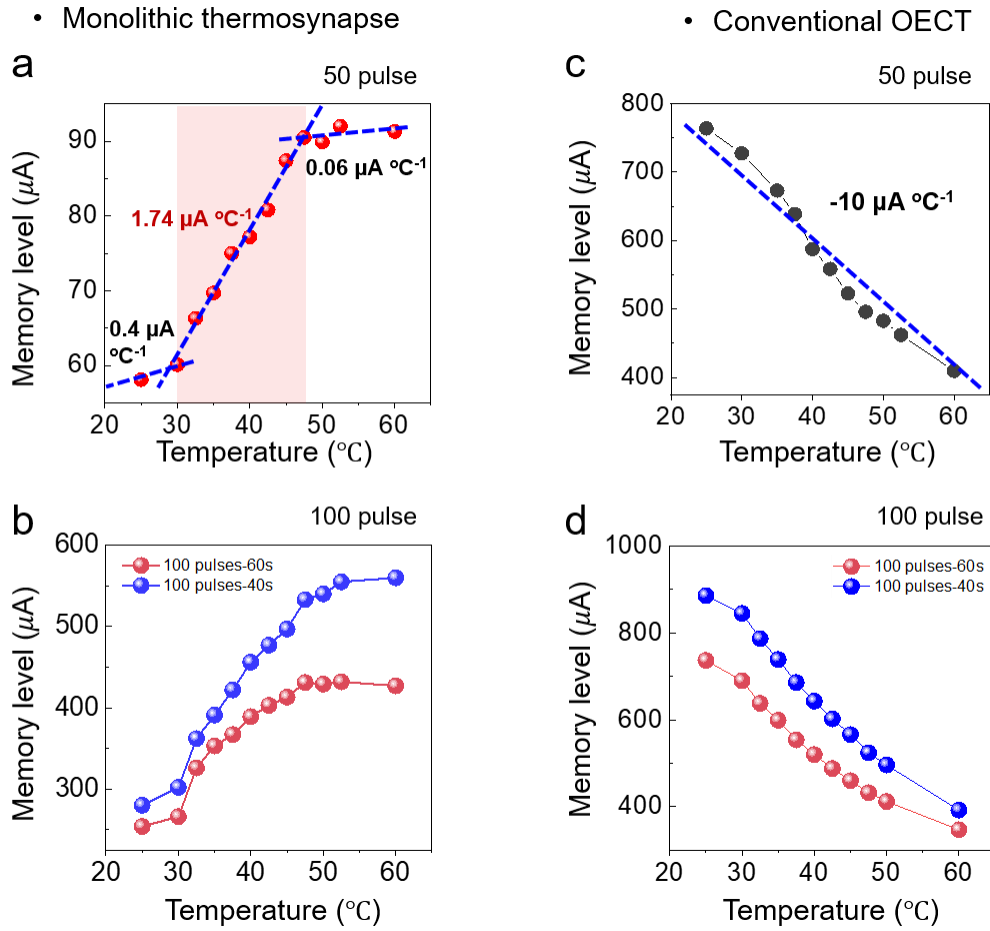
- Zwitterionic gel_w/o UCST (5 or 10 mol% LiTFSI)



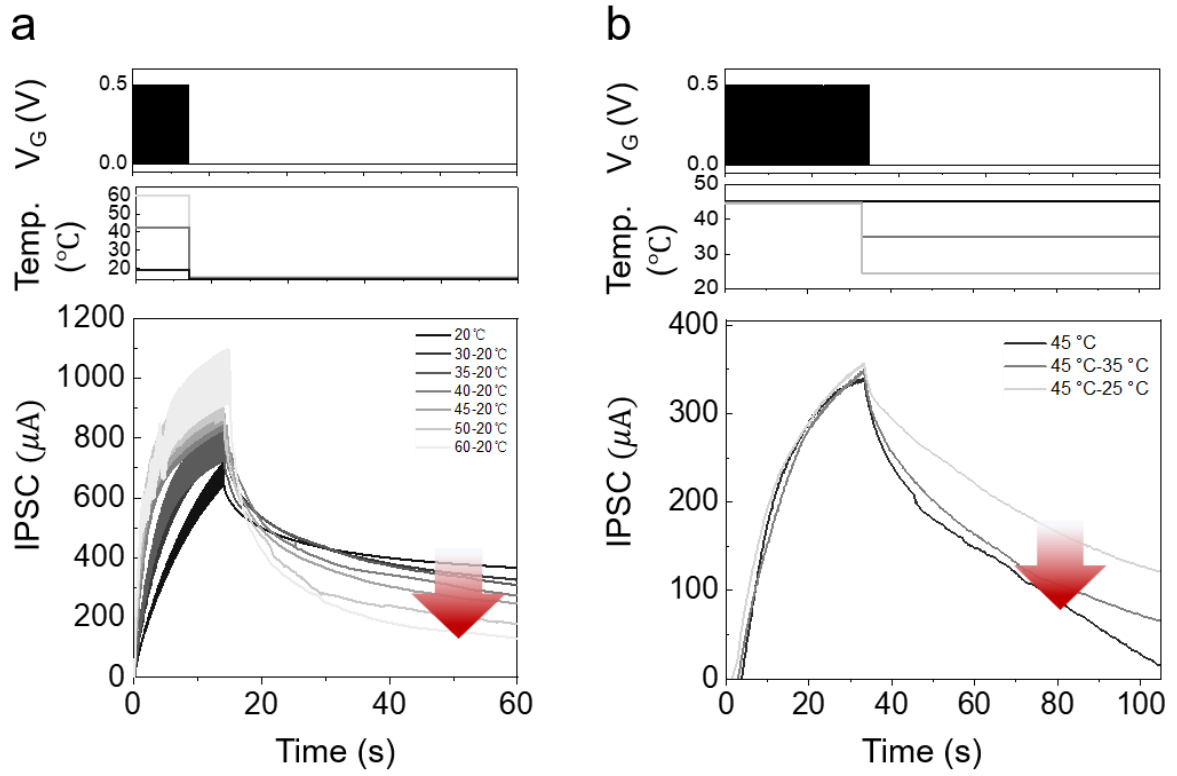
Supplementary Fig. 16 | Polarization behavior of zwitterionic gels with different ion concentrations. P-E hysteresis loops of zwitterionic gels **a**, without LiTFSI, **b**, with 0.05 mol% LiTFSI under the UCST condition, and **c**, with high LiTFSI concentration under the out-of-UCST condition measured at different frequencies.



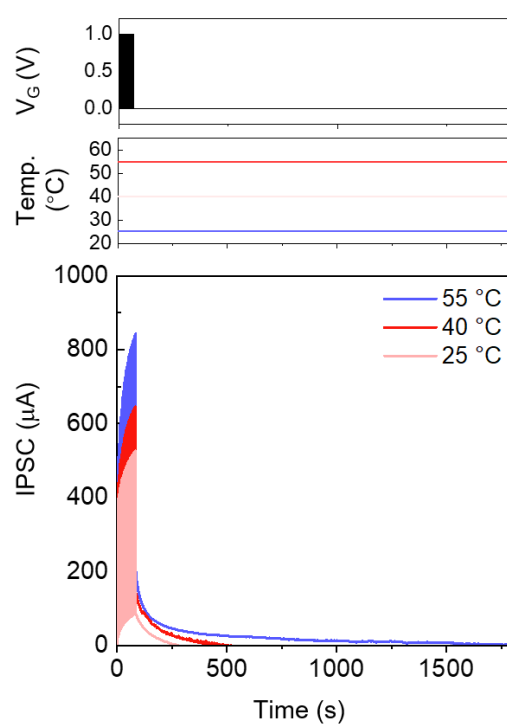
Supplementary Fig. 17 | Temperature-dependent stimulation and retention behavior under 50 consecutive gate pulses. IPSC responses of **a**, monolithic thermosynapse and **b**, conventional OECT at different temperatures.



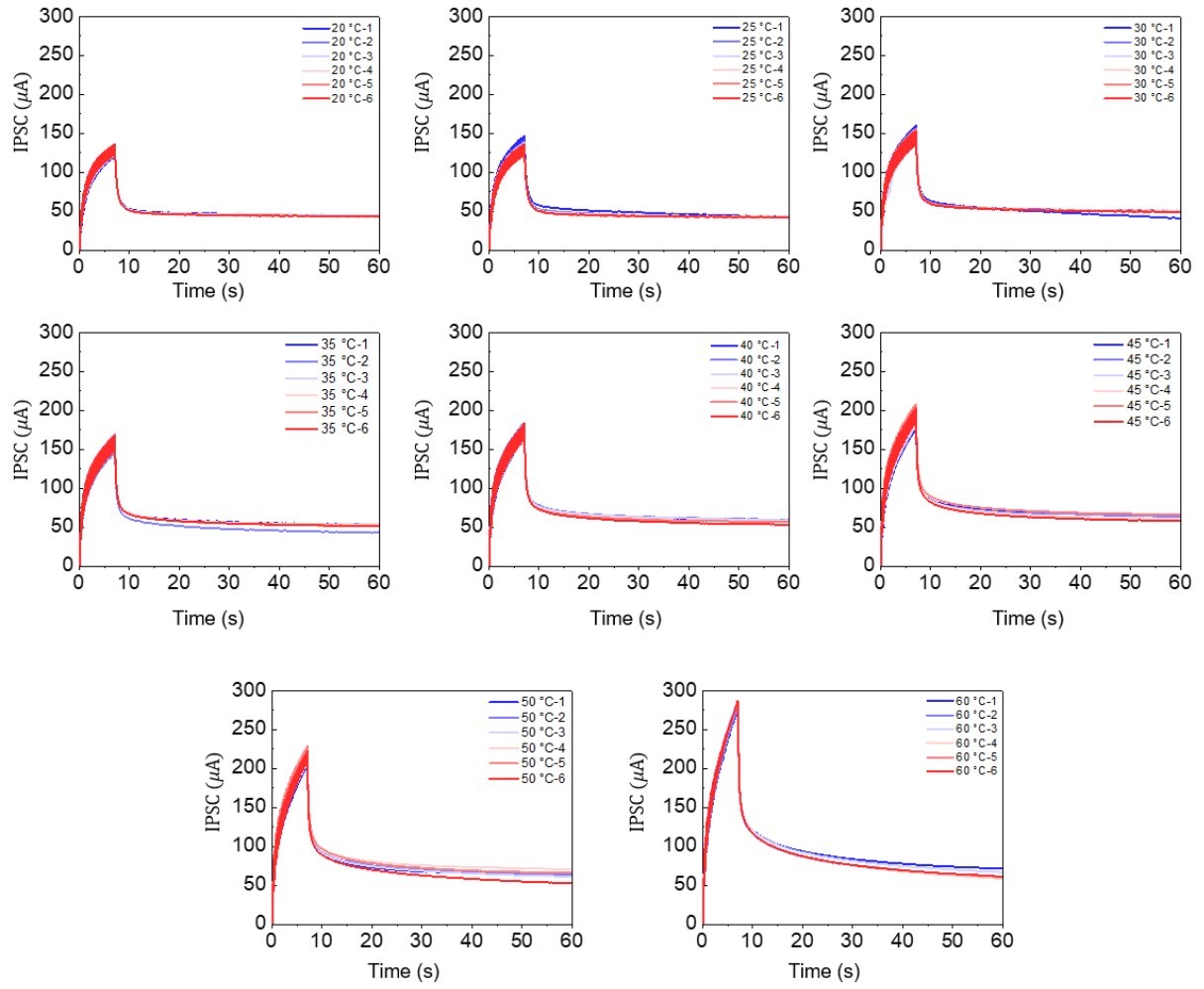
Supplementary Fig. 18 | Temperature-dependent memory levels. Memory levels of monolithic thermosynapse after **a**, 50 consecutive gate pulses and **b**, 100 consecutive gate pulses, evaluated as a function of temperature. Memory levels of conventional OECT after **c**, 50 consecutive gate pulses and **d**, 100 consecutive gate pulses, evaluated as a function of temperature. Memory levels in **b** and **d** were extracted after retention times of 40 and 60 s.



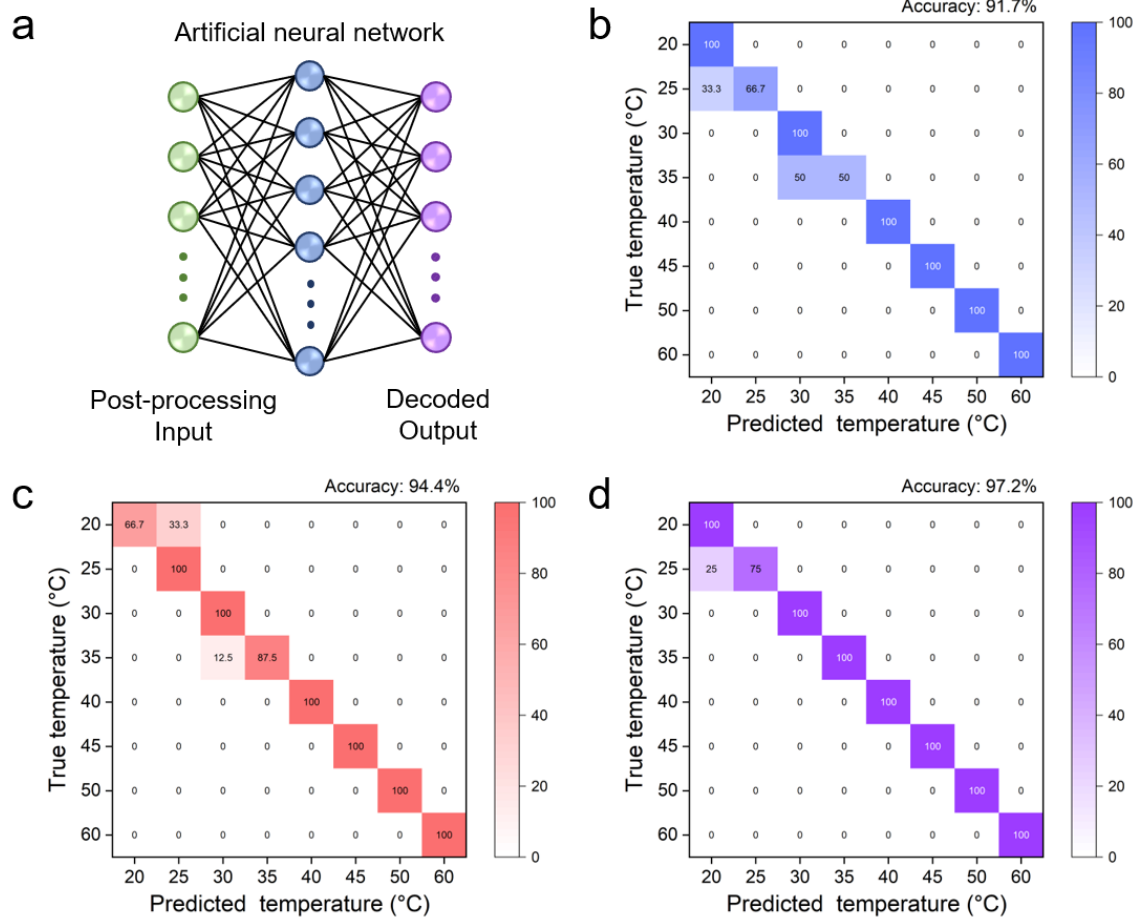
Supplementary Fig. 19 | Decoupled temperature-application protocols for conventional OEET. a, IPSC responses measured by varying the temperature during gate-pulse stimulation while keeping the retention condition identical after gate-pulse removal. **b,** IPSC responses measured by keeping the stimulation temperature identical during gate-pulse stimulation while varying the retention temperature after gate-pulse removal.



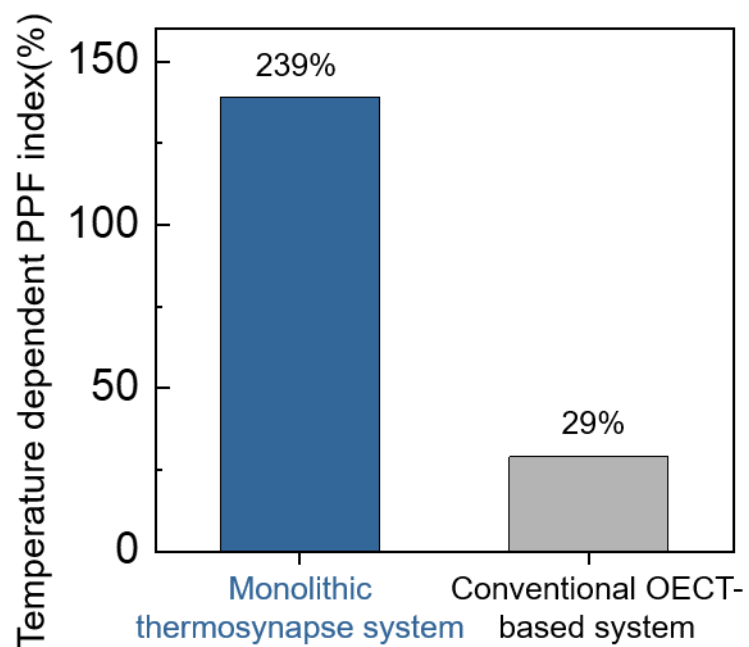
Supplementary Fig. 20 | Temperature-dependent memory accumulation and retention in monolithic thermosynapse. IPSC responses measured at 25, 40 and 55 °C under 30 consecutive 1 V gate pulses, followed by post-stimulus relaxation after removal of the gate bias.



Supplementary Fig. 21 | Reproducibility of temperature-dependent IPSC responses in monolithic thermosynapse. IPSC responses repeatedly measured six times at each temperature (20, 25, 30, 35, 40, 45, 50 and 60 °C) after 50 consecutive gate pulses.

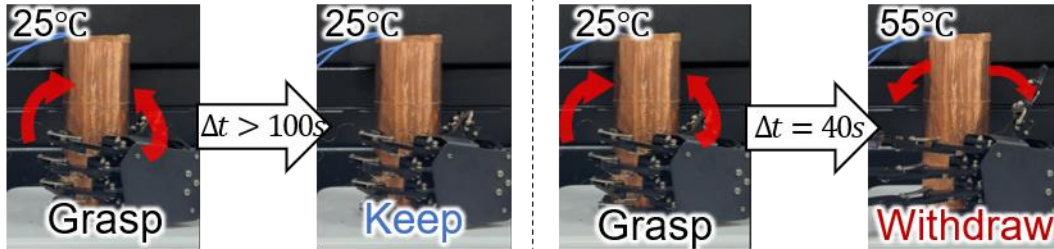


Supplementary Fig. 22 | ANN-based temperature classification. **a**, Schematic of the artificial neural network (ANN) used to classify temperature-dependent device responses. **b-d**, Confusion matrices obtained using pre-synaptic signals only (**b**, accuracy: 91.7%), post-synaptic signals only (**c**, accuracy: 94.4%), and combined pre- and post-synaptic signals (**d**, accuracy: 97.2%). Selected temperature states ranging from 20 to 60 °C were classified.

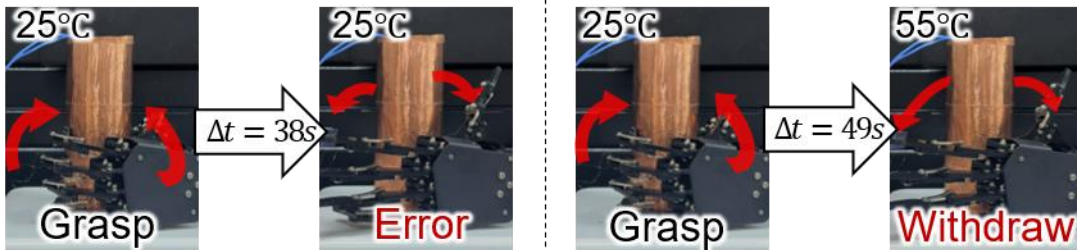


Supplementary Fig. 23 | Temperature-dependent paired-pulse facilitation of the monolithic thermosynapse system and conventional OECT-based system.

Monolithic thermosynapse system

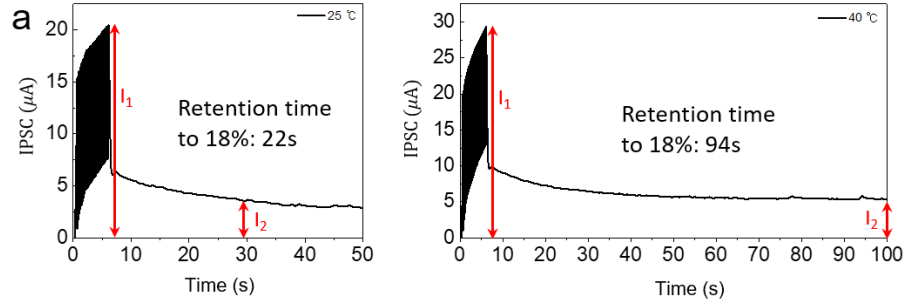


Conventional OECT-based system

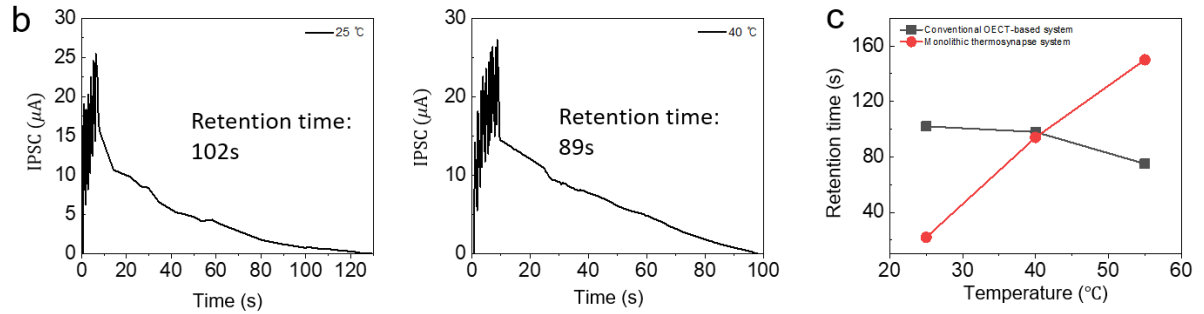


Supplementary Fig. 24 | Temperature-selective actuation of the robotic system. Robotic operation under sequential thermal stimulation, including grasping at 25 °C and withdrawal upon exposure to a 55 °C heat source. The monolithic thermosynapse system enables temperature-selective grasping and withdrawal, whereas the conventional OECT-based system exhibits erroneous actuation at 25 °C and loses temperature selectivity.

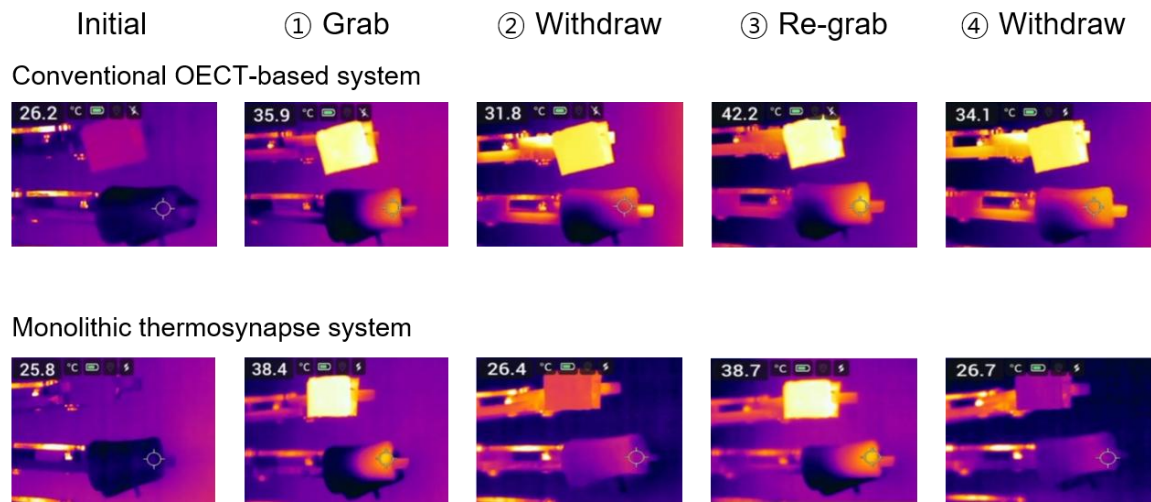
- Monolithic thermosynapse system



- Conventional OECT-based system



Supplementary Fig. 25 | Temperature-dependent retention-controlled waiting time in the self-adaptable robotic system. IPSC responses of **a**, monolithic thermosynapse system and **b**, conventional OECT-based system at 25 and 40 °C. **c**, Comparison of retention time as a function of temperature.



Supplementary Fig. 26 | Infrared thermographic comparison of thermal accumulation during robotic operation. Infrared images showing the temperature evolution of the porcine skin during repeated grasping cycles, highlighting reduced thermal accumulation in monolithic thermosynapse system and cumulative heating in the conventional OECT-based system.

Supplementary Table 1. Comparison of the temperature-dependent retention times of previously reported conventional synapses.

Reference no.	System	Materials	Operating voltage	Retention time of LTM (retention ratio) (Temperature)
42	Thin-film transistor	Dielectric: SiO ₂ channel: IGZO	1 V	0.72s (0%) (30°C) 0.16s (0%) (50°C)
43	Field-effect transistor	Dielectric: SU-8 solid channel: s-CNT network	2.5 V	30s (25%) (10°C) 8s (0%) (40°C)
44	Thermally tunable photonic synaptic transistor	Dielectric: P ⁺ Si/SiO ₂ channel: IGZO	-2 V	48.2s (0%) (20°C) 8.7s (0%) (80°C)
45	Integration of thermistor & actuator	Chitosan/Guar gum/Cellulose acetate	-0.1 V	420s (0.3%) (57°C) 780s (0%) (>80°C)
46	Thin-film transistor	Dielectric: PVA/SiO ₂ channel: S-CNTs	-1 V	100s (85%) (50°C)
	Our work	Dielectric: PDMAPS-based hydrogel channel: PEDOT:PSS	1 V	277s (0%) (25°C) 472s (0%) (40°C) 1800s (0%) (55°C)

Supplementary Video 1. Thermal Sensing Demonstration of the Zwitterionic gel-based OECT. The robotic hand maintains its grip on the object at 25 °C, whereas at 55 °C the amplified ionic response drives the current across the release threshold and triggers withdrawal.

Supplementary Videos 2. Thermal Sensing Demonstration of the PEO-based OECT. Under the same conditions, progressive potentiation occurs even at 25 °C, causing the hand to release the object erroneously and lose temperature selectivity.

Supplementary Videos 3. Thermosynapses for robotic systems. Thermal-history-dependent operation of the monolithic thermosynapse system during repeated interaction. Guided by its retained ionic state, the robotic hand delays recontact until thermal recovery, suppressing cumulative heating of the skin and preserving a stable pressure response across repeated grab-withdraw-regrasp cycles.