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Significantly Improved High-temperature Energy Storage Performance of PP Films by Grafting-cross-linking Modification

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Materials

The materials and reagents used in this experiment are PP masterbatch (Borealis; HC300BF), triallyl isocyanurate(TAIC purity≥98%), dicumyl peroxide(DCP purity≥99%), benzophenone (BP purity≥99%), acrylic acid (AA purity≥99.7%)(Shanghai Aladdin Biochemical Technology Co., Ltd.). The above materials and chemical reagents are directly used for experimental preparation without further purification.

Preparation of Hg-XLPP films

The cross-linking agent is added from the feed port along with the PP, and the mass fraction of the cross-linking agent TAIC is controlled at 0.4%, the mass fraction of AA is controlled at 0.2%, 0.4%, 0.6%, 0.8%, the mass fraction of Initiator DCP is controlled at 0.4%. Then it enters the extruder barrel, the extruder barrel can be divided into six zones according to the different heating temperatures, where the first zone is 190°C and the temperatures from the second to sixth zones can be set as 200°C, 210°C, 210°C, 210°C, 210°C. While the temperature of the tape casting temperature of chilling roll are set as 140°C. Finally, the film thickness is controlled by adjusting the stretching rate during the stretching process, the resulting films have a thickness of 8-10 μm. The above films are named Hg-XLPP-Y (0.2%, 0.4%, 0.6%, 0.8%). Abbreviated as Hg-XLPP1, Hg-XLPP2, Hg-XLPP3, Hg-XLPP4.

Preparation of Ug-XLPP films

The cross-linking agent is added from the feed port along with the PP, and the mass fraction of the cross-linking agent TAIC is controlled at 0.4%, the mass fraction of AA is controlled at 0.2%, 0.4%, 0.6%, 0.8%, the mass fraction of Initiator BP is controlled at 0.4%. The remaining sections are identical to those described the previous section. The above films are named Ug-XLPP-Y (0.2%, 0.4%, 0.6%, 0.8%). Abbreviated as Ug-XLPP1, Ug-XLPP2, Ug-XLPP3, Ug-XLPP4.

Characterization

X-ray diffraction (XRD) patterns of the PP films were all tested by the EMPYREAN X-ray diffractometer, which adopted a copper target as the radiation source, and the operating voltage and current were 40 kV and 40 mA, respectively.

Fourier Transform infrared spectroscopy (FTIR) (NEXUS 670) was used to characterize and analyze the physical structure and the surface properties of the dielectric. The element composition and chemical bonds of the surface were tested by X-ray photoelectron spectroscopy (XPS) with the Thermo Scientific K-Alpha. A contact angle meter (JY-82) was used to measure the water contact angles of PP films. The temperature dependences of modulus ranging from 0°C to 160°C were measured by a dynamic mechanical analyzer (DMA, TA Q800). The samples sized 50×10×0.02 mm^3 were fixed by dual cantilever beam fixture and tested at the stress frequency of 1 Hz. The heating rate was 3°C/min. Differential scanning calorimetry (DSC) was performed using a METTLER DSC1 with a constant nitrogen flow rate of 10 mL/min. The PP was heated from 25°C to 200°C at a heating rate of 4°C/min, and the weight of the examined samples was 8–10 mg. The molecular weight distribution of the PP films was measured by gel permeation chromatography (PL-GPC220). Aluminum electrodes were evaporated on both sides of the prepared film before testing the electrical properties. The electrode size with a diameter of 3 mm was used for testing the D-E loop, DC breakdown field strength and leakage current density, and the electrode size with a diameter of 9 mm was used for testing the dielectric constant and dielectric loss.The current density was characterized by a precision LC ferroelectric test system (Radiant Technologies, USA). Furthermore, the DC breakdown test system was used to examine the breakdown strength of thin films, and the experimental data were analyzed using the two-parameter Weibull statistic:

$$P(E) = 1 - \exp(-(\frac{E}{E_b})^{\beta}) \qquad \text{(Eq. S1)}$$

A modified Sawyer-Tower circuit was used for the cyclic rapid charge–discharge testing. The fast discharge tests were performed through a capacitor charge–discharge test system with a load resistor of 10 kΩ. Leakage current and TSDC were measured using a high-voltage leakage current system (PolyK Technologies, United States), which includes a Keithley 6517B pA meter. The samples were polarized for 30 min at 80°C in a 40 kV/mm DC electric field before being abruptly chilled to −30°C in the same electric field. Afterward, the samples were placed at −30°C for 5 min, and then the electric field was removed. Finally, the samples were short-circuited and heated to 160°C at a rate of 4°C/min while the current was recorded. Trap energy level (E) and trapped charge quantity (Q) were derived based on peak location and intensity using the half-width method:

$$j(T) = B\exp(-\frac{E_a}{K_B T} - \frac{1}{\beta\tau_0}\int_{T_0}^{T'}\exp(-\frac{E_a}{K_B T})dt) \qquad \text{(Eq. S2)}$$

The density of traps(N_t) can be represented as follows:

$$N_t = \frac{1}{\beta e d}\int_{T_0}^{T} j(T)dT \qquad \text{(Eq. S3)}$$

$j(T)$ is thermal stimulation current density, A/m^2. E_a is relaxation activation energy, eV. β is heating rate, K/s. τ_0 is relaxation time constant, s. T_0 and T' are the starting and terminating temperatures of depolarizing current, K. K_B is the boltzmann constant. e is the elementary charge, C. d is the film thickness, m.

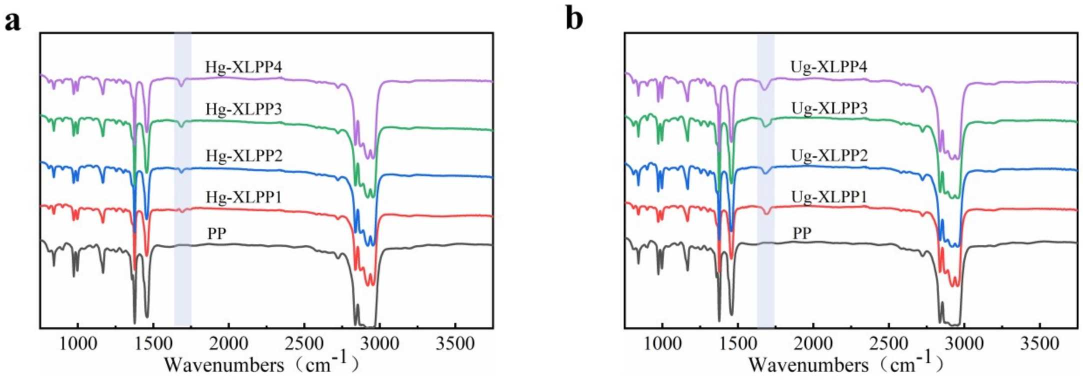

Figure S1. FTIR of (a) Hg-XLPP films. (b) Ug-XLPP films.

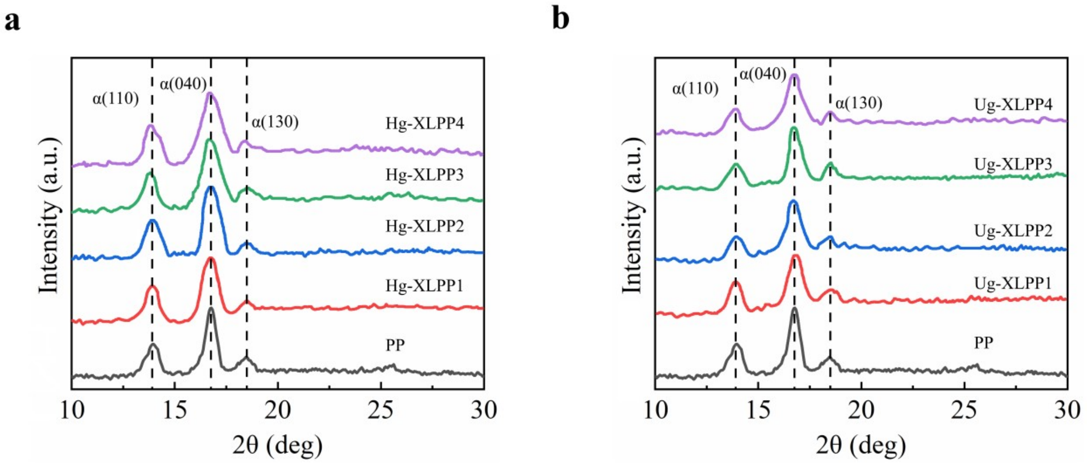

Figure S2. XRD of (a) Hg-XLPP films. (b) Ug-XLPP films.

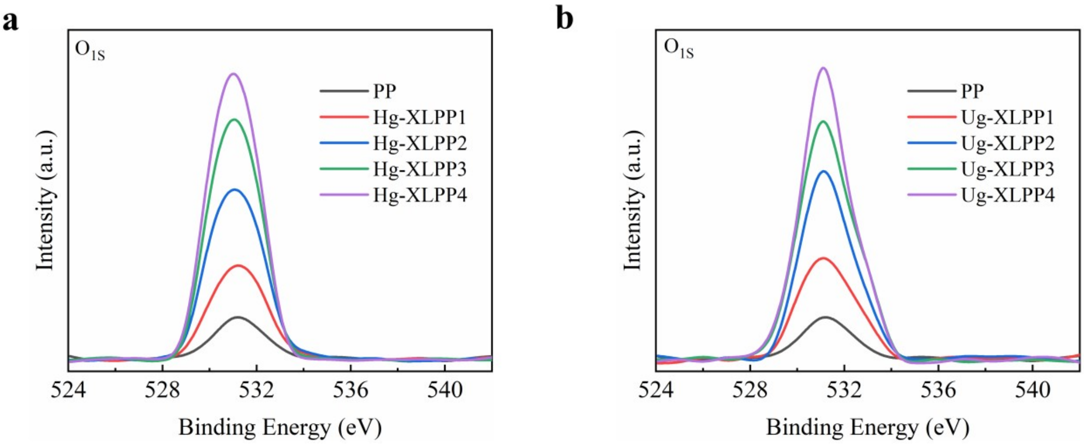

Figure S3. High-resolution O_{1S} of (a) Hg-XLPP films and (b) Ug-XLPP films.

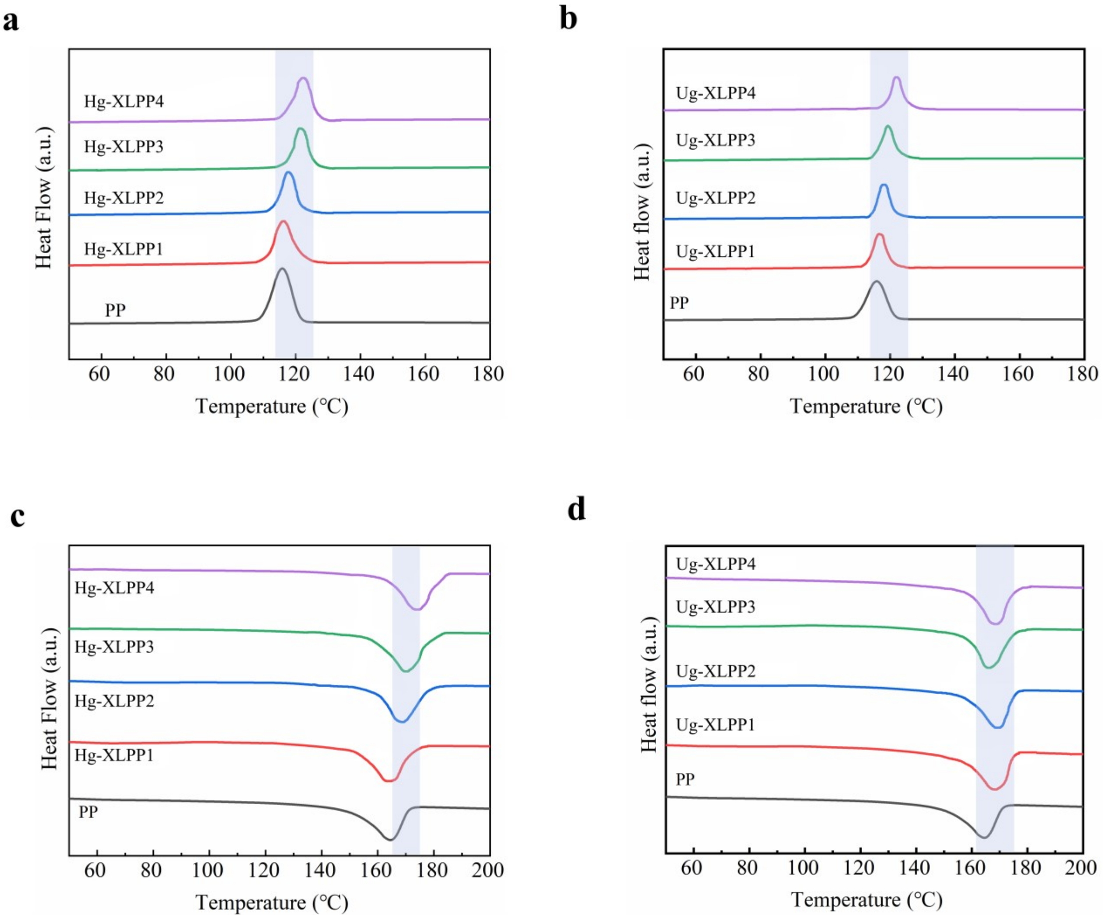

Figure S4. (a) DSC crystallization curves of Hg-XLPP films. (b) DSC crystallization curves of Ug-XLPP films. (c) DSC melting curves of Hg-XLPP films. (d) DSC melting curves of Ug-XLPP films.

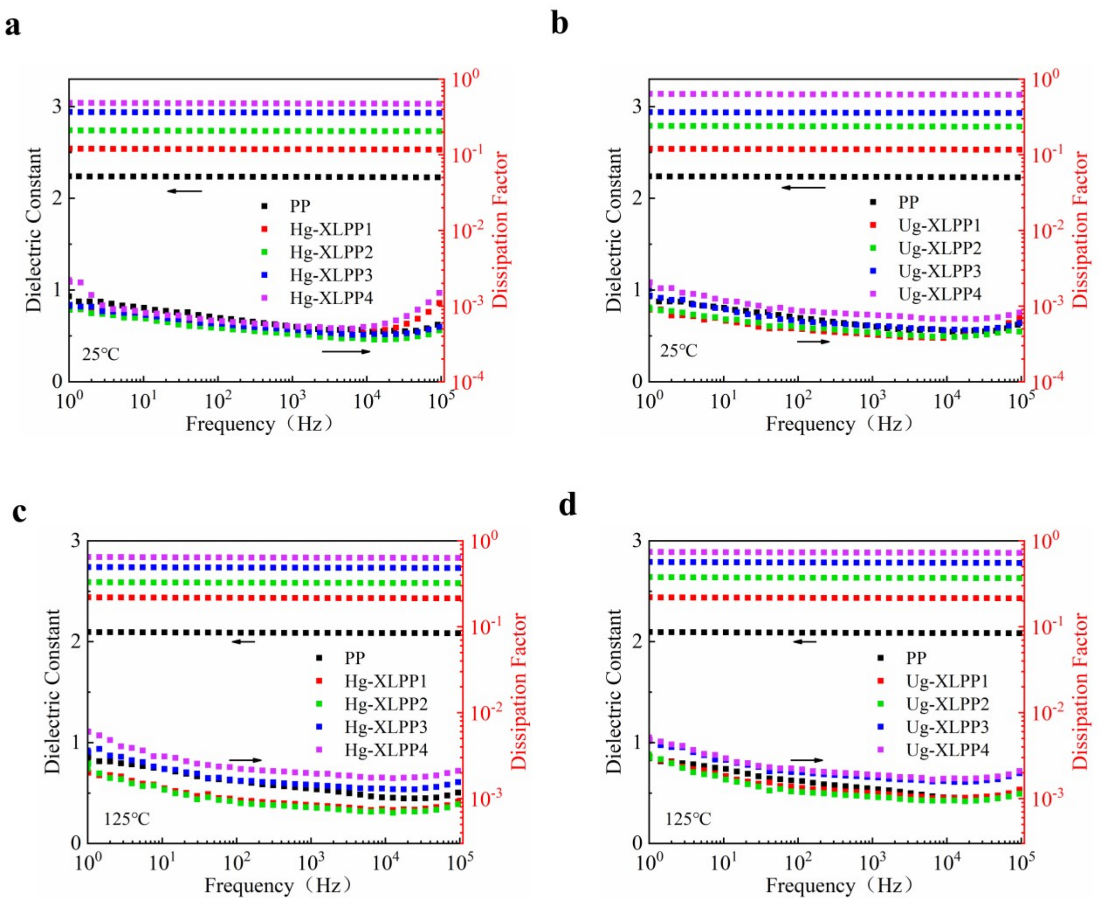

Figure S5. Frequency dependence of dielectric constant and dissipation factor of (a) Hg-XLPP at 25°C. (b) Ug-XLPP at 25°C. (c) Hg-XLPP at 125°C. (d) Ug-XLPP at 125°C.

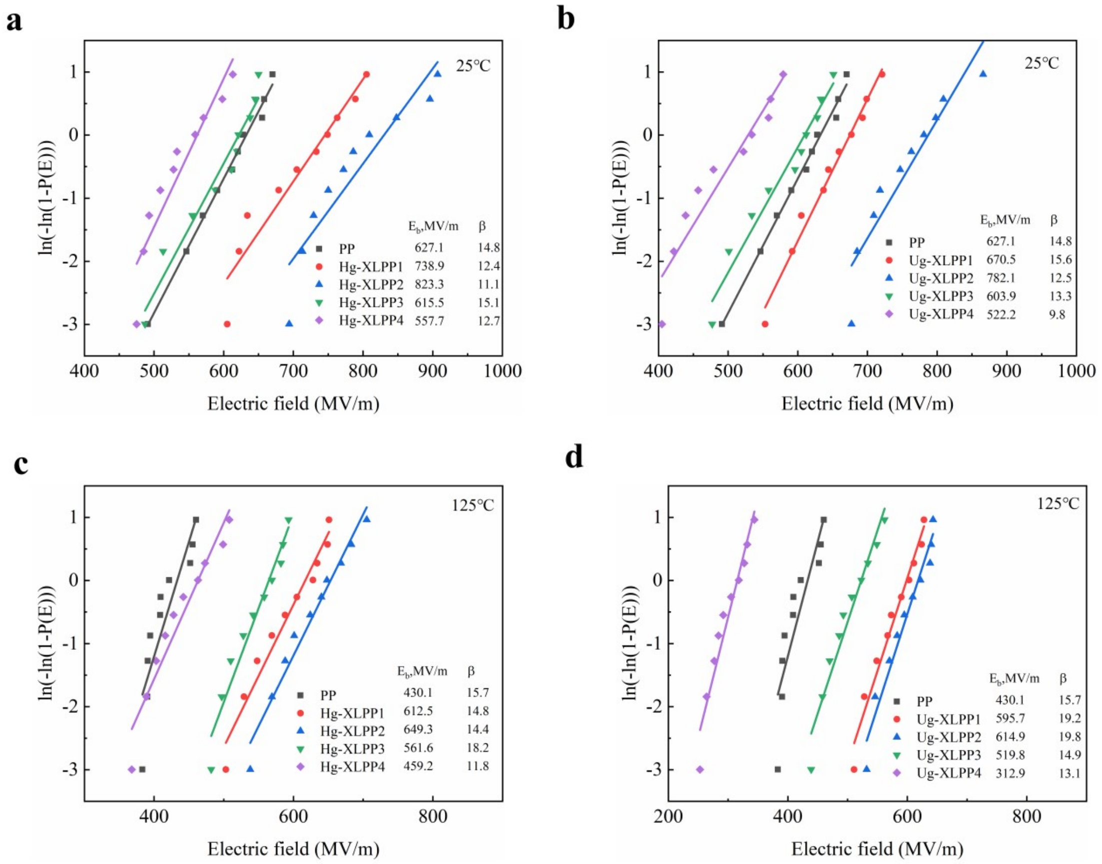

Figure S6. Weibull distribution of the dielectric breakdown strength of (a) Hg-XLPP at 25°C. (b) Ug-XLPP at 25°C. (c) Hg-XLPP at 125°C. (d) Ug-XLPP at 125°C.

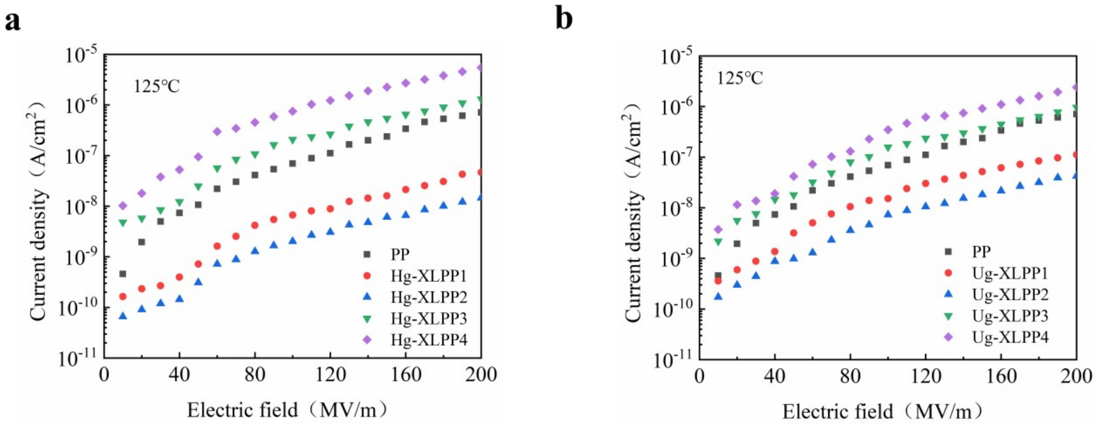

Figure S7. Leakage current density of (a) Hg-XLPP at 125°C. (b) Ug-XLPP at 125°C.

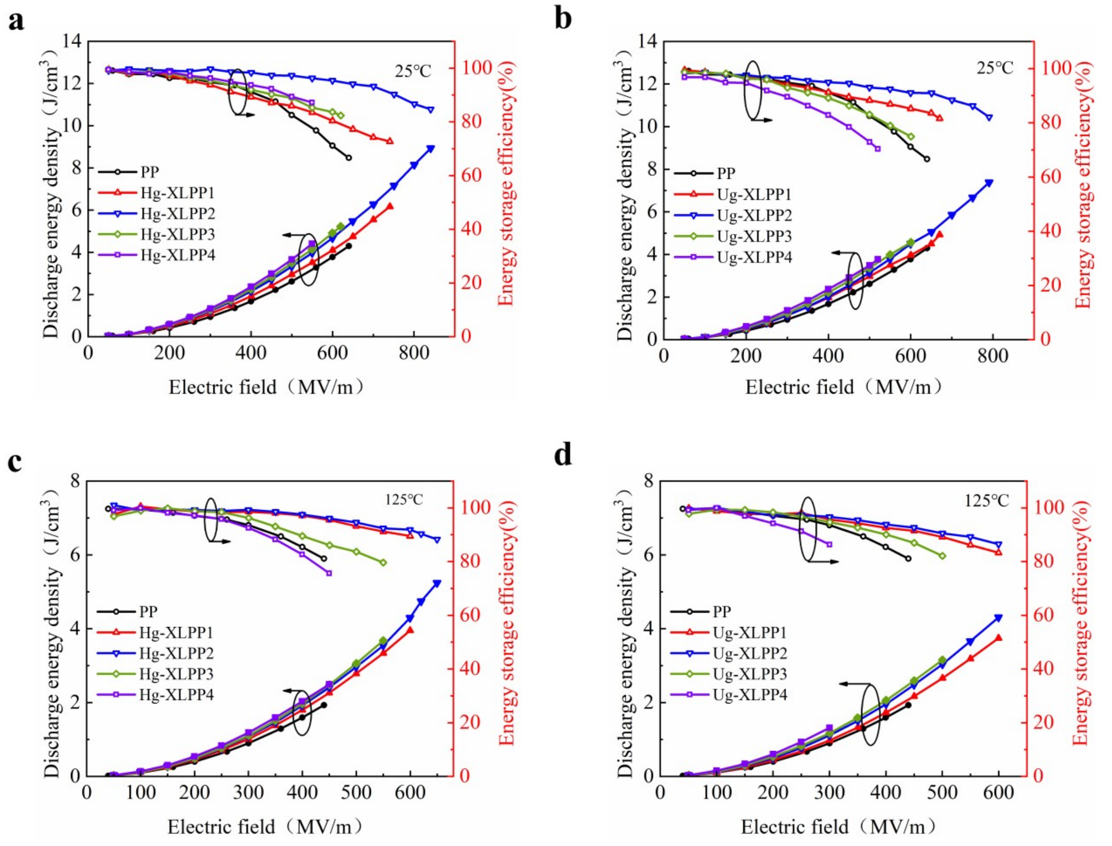

Figure S8. Charge-discharge efficiency and discharged energy density of (a) Hg-XLPP at 25°C. (b) Ug-XLPP at 25°C. (c) Hg-XLPP at 125°C. (d) Ug-XLPP at 125°C.