Supplementary Information (SI) for Journal of Materials Chemistry C.

Supplementary Material for

Ultra-High Energy Density in All-Organic Copolymeric Blends by Grain Refinement

This PDF file includes:

Supplementary Note 1

The intensity of the characteristic FTIR absorption peaks of the three phases was calculated to quantify the content of the three phases. The characteristic peaks of each phase corresponded to the following: α-phase: 408, 532, 614, 764, 795, 855, 975 cm^{-1}, β-phase: 510, 840, 1275 cm^{-1}, and γ-phase: 431, 512, 776, 812, 833, 840, 1234 cm^{-1}.

For the samples containing α, β and γ phases, the content of the polar phase was first calculated:

$$F(\beta,\gamma) = \frac{A_{\beta,\gamma}}{\left(\frac{K_{\beta,\gamma}}{K_\alpha}\right)A_\alpha + A_{\beta,\gamma}} = \frac{A_{\beta,\gamma}}{1.26A_\alpha + A_{\beta,\gamma}}$$

where K_α and $K_{\beta,\gamma}$ are the corresponding absorbance coefficients of 6.1×10^4 and 7.7×10^4 cm^2/mol, respectively, and A_α and $A_{\beta,\gamma}$ are the absorbances at 764 and 840 cm^{-1}, respectively.

Then, calculate the content of the α phase using:

$$F(\alpha) = 1 - F(\beta,\gamma)$$

Finally, the β phase and γ phase contents were obtained by further calculating the characteristic absorbance peaks at 1275 cm^{-1} and 1234 cm^{-1}:

$$F(\beta) = F(\beta,\gamma) \times \frac{A_{1275}}{A_{1275} + A_{1234}}$$

$$F(\gamma) = F(\beta,\gamma) \times \frac{A_{1234}}{A_{1275} + A_{1234}}$$

Supplementary Note 2

The breakdown strength is critical to the energy storage properties of dielectrics. In order to accurately measure the breakdown strength (E_b) of a material, the measured data are usually analyzed using the Weibull distribution describing the cumulative probability of failure (P (E)), which is expressed as a function of the following:

$$P(E) = 1-exp\left[-\left(\frac{E_i}{E_b}\right)^{\beta}\right]$$

where E_i is the experimental breakdown voltage. The breakdown strength E_b is obtained by fitting the experimental breakdown voltage to the cumulative failure probability function, defining the breakdown electric field when the cumulative failure probability P(E) is 63.2% as the Weibull breakdown strength; β is the shape factor, which indicates the stability of the measured value. The Weibull distribution is a continuous probability distribution, and its logarithmic form is usually used to calculate the Weibull characteristic breakdown strength for ease of calculation. When the estimator is used for P(E), the distribution function can be expressed as:

$$ln(-ln(1-P(E))) = \beta ln(E_i) - \beta ln(E_b)$$

$$X_i = ln(E_i)$$

$$Y_i = ln\left(-ln\left(1-\frac{i}{n+1}\right)\right)$$

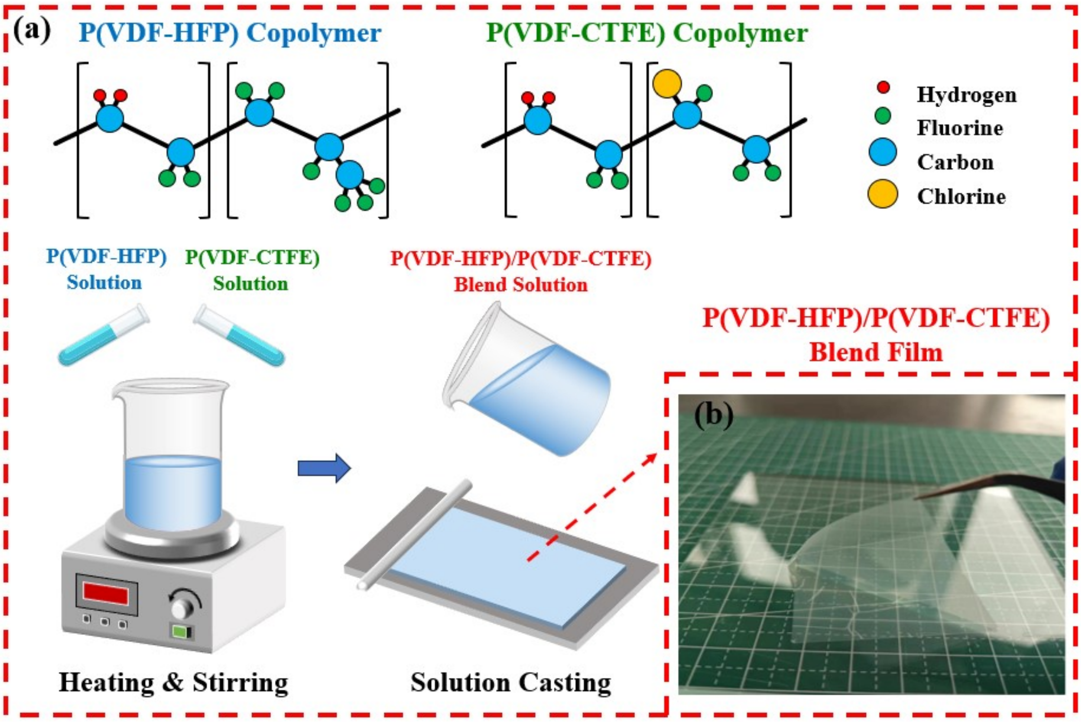

Fig. S1. Blend films preparation. (a) Schematic diagram of the fabrication of P(VDF-HFP)/P(VDF-CTFE) blend films. (b) Photograph of P(VDF-HFP)/P(VDF-CTFE) 50/50 wt.% blend film.

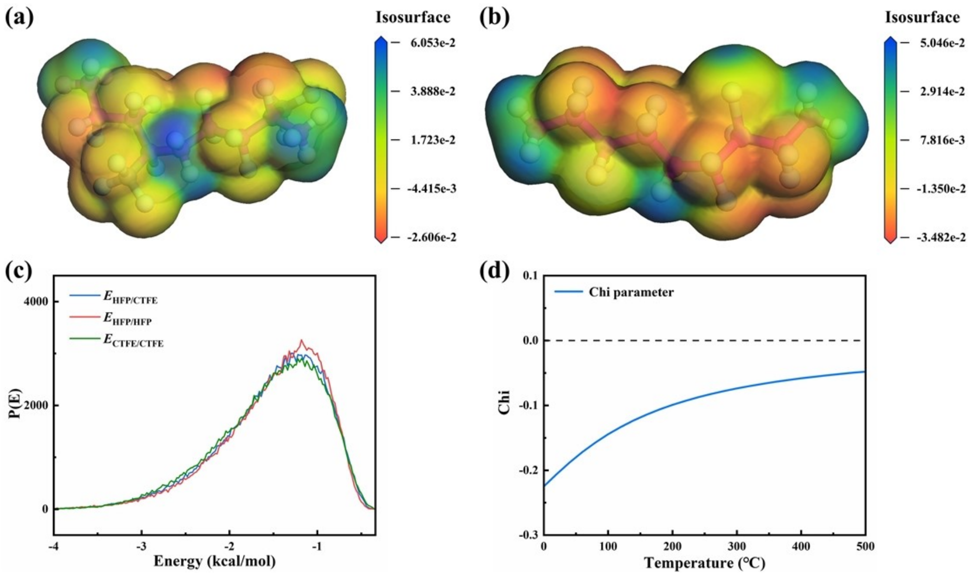

Fig. S2. Molecular simulation results of the blend system. Structural formula for one TTTGTTTG′ conformation of (a) P(VDF-HFP) and (b) P(VDF-CTFE) with the electrostatic potential plotted on the isosurface of the total electron density of the cluster (in Hartree/e). P(VDF-HFP) exhibits a stronger positive charge center for the methylene group and P(VDF-CTFE) has a stronger negative charge center for the fluorine group. (c) Binding energy distribution of P(VDF-HFP) and P(VDF-CTFE) blend system. The similar binding energy distributions of the blend phase and the pure phase indicate that the two phases have good compatibility. The bonding energy between copolymerized monomers was calculated by Dmol3 and Forcite modules of Materials Studio simulation software, and the results are shown in Table S1 and Table S2. (d) Curve of Chi value versus temperature for P(VDF-HFP)/P(VDF-CTFE) blend system. The Chi value is close to 0 and tends to 0 as the temperature increases, which indicates that the blend system has good mixability in the temperature range.

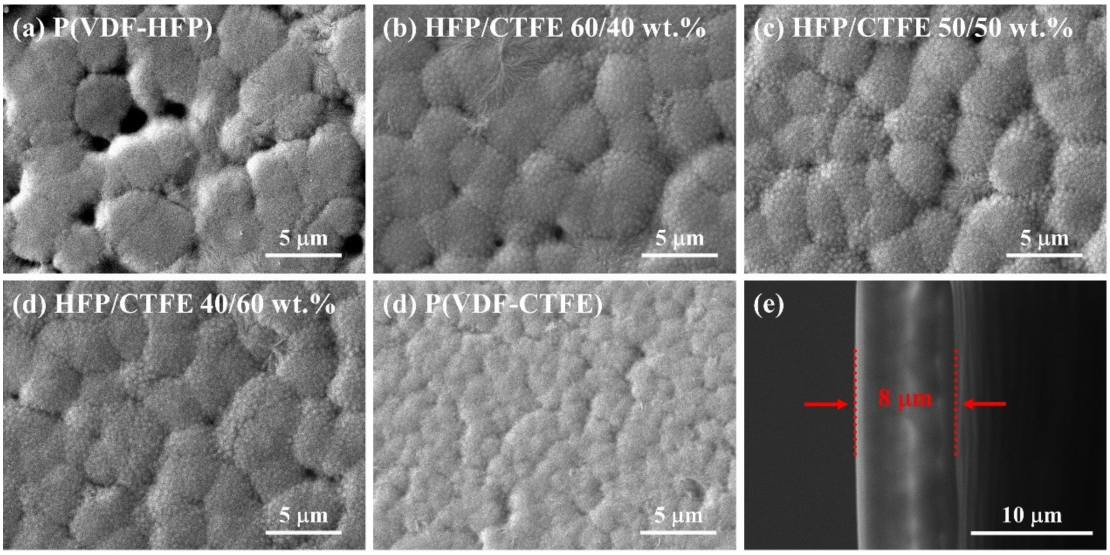

Fig. S3. SEM images of surface and cross section. 5kx SEM images of (a) P(VDF-HFP), (b) P(VDF-HFP)/P(VDF-CTFE) 60/40 wt.%, (c) P(VDF-HFP)/P(VDF-CTFE) 50/50 wt.%, (d) P(VDF-HFP)/P(VDF-CTFE) 40/60 wt.%, (e) P(VDF-CTFE). (f) SEM image of cross section of P(VDF-HFP)/P(VDF-CTFE) 50/50 wt.% with thickness of about 8 μm.

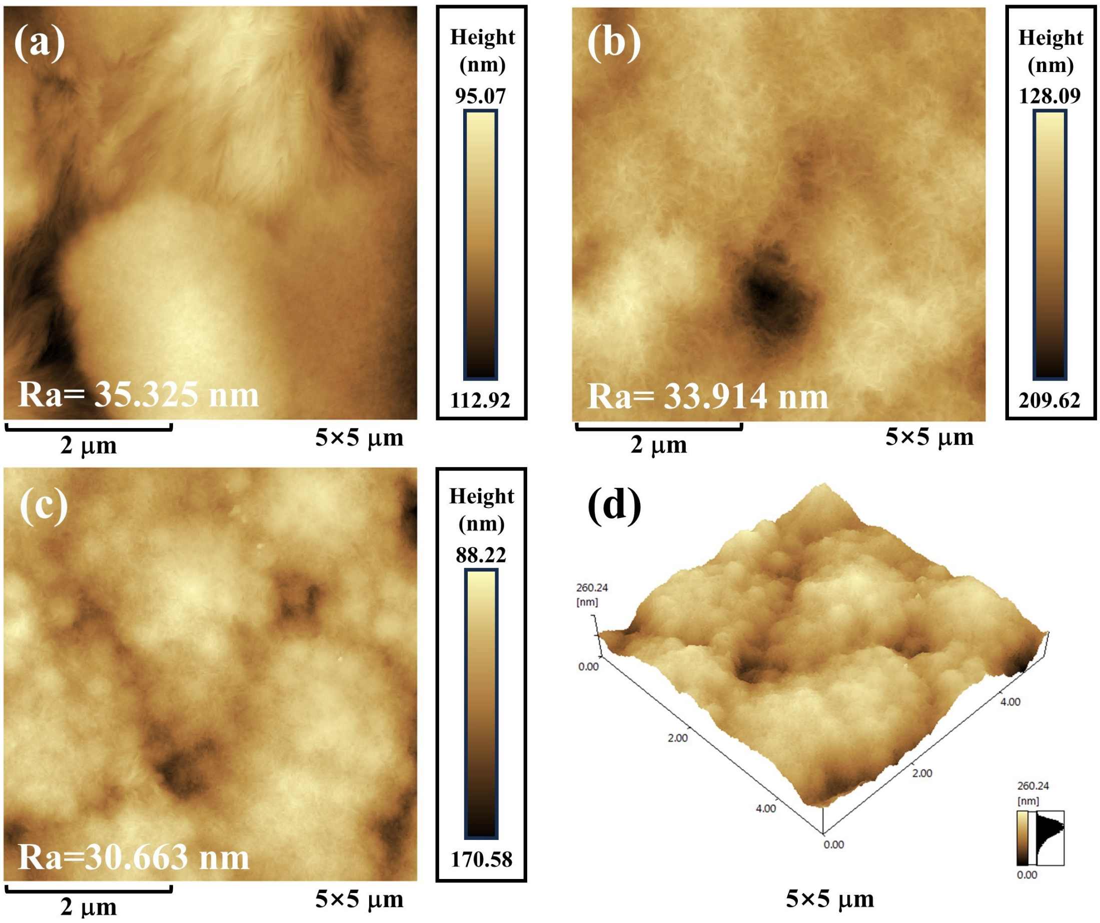

Fig. S4. AFM image of the surface. AFM morphology images of (a) P(VDF-HFP), (b) P(VDF-CTFE), (c) P(VDF-HFP)/P(VDF-CTFE) 50/50 wt.% films (5 μm × 5 μm). The surface roughness (Ra) of P(VDF-HFP)/P(VDF-CTFE) 50/50 wt.% films was reduced to 30.663 nm, which implies a reduction of surface defects and an increase in the uniformity of the blend film. (d) AFM 3D images of P(VDF-HFP)/P(VDF-CTFE) 50/50 wt.% films.

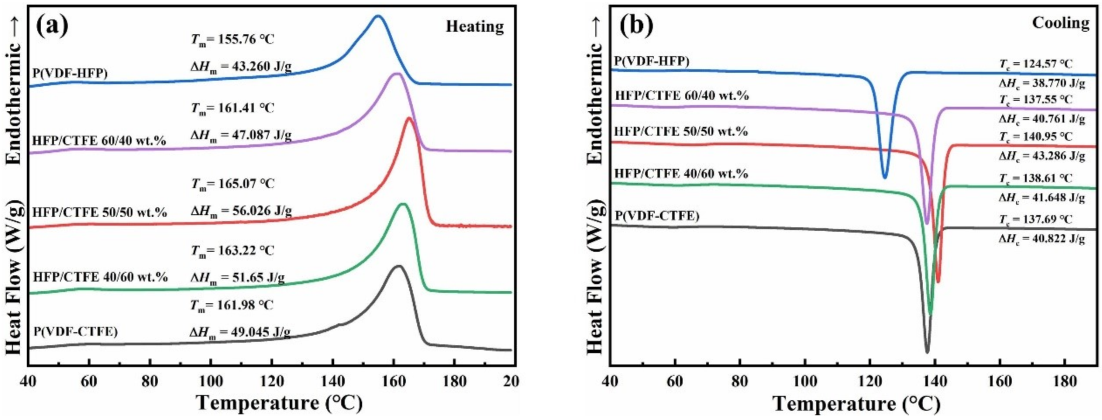

Fig. S5. DSC curves of the first (a) heating and (b) cooling of the blend gradients. The peaks in the heating and cooling curves are the endothermic peaks of melting and the exothermic peaks of crystallization, respectively, and the peak temperatures are the melting temperature (T_{m}) and the crystallization temperature (T_{c}).

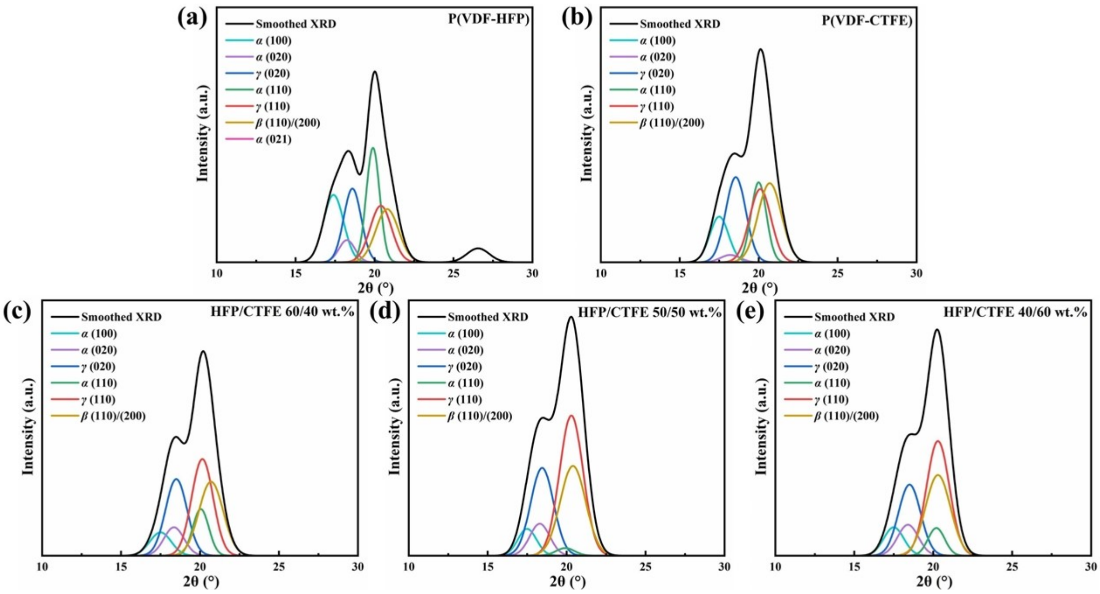

Fig. S6. XRD spectra of films with different blend compositions. All data were analyzed using Origin software with Gaussian fitting function. The crystal size of the samples calculated from the Scherrer equation decreases as the blend composition towards to 50/50 wt.% and the specific data are recorded in Table S. The spectra of all samples show fitted peaks with crystal orientations of α (100), α (020), γ (020), α (110), γ (110), and β (110)/(200) at six positions at about 17.66, 18.30°, 18.5°, 19.90°, 20.04, 20.26, and 20.04°, respectively.

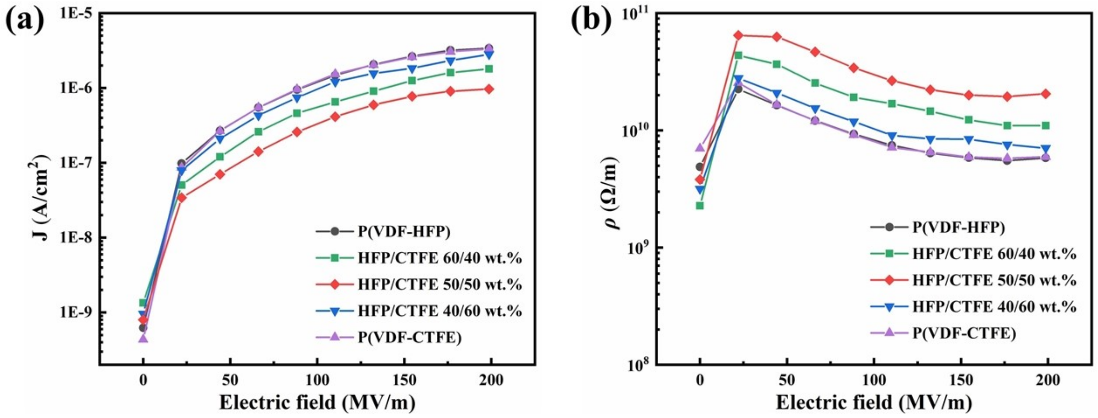

Fig. S7. (a) Leakage current and (b) resistivity of different blend components under varying electric field.

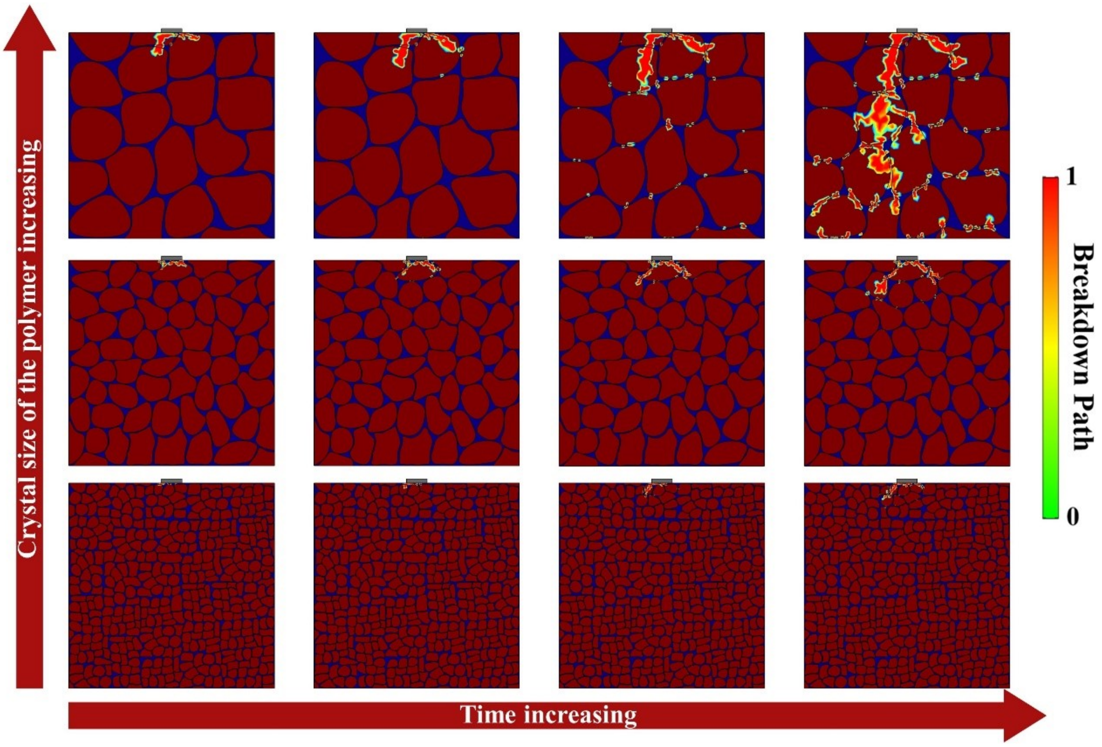

Fig. S8. Finite element simulation of conductive pathways at different grain sizes. The simulation results are consistent with the design and experiments, as the grain size decreases, the grain boundaries increase, which hinders the formation of conductive pathways thus increasing the breakdown strength.

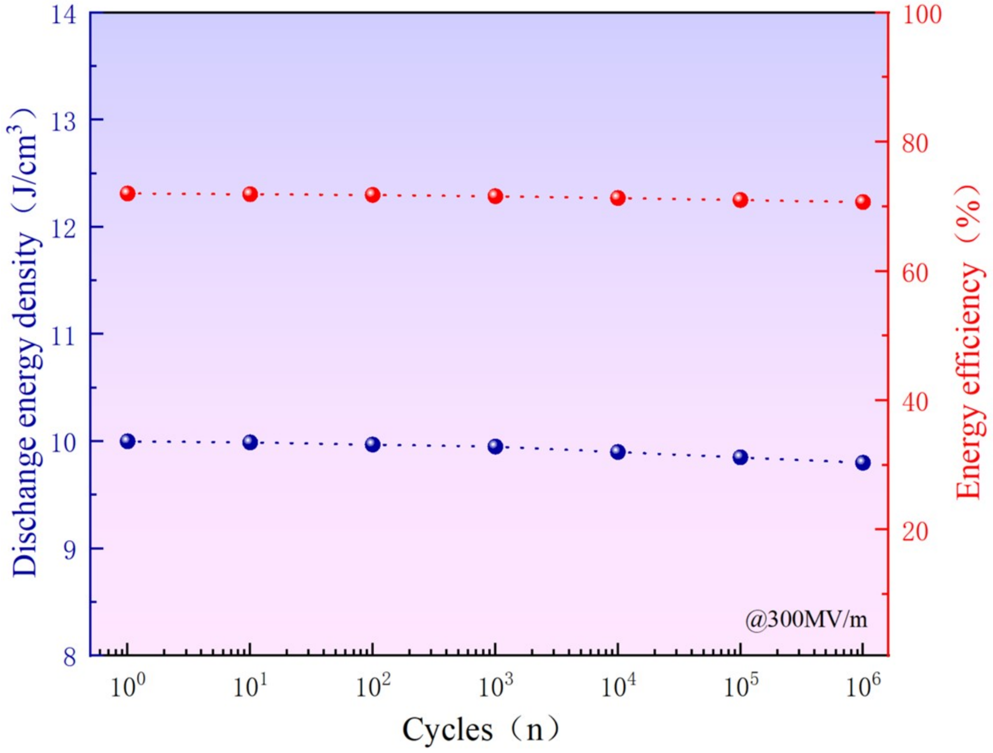

Fig. S9. Charge/discharge cycle performance of P(VDF-HFP)/P(VDF-CTFE) 50/50 wt.% at 300MV/m

Table S1. Simulation results of binding force between P(VDF-HFP) and P(VDF-CTFE). The intermolecular binding forces of the blend system and the pure phase system were simulated by the Dmol3 module of the Materials Studio molecular simulation software. The binding energy between P(VDF-HFP) and P(VDF-CTFE) was -8.76 KJ/mol, which was much smaller than that of the pure polymer, indicating that a strong interaction force was generated between each other.

Components	E_{AB} **(Ha)**	E_{A} **(Ha)**	E_{B} **(Ha)**	E_{int} **(Ha)**	E_{int} **(KJ/mol)**
HFP-HFP	-4991.316258	-2495.655853	-2495.658714	-0.001691	-1.1372144
CTFE-CTFE	-4530.947526	-2265.472802	-2265.472977	-0.001747	-1.1748750
HFP-CTFE	-4761.145581	-2495.659300	-2265.473251	-0.013030	-8.7628053

Table S2. Simulation results for the internal energy of the blend gradient. The internal energy of the blend system and the pure phase system were simulated by the Forcite module of the Materials Studio. The internal energy of the blend system is -135.99 kcal/mol, implying the formation of a more stable structure.

Components	**Valence energy (diag.terms)**	**Valence energy (cross terms)**	**Non-bond energy**	**Total energy (kcal/mol)**
HFP-HFP	-128.580	-87.443	103.253	-112.770
CTFE-CTFE	-86.696	-28.671	8.458	-123.625
HFP-CTFE	-99.001	-73.452	36.461	-135.993

Table S3. The fraction of *α*-, *β*-, and *γ*-phase of the films in the different blend compositions. Phase content results calculated from FTIR images and Supplementary Note 1.

Content	P(VDF-HFP)	60/40 wt.%	50/50 wt.%	40/60 wt.%	P(VDF-CTFE)
F(α)	49.07	24.65	17.52	21.59	27.70
F(β)	16.96	24.30	25.75	25.14	25.02
F(γ)	33.97	51.05	56.73	53.27	47.28

Table S4. Grain sizes of different blend compositions. The grain size of each fitted peak was calculated from the peak splitting results of Fig. S6 and the Scherrer equation.

Sample	**Grain size α (100) (nm)**	**Grain size α (020) (nm)**	**Grain size γ (020) (nm)**	**Grain size α (110) (nm)**	**Grain size γ (110) (nm)**	**Grain size β (020) (nm)**
P(VDF-HFP)	53	66.31	61.27	79.76	49.86	46.94
60/40 wt.%	49.69	53.05	49.75	66.47	48.82	44.34
50/50 wt.%	49.08	52.35	46.82	56.97	44.32	42
40/60 wt.%	52.46	51.34	48.24	63.81	46.93	43.14
P(VDF-CTFE)	56.79	54.88	53.06	69.36	52.26	47.85