Supplementary Information for

Enhanced high-temperature capacitive energy storage in PMIA-based dielectric films by tailoring a short-range ordered conformation

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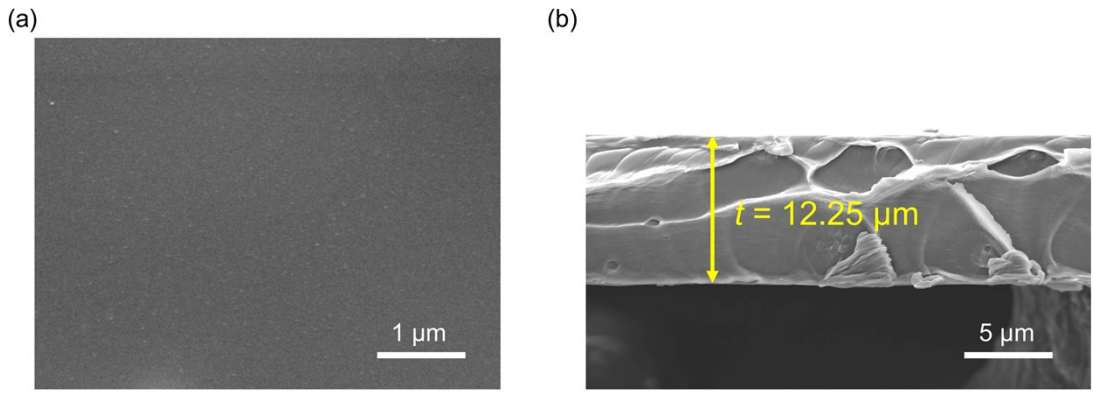

Figure S1. (a) Surface and (b) cross-sectional morphologies of the 0.10 wt% film.

Note 1. The free volume fraction and the quantity of hydrogen bonds in *Molecular Dynamics* models

The calculations are conducted using the *Forcite* module implanted in *Materials Studio* software at 298.15K. MD models of pure PMIA, 0.05 wt% PMIA/BzP, 0.10 wt% PMIA/BzP, 0.20 wt% PMIA/BzP, and 0.30 wt% PMIA/BzP are constructed. The PMIA chains are polymerized at a degree of 15, with each amorphous cell containing 20 chains. BzP is incorporated in each cell at the specified doping ratios. Geometric optimization is then performed to all amorphous cells to rationalize the conformation. Subsequently, the constant pressure and temperature (NPT) relaxation and the constant volume and temperature (NVT) relaxation are successively performed to minimize the system energy, with each relaxation lasting for 500 ps.

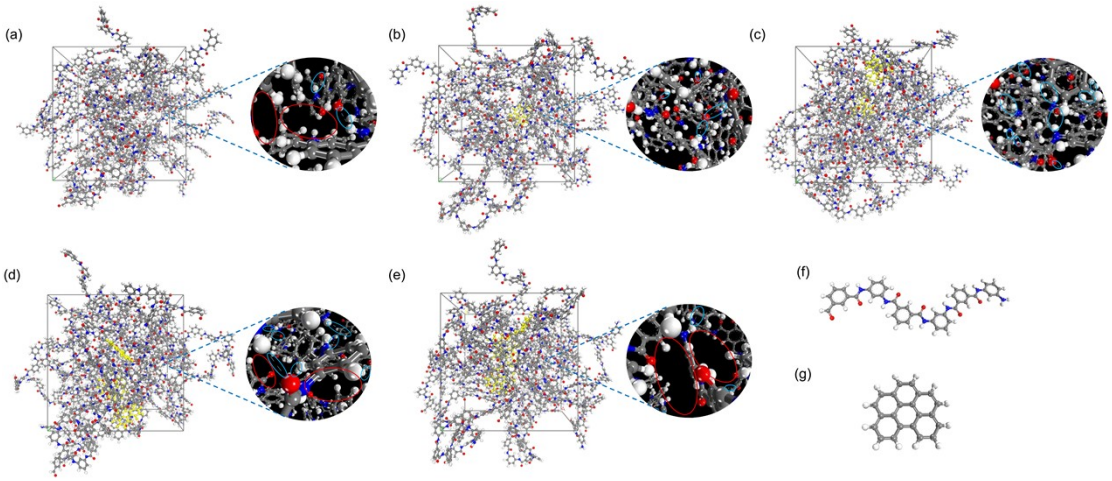

Figure S2. The free volume distribution and hydrogen bonds in each MD model of (a) PMIA, (b) 0.05 wt% PMIA/BzP, (c) 0.10 wt% PMIA/BzP, (d) 0.20 wt% PMIA/BzP, and (e) 0.30 wt% PMIA/BzP. BzP is highlighted by the yellow color, with blue circles representing the smaller interchain spacing where hydrogen bonds are formed between PMIA chains, red circles denoting the larger interchain spacing where hydrogen bonds are absent. (f) PMIA chain structure. (g) BzP molecular structure.

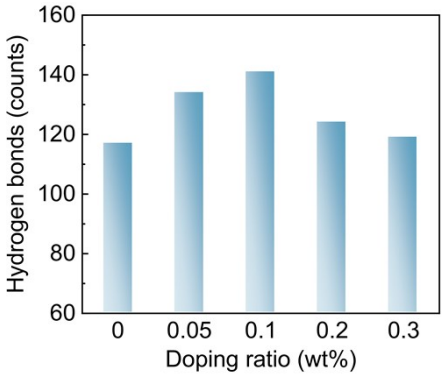

Figure S3. The quantity of hydrogen bonds in each model.

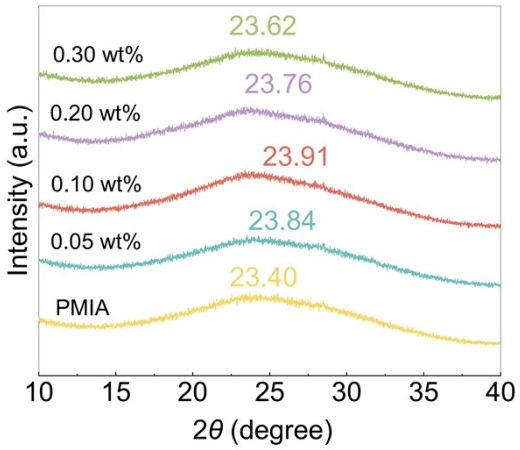

Figure S4. XRD patterns of various films.

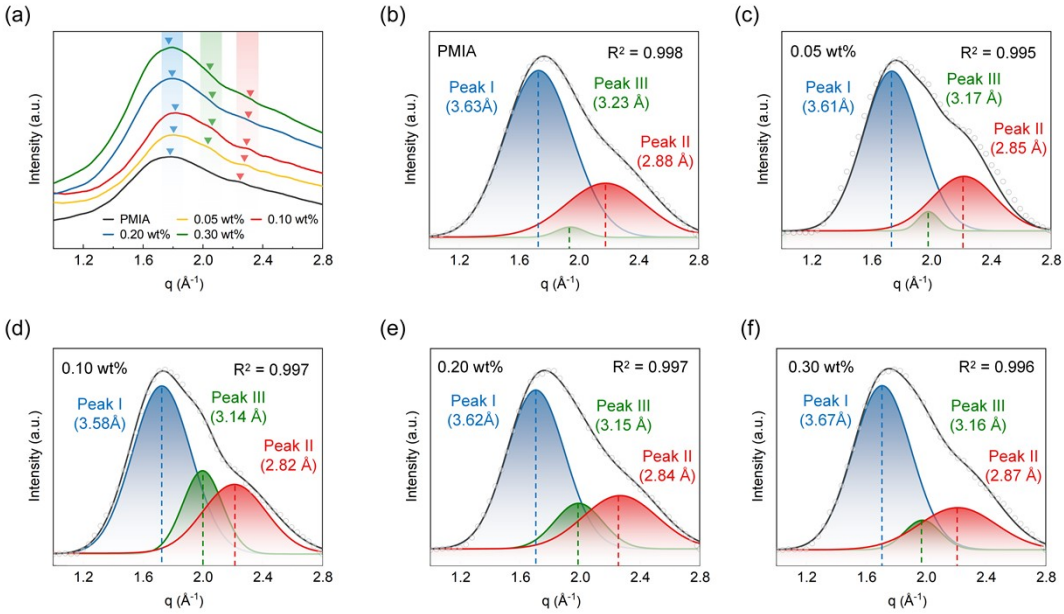

Figure S5. WAXS patterns and their peak fitting for various films.

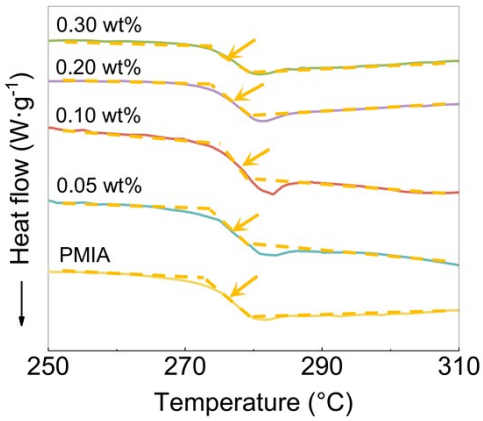

Figure S6. DSC curves of various films.

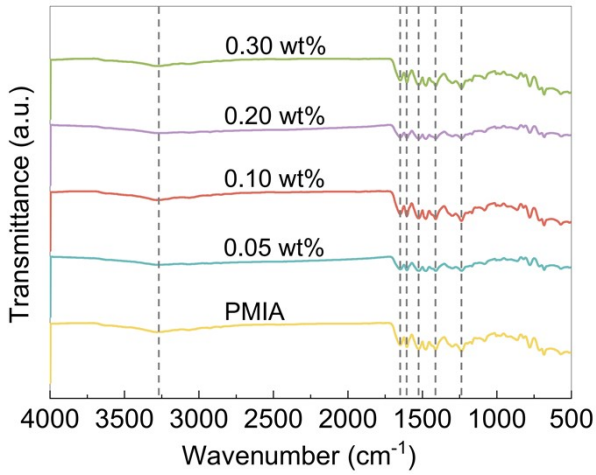

Figure S7. FTIR spectra of various films.

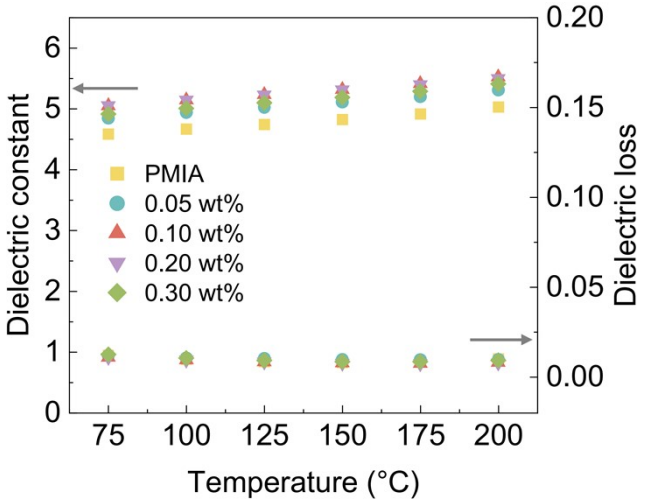

Figure S8. Temperature-dependent dielectric constant and loss of various films.

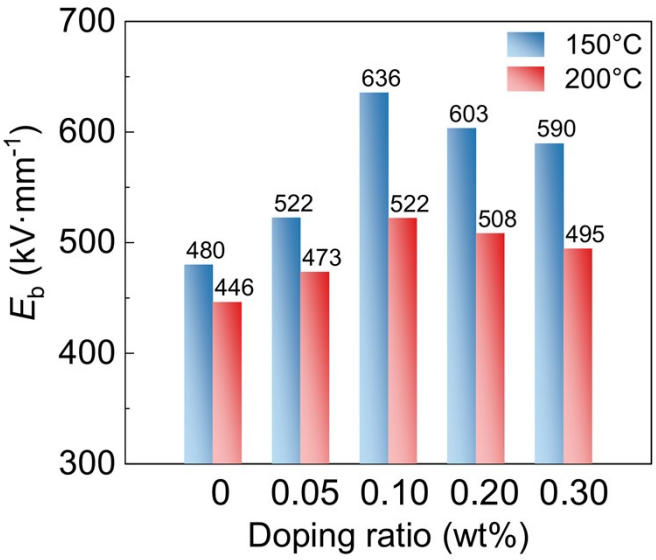

Figure S9. The characteristic E_b of various films at 150°C and 200°C.

Note 2. Fitting with the leakage current density based on the hoping conduction model

When charge transfer is primarily dominated by the hopping conduction, leakage current correlates with both the electric field (E) and temperature (T) as

$$J(E,T) = 2ne\lambda v \times \exp\left(\frac{-E_a}{kT}\right) \times \sinh\frac{\lambda eE}{2kT} \tag{1}$$

where n is the carrier concentration, e is the unit charge, λ is the hopping distance, v is the carrier hopping probability, E_a is the activation energy, and k is the Boltzmann constant.

At a specific temperature, the leakage current density (J) is mainly determined by E, and the equation (1) can be simplified as,

$$J = J_0 \times A \times \sinh(A \times E) \tag{2}$$

$$A = \frac{\lambda e}{2kT} \tag{3}$$

$$J_0 = 2kT \times 2nv \times \exp\left(\frac{-E_a}{kT}\right) \tag{4}$$

Note 3. Arrhenius function for fitting temperature-dependent conductivity

The electrical conductivity (σ) is determined based on the leakage current density (J) by the equation,

$$\sigma = \frac{J}{E} \tag{5}$$

where E is the electric field strength and J is the leakage current density at the given E.

The σ is a temperature-dependent property, following the Arrhenius equation,

$$\sigma(T) = \sigma_0 \times \exp\left(-\frac{E_a e}{kT}\right) \tag{6}$$

where σ_0 is the prefactor. By plotting $ln\sigma$ as the y-axis and $1/T$ as the x-axis, a linear fitting curve can be obtained, with its slop being E_a.

Note 4. Calculations based on the DFT method

For both BzP and PMIA, their electrostatic potential (ESP) distributions and energy band structures are calculated based on the DFT method, utilizing Gaussian 16.0. The B3LYP hybrid functional and 6-31G(d) basis set are performed. Additionally, the quantitative analysis of the specific surface potential is displayed through *Multiwfn* program, during which the grid spacing is set to 0.25 bohr, and the isosurface of electron density is set as 0.001 e/bohr^3.

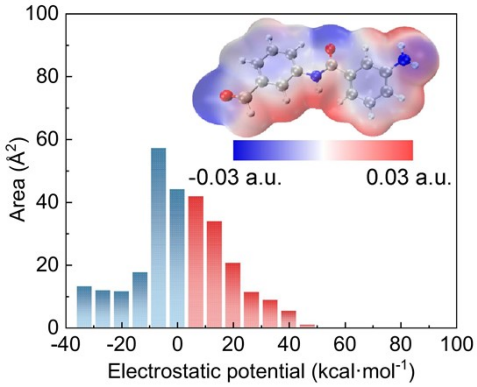

Figure S10. The electrostatic potential (ESP) distribution of PMIA.

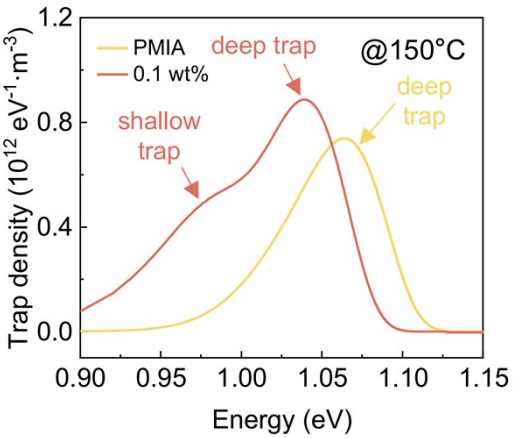

Figure S11. The charge trap characteristic curves of the pure PMIA film and the 0.10 wt% film.

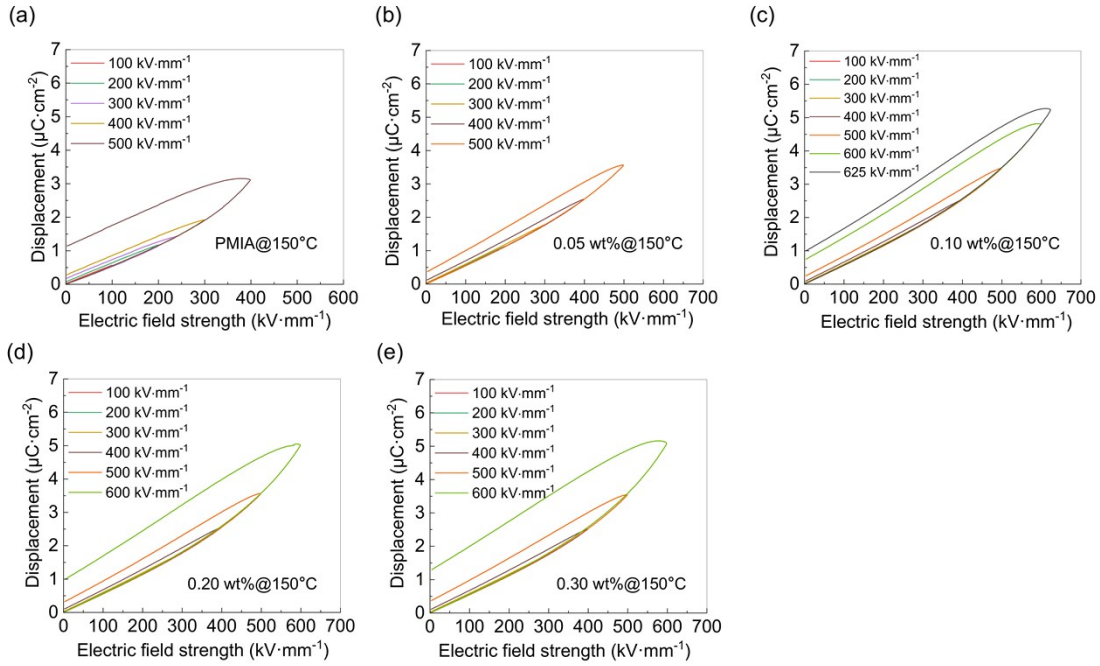

Figure S12. The *D*-*E* loops for (a) PMIA, (b) 0.05 wt% PMIA/BzP, (c) 0.10 wt% PMIA/BzP, (d) 0.20 wt% PMIA/BzP, and (e) 0.30 wt% PMIA/BzP films at 150°C.

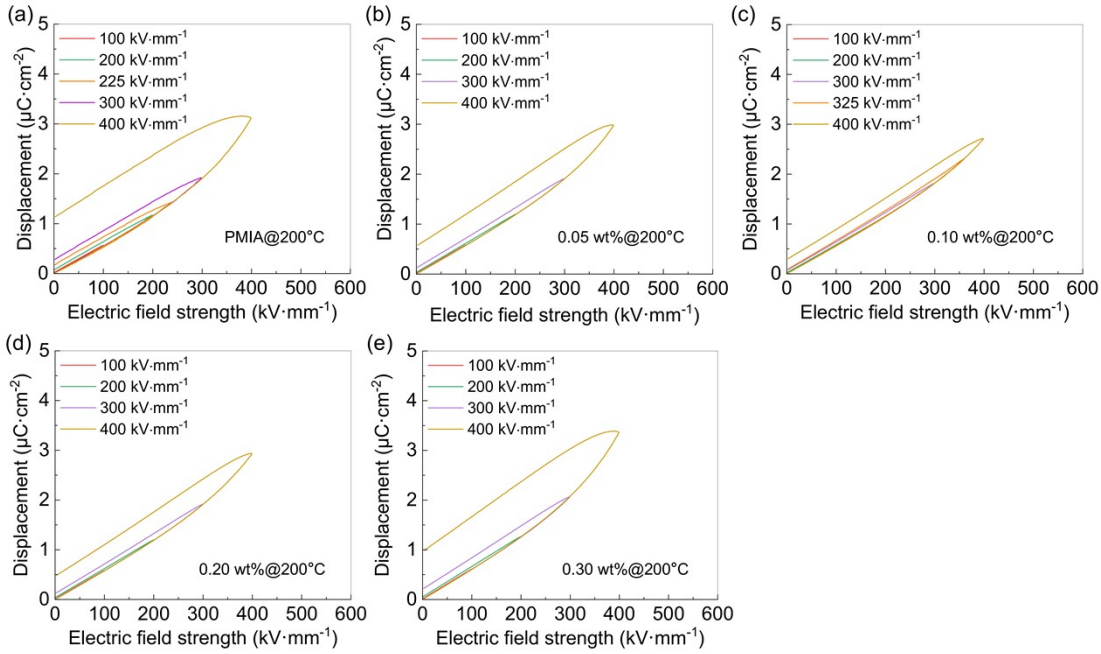

Figure S13. The *D-E* loops for (a) PMIA, (b) 0.05 wt% PMIA/BzP, (c) 0.10 wt% PMIA/BzP, (d) 0.20 wt% PMIA/BzP, and (e) 0.30 wt% PMIA/BzP films at 200°C.