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Achieving synergistic improvement in dielectric constant and energy storage properties of all-organic liquid crystal molecule/PVDF composites

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Characterization

The morphology of the all-organic PVDF-based films with different weight fraction of 5CB were characterized by scanning electron microscopy (SEM, JSM-6390). The diffusion of 5CB within the PVDF was analyzed by means of energy dispersive X-ray spectrometer (EDS) equipped with SEM.

The contact angle was measured by using the contact angle goniometer (POWEREACH JC20000D1). The uniform PVDF-based solution was evenly scraped on the clean glass surface. Water and N, N'-dimethylformamide (DMF) were used as test solvents, and contact angle images were taken immediately after the entire droplet fell onto the sample surface at a constant height. Each sample was measured at least five times.

The optical microscopy studies were carried out via polarized light microscope

(POM, Leica DM-LMP) equipped with a Mettler-Toledo hot stage (FP82HT). The images displayed in this paper were taken under crossed polarizers.

XRD experiments were performed on an X-ray diffractometer (SmartLab SE, Rigaku) employing Cu-Kα radiation at a scanning rate of 10 °/min over the range from 5 ° to 45 °. Its voltage and current ratings were 40 kV and 40 mA.

The structure analysis of the pristine PVDF film and all 5CB/PVDF nanocomposite films were identified by Fourier-transform infrared (FTIR) spectroscopy (Nicolet 6700 instrument) with scanning range from 4000 cm^{-1} to 6000 cm^{-1}. FT-IR results were also used to determine the content of γ-phase in the pristine PVDF film and all 5CB/PVDF nanocomposite films. The calculation formula is as follows [1]:

$$F(\gamma) = \frac{A_\gamma}{\left(K_\gamma/K_\alpha\right)A_\alpha + A_\gamma} \tag{1}$$

Where F(γ) represents the γ-phase content; A_γ and A_α represent the absorbance at 763 and 833 cm^{-1}, respectively; K_γ and K_α are the absorption coefficients at the respective wavenumber, whose values are 6.1×10^4 and 7.7×10^4 cm^2·mol, respectively.

Differential scanning calorimetry (DSC) traces of the pristine PVDF film and all 5CB/PVDF nanocomposite films were obtained using a TA Q25 DSC instrument at a heating rates of 10 ℃/min. The degree of crystallinity was calculated by the following formula of polymer matrix nanocomposites, as below [2]:

$$\mathrm{X}_c(\%) = \frac{\Delta H_m}{(1-\phi)\Delta H_m^{100}} \times 100\% \tag{2}$$

Where ΔH_m and ΔH_m^{100} represent the melting enthalpy of the composite measured from

the DSC and the melting enthalpy for a 100% crystalline PVDF (104.7 J/g). X_c is the weight fraction of nanofillers.

Thermogravimetric analysis (TGA) was performed on a TA SDT Q600 instrument at a heating rate of 10 °C/min in a nitrogen atmosphere.

The Young's modulus of the PVDF-based nanocomposite films was measured by a MML Nano Test Vantage.

The dielectric performance was measured using an Agilent 4294A LCR meter with a frequency range from 100 Hz to 10 MHz. The temperature-dependence of dielectric properties of all nanocomposites was also studied by Partulab DMS-500 dielectric measuring instrument with temperature range from 25 °C to 150 °C. The polarization-electric field hysteresis loops, leakage current and cycle stability of the composites were performed by a TF analyzer 2000 ferroelectric polarization tester (aixACT, Germany). The energy storage performance was calculated according to the P-E loops.

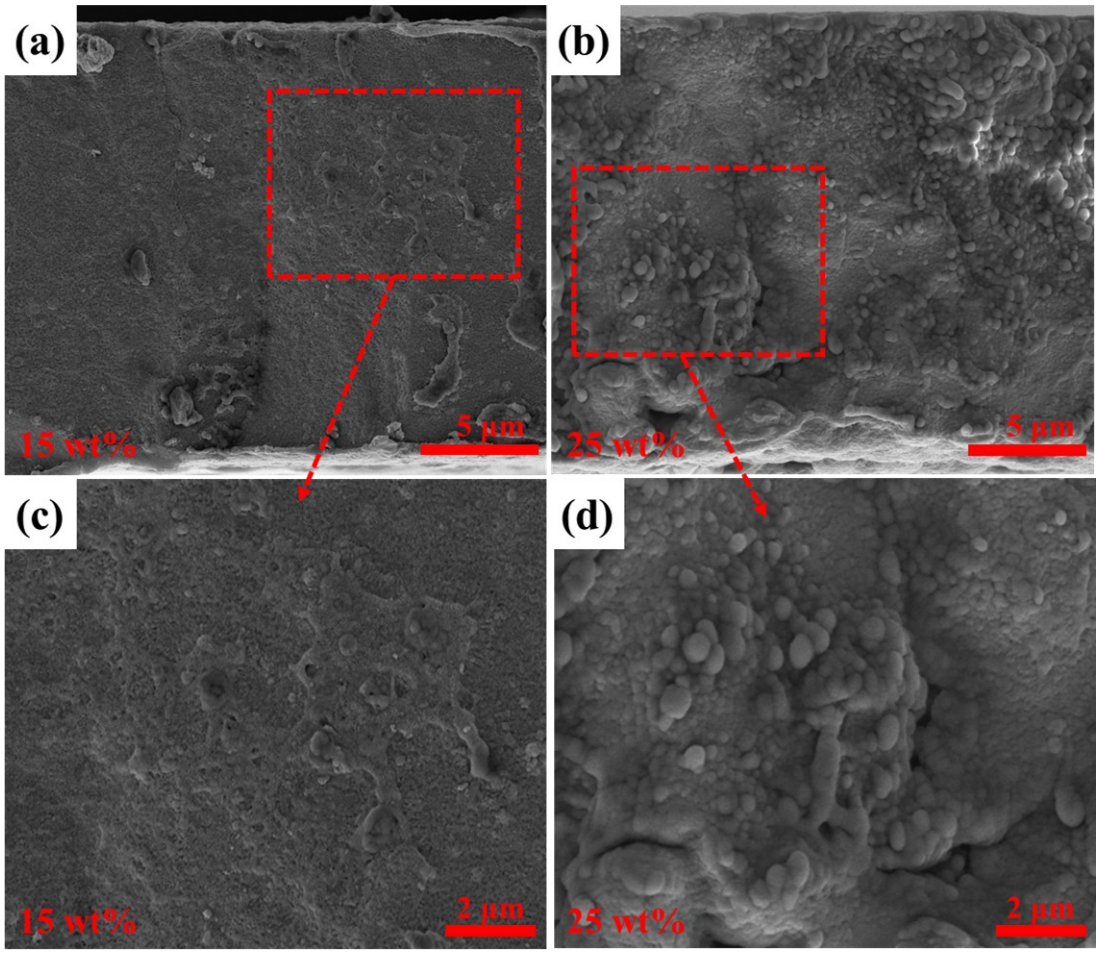

Fig. S1. SEM images of the freeze-fractured cross-sectional morphologies of the nanocomposite films with (a) 15 wt% 5CB and (b) 25 wt% 5CB; Local magnification of SEM image of the composite films with (c) 15 wt% 5CB and (d) 25 wt% 5CB.

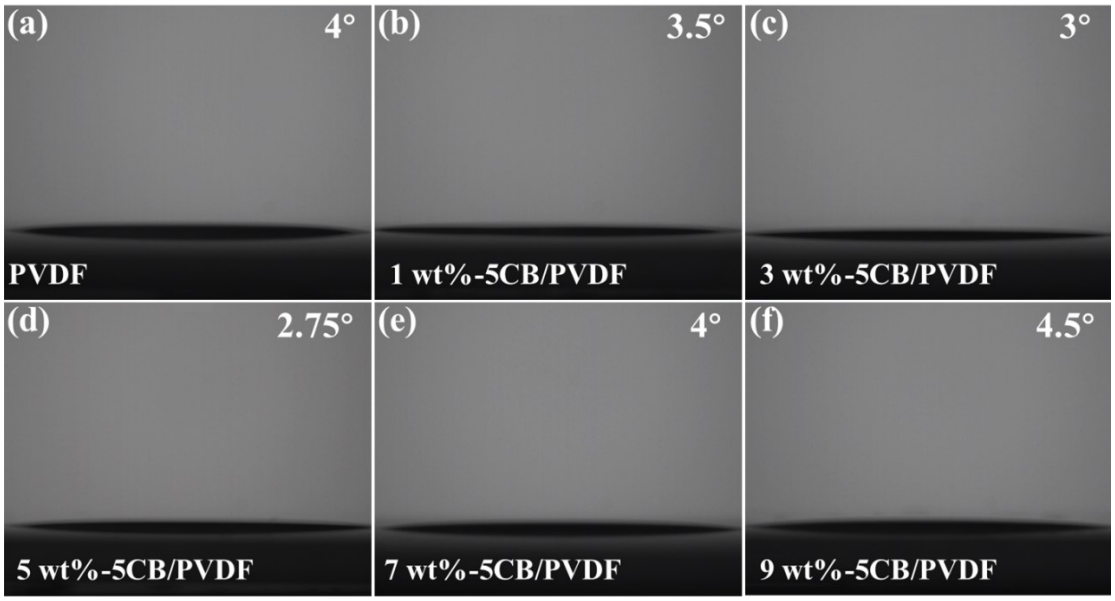

Fig. S2. The DMF contact angle of all PVDF-based composites with different 5CB loading.

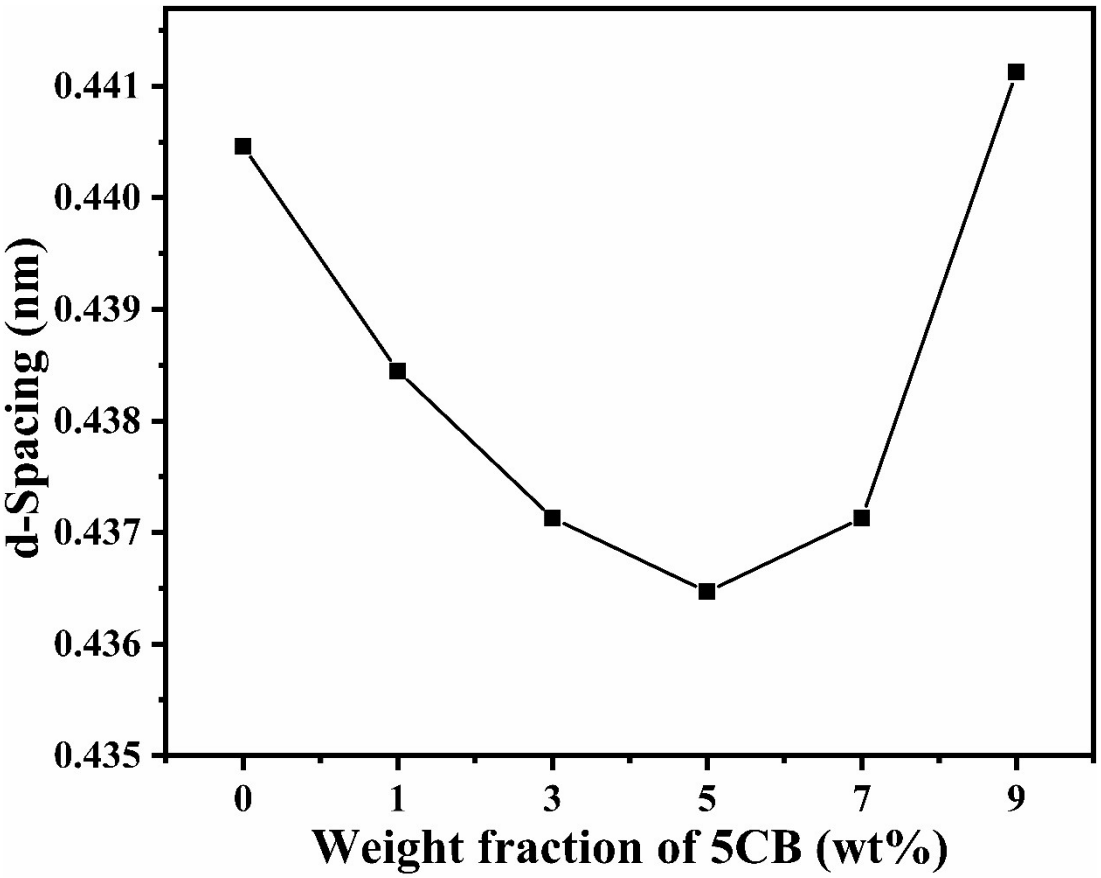

Fig. S3. The average interchain spacing (calculated from the XRD spectra in Fig 6c) of the composite films with different 5CB content.

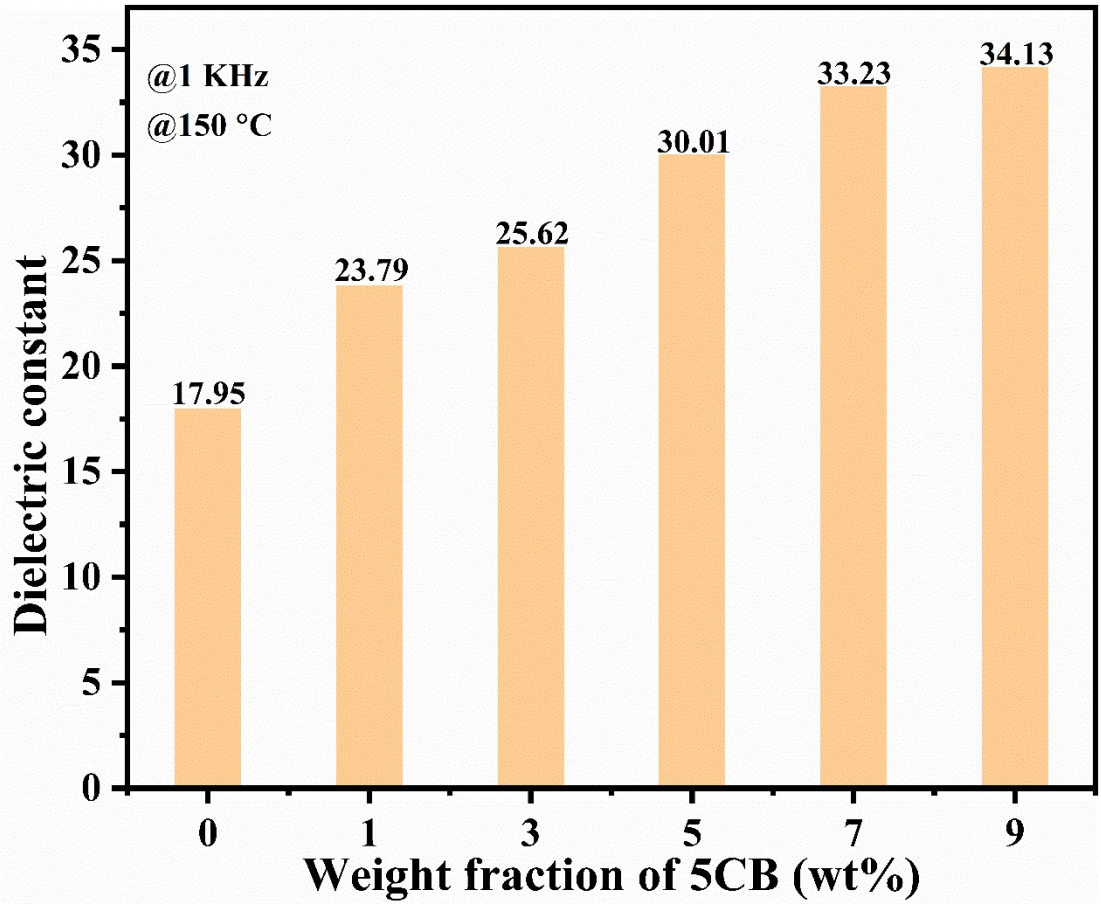

Fig. S4. Dielectric constant of all PVDF-based composites with different 5CB loading at 1 KHz and 150 °C.

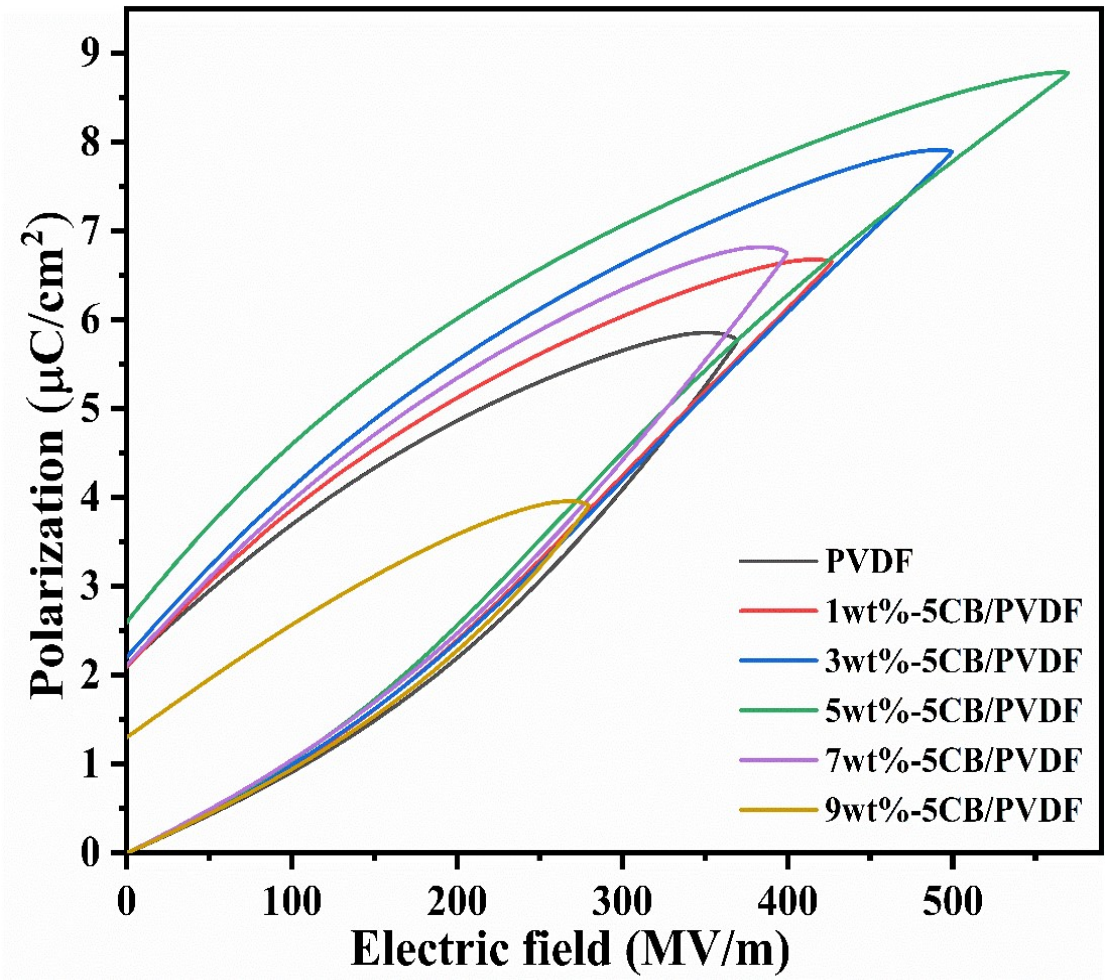

Fig. S5. The P-E loops of all 5CB/PVDF films with different 5CB loading at highest electric field.

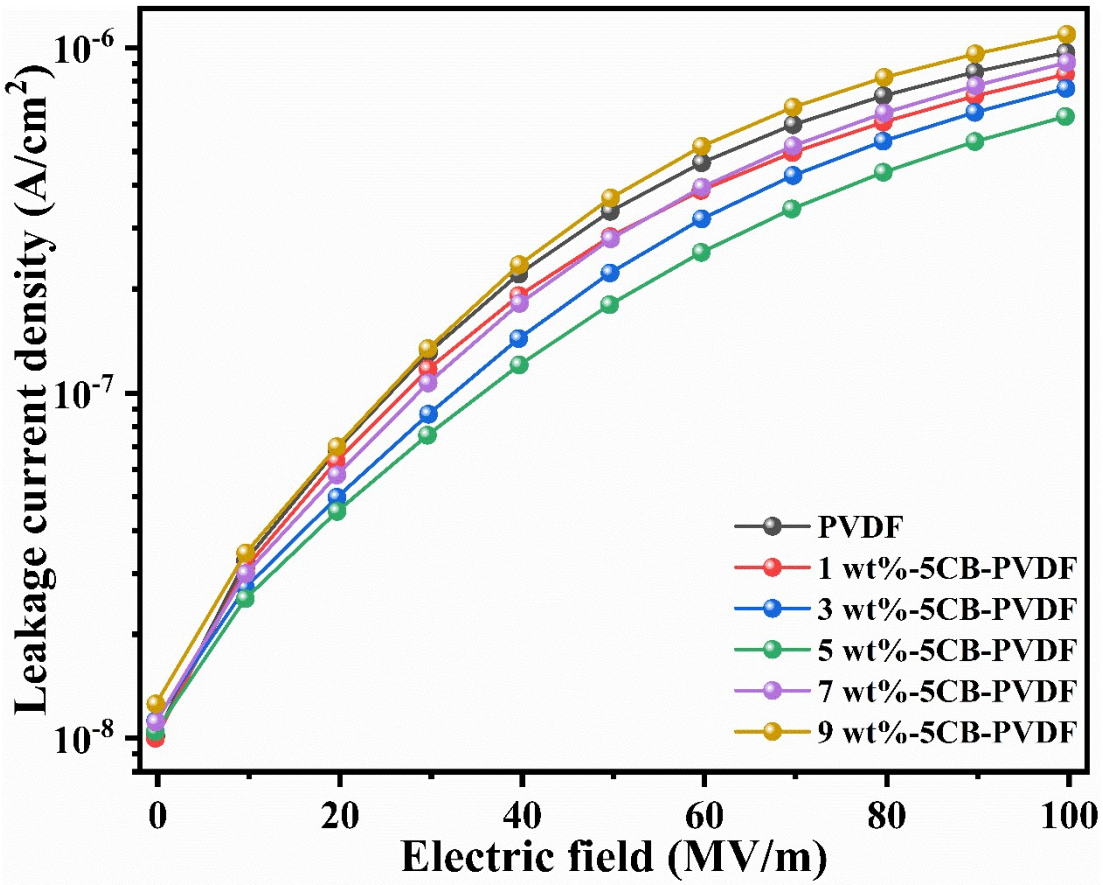

Fig. S6. The leakage current density of the composite films with different 5CB content.

Table S1. Physical properties of the 5CB/PVDF composite films with different filling ratio

Sample	T_c (°C) [a]	T_m (°C) [b]	$\triangle H_m$ (J/g) [c]	X_c (%) [d]
PVDF	143.94	172.69	49.18	47.02
1 wt%-5CB/PVDF	144.31	170.88	50.01	48.30
3 wt%-5CB/PVDF	145.24	170.65	52.97	52.21
5 wt%-5CB/PVDF	143.82	170.54	51.15	51.48
7 wt%-5CB/PVDF	142.96	169.11	48.10	49.45
9 wt%-5CB/PVDF	141.89	168.81	45.33	47.62

[a] The crystallization temperature (T_c) was measured by DSC at a cooling rate of 10 °C/min under N_2 during the first cooling process.

[b] The melting temperature (T_m) was measured by DSC at a heating rate of 10 °C/min under N_2 during the second heating process.

[c] The melting enthalpy ($\triangle H_m$).

[d] The crystallinity (X_c).

Table S2. Summary table about the LUMO, HOMO and energy gap values of PVDF and 5CB (calculated in the Gaussian09)

Sample	LUMO (eV)	HOMO (eV)	Electronic bandgap (eV)
PVDF	1.21 eV	-8.73 eV	9.94 eV
5CB	-1.60 eV	-6.31 eV	6.31 eV

References

[1] Z.X. Liu, H.J. Wang, K. Liu, H.H. Li, X.L. Sun, J. Hu, S.J. Wang, C.L. Yuan, S.K. Yan, Ionic Liquid Assisted α–γ′ Phase Transition of Poly(vinylidene fluoride) Thin Films, Macromolecules. 55 (2022) 2160-2170. https://doi.org/10.1021/acs.macromol.1c02653.

[2] A. Bužarovska, M. Kubin, P. Makreski, M. Zanoni, L. Gasperini, G. Selleri, D. Fabiani, C. Gualandi, PVDF/$BaTiO_3$ composite foams with high content of β phase by thermally induced phase separation (TIPS), J Polym Res. 29 (2022) 272. https://doi.org/10.1007/s10965-022-03133-z.