Remarkable Dielectric Breakdown Strength Enhancement of PVDF Terpolymer Using A 2D Hybrid Organic Inorganic Perovskite as Functional Additive

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1. Experimental details

Materials: The PVDF terpolymer (PVDF-t), poly(vinylidene fluoride-trifluoroethylene chlorofluoroethylene), was purchased from PolyK Co. Ltd. (USA). All other materials were of reagent grade and purchased from Sigma-Aldrich. The chemicals used as received unless stated otherwise.

Preparation of $(PEA)_2PbI_4$: $(PEA)_2PbI_4$ bulk crystals were prepared using a solution-growth method. Solid lead iodide (0.25 mmol) and phenyl ethyl ammonium (0.50 mmol) were placed into a 4 mL vial. Subsequently, γ-butyrolactone (1.5 mL) was added and the resulting mixture was sonicated for 10 mins to afford a clear yellow solution. The vial was then transferred into a 20 mL vial containing dichloromethane (DCM). Slow solvent evaporation over 1 week of the precursor solution gave orange $(PEA)_2PbI_4$ crystals.

Film fabrication: The powdered PVDF-t was dissolved in DMF at a concentration of 50 mg/mL and stirred overnight at room temperature to make a transparent solution. Then $(PEA)_2PbI_4$ was dissolved in DMF completely to make the additive solution (1mg/mL). The additive solution was added to the polymer solution by weight ratio (0.05, 0.1, 0.15, 1 and 10 wt%) of perovskite to polymer matrix. The obtained solution was mixed homogeneously, and 2.5 mL of the solution was transferred to a petri dish which was subsequently dried at 95 ℃ for 16 h under vacuum. After cooling down to room temperature, the resulting film was peeled off followed by annealing at 105 ℃ for 12 h. The obtained films with thickness of ~30 μm were used to measure DC BDS and films with thickness of ~60 μm were used to probe the THz-TDS properties. Note: For the fabrication of PVDF-t/C60 film, C60 was directly added into DMF solution and ultrasonication was employed for 30 min to make the additive solution.

Characterization and measurements: Raman spectra were recorded on a WITec alpha 300RAS confocal Raman microscope. 633 nm He−Ne gas laser line was used for Raman scattering to avoid absorption. Laser power was 5mW with a laser spot size of about 1 μm. Spectra were collected by an Acton spectrometer with a diffraction grating of 1800 grooves/mm and a thermo-electrically cooled Andor CCD detector. The spectra were collected in the backscattered geometry and Rayleigh scattering was removed by two ultra-low wavenumber 633 nm BragGrate Notch Filters (BNF). The morphology of cryo-fractured surfaces of as-prepared samples was studied by field emission scanning electron microscope (FESEM) (JEOL JSM-7600F). The size of nano $(PEA)_2PbI_4$ was examined using transmission electron microscope (TEM) (JEOL JEM-2100F). Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) spectra were recorded by Perkin Elmer Frontier FTNIR/MIR spectrometers, with resolution of 2 cm^{-1} for 16 scans. Differential scanning calorimetry (DSC) (TA Instruments 2010) was performed from room temperature to 200 ℃ at a constant heating rate of 10 ℃/min under nitrogen atmosphere. Dielectric breakdown strength

was measured using a Hipotonics 880PL DC Hipot tester by sweeping the applied voltage from 50 V_{DC} at approximately 200V/sec until the point of catastrophic failure, as evidenced by spurious current changes and pitting of the top electrode. The measurements were done at room temperature with a 6 mm cylinder shaped electrode geometry in silicone oil to prevent flashover. THz time-domain spectroscopy (THz-TDS) measurements of polymer films were carried out using a TeraView Spectra 3000, incorporated with a Janis ST-100-FTIR cryostat at room temperature. THz conductivity ($\tilde{\sigma}$) was measured in the 0.2 - 2.8 THz range. The samples were kept under vacuum ($\sim 10^{-2}$ mbar) during the entire duration of THz-TDS measurement. The *D-E* hysteresis loop measurements were carried out using a Premiere II ferroelectric tester (Radiant Technologies, Inc.) in combination with a Trek 10/10B-HS high voltage amplifier. The applied voltage had a bipolar sinusoidal waveform in a frequency range 0.1-1000 Hz. Gold electrodes (ca. 2.5 mm^2 diameter) with a thickness around 40 nm were evaporated onto both sides of the film samples. The metallized film samples were immersed in a silicone oil bath to avoid corona discharge in air.
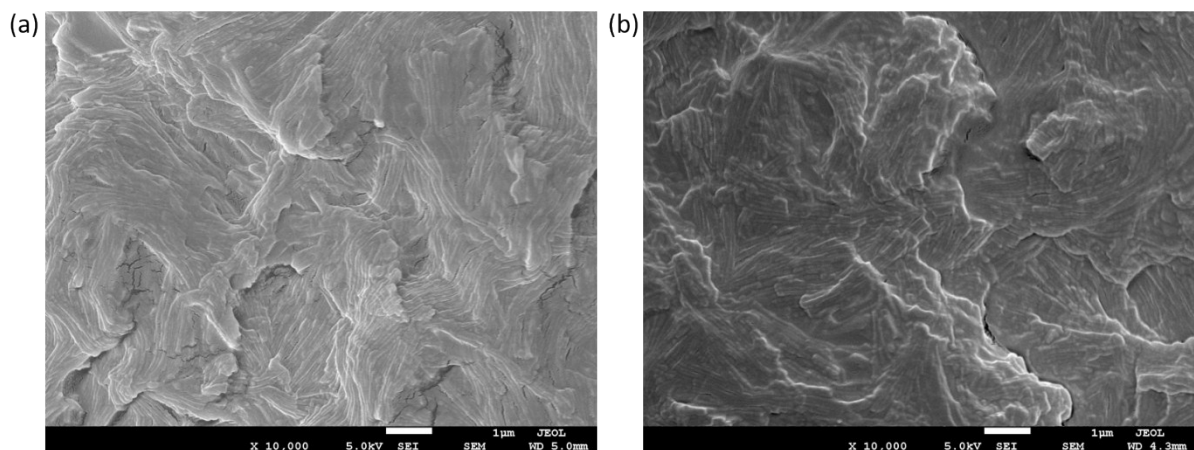
2. Figures

Fig. S1 SEM images of cross section of PVDF-t polymer films with $(PEA)_2PbI_4$ additive in (a) 0 wt% (b) 0.1 wt%.
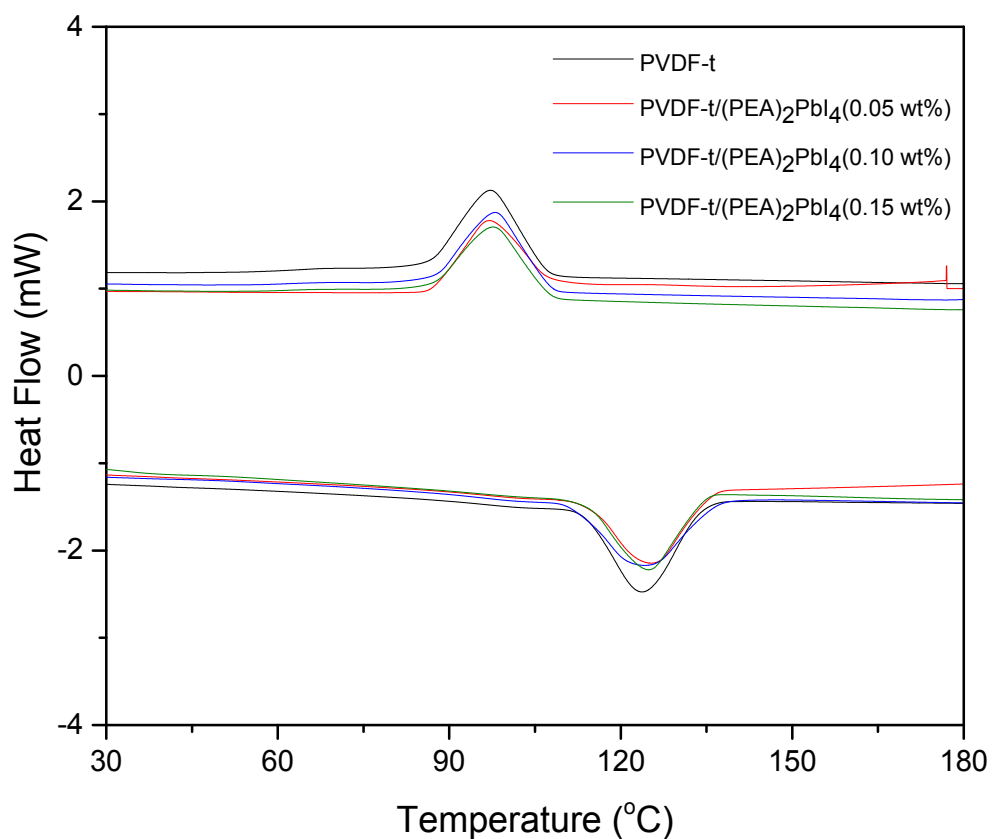
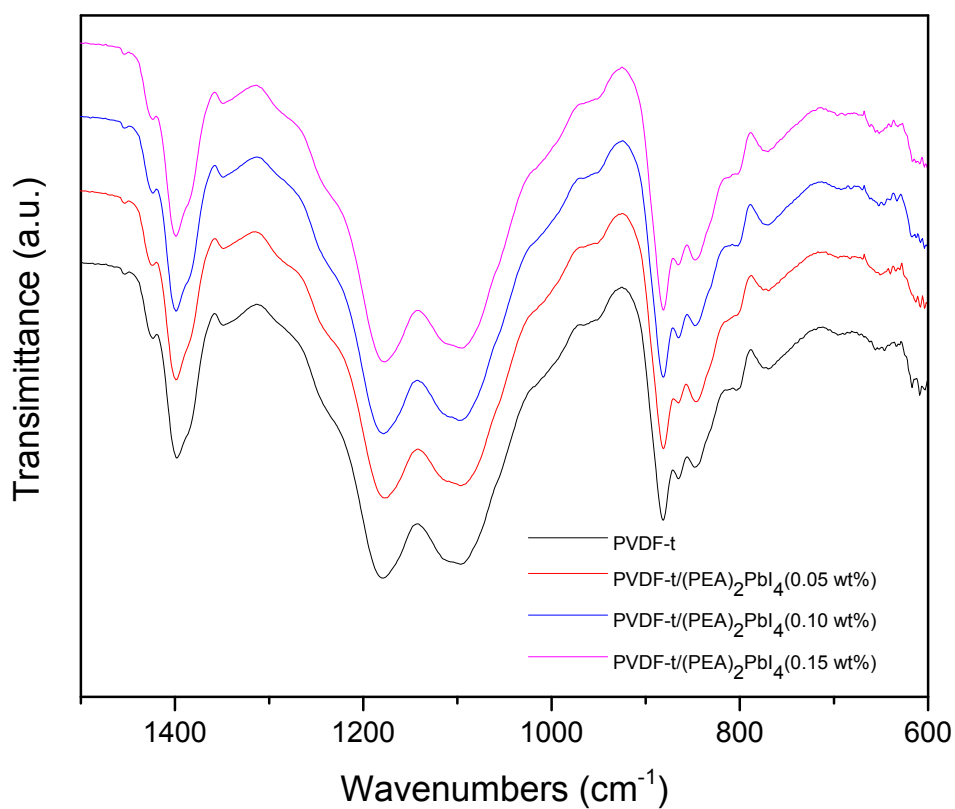**Fig. S2** DSC curves of PVDF-t with $(PEA)_2PbI_4$ additive in different content.

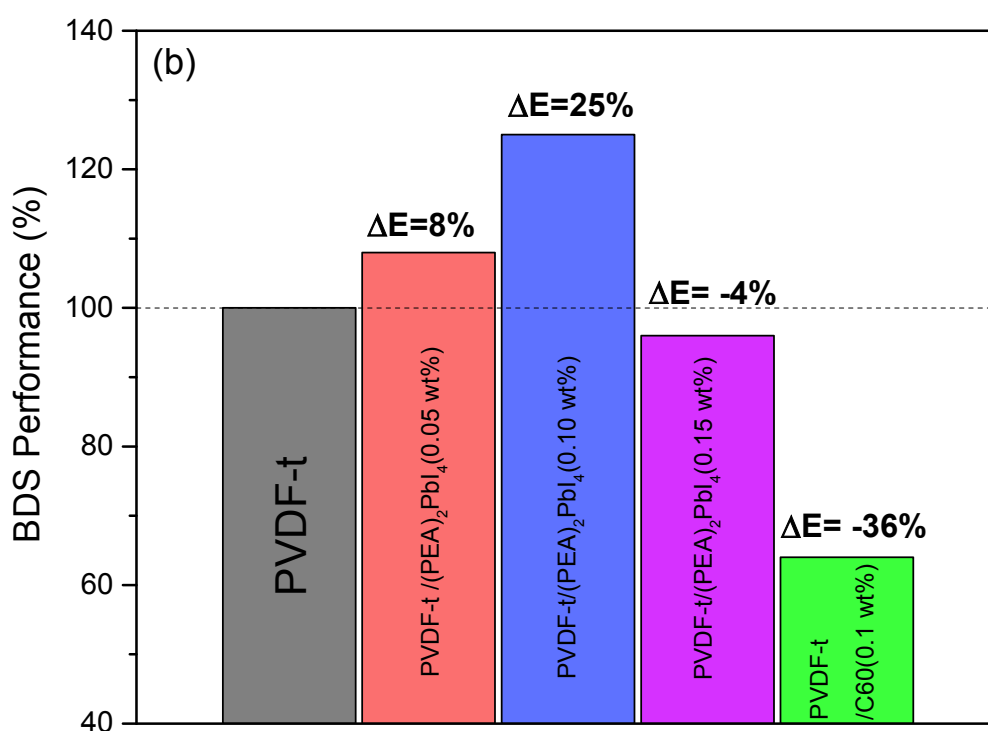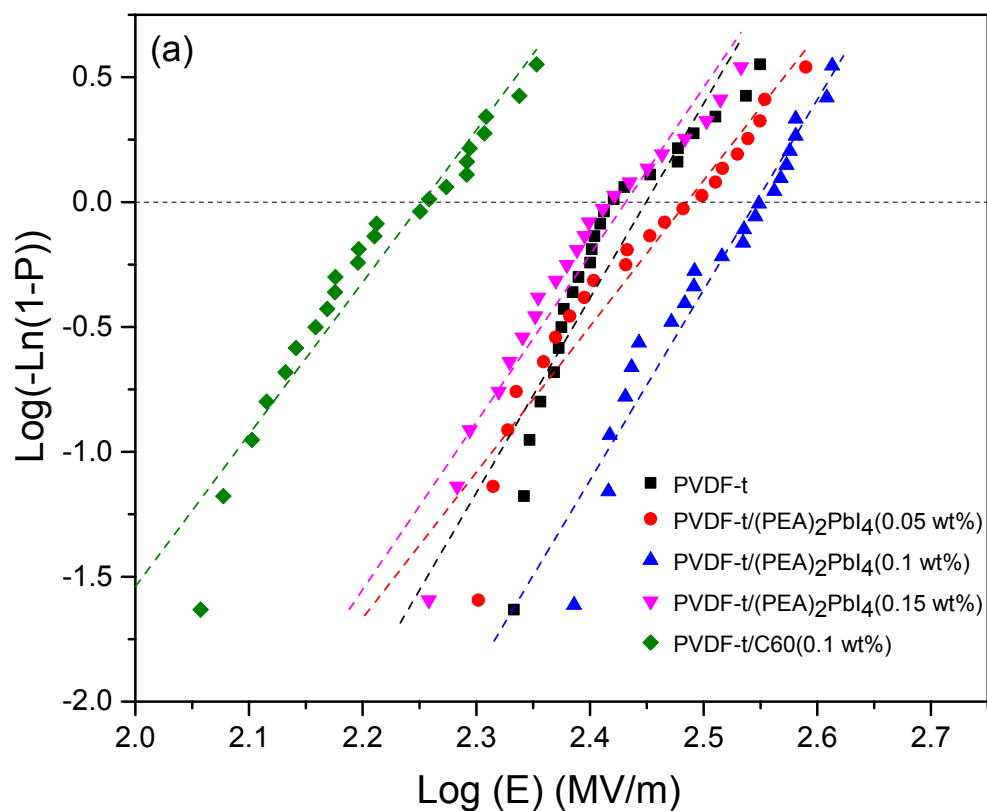**Fig. S3** FT-IR spectra of PVDF-t with $(PEA)_2PbI_4$ additive in different content.

Fig. S4 (a) Weibull distribution of BDS of PVDF-t/(PEA)$_2$PbI$_4$(0, 0.05, 0.1 and 0.15 wt%) film and PVDF-t/C60(0.1 wt%) film. (b) Percentage enhancement of BDS of PVDF-t with (PEA)$_2$PbI$_4$ or C60 as additive.
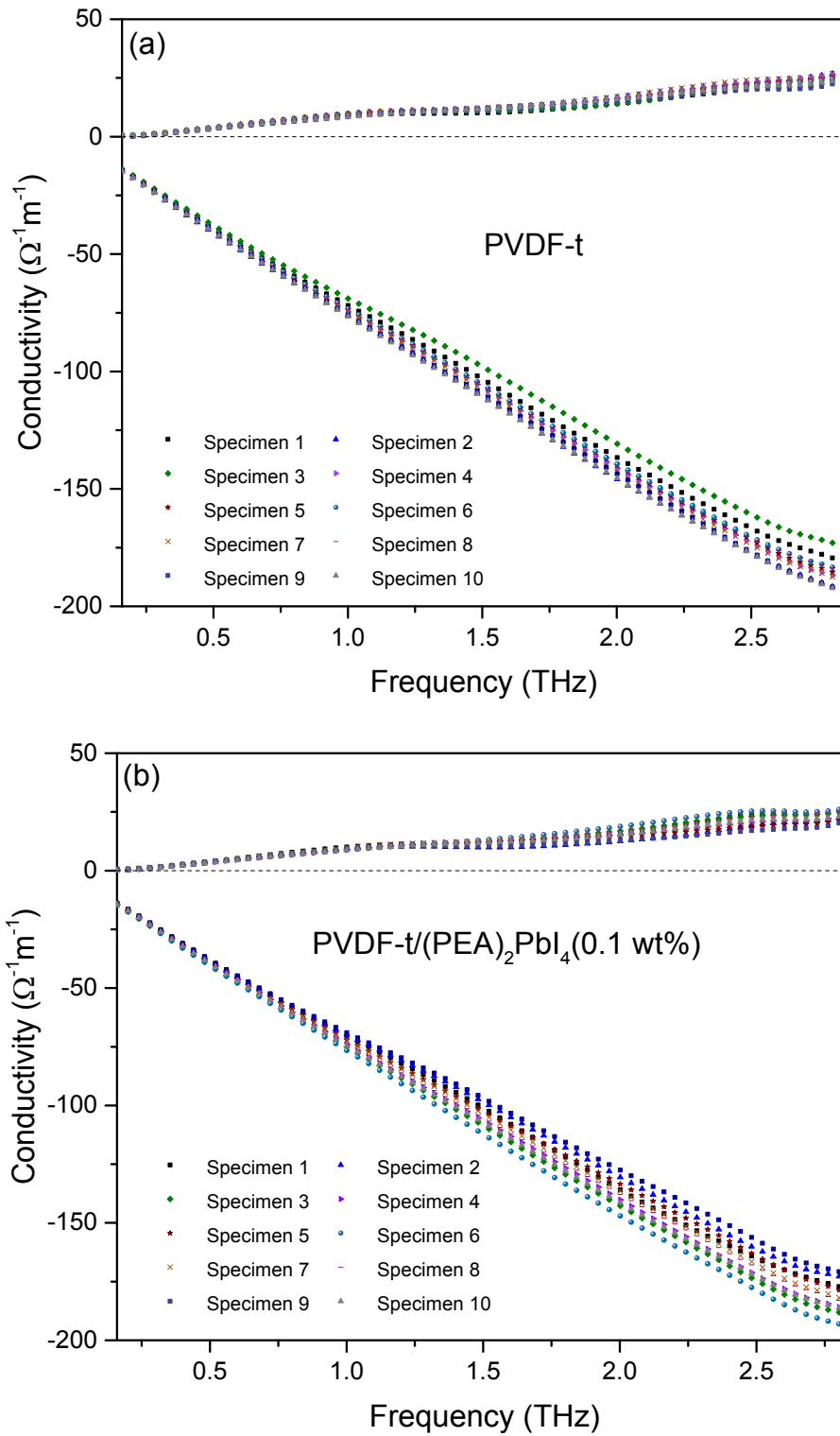
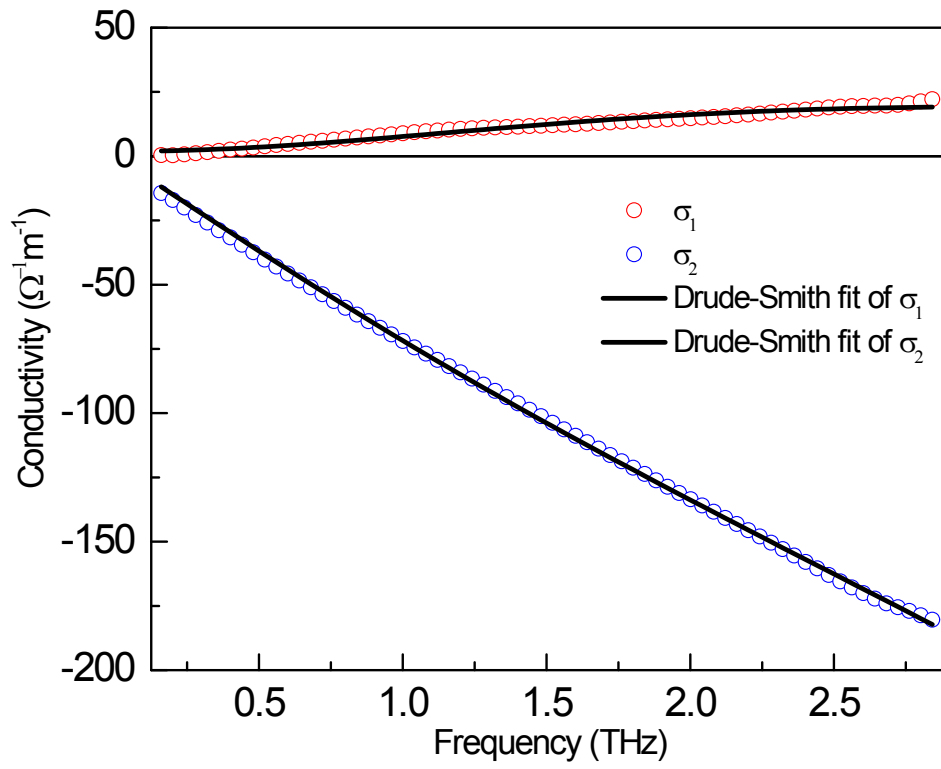**Fig. S5** THz-TDS of (a) neat PVDF-t films and (b) PVDF-t/(PEA)$_2$PbI$_4$(0.1 wt%) films.

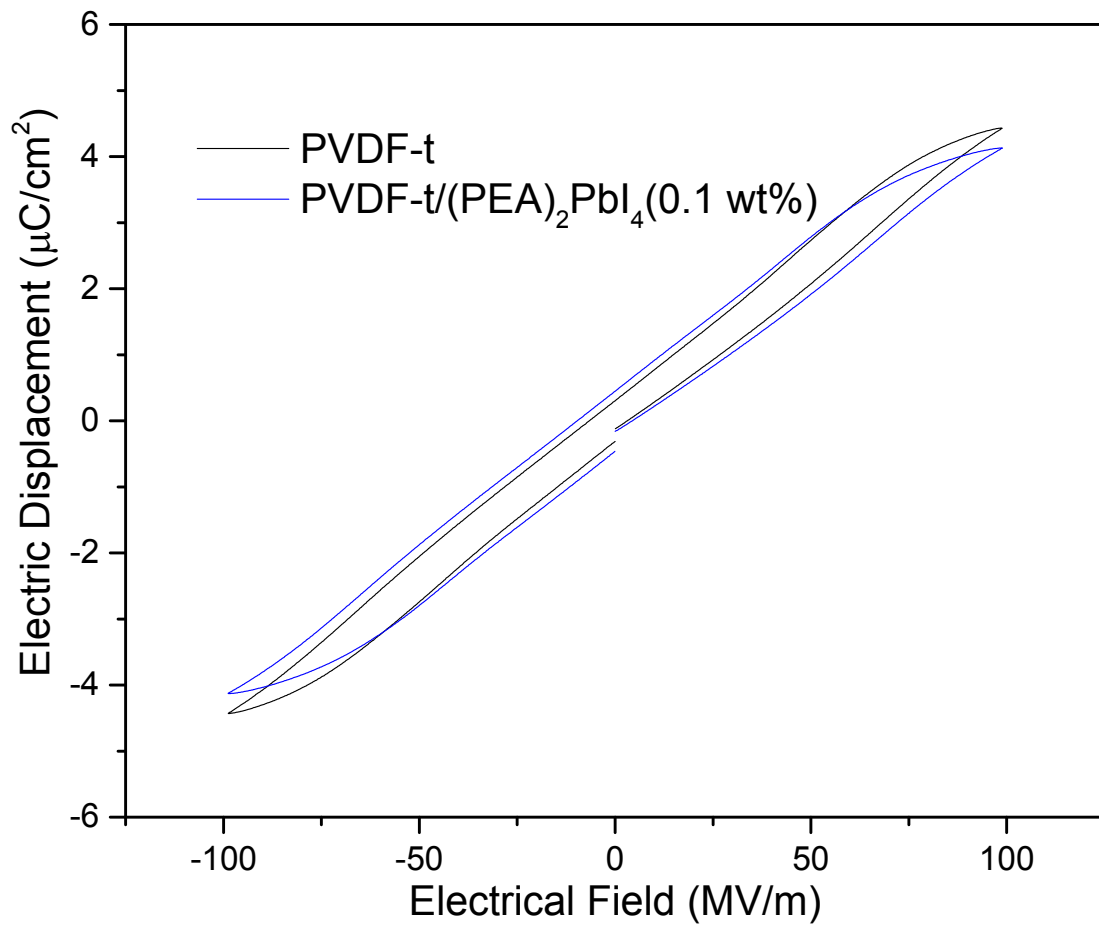**Fig. S6** Typical THz-TDS and its corresponding Drude-Smith fit.

Fig S7. Electric displacement - electric field hysteresis loops of neat PVDF-t film and PVDF-t/(PEA)$_2$PbI$_4$(0.1 wt%) film. The poling frequency is 10 Hz.
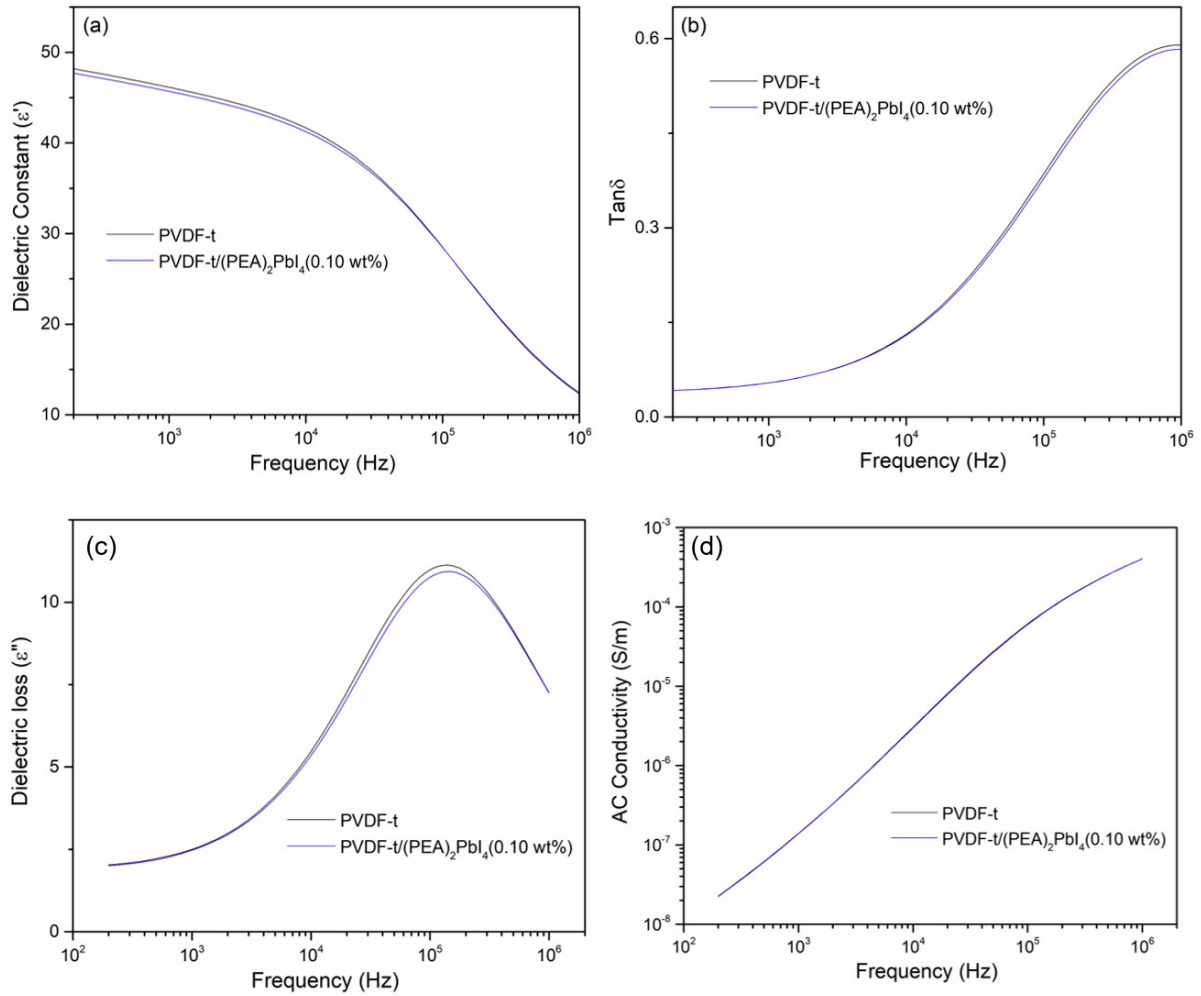
Fig. S8 Frequency dependence dielectric properties of PVDF-t with addition of 0.1 wt% $(PEA)_2PbI_4$ additive.

3. Analysis of THz-TDS and Drude-Smith fits to THz conductivity:

Localized charge carriers are not able to travel enough long distances between electrodes to be detected by DC measurements. However, these localized carriers can absorb an alternating electric field (e.g. THz) and oscillate within the grains where they reside, with the resultant response given by the frequency-dependent complex optical conductivity $\tilde{\sigma}(\omega)$. In the terahertz (THz) range, the carriers interact efficiently with external electromagnetic radiation via the Drude-type mechanism, yielding the complex THz conductivity spectra, from

which we can disentangle the carrier density n and carrier mobility μ by fitting the spectra with appropriate models. In this study, the Drude-Smith (DS) model is employed to fit the complex THz conductivity for both samples.

The THz complex conductivity $([(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)]$ is obtained from the relation $\tilde{\sigma}(\omega) = i\omega\varepsilon_0[1 - \tilde{n}(\omega)^2]$ and $\tilde{n}(\omega) = n_1(\omega) + in_2(\omega)$. $\tilde{n}$ is extracted from the transmission function:

$$\tilde{T} = \frac{4\tilde{n}\ exp[\dfrac{i\omega d(\tilde{n} - 1)}{c}]}{(\tilde{n} + 1)^2 + (\tilde{n} - 1)^2 exp(\dfrac{2i\omega d\tilde{n}}{c})} \tag{S1}$$

where T is THz transmission function, ω is frequency, $\tilde{n}$ is the complex refractive index of specimen, d is the film thickness and c the speed of light in vacuum. Multi-reflection within the sample is considered in this equation.

For both PVDF-t and PVDF-t/(PEA)$_2$PbI$_4$(0.1 wt%) films, we observe $\sigma_1(\omega)$ increases with increasing frequency and $\sigma_2(\omega)$ is negative (Fig. S6). The negative $\sigma_2(\omega)$ implies a restoring force in these films, which origins from the localized potential well near the charge carriers. According to the DS model (Equation 2) that fits the complex conductivity for both samples, the parameter c_1, defined as the fraction of retained initial velocity of carriers after a collision, describes the strength of backscattering due to localization, and ranges between $^-1$ (complete backscattering) and 0 (no backscattering). The parameter c_1 obtained from both sets of spectra is about $^-0.95$, implying that carriers in two films are strongly localized. Therefore, if the applied electric field (e.g. our THz-TDS) is far below the BDS, carrier mobility is not to be considered but the localized carrier density can strongly affect the dielectric strength by means of the breakdown probability. The extracted n from ω_p^2 for both samples are listed in **Tab. S1**.

Tab. S1 The Carrier Density n in PVDF-t and PVDF-t/(PEA)$_2$PbI$_4$(0.1 wt%) Films

Specimen No.	Carrier density ($\times 10^{24}\ \varepsilon_0 m^*/e^2$)	
	PVDF-t film	PVDF-t/(PEA)$_2$PbI$_4$(0.1 wt%) film
1	122.0 ± 7.0	69.3 ± 4.9
2	142.5 ± 8.3	87.0 ± 4.3
3	147.9 ± 15.5	124.8 ± 15.9
4	170.3 ± 16.2	135.2 ± 9.5
5	196.9 ± 19.4	135.6 ± 10.6
6	203.2 ± 20.5	138.5 ± 9.7
7	208.3 ± 18.0	156.6 ± 10.9
8	208.4 ± 21.4	183.7 ± 14.0
9	228.8 ± 21.6	207.7 ± 12.3
10	236.4 ± 39.3	257.6 ± 36.8

The bin size h in Fig. 4 was chosen using Scott's rule: $h = 3.49\ s\ N^{-1/3}$, where s is a rough estimate of the standard deviation and N is the sample size.[1] In our case, for the data set of PVDF-t film in Tab. S1, s is 38.7 and N is 10, yielding the bin size h to be ~60.

4. Reference:

[1]. David W. Scott, *Biometrika* **1979**, *66*, 605.