

## Supporting Information

### **Interfacial engineering tailoring the dielectric behavior and energy density of BaTiO<sub>3</sub>/P(VDF-TrFE-CTFE) nanocomposites by changing liquid-crystalline polymer modifier structure**

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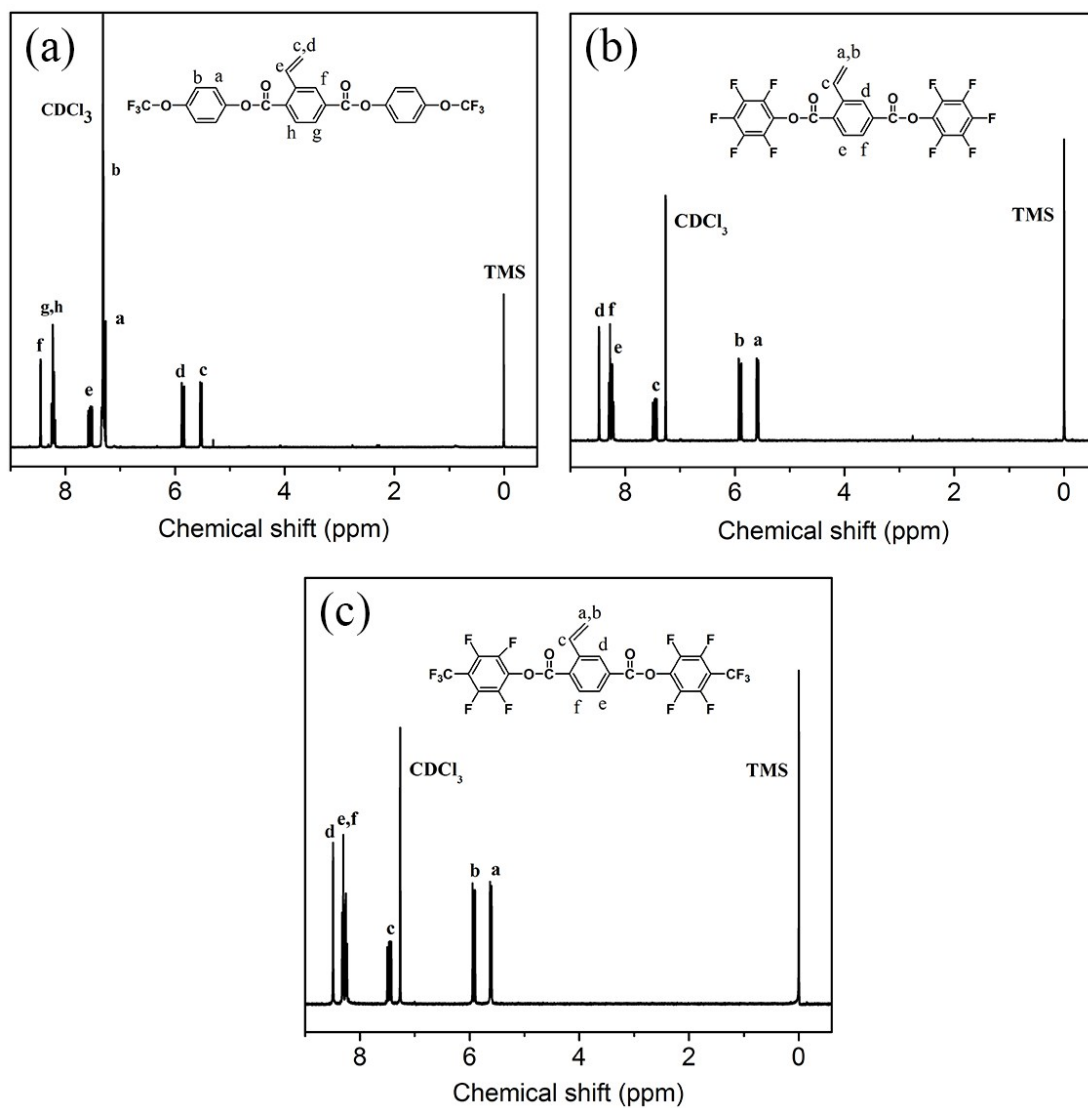
## Characterization

Nuclear magnetic resonance (NMR) measurements were performed on a Bruker ARX400 MHz spectrometer using with  $\text{CDCl}_3$  as solvent, tetramethylsilane (TMS) as the internal standard at room temperature. Fourier-transform infrared (FT-IR) spectroscopy was performed with a Nicolet 6700 instrument over the range of 4000-600  $\text{cm}^{-1}$  to determine the functionalization of the samples. Thermogravimetric analysis (TGA) was performed on a TA SDT 2960 instrument at a heating rate of 20  $^{\circ}\text{C min}^{-1}$  in a nitrogen atmosphere. X-ray photoelectron spectroscopy (XPS) was recorded with an Axis Ultra spectrometer (Kratos Analytical, UK) with a monochromated Al  $K\alpha$  source. Survey scans over a binding energy range of 0-1150 eV were taken for each sample with a constant detector pass energy range of 160 eV, followed by high-resolution XPS measurement (pass energy 40 eV) for quantitative measurements of binding energy and atomic concentration. The morphology of the composites was performed by scanning electron microscopy (SEM, JSM-6390). Liquid crystalline texture of the polymers was examined under POM (Leica DM-LM-P) equipped with a Mettler-Toledo hot stage (FP82HT). Transmission electron microscopy (TEM) images were obtained from a JEOL JEM-2100 instrument operated at an accelerating voltage at 200 kV. The samples were prepared by dropping the sample solutions onto carbon-coated copper grids and air-drying before measurement. Frequency-dependent dielectric constant and dielectric loss were measured using an Agilent 4294A LCR meter with a frequency range from 100 Hz to 10 MHz. Electric displacement-electric field loops was measured by a Precision Premier II ferroelectric polarization tester (Radiant, Inc.).

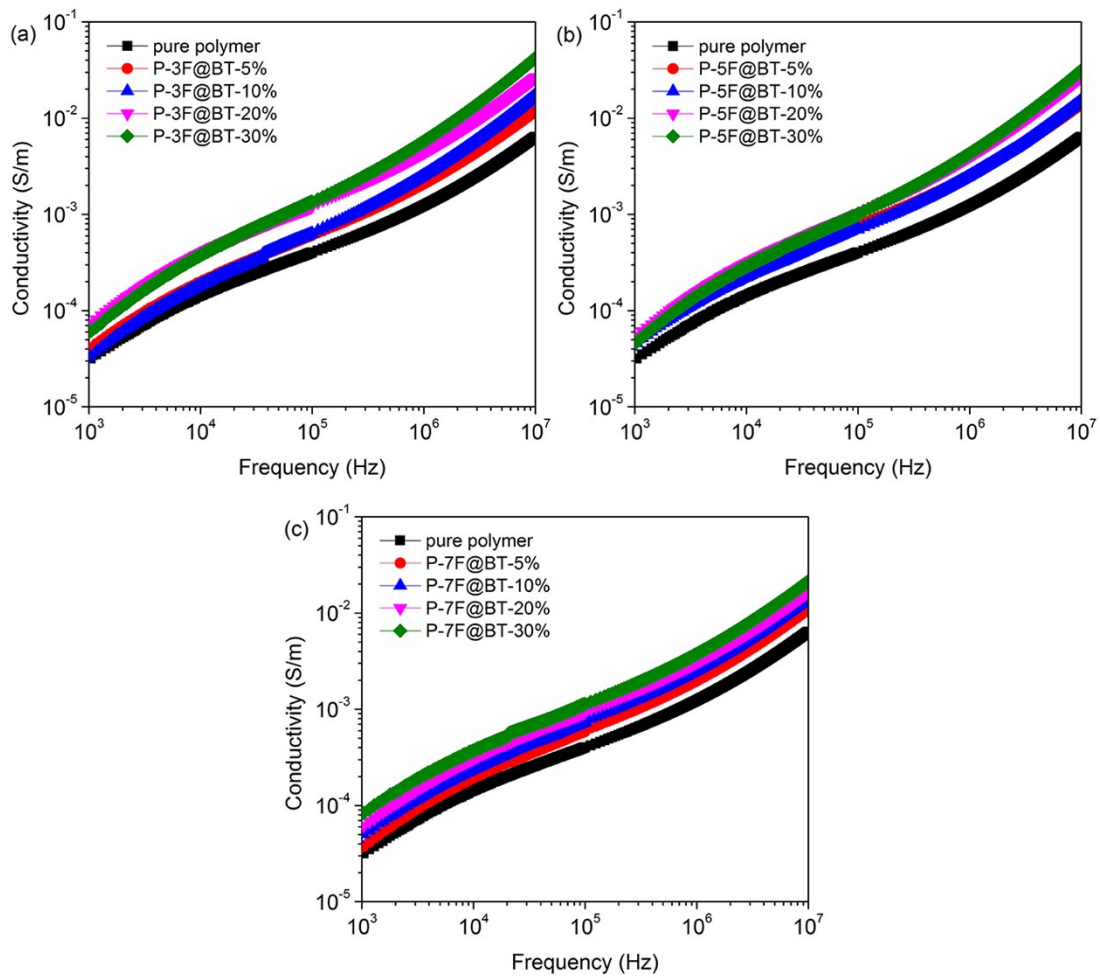
### Surface functionalization of $\text{BaTiO}_3$ nanoparticles

The experimental details of modified  $\text{BaTiO}_3$  nanoparticles were described as followed: (1) The first step was hydroxylation functionalization of  $\text{BaTiO}_3$  nanoparticles. 4 g of  $\text{BaTiO}_3$  nanoparticles was added into a 100 ml aqueous solution of  $\text{H}_2\text{O}_2$  (30 wt%) in a round-bottomed flask. The mixture was sonicated for 30 min and was then refluxed at 105  $^{\circ}\text{C}$  for 6 h. The nanoparticles were recovered by centrifugation at 4000 rpm for 10 min, and then washed with deionized water three times followed by dried under vacuum at 80  $^{\circ}\text{C}$  for 24 h to obtain the surface hydroxylated BT nanoparticles (BT-OH). (2) The second step was amino

functionalization of BT-OH. 3.5 g BT-OH were poured into 100 ml tetrahydrofuran (THF) in a round-bottomed flask and sonicated for 30 min. After 3 g  $\gamma$ -APS was added, the mixture was heated to 80 °C for 24 h under N<sub>2</sub> atmosphere. The nanoparticles were recovered by centrifugation at 4000 rpm for 10 min, and washed with THF three times and followed by dried under vacuum at 80 °C for 24 h to gain the amino-functionalized BT nanoparticles (BT-NH<sub>2</sub>). (3) The third step was that the activation of a RAFT agent (CPDB-NHS) anchored the surface of BT nanoparticles. An amount of 3.3 g of BT-NH<sub>2</sub> was dispersed in THF and sonicated for 0.5 h, and then the mixture was added dropwise to the THF solution of CPDB-NHS at room temperature with vigorous stirring. After reaction of 12 h, the BT-CPDB was collected by centrifugation and washed with THF three times. Then the BT-CPDB was dried at 60°C for 24 h. (4) Finally, the three different liquid crystalline polymers (P-3F, P-5F and P-7F) were introduced onto the surface of BT nanoparticles via RAFT surface-initiated polymerization, denoted as P-3F@BaTiO<sub>3</sub>, P-5F@BaTiO<sub>3</sub> and P-7F@BaTiO<sub>3</sub>. The typical process were as follows: BT-CPDB (1 g), monomer M-3F (1 g, 1.8 mmol), AIBN (2.6 mg, 0.015mmol), and chlorobenzene (7.5 g) were mixed into a glass test tube. The glass tube was purged with nitrogen and subjected to four freeze-thaw cycles to remove the dissolved oxygen. After that, the glass tube was end-capping by alcohol blast burner and then immersed into an oil bath at 80 °C with magnetic stirring. After reaction for 18 h, the glass tube was broken with an iron bar when rapidly cooling to 0 °C with the ice bath. The solution was diluted with THF and centrifuged. The procedure recycled for three times to obtain the P-3F@BaTiO<sub>3</sub>. The synthesized step of the P-5F@BaTiO<sub>3</sub> and P-7F@BaTiO<sub>3</sub> was similar with P-3F@BaTiO<sub>3</sub>.



**Fig. S1.** <sup>1</sup>H NMR spectra of the monomers (a) M-3F, (b) M-5F, and (c) M-7F in CDCl<sub>3</sub>.



**Fig. S2.** Frequency dependence of conductivity of the P-nF@BT/P(VDF-TrFE-CTFE) nanocomposite films with (a) P-3F@BaTiO<sub>3</sub>, (b) P-5F@BaTiO<sub>3</sub>, and (c) P-7F@BaTiO<sub>3</sub>.