Supplementary Information

Flexible Thiophene Polymers: A Concerted Macromolecular Architecture for Dielectrics

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S1. Materials and Methods

Materials: Exo-5-norbornenecarboxylic acid (97%, Aldrich), Grubbs catalyst (2nd Generation, Aldrich), triethylamine (TEA, 99%, Alfa Aesar), p-toluenesulfonyl chloride (TsCl, 98%, Alfa Aesar), 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (Aldrich), 2-([2,2'-bithiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (TCI america), 2-(thiophen-2-yl)ethan-1-ol (Alfa Aesar) were used as received. Grubbs catalyst (3rd generation) was prepared according to a previous report.[1] All other reagents were from commercial resources and used as received unless otherwise mentioned.

Physical Characterization: 300 MHz ^{1}H NMR and 75 MHz ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer with tetramethylsilane (TMS) as an internal reference. Molecular weight information of polymers was determined using a gel permeation chromatography (GPC) equipped with a 2414 RI detector, a 1525 Binary Pump and three Styragel columns. The columns consisted of HR 1, HR 3 and HR 5E in the effective molecular weight ranges of 100,000–5,000 Daltons, 500,000–30,000 Daltons, and 2,000–4,000,000 Daltons respectively. Tetrahydrofuran (THF) was used as eluent at 35 °C with a flow rate of 1.0 mL min^{-1}. The system was calibrated with polystyrene standards obtained from Polymer Laboratories. GPC samples were prepared by dissolving samples in THF with a concentration

of 3.0 mg mL^{-1} and passing through microfilters with an average pore size of 0.2 μm. Fourier transform infrared spectrometry (FTIR) spectra were taken on a PerkinElmer spectrum 100 FTIR spectrometer. The thermal properties of polymers was measured through differential scanning calorimetry (DSC) conducted on a DSC 2000 instrument (TA Instruments). Samples were first heated from −70 to +200 °C at a rate of 10 °C min^{-1}. After cooling down to −70 °C at the same rate, the data were collected from the second heating scan. A 3~5mg amount of each sample was used for the DSC test under nitrogen at a flow rate of 50 mL min^{-1}. Thermogravimetric analysis (TGA) was conducted on a Q5000 TGA system (TA Instruments), ramping from 25 to 600 °C with a rate of 10 °C min^{-1}. Each test needed ~10 mg of samples. Tensile stress-strain testing was carried out with an Instron 5543A testing instrument. The films were prepared by casting a dichloromethane (DCM) solution of polymers in a PTFE mold. After the evaporation of DCM, the film was put under vacuum for 4 h at room temperature and then 4 h at 60 °C. Dog-bone shaped specimens were cut from the film with a length of 20 mm, a width of 5 mm, and a thickness of 50~70 μm before tested at room temperature with the crosshead speed of 20 mm min^{-1}.

Fabrication of Free-Standing Films: Films of hydrogenated and unhydrogenated poly(oligothiophene-norbornene)s for dielectric property characterization were prepared by a solution casting method. Generally, polymer samples were dissolved in THF (50 mg mL^{-1}), stirred at room temperature for half an hour, then filtered (using microfilters with a pore size 0.22 μm). The filtrate was then poured onto clean glass slides (3 inch × 1 inch) at room temperature. After being dried at room temperature under ambient conditions for 12 h, the films were transferred into a vacuum oven and baked at 80 ºC for 12 h in order to remove the remaining trace of solvents and to enhance the film quality by thermal annealing. The resulting films were cooled down to room temperature, and directly peeled off from glass slide to obtain the free-standing films, which are highly flexible and transparent. These films have a uniform

2

thickness, free of bubbles, cracks, or other defects (visually). The film thickness was measured at multiple positions with a micrometer and found to be ca. 20 μm.

Dielectric and Polarization Characterization: The characterization is very similar to those reported in our early publications, and thus no substantial change is made here.[2, 3] To fabricate parallel film capacitors, circular gold electrodes (area 0.0531 cm^2) was sputter-coated under argon atmosphere through a shadow mask on the both sides of the free-standing films. The complex impedance of film samples was measured using an impedance analyzer (Agilent LCR meter E4980A). Measurements were carried out at a fixed applied voltage (20 mV) and varying frequency (typically 10^2 to 2×10^6 Hz). Impedance spectra were collected for 3–5 specimens of each sample to ensure reproducibility; average values are reported. The real and complex parts of the impedance, expressed as impedance magnitude and phase angle, were analyzed using a parallel RC circuit model describing a "leaky" capacitor, yielding values of relative permittivity (ε_{eff}) and loss tangent (tan δ) as functions of frequency.

Polarization measurements at higher applied voltages employed a Precision Multiferroic polarization tester (Radiant, Inc.). Polarization data (*D* versus *E*) were obtained with a cycle frequency of 10 Hz. The maximum applied field strength depended on the sample film thickness and breakdown strength. Stored energy density $(\widehat{W}_s)$, was determined by numerical integration of *E*, according to $\widehat{W} = \int E dD$, from *D* = 0 to the maximum value of *D* (D_{max}) achieved in the hysteresis loop. Recovered energy density $(\widehat{W}_r)$ was determined by numerically integrating *E* from D_{max} to the value of *D* where *E* = 0. Percentage energy loss is computed as $100 \times (\widehat{W}_s - \widehat{W}_r)/\widehat{W}_s$. Dielectric breakdown strength measurements were performed on a TREK P0621P instrument using the electrostatic pull-down method under a DC voltage ramp of 500 Vs^{-1}.

Two-parameter Weibull statistic: Weibull statistic can be described as: $P(E)$ = 1-exp(-$(E/\alpha)^\beta$), where *P(E)* is the cumulative probability of electric failure, *E* is the measured breakdown field,

scale parameter α is the field strength for which there is a 63% probability for the sample to breakdown (Weibull breakdown strength), and shape parameter β evaluates the scatter of data and a higher value of β represents higher level of dielectric reliability.

General synthesis of monomer: Terthiophene ethanol (0.85 g, 2.91 mmol), pivalic anhydride (0.6 g, 3.2 mmol, *exo*-5-norbornenecarboxylic acid (0.441 g, 3.2 mmol) and DMAP (3.7 mg, 0.03 mmol) were dissolved in 3 mL THF and stirred in an oil bath of 60 °C. After stirring for 20 h, 1.0 mL water was added into the solution and stirred for 1 more hour. DCM was added to dissolve the product and washed with $NaHCO_3$ and NaCl aqueous solution. The crude product was obtained after drying the organic phase and evaporating the solvent, and further purifing by silica gel column (dichloromethane:Hexane = 1:5) to obtain monomer 2-([2,2':5',2''-terthiophen]-5-yl)ethyl-bicyclo[2.2.1]hept-5-ene-2-carboxylate (**TTEN**) as light yellow powder (0.96g, yield: 80%). Monomers 2-([2,2'-bithiophen]-5-yl)ethyl-bicyclo[2.2.1]hept-5-ene-2-carboxylate (**BTEN**) (yield: 75%) and 2-(thiophen-2-yl)ethyl-bicyclo[2.2.1]hept-5-ene-2-carboxylate (**TEN**) (yield: 80%) were prepared using the same method.

TTEN ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.16 (d, J = 3.6 Hz, 1H), 7.06 (d, J = 3.7 Hz, 1H), 7.04 – 6.96 (m, 3H), 6.77 (d, J = 3.2 Hz, 1H), 6.19 – 6.07 (m, 2H), 4.33 (t, J = 6.6 Hz, 2H), 3.14 (t, J = 6.6 Hz, 2H), 3.05 (s, 1H), 2.93 (s, 1H), 2.33 – 2.18 (m, 1H), 1.93 (dt, J = 12.2, 4.0 Hz, 1H), 1.50 (s, 1H), 1.45 – 1.30 (m, 2H). ^{13}C NMR (75 MHz, CDCl$_3$, δ): 176.12, 139.63, 138.12, 137.17, 136.36, 135.93, 135.76, 127.88, 126.41, 124.44, 124.30, 123.91, 123.65, 123.46, 77.47, 77.05, 76.63, 64.38, 46.62, 46.42, 43.19, 41.67, 30.38, 29.69.

BTEN ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.19 (d, J = 5.1 Hz, 1H), 7.11 (d, J = 3.5 Hz, 1H), 7.04 – 6.97 (m, 2H), 6.77 (d, J = 3.5 Hz, 1H), 6.22 – 6.02 (m, 2H), 4.33 (t, J = 6.5 Hz, 2H), 3.14 (t, J = 6.6 Hz, 2H), 3.05 (s, 1H), 2.92 (s, 1H), 2.25 (dd, J = 9.5, 4.4 Hz, 1H), 1.93 (dt, J = 12.2, 3.9 Hz, 1H), 1.51 (d, J = 8.3 Hz, 1H), 1.44 – 1.30 (m, 2H). ^{13}C NMR (75 MHz, CDCl$_3$, δ): 176.15, 139.42, 138.12, 137.55, 136.04, 135.76, 127.76, 126.30, 124.11, 123.50, 123.37, 77.48, 77.06, 76.63, 64.43, 46.62, 46.41, 43.18, 41.66, 30.37, 29.65.

TEN ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.17 (d, *J* = 5.1 Hz, 1H), 6.98 – 6.91 (m, 1H), 6.87 (d, *J* = 3.2 Hz, 1H), 6.17 – 6.07 (m, 2H), 4.32 (t, *J* = 6.6 Hz, 2H), 3.17 (t, *J* = 6.7 Hz, 2H), 3.04 (s, 1H), 2.92 (s, 1H), 2.24 (dd, *J* = 10.0, 4.3 Hz, 1H), 1.92 (dt, *J* = 12.2, 4.0 Hz, 1H), 1.50 (d, *J* = 8.3 Hz, 1H), 1.43 – 1.29 (m, 2H). ^{13}C NMR (75 MHz, CDCl$_3$, δ): 176.13, 140.09, 138.11, 135.76, 126.86, 125.53, 124.02, 77.50, 77.08, 76.65, 64.65, 46.59, 46.40, 43.18, 41.65, 30.34, 29.41.

General synthesis of poly(oligothiophene-norbornene): Synthesis of Polymers **PTEN**, **PBTEN**, **PTTEN** by ROMP. Norbornene monomer **TTEN** (0.8 g, 1.9 mmol) was dissolved in 5.0 mL DCM and nitrogen was purged through the solution for 10 min. Grubbs third-gen catalyst (3.7 mg, 0.005 mmol) dissolved in 1.0 mL was purged with nitrogen and transferred into the monomer solution to start the polymerization. To the reacting solution, several drops of ethyl vinyl ether were added to stop the polymerization after 30 min and stirred for another 10 min when full conversion of the monomer was confirmed by ^{1}H NMR. Methanol was added into the concentrated solution to precipitate the polymer out followed by washing with methanol for twice. The polymers were dried under vacuum overnight to get **PTEN**. **PBTEN** and **PTTEN** were prepared from monomers **BTEN** and **TTEN**.

PTTEN M_n: 150,000 g mol^{-1} (GPC), Đ: 1.15 (GPC). ^{1}H NMR (300 MHz, CDCl$_3$, δ): 6.68– 7.15 (multiple peaks, aromatic proton from terthiophene side-chain), 5.0–5.5 (broad, proton on double bond), 4.23 (s, –CH$_2$O–), 3.04 (s, –CH$_2$ in side-chain), 1.0–2.75 (multiple peaks, proton on cyclopentane backbone)

**PBTEN** M_n: 120,000 g mol^{-1} (GPC), Đ: 1.12 (GPC). ^{1}H NMR (300 MHz, CDCl$_3$, δ): 6.68– 7.15 (multiple peaks, aromatic proton from bithiophene side-chain), 5.0–5.5 (broad, proton on double bond), 4.23 (s, –CH$_2$O–), 3.04 (s, –CH$_2$ in side-chain), 1.0–2.75 (multiple peaks, proton on cyclopentane backbone)

PTEN M_n: 140,000 g mol^{-1} (GPC), Đ: 1.12 (GPC). ^{1}H NMR (300 MHz, CDCl$_3$, δ): 6.68–7.15 (multiple peaks, aromatic proton from thiophene side-chain), 5.0–5.5 (broad, proton on double

bond), 4.23 (s, –CH$_2$O–), 3.04 (s, –CH$_2$ in side-chain), 1.0–2.75 (multiple peaks, proton on cyclopentane backbone)

Hydrogenation of PTTEN after ROMP (**HPTTEN**): Into a dry flask was charged with 0.5 g of **PTTEN** (M_n = 150,000 g mol^{-1}, Đ = 1.15), 1.47 g of tosyl hydrazide (7.9 mmol, 6.5 equiv per double bond), 10 mL of toluene, and 1 mL of Et$_3$N. The mixture was degassed by three freeze-pump-thaw cycles, and a reflux condenser was attached to the flask under argon. The reaction was heated to reflux for 3 h. The solution was cooled to room temperature and then precipitated into 100 mL of stirring MeOH. The light yellow polymer precipitate was washed several times with MeOH and then dried in vacuo overnight; yield 0.49 g (99%). M_n = 150,000 g mol^{-1}, Đ = 1.21. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 6.68–7.15 (multiple peaks, aromatic proton from thiophene side-chain), 4.26 (s, –CH$_2$O–), 3.06 (s, –CH$_2$ in side-chain), 1.0–2.3 (multiple peaks, proton on cyclopentane backbone).

S2. ^{1}H NMR and ^{13}C NMR Spectra

^{1}H NMR spectrum (CDCl$_3$, 25°C) of TEN
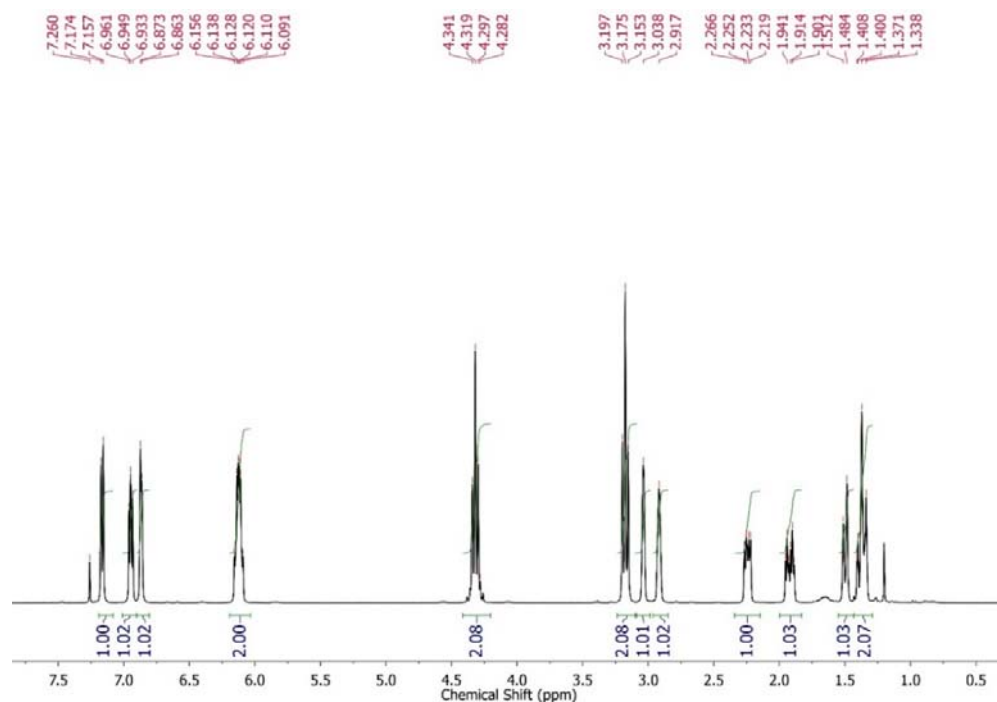
^{13}C NMR spectrum (CDCl$_3$, 25°C) of TEN
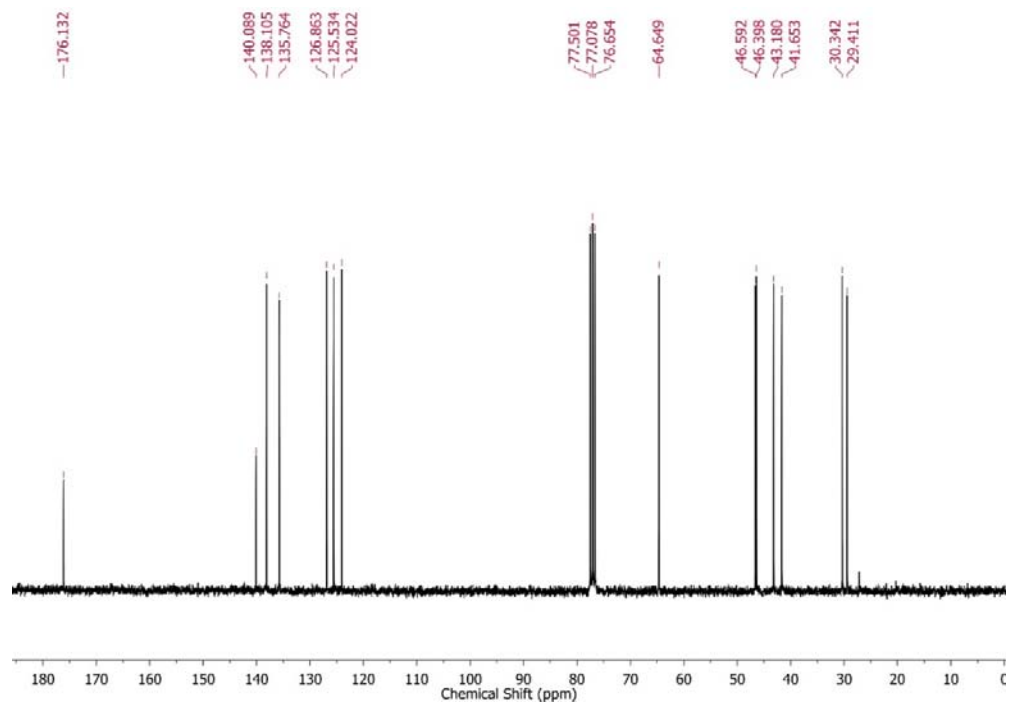
^{1}H NMR spectrum (CDCl$_3$, 25°C) of BTEN
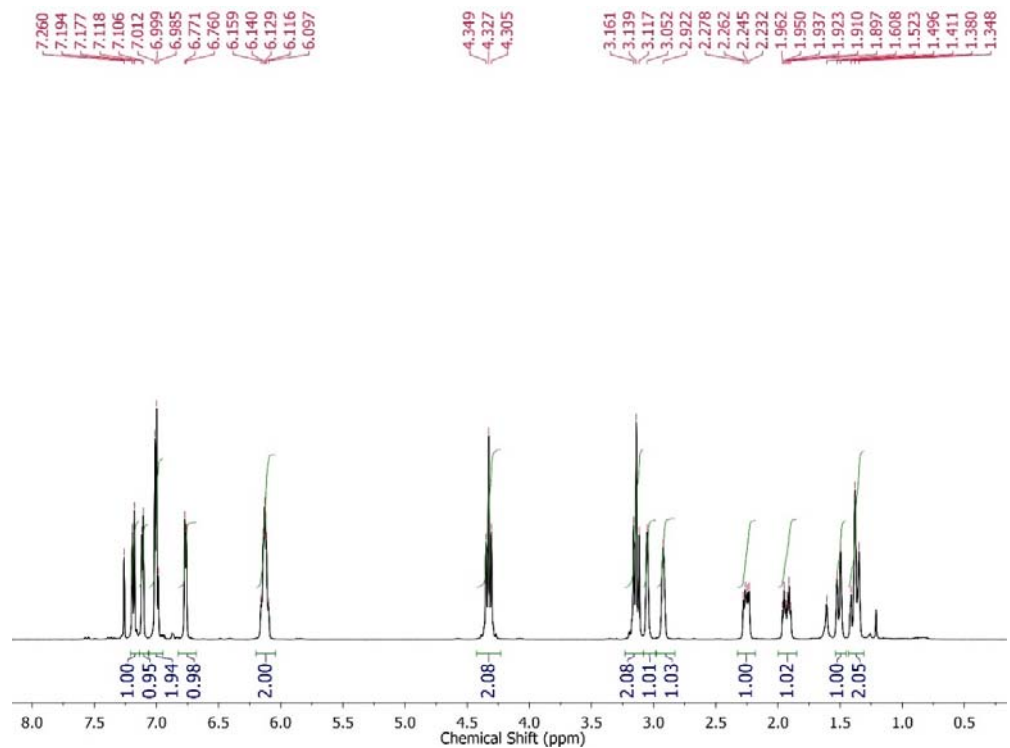
^{13}C NMR spectrum (CDCl$_3$, 25°C) of BTEN
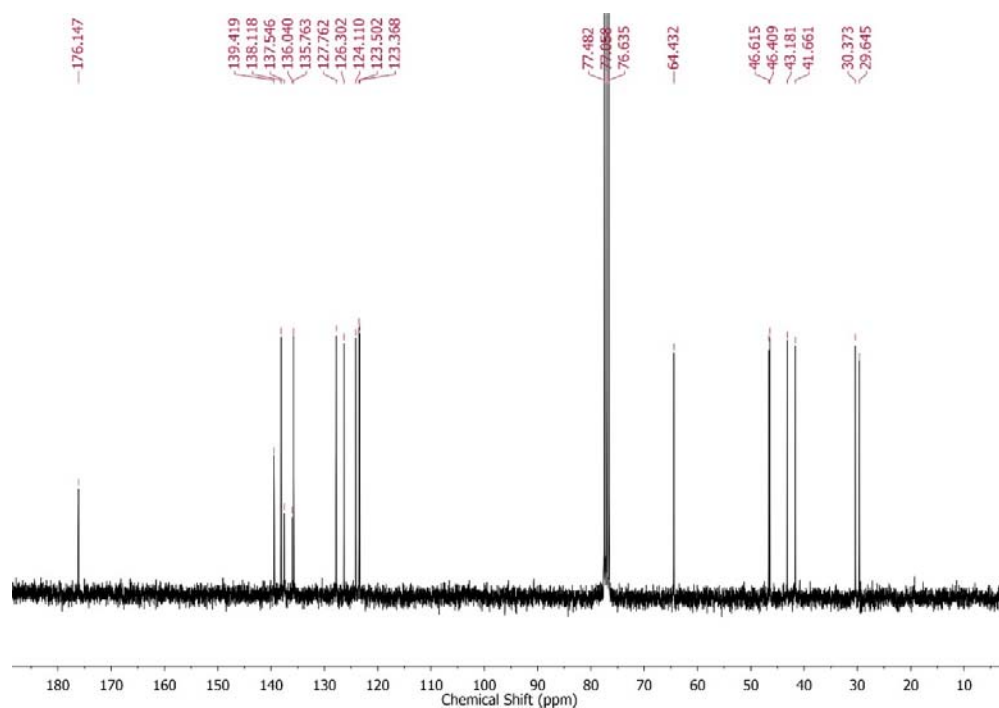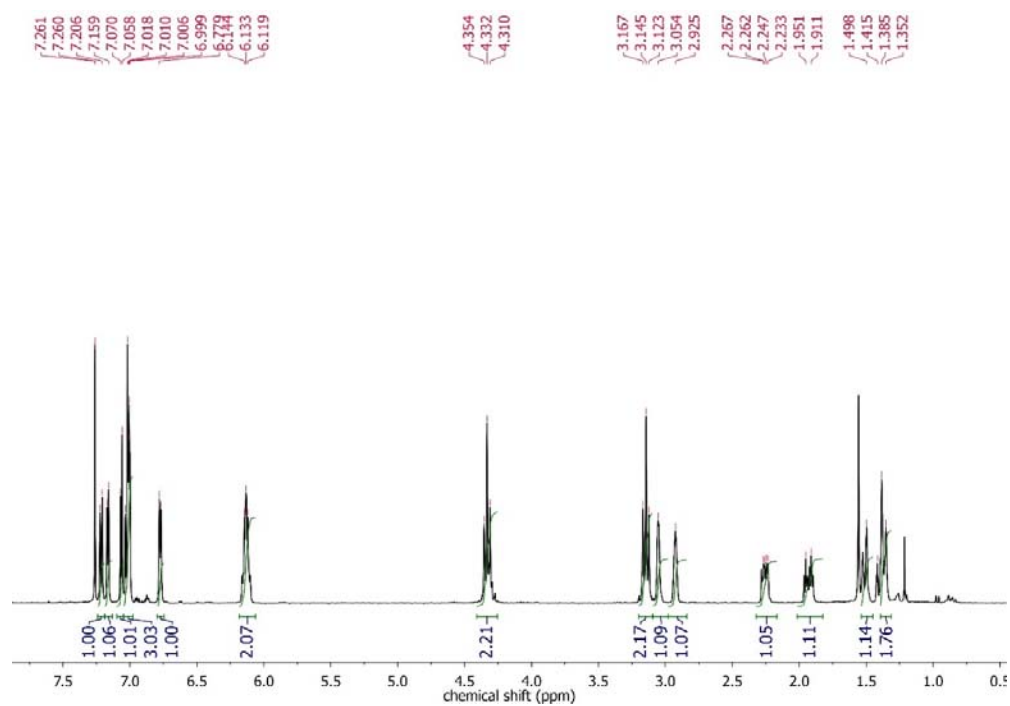
^{1}H NMR spectrum (CDCl$_3$, 25°C) of TTEN

8

^{13}C NMR spectrum (CDCl$_3$, 25ºC) of BTEN

^{1}H NMR spectrum (CDCl$_3$, 25ºC) of PTEN

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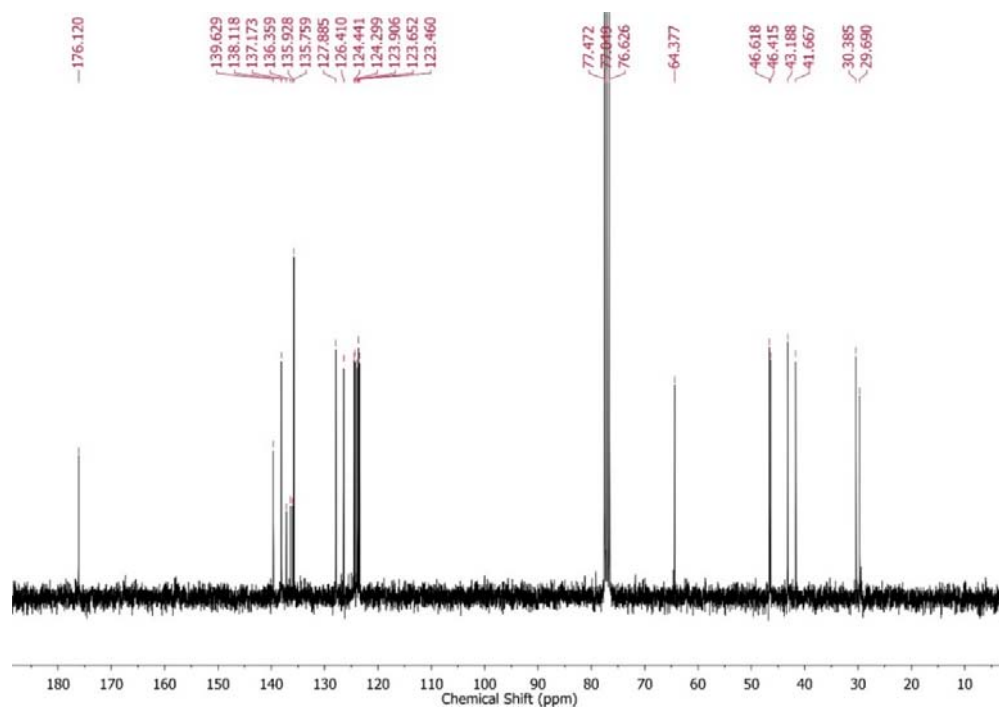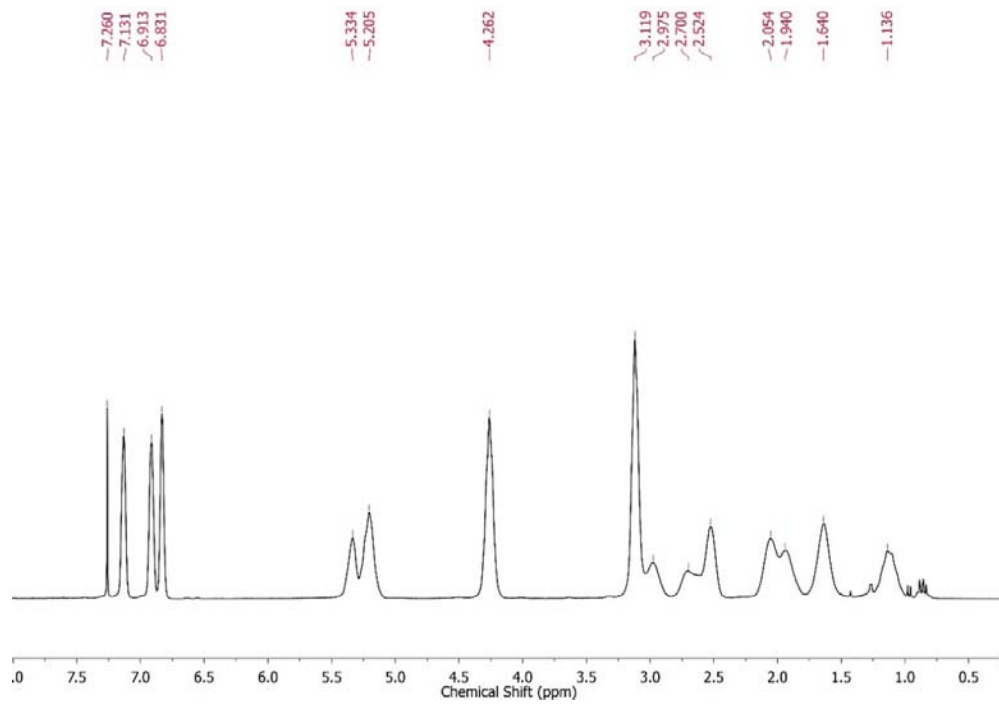
¹H NMR spectrum (CDCl₃, 25°C) of PBTEN
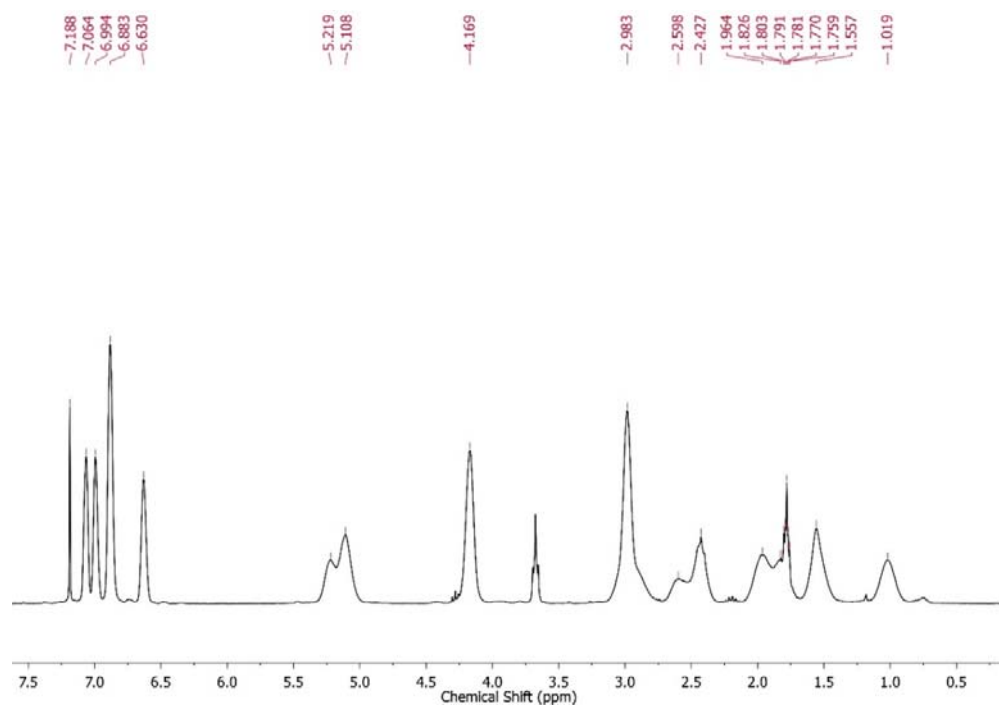
¹H NMR spectrum (CDCl₃, 25°C) of PTTEN
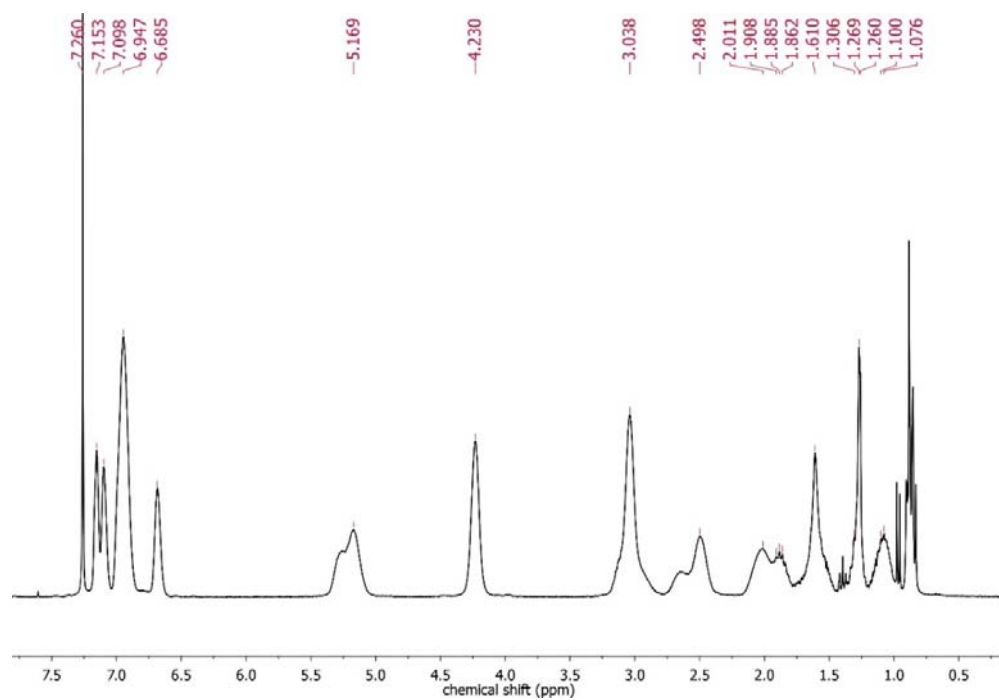
^{1}H NMR spectrum (CDCl$_3$, 25°C) of HPTTEN
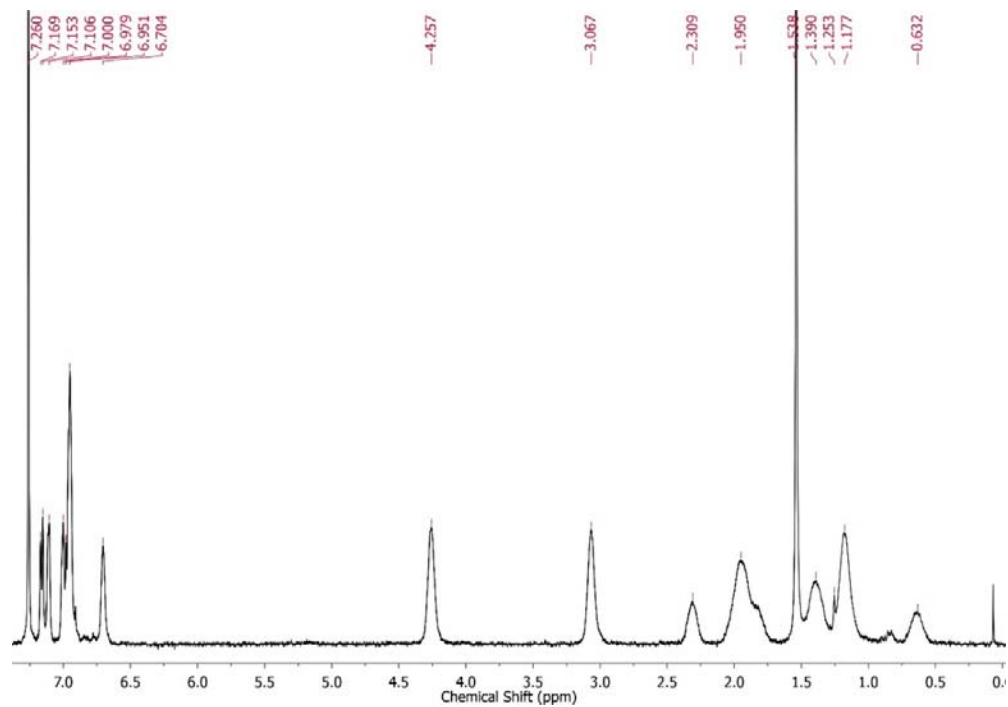
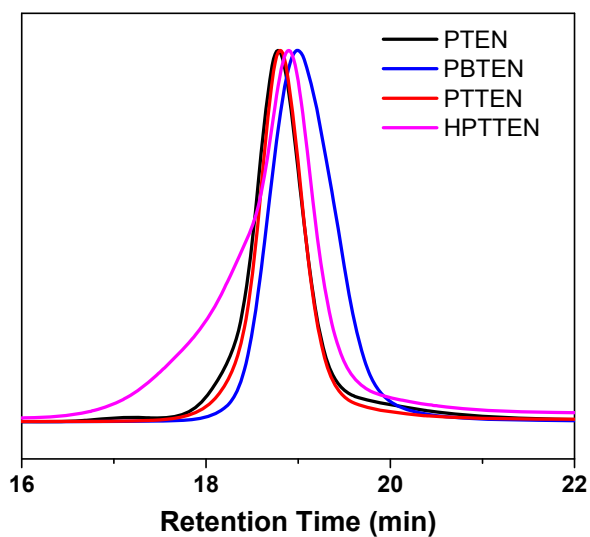**S3. Experimental Results**

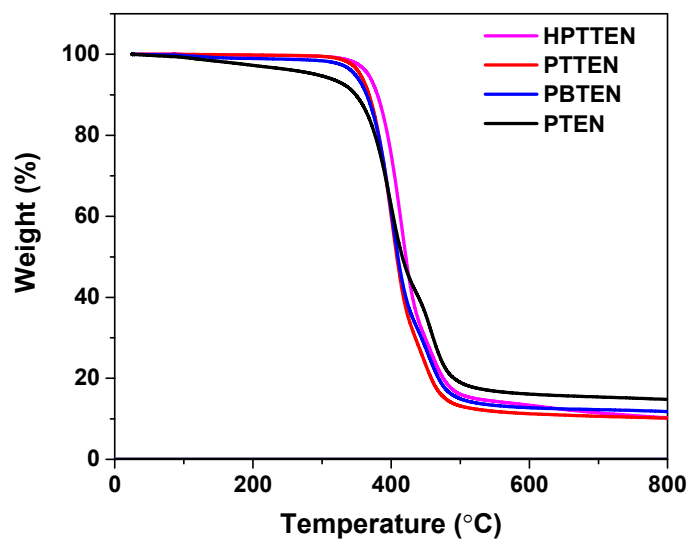**Figure S1**. GPC traces of **PTEN**, **PBTEN**, **PTTEN**, and **HPTTEN**.

Table S1. Molecular weight information and thermal properties of **PTEN**, **PBTEN**, **PTTEN**, and **HPTTEN**.

| Polymer	$M_n{}^a$ (g mol^{-1})	DP^b	Đ	T_g(°C)
PTEN	140,000	564	1.15	6
PBTEN	120,000	363	1.12	25
PTTEN	150,000	378	1.12	49
HPTTEN	130,000	314	1.20	45

^{a} Molecular weight obtained from GPC in THF by using polystyrenes as standards. ^{b} DP is determined by M_n of polymers and molecular weight of corresponding monomers.
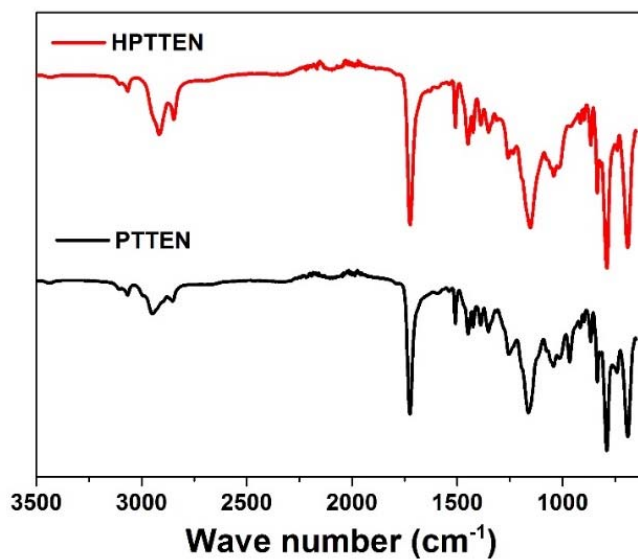
Figure S2. FT-IR spectra of **PTTEN** and **HPTTEN**.

Figure S3. Thermogravimetric analysis (TGA) of **PTEN**, **PBTEN**, **PTTEN and HPTTEN**.
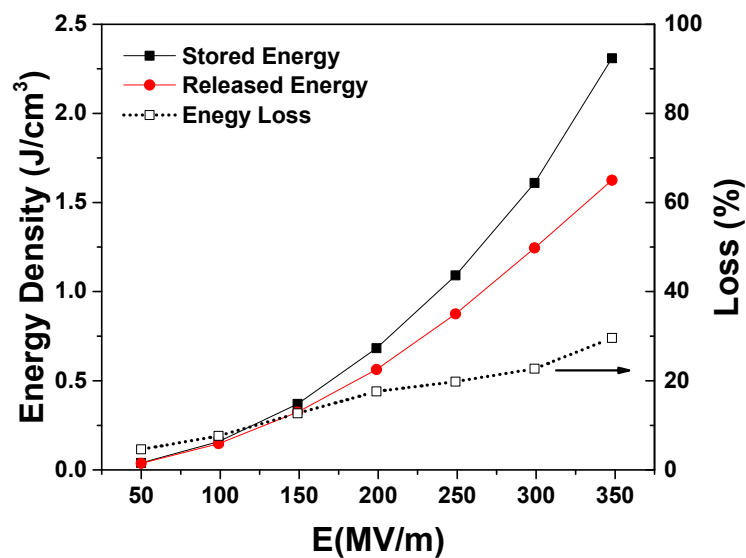
Figure S4. Energy density (stored and released) and hysteresis loss of **HPTTEN** versus the electric field.

S4. References

1. M. S. Sanford, J. A. Love and R. H. Grubbs, *Organometallics*, 2001, **20**, 5314-5318.
2. Y. Qiao, M. S. Islam, K. Han, E. Leonhardt, J. Zhang, Q. Wang, H. J. Ploehn and C. Tang, *Adv. Funct. Mater.*, 2013, **23**, 5638-5646.
3. Y. Qiao, M. S. Islam, L. Wang, Y. Yan, J. Zhang, B. C. Benicewicz, H. J. Ploehn and C. Tang, *Chem. Mater.*, 2014, **26**, 5319-5326.