Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information for

Azobenzene-functionalized polymers by ring-opening metathesis polymerization for high dielectric and energy storage performance

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Experimental

Materials

4-Trifluoromethylaniline, 4-nitroaniline, acetic acid (HOAc), sodium nitrite ($NaNO_2$), and sodium hydroxide (NaOH) were purchased from Energy Chemical or Adamas-beta Company. Ethyl acetate (EtOAc), magnesium sulfate ($MgSO_4$), and sodium acetate (NaOAc) were purchased from Shanghai Chemical Reagents Company. The third generation Grubbs catalyst (**Ru-III**) was prepared according to the literature.[S1] Solvents were distilled over drying agents under nitrogen prior to use: dichloromethane (CH_2Cl_2) from calcium hydride (CaH); tetrahydrofuran (THF) and diethylether (Et_2O) from sodium/benzophenone. N-phenyl-norbornene-pyrrolidine (**PNP**) was synthesized according to the literature.[S2] All reactions were performed under dry nitrogen atmosphere using standard Schlenk-line technique.

Characterization

^1H (500 MHz), ^{13}C (125MHz), and ^{19}F (471 MHz) NMR spectra were recorded on a Bruker DPX500 spectrometer using tetramethylsilane as an internal standard in $CDCl_3$. IR spectra were recorded on a Perkin Elmer Spectrum using KBr pellets. UV-vis absorption spectra were measured on a UV-1800 spectrometer with the concentration of 1.0×10^{-3} mg mL^{-1}. Gel permeation chromatography (GPC) was used to calculate relative molecular weight and molecular weight distribution equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (7.8×300 mm, 5 mm bead size; 10^3, 10^4, and 10^5 Å pore size). GPC measurements were carried out at 35 ^{o}C using THF as the eluent with a flow rate of 1.0 mL/min. The hydrodynamic diameter was determined by means of dynamic light scattering (DLS) analysis using a Malvern Zetasizer Nano-ZS light scattering apparatus (Malvern Instruments, U.K.) with a He-Ne laser (633 nm, 4 mW). The Nano ZS instrument incorporates noninvasive backscattering (NIBS) optics with a detection angle of 173°. The z-average diameter of the sample was automatically provided by the instrument using cumulate analysis. Transmission electron microscopy (TEM) images were recorded on the JEOL2100F microscopes operating at 120 kV. Samples for TEM measurement were prepared by depositing a drop of THF solution with different concentration on the copper grids coated with carbon, followed by air-drying. Additionally, the samples were not stained before measurement because the electron density difference between the two blocks provided sufficient contrast for TEM imaging. Thermal gravimetric analysis (TGA) was performed by an SDT851e/SF/1100 °C TGA instrument under nitrogen flow at a heating rate of 20 °C min^{-1} from 25 to 800 °C. Differential scanning calorimeter (DSC) was performed on a Q2000 DSC system in nitrogen atmosphere. An indium standard was used for temperature and enthalpy calibrations. All the samples were first heated from 30 to 240 °C and held at this temperature for 3 min to eliminate the thermal history, and then, they were cooled to room temperature and heated again from 30 to 240 °C at a heating or cooling rate of 10 °C min^{-1}. Dielectric measurements were carried out by a Novocontrol BDS40 dielectric spectrum analyzer over the frequency range of 100 Hz to 1 MHz at room temperature, and a contacting electrode method was used. The electric displacement (D)-electric field (E) hysteresis loops were recorded for applied voltages up to 10000 V with a cycle frequency of 100 Hz.

Film fabrication for dielectric measurements

Film of polymer for dielectric property characterization was prepared by a solution casting method. Generally, polymer was dissolved in THF or $CHCl_3$ (20 mg mL^{-1}), and the mixture was stirred for 4 h at room temperature. The solution poured onto clean glass slide (2 cm×2 cm) at room temperature and dried in air overnight, then the film was transferred into a vacuum oven and dried at room temperature for 12 h in order to remove the remaining solvent and to enhance the film quality by thermal annealing. Finally, the free-standing film was peeled off from glass slide, and the typically thickness was about 20-30 μm. The dielectric constant (k) can be calculated by equation (1):

$$k = C_p l/\varepsilon_0 A \qquad (1)$$

where l is the thickness of film, ε_0, the permittivity of the free space, is 8.85×10^{-12} F m^{-1}, and A is the guarded electrode area, $A = \pi d^2$. The conductivity (σ) is calculated according to the following equation (2):

$$\sigma = G{\cdot}A/l \qquad (2)$$

Where G is the conductance.

*Synthesis of N-(4-trifluoromethylazophenyl)-norbornene-pyrrolidine (**FANP**)*: 4-aminobenzotrifluoride (3.22 g, 20 mmol) was dissolved in 6 M hydrochloric acid (14 mL), keeping the temperature below 5 °C, and a solution of sodium nitrite (1.49 g, 21.6 mmol in 18 mL H_2O) was added dropwise into the solution and stirred for 1 h. The diazonium salt solution was added into a solution of N-phenyl-norbornene-pyrrolidine (PNP) (4.22 g, 20 mmol) in 100 mL THF, keeping the temperature below 5 °C. After 6 h, the reaction mixture was neutralized with NaOAc and filtered. After recrystallization from ethanol, the product **FANP** was obtained in a red powder (5.9 g, 78% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.91 (t, 4H, NAr*H*CF_3), 7.73 (d, 2H, m-NAr*H*N), 6.53 (d, 2H, *o*-NAr*H*N), 6.22 (t, 2H, CHC*H*=C*H*CH), 3.46-3.32 (m, 2H, C*H*CHCH_2N), 3.21-3.11 (m, 2H, C*H*CH_2N), 3.10-2.91(m, 4H, CHCH_2N), 1.60-1.58 and 1.51-1.49 (m, 2H,CHCH_2CH). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 154.83, 150.14, 143.27, 135.86, 130.35, 126.18, 125.71, 123.16, 122.22, 111.76, 52.12, 50.74, 46.67, 45.47. ^{19}F NMR (471 MHz, $CDCl_3$, ppm): δ = -62.21; elemental analysis calcd (%) for $C_{22}H_{20}F_3N_3$: C 68.92, H 5.26, N 10.96; found: C 68.85, H 5.20, N 10.93. IR (KBr): 2947 (CH_2), 2860 (C=C), 1602 (N=N), 1517, 1473, 1425, 1380, 1365, 1320 (C-F), 1255, 1167, 1132, 1115, 1062, 854, 817, 727, 680, 602 cm^{-1}.

Synthesis of N- (4-nitroazophenyl)-norbornene-pyrrolidine (NANP): **NANP** was synthesized by a procedure similar to that for **FANP**, the reaction of the diazonium ion, prepared from 4-nitroaniline (1.38 g, 10 mmol), with PNP (2.11 g, 10 mmol) afforded **NANP** as dark red powder (2.7 g, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.33 (m, 2H, *o*-NAr*H*N), 8.02-7.84 (m, 4H, NAr*H*NO_2), 6.53 (d, 2H, m-NAr*H*N), 6.22 (t, 2H, CHC*H*=C*H*CH), 3.50-3.35 (m, 2H, C*H*CHCH_2N), 3.26-3.12 (m, 2H, C*H*CH_2N), 3.07 (dd, J = 13.6, 11.7 Hz, 4H, CHCH_2N), 1.71-1.65 and 1.60-1.55 (m, J = 8.1 Hz, 2H,CHCH_2CH). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 156.96, 150.54, 147.18, 143.56, 135.87, 126.23, 124.69, 122.50, 111.89, 52.12, 50.80, 46.68, 45.45; elemental analysis calcd (%) for $C_{21}H_{20}N_4O_2$: C 69.98, H 5.59, N 15.55; found: C 69.95, H 5.53, N 15.60. IR (KBr): 2958 (CH_2), 2863 (C=C), 1605 (N=N), 1504, 1475, 1379, 1358, 1336 (NO_2), 1255, 1149, 1106, 860, 824, 754, 727, 685 cm^{-1}.

General procedure for polymerization

Syntheses of homopolymers via ROMP

Homopolymers were prepared by ROMP using **Ru-III** as the catalyst and a typical procedure was as follows. In a dry nitrogen-filled Schlenk tube, a solution of **Ru-III** (2.2 mg, 2.5 μmol) in 1 mL of CH_2Cl_2, which was degassed in three freeze-vacuum-thaw cycles, was added to a degassed solution of **FANP** (191 mg, 0.5 mmol) in 4 mL of CH_2Cl_2 to give a monomer concentration of 0.1 mol L^{-1}. After 1 h, the polymerization was quenched by adding 0.5 mL ethyl vinyl ether with stirring for 30 min, and then precipitated into an excess of methanol. Polymer was dissolved in $CHCl_3$, and precipitated once again from methanol. The obtained polymer **PFANP**$_{200}$ was dried in a vacuum oven at 30 °C to a constant weight. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 7.90 (d, NAr*H*CF_3), 7.68 (d, m-NAr*H*N), 6.65 (s, *o*-NAr*H*N), 5.53-5.22 (m, *trans*-C*H*=C*H* on polymer chain), 3.44-3.32 (d, C*H*CHCH_2N), 3.17-2.96 (m, C*H*CH_2N), 2.85-2.76 (s, CHCH_2N), 2.10-1.95 and 1.53-1.40 (m, CHCH_2CH). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 155.16, 150.39, 143.75, 132.35, 125.89, 125.65, 125.26, 123.10, 122.36, 112.25, 49.62, 44.05, 36.25, 31.11; IR (KBr): 2940 (CH_2), 2850 (C=C), 1602 (N=N), 1515, 1481, 1375, 1322 (C-F), 1163, 1140, 1062, 965, 848, 816, 597, 532 cm^{-1}. GPC: M_n = 55.1 kDa, M_w/M_n =1.28.

Syntheses of block copolymers via ROMP

The block copolymers were prepared by ROMP followed by ROMP with the sequential addition of monomers, and a typical procedure was as follows. In a nitrogen-filled Schlenk tube, a solution of **Ru-III** (2.2 mg, 2.5 μmol) in 0.5 mL of CH_2Cl_2, which was degassed in three freeze-vacuum-thaw cycles, was added to a degassed solution of the first **FANP** (191.5 mg, 0.5 mmol) in 5 mL of CH_2Cl_2 to give a monomer concentration of 0.1 mol L^{-1}. After stirring for 20 min at 30 °C, a degassed solution of the second monomer **NANP** (90 mg, 0.25 mmol) in 5 mL of CH_2Cl_2 was then added under nitrogen. After stirring for 1 h, the polymerization was quenched by adding 0.5 mL ethyl vinyl ether with stirring for further 30 min, and the solution was then poured into an excess of methanol. The solid was redissolved in $CHCl_3$ and precipitated once again from methanol, dried under vacuum for 24 h at 30 °C to give the block copolymer **PFANP**$_{200}$-*b*-**PNANP**$_{100}$ with a constant weight. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 7.90 (d, NAr*H*CF_3), 7.66 (d, m-NAr*H*N), 6.65 (s, *o*-NAr*H*N), 5.53-5.22 (m, *trans*-C*H*=C*H* on polymer chain), 3.50-3.32 (d, C*H*CHCH_2N), 3.17-2.96 (m, C*H*CH_2N), 2.85-2.76 (s, CHCH_2N), 2.08-1.93 and 1.53-1.40 (m, CHCH_2CH). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 162.48, 148.66, 144.75, 138.40, 133.74, 131.68, 131.20, 130.05, 129.08, 128.84, 128.50, 128.04, 118.05, 116.77, 47.65, 45.93, 42.28, 34.73; IR (KBr): 2940 (CH_2), 2850 (C=C), 1602 (N=N), 1514, 1481, 1375, 1322 (C-F), 1160, 1138, 1101, 1062, 965, 850, 821, 601, 537 cm^{-1}. GPC: M_n = 70.2 kDa, M_w/M_n = 1.09.

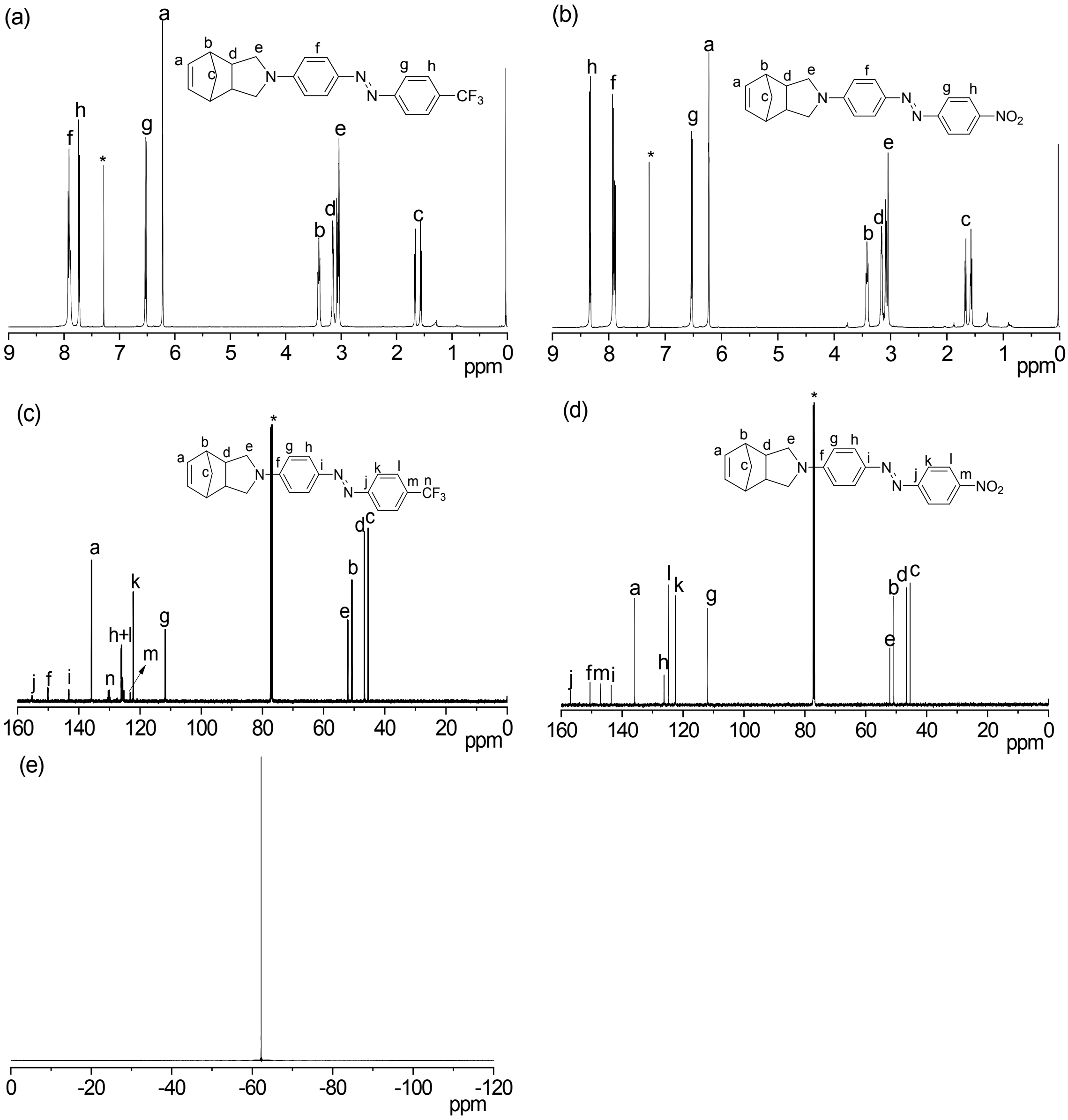


Figure S1. ^{1}H NMR spectra of (a) **FANP**, (c) **NANP**; ^{13}C NMR spectra of (b) **FANP**, (d) **NANP**; ^{19}F NMR spectra of (e) **FANP**.

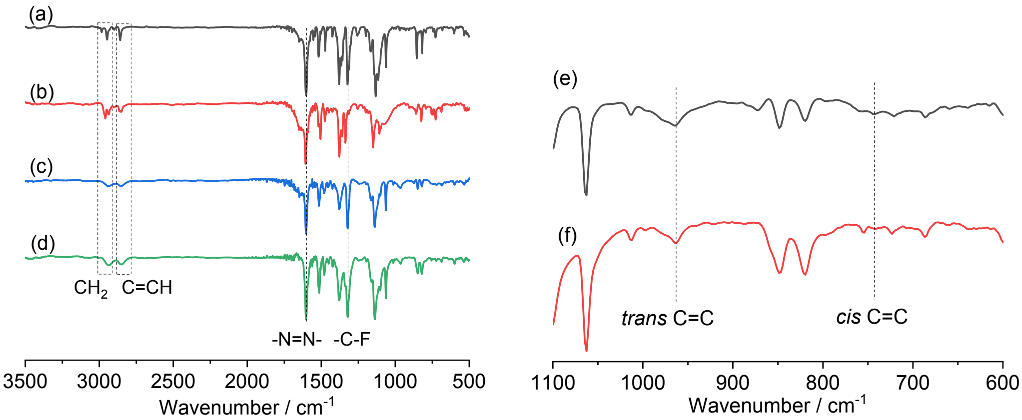


Figure S2. IR spectra of (a) **FANP**, (b) **NANP**, (c) **PFANP$_{200}$**, and (d) **PFANP$_{200}$-*b*-PNANP$_{100}$**. Amplified IR spectra of (e) **PFANP$_{200}$** and (f) **PFANP$_{200}$-*b*-PNANP$_{100}$**.

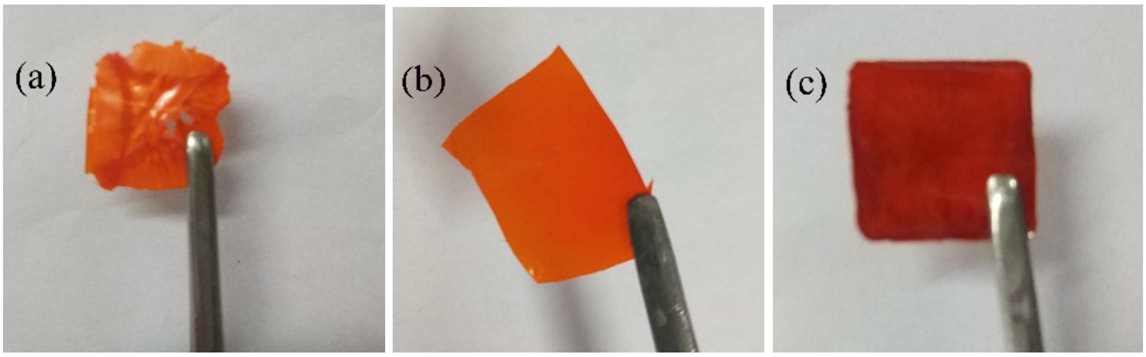


Figure S3. Photographs for free-standing films of (a) **PFANP$_{100}$**, (b) **PFANP$_{200}$**, and (c) **PFANP$_{200}$-*b*-PNANP$_{100}$**.

Table S1. Solubility of polymers in various solvents at room temperature*

Samples	CH_2Cl_2	$CHCl_3$	THF	CH_3OH	Acetone
PFANP$_{200}$	++	++	++	–	–
PNANP$_{100}$	+–	+–	+–	–	–
PFANP$_{200}$-*b*-PNANP$_{50}$	+	+	+	–	–
PFANP$_{200}$-*b*-PNANP$_{100}$	+	+	+	–	–

*1 mg of polymers in 1 mL of solvent.

–: insoluble; +–: partially soluble; +: soluble; ++ easily soluble.

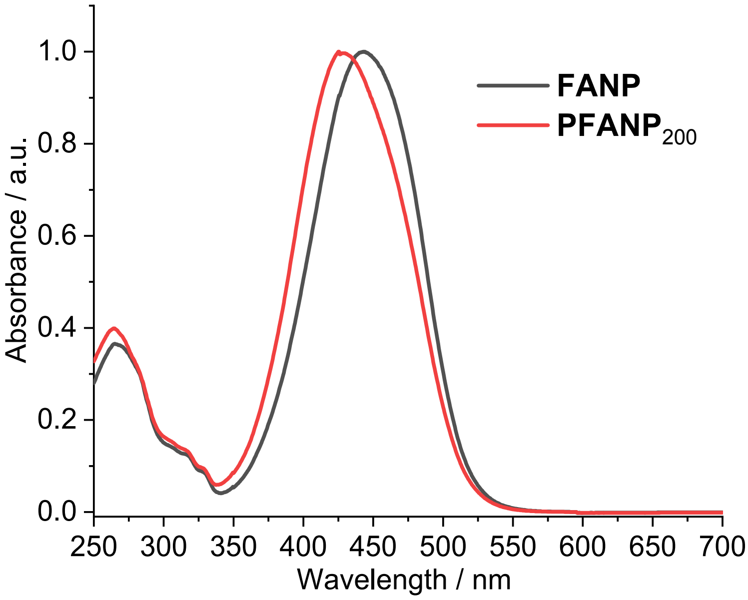


Figure S4. UV-vis absorption spectra of **FANP** and **PFANP$_{200}$** in THF solution at 0.001 mg mL^{-1}.

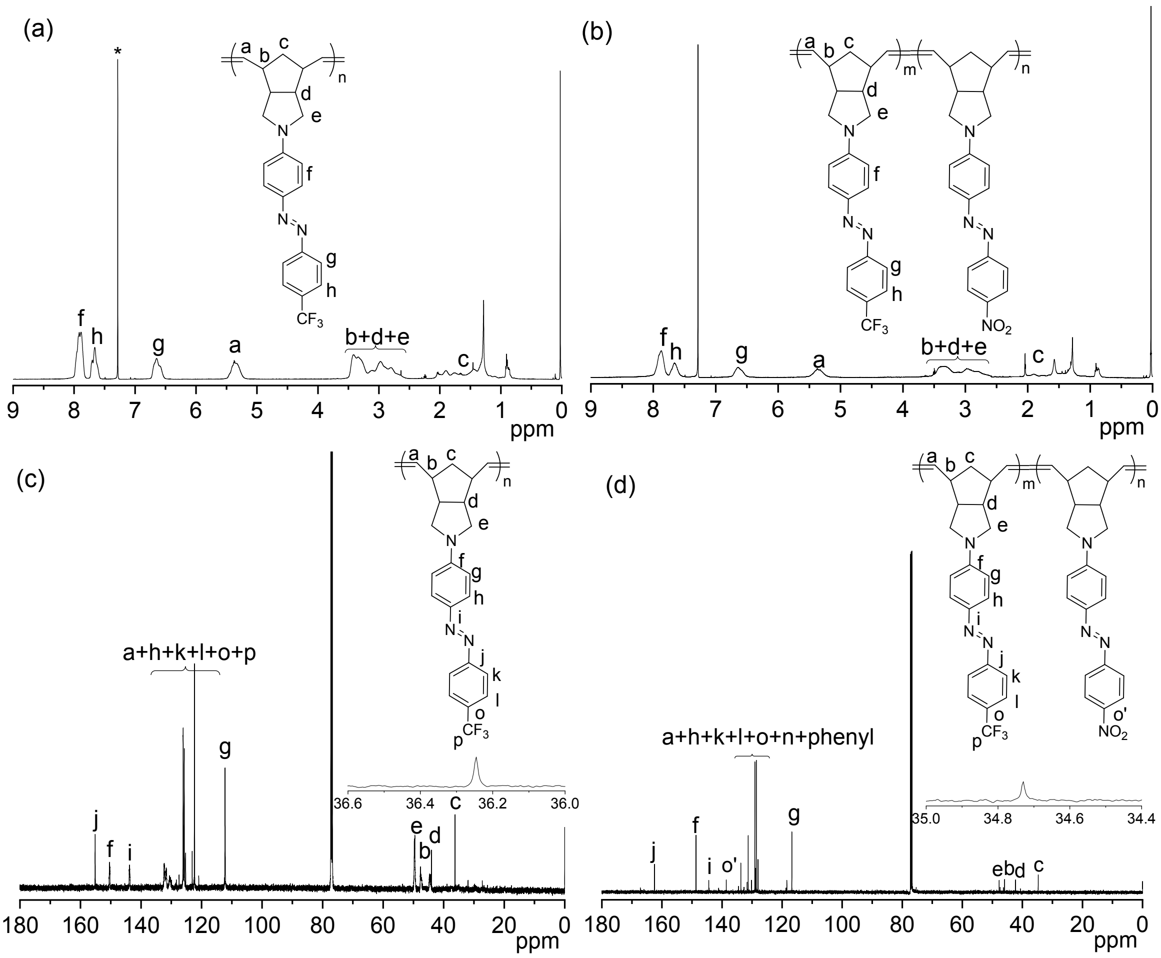


Figure S5. ^{1}H NMR spectra of (a) **PFANP$_{200}$** and (b) **PFANP$_{200}$-*b*-PNANP$_{100}$**; ^{13}C NMR spectra of (c) **PFANP$_{200}$** and (d) **PFANP$_{200}$-*b*-PNANP$_{100}$**.

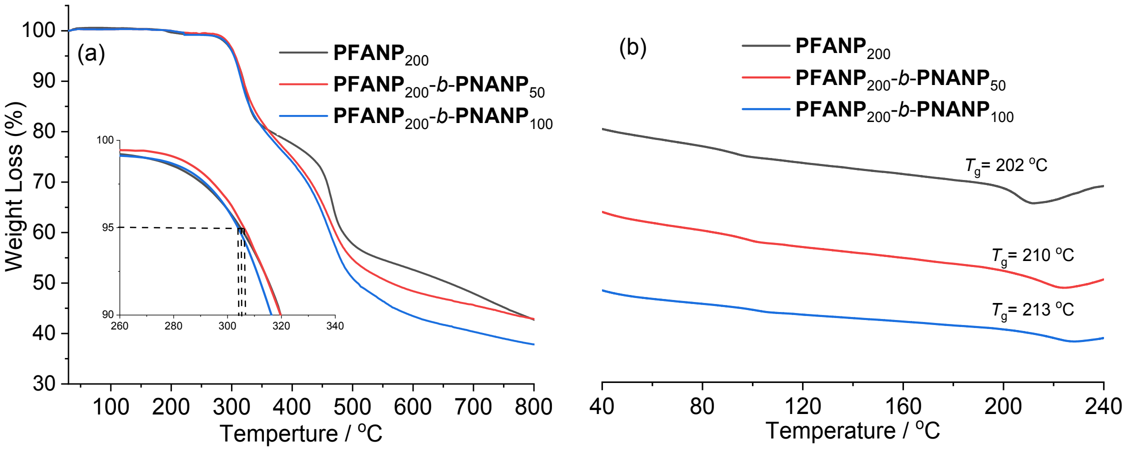


Figure S6. TGA (a) and DSC (b) curves of polymers.

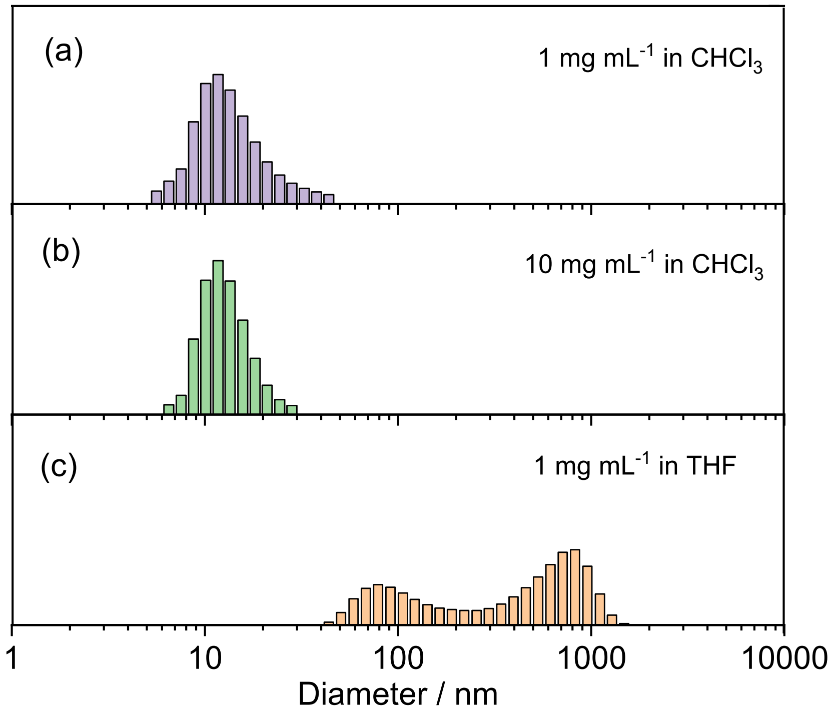
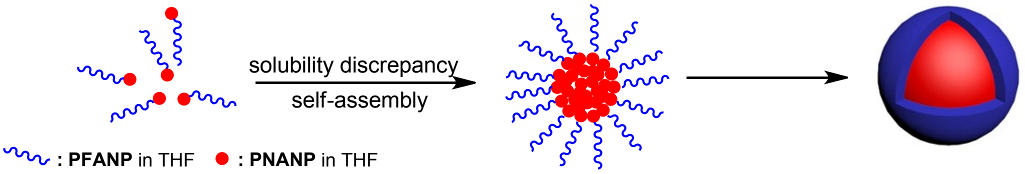


Figure S7. DLS diagrams of **PFANP$_{200}$-*b*-PNANP$_{100}$** in $CHCl_3$ (a,b) and THF (c).

Table S2. Size (D_h) of polymers in different solvents at varied concentrations determined by DLS

Polymer	in $CHCl_3$		in THF
	1 mg mL^{-1}	10 mg mL^{-1}	1 mg mL^{-1}
PFANP$_{200}$-*b*-PNANP$_{100}$	11 nm	11 nm	79/805 nm



Scheme S1. Schematic processes of the regular core-shell nanostructure in THF by the self-assembly of **PFANP$_{200}$-*b*-PNANP$_{100}$**.

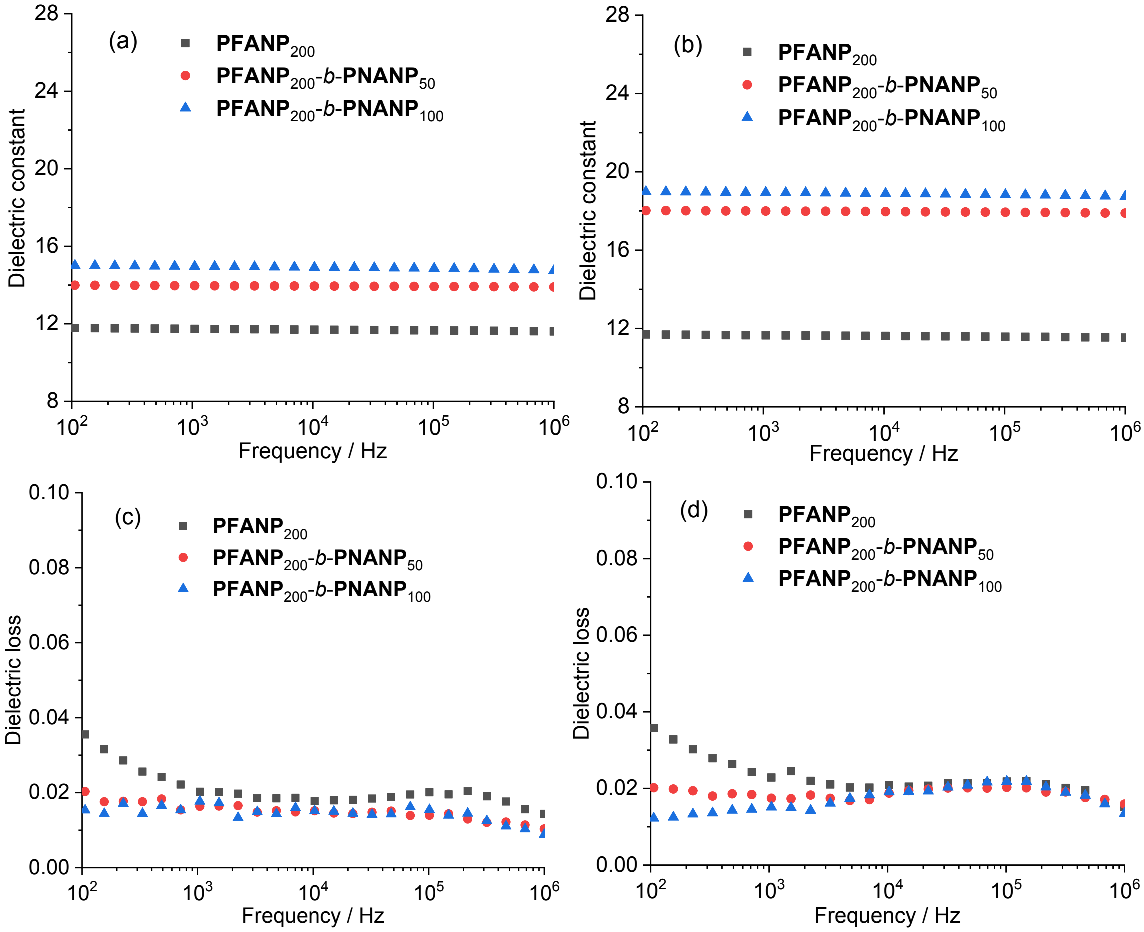


Figure S8. Dielectric constant (a,b) and dielectric loss (c,d) of the films made from polymers in $CHCl_3$ (a,c) and THF (b,d) versus frequency.

Table S3. The dielectric constant (k), dielectric loss ($\tan\delta$), stored energy density (U_s, J cm^{-3}), released energy density (U_r, J cm^{-3}), and charge-discharge efficiency ($\eta = U_r/U_s$, %) of polymer films made from different solutions

Polymer	$CHCl_3$			THF		
	$k/\tan\delta$	U_s/U_r	η	$k/\tan\delta$	U_s/U_r	η
PFANP$_{200}$	11.6/0.03	2.04/1.91	93.4	11.7/0.03	3.43/3.06	89.2
PFANP$_{200}$-*b*-PNANP$_{50}$	13.9/0.02	2.49/2.23	90.1	17.9/0.02	4.21/3.60	85.5
PFANP$_{200}$-*b*-PNANP$_{100}$	14.7/0.02	3.73/3.25	87.1	19.1/0.02	5.54/4.55	82.1

Conductivity of polymers

The insulating behavior is a great important property of dielectric materials.[S3] The conductivity values of **PFANP$_{200}$**, **PFANP$_{200}$-*b*-PNANP$_{50}$**, and **PFANP$_{200}$-*b*-PNANP$_{100}$**

films made from $CHCl_3$ solution were 1.8×10^{-10}-8.3×10^{-7}, 1.1×10^{-10}-7.1×10^{-7}, and 6.1×10^{-11}-6.7×10^{-7} S cm^{-1} (Figure S9a), as well as the films made from THF solution were 2.0×10^{-10}-8.2×10^{-7}, 8.4×10^{-11}-7.0×10^{-7}, and 3.9×10^{-11}-4.9×10^{-7} S cm^{-1} (Figure S9b), respectively, in a wide range frequency from 100 Hz to 1 MHz. As a whole, the conductivity values of the polymer films made from THF solution were smaller than those of the polymer films made from $CHCl_3$ solution. As shown in Scheme S2, each solid nanosphere in the polymer films made from THF solution could form a small electrode in an electric field, the impedance of film increased because the electrode polarization was enhanced under low frequency electric field, thus restrained the leakage current. The conductivity of polymer films increased rapidly with the increase of frequency when the frequency was more than 10^4 Hz, because the electrode polarization weakened gradually, thus the electric charges were hardly accumulated at electrodes under high frequency electric fields.[S4,S5]

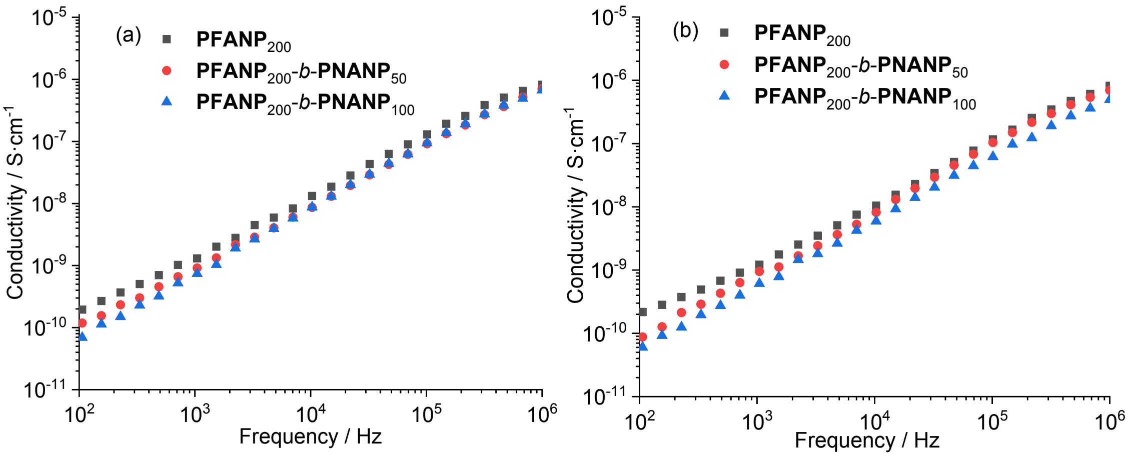
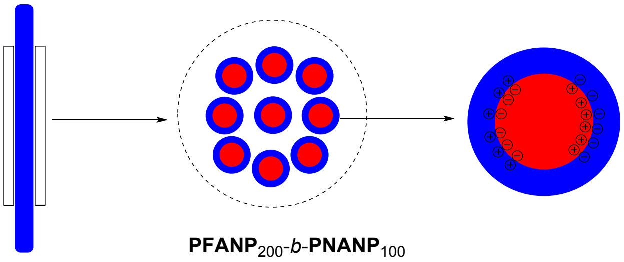


Figure S9. Conductivity of the films made from polymers in $CHCl_3$ (a) and THF (b) versus frequency at room temperature.



Scheme S2. Schematic illustration of small relative displacements of the electrons under the applied electric field.

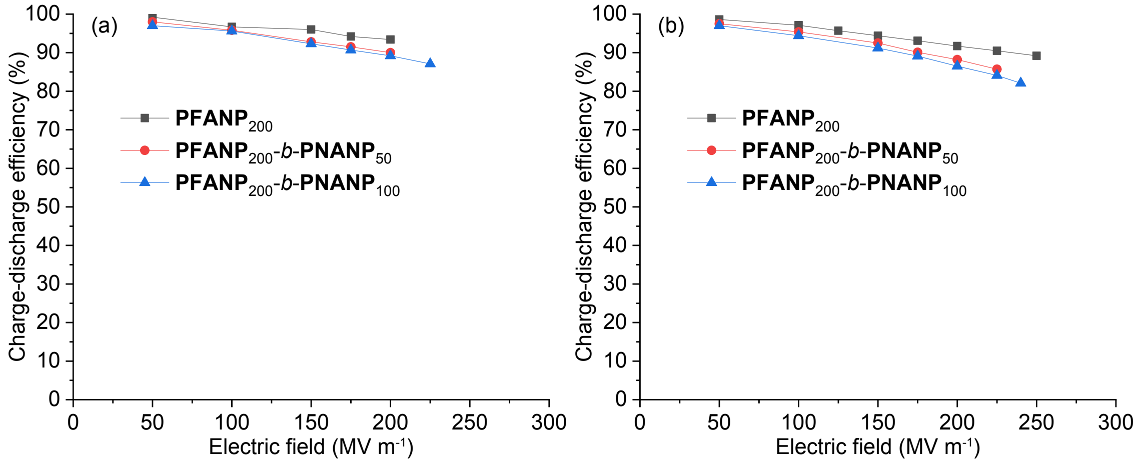


Figure S10. Charge-discharge efficiency of the films made from polymers in $CHCl_3$ (a) and THF (b) versus frequency at room temperature.

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