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Electronic Supplementary Information (ESI):

Polyimide Complexes with High Dielectric Performance: Toward Polymer Film Capacitor Application

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1. Experimental

1.1 Materials

2,2'-bipyridine (99.0%), 4-aminophenol (99.0%), bromine(99.5%), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA, 99.0%), were purchased from J&K Chemical Ltd. 1-methyl-2-pyrrolidinone (NMP) and N,N-diethylacetamide (DMAc) were purified using CaH_2 and then distilled under reduced pressure and then stored in the presence of 4 Å molecular sieves. All other reagents and solvents were obtained from China National Pharmaceutical Group Corporation.

1.2 Measurements

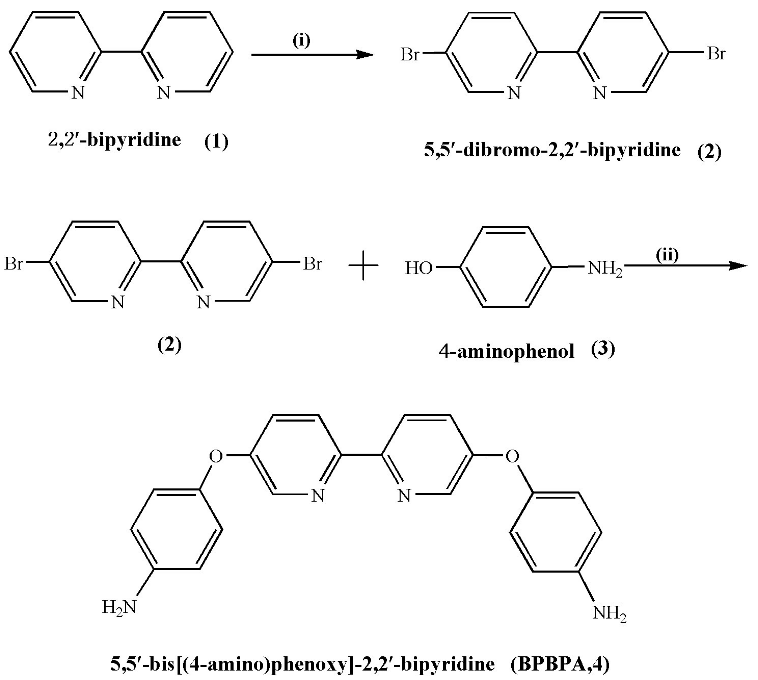
Proton and carbon nuclear magnetic resonance (^1H and ^{13}C-NMR) spectra were measured at 400 MHz and 100 MHz respectively on Bruker Avance-400 spectrometers. FT-IR spectra were obtained with Perkin-Elmer SP one FT-IR. Elemental analyses were determined by a Perkin-Elmer model 2400 CHN analyses. The intrinsic viscosity was measured in DMAc with an Ubbelohde viscometer at 25 °C. Thermal gravimetric analysis (TGA) was carried out using approximately 6-8 mg film samples with a Perkin Elmer Pyris 1 TGA in nitrogen at a heating rate of 10°C/min. A Perkin-Elmer Diamond dynamic thermomechanical analysis (DMA) instrument was used to determine the glass transition temperatures. During the test, a load of 10 g (stress, 0.125 MPa) and a heating rate of 10 °C/min in air were applied. Tensile tests of polymer films were performed using SANS CMT8012 (Shenzhen, China) instrument at 5 mm/min on strips (0.5 cm wide, 2 cm long, and about 0.05 mm thick). The dielectric properties were measured on an Agilent E4980 LCR (20Hz-2MHz) electrometer with 16451 B test fixture at different frequencies and conductive tapes were served as electrodes to clamp our samples with 10 mm in diameter. Dielectric breakdown strength was tested using an electric breakdown strength test machine (DDJ- 20 kV, China) under DC high-voltage power with 20×20 mm in size. Scanning electron microscope (SEM, TESCAN vega3) was employed to observe the morphology and cross-section of PICuCs films, and to obtain the films thickness. The polarization-electric field (P-E) loop was measured using a function generator (FG300, Yokogawa, Japan), a digital oscilloscope (DL7100, Yokogawa, Japan), and a voltage amplifier (610E, Trek, USA).

1.3 Synthesis of diamine monomer (5,5'-bis[(4-amino) phenoxy]-2,2'-bipyridine)

1.3.1 Synthesis of 5,5'-dibromo-2,2'-bipyridine

2,2'-bipyridine (**1**, 4.99 g, 0.032 mol) and bromine (10.24 g, 0.064 mol) were first added in a hydrothermal reaction container and heated to 150 ^{o}C and annealed for 15 h. Then, the mixture was cooled and the hard solid was powdered and following treated with Na_2SO_3 solution to remove the unreacted bromine. Finally it was basified with sodium hydroxide and filtered. The white solid product 5,5'-dibromo-2,2'-bipyridine was obtained by the chromatography on silica (CH_2Cl_2). 5,5'-dibromo-2,2'-bipyrimidin, 8.64g (86%). m.p. 221.6-222.1 ^{o}C. ^1H-NMR (400 MHz, $CDCl_3$, δ): 7.95 (d, 2 H), 8.28 (s, 2H),8.71 (d, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 121.47 (C5), 122.25 (C3), 139.64

(C4); 150.28 (C6),153.64 (C2); IR (KBr): 3049 (C-H, stretching), 1562, 1453, 1356 (Ar, stretching), 636 (C-Br, stretching). Anal. calcd for $C_{10}H_6N_2Br_2$: C 38.22, H 1.91, N 8.92, Br 50.95; found: C 38.26, H 1.94, N 8.90, Br 50.97.



Scheme S1. Synthesis of 5, 5'-bis[(4-amino) phenoxy]-2,2'-bipyridine (BPBPA). The reagents and conditions are described as follows: (i) Br_2 (liquid), 150 °C, 15 h; (ii) K_2CO_3, NMP, 175 °C for 12 h.

1.3.2 Synthesis of 5,5'-bis[(4-amino) phenoxy]-2,2'-bipyridine (BPBPA)

5,5'-dibromo-2,2'-bipyridin (**2,** 6.28g, 0.02 mol) and 4-aminophenol (**3**, 5.23g, 0.048 mol) were dissolved in 100 mL NMP. Anhydrous K_2CO_3 (2.73 g, 0.02 mol) was added to the solution, and the mixture was heated at 175 °C for 12 h. After cooling to room temperature, the mixture was poured into 5 wt % sodium hydroxide solution, and stirred for 1 h. The solution was filtered, and the filter cake was washed repeatedly with distilled water. The white crystals of 5,5'-bis[(4-amino)phenoxy]-2,2'-bipyrimidine (BPBPA, **4**) was recrystallized from H_2O/ethanol. 6.44g (87%), m.p. 204.0-204.6 °C. ^{1}H-NMR (400 MHz, DMSO-d_6, δ): 5.06 (s, 4H), 6.61 (d, 4H), 6.85 (d, 4H), 7.29 (d, 2H), 8.21 (s, 2H), 8.29 (d, 2H). ^{13}C-NMR (100 MHz, DMSO-d_6, δ): 114.89 (C3'), 120.82 (C2'), 123.92 (C3, C4), 138.43 (C6), 144.75 (C4'), 146.04 (C1'), 148.84 (C2), 155.36 (C5); FTIR (KBr): 3396, 3302 (N-H, stretching), 1633, 1558, 1503, 1455 (Ar, stretching). Anal. calcd for $C_{22}H_{18}N_4O_2$: C 71.35, H 4.86, N 15.14, O 8.65; found: C 71.31, H 4.89, N 15.11, O 8.70.

1.4 Synthesis of polyimide and polyimide complexes

The polyamic acid containing bipyridine units (PAA, **3**, scheme 1 in main text) was prepared by the reaction of diamine (5,5'-bis [(4-amino) phenoxy]-2,2'-bipyridine (**2**, BPBPA) and biphenyl dianhydride (BPDA, **1**). In a round bottom flask, BPBPA (3.70 g, 0.01 mol) and BPDA (2.94 g, 0.01 mol) were added to 63.7 mL of DMAc and the mixture was allowed to react for 12 h at room temperature. The intrinsic viscosity of the polyamic acid is 3.5 dL/g, measured by an Ubbelohde viscometer in DMAC at 25 °C. The resulting PAA (**3**) solution (9.44%) was used to prepare the PAA-Cu complexes in the next step.

The anhydrous Cupric(II) acetylacetonate ($Cu(C_5H_7O_2)_2$, 2.0 g) was added to the 20 g anhydrous solvent (DMAc) and stirred vigorously for 24 h at room temperature under argon. From this $Cu(C_5H_7O_2)_2$-DMAC stock solution, 3.20 g was taken out, and added to the round bottom flask containing PAA-DMAc (15 g, 9.44%) solution and stirred for 48 h at room temperature to prepare PAACuCs (1:2, **4a**). Similarly 1.60 g, 1.17 g, and 0.40 g of $Cu(C_5H_7O_2)_2$ -DMAc solution was added separately to 3 round bottom flasks containing freshly prepared PAA-DMAC (15 g) solution and stirred for 48 h at room temperature under argon, to respectively prepare PAACuCs (1:4, **4b**), PAACuCs (1:6, **4c**), and PAACuCs (1:8, **4d**). The solutions were cast onto clean glass substrates (80mm×30mm). The glass substrates were immediately placed into vacuum oven for 6h at 80°C.

The four PAACuCs (**4a**, **4b**, **4c**, and **4d**, scheme 1) were then imidized to obtain the final four polyimide-Cupper complexes (PICuCs, **5a**, **5b**, **5c**, and **5d**, scheme 1) in a high-temperature furnace according to the following protocols: (1) holding at 160 °C for 2h to remove the residual solvent, (2) heating at a rate of 10 °C/min and annealing at 250 °C for 15min, (3) heating at a rate of 5 °C/min and annealing at 350 °C in for 2h.

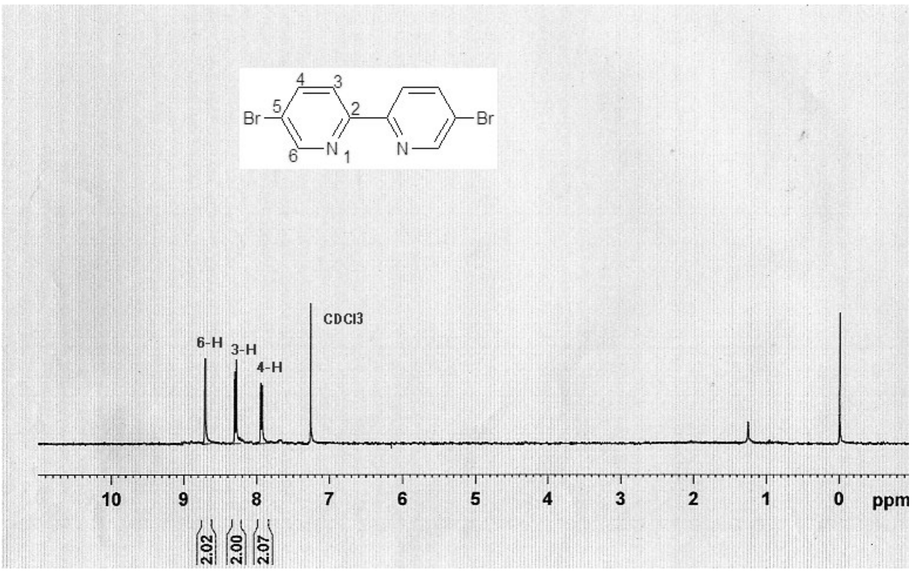


Figure S1. ^1H NMR of 5,5'-dibromo-2,2'-bipyridine in $CDCl_3$ solution.

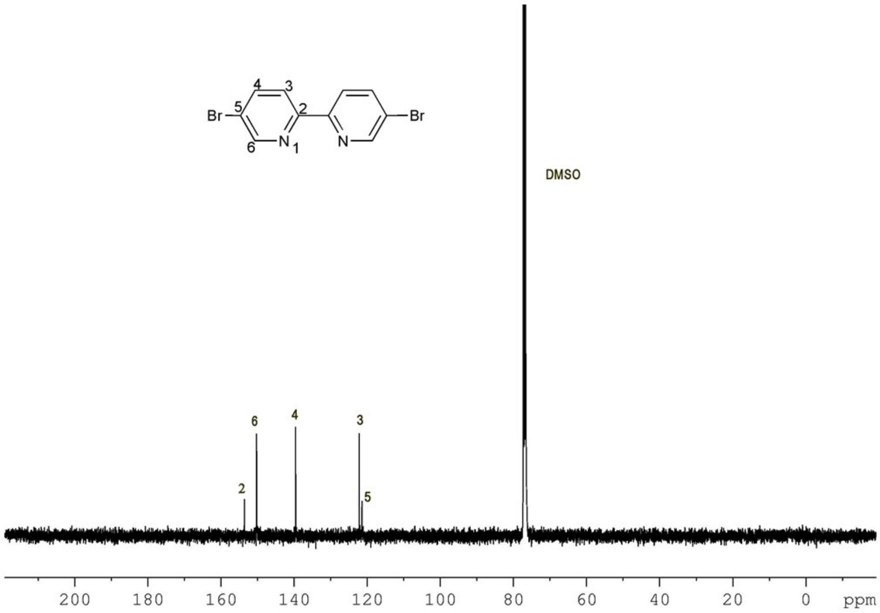


Figure S2. ^{13}C NMR of 5,5'-dibromo-2,2'-bipyridine in DMSO-d_6 solution.

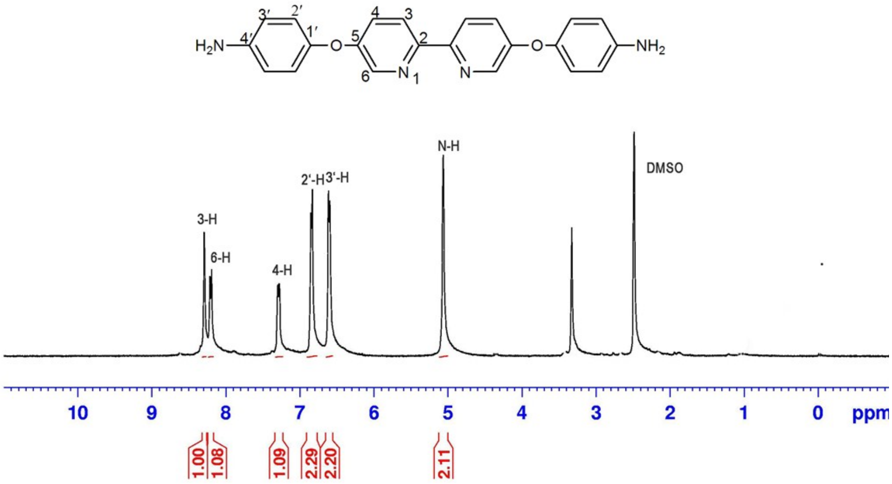


Figure S3. ^{1}H NMR of 5, 5'-bis[(4-amino)phenoxy]-2, 2'-bipyridine in DMSO-d_6 solution.

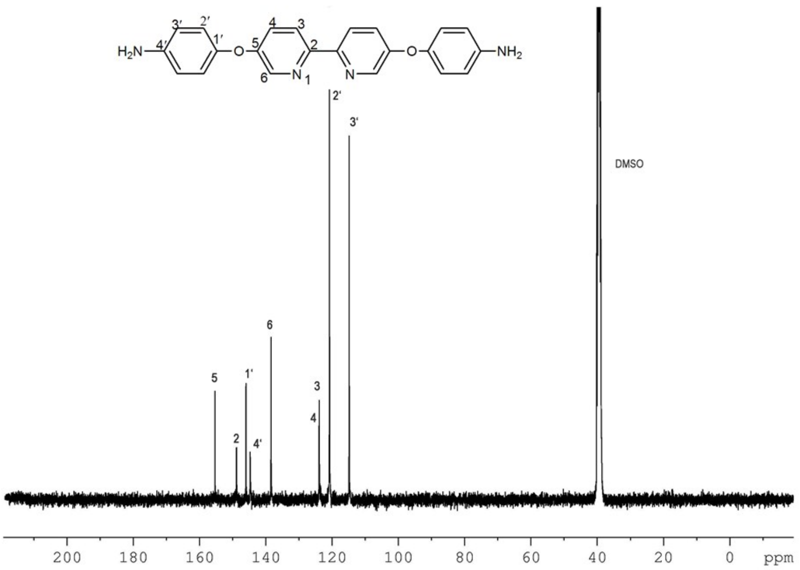


Figure S4. ^{13}C NMR of 5, 5'-bis[(4-amino)phenoxy]-2, 2'-bipyrimidine in DMSO-d_6 solution.

2. Properties of polyimide derived from 5,5′-bis[(4-amino) phenoxy]-2,2′-bipyridine

The polyimide containing bipyrimidine units was prepared from a newly synthesized 5,5′-bis[(4-amino) phenoxy]-2,2′-bipyridine (BPBPA) and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) *via* a two-step method. The dielectric constant of the polyimide (BPDA-BPBPA) from 10^2 Hz to 10^5 Hz was 6.78-6.36 (**Figure.S5**). Dielectric loss of the bipyridine-contained polyimides remained below 0.04 (**Figure.S5**). The electrical breakdown strength is 282 kV/mm and the maximum energy storage density of the PI is as high as 2.22 J/cm^3. The PI films had $T_{d5\%}$ values of 544 °C and $T_{d10\%}$ values of 561 °C (**Figure.S7**), and the PI showed high glass transition temperature of 285°C (**Figure.S8**). The polyimide films containing bipyridine units showed good mechanical properties, that the tensile strengths was 221 MPa and the elongation at break was 19.8% (**Figure.S9**).

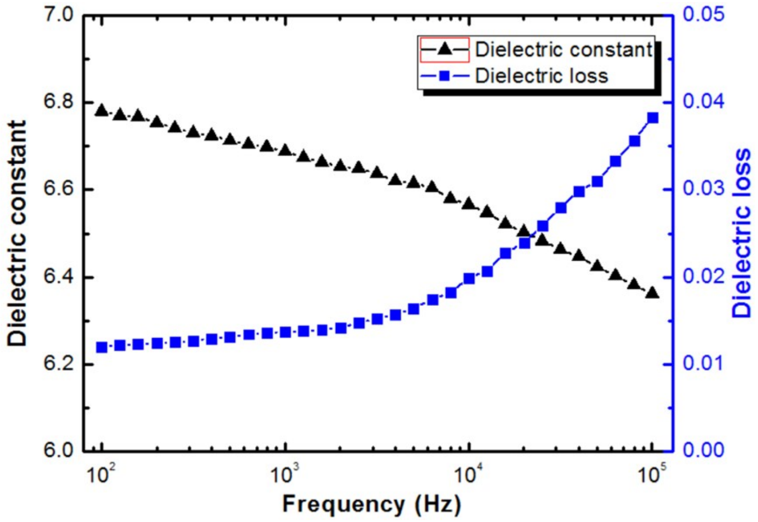


Figure S5. Dielectric constant and dielectric loss of the neat polyimide measured at the frequency from 10^2 Hz to 10^5 Hz

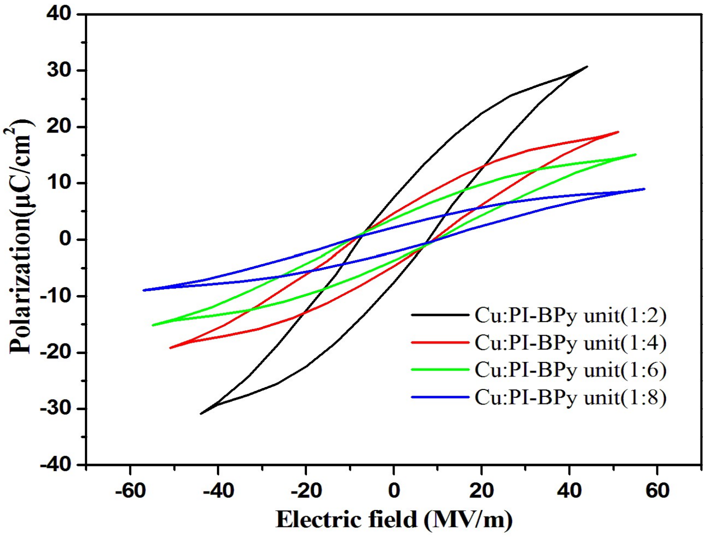


Figure S6. Polarization-electric field (P-E) hysteresis loops

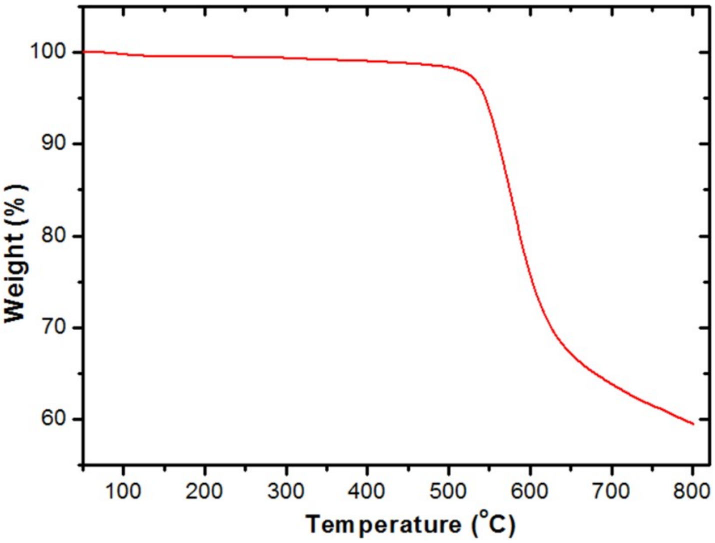


Figure S7. TGA curve of the neat polyimide at a scan rate of 10 °C/min under nitrogen atmosphere.

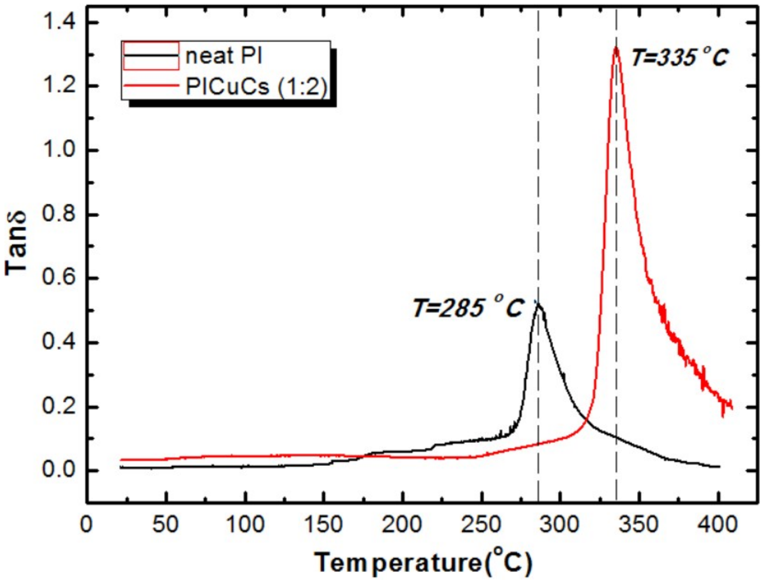


Figure S8. Dynamic mechanical analysis (DMA) curves of neat PI and PICuCs (Cu:PI-BPy unit is 1:2) at a heating rate of 5 °C/min

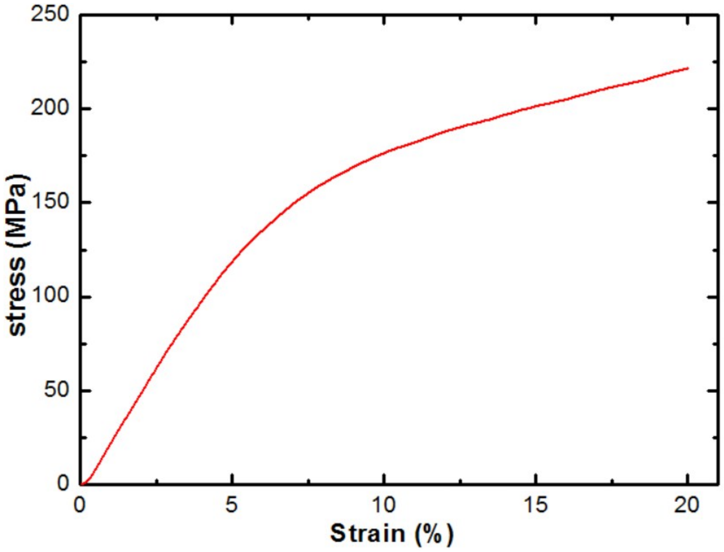


Figure S9. Typical stress-strain curves of neat PI film

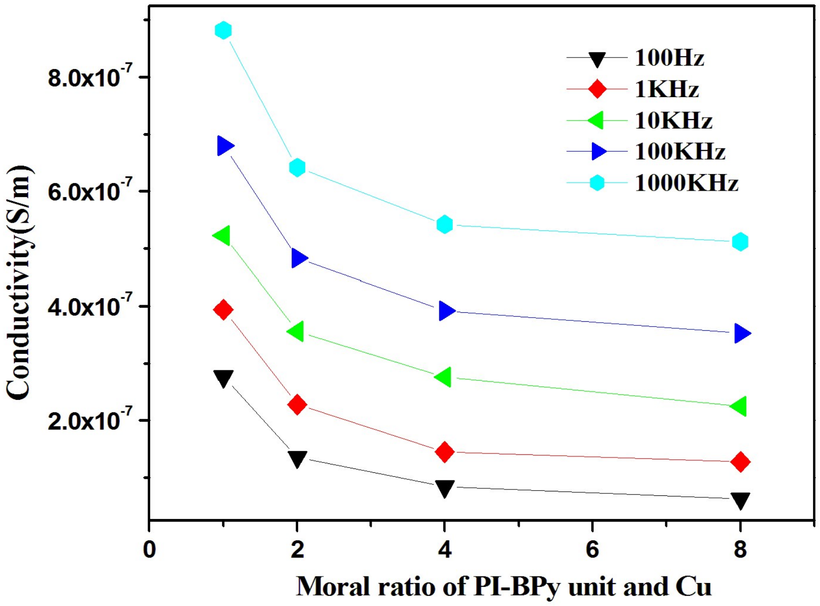


Figure S10. AC conductance of the different PICuCs

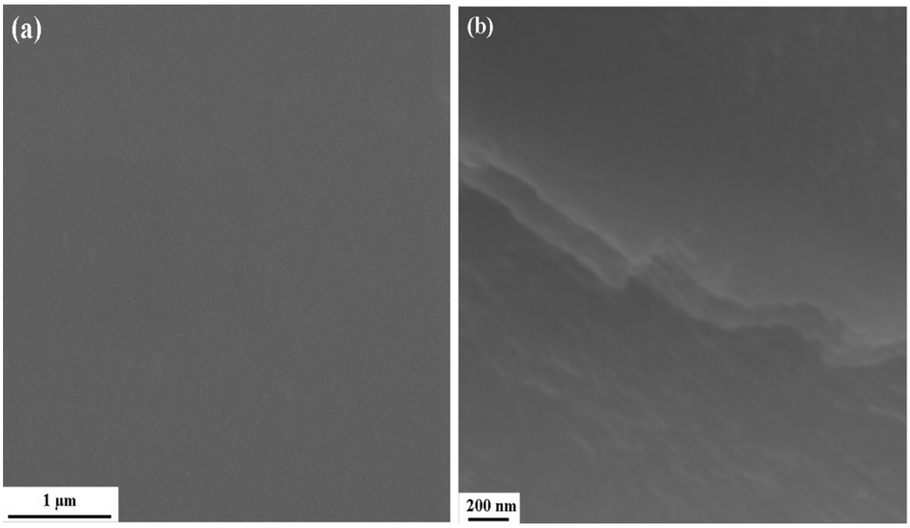


Figure S11 SEM images of the surface **(a)** and cross section **(b)** of the PICuCs (1:2) film.

Table S1. Dielectric properties (room temperature) of the PICuCs

Sample	**ε (100 Hz)**	**tanδ (100 kHz)**	**Breakdown strength (kV/mm)**	**Maximum energy storage density (J/cm^3)**
Cu:PI-BPy unit (1:2)	133	0.077	44	11.39
Cu:PI-BPy unit (1:4)	87	0.061	51	10.10
Cu:PI-BPy unit (1:6)	70	0.041	55	9.40
Cu:PI-BPy unit (1:8)	41	0.012	57	8.31

Table S2. Thermal properties of the PICuCs

Sample	**$T_{5\%}$ (℃)**	**Tg (℃)**	**Char yield**
Cu:PI-BPy unit (1:2)	589	335	66%
Cu:PI-BPy unit (1:4)	578	325	62%
Cu:PI-BPy unit (1:6)	568	318	57%
Cu:PI-BPy unit (1:8)	560	309	55%