Electronic Supplementary Information

Synthesis and Properties of A High Dielectric Constant Copolymer of Copper Phthalocyanine Oligomer Grafted to Amino-capped Polyimide

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1. Experimental

1.1 Materials

Pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), and 4,4'-oxydianiline (ODA) were purchased from Changzhou Sunlight Pharmaceutical Co., Ltd. (Changzhou, China). N,N′-dimethylacetamide (DMAc), N-methyl pyrrolidone (NMP), nitrobenzene ($PhNO_2$, AR), methanol (AR), and HCl (AR) were purchased from the Shanghai Chemical Reagents Co. (Shanghai, China). Urea (AR), $CuSO_4$ (CP), NH_4Cl (CP), and $(NH_4)_2MoO_4$ (AR) were purchased from Sinopharm Chemical Reagent Co.,Ltd. (Shanghai, China). NaOH (AR) and NaCl (AR) were purchased from Nanjing Chemical Reagents Co. (Nanjing, China). PMDA, BPDA, and ODA were purified using vacuum sublimation prior to use; $PhNO_2$ was pre-treated with anhydrous $MgSO_4$ prior to use; and other chemicals were used as received.

1.2 Synthesis of copper phthalocyanine anhydride oligomer (o-CuPcA)

***o-CuPc synthesis**:* The copper phthalocyanine oligomer (o-CuPc) (**Figure S1**) was synthesized by a solution method following a previously reported procedure.[1, 2] Specifically, $CuSO_4$ (3.9 g), urea (30 g), PMDA (9.6 g), NH_4Cl (2.5 g), and $(NH_4)_2MoO_4$ (0.5 g) were mixed together and finely ground, and then transferred to a 250 mL three-necked flask equipped with a thermometer, condenser, and mechanical stirrer. Subsequently, 25 mL $PhNO_2$ was added into the flask and the flask was then gradually heated to 180 ºC and held for at least 12 h. During the reaction, the color of the solution gradually becomes dark blue, and the dark-blue solid material was precipitated in the flask, which is the formed o-CuPc. Please note that during the reaction, a large amount of white crystalline solid is formed in the condenser, which is caused by the sublimation of ammonium salt under high temperature. Therefore, the condenser should be paid attention to remove the white solid in time to avoid explosion. Thereafter, the resulting solid product was treated with the following procedure to give the final product: 1) washed with methanol and filtered; 2) boiled with 2 N HCl (saturated with NaCl), then cool to room temperature and filtered; 3) boiled with 2 N NaOH (saturated with NaCl) until all the ammonia was evaporated, and then cool to room

temperature and filtered; 4) treated with 2 N HCl and filtered; 5) dissolved in 2 N NaOH and filtered to separate the insoluble components; 6) the above solution was precipitated with 2 N HCl and filtered; 7) the solid was washed with DI water until it was neutral; 8) dried in a vacuum oven, room temperature. **Figure S2a** shows the chemical synthesis.

o-CuPcA synthesis*:* The as-synthesized o-CuPc was heat treated to dehydration to form copper phthalocyanine anhydride oligomer (o-CuPcA). In detail, the obtained o-CuPc powder was heated in a vacuum oven under 200 ºC overnight (~10 h), and then cool down to room temperature in the vacuum oven. **Figure S2b** shows the conversion from o-CuPc to o-CuPcA.

1.3 Preparation of CuPc-PI film

Synthesis of amino-capped polyamic acid (PAA): The precursor of PI (PAA) was synthesized by polycondensation of BPDA and ODA at a low temperature (0~5 ºC), and the molar ratio of BPDA and ODA was 0.95:1 to obtain a 20 wt% amino-capped PAA solution. **Figure S7** shows the chemical synthesis.

Preparation of CuPc-PI film: The o-CuPcA was dispersed in NMP by ultra-sonication for 3 h until a stable suspension was formed. Then, pre-calculated amount of PAA solution and o-CuPcA dispersion were added together in a dry flask equipped with a mechanical stirrer, followed by vigorously stirring for 1 h at room temperature. o-CuPcA-PAA solutions with the o-CuPcA content of 10 wt%, 20 wt%, 30 wt%, 40 wt%, and 50 wt% were prepared. Subsequently, the resulting o-CuPcA-PAA solutions were cast onto clean glass slides to obtain smooth and uniform films. The films were then dried in a vacuum oven at 60 ºC for 12 h to completely remove the residual solvent. The thermal imidization process is performed as follows: 1) heating to 120 ºC with the heating rate of 5 ºC/min (in nitrogen) and annealing for 1h; 2) heating to target temperature (240, 270, 300, 330, 350, and 380 ºC) with the heating rate of 2 ºC/min (in nitrogen) and annealing for 1h.

1.4 Characterization

Scanning Electron Microscope (SEM, TESCAN vega3) was employed to observe the morphology of the o-CuPcA and CuPc-PI films, and SEM-EDS analysis was used to analyze the element information. The chemical structures were studied by using Fourier transform infrared spectroscopy (FT-IR, Bruker tensor 27) and UV-vis (U-3310, Hitachi). Dielectric properties were measured using a TH2819-A precision LCR meter (Tong hui Electronic Co., Ltd) at a frequency range from 100 Hz to 100 kHz. The dielectric breakdown strength of the films was performed on the electric breakdown strength test machine (KP8048, Dongguan, China). Thermal Gravimetric Analysis (TGA) was carried out on a thermogravimetric analyzer (WRT-3P, Shanghai, China) with the heating rate of 10 ºC/min in N_2. Tensile test is carried out using CMT-8102 electromechanical testing machine (Shenzhen, China) with stretching rate of 5 mm/min. The thickness of the samples was measured by screw micrometer.

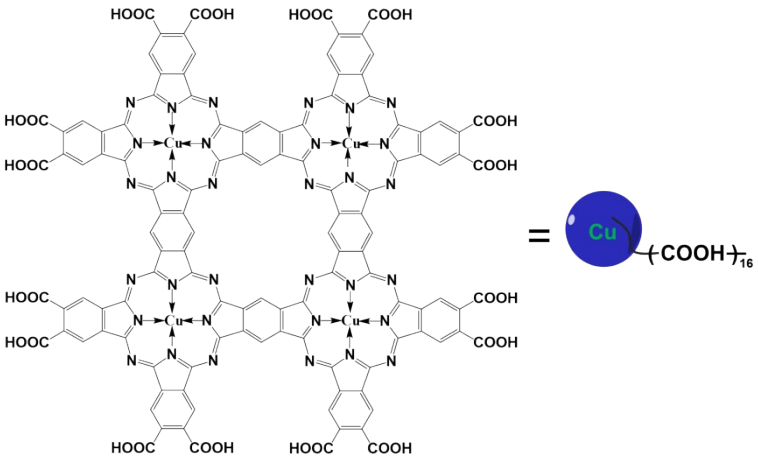

Figure S1 The chemical structure of copper phthalocyanine oligomer (o-CuPc).

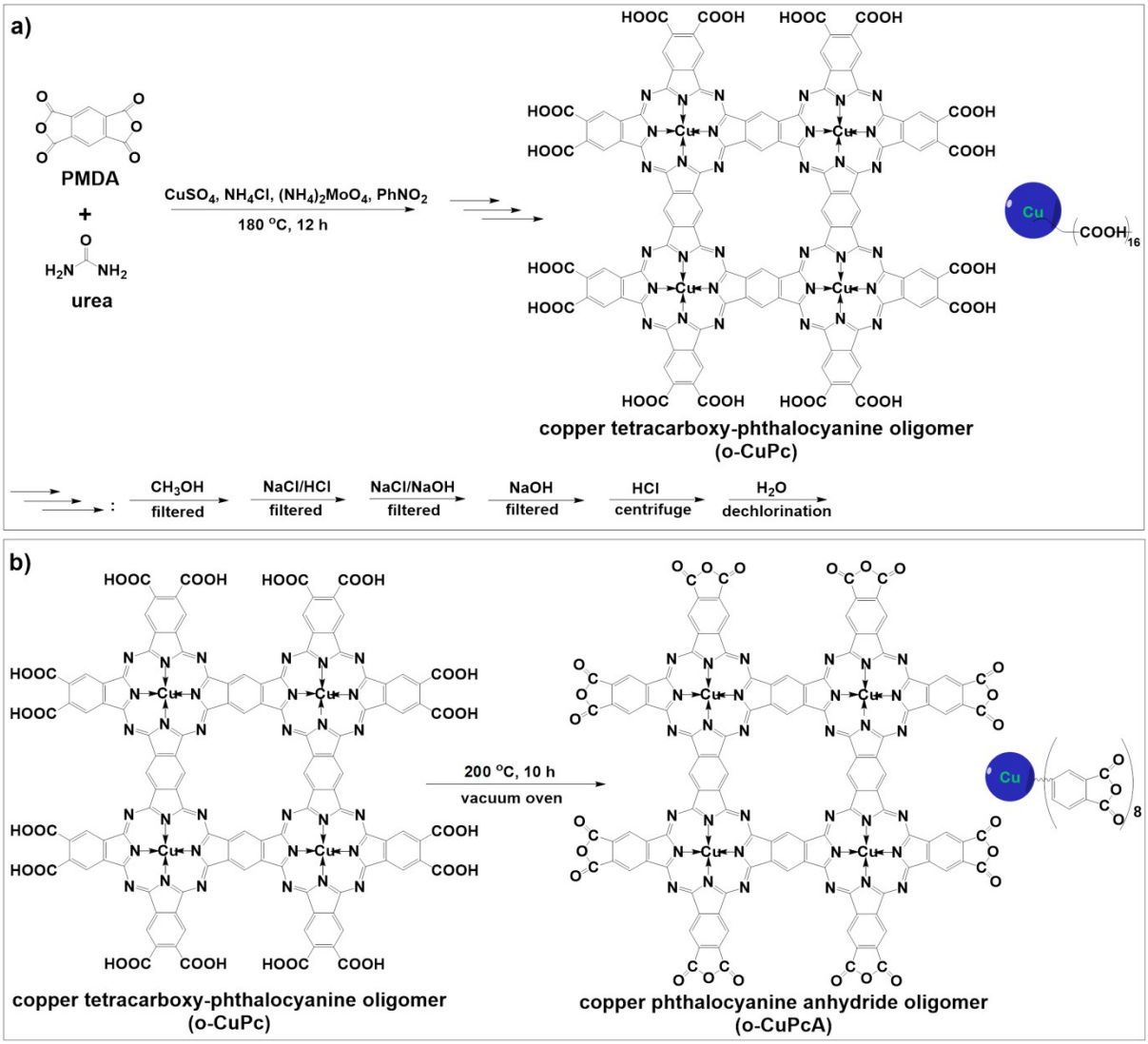

Figure S2 a) Synthesis of o-CuPc, **b)** conversion of o-CuPc to copper phthalocyanine anhydride oligomer (o-CuPcA) by thermal dehydration.

2. Results and Discussion

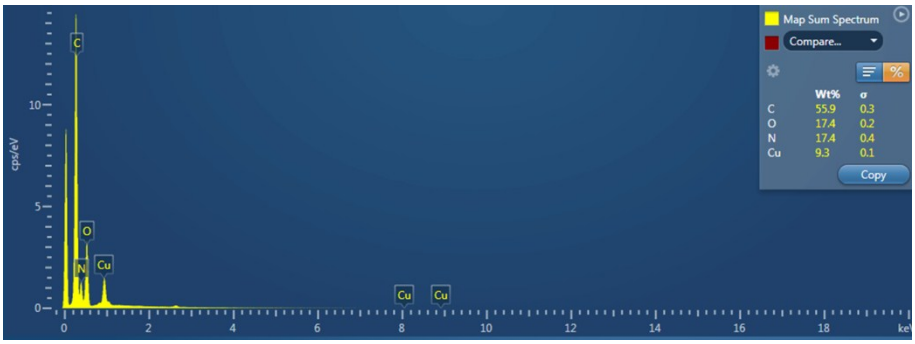

Figure S3 SEM-EDS element analysis of the synthesized o-CuPcA.

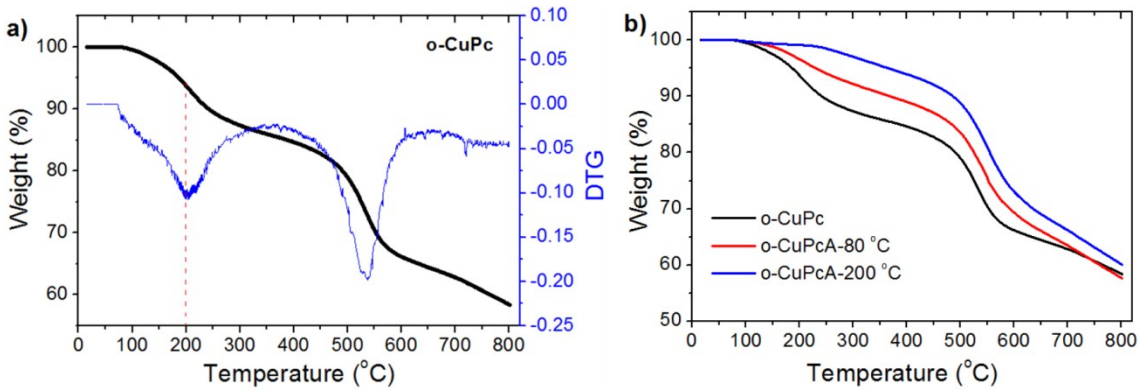

Figure S4 a) TGA and DTG curves of the synthesized o-CuPc; **b)** TGA curves of the o-CuPc, and o-CuPc treated at 80 ºC (o-CuPcA-80) and 200 ºC (o-CuPcA-200).

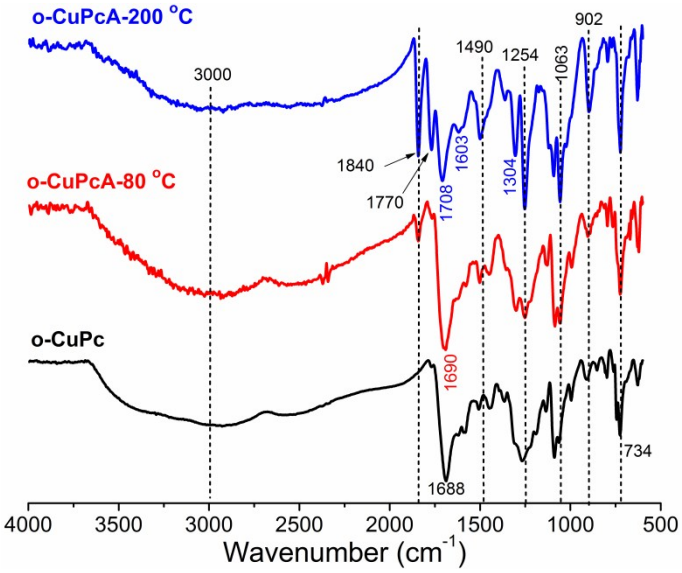

Figure S5 FT-IR spectrum of the synthesized o-CuPc, and o-CuPc treated at 80 ºC (o-CuPcA-80) and 200 ºC (o-CuPcA-200).

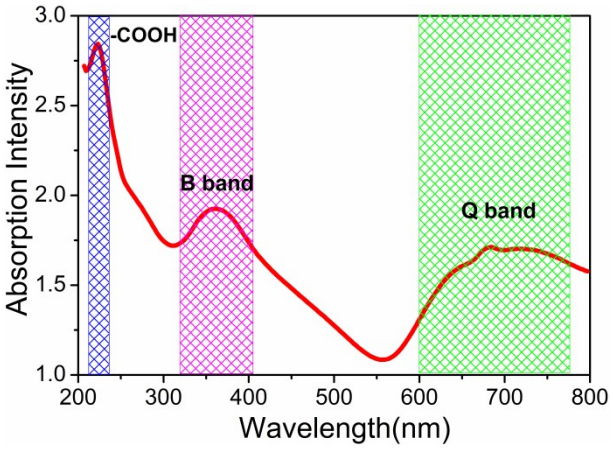

Figure S6 UV-vis spectrum of the synthesized o-CuPcA.

2.1 Characterization of as-synthesized o-CuPcA

The o-CuPc is a carboxylic-capped oligomeric molecule containing a rich ortho-dicarboxylic acid group, in which the ortho-dicarboxylic acid can be converted into dianhydride group through thermal dehydration to give the copper phthalocyanine anhydride oligomer (o-CuPcA). **Figure S4a** shows the TGA and DTG curves of the synthesized o-CuPc, it can be seen that the on-set weight loss temperature is about 80 ºC, and the DTG peak temperature is about 200 ºC. Those weight losses should be attributed to the dehydration. Therefore, we have investigated the conversion of o-CuPc to o-CuPcA at the heat treatment temperature of 80 and 200 ºC (in vacuum, 10 h). **Figure S4b** shows the TGA curves of original o-CuPc, and o-CuPc treated at 80 ºC (o-CuPcA-80) and 200 ºC (o-CuPcA-200), it is obvious that the o-CuPcA-80 still has a significant weigh loss above 150 ºC, indicating that there are still carboxylic acid groups in the o-CuPcA-80 and can be further dehydrated; while the o-CuPcA-200 shows negligible weight loss until 250 ºC, indicating most dicarboxylic acid groups should be converted to dianhydride groups. The further weight loss above 250 ºC might be attributed to the dehydration of some residual carboxylic acid groups and the decomposition of the molecule skeleton. The 5% weight loss temperature of the o-CuPcA-200 is about 352 ºC, showing good thermal stability. In the following preparation of CuPc-PI, the o-CuPcA-200 was used.

The chemical structure was investigated by using FT-IR, and **Figure S5** shows the FT-IR spectrum of the o-CuPc, o-CuPcA-80, and o-CuPcA-200. In the spectrum of o-CuPc, the broad peak around 3000 cm^{-1} corresponds to the stretching vibration of –OH, the strong absorption band at 1688 cm^{-1} corresponds to the stretching vibration of carbonyl group of –COOH, the absorption peaks at 1603, 1490, 1304, and 1254 cm^{-1} correspond to the heteroaromatic skeleton (-C-N, -C=N, and C=C), and the absorption peaks at 902 and 734 cm^{-1} correspond to the phthalocyanine skeleton.[2, 3] The above absorptions should demonstrate the formation of o-CuPc. After heat treatment at 80 ºC, a weak peak appeared at 1840 cm^{-1}, which corresponds to the asymmetric stretching of carbonyl group of anhydride, indicating the formation of dianhydride. After heat treatment at 200 ºC, the absorptions of

heteroaromatic skeleton and phthalocyanine skeleton were maintained. In addition, two strong peaks appeared at 1840 and 1770 cm^{-1}, which correspond to the asymmetric stretching and symmetric stretching of carbonyl group of anhydride; and a strong peak at 1063 cm^{-1}, which corresponds to the stretching vibration of C-O in anhydride. In addition, there was still a broad peak near 3000 cm^{-1}, and the peak at 1688 cm^{-1} shifted to 1708 cm^{-1}, indicating the presence of some unreacted –COOH in o-CuPcA-200.

Moreover, the chemical structure of o-CuPcA was further confirmed by UV-vis. In general, there are two characteristic peaks in the o-CuPc: one absorption in the UV region (~200-300 nm) which known as the Soret (B) band, and another broad absorption in the visible region (~550-750 nm) which known as the Q band.[3] The B band is equivalent to the γ or Soret band in porphyrins, and the Q band is equivalent to α band in porphyrins. The B band and Q band are attributed to the n-π* transition and π-π* transition on the phthalocyanine, respectively.[4] As shown in **Figure S6**, those two peaks are observed in the o-CuPcA-200. In addition, there is another peak appearing at 220-230 nm, which corresponds to the absorption of –COOH.

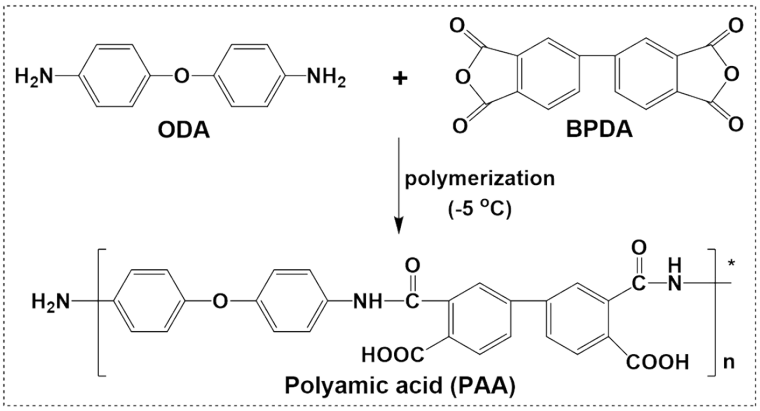

Figure S7 Synthesis of amino-capped polyamic acid (PAA) by the polycondensation between ODA and BPDA.

2.2 Thermal imidization investigation (Chemical structure of CuPc-PI)

The conversion from o-CuPcA-PAA to CuPc-PI by thermal treatment is confirmed by FT-IR. As shown in **Figure 8**, the amino-capped PAA shows the characteristic absorptions at 1710, 1603 and 1546 cm^{-1}, which correspond to the –C=O stretching in –COOH group, –C=O stretching in –CONH group, and –NH stretching in –CONH group, respectively; the peak at 1490 cm^{-1} corresponds to the C–N stretching, and wide weak peak around 3000~3500 cm^{-1} corresponds to absorption of –NH– and –OH groups, and the absorptions at 1406 and 1217 cm^{-1} correspond to –OH stretching. For the o-CuPcA-PAA, it not only has the characteristic absorptions of both PAA and o-CuPcA, but also appears significant absorptions near 3340

and 2976 cm^{-1}, which should be attributed to the rich–COOH groups after the reaction of o-CuPcA and amino capped PAA. After heat treatment (thermal imidization), the CuPc-PI shows the characteristic absorptions of PI, peaks at 1780 cm^{-1} (–C=O in imide, asymmetric stretching), 1708 cm^{-1} (–C=O in imide, symmetric stretching, 1370 cm^{-1} (C-N stretching), and 1217 and 1063 cm^{-1} (C-O-C stretching).[5-7] The peak at 734 cm^{-1} is contributed to the deformation of imide ring or imide carbonyl groups,[5] and the peaks at 1603 and 1490 cm^{-1} are correspond to the heteroaromatic skeleton structure (-C-N, -C=N, and C=C)[2] in CuPc or PI component.

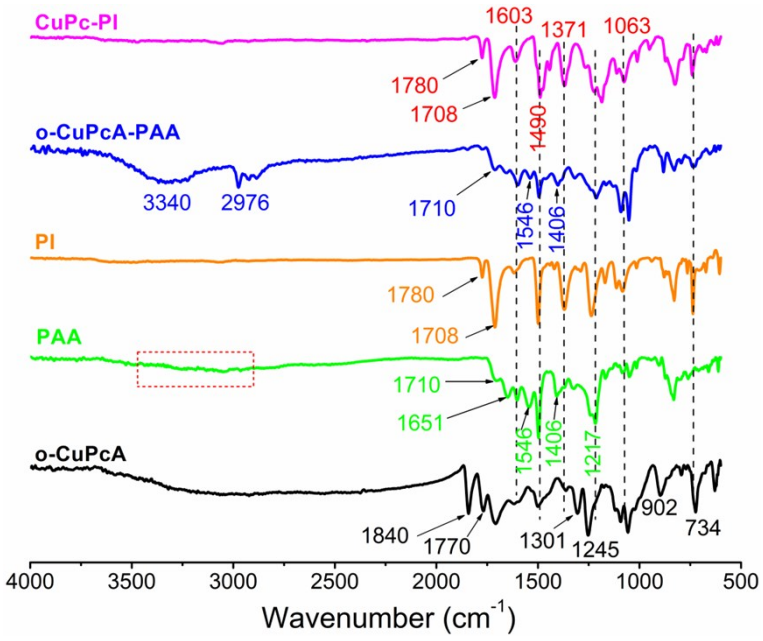

Figure S8 FT-IR spectrum of o-CuPcA, PAA, PI (thermal imidization temperature: 300 ºC), o-CuPcA-PAA, and CuPc-PI (thermal imidization temperature: 300 ºC).

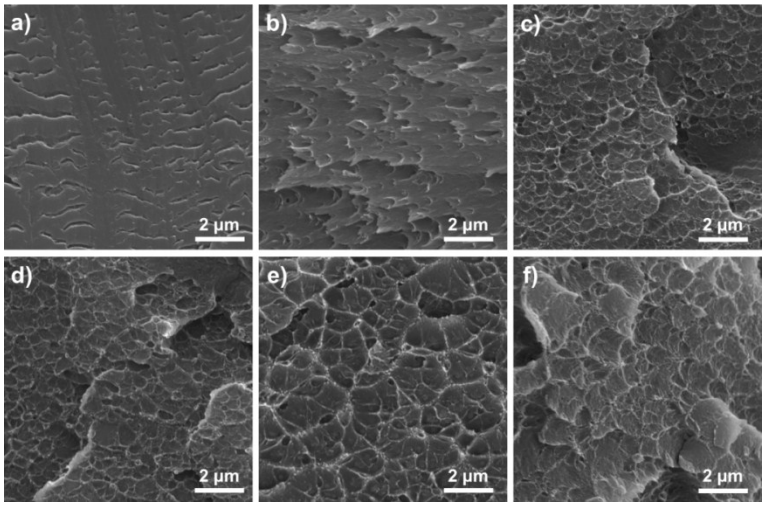

Figure S9 SEM images of neat PI **(a)**, and CuPc-PI film with the o-CuPcA content of 10 wt% **(b)**, 20 wt% **(c)**, 30 wt% **(d)**, 40 wt% **(e)**, and 50 wt% **(f)**.

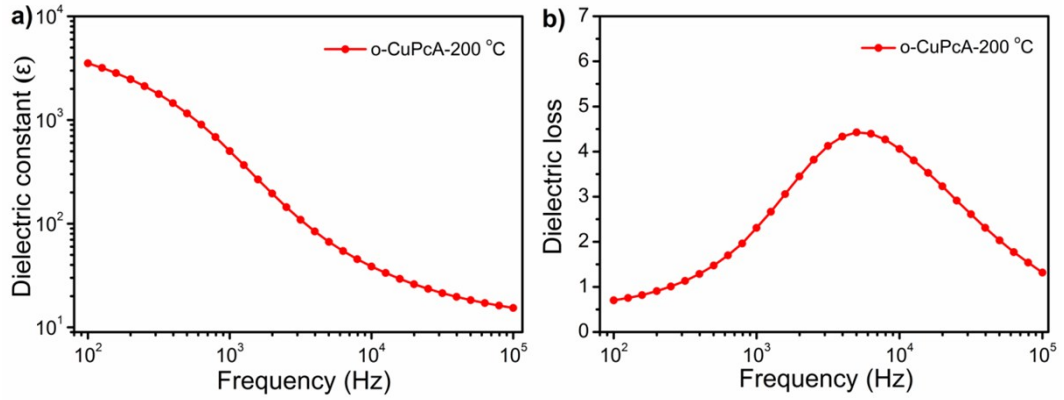

Figure S10 Frequency dependent **a)** dielectric constant and **b)** dielectric loss of the synthesized o-CuPcA.

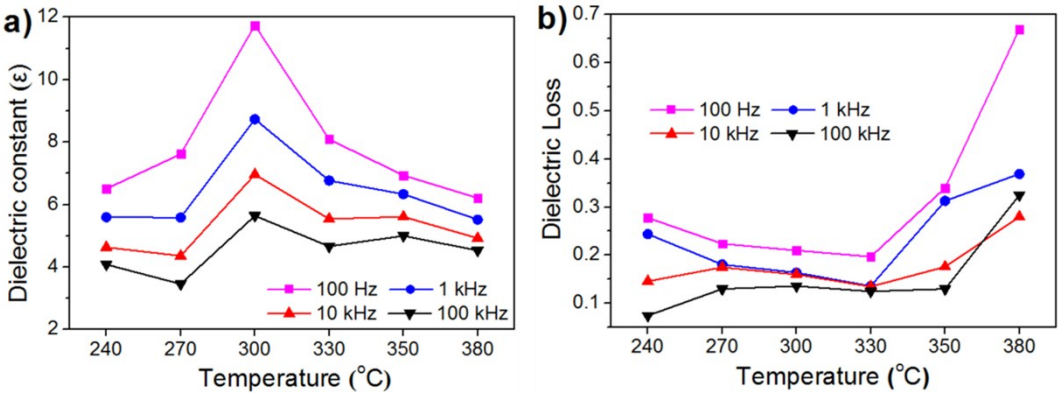

Figure S11 Dependence of **a)** dielectric constant and **b)** dielectric loss of the CuPc-PI film (20 wt%) on thermal imidization temperature, measured at 100 Hz, 1 kHz, 10 kHz and 100 kHz.

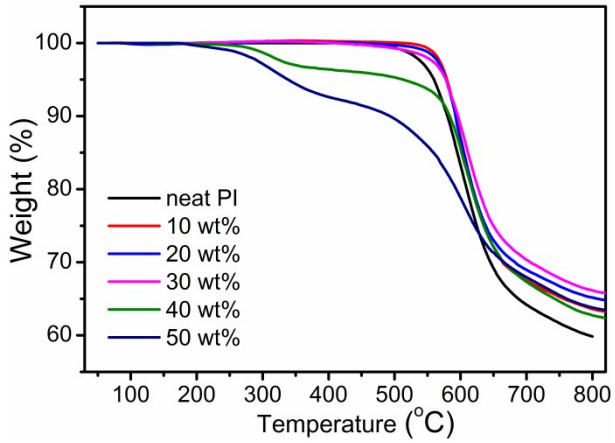

Figure S12 TGA curves of neat PI and the prepared CuPc-PI films with different content of o-CuPcA.

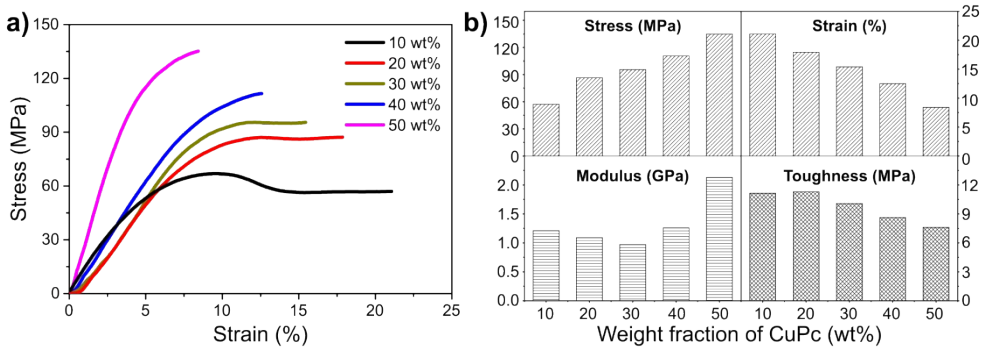

Figure S13 a) Typical stress-strain curves of the CuPc-PI films; **b)** Histogram comparison of the tensile stress, strain, elastic modulus, and toughness of the CuPc-PI films.

2.3 Thermal and mechanical property of CuPc-PI film

Good thermal stability and mechanical properties are essential for the practical application of modern flexible electronics. In this work, the prepared CuPc-PI films present an excellent thermal stability with the 5% weight loss temperature ($T_{5\%}$) of CuPc-PI (10-40 wt%) higher than 500 °C (see TGA curves shown in **Figure 12**), which is comparable to those polyimide dielectric composites using inorganic fillers.[8-10] When the content of o-CuPcA is 10-30 wt%, the 5% weight loss temperatures of the CuPc-PI films are higher than that of neat PI, which are about 580 °C. The increase is because the synthesized CuPc-PI copolymer is a highly crosslinked polymer, that it has a higher molecular weight than both oligomers and the CuPc components should be encapsulated by polyimide molecules when at a low content CuPc. When at a higher content of o-CuPcA (40-50 wt%), the $T_{5\%}$ is decreased to about 513 and 340 °C, respectively. The reason should be that the CuPc component is decomposed first when at a high content, since the CuPc has a relative low decompose temperature (~350 °C, Figure S4b). **Figure 13a** shows the typical stress-strain curves of the CuPc-PI films. It can be seen that the tensile stress of CuPc-PI increases with the increase of o-CuPcA, which is different with the decrease of mechanical strength for conventional dielectric composites using inorganic fillers.[8-10] The improved mechanical strength is attributed to the high molecular weight of CuPc-PI copolymer and the increased crosslinking degree. On the other hand, the tensile strain of CuPc-PI copolymer decreases with the increase of o-CuPcA content, attributing to the increased rigidity because of the highly crosslinked structure. The histogram comparison of tensile stress, strain, modulus, and toughness of the CuPc-PI films are displayed in **Figure 13b**.

Table S1 Dielectric constant (@ 1kHz), electrical breakdown strength, and the maximum energy storage density of the CuPc-PI films

Sample	Dielectric constant (1 kHz)	Breakdown strength (kV/mm)	Maximum energy density (J/cm^3)
neat PI	3.55	139.6	0.306
10 wt%	5.52	127.5	0.397
20 wt%	8.74	114.3	0.505
30 wt%	13.10	97.4	0.550
40 wt%	17.75	78.9	0.489
50 wt%	24.10	64.8	0.448

Movie S1. A video showing a bending test of bending the CuPc-PI (50 wt%) up to ~100 cycles to demonstrate the mechanical flexibility.

References

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