Electronic Supplementary Information

Molecular engineering of polyimide copolymer enables excellent dielectric and energy storage performance

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Experimental section

Materials

3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA), 4,4′-Oxydianiline (ODA), 5,10,15,20-tetraphenylporphyrin (TPP) and trifluoroacetic acid (TFA) were purchased from J&K Chemical Ltd. Sodium nitrite ($NaNO_2$), stannous chloride ($SnCl_2$) and tetrahydrofuran (THF) were provided by Aladdin. Zinc acetylacetonate (ZAA) was purchased from Beijing Jinming Biotechnology Co., Ltd, Beijing, China. All other chemicals and solvents were obtained from Tianjin Zhi Yuan chemical reagents, LTD, Tianjin, China. N, N-dimethyllformamide (DMF) was purified with CaH_2 and vacuum distilled, and then stored in the presence of 4 Å molecular sieves.

Synthesis of TPP-2NH_2

TPP (0.6g, 0.001mol) and $NaNO_2$ (0.55 g, 0.008 mol) were completely dissolved in 25 mL TFA under nitrogen atmosphere, and magnetically stirred at room temperature for 0.5 h to obtain homogeneous solution. After reaction of 0.5 h, 100 mL of deionized water has been added to stop the reaction and then extracted with dichloromethane and dried. The obtained powder and $SnCl_2$ (1.6 g, 0.007 mol) were added to 80 ml of concentrated hydrochloric acid under nitrogen atmosphere with 65 ℃ and magnetically stirred for 3 h. Subsequently, ammonia water was added to the solution until the pH reached 8~9. Then the powder was filtered, washed and dried. Finally, the tetraphenylporphyrin diamine (TPP-2NH_2) was obtained via column chromatography on silica gel with methanol/dichloromethane (1:100, v/v) as the eluent.

Synthesis of ZnTPP-2NH_2

The obtained TPP-2NH_2 (200 mg, 0.31 mmol) was dissolved in 60 mL of THF solution, and then ZAA (400 mg, 1.52 mmol) was added into above solution and heated to reflux for 3 h. Subsequently, the organic solvent was removed through rotary evaporation to obtain powder. Finally, the powder was dissolved in methanol overnight at low temperature, and then filtered, washed and dried to obtain zinc tetraphenylporphyrin diamine (ZnTPP-2NH_2). The synthetic route of ZnTPP-2NH_2 is shown in Figure 1A.

Preparation of the ZnTPP-PI film

The ZnTPP-PI film was prepared by the following two steps (Figure 1B). First, ODA (56.1 mg, 0.28 mmol) was completely dissolved in 3.0 g DMF. Then BPDA (164.4 mg, 0.56 mmol) was added into the DMF solution under strong mechanical stirring at 0 °C in N_2 atmosphere for 2 h to obtain homogeneous solution. Subsequently, ZnTPP-2NH_2 with the same molar ratio as ODA was added into above solution under strong mechanical stirring at 60 °C in N_2 atmosphere for 2 h to obtain the polyamic acid (PAA) solution. After that, the obtained PAA solution was coated on glass plate and dried as well as followed with imidization at 350 °C under N_2 atmosphere to obtain the ZnTPP-PI film. For comparison, the ZnTPP-PI film with different amounts of ZnTPP-2NH_2 was also prepared via the same operation processes, respectively, which were named as ZnTPP-PI-0, ZnTPP-PI-10, ZnTPP-PI-30, ZnTPP-PI-50 and ZnTPP-PI-70 according to the different contents of ZnTPP-2NH_2, respectively.

Characterizations

Chemical compositions and structures of different samples were characterized via

nuclear magnetic resonance (NMR, Bruker AVANCE 400) and Fourier transform infrared (FTIR, Bruker tensor-27). The dielectric properties of different ZnTPP-PI films were analysed by a TH-2819A precision LCR meter (Tong Hui Electronic Co., Ltd.) from 10^2 to 10^5 Hz at ambient temperature. The breakdown strength of different ZnTPP-PI films with 20×20 mm in size and thickness of 25 μm was tested using an electric breakdown strength test machine (DDJ-20 kV, China) under DC high-voltage power. The tensile test of different ZnTPP-PI films was characterized by SANS CMT8012 (Shenzhen, China) instrument. Thermal stability of different ZnTPP-PI films was measured by thermogravimetric analyzer (TGA, WRT-3P, China) with a temperature ramp of 10 °C min^{-1} under N_2 atmosphere.

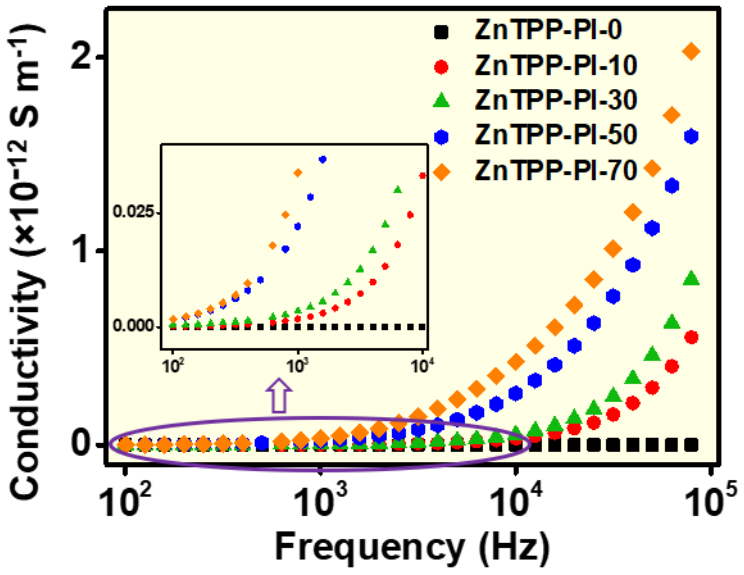

Fig. S1 Conductivity of different ZnTPP-PI films.

Table 1 Thermal stability of the different ZnTPP-PI films

Different ZnTPP-PI films	5% weight-loss temperature (°C)	10% weight-loss temperature (°C)	Char yield of 800 °C [%]
ZnTPP-PI-0	550	570	57.6
ZnTPP-PI-10	548	567	59.0
ZnTPP-PI-30	540	562	61.4
ZnTPP-PI-50	537	556	62.3