Supporting Information

Dual Cross-linking Strategy to prepare fluorine-containing poly(arylene ether nitrile) films with low dielectric constant and ultra-low water uptake

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1. Materials

4,4'-(Hexafluoroisopropylidene) diphenol (bisphenol AF, 99%), 2,2'-diallylbisphenol-A (DBA) (AR) were all purchased from Adamas-beta®. 2,6-difluorobenzonitrile (DFBN) from Shanghai Dibai Biotechnology Co., Ltd. N-Methylpyrrolidone (NMP, AR), hydrochloric acid (HCl, AR), N, N-dimethylacetamide (DMAc, AR), N, N-dimethylformamide (DMF, AR), dimethylsulfoxide (DMSO, AR), tetrahydrofuran (THF, AR), toluene (AR), chloroform ($CHCl_3$, AR), acetone (AR), and K_2CO_3 (AR) were supplied by Chengdu Kelong Chemical Co, Ltd, Chengdu, China. All the materials were used without further purification.

2. Characterization

The Fourier transform infrared (FTIR) spectra were recorded on a Thermo Fisher Nicolet Is5 with a resolution of 1.0cm^{-1} between 4000 and 400 cm^{-1} to prove the structure of PEN and PEN-E crosslinked membrane. The selected test mode is attenuated total reflectance. The proton nuclear magnetic resonance (^1H NMR) spectra were recorded with a Bruker 600 MHz spectrometer (Billerica, Massachusetts, USA) with DMSO as solvent to prove structure of DnAF-PEN. SEM samples were fractured in liquid nitrogen and then sputtered with gold on the fractured surface. The morphology of the porous crosslinked membrane was observed with a JMS-6490 LV scanning electron microscope (SEM, Japan) at 20 KV. The elemental composition of the

membrane surface was evaluated via X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). Dielectric property testing was performed on a broad frequency dielectric spectrometer Concept 50 (Novocontrol, Germany) at room temperature from 1 Hz to 10^6 Hz. The sample size for dielectric test is 20 mm in diameter and 0.050 mm in thickness in round shape. TA Instrument DSC Q100 equipment (New Castle, USA) was used for the tests of differential scanning calorimetry (DSC) under nitrogen at a flow rate of 50 mL·min^{-1} with a heating rate of 10 °C·min^{-1} from room temperature to 300°C. Thermogravimetric analysis (TGA) was carried out on a TA Instruments TGA Q50 (New Castle, USA) with a heating rate of 20 °C min^{-1} from room temperature to 800 °C under nitrogen at a flow rate of 40 mL·min^{-1}. The mechanical properties of PEN foams were obtained from a universal testing machine (SANS CMT6104, China) at a strain speed of 5 mm min^{-1} at room temperature, and the results were recorded as average values from five samples. The hydrophilicity of the membranes was evaluated by water contact angle (WCA) measurement on a Drop Shape Analysis System DSA 30 at 25°C. The gel contents of the crosslinked films were measured by Soxhlet extraction, and it can be obtained by the following formula：$Gc\%=(m_1/m_2) * 100\%$. m_1 is the mass of film fragments before Soxhlet extraction; m_2 is the mass of the film fragments after 12 hours of Soxhlet extraction and vacuum drying. The water absorption is defined by $(W-W_0)/W_0$ x 100 (%), in which W is the weight of the sample after placing in water for a certain time, and W_0 is the weight of the sample before placing in water.

3. Detailed materials for polymer synthesis

Table S1 Composition, the inherent viscosities, and GPC of DnAF-PEN copolymers.

Polymers	DFBN(mol)	DBA(mol)	BPAF(mol)	η_{inh}(dlg^{-1})	M_n	M_w/M_n
D_0AF-PEN	0.128	0	0.128	0.76	67301	1.7109
D_5AF-PEN	0.128	0.0064	0.1216	0.48	72216	2.2341
D_{10}AF-PEN	0.128	0.0128	0.1152	0.74	46195	2.0230
D_{20}AF-PEN	0.128	0.0256	0.1024	0.33	33362	2.3884

η_{inh}: inherent viscosity; GPC: gel permeation chromatography; DFBN: 2,6-Difluorobenzonitrile; DBA: 2,2'-diallylbisphenol A; BPAF: Bisphenol AF; M_n: number-average molecular weight; M_w: weight-average molecular weight.

4. D20AF-PEN-300 physical image

Fig. S1 D20AF-PEN-300 physical image

5. ^{1}H NMR spectra of D10AF-PEN

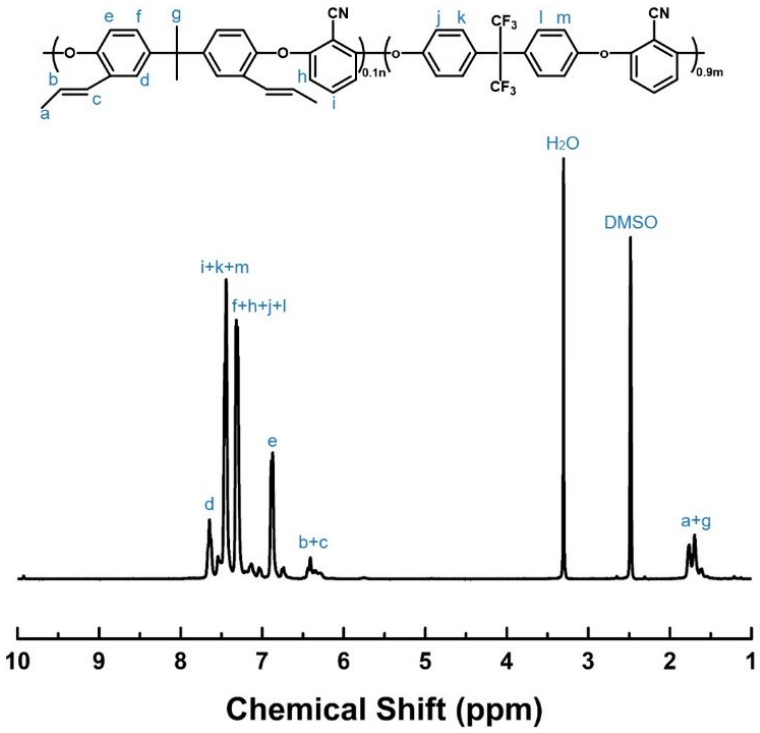

Fig. S2 ^{1}H NMR spectra of D10AF-PEN

6. FTIR spectra of D0AF-PEN-200, D0AF-PEN-280 and D20AF-PEN-280

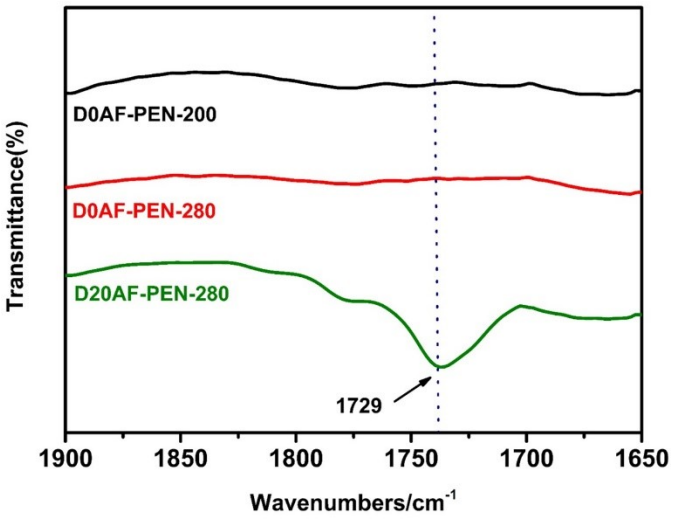

Fig. S3 FTIR spectra of D0AF-PEN-200, D0AF-PEN-280 and D20AF-PEN-280.

7. N 1s XPS of spectra of (a) D0AF-PEN-200 and (b) D0AF-PEN-280

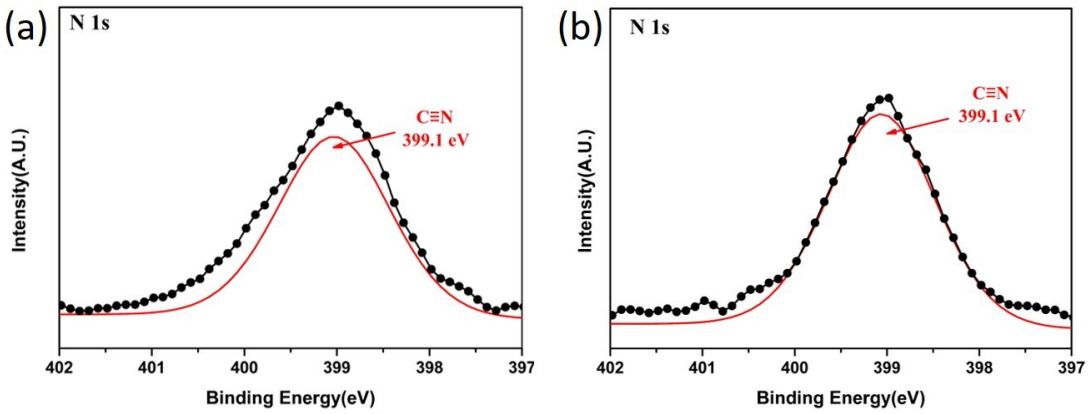

Fig. S4 N 1s XPS of spectra of (a) D0AF-PEN-200 and (b) D0AF-PEN-280

8. Solubility of the PEN films

Table S2 Solubility of the DnAF-PEN films

	NMP	DMF	DMSO	THF	$CHCl_3$	Acetone
D0AF-PEN-200	++	++	++	++	+	+
D0AF-PEN-280	++	++	+	++	+	+
D5AF-PEN-200	+	+	+	+	+	+
D5AF-PEN-280	-	-	-	-	-	-
D10AF-PEN-200	+-	+-	+-	+-	-	-
D10AF-PEN-280	-	-	-	-	-	-
D20AF-PEN-200	+-	+-	+-	+-	+-	+-
D20AF-PEN-230	+-	+-	+-	+-	-	-
D20AF-PEN-260	+-	+-	-	+-	-	-
D20AF-PEN-280	-	-	-	-	-	-

Note: "++" indicates complete dissolution at room temperature, "+" indicates complete dissolution under heating conditions, "+-" indicates partial dissolution under heating conditions, and "-" means no dissolution under heating conditions.

9. SEM

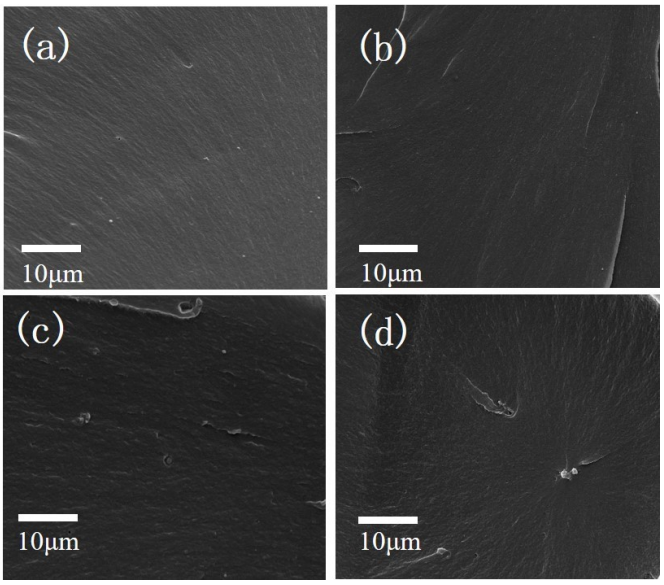

Fig. S5 SEM cross-sectional images of (a) D0AF-PEN-200, (b) D5AF-PEN-200, (c) D10AF-PEN-200, (d) D20AF-PEN-200

10. DTG curves of the D20AF-PEN films

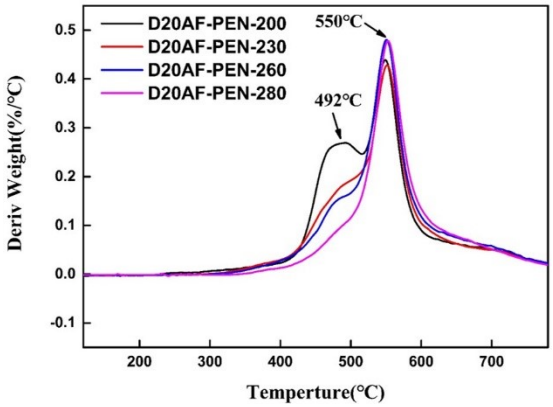

Fig. S6 DTG curves of the D20AF-PEN films

11. Conductivity of the D20AF-PEN films

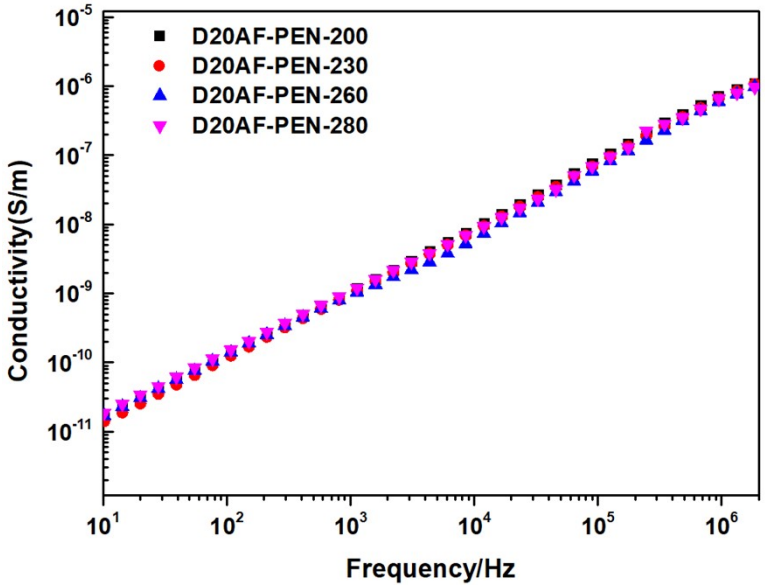

Fig. S7 Conductivity of the D20AF-PEN films

The conductivity of the D20AF-PEN film at room temperature is shown in **Fig. S7**. The conductivity does not change greatly with the increase of crosslinking temperature. It is noted that all films show good insulation at low frequencies.