

## Electronic Supplementary Information

### Additionally cross-linked organic-inorganic hybrid polybenzoxazine with a high $T_g$

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## Experimental

### Materials

Paraformaldehyde was purchased from Tianjin Kermel Chemical Reagent Co., Ltd.  $\gamma$ -Aminopropylmethyldiethoxysilane was received from Qufu Chenguang Chemical Co., Ltd. Bisphenol-A was purchased from Tianjin Guangfu Fine Chemical Institute. Chloroform, dichloromethane, and ethyl acetate were purchased from Tianjin Fuyu Fine Chemical Reagent Co., Ltd. All other reagents and solvents were obtained commercially and used as received.

### Synthesis of 6,6'-(propane-2,2-diyl)bis(3-(3-(diethoxy(methyl)silyl)propyl)-3,4-dihydro-2H-benzo[e][1,3]-oxazine) (BA-mdes)

Chloroform (20 ml),  $\gamma$ -aminopropylmethyldiethoxysilane (0.1 mol, 19.13 g) and bisphenol-A (0.05 mol, 11.41 g) were added into a 100-mL single-mouth flask fitted with a magnetic stirrer and an allihn condenser. The mixture was heated at 50 °C until a transparent solution was formed, and then a suspension of paraformaldehyde (0.2 mol, 6 g) in chloroform (10 ml) was poured into it. The mixture was then refluxed for 5 h. After cooling to room temperature, the mixture was dried by anhydrous magnesium sulfate ( $\text{MgSO}_4$ ) overnight and filtered. The solvent was removed through a rotary evaporator. The residue was chromatographed on a silica gel column (100-200) with a mixture of dichloromethane and ethyl acetate (2: 1) as the mobile phase to give pure BA-mdes as a yellowish oil. Yield: 89 %.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 6.69 (d, 2H, aromatic), 6.83 (s, 2H, aromatic), 6.94 (d, 2H, aromatic), 4.84 (s, 4H, O- $\text{CH}_2$ -N), 3.95 (s, 4H, Ar- $\text{CH}_2$ -N), 3.78 (m, 8H, Si-O- $\text{CH}_2$ - $\text{CH}_3$ ), 2.75 (t, 4H, N- $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ -Si), 1.65 (m, 4H, N- $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ -Si), 1.60 (s, 6H, C-( $\text{CH}_3$ ) $_2$ ), 1.22 (t, 12H, Si-O- $\text{CH}_2$ - $\text{CH}_3$ ), 0.64 (t, 4H, N- $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ -Si), 0.13 (s, 6H, Si- $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = -4.87, 11.25, 18.42, 21.64, 31.08, 41.63, 50.49, 54.44, 58.07, 82.46, 115.76, 119.40, 125.37, 126.12, 154.27.  $^{29}\text{Si}$  NMR (59 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = -5.51. FTIR (KBr,  $\text{cm}^{-1}$ ): 1501 (stretching of trisubstituted benzene ring), 1231 (C-O-C asymmetric stretching), 1077 (Si-O-C stretching), 1016 (C-O-C symmetric stretching), 933 (oxazine ring mode).

### Preparation of the poly(BA-mdes)

The poly(BA-mdes) was obtained in the way below. The monomers were first poured into tetrafluoroethylene mold. The sample was then thermally cured at 140 °C for 3h, 160 °C for 1h,

180 °C for 1 h, 200 °C and 220 °C for 2 h, and then post-cured at 250 °C for 1 h to obtain the polybenzoxazine.

### **Characterizations**

Fourier Transform infrared (FTIR) spectra were recorded on a Bruker Tensor 27 FTIR spectrometer (Bruker, GM) in the range of 4000 to 400 cm<sup>-1</sup>. Samples were prepared as KBr pellets.

<sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si-NMR spectra were recorded on a Bruker Avance-300 instrument (Bruker). The CDCl<sub>3</sub> was used as the deuterated solvent.

On a Bruker Avance-300 instrument, the solid-state <sup>29</sup>Si-NMR spectra were recorded.

X-ray photoelectron spectroscopy (XPS) measurements of all samples were carried out on a ESCALABXi+ XPS instrument. All of the binding energies were calibrated by the C1s peak at 284.8 eV.

Differential scanning calorimetry (DSC) thermogram was recorded with a TA DSC Q10 instrument at a heating rate of 10 °C/min under a nitrogen atmosphere.

Dynamic mechanical analysis (DMA) was performed on a Mettler-Toledo DMA/SDTA861<sup>e</sup> instrument (Mettler-Toledo, CH). A specimen with dimensions of approximately 5.0 × 5.0 × 1.0 mm<sup>3</sup> was tested in shear mode. The frequency is 1 Hz, and the sample was heated from 30 °C to 400 °C with a heating rate of 3 °C/min.

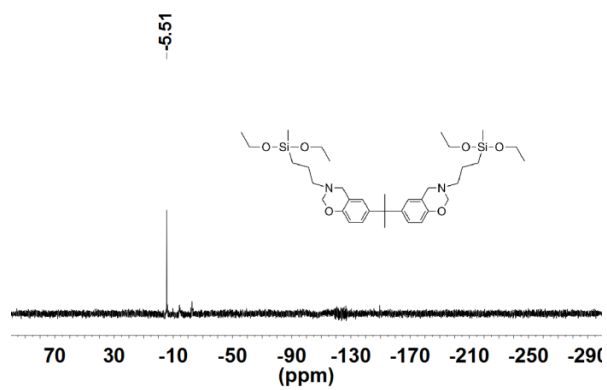
The cross-linking density of poly(BA-mdes) after cured at 220 °C and 250 °C were tested by a cross-linking density NMR analyzer (VTMR20-010V-T, NIUMAG). An average value of at least three tests was used to determine the cross-linking density of each sample. The powdered sample at room temperature was placed in a special sample tube and evaluated at 100 °C.

Thermogravimetric analysis (TGA) was performed on a TGA/DSC STAR<sup>e</sup> instrument (Mettler-Toledo, CH) from 30 °C to 800 °C under nitrogen and air atmospheres. The heating rate was 10 °C/min and the gas flow rate was 100 mL/min.

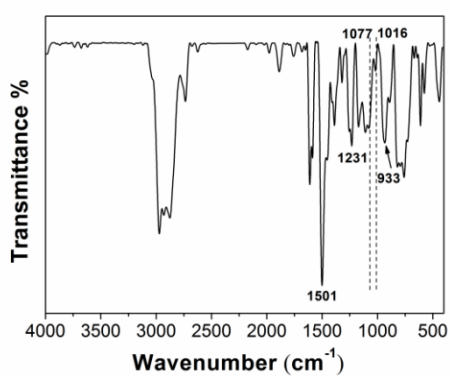
Isothermal TGA was performed on a TGA/DSC STAR<sup>e</sup> instrument (Mettler-Toledo, CH) at 260 °C for 2 h under nitrogen atmosphere. The gas flow rate was 100 mL/min.

Contact angles (CA) were recorded on a Dataphysics OCA-20 contact angle analyzer interfaced with image capture software at 25 °C after injecting a 3 μL liquid drop. Distilled water was used as the test liquid.

The dielectric property was evaluated by the impedance method using an Agilent 4263B and HP4194A impedance/Gain-Phase Analyzer at frequencies of 1 kHz, 10 kHz, 100 kHz and 1 MHz at room temperature. Both sides of the sample were sputtered with platinum to form a parallel plate capacitor.

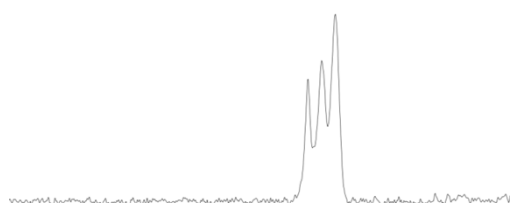


**Fig. S1**  $^{29}\text{Si}$ -NMR spectrum of BA-mdes

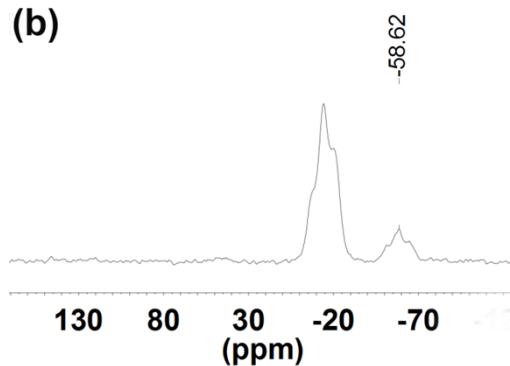


**Fig. S2** FTIR spectrum of BA-mdes

**(a)**

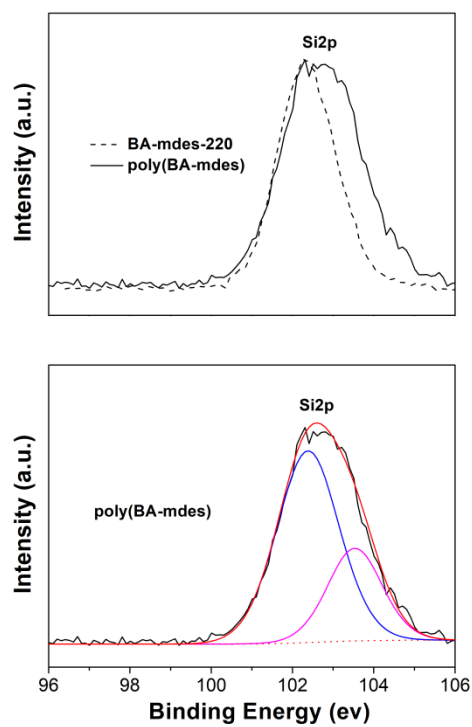


**(b)**



**Fig. S3** Solid-state  $^{29}\text{Si}$  NMR spectra of the poly(BA-mdes) samples cured at (a) 220 °C and (b)

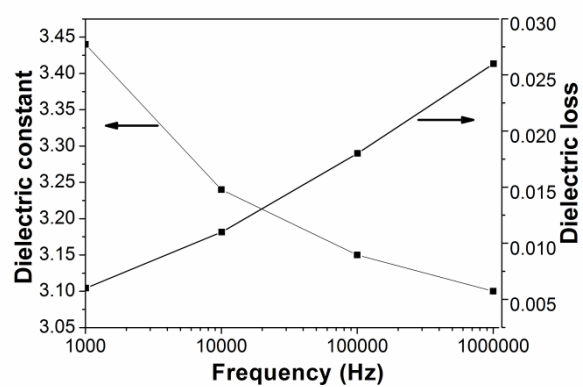
250 °C



**Fig S4** Si2p XPS spectra of BA-mdes-220 (after thermal treatment at 180 °C for 1 h, 200 °C for 2 h, and 220 °C for 2 h) and poly(BA-mdes) samples



**Fig. S5** Water contact angle of poly(BA-mdes)



**Fig. S6** Dielectric constant and dielectric loss of poly(BA-mdes)