Supporting information for:

Synthesis of novel furan-containing tetrafunctional fluorene-based benzoxazine monomer and its high performance thermoset

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Materials and methods

Materials

2,7-Dihydroxy-9-fluorenone, methylsulfonic acid, trifluoroacetic anhydride (TFA), 4-chlorobenzene, sodium borohydride, 2-hdyroxybenzaldehyde, and paraformaldehyde were obtained from Shanghai Jingchun Reagent Co., Ltd (China). Cardanol, distilled technical grade, was kindly supplied by Shandong haobo Corporation, and used as received without purification. 2-furfurylamine and all solvents were purchased from Tianjin Kermel Chemical Reagent Co., Ltd (China), and used without further purification.

Monomer synthesis

Furan-containing tetrafunctional asymmetric fluorene-based benzoxazine monomer (*t*-BF-f) with bisphenol- and diamine-type oxazine rings in single-molecule structure is prepared using two approaches. The first synthesis route is shown in Scheme S1.

The first approach is descripted as follows.

***Preparation of b*-AHF**

2,7-Dihydroxy-9-fluorenone (21.2 g, 0.10 mol), aniline (74.6 g, 0.80 mol) and methylsulfonic acid (4.80 g, 0.050 mol) were added to a 250 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, reflux condenser, thermometer and nitrogen inlet. A stream of nitrogen was introduced and the mixture was heated at 150 ^{o}C for 14 h with vigorous stirring. The water formed in the condensation reaction was retained in the flask throughout the reaction. The flask was cooled and its contents were poured into 300 mL of ethanol containing 2.0 g of sodium hydroxide. The off-white precipitated product was filtered, washed with ethanol until the effluent was colorless. The product was dried under vacuum at 100 ^{o}C for 24 h. A yellow powder was obtained (yield 86%). ^{1}H NMR (500 MHz, DMSO, ppm): 9.24 (s, 2H, –O**H**), 6.40-7.45 (m, 14H, Ar–**H**), 4.83 (s, 4H, –N**H**$_2$).

***Preparation of b*-PAHF**

b-AHF (19.0 g, 0.05 mol) and THF (200 mL) were added into a 250 mL round flask and cooled in an ice bath for 30 min. Trifluoroacetic anhydride (23.1 g, 0.11 mol) was added dropwise with stirring in 30 min. Then, the reaction mixture was stirred in the ice bath for an additional 2 h. The solvent was removed by a rotary evaporator, followed by dissolving the residue in ethyl acetate. The solution was washed five times with saturated aqueous sodium bicarbonate solution and finally three times with distilled water. The obtained solution was dried using sodium sulfate, filtered, and concentrated under vacuum. The resulted product was precipitated in 500 mL of hexanes, filtered, and dried under vacuum overnight to give the yellowish powder (yield 92%). ^{1}H NMR (500 MHz, DMSO, ppm): 11.31 (s, 2H, –N**H**–Ar), 9.44 (s, 2H, –O**H**), 6.71-7.58 (m, 14H, Ar–**H**).

***Preparation of b*-PABF-f**

b-PAHF (5.72 g, 0.01 mol), 2-furfurylamine (1.94 g, 0.02 mol), paraformaldehyde (1.20 g, 0.04 mol) and 30 mL of chlorobenzene/xylenes (1:1) were added to a 100 mL three neck round-bottomed flask equipped with a magnetic stirrer, reflux condenser, and thermometer. Firstly, the mixture was stirred at 130 ^{o}C for 4 h. After that, the mixture was cooled to room temperature and then poured into hexane. The precipitated yellowish powder was isolated by filtration and washed thoroughly with ethanol before it dried under vacuum. The crude

product was then dissolved in 100 mL of dichloromethane, followed by washing with 5 wt % of aqueous Na_2CO_3 solution and finally several times with distilled water for neutralization. The solution was dried over anhydrous sodium sulfate, followed by the evaporation of the solvent under vacuum to afford white powder (yield 83%). ^{1}H NMR (500 MHz, DMSO, ppm): 11.30 (s, 2H, –N**H**–), 6.35, 6.41 and 7.14 (m, 6H, the protons of furan ring), 6.78-7.66 (m, 10, Ar–**H**), 4.84 (s, 4H, O–C**H**$_2$–N), 4.00 (s, 4H, Ar–C**H**$_2$–N), 3.86 (s, 4H, the protons of methylene in furfurylamine).

***Preparation of b*-PAF-f**

Into a 500 mL flask *b*-PABF-f (7.11 g, 0.01 mol) was dissolved in a mixture of ethyl acetate/methanol at a ratio of 100:1, followed by addition of $NaBH_4$ (3.78 g, 0.10 mol) (6.9 g K_2CO_3, or 3.5 g $NH_3 \cdot H_2O$). The resulting mixture was stirred for 5 h at room temperature under a nitrogen atmosphere. Then, the reaction mixture was washed with brine and water. After that, ethyl acetate was removed using a rotary evaporator. The product was dried under vacuum at 60 ^{o}C for 24h (yield 71%).^{1}H NMR (500 MHz, DMSO, ppm): 6.30-7.61 (m, Ar–**H**), 4.84 (m, O–C**H**$_2$–N), 4.00 (m, Ar–C**H**$_2$–N), 3.86 (m, the methylene protons in furfurylamine), . 3.65-3.81 (m, the methylene protons in Mannich linkages).

The fllowing is the second synthesis method.

***Preparation of b*-SHF**

All the reactant including *b*-AHF (7.6 g, 0.02 mol), 2-hdyroxybenzaldehyde (4.9 g, 0.04 mol), sulfuric acid (0.2 mL) and ethanol (150 mL) were placed in a suitable flask. The mixture refluxed for 8 h and then cooled down to the room temperature. $NaBH_4$ (2.27 g, 0.06 mmol) was added to this mixture in small portions. After the reduction was completed, a 100 mL of water was added, and the resulting mixture was extracted with diethyl ether, washed with deionized water, dried over anhydrous Na_2SO_4, filtered and the solvent was removed. The resulting intermediate (*b*-SHF) was obtained as yellow-green powder with 78 % yield. ^{1}H NMR (500 MHz, DMSO, ppm): 9.45 (s, 2H, the protons of –O**H** attached with cardo ring),

9.21 (s, 2H, the protons of –O**H** in 2-hdyroxybenzaldehyde), 6.42-7.454 (m, 22H, Ar–**H**), 5.88 (s, 2H, –N**H**–Ar), 4.11 (s, 4H, –C$\mathbf{H}_2$–Ar).

Preparation of t-BF-f

2-furfurylamine (1.94 g, 0.02 mol), paraformaldehyde (1.8 g, 0.06 mol), *b*-SHF (5.92 g, 0.01 mol) and 80 mL of chloroform were added to a 150 mL three-necked round-bottomed flask. The content was refluxed for 24 h. After that, the reaction mixture was cooled and washed repeatedly with 1 N sodium hydroxide and finally washed several times using the distilled water for neutralization. The remaining chloroform solution was dried with Na_2SO_4, filtered and dried under vacuum. Yellow power was obtained in 79% yield. ^{1}H NMR (500 MHz, DMSO, ppm): 7.30, 6.29, 6.16 (m, 6H, the protons of furfuran ring), 6.35-7.16 (m, 20H, Ar–**H**), 5.38 (s, 4H, the protons of O–C$\mathbf{H}_2$–N attached with benzene ring), 4.75 (s, 4H, the protons of O–C$\mathbf{H}_2$–N attached with cardo ring), 4.56 (s, 4H, the protons of Ar–C$\mathbf{H}_2$–N attached with benzene ring), 3.98 (s, 4H, the protons of Ar–C$\mathbf{H}_2$–N attached with cardo ring), 3.80 (s, 4H, the protons of methylene in furfurylamine). ^{13}C NMR (500 MHz, DMSO, ppm): 108.70-154.52 (22C, the carbons of benzene and furan rings), 82.09 (2C, the carbons of O–**C**H_2–N attached with benzene ring), 79.10 (2C, the carbons of O–**C**H_2–N attached with fluorene ring), 63.77 (1C, the quaternary carbon in the fluorene ring), 50.33 (2C, the carbons of Ar–**C**H_2–N attached with benzene ring), 49.23 (2C, the carbons of Ar–**C**H_2–N attached with fluorene ring), 48.08 (2C, the carbons of methylene in furan ring).

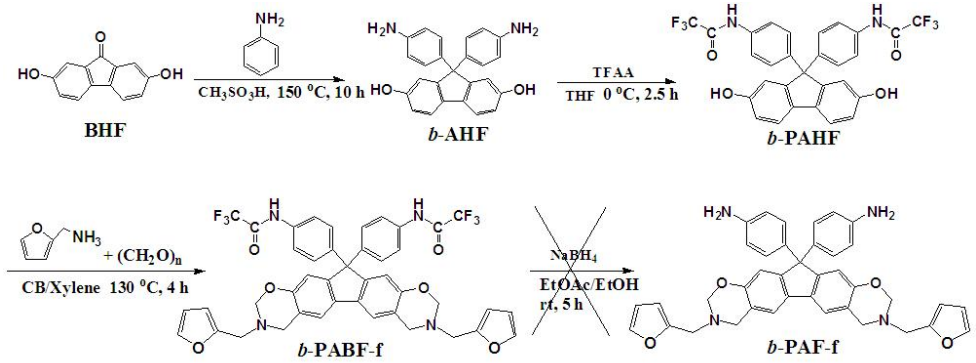
Preparation of polybenzoxazine resins

t-BF-f was polymerized without initiator or catalyst according to the followings schedule: 150 ^{o}C/2h, 180 ^{o}C/2h, 210 ^{o}C/2h, 240 ^{o}C/2h and 260 ^{o}C/3h in an air-circulating oven.

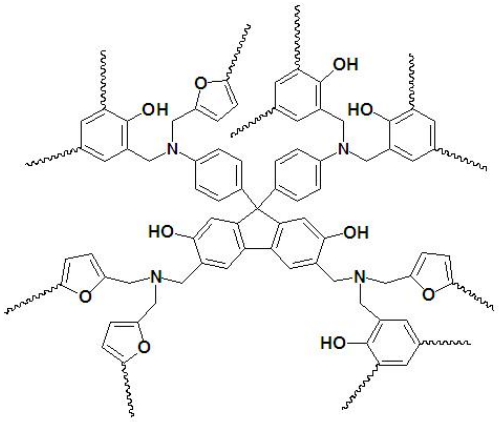
Characterization

Fourier transform infrared (FTIR) spectra were recorded by a Perkin-Elmer Spectrum 100 spectrometer in the range of 4000-650 cm^{-1}, which was equipped with a deuterated triglycine sulfate (DTGS) detector and KBr optics. Transmission spectra were obtained at a resolution of 4 cm^{-1} after averaging two scans by casting a thin film on a KBr plate for monomers and cured samples. ^{1}H NMR characterizations were performed by a Bruker AVANCE-500 NMR spectrometer using deuterated

DMSO as solvent at 25 °C. DSC measurements were evaluated by a TA Q200 differential scanning calorimeter under a 50 mL·min^{-1} constant flow of nitrogen. The instrument was calibrated with a high-purity indium standard, and α-Al_2O_3 was used as the reference material. About 5 mg of sample was put into a hermetic aluminum sample pan at 25 °C, which was then sealed and tested immediately. The dynamic scanning experiments ranged from 30 to 480 °C at a heating rate of 20 °C min^{-1}. The thermogravimetric measurements were carried out by a TA Instruments Q50 at a heating rate of 20 ºC·min^{-1} from 30 to 820 ºC under nitrogen atmosphere at a flow rate of 50 mL·min^{-1}. The dynamic mechanical thermal properties of the polybenzoxazine films were performed by a TA Q800 dynamic mechanical analyzer at a frequency of 1 Hz and amplitude of 10 μm.



Scheme S1. The first synthesis approach of *t*-BF-f.



Scheme S2. The network structure of poly(*t*-BF-f).

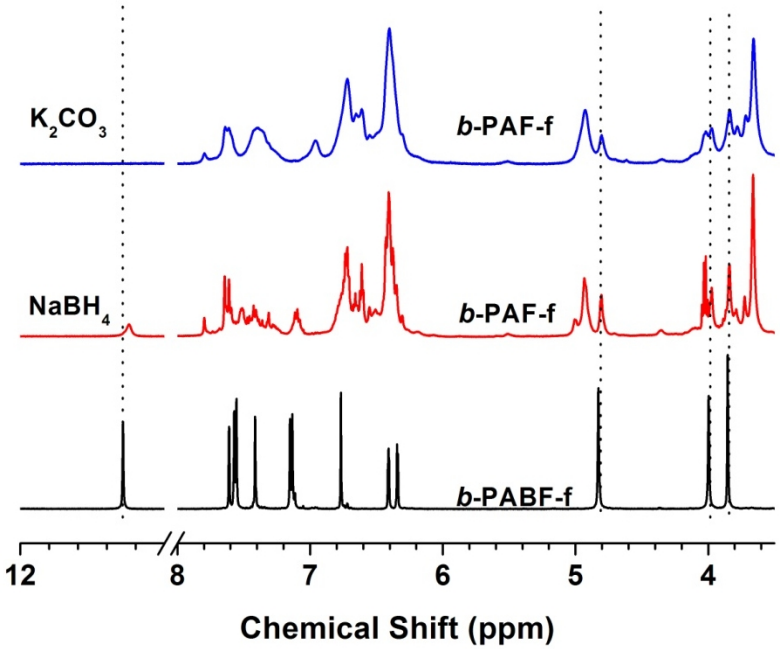


Figure S1. ^{1}H NMR spectra of *b*-PABF-f and the deprotecting samples with different deprotecting agents.

In Figure S1, the peaks at 11.24 ppm are due to the protons of CF_3CONH–. The chemical shifts at 3.81, 4.00 and 4.84 ppm are assigned to the methylenes connected with furan group and the methylenes of oxizane ring (Ar–CH_2–N and O–CH_2–N), respectively. Althrough the protons of amine located at 4.9 ppm occur after removing the protecting groups, the peak intensities of protons corresponded to O–CH_2–N and Ar–CH_2–N decrease dramaticlly. In the meantime, the peaks attributed to the ring-opening products (3.7 ppm) can be observed. Despite the protecting groups can be successfully removed during the deprotecting reaction, the oxazine ring is destroyed simutaneously. Thus, this approach is not suitable to prepare the furan-containing tetrafunctional fluorene-based benzoxazine monomer.

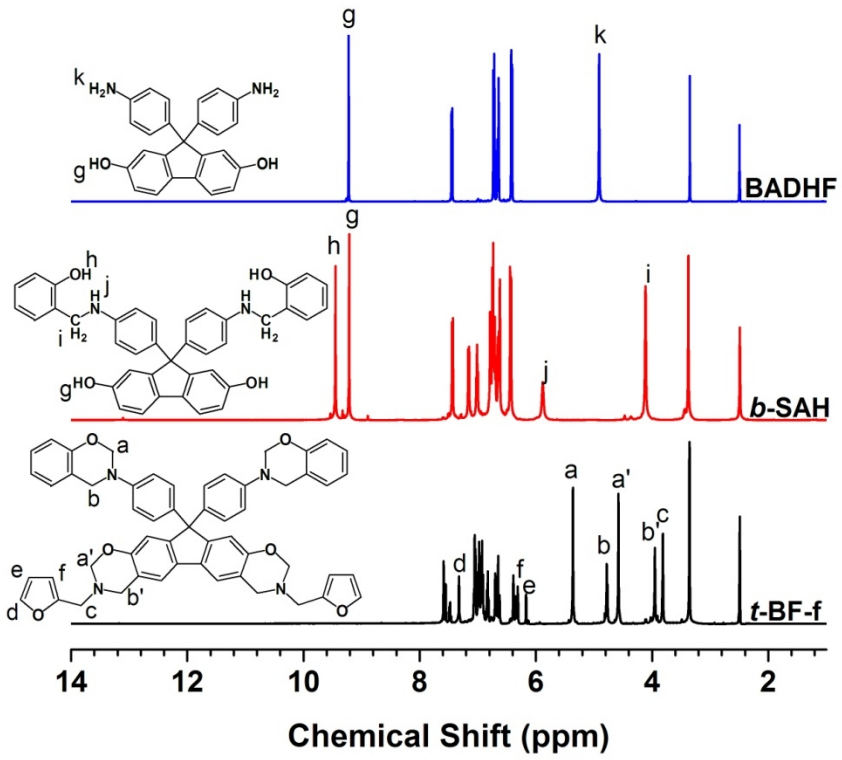


Figure S2. ^{1}H NMR spectra of *t*-BF-f and its intermediates.

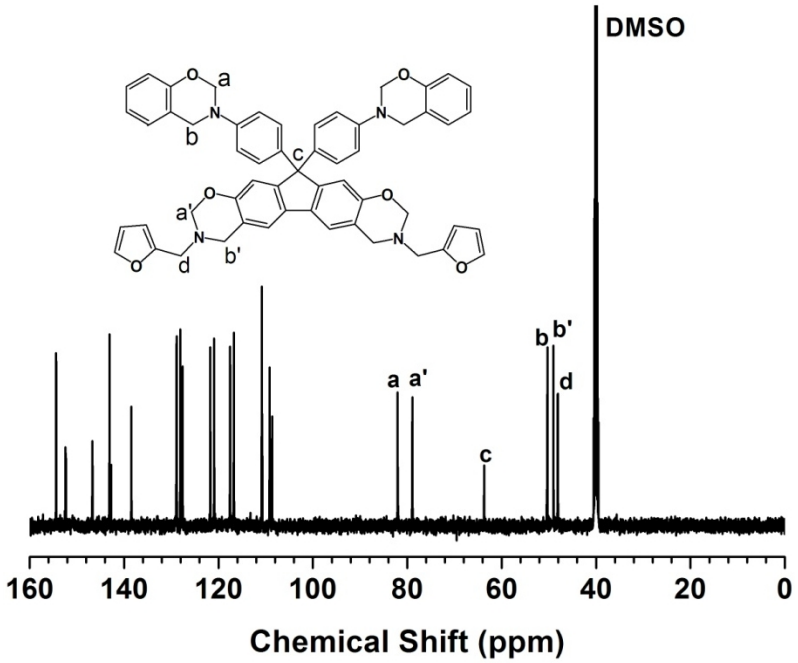


Figure S3. ^{13}C NMR spectra of *t*-BF-f.

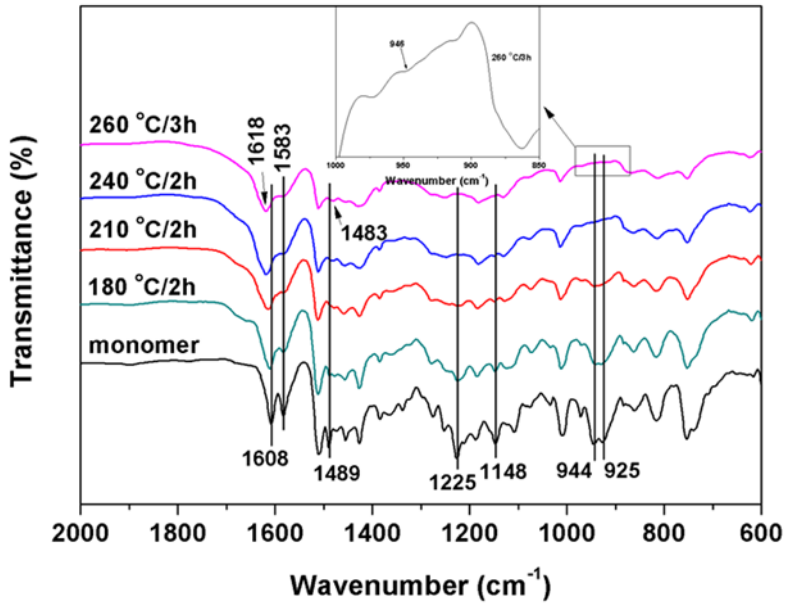


Figure S4. FTIR spectra of *t*-BF-f at each curing stage.

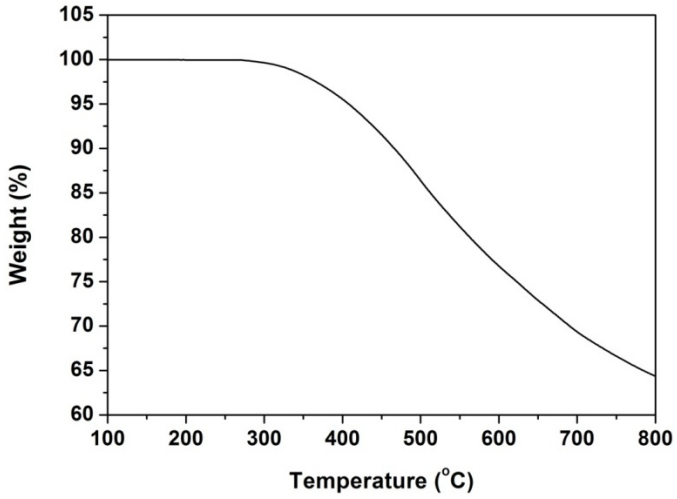


Figure S5. TGA curve of poly(*t*-BF-f) under nitrogen atmosphere.