Supporting Information

Modification of Benzoxazine with Aryl-Ether-Ether-Ketone Diphenol: Preparation and Characterization

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1. Synthesis and Characterization of Bisphenol A-aniline benzoxazine (BA-a)

1.1 **Synthesis of Bisphenol A-aniline benzoxazine (BA-a)**

To a 500 mL of flask were added sequentially toluene (100 mL), 37% formaldehyde solution (71.4 g, 0.88 mol), aniline (37.2 g, 0.4 mol) and Bisphenol-A (45.6 g, 0.2 mol). Then the mixture was slowly heated to 80 ^{o}C and hold for 5 h. When the reaction was completed, the reaction mixture was cooled and washed with 1 N aqueous solution of sodium hydroxide. Then the organic layer was washed several times with deionized water and crystallized at 5^{o}C. The precipitate product was collected by filtration and recrystallized twice from a toluene-ethanol mixed solvent. Finally, the BA-a crystal was washed with ethanol and obtained product in 78% yield.

1.2 **Characterization of Bisphenol A-aniline benzoxazine (BA-a)**

BA-a: mp. 109.2^{o}C;

^{1}H NMR (400 MHz, DMSO-d_6, δ): 7.26, 7.24, 7.22 (4H, H^{h}, t), 7.13, 7.11 (4H, H^{g}, d), 7.00 (2H, H^{b}, s), 6.90, 6.88, 6.86, 6.84 (4H, H^{f}), 6.65, 6.63 (2H, H^{i+e}), 5.41 (4H, H^{d}, s), 4.61 (4H, H^{c}, s), 1.55 (6H, H^{a}, s).

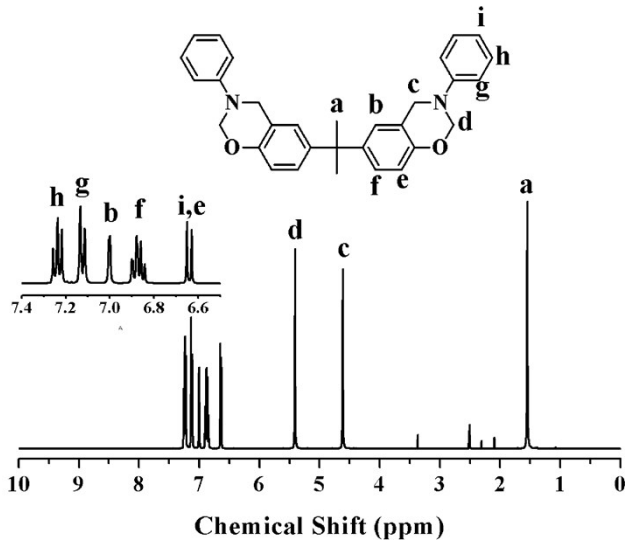

Figure S1 ^{1}H-NMR spectra of BA-a

FT-IR (KBr, cm^{-1}): 2965 (stretching vibration of CH_3); 1600 cm^{-1} (framework vibration of benzene), 1496 cm^{-1} (1,2,4-substitutation), 1232 and 1030 cm^{-1} (symmetrical stretching and asymmetrical stretching of ether), 948 cm^{-1} (benzoxazine ring).

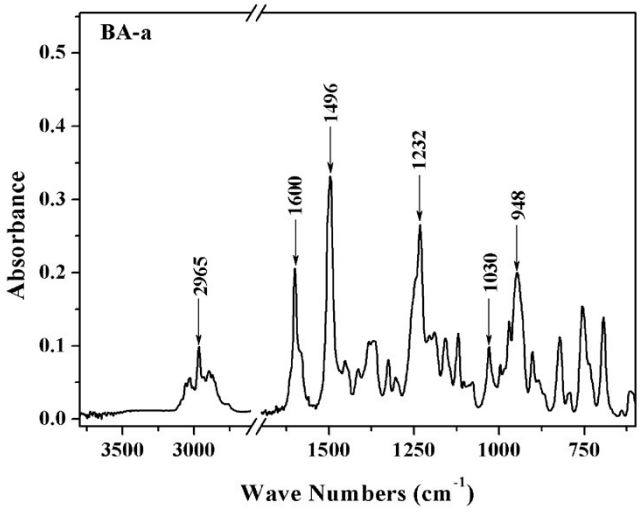

Figure SII FT-IR spectra of BA-a

2. Characterization of 4,4'-bis(m-hydroxyphenoxy) benzophenone (m-DHPBP)

^{1}H NMR (400 MHz, DMSO-d_6, $(CH_3)_4Si$, $\delta_{H,}$ ppm): 9.78 (4H, Ar-OH, s), 7.79, 7.77

(12H, H^a, d), 7.55, 7.53, 7.51 (1H, H^b, t).

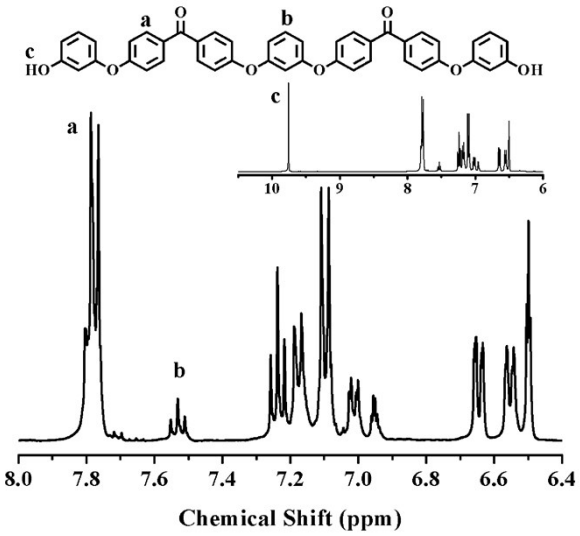

Figure SIII ^{1}H-NMR spectra of m-DHPBP

FI-TR (KBr, cm^{-1}): 3500~3200 cm^{-1} (Ar-OH symmetrical stretching), 1644 (C=O symmetrical stretching), 1590 cm^{-1} (framework vibration of benzene), 1230 and 1160 cm^{-1} (symmetrical stretching and asymmetrical stretching of ether), 770 and 677 cm^{-1} (1,3-substitutation).

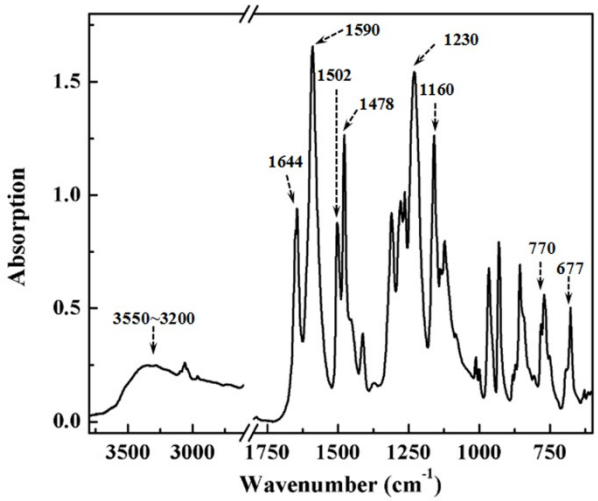

Figure SIV FT-IR spectra of m-DHPBP

Gel Permeation Chromatography (GPC): GPC experiments were performed using a Waters 2414 system, equipped with two consecutive polystyrene gel columns (Waters Styrage HR 2 DMF 7.8×300 mm and Waters Styrage HR 4 DMF 7.8×300 mm) and

refractive index (RI)) detectors, using DMF as an eluent, at a flow rate of 1.0 mL/min, calibrated with polystyrene standards. The sample concentration in each injection solution was 0.40 wt%, and the solutions were filtered through a 0.45-um filter prior to injection. DMF at 35 °C was used as the eluent. The results obtained with the RI detector were used along with a calibration curve generated using 9 polystyrene standards to calculate the M_n values for the polymers. The peak molecular weights of the polystyrene tandards were 176000, 116000, 42400, 10700, 6520, 2650, 890, 470 and 373 g·mol^{-1}. The GPC curve showed two peaks and M_ns of peak^1 and peak^2 were 3258 g/mol and 2342 g/mol, respectively.

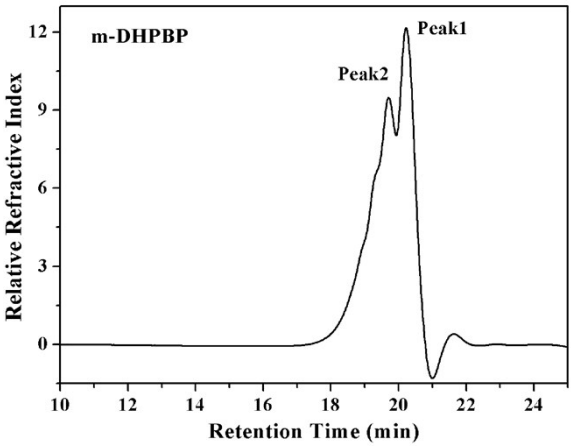

Figure SV GPC curve of m-DHPBP