

Supporting Information

A facile method to introduce phosphoester groups into polybenzoxazines backbone as multifunctional modifiers

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Chemicals

1,1,1-tris(4-hydroxyphenyl)ethane (98%) was purchased from TCI (Shanghai) Development Co., Ltd. Paraformaldehyde (95%), aniline (99%), diethyl phosphate (DEP, 99%), sodium hydroxide (99%) and Cadmium sulfate (99%) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. 1,4-dioxane (99%) was also purchased from Sinopharm and purified by distillation over calcium hydride (from Sinopharm) and stored over molecular sieves. Standard stock solutions of Cd(II) was prepared by dissolving Cadmium sulfate in deionized water.

Synthesis of tri-functionalbenzoxazine monomer TBOZ

TBOZ was prepared according to reported method⁴⁴ with a few modification. The typical procedure was as follows: Aniline (8.21 g, 0.09 mol) and paraformaldehyde (5.94 g, 0.198 mol) were mixed in 250 mL three-neck flask and stirred in ice bath for 1 h. Then 150 mL toluene, 1,1,1-Tris(4-hydroxyphenyl)ethane (9.19 g, 0.03 mol) were added into the mixture under stirring. The mixture was gently heated to 110 °C and refluxed for 10 h. Water produced during reaction was separated out by azeotropic distillation with toluene. At the end of reaction, toluene was removed by rotary evaporation and the residues were extracted with chloroform. The chloroform solution was washed with 0.5 M NaOH and distilled water successively, then dried with anhydrous Na₂SO₄ over night. After filtration the filtrate was concentrated and dropped into petroleum ether under stirring. White powder was collected and dried in vacuum at 50 °C for 48 h. (Scheme 1)

Yield: 91.6%. MP. 57-59 °C [Fig. S2]. ¹H NMR (CDCl₃, TMS, ppm): 6.64-6.93(24H, Ar-H), 4.52 (6H, Ar-CH₂-N), 5.34 (6H, O-CH₂-N), 2.04(3H, -CH₃). ¹³C NMR (DMSO-d₆, TMS, ppm):152.4 (C-O), 148.3 (C-N), 141.7 (C-O), 129.6 (CH), 128.3 (CH), 126.9 (C), 120.8 (CH), 117.6 (CH), 115.9 (CH), 50.8 (Ar-CH₂-N), 78.9 (O-CH₂-N), 49.6(C). [Fig. S1]

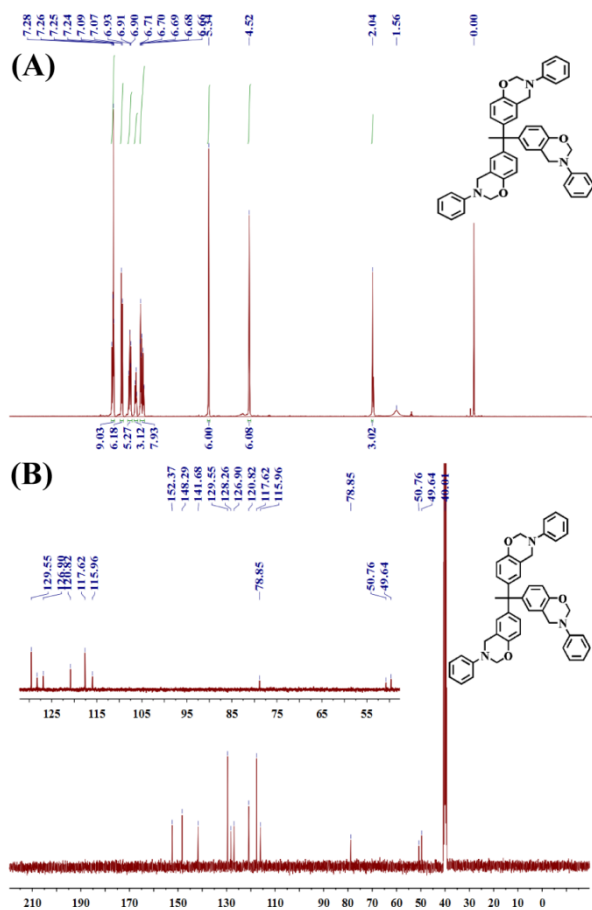


Fig. S1 (A) ^1H and (B) ^{13}C NMR spectra of TBOZ

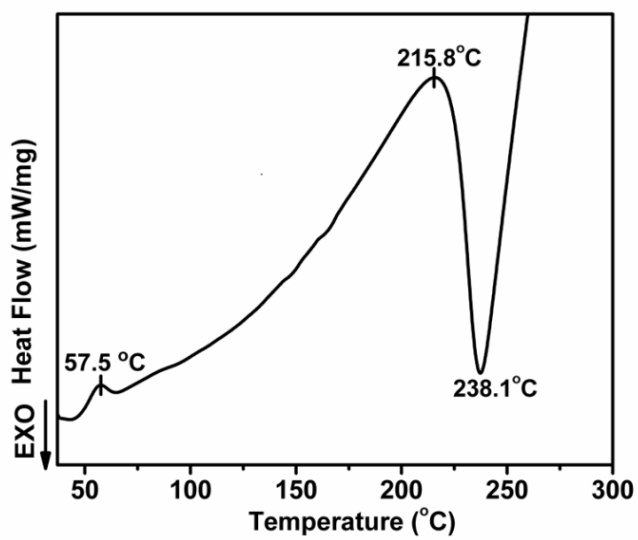


Fig. S2 DSC plot of TBOZ