

Supporting Information

Dendritic organic-inorganic hybrid polyphenol and branched benzoxazine monomers with low curing temperature

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Synthesis of T1

T1 was prepared according to the reported method³⁶ with a few modifications. A mixture of $[\text{N}_3\text{P}_3\text{Cl}_6]$ (8 g, 23 mmol), p-hydroxybenzaldehyde (20.16 g, 165 mmol) and K_2CO_3 (34.6 g, 264 mmol) in tetrahydrofuran (60 mL) was heated under reflux for 48 h. The volatile materials were removed by rotary evaporation and the residue was precipitated in hot water, the resulting white solid was filtered off and washed with large amount of hot water, a little ethanol and hexane, and dried in vacuum at 50 °C for 48 h. The crude product was recrystallized from ethyl acetate. White crystals were collected and dried in vacuum at 50 °C for 48 h. (Scheme 1)

Yield: 82%. M.P. = 160-162 °C. ¹H NMR (DMSO-d₆, TMS, ppm): 6.74-7.78 (Ar-H, 8H, m), 9.48 (CH=N, 1H, s), 8.52(CH=N, 1H, s). ¹³C NMR (DMSO-d₆, TMS, ppm): 156.8 (C-OH), 156.0 (C=N), 151.8 (C-O), 142.7 (C-N), 134.4 (CH), 131.9 (CH), 129.9 (CH), 123.1 (CH), 121.0(C), 116.1 (CH), 115.5 (CH). ³¹P NMR (DMSO-d₆, ppm): 8.75. [Fig. S1-3]

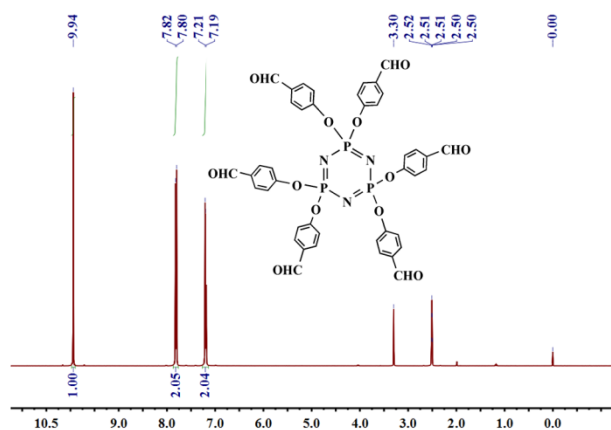


Fig. S1 ¹H NMR spectra of T1 (solvent: DMSO-d₆)

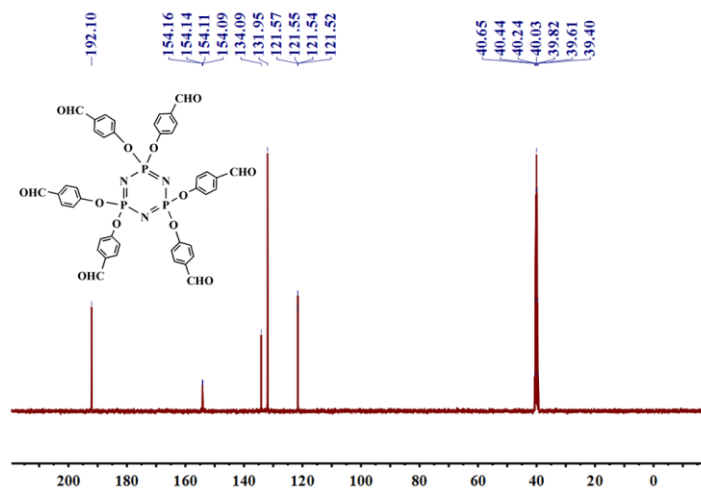


Fig. S2 ^{13}C NMR spectra of T1 (solvent: DMSO-d6)

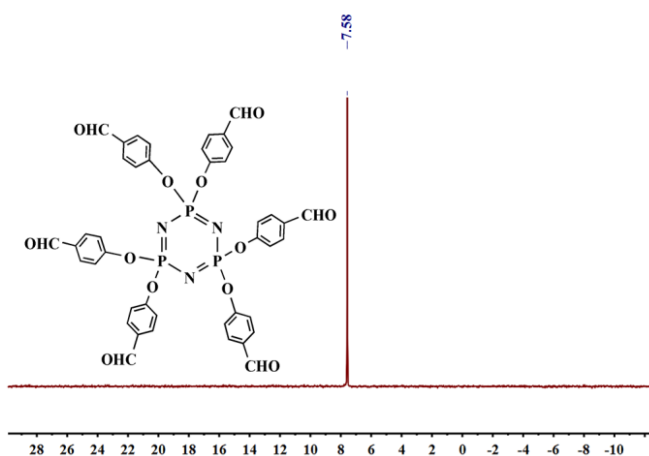


Fig. S3 ^{31}P NMR spectra of T1 (solvent: DMSO-d6)

Synthesis of dendritic polyphenol T2

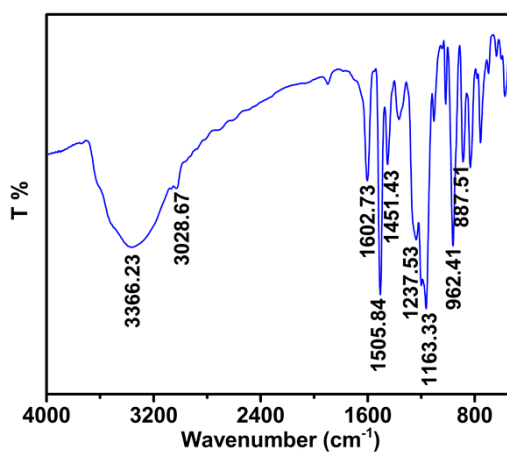


Fig. S4 FT-IR spectrum of T2

IR spectrum of T2 was shown in Fig. S4. The wide peaks around 3366.2 cm^{-1} attributed to the phenolic groups. The peaks at 1602.73 cm^{-1} , 1505.84 cm^{-1} and 1451.43 cm^{-1} ascribed to the benzene ring. The peaks at 1163.33 cm^{-1} , 887.51 cm^{-1} and 962.41 cm^{-1} were due to P=N, P-N and P-O absorption, respectively.^{34,35} These results further certified that T2 was successfully prepared.

Synthesis of branched benzoxazine monomers

Table S1 Different oxazine ring content at given time interval

reaction time(h)	integral area of protons in T3			
	ratio of O-CH ₂ -N and Ar-H protons in theoretical value	ratio of O-CH ₂ -N and Ar-H protons in experiment value	unreacted Ar- OH	oxazine ring content (%)
3	4/20	1.36/20	2.81	23.6
9	4/20	2.11/20	2.45	40.1
15	4/20	2.22/20	2.02	42.8
24	4/20	2.37/20	1.70	46.6
48	4/20	2.89/20	2.00	60.9
60	4/20	2.94/20	1.12	62.5
72	4/20	3.34/20	1.17	75.2