

## Electronic Supplementary Information

### A Novel High Temperature vinylpyridine-based Phthalonitrile Polymer with A Low Melting Point and Good Mechanical Properties

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#### Synthesis

**Synthesis of BHSP monomer.** 2,6-Bis(4-hydroxystyryl)pyridine (BHSP) was synthesized by a modified literature procedure.<sup>24,25</sup> A mixture of 2,6-dimethylpyridine (21.43 g, 0.2 mol), 4-hydroxybenzaldehyde (61.06 g, 0.5 mol) and acetic anhydride (81.67 g, 0.8 mol) was refluxed for 24 h at 140 °C under N<sub>2</sub>. Then the mixture was poured into deionized water (1 L) and stirred overnight. The suspension was suction filtrated to give gray solid which was collected and washed with plenty of distilled water to eliminate excess acetic anhydride. The mixture of collected 2,6-bis-(4-acetoxystyryl)pyridine (48.42 g) and 0.75 mol L<sup>-1</sup> of alcoholic potassium hydroxide (300 mL) was refluxed 2 h in a three-necked flask. At last, hydrochloric acid (HCl, AR, 35 wt.%) was introduced to the mixture to precipitate out golden solid, which was added to 10 % of aqueous NaOH solution (140 mL) and then acidified with acetic acid (100 mL). After filtrated and washed with distilled water, the raw product was recrystallized from ethanol to obtain golden powder of BHSP. Yield 35 %. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ(ppm): 10.15 (s, 2H, OH), 8.26 (s, 1H, Py), 7.97 (d, *J*= 16.71 Hz, 4H, Ar and CH=CH), 7.56 (d, *J*= 8.65 Hz, 4H, Ar), 7.45 (d, *J*= 16.31 Hz, 2H, CH=CH), 6.91 (d, *J*= 8.44 Hz, 4H, Ar). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ(ppm): 159.14 (C 9), 149.77 (C 3), 142.95 (C 1), 139.12 (C 5), 128.97 (C 7), 127.94 (C 4), 125.30 (C 6), 118.79 (C 2), 115.39 (C 8). Calc. for (C<sub>21</sub>H<sub>17</sub>NO<sub>2</sub>) 315.37. Mass calculated from observed ESI-MS *m/z* ratio was 316.10.

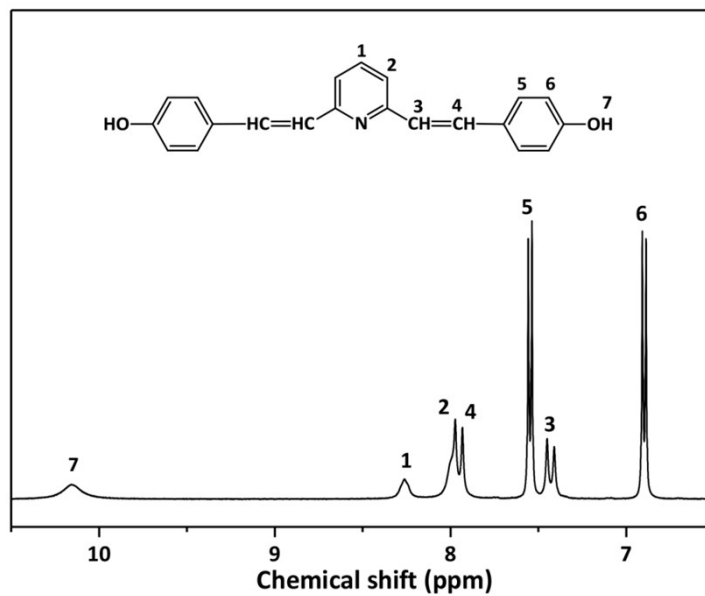


Fig. S1.  $^1\text{H}$  NMR spectrum of BHSP intermediate.

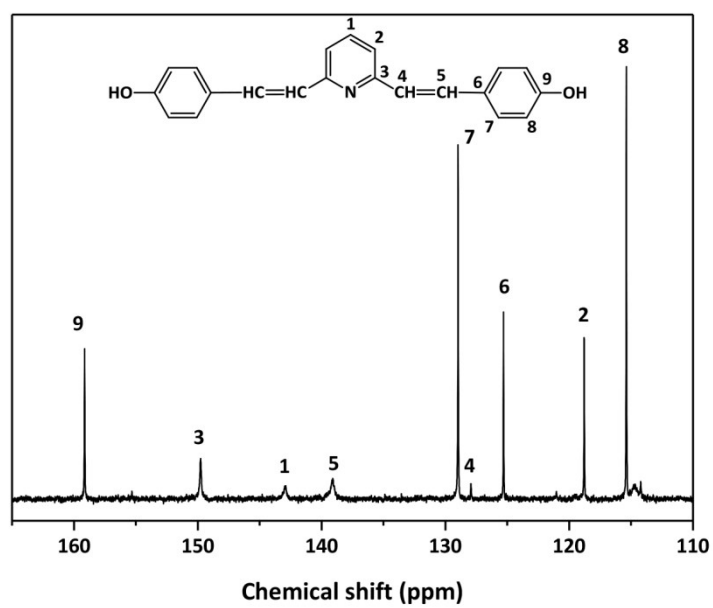


Fig. S2.  $^{13}\text{C}$  NMR spectrum of BHSP intermediate.



Fig. S3. MSI-MS spectrum of BHSP intermediate.

**Synthesis of BCSP monomer.** BHSP (20 g, 0.0635 mol) and anhydrous potassium carbonate (22 g, 0.1588 mol) were added to 100 mL of dry N,N-dimethylformamide (DMF) under a constant flow of nitrogen. The reaction mixture was stirred at 90 °C. After 2 h, 4-nitrophthalonitrile (22 g, 0.13 mol) was introduced and the reaction mixture was stirred for an additional 6 h at the same temperature. Lastly, after cooled to room temperature, the resulted brown mixture was slowly poured into 1.5 L of distilled water, and 2,6-bis[4-(3,4-dicyanophenoxy)styryl]pyridine (BCSP) monomer was deposited consequently. The precipitated solid product was collected by suction filtration, washed with plenty of deionized water, dried at 80 °C under vacuum for 48 h and then used for polymerization. Yield 90 %. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ(ppm): 8.14 (d, *J*= 8.68 Hz, 2H, Ar), 7.88–7.79 (m, 9H, Py, Ar and CH=CH), 7.48 (d, *J*= 2.40 Hz, 2H, Ar), 7.46 (d, *J*=2.79 Hz, 2H, Py), 7.38 (d, *J*= 16.22 Hz, 2H, CH=CH), 7.26 (d, *J*= 8.57 Hz, 4H, Ar). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ(ppm): 158.48 (C 10), 152.33 (C 9), 151.51 (C 3), 135.18 (C 1), 134.01 (C 12), 131.74 (C 5), 128.89 (C 6), 126.94 (C 7), 126.15 (C 4), 120.57 (C 8), 119.94 (C 2), 118.84 (C 11), 118.29 (C 15), 114.44 (C 17), 113.59 (C 16), 113.08 (C 14), 106.11 (C 13). Calc. for (C<sub>37</sub>H<sub>21</sub>N<sub>5</sub>O<sub>2</sub>) 567.59. Mass calculated from observed ESI-MS m/z ratio was 568.15.

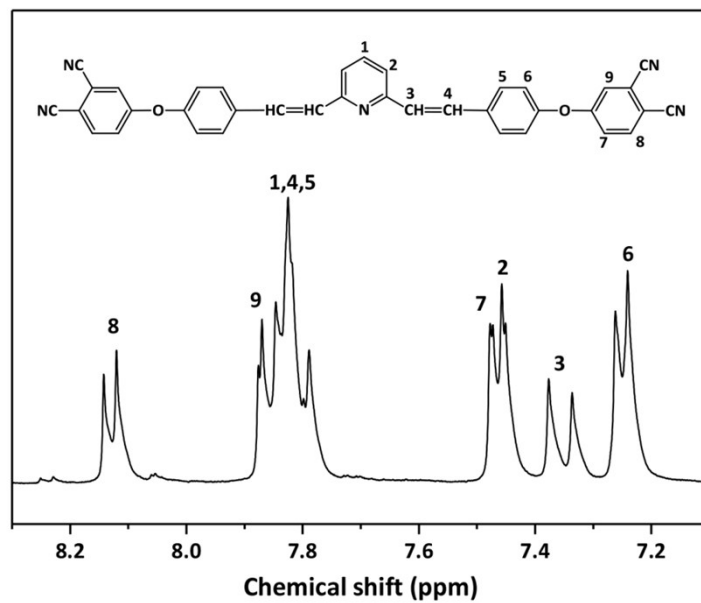


Fig. S4. <sup>1</sup>H NMR spectrum of BHP intermediate.

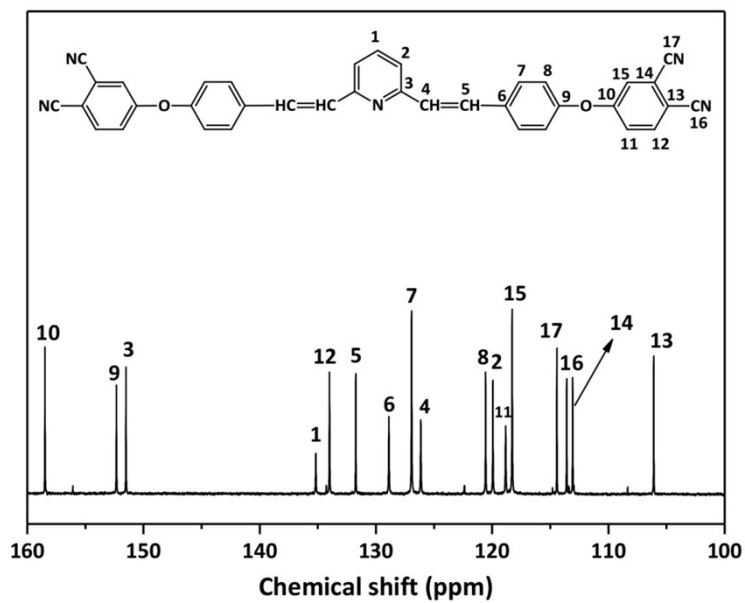


Fig. S5. <sup>13</sup>C NMR spectrum of BCBP monomer.

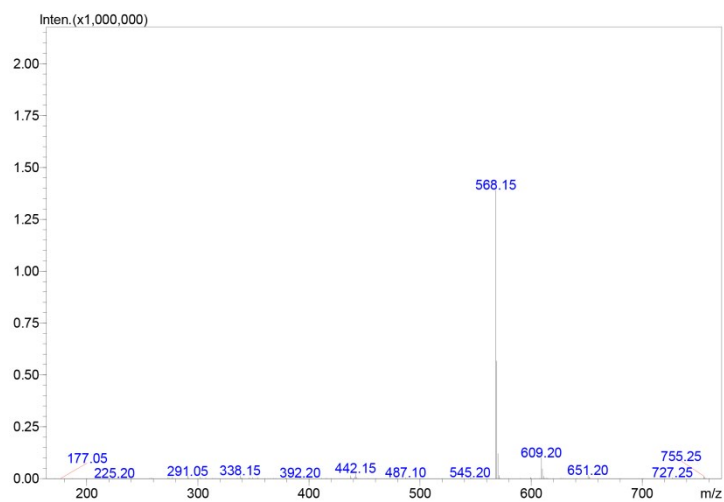


Fig. S6. MSI-MS spectrum of BCBP monomer.

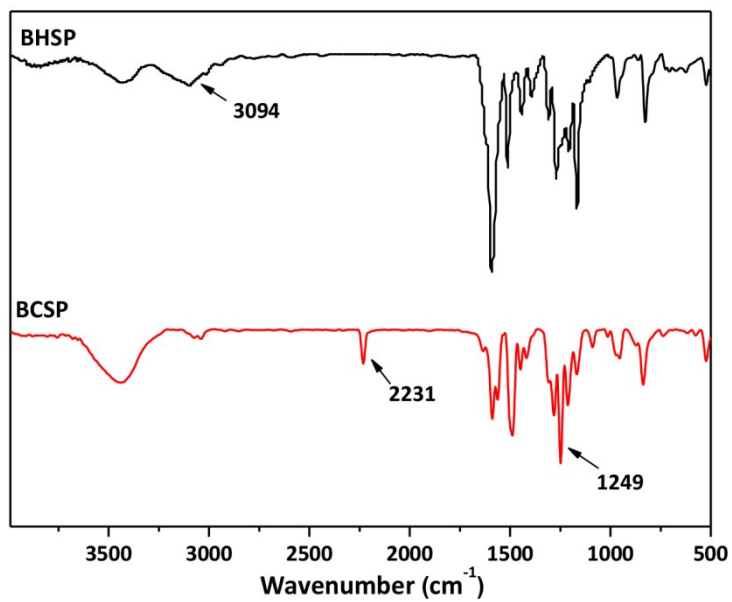


Fig. S7. FTIR spectra of intermediate BHSP, monomer BCSP.

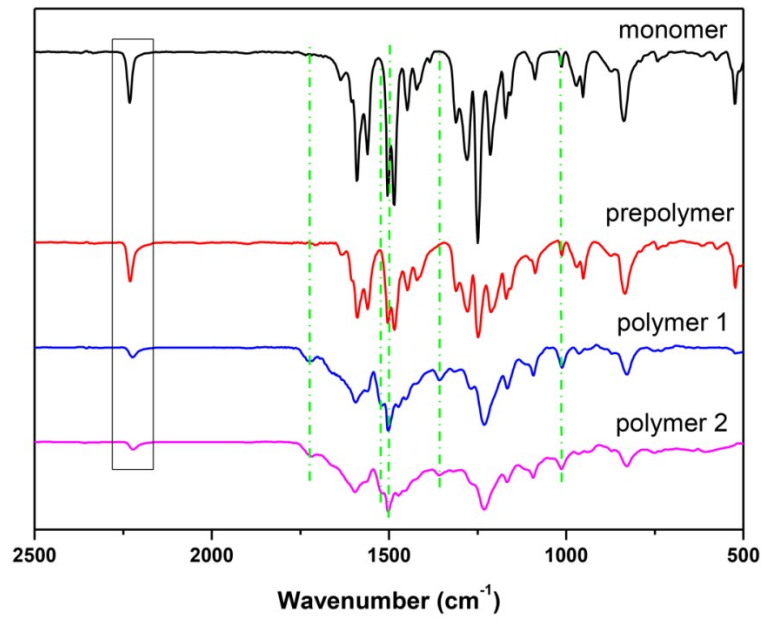


Fig. S8. FTIR spectra of monomer BCSP, prepolymer and polymers.

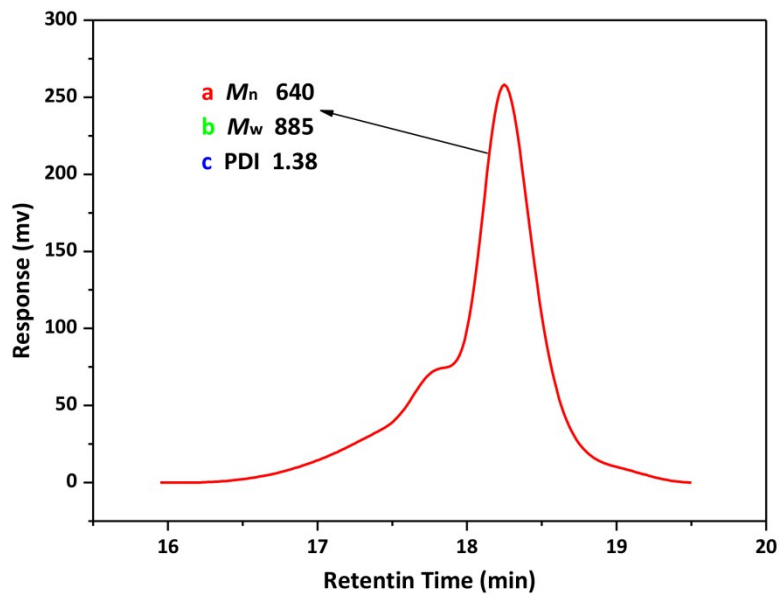


Fig. S9. GPC spectrum of BCSP proepolymer.