

## A new molecular design platform for high performance polymer from versatile bio-based tyramine: a case study on tyramine-derived phthalonitrile resin

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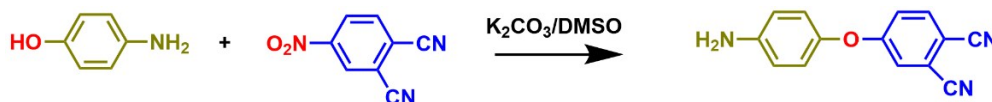
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### 1 Synthesis of PAP-CN



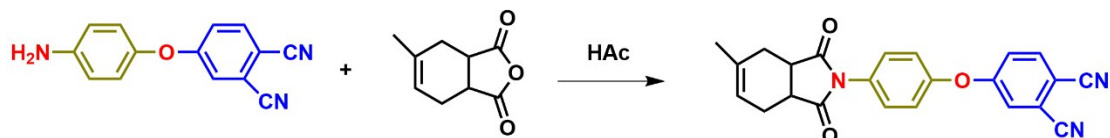
Scheme S1. The Synthesis of PAP-CN

The synthetic route of PAP-CN is shown in **scheme S1**. PAP 5.675g(0.052mol), 4-Nitrophthalonitrile 8.65g (0.05mol), 18-crown-6 0.687g (0.0026mol) and 41ml DMSO were added to a 100 ml three-necked bottle. Then the mixture was heated to 60°C, and the mixture was stirred until the raw materials are completely dissolved, then the K<sub>2</sub>CO<sub>3</sub> 7. (0.052mol) was added to the mixture to react 7h at 60°C. Then the mixture was deposited in deionized water the product was collected by suction filtration when the reaction solution was cooled to room temperature. The product was washed with deionized water and ethanol to neutrality, and then the product was dried in a vacuum oven at 80°C for 12h to obtain the PAP-CN (8.88g, 75.6%).

$^1\text{H}$  NMR (DMSO- $d_6$ , ppm)  $\delta$  8.04 (d, 1H, Ar-H), 7.62 (d, 1H, Ar-H), 7.26 (dd, 1H, Ar-H), 6.86 (d, 2H, Ar-H), 6.64 (t, 2H, Ar-H), 5.19 (s, 2H, N-H).

FTIR (KBr,  $\text{cm}^{-1}$ ): 3457 and 3351 (free state N-H), 3232 (associate state N-H), 3100-3010 ( $\text{sp}^2$  C-H), 2230 (-CN), 1253 (C-O).

## 2 The synthesis of Me-THPA -PAP-CN



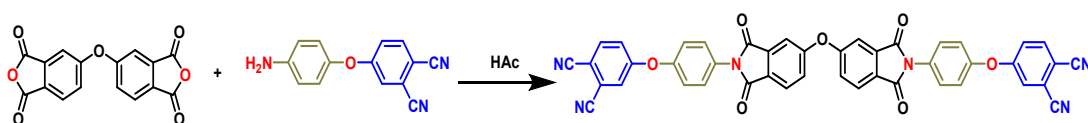
Scheme S2. The synthesis of Me-THPA-PAP-CN

The synthetic route of Me-THPA-PAP-CN is shown in **scheme S2**. PAP-CN 4.705g (0.02mol), Me-THPA 3.7g(0.024mol) and 56ml acetic acid were added to a 100 ml three-necked bottle. Then slowly heated to 116 °C for reflux, the reaction was refluxed for about 6h to terminate the reaction. Then the product was collected by suction filtration when the reaction solution was cooled to room temperature. The product was washed with deionized water and ethanol to neutrality, and then the product was dried in a vacuum oven at 80°C for 12h to obtain the ODPA-TA (7.00g, 91.4%). Elemental analysis: Cal. %: C: 72.08, H: 4.47, N: 10.98; Found %: C: 72.26, H: 4.49, N: 11.30.

$^1\text{H}$  NMR (DMSO- $d_6$ , ppm)  $\delta$  8.13 (d, 1H, Ar-H), 7.89 (d, 1H, Ar-H), 7.45 (d, 1H), 7.31 (dd, 4H, Ar-H), 5.59 (t, 1H, aliphatic C-H), 3.28 – 3.10 (m, 1H, aliphatic C-H), 2.47 – 2.15 (m, 4H, aliphatic C-H), 1.71 (d, 3H, aliphatic C-H).

FTIR (KBr,  $\text{cm}^{-1}$ ): 3094 and 3043 ( $\text{sp}^2$  C-H), 2962-2854 ( $\text{sp}^3$  C-H), 2230 (-CN), 1706 (C=O), 1380 (C-N of imide), 1253 (C-O)

## 3 The synthesis of ODPA -PAP-CN



Scheme S3. The synthesis of Me-THPA-PAP-CN

The synthetic route of ODPA- is shown in **scheme S3**. ODPA 4.14g (0.0281mol), PAP-CN 6.6g (0.105mol) and about 71.6ml acetic acid were added to a 150ml three-necked bottle. Then slowly heated to 116 °C for reflux, the reaction was refluxed for about 6h to terminate the reaction. The product is insoluble in glacial acetic acid. Then the product was collected by suction filtration when the reaction solution was cooled to room temperature. The product was washed with deionized water and ethanol to neutrality, and then the product was dried in a vacuum oven at 80°C for 12h to obtain a white product ODPA-TA (9.26g, 93.06%). Elemental analysis: Cal. %: C: 70.97, H: 2.71, N: 11.29; Found %: C: 71.31, H: 2.77, N: 11.59.

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm) δ: 8.15 (d, 1H, Ar-H), 8.1 (d, 1H, Ar-H), 7.92 (s, 1H), 7.67 (d, 1H, Ar-H), 7.63 (s, 1H, Ar-H), 7.58 (d, 2H, Ar-H), 7.49 (d, 1H, Ar-H), 7.3758 (d, 2H, Ar-H).

FTIR (KBr, cm<sup>-1</sup>): 3075 (sp<sup>2</sup> C-H), 2232 (-CN), 1778 and 1714 (C=O of imide), 1250 (C-O-C)

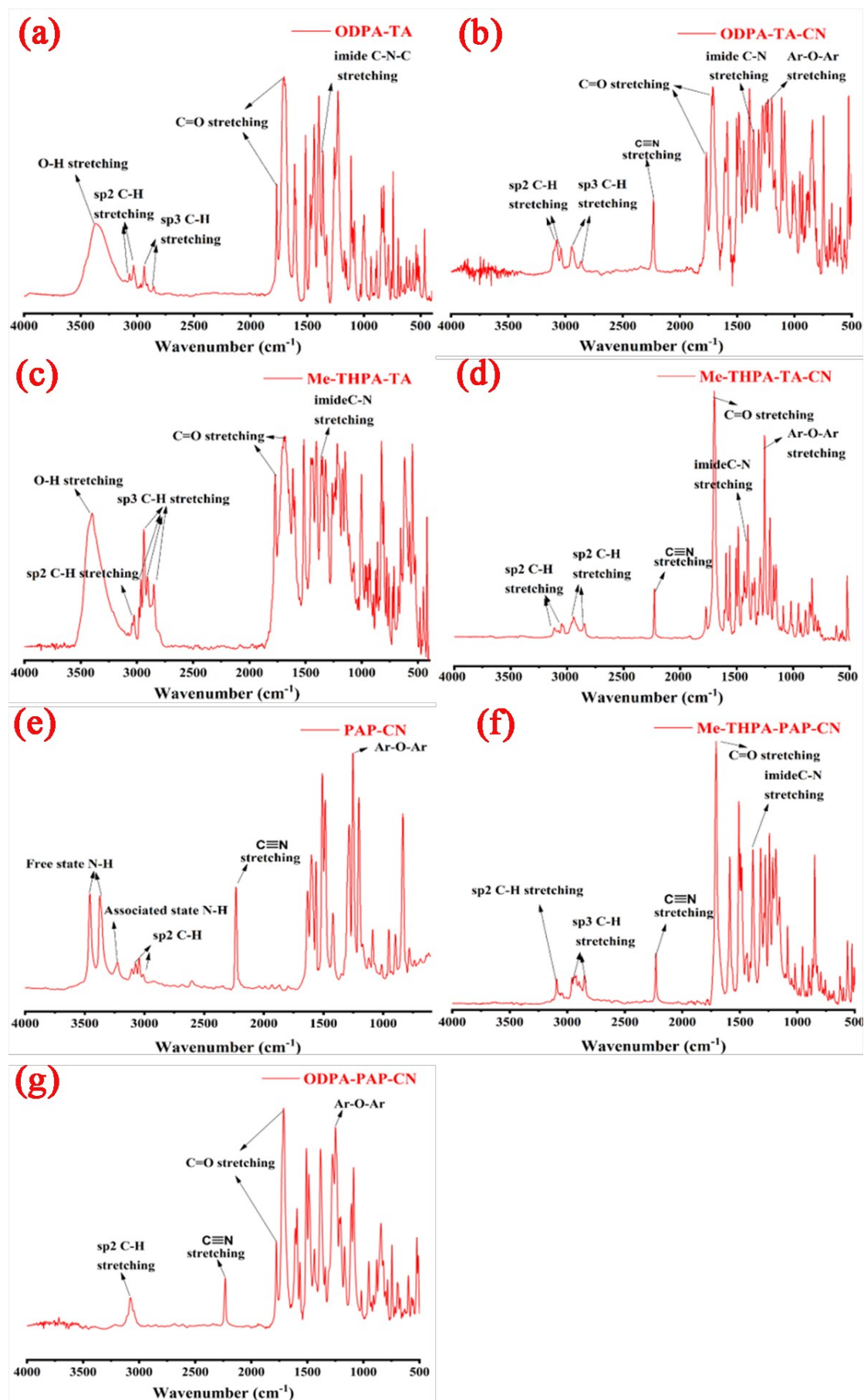


Fig. S1. FTIR spectra of monomers. (a): FTIR spectrum of ODPA-TA; (b): FTIR spectrum of ODPA-TA-CN; (C): FTIR spectrum of Me-THPA-TA; (d): FTIR spectrum of Me-THPA-TA-CN; (e): FTIR spectrum of PAP-CN; (f): FTIR spectrum of Me-THPA-PAP-CN; (g) FTIR spectrum of ODPA-PAP-CN.

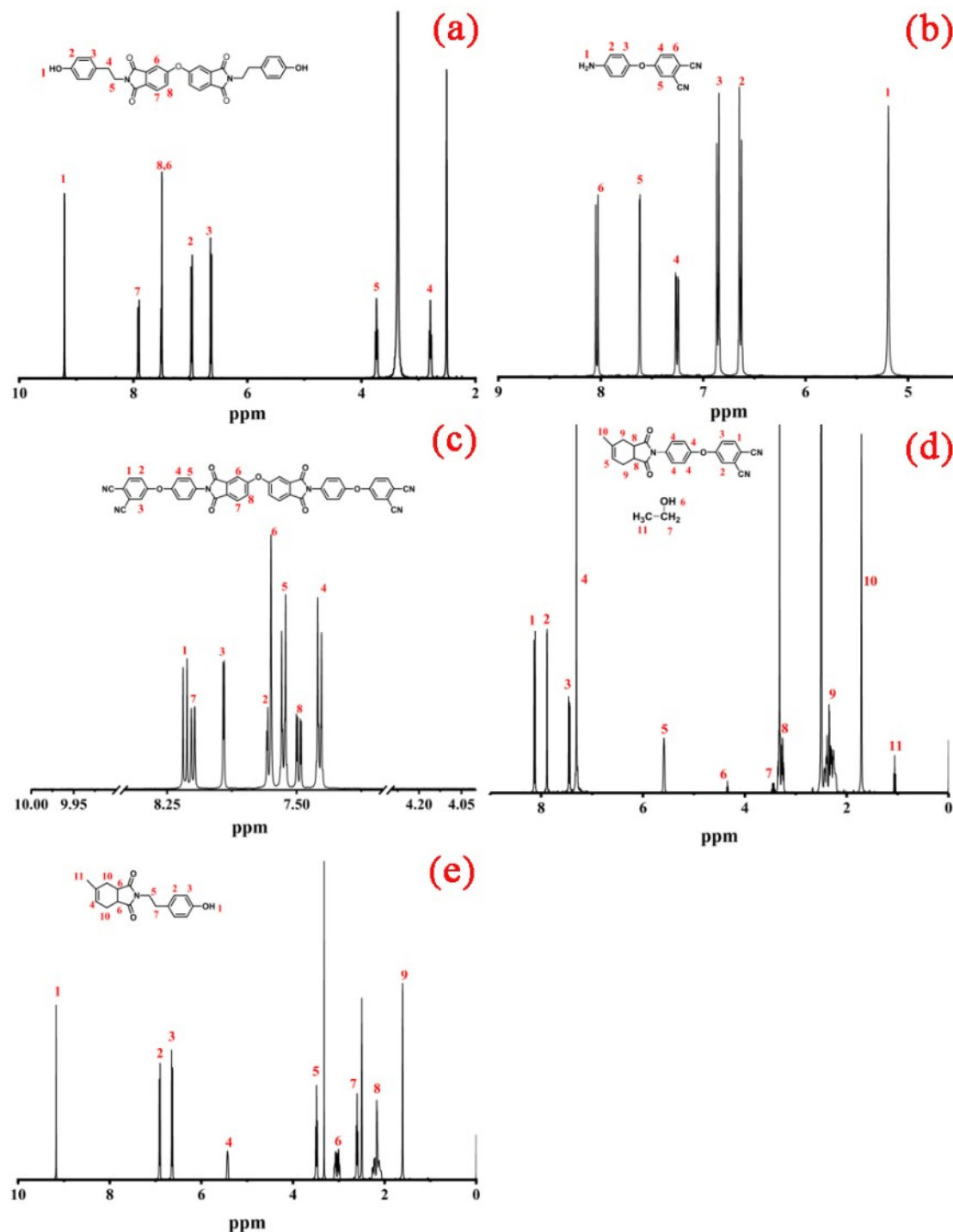


Fig. S2.  $^1\text{H}$  NMR spectra of monomers. (a):  $^1\text{H}$  NMR spectrum of ODPA-TA; (b):  $^1\text{H}$  NMR spectrum of PAP-CN; (c):  $^1\text{H}$  NMR spectrum of ODPA-PAP-CN; (d):  $^1\text{H}$  NMR spectrum of Me-THPA-PAP-CN; (e):  $^1\text{H}$  NMR spectrum of Me-THPA-TA

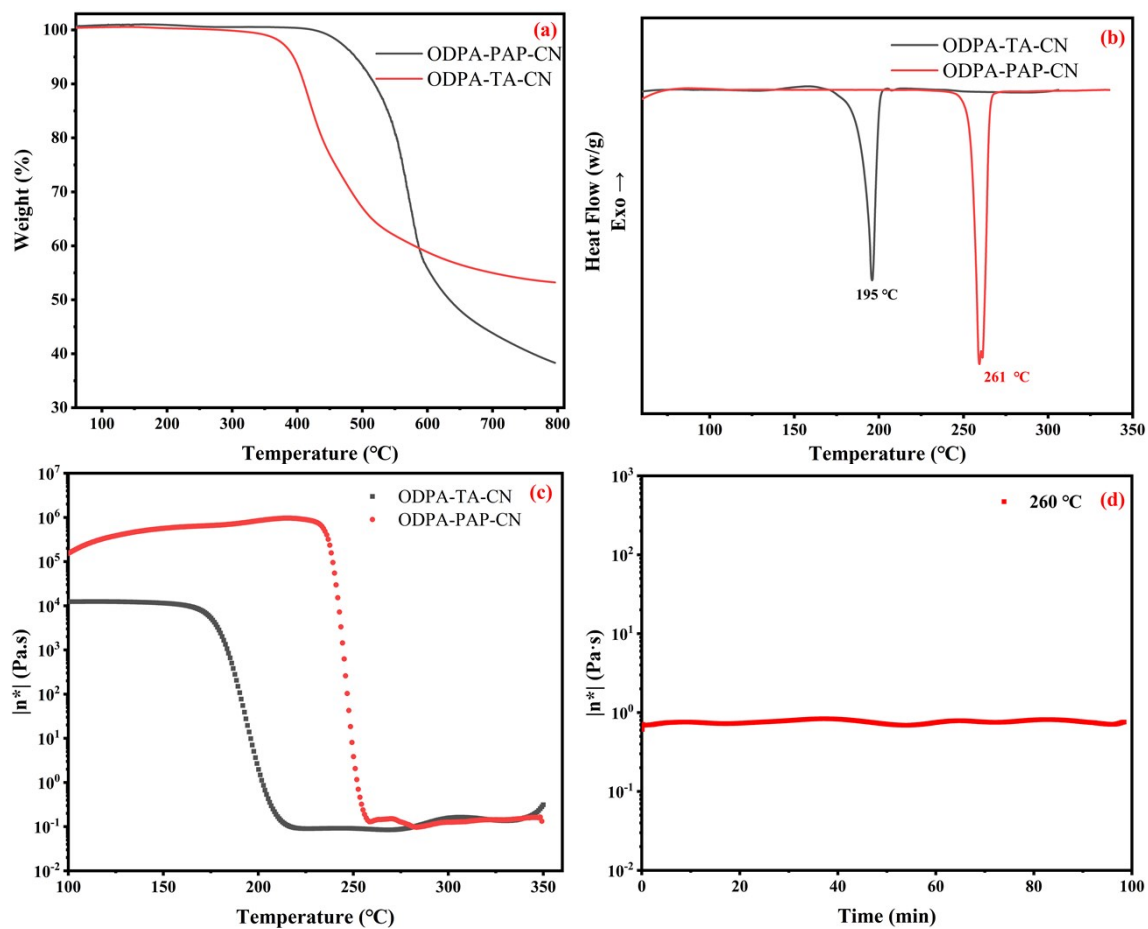


Fig. S3. (a) TGA curves of ODPA-TA-CN and ODPA-PAP-CN; (b) DSC curves of ODPA-TA-CN and ODPA-PAP-CN; (c) Complex viscosity vs. temperature curves for ODPA-TA-CN and ODPA-PAP-CN; (d) Complex viscosity vs. time curve for ODPA-TA-CN.

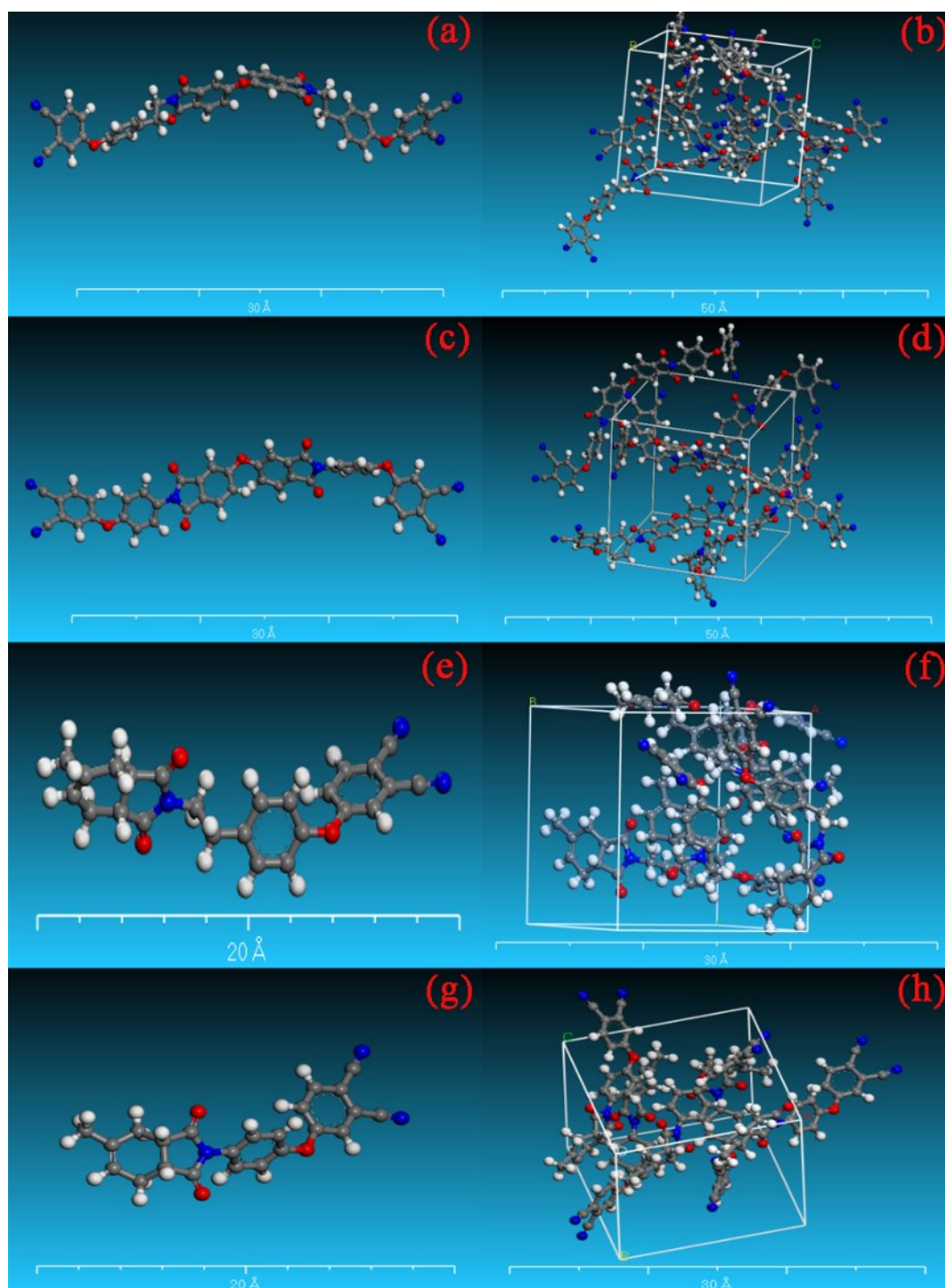


Fig. S4. Geometry-optimization spatial structure of monomers was obtained by molecular simulation. (a) Geometry-optimization molecular structure of ODPA-TA-CN; (b) Geometry-optimization packed structure of ODPA-TA-CN cell; (c) Geometry-optimization molecular structure of ODPA-PAP-CN; (d) Geometry-optimization packed structure of ODPA-PAP-CN cell; (e) Geometry-optimization molecular

structure of Me-THPA-TA-CN; (f) Geometry-optimization packed structure of Me-THPA-TA-CN cell; (g) Geometry-optimization molecular structure of Me-THPA-PAP-CN; (f) Geometry-optimization packed structure of Me-THPA-TA-CN cell;



Fig. S5. (a) and (b) were the 375 °C cured resin before DMA test; (c) and (d) were the 375 °C cured resin after DMA test



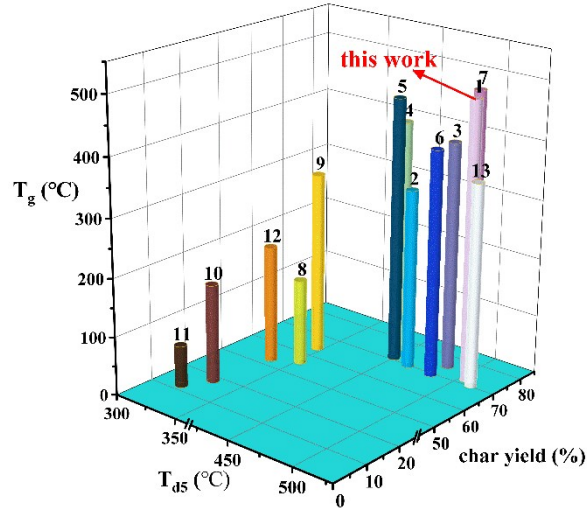


Fig. S6. A comparison of this work to recent works about thermosets. Number 1 is this work; Number 2,4,6,7(1000°C char yield) and 13(1000 °C char yield) -petroleum-based PN<sup>1-5</sup>; Number 3 and 5-bio-based PN<sup>6, 7</sup>; Number 8 and 9 (600 °C char yield)-bio-based benzoxazines<sup>8, 9</sup>; Number 10 and 11(600°C char yield)-bio-based epoxy resins<sup>10, 11</sup>; Number 12 (400 °C char yield)-bio-based cyanate esters <sup>12</sup>;

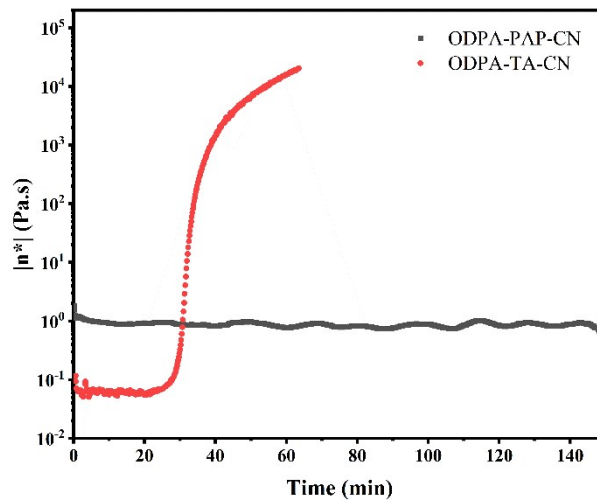


Fig. S7. Complex viscosity vs. time curve for the ODPA-TA-CN and ODPA-PAP-CN at 320 °C

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