Supporting Information for

Highly Thermostable Phthalonitrile Networks Constructed from an Unsymmetrical Bisphthalonitrile Bearing Phthalazinone Moieties

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Molecular simulation and measurement details for monomers and polymers

The molecular simulation was applied to calculate the charge density on the N atom of diamine additives. All calculations, including geometry optimizations for all diamine structures were performed with the B_3LYP exchange correlation corrected functional with the 6-311+G(d,p) basis set using the Gaussian 03W package. H H cosy NMR (400 MHz) spectrum was obtained with a Varian Unity Inova 400 spectrometer at an operating temperature of 25 °C using DMSO-d_6 as a solvent and were listed in parts per million downfield from tetramethylsilane (TMS).

Syntheses for some monomers and polymers

Procedure for polymerization of 5 with diamines (6b-6c) to prepolymers (7b-7c)

The prepolymers **7b** and **7c** were separately prepared by the reaction of **5** with diamines **6b** and **6c** (1.0 wt%) in a similar procedure as for **7a**. For synthesis of **7b,** it took about 3 minutes at temperature 250 °C to evenly disperse **6b** and the polymerization was kept at this temperature for 15 minutes. Selected data of **7b**: Yield: 97wt%. FTIR (KBr, cm^{-1}): 3452 (w, N–H), 3069 (w, Ar–H), 2891 (w, Ar–H), 2226 (m, C≡N), 1671(s, C=O), 1578 (s, C=C), 1502 (s, C=N), 1483 (s, C=C), 1445, 1401, 1352 (s, C–N)., 1252 (s, C–O), 1015. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 12.79 (s, 1H), 8.46~8.49 (d, 2H), 8.22~8.29 (m, 2H), 8.11~8.16 (m, 2H), 7.99~8.10 (m, 2H), 7.89~7.95 (m, 4H), 7.82~7.85 (m, 2H), 7.57~7.61 (m, 4H), 7.27~7.35 (m, 6H), 7.12~7.21 (m, 4H).

For synthesis of **7c,** it took about 3 minutes at temperature 250 °C to evenly disperse **6c** and the polymerization was kept at this temperature for 15 minutes. Selected data of **7c**: Yield: 97 wt%. FTIR (KBr, cm^{-1}): 3397 (w, N–H), 3046 (w, Ar–H), 2234 (m, C≡N), 1667(s, C=O), 1587 (s, C=C), 1505 (s, C=N), 1492 (s, C=C), 1465, 1397, 1345 (s, C-N), 1247 (s, C–O), 1012. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 12.94 (s, 1H), 8.31~8.41 (d, 2H), 8.28~8.32 (m, 2H), 8.11~8.23 (m, 2H), 7.98~8.10 (m, 2H), 7.92~7.99 (m, 4H), 7.86~7.90 (m, 2H), 7.67~7.71 (m, 4H), 7.45~7.63 (m, 6H), 7.09~7.21 (m, 4H).

Characterization for monomers and polymers

Characterization for monomer 4 and 5

FTIR, NMR, GC-TOF and elemental analysis were applied to determine the chemical structure of **4** and **5**.

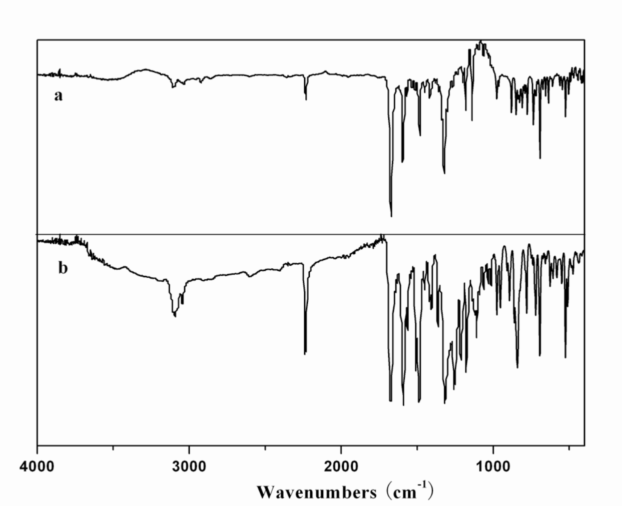

Figure S1. FTIR spectra of **4** (a) and **5** (b).

IR spectra in KBr pellet of **4** and **5** showed absorption bands around 3021 cm^{-1} and around 1764 cm^{-1} indicative of aromatic C–H stretch and C=O stretch, respectively, in addition to the sharp peak at 2222 cm^{-1}, which confirmed the presence of nitrile groups (Figure S1). Disappearance of absorptions in the range of 3200-3500 cm^{-1} indicates the complete conversion of lactam N–H groups of the phthalazinones. As shown in Figure S1a, compound **4** showed absorption bands at 2958 and 2855 cm^{-1} corresponding to the ν_{as} CH_3 and ν_s CH_3 vibrations, respectively. No absorption peak corresponding to aromatic ether linkage at around 1200-1300 cm^{-1} was observed, revealing the purity of compound **4**.

The chemical shifts and proton-proton spin coupling constants (*J*) obtained by ^{1}H NMR spectra provide helpful evidence in identifying the chemical structure of **4** and **5** (Figure S2). The characteristic peaks splitting and shifting downfield at 8.48 and 8.50 ppm, which can always be used as the reference signal to assign the other atoms, is diagnostic for the presence of *ortho*-hydrogen (H-4) of lactam in phthalazinone. As shown in Figure S2a, ^{1}H NMR spectrum of **4** shows a singlet at around 2.33 ppm assigned to hydrogen protons of CH_3 groups. As shown in a representative H-H cosy NMR spectrum of **7a** (Figure S3), the protons of nitrogen-bridged phthalonitrile appear at around 8.60, 8.35~8.39 and 8.26~8.31, whereas those of oxy-bridged phthalonitrile appear at 8.14-8.18, 7.94~7.98, and 8.26~8.31, confirming the FTIR analysis. The signals for hydrogen protons (H-1, H-2 and H-3) of nitrogen-bridged phthalonitrile appear at high frequencies, due to the deshielding effect of the electron-withdrawing phthalazinone. The NMR spectra provide powerful evidence for identifying the generation of the phthalonitrile-functional phthalazinone. The tested values by the element analysis and TOF/MS are respectively in reasonable agreement with the theoretical calculated values.

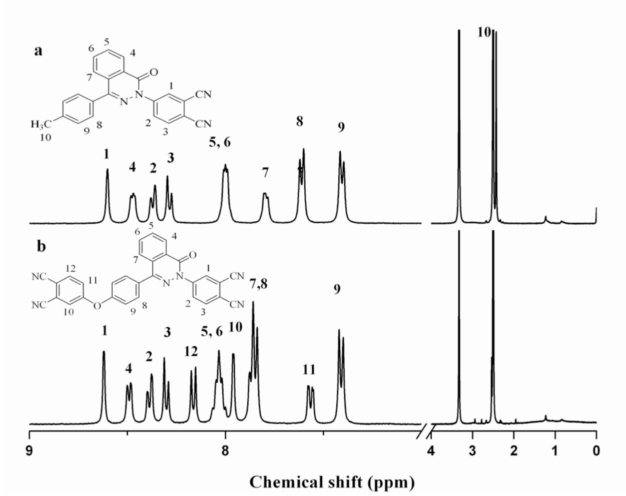

Figure S2. ^{1}H NMR spectra of **4** (a) and **5** (b).

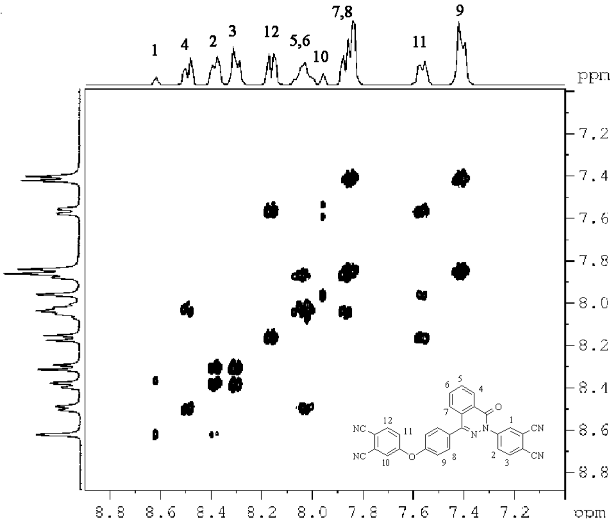

Figure S3. H-H cosy NMR spectrum of **5**.

Molecular simulation of 6a-6c

To determine the basicity of diamine additives, the molecular simulation was conducted to calculate the charge density on their N atoms. As shown in Figure S4, Figure S5 and Figure S6, calculated charge density on the N atom of 6a, 6b and 6c were 0.355, 0.364 and 0.373 ev, respectively. Therefore, the charge density of 6a according to the molecular simulation was higher than that of 6b and 6c, which is in good agreement with the basicity order concluded from GPC analysis in the main text.

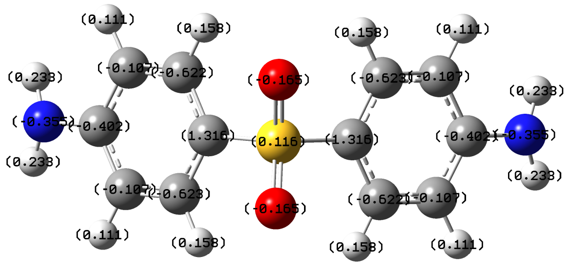

Figure S4. Mulliken analysis on charge density of **6a**.

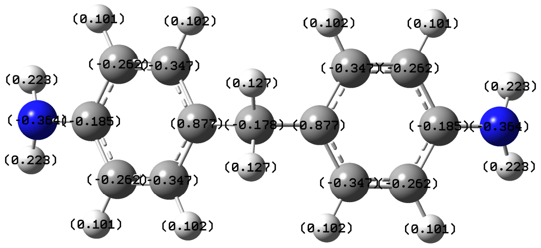

Figure S5 Mulliken analysis on charge density of **6b**.

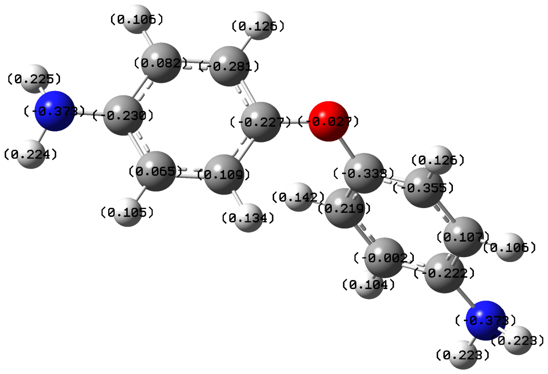

Figure S6. Mulliken analysis on charge density of **6c**.

Characterization for polymer 7a-7c and 8a-8c

The nitrile absorption of **7b** at around 2226 cm^{-1}, which is recorded to be about 69% of the origin intensity of **5**, decreases with the prolonged polymerization at 250 ^{o}C, normalized to the lactam carbonyl bands at 1771 cm^{-1}. Instead, the intensity of the absorption at 1502 attributed to C=N stretch obviously increases in the IR spectra. The emergence of small peaks around and 1352 cm^{-1} and around 1015 cm^{-1} are possibly contributed to the formation of *N*-substituted-3-iminoisoindoline units. Besides these characteristic absorptions, a weak band centered at 3452 cm^{-1} suggests the presence of N–H in the polymer chain. The N–H chain ends is also clearly identified by signals at 12.81 ppm as shown in a representative 1H NMR spectrum of 7a (Figure S7). These results also provides powerful evidence for identifying the formation of the *N*-substitued-3-iminoisoindolenine intermediate or poly(iminoisoindolenine)s. Similarly, **7c** which was obtained by the polymerization of **5** in its melt phase with the charge of a minute mount of **6c**, and with concurrent cyclization a mixture of poly(iminoisoindolenine) oligomers was produced.

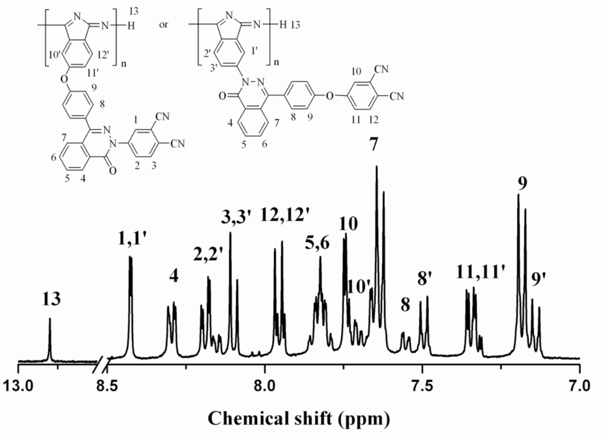

Figure S7. ^{1}H NMR spectrum of **7a** in DMSO-d_6.

In the IR spectrum of **8a** (Figure 4), the intensity of nitrile absorption is about 33% of that of **5** after thermal curing cycles, normalized to the lactam carbonyl bands. Instead, the intensity of both the absorption at 1592 cm^{-1} attributed to C=N and the absorption at 1483 cm^{-1} attributed to C–N significantly increases, indicative of the formation of triazines. Additionally, the characteristic absorption band corresponding to N–H in the range of 3400-3500 disappears, implying the completely conversation of poly(iminoisoindolenine) to s-triazine networks (Scheme 2). Similar results were also exhibited by FTIR spectra of **8b** and **8c**.

Figure S8 shows the UV-visible absorption of compound **5** and a representative **7a** in chloroform. Prepolymer **7a**-**7c**, are deep green to blue in their diluted chloroform solution with two intensive absorptions at round 667 and 704 nm in the long wave length ultraviolet region. The absorption is at a slightly longer wavelength than for the prazinoporphyrazine and phthalocyanines previously. In summary, our experimental results demonstrated that certain polymerization of phthalonitrile occurred, resulting in prepolymers, and their spectra also gave the characteristic absorption of phthalazinone-containing poly(iminoisoindolenine)s.

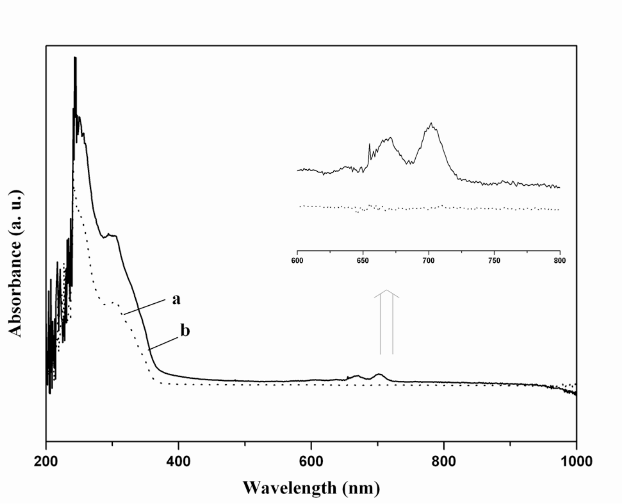

Figure S8. UV-vis spectrum of **5** (a) and **7a** (b).