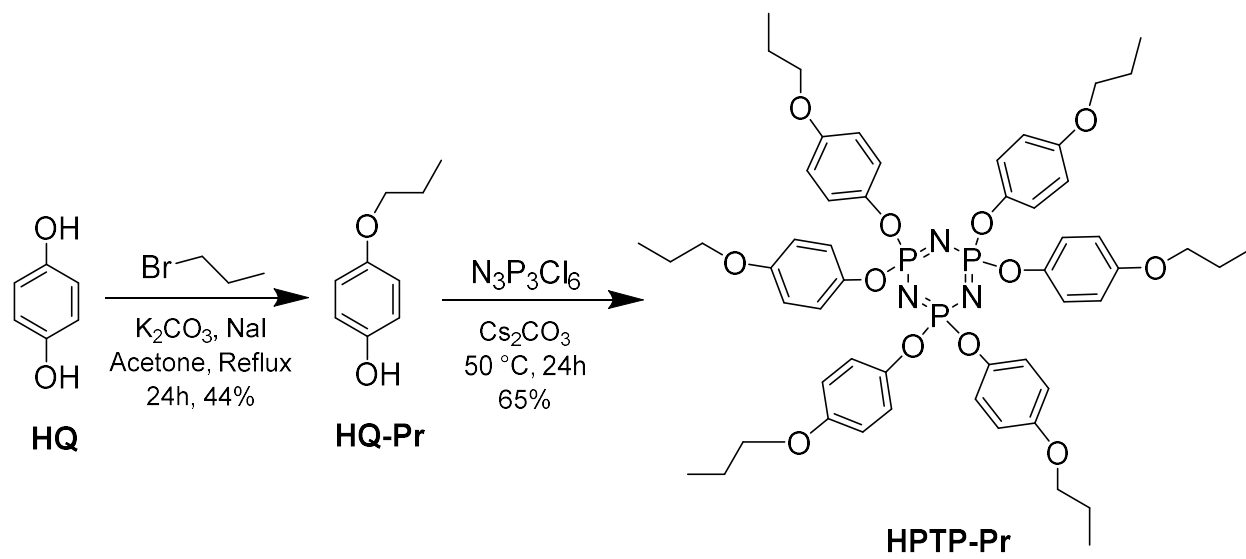


SUPPORTING INFORMATION

Annealing of Acetylene Containing Cyclotriphosphazene to Generate Nitrogen- and Phosphorus-Containing Layered Graphitic Materials

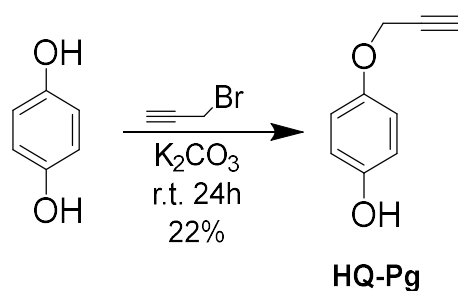
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Scheme S1: Synthesis of a **HPTP-Pr**, a reference compound without terminal acetylene

Synthesis of 4-(prop-2-yn-1-yloxy)phenol (**HQ-Pg**)^{1,2}



Hydroquinone (HQ, 10.28 g, 93.37 mmol) was dissolved in acetone (150 mL) followed by the addition of K_2CO_3 (15.42 g, 111.58 mmol) and propargyl bromide (PgBr, 80% in toluene, 10.28 mL, 93.50 mmol, 0.98 eq.) and the mixture was stirred over night at room temperature. After that, mixture was filtered, and solvent was evaporated under reduced procedure. Residue was dissolved in dichloromethane (DCM, 100 mL) and washed with water (3X50 mL) and brine (3X50 mL). Monosubstituted propargyl hydroquinone (**Hq-Pg**) was further purified by flash column chromatography using EtOAc/*n*-hexane (0 to 20%), 3.11 g, 20.96 mmol, 22% yield. ¹H NMR (300 MHz, CDCl₃) δ 6.90 (m, 2H, aromatic), 6.80 (m, 2H, aromatic), 4.66 (d, *J* = 2.4 Hz, 2H, CH₂), 4.61 (br, 1H, -OH), 2.53 (t, *J* = 2.4 Hz, 1H, ≡CH). ¹³C NMR (75 MHz, CDCl₃) δ 151.80 (C-OH), 150.34 (C-O-C), 116.56 and 115.22 (CX₄ arom), 78.94 (C≡CH), 75.57 (C≡CH), 56.87 (C-O-C_{arom}). HRMS (ESI) *m/z* calculated for C₉H₈O₂ [M+H]⁺: 148.0524, found 148.0524.

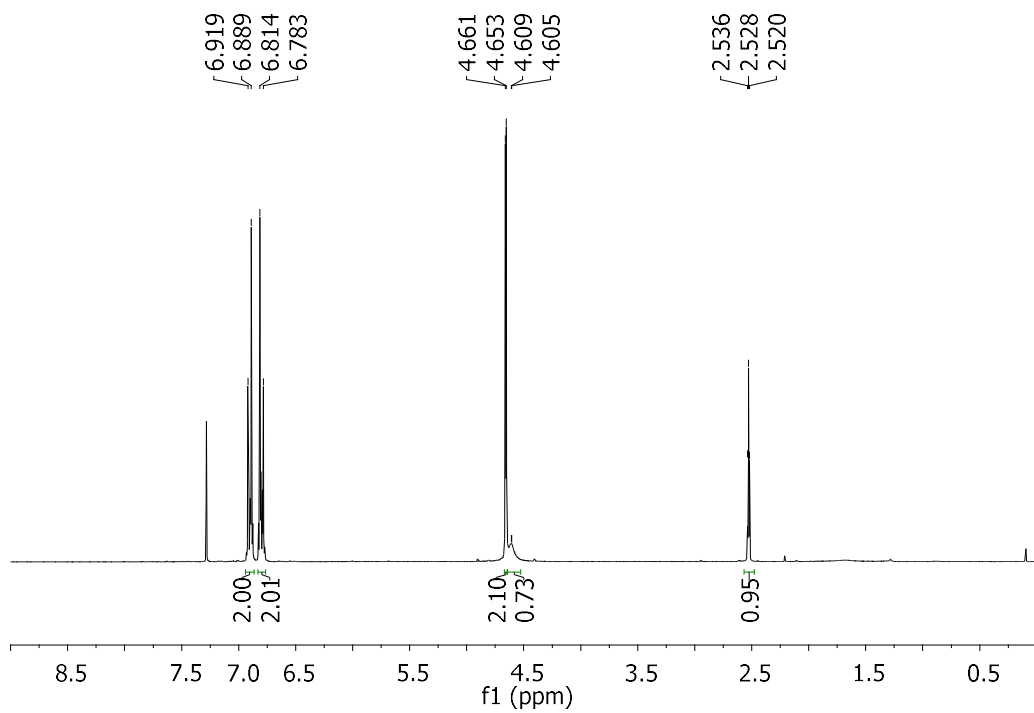


Figure S1: ¹H-NMR spectrum (300 MHz, CDCl₃) of HQ-Pg

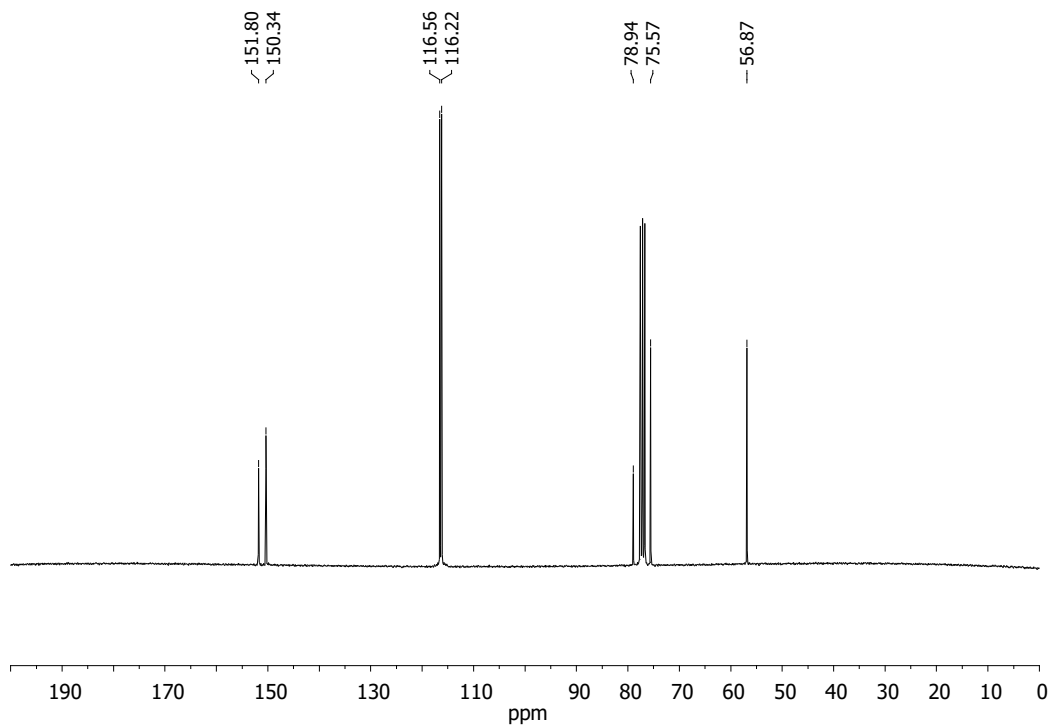
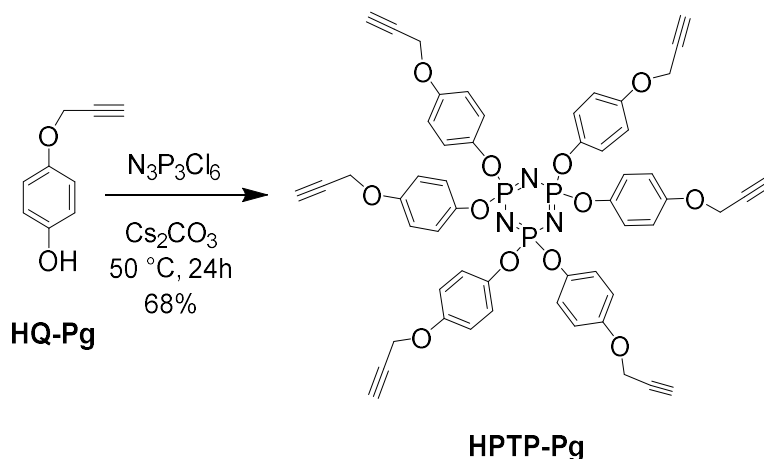


Figure S2: ¹³C-NMR spectrum (75 MHz, CDCl₃) of HQ-Pg

Synthesis of 2,2,4,4,6,6-hexakis(4-(prop-2-yn-1-yloxy)phenoxy)-1,3,5,215,415,615-triazatriphosphinine (**HPTP-Pg**)^{1, 3-8}



$N_3P_3Cl_6$ (0.99 g, 2.86 mmol) and Pg-HQ (**1**, 3.11 g, 20.96 mmol, 7.33 eq.) were dissolved in THF (150 mL) followed by the addition of CS_2CO_3 (11.11 g, 34.09 mmol). Reaction mixture was stirred over night at $50\text{ }^\circ\text{C}$. After that, the mixture was filtered, and solvent was evaporated under reduced pressure to obtain the product which was further purified by flash column chromatography using EtOAc/n-hexane (0 to 30%) to get a whitish solid (1.99 g, 1.95 mmol, 68 %). ^1H NMR (300 MHz, $CDCl_3$) δ 6.85 – 6.76 (m, 4H, aromatic), 4.65 (d, $J = 2.4$ Hz, 2H, $-CH_2$), 2.52 (t, $J = 2.4$ Hz, 1H, $\equiv CH$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.58 (C-O-C), 144.90 (C-O-P), 126.96 and 115.61 (arom), 78.61 ($C\equiv CH$), 75.87 ($C\equiv CH$), 56.27 (C-O-C_{arom}). ^{31}P NMR (122 MHz, $CDCl_3$) δ 9.82 (s). HRMS (ESI) m/z calculated for $C_{54}H_{42}N_3O_{12}P_3$ $[M+H]^+$: 1018.2059, found 1018.2059.

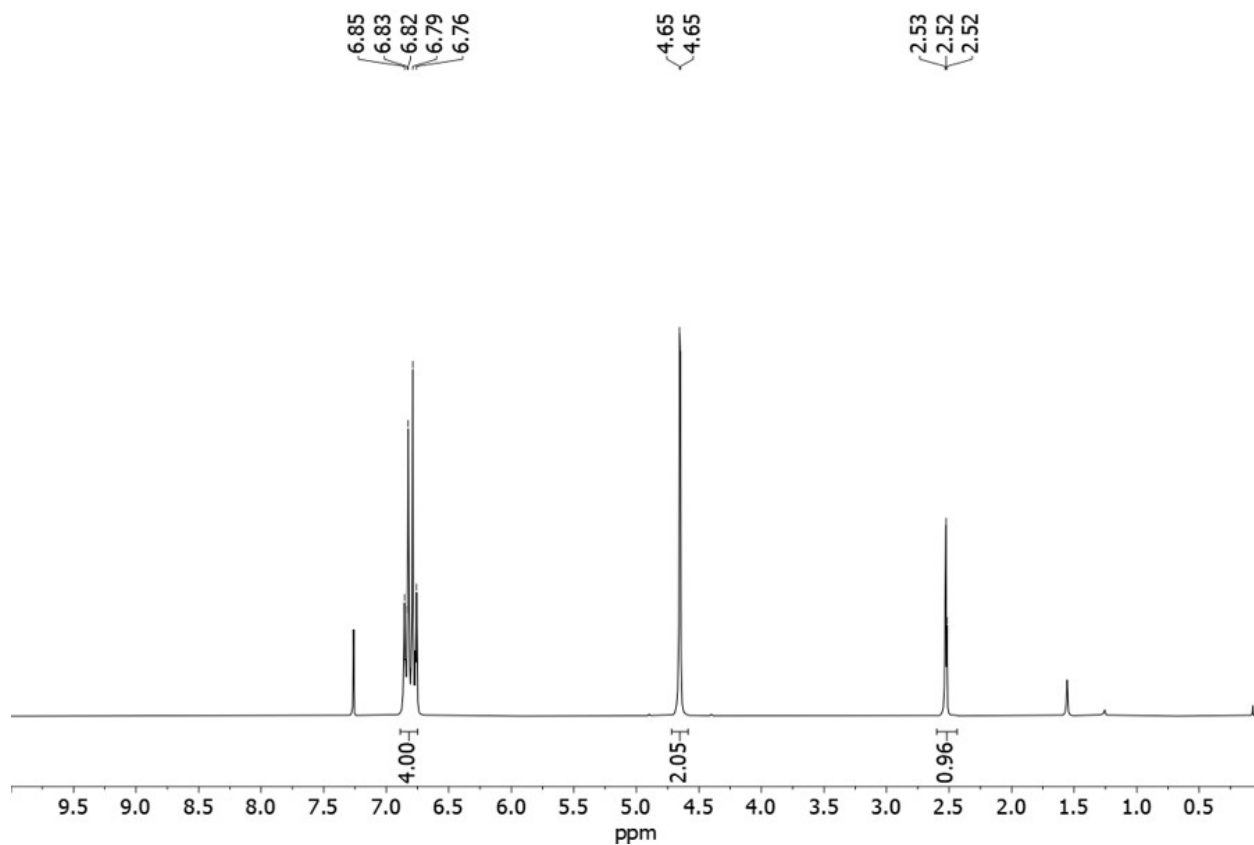


Figure S3: ^1H -NMR spectrum (300 MHz, CDCl_3) of **HPTP-Pg**

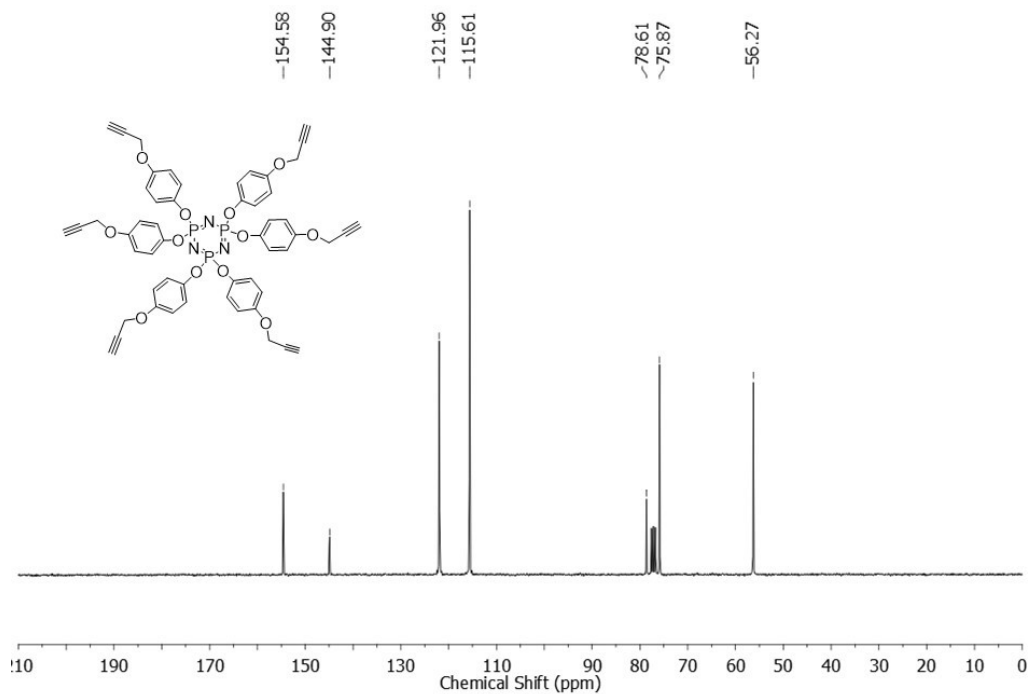


Figure S4: ^{13}C -NMR spectrum (75 MHz, CDCl_3) of **HPTP-Pg**

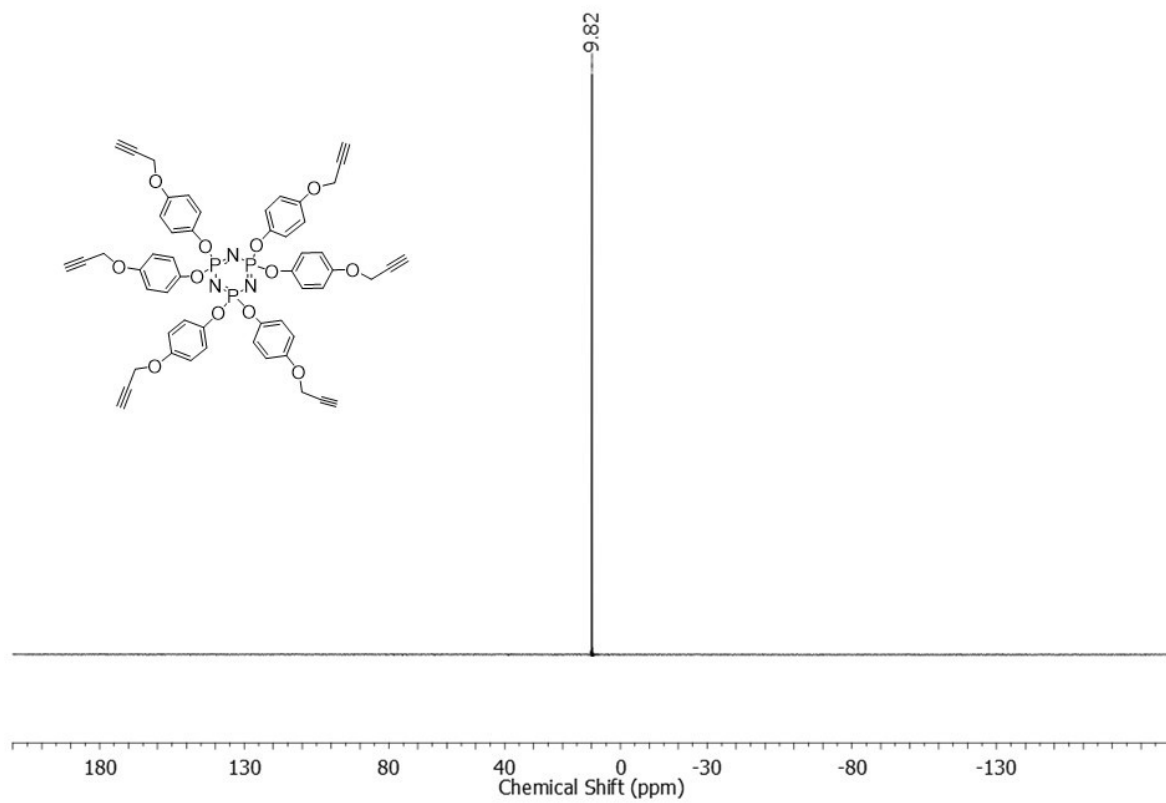
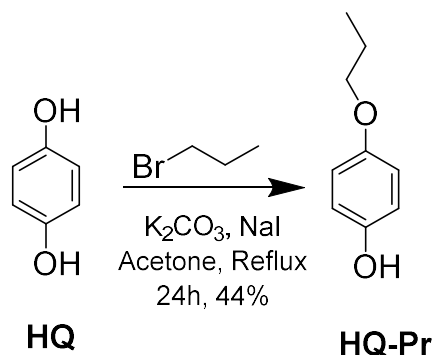


Figure S5: ^{31}P -NMR spectrum (122 MHz, CDCl_3) of **HPTP-Pg**

Synthesis of 4-propoxyphenol (**HQ-Pr**)



Hydroquinone (HQ, 10 g, 90.82 mmol) was dissolved in acetone (50 mL) followed by the addition of K₂CO₃ (62.5 g, 452.23 mmol, 5 eq.), NaI (53 g, 353.59 mmol, 3.9 eq.) and 1-bromo propane (14.5 g, 117.89 mmol, 1.3 eq.) and the mixture was refluxed for 24h. After that, mixture was filtered, and solvent was evaporated under reduced procedure. Residue was dissolved in dichloromethane (DCM, 50 mL) and washed with water (3X50 mL) and brine (3X50 mL). Monosubstituted product (**HQ-Pr**) was further purified by flash column chromatography using EtOAc/*n*-hexane (0 to 20%), 6.1 g, 40.08 mmol, 44%. ¹H NMR (300 MHz, CDCl₃) δ 6.78-6.76 (m, 4H, arom.), 4.42 (br, 1H, -OH), 3.86 (t, *J* = 6.57, 2H, O-CH₂), 1.77 (m, 2H, O-CH₂-CH₂), 1.02 (t, *J* = 7.40, 3H, CH₃). ¹³C NMR (75 MHz, CDCl₃) δ 153.53 (C-OH), 149.45 (C-O-C), 116.13 and 115.78 (4XC arom), 70.39 (O-CH₂), 22.82 (CH₂-CH₃), 10.66 (CH₃). HRMS (ESI) *m/z* calculated for C₉H₁₂O₂ [M+H]⁺: 152.0837, found 152.0837.

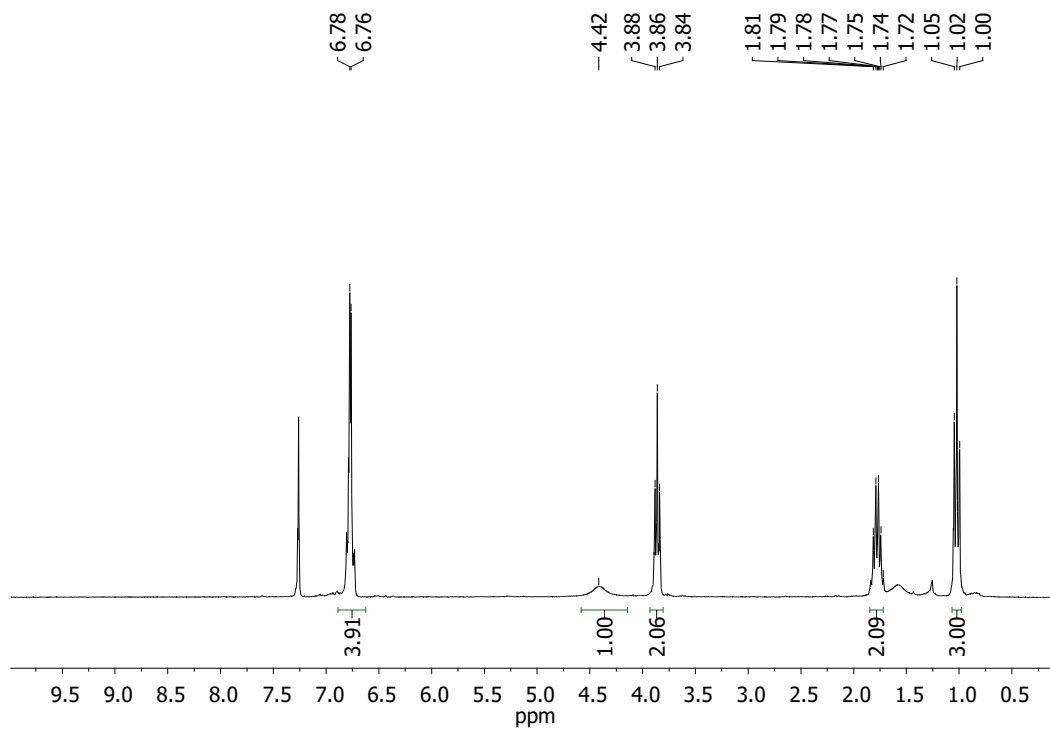


Figure S6: ^1H -NMR (300 MHz, CDCl_3) of **HQ-Pr**

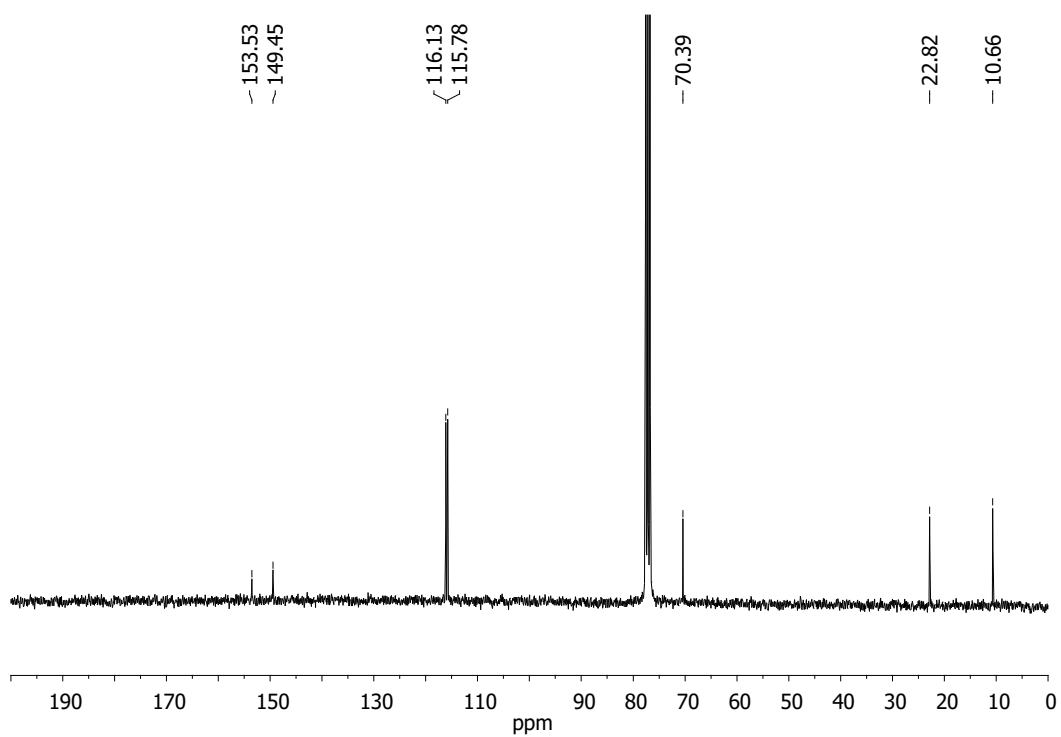
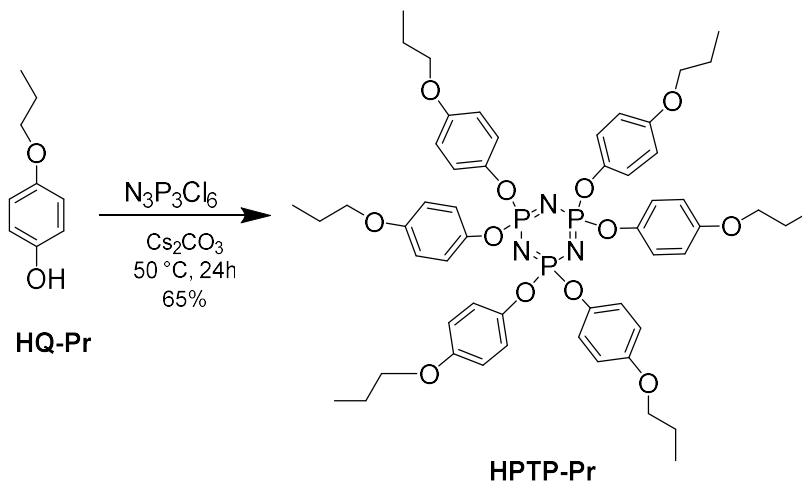
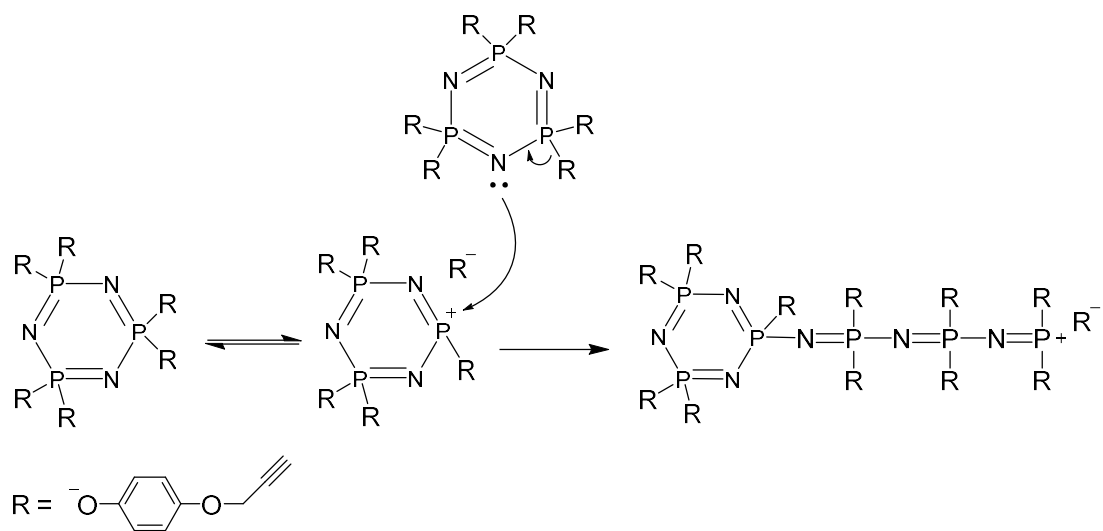


Figure S7: ^{13}C -NMR (75 MHz, CDCl_3) of **HQ-Pr**

Synthesis of 2,2,4,4,6,6-hexakis(4-propoxyphenoxy)-1,3,5,2λ⁵,4 λ⁵,6 λ⁵-triazatriphosphinine
(**HPTP-Pr**)



N₃P₃Cl₆ (1 g, 2.87 mmol) and **HQ-Pr** (3.28 g, 21.57 mmol, 7.5 eq.) were dissolved in THF (150 mL) followed by the addition of Cs₂CO₃ (11.25 g, 34.51 mmol). Reaction mixture was stirred for 24h at 50 °C. After that, the mixture was filtered, and solvent was evaporated under reduced pressure to obtain the product which was further purified by flash column chromatography using EtOAc/*n*-hexane (0 to 30%) to get a viscous yellow oil (1.95 g, 1.87 mmol, 65 %). ¹H NMR (300 MHz, CDCl₃) δ 6.94-6.60 (m, 4H, arom.), 3.79 (t, *J* = 6.51, 2H, O-CH₂), 1.70 (m, 2H, O-CH₂-CH₂), 0.96 (t, *J* = 7.32, 3H, CH₃). ¹³C NMR (75 MHz, CDCl₃) δ 156.55 (C-OH), 144.04 (C-O-C), 122.26 and 115.13 (4XC arom), 70.00 (O-CH₂), 22.77 (CH₂-CH₃), 10.64 (CH₃). HRMS (ESI) *m/z* calculated for C₅₄H₆₆N₃O₁₂P₃ [M+H]⁺: 1041.3859, found 1041.3859.



Scheme S2: Mechanism of the thermal ring-opening polymerization for **HPTP-Pg**.⁹

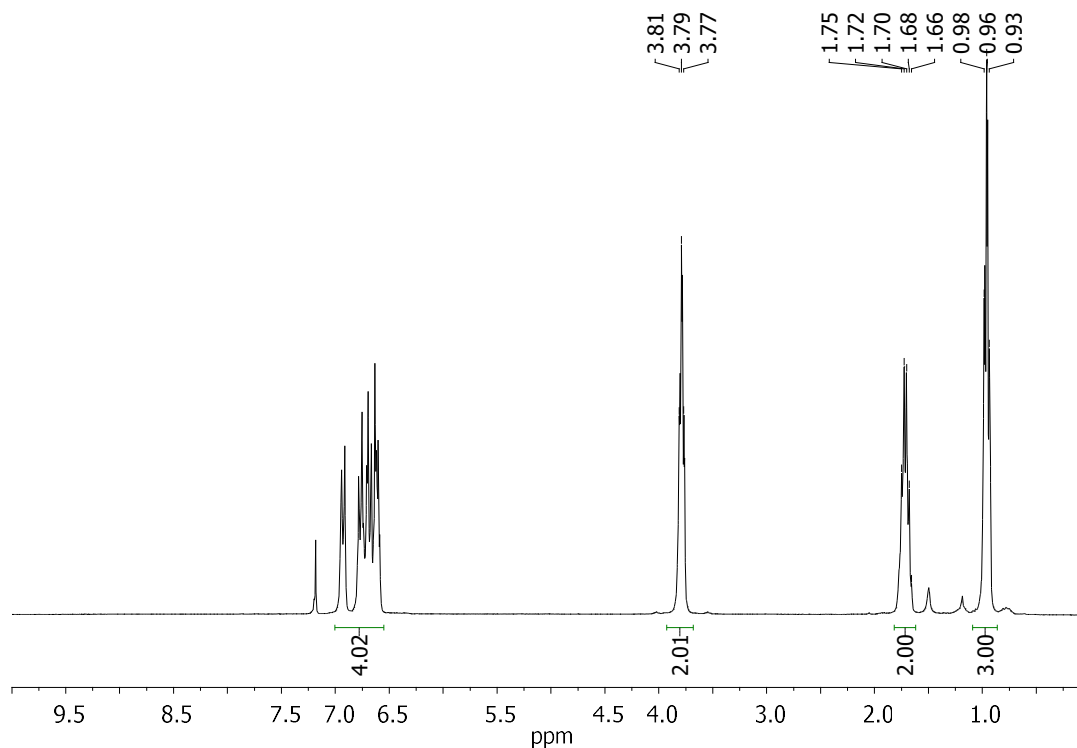


Figure S8: $^1\text{H-NMR}$ (300 MHz, CDCl_3) of HPTP-Pr

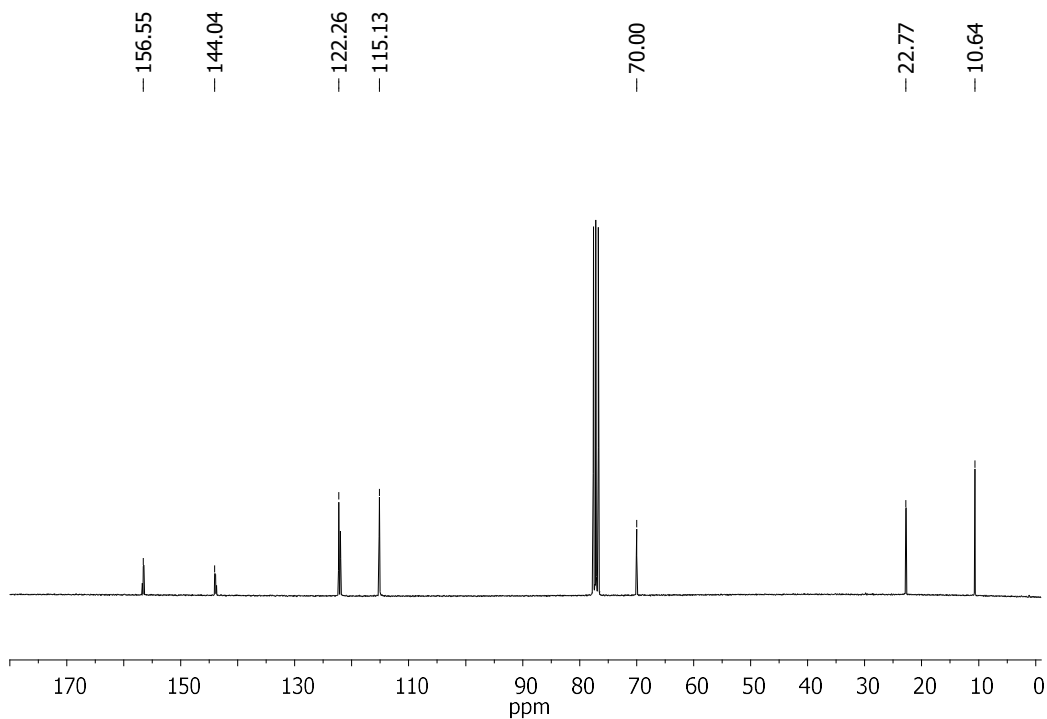


Figure S9: $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) of HPTP-Pr

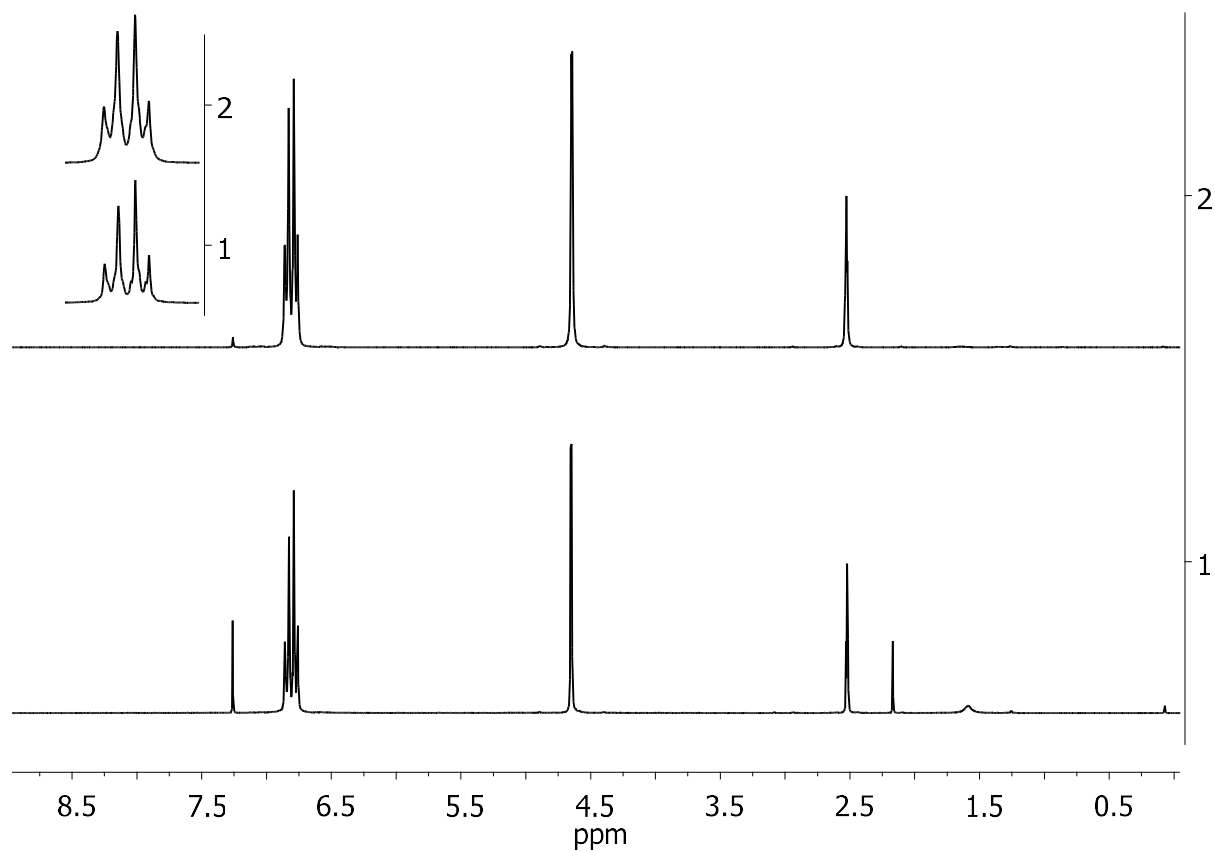


Figure S10: ^1H -NMR of **HPTP-Pg** before (upper) and after (lower) recording DSC up to 110 °C. (see Fig. 1c). In the inset are the enlarged NMR signals at 6.5-7.1 ppm (Note: at 2.18 ppm is the acetone).

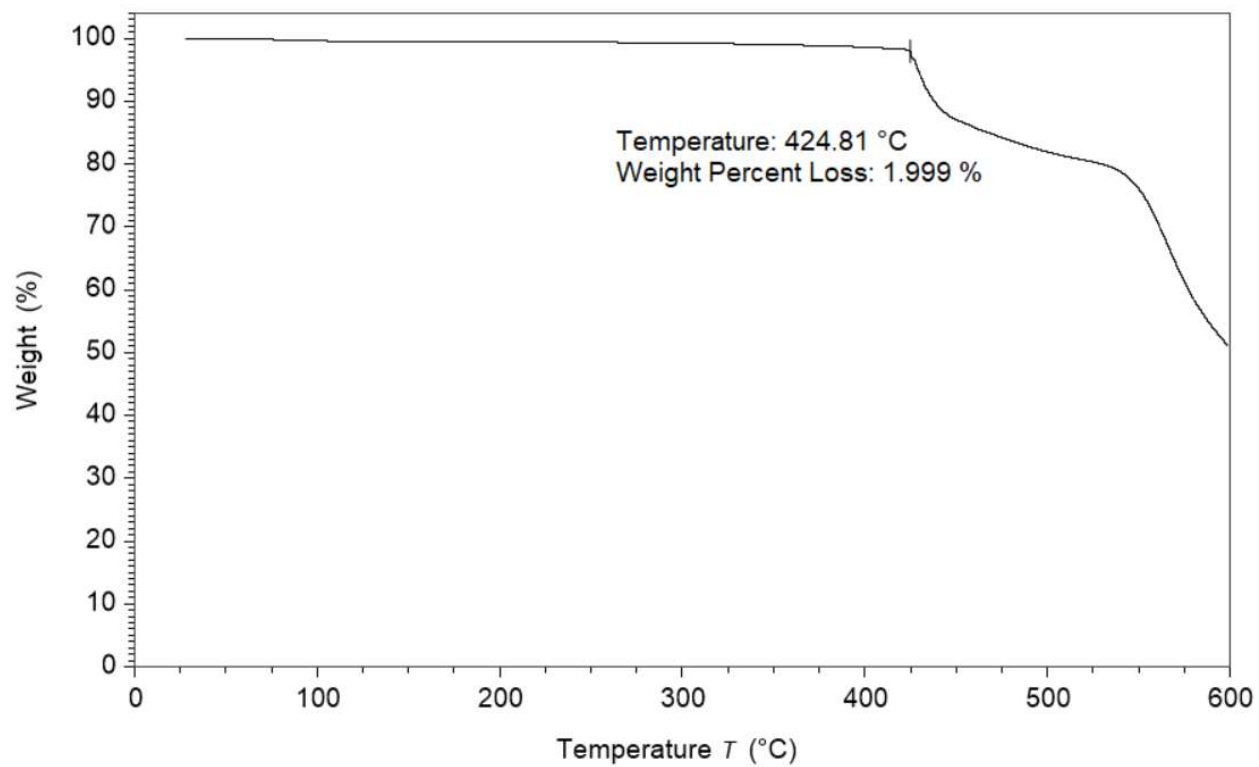


Figure S11: Thermogravimetric analysis (TGA) of **HPTP-Pg** at a heating rate of 10 °C/min under air.

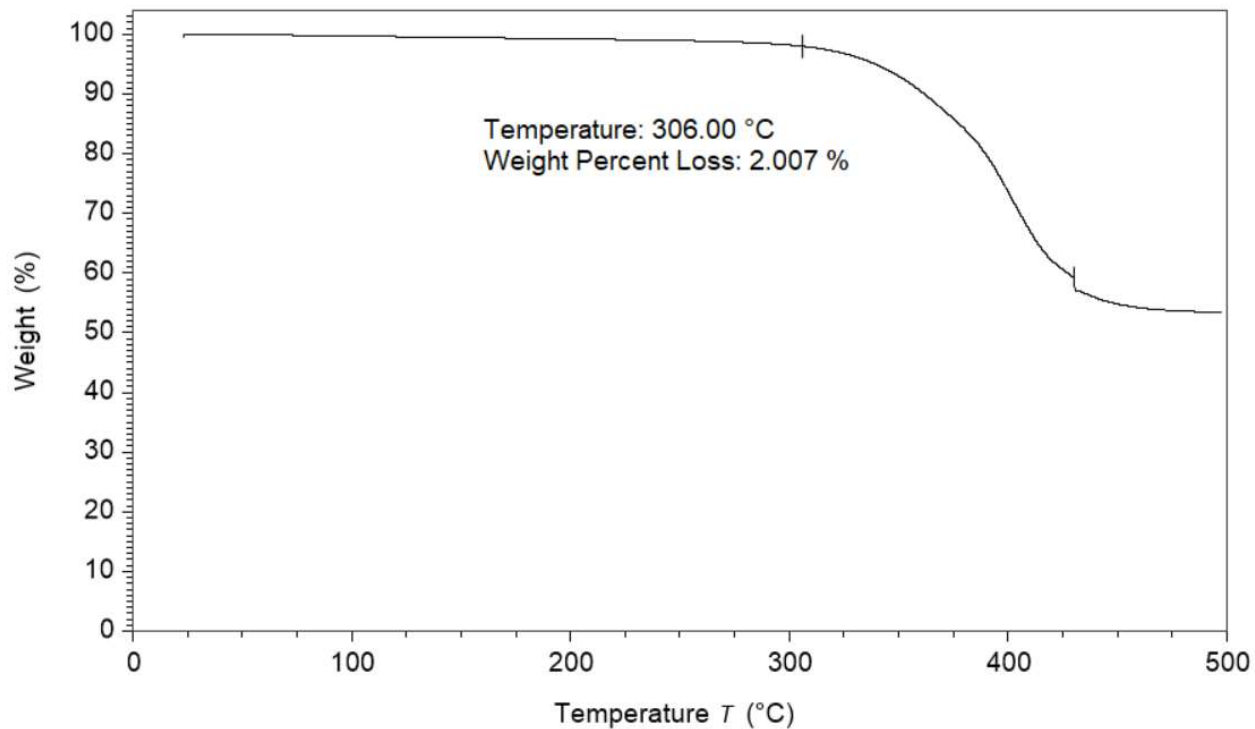


Figure S12: Thermogravimetric analysis (TGA) of **HPTP-Pr** at heating rates of 10 °C/min under N₂.

Table S1: Decomposition temperatures of **HPTP-Pg** before and after polymerization based on a 2% mass loss as the onset of decomposition.

Sample	Decomposition Temperature
HPTP-Pg	440 °C – Under N ₂
HPTP-Pg	425 °C – Under air
HPTP-Pg-X	489 °C – Under N ₂
HPTP-Pr	306 °C – Under N ₂

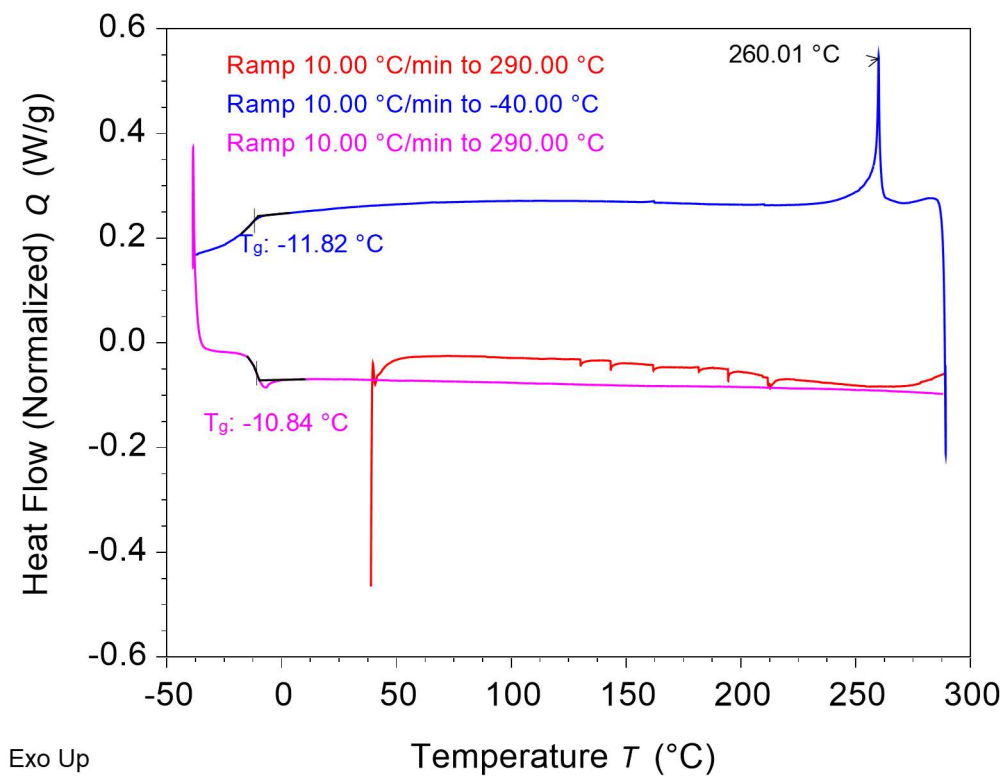


Figure S13: DSC curves of **HPTP-Pr** on first (red) and second (pink) heating and first (blue) cooling at 10 $^{\circ}\text{C}/\text{min}$ under N_2 .

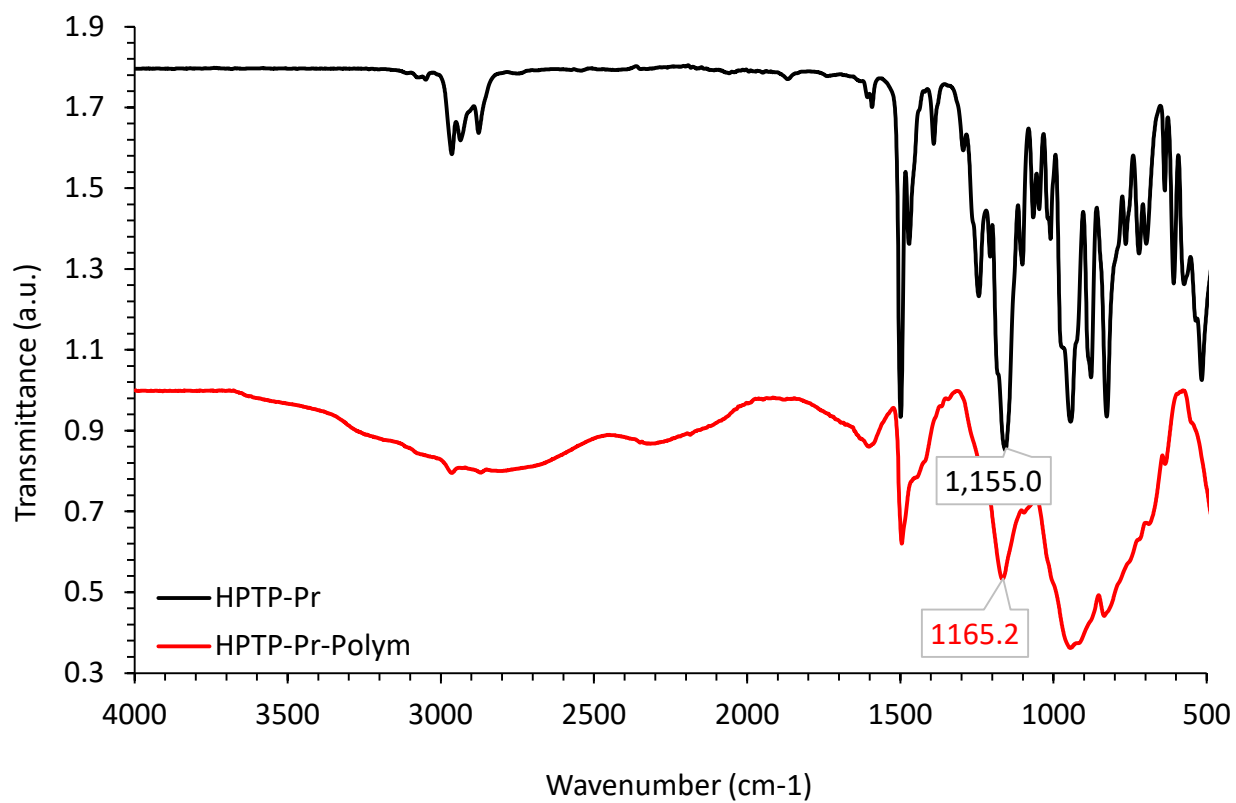


Figure S14: ATR-IR spectra of **HPTP-Pr** fresh and that of after thermal annealing at 295 °C (**HPTP-Pr-Polym**).

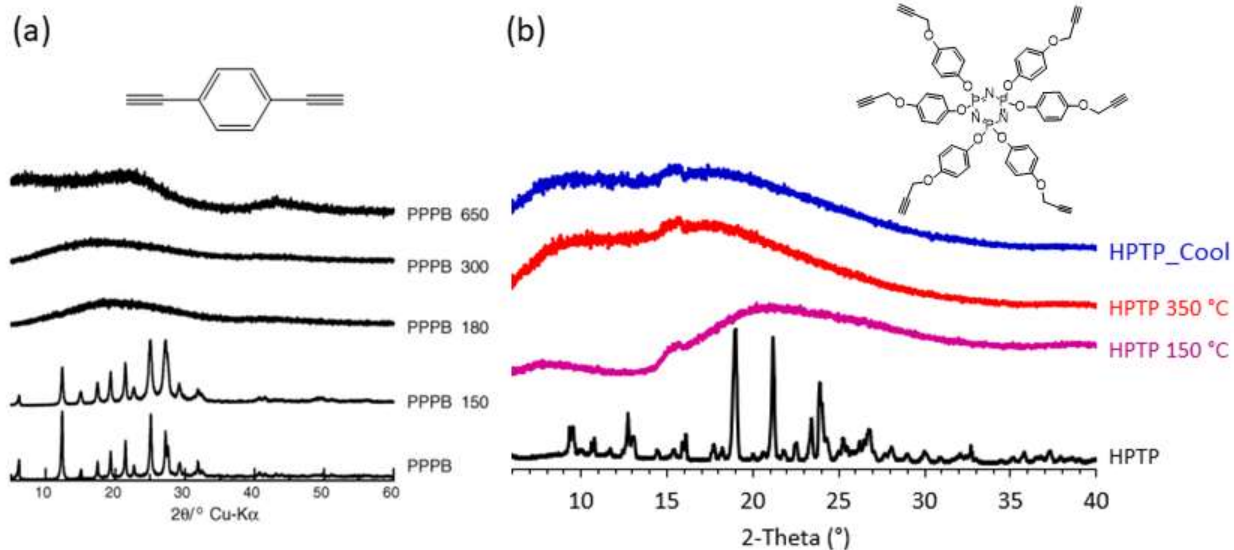


Figure S15: Variable-temperature X-ray diffraction (vt-XRD) recorded at different temps for a 1,4-diethynylbenzene thermally crosslinked material reported by Ozaki et al.¹⁰ (a) and its comparison with the vt-XRD of **HTP-Pg** at comparable temperatures and after cooling back to room temperature (b).

Table S2: SEM/EDX of **HTP-Pg** before and after polymerization/crosslinking (**HTP-Pg-X**)

Sample	C	N	O	P
HTP-Pg	66.43	6.48	20.63	6.47
HTP-Pg-X	64.08	0.92	28.25	6.76

All values are average of 5 measurements from different spots

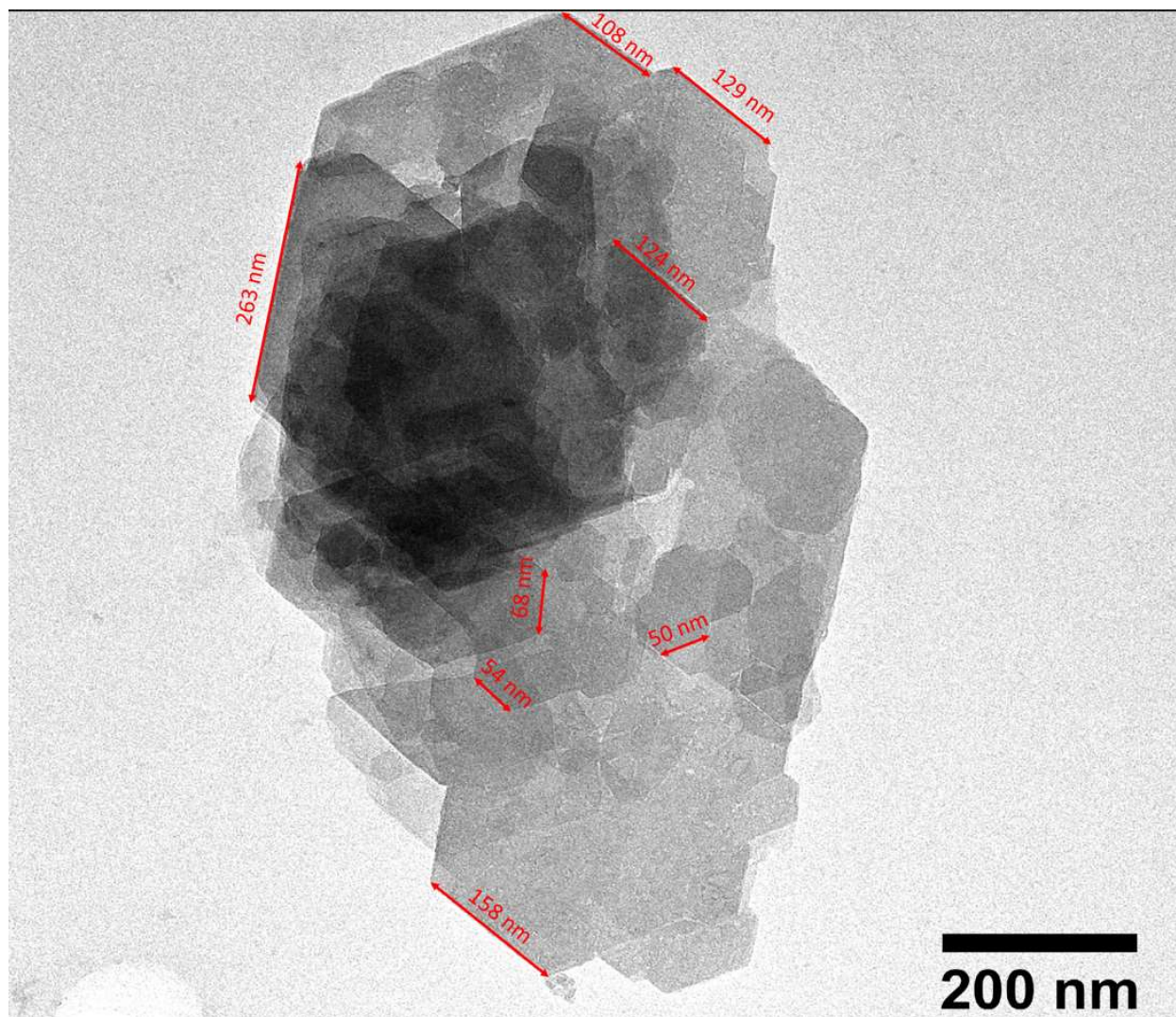


Figure S16: Transmission electron microscopy (TEM) images of **HPTP-Pg-X** with lateral sizes labeling. The scale bar is 200 nm.

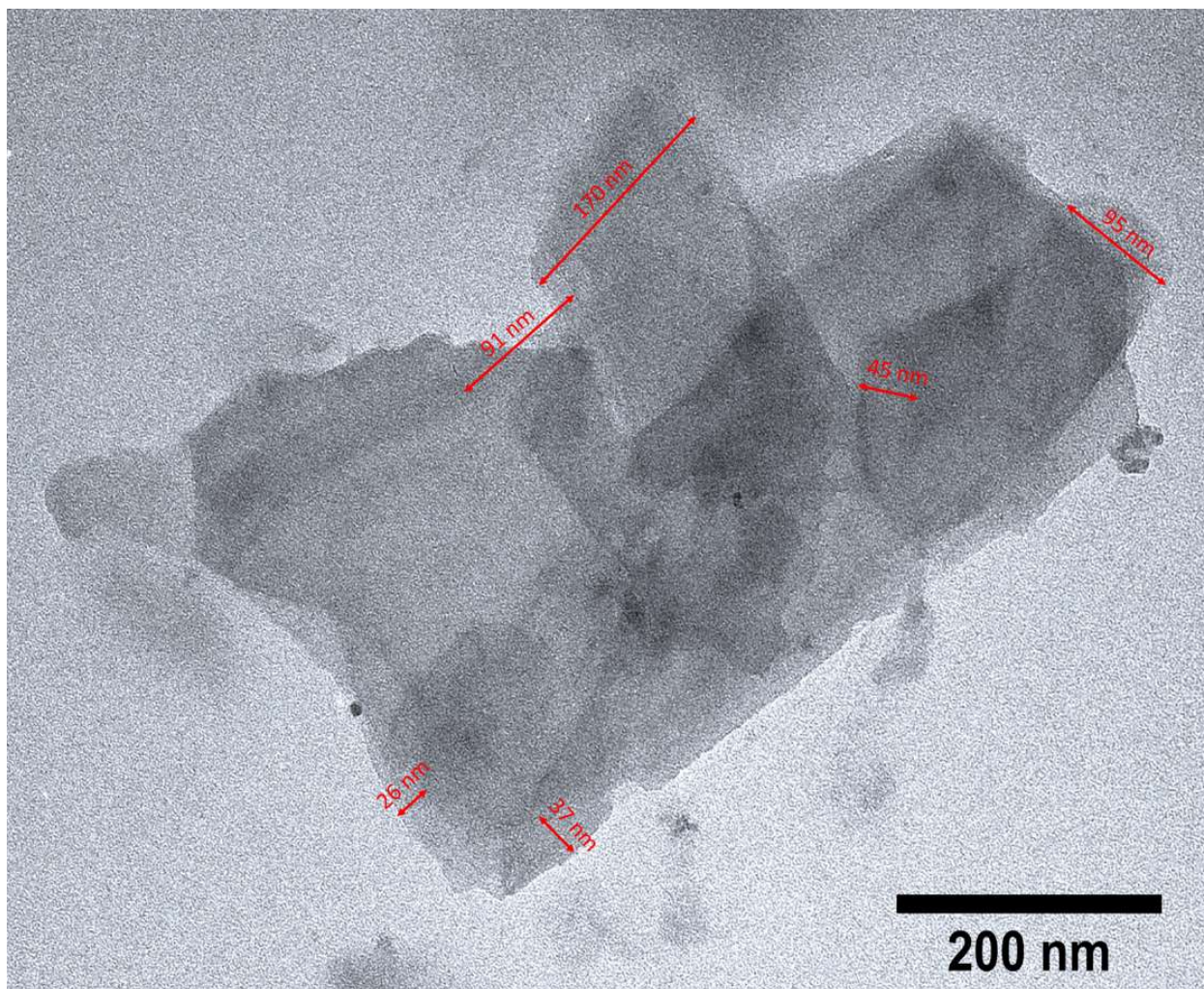


Figure S17: Transmission electron microscopy (TEM) images of **HPTP-Pg-X** with lateral sizes labeling. The scale bar is 200 nm.

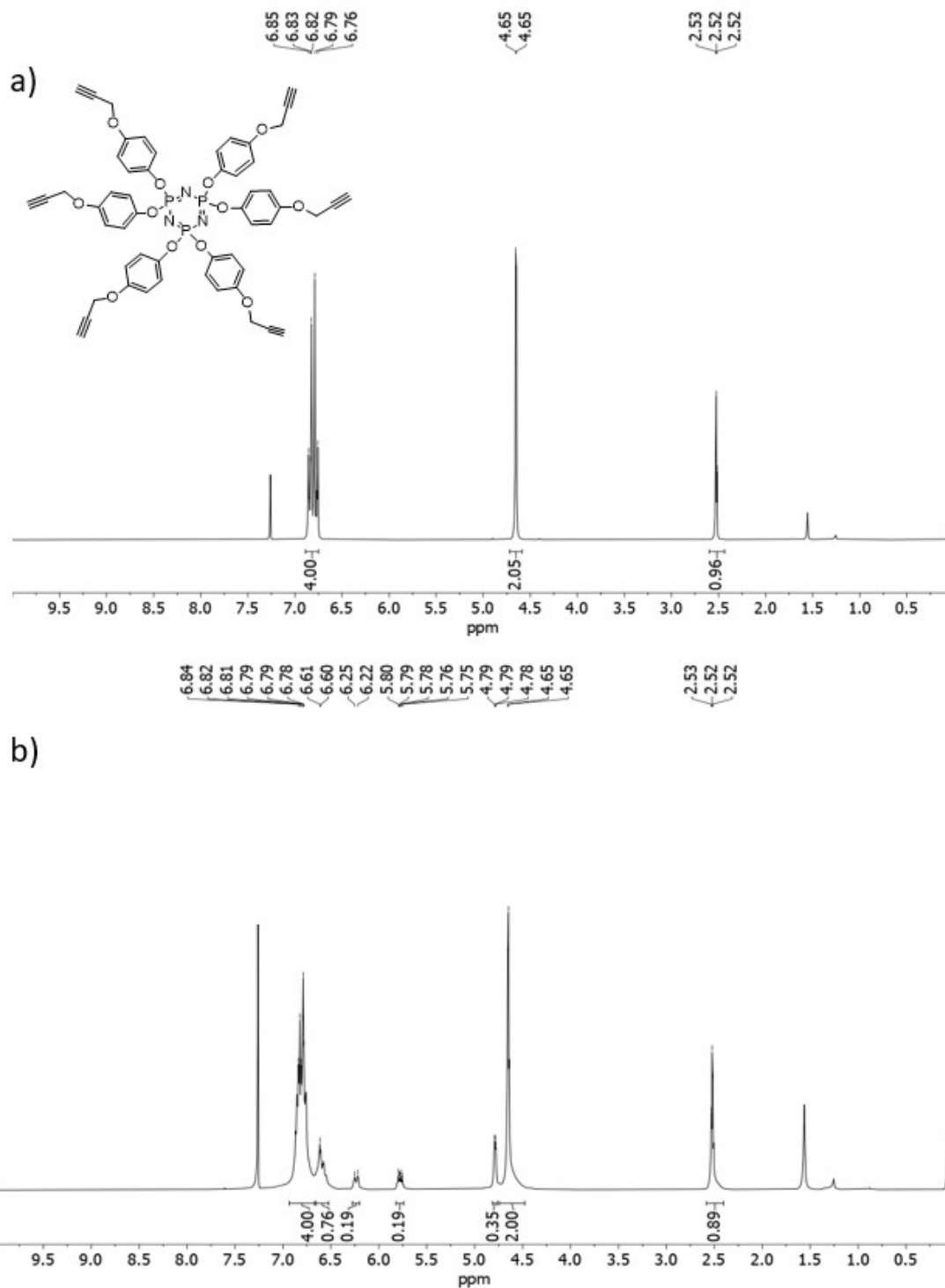


Figure S18: $^1\text{H-NMR}$ spectrum (300 MHz, CDCl_3) of **HPTP-Pg** (a) fresh and (b) recovered from DSC pan where sample was heated beyond the onset of the DSC transition starting at 238 °C (see Figure 1b) and stopped at 250 °C. Signal at 1.55 ppm is moisture in the solvent/sample.

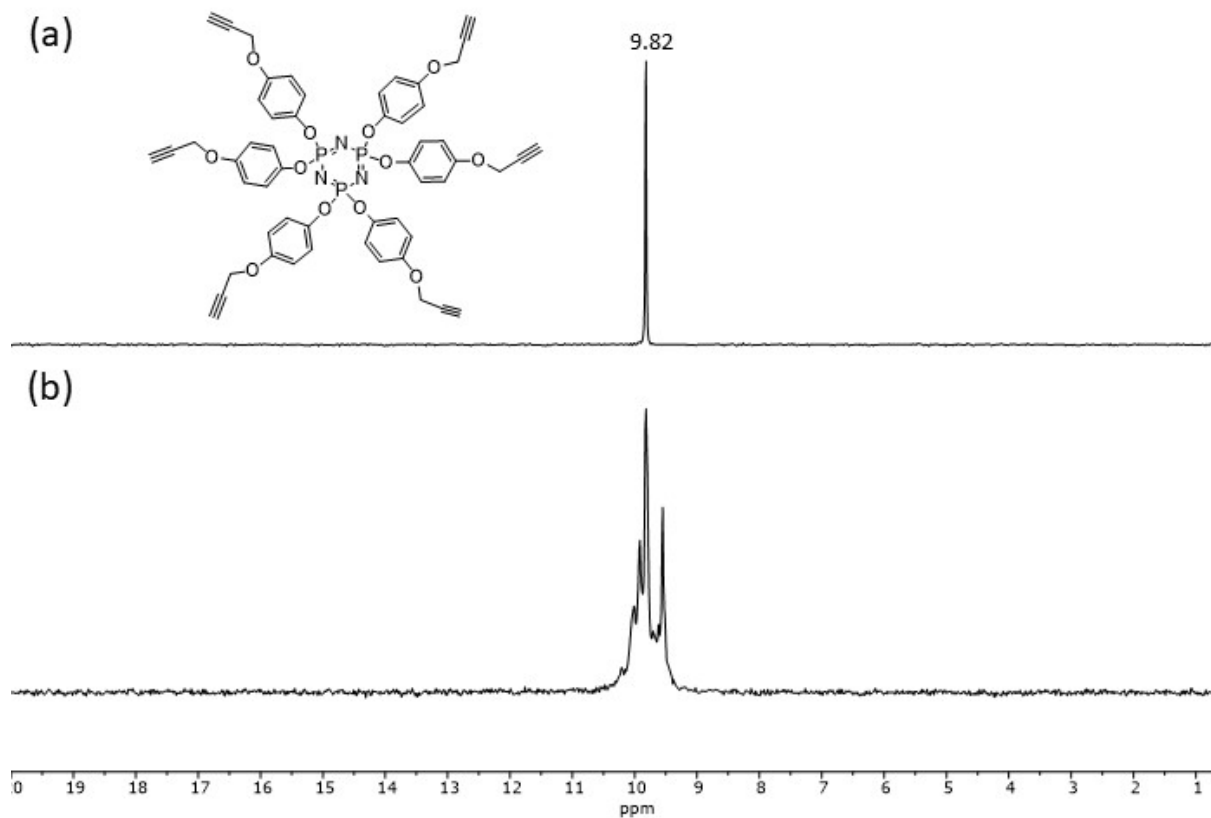


Figure S19: ^{31}P -NMR spectrum (122 MHz, CDCl_3) of **HPTP-Pg** (a) fresh and (b) recovered from DSC pan where sample was heated beyond the onset of the DSC transition starting at 238 °C (see Figure 1b) and stopped at 250 °C.

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