Design and synthesis of thiophene-engineered phenanthroimidazoles with vinyl functionality for polymer integration

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Content

General information

All reagents and solvents were obtained from commercial suppliers (Merk, TCI, BLD, and Penta) and used without further purification unless otherwise specified. Phenanthrene-9,10-dione, 4-iodoaniline, 4-bromoaniline, and (4-vinylphenyl)boronic acid were of analytical grade. Ammonium acetate, glacial acetic acid, potassium carbonate, toluene, and ethanol were used as received. Palladium tetrakis(triphenylphosphine) $[Pd(PPh_3)_4]$ was used as a catalyst for Suzuki-Miyaura coupling reactions. Thin-layer chromatography (TLC) was performed on silica gel 60 F254 plates (Merck) and visualized under UV light (254 nm). Column chromatography was performed using silica gel (40-63 µm particle size).

^{1}H and ^{13}C NMR spectra were recorded at 295 K on a Bruker Ascend 500 spectrometer operating at 500.13 MHz for ^{1}H and 125.76 MHz for ^{13}C nuclei. Samples were prepared in $CDCl_3$, and chemical shifts (δ) are given in ppm relative to residual solvent signals: δ(^{1}H) = 7.26 ppm and δ(^{13}C) = 77.23 ppm. Infrared spectra (4500-500 cm^{-1}, resolution 2 cm^{-1}) were obtained using a Vertex 70V FT-IR spectrometer (Bruker, Germany) equipped with a single-bounce diamond ATR crystal.

Diffraction data were collected using a Bruker Venture D8 diffractometer at 150 K with graphite-monochromated Mo-Ka (0.7107 Å) radiation. The frames were integrated with the Bruker SAINT software package using a narrow frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The obtained data were treated by the XT-version 2014/5 and SHELXL-2019/1 software implemented in APEX4 v2021.10-0 (Bruker AXS) system.51 All non-hydrogen atoms were refined using anisotropic displacement parameters. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 2528847-2528849. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Thermal properties of the synthesized compounds were investigated by simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) using a NETZSCH STA 449 F5 Jupiter instrument. The DSC signal was used exclusively for the determination of melting temperatures (T_m) of the monomers. The DTG curves were obtained as the first derivative of the corresponding TGA curves. Measurements were carried out under a nitrogen atmosphere with a constant gas flow of 50 mL·min^{-1}. Samples (≈ 10 mg) were placed in open alumina crucibles and heated from 35 to 1250 °C at a constant heating rate of 10 °C·min^{-1}. The temperature accuracy of the instrument is better than ±1 °C, and the mass measurement uncertainty is within ±0.1 % of the initial sample mass. The instrument was calibrated using the melting points of standard pure metals.

The size exclusion chromatography (SEC) experimental set-up consisted of a Waters Arc HPLC coupled with a multi-angle light scattering (MALS) detector DAWN, a refractive index (RI) detector Optilab, and an online viscometer ViscoStar. The detectors were from Waters | Wyatt Technology. The SEC columns were two Agilent PLgel Mixed-C 300 × 7.5 mm with tetrahydrofuran (THF) at a flow rate of 1 ml/min as the mobile phase. The samples were prepared in THF at the concentrations of ≈ 6 mg/ml and the obtained solutions were filtered with 0.45 µm filters; the injection volume was 100 µl.

Optical measurements were performed using a Shimadzu UV-3600 spectrophotometer (200-800 nm range) for UV-Vis absorption and a PTI QuantaMaster 400 fluorometer (Horiba, Germany) for photoluminescence (PL) measurements in the 300-850 nm range, with excitation wavelengths between 300 and 350 nm. Time-resolved PL decay profiles were obtained by the time-correlated single-photon counting (TCSPC) method using the same fluorometer equipped with NanoLED-390 excitation source (pulse width < 1.3 ns).

General procedure for the synthesis of halogenated phenanthroimidazoles (Debus–Radziszewski condensation)

A mixture of phenanthrene-9,10-dione (0.01 mol), the corresponding aniline (4-iodo- or 4-bromoaniline, 0.03 mol), and ammonium acetate (0.02 mol) was suspended in glacial acetic acid (50 ml) under an argon atmosphere. While stirring, the corresponding aldehyde (0.01 mol) was added, and the reaction mixture was stirred for 10 min at room temperature, then refluxed for 4 – 6 hours until complete conversion (monitored by TLC in dichloromethane). After cooling to room temperature, the mixture was diluted with an equal volume of water. The precipitated solid was filtered, washed with water and ethanol, and air-dried. The crude product was purified by column chromatography on silica gel using dichloromethane as the eluent.

Synthesis of 1-(4-iodophenyl)-2-(thiophen-2-yl)-1H-phenanthro[9,10-d]imidazole ***Th-PPI-I***

Beige powder; yield: 84%. ^{1}H NMR (500.13 MHz, $CDCl_3$), δ: 8.79-8.78 (d, $^3J_{H,H}$ = 7.92 Hz, 1H), 8.66-8.65 (d, $^3J_{H,H}$ = 8.30 Hz, 1H), 8.60-8.58 (d, $^3J_{H,H}$ = 8.30 Hz, 1H), 7.95-7.94 (d, $^3J_{H,H}$ = 8.30 Hz, 2H), 7.67 (t, $^3J_{H,H}$ = 7.50 Hz, 1H), 7.57 (t, $^3J_{H,H}$ = 7.72 Hz, 1H), 7.43 (t, $^3J_{H,H}$ = 7.72 Hz, 1H), 7.28-7.22 (m, 4H), 7.09-7.08 (d, $^3J_{H,H}$ = 8.30 Hz, 1H), 6.87-6.84 (m, 2H). ^{13}C NMR (125.76 MHz, $CDCl_3$), δ: 145.68; 139.77; 138.01; 137.52; 132.61; 131.11; 129.16; 128.23; 127.85; 127.67; 127.48; 127.38; 127.26; 126.76; 126.45; 125.77; 125.03; 124.15; 123.03; 122.86; 122.52; 120.34; 96.30. IR (ATR, cm^{-1}): 3080 (Ar-C-H), 1610 (C=N, imidazole), 1513, 1488 (C=C_{arom}), 1386 (C-N), 1230 ($\delta_{C-H+C-N}$), 1133, 1095, 1053 (C-H/C-C), 1010, 938 (ring breathing), 854, 833 (γ_{CH}, p-substituted Ph-I), 749 (γ_{CH}, phenanthrene), 680 (ν_{C-S}, thiophene), 534 (ν_{C-I}), 428 (skeletal deformation).

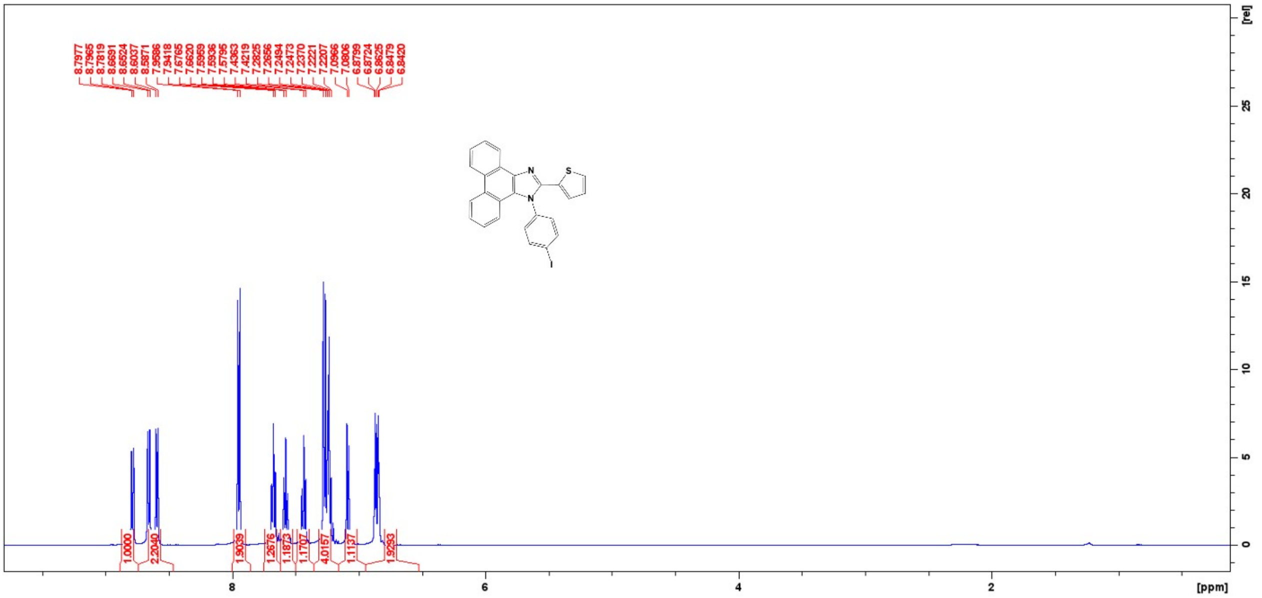


Figure S1. ^{1}H NMR spectrum of Th-PPI-I in $CDCl_3$ at room temperature.

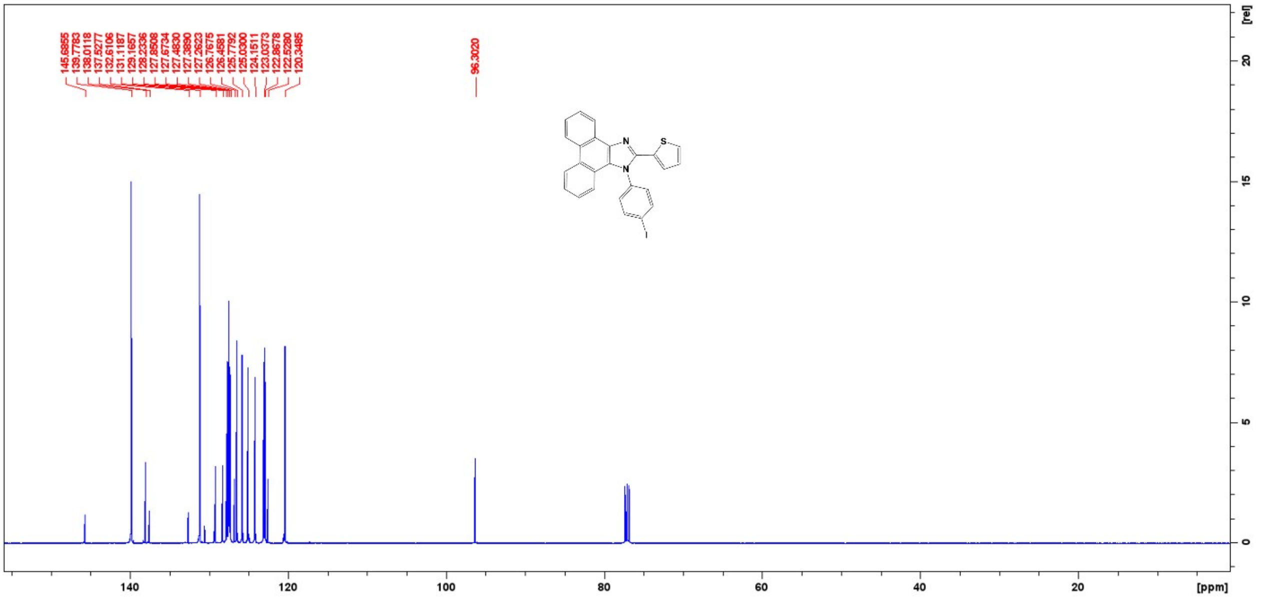


Figure S2. ^{13}C NMR spectrum of Th-PPI-I in $CDCl_3$ at room temperature.

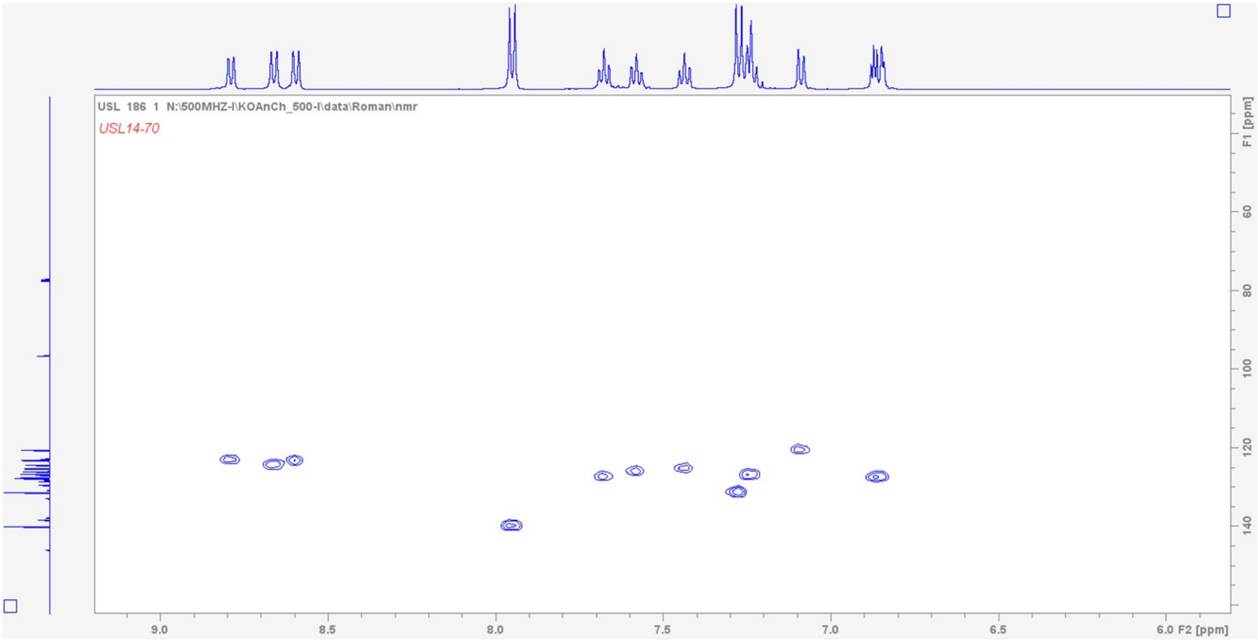


Figure S3. Partial ^1H-^{13}C-HSQC NMR spectrum of Th-PPI-I in $CDCl_3$ at room temperature.

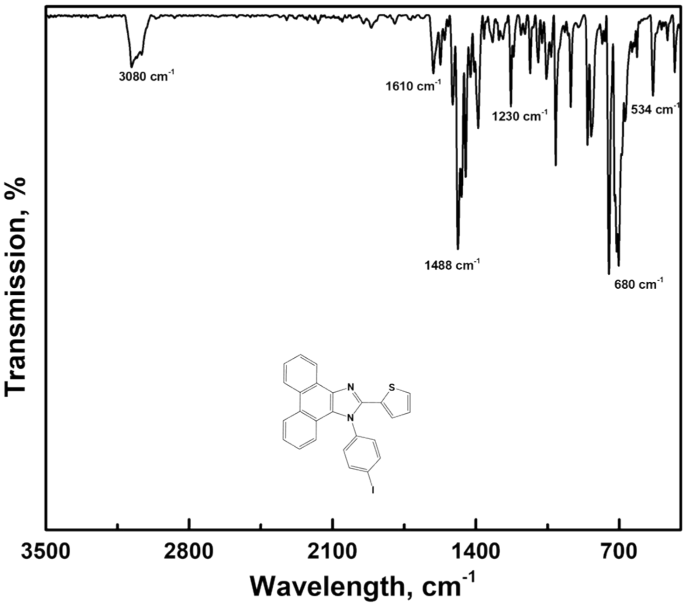


Figure S4. IR (ATR) spectrum of Th-PPI-I.

Synthesis of 2-(benzo[b]thiophen-2-yl)-1-(4-iodophenyl)-1H-phenanthro[9,10-d]imidazole ***BTh-PPI-I***

Beige powder; yield: 89%. ^{1}H NMR (500.13 MHz, $CDCl_3$), δ: 8.81-8.80 (d, $^{3}J_{H,H}$ = 7.92 Hz, 1H), 8.69-8.68 (d, $^{3}J_{H,H}$ = 8.30 Hz, 1H), 8.62-8.60 (d, $^{3}J_{H,H}$ = 8.30 Hz, 1H), 8.02-8.00 (d, $^{3}J_{H,H}$ = 8.30 Hz, 2H), 7.73-7.68 (m, 2H), 7.62-7.58 (m, 2H), 7.47 (t, $^{3}J_{H,H}$ = 7.92 Hz, 1H), 7.36-7.34 (d, $^{3}J_{H,H}$ = 8.30 Hz, 2H), 7.28-7.25 (m, 3H), 7.11-7.10 (d, $^{3}J_{H,H}$ = 8.30 Hz, 1H), 7.02 (s, 1H). ^{13}C NMR (125.76 MHz, $CDCl_3$), δ: 145.37; 140.17; 139.89; 139.46; 137.91; 131.08; 129.40; 128.37; 128.31; 127.33; 126.72; 126.51; 125.92; 125.26; 124.52; 124.20; 124.19; 123.73; 123.04; 122.89; 122.46; 121.93; 120.47; 96.43. IR (ATR, cm^{-1}): 3058, 3029 (Ar-C-H), 1610 (C=N, imidazole), 1513, 1488 ($C=C_{arom}$), 1450, 1403 (ring skeletal vibrations), 1192 [$\delta_{C\text{-}H+C\text{-}N}$], 1011 (ring breathing), 930 [δ_{CH}, aromatic], 830 [γ_{CH}, p-substituted Ph-I], 741 (γ_{CH}, phenanthrene unit), 680 [$\nu_{C\text{-}S}$, benzo[*b*]thiophene], 534 ($\nu_{C\text{-}I}$), 437 (skeletal deformation).

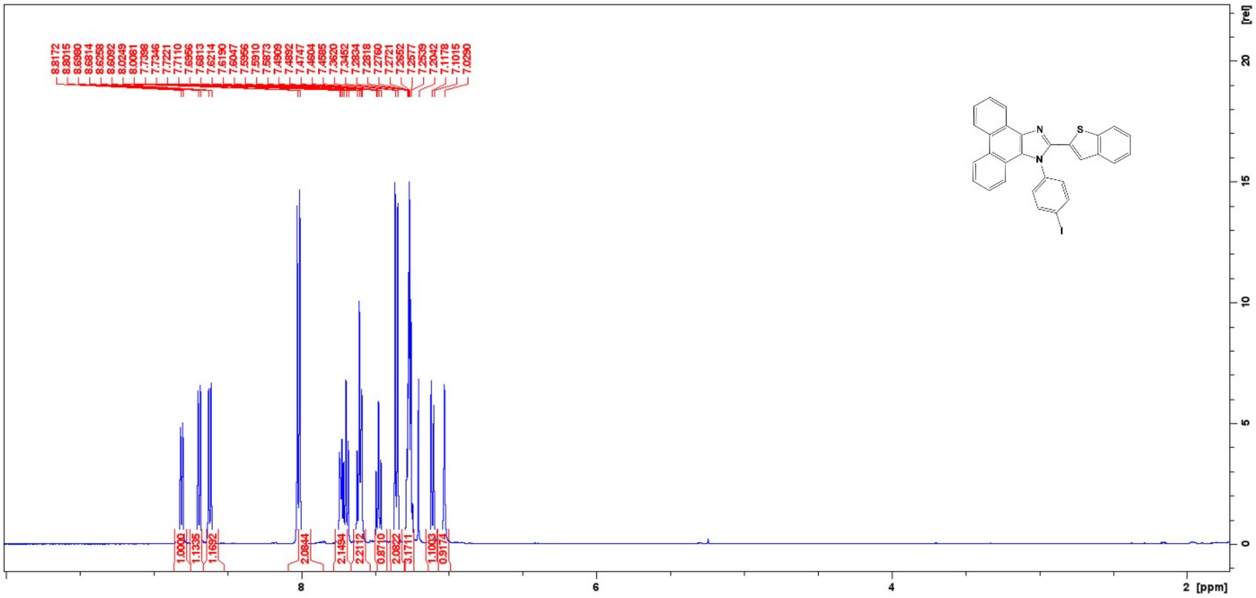


Figure S5. ^{1}H NMR spectrum of BTh-PPI-I in $CDCl_3$ at room temperature.

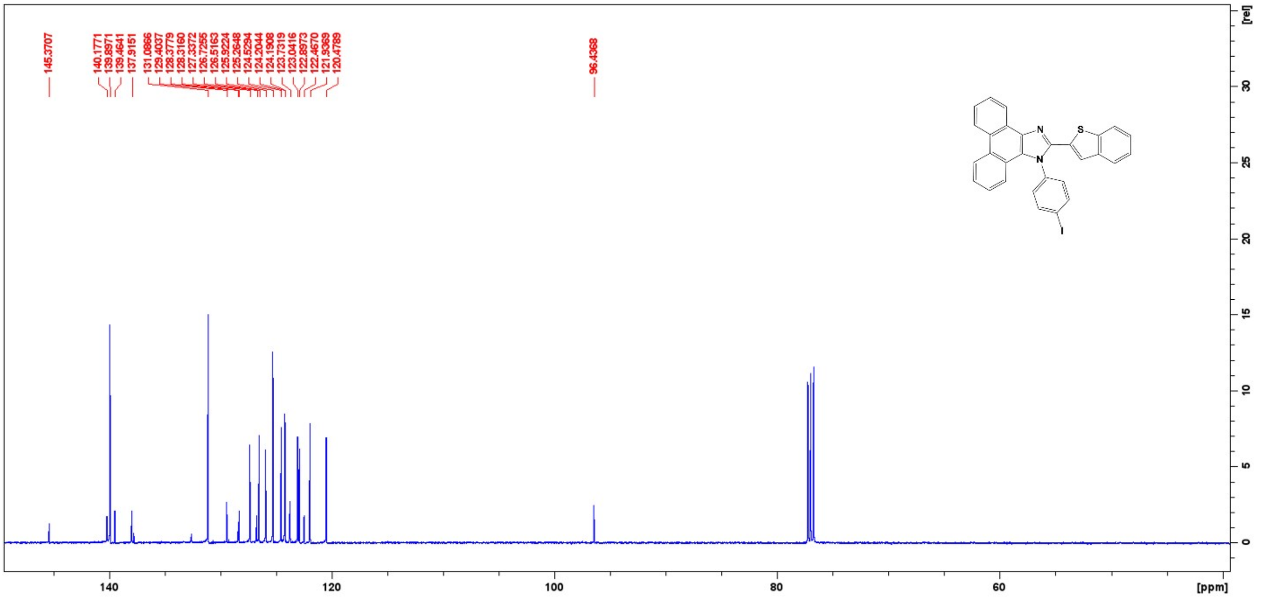


Figure S6. ^{13}C NMR spectrum of BTh-PPI-I in CDCl$_3$ at room temperature.

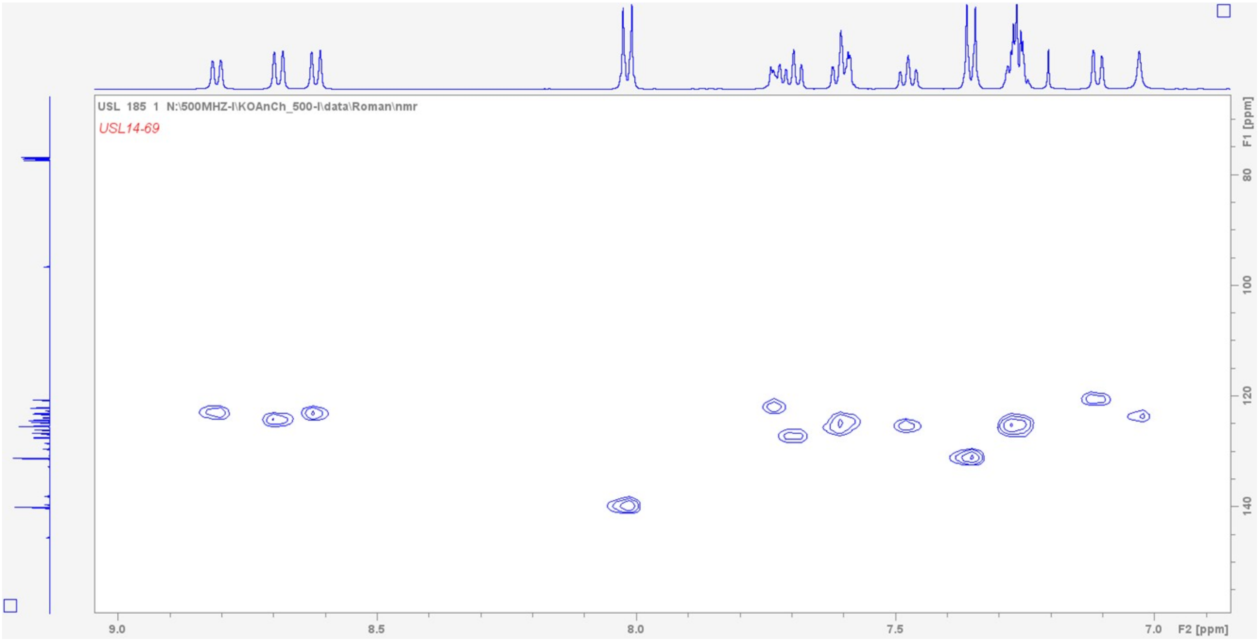


Figure S7. Partial ^{1}H-^{13}C-HSQC NMR spectrum of BTh-PPI-I in CDCl$_3$ at room temperature.

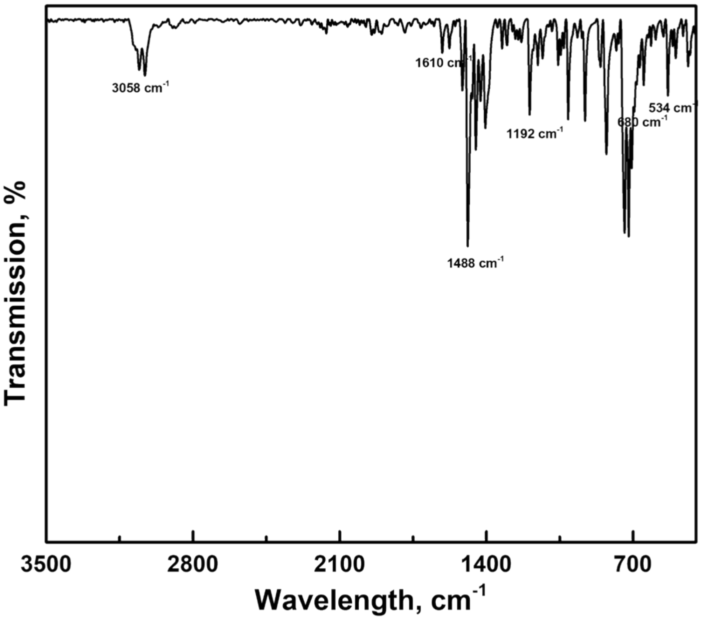


Figure S8. IR (ATR) spectrum of BTh-PPI-I.

Synthesis of 1-(4-bromophenyl)-2-(thieno[3,2-b]thiophen-2-yl)-1H-phenanthro[9,10-d]imidazole ***TTh-PPI-Br***

Beige powder; yield: 79%. ^{1}H NMR (500.13 MHz, CDCl$_3$), δ: 8.86-8.85 (d, $^3J_{H,H}$ = 7.81 Hz, 1H), 8.78-8.76 (d, $^3J_{H,H}$ = 8.15 Hz, 1H), 8.71-8.69 (d, $^3J_{H,H}$ = 8.15 Hz, 1H), 7.90-7.88 (d, $^3J_{H,H}$ = 8.15 Hz, 2H), 7.76 (t, $^3J_{H,H}$ = 7.47 Hz, 1H), 7.68 (t, $^3J_{H,H}$ = 7.81 Hz, 1H), 7.56-7.53 (m, 3H), 7.43-7.42 (d, $^3J_{H,H}$ = 5.43 Hz, 1H), 7.33 (t, $^3J_{H,H}$ = 7.47 Hz, 1H), 7.25-7.24 (d, $^3J_{H,H}$ = 5.43 Hz, 1H), 7.16-7.14 (d, $^3J_{H,H}$ = 7.81 Hz, 1H), 7.06 (s, 1H). ^{13}C NMR (125.76 MHz, CDCl$_3$), δ: 145.71; 140.69; 139.41; 137.76; 137.29; 134.46; 134.06; 131.00; 129.34; 128.88; 128.35; 128.27; 127.37; 126.79; 126.56; 125.92; 125.18; 124.94; 124.26; 123.11; 122.92; 122.55; 120.41; 119.45; 119.32. IR (ATR, cm^{-1}): 3105, 3046 (Ar-C-H), 1610 (C=N, imidazole), 1573, 1547, 1488 (C=C$_{\text{arom}}$), 1450, 1395 (C-N), 1234, 1200, 1167 ($\delta_{\text{C-H+C-N}}$), 1066, 1015 (C-H), 952, 893 [γ_{CH}, thiophene/phenanthrene], 838 [γ_{CH}, p-substituted Ph-Br], 741 [γ_{CH}, phenanthrene], 690, 626 [$\nu_{\text{C-S}}$), thieno[3,2-*b*]thiophene], 517 ($\nu_{\text{C-Br}}$), 466, 429 (skeletal deformations).

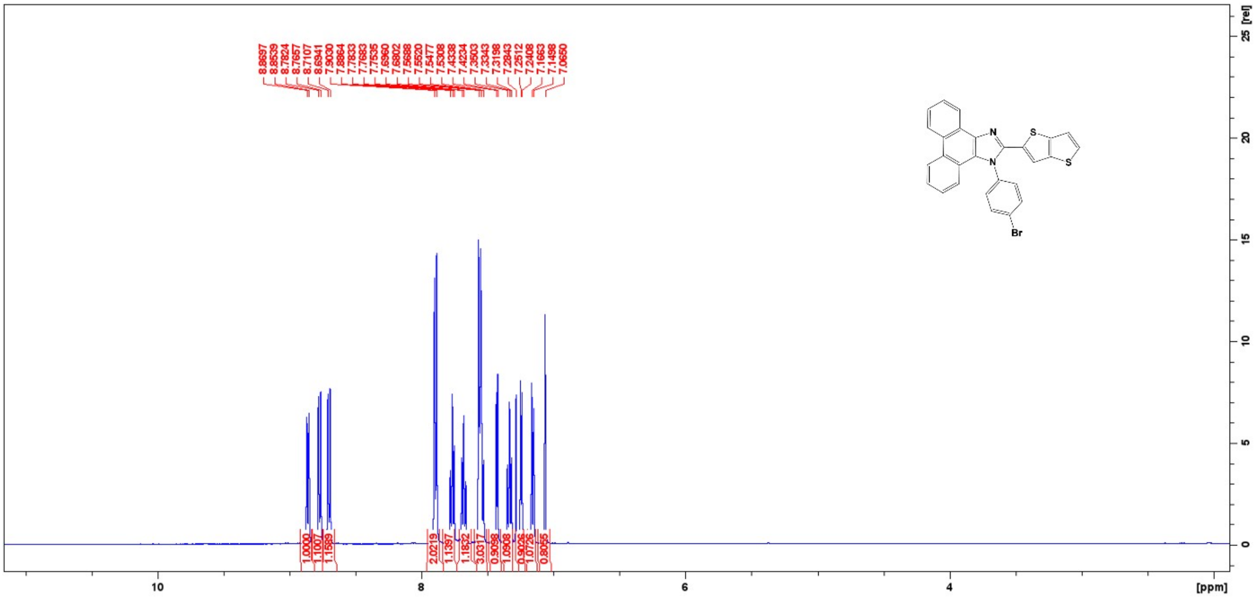


Figure S9. ^{1}H NMR spectrum of TTh-PPI-Br in $CDCl_3$ at room temperature.

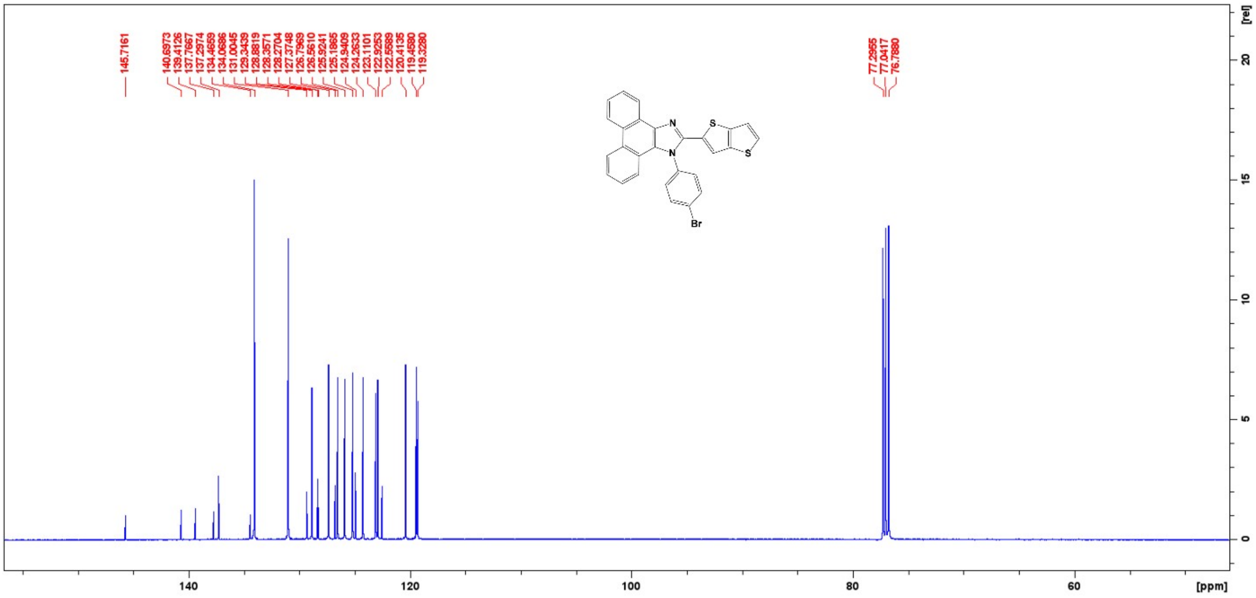


Figure S10. ^{13}C NMR spectrum of TTh-PPI-Br in $CDCl_3$ at room temperature.

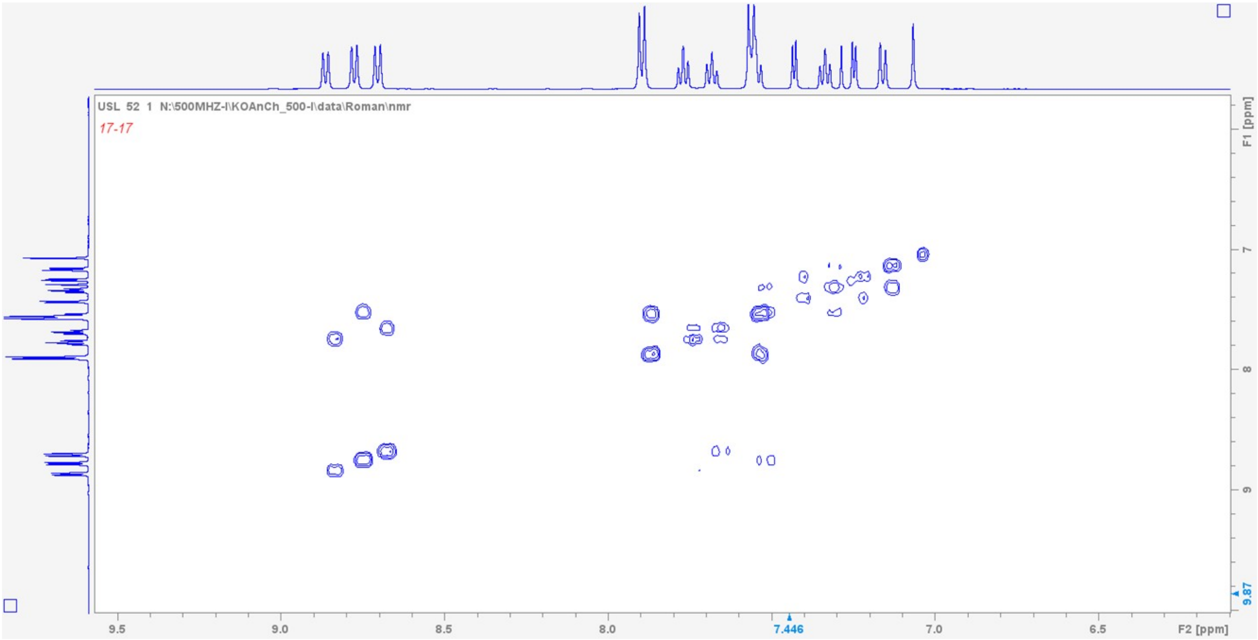


Figure S11. ^{1}H-^{1}H-COSY NMR spectrum of TTh-PPI-Br in CDCl$_3$ at room temperature.

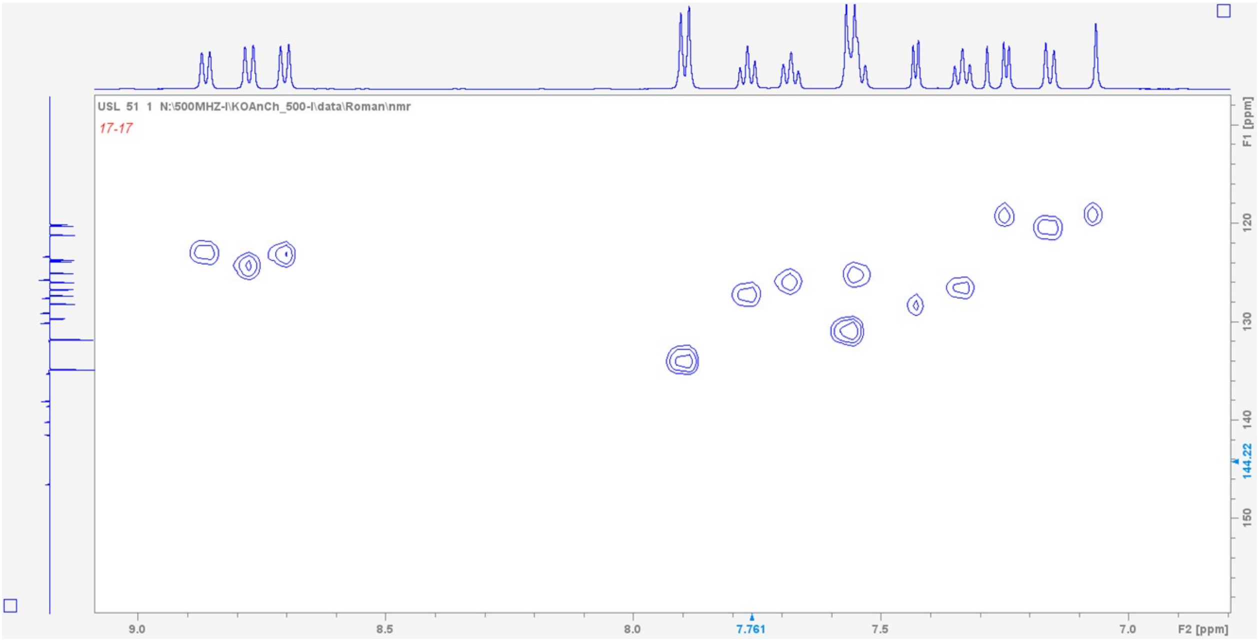


Figure S12. Partial ^{1}H-^{13}C-HSQC NMR spectrum of TTh-PPI-Br in CDCl$_3$ at room temperature.

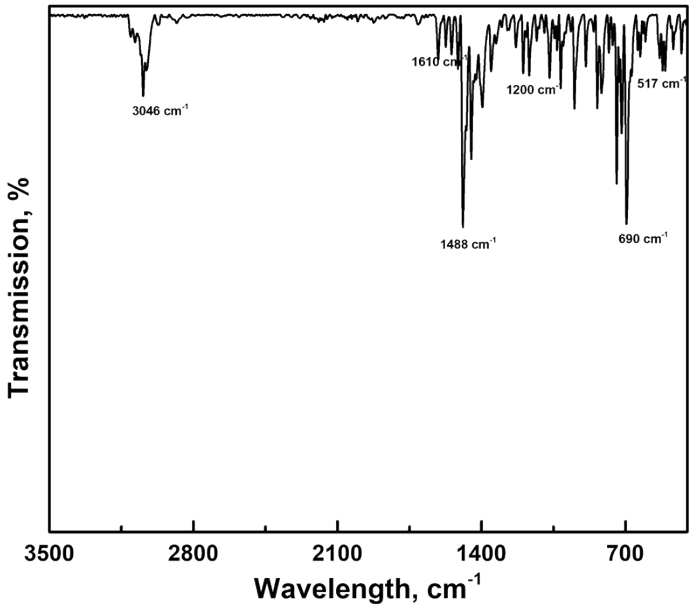


Figure S13. IR (ATR) spectrum of TTh-PPI-Br.

General procedure for the Suzuki–Miyaura cross-coupling

A halogenated phenanthroimidazole (0.005 mol) was placed in a round-bottom flask along with toluene (60 ml) and ethanol (20 ml). A solution of potassium carbonate (0.015 mol) in water (7.5 ml) was added, and the resulting biphasic mixture was degassed by several argon purges. Then, (4-vinylphenyl)boronic acid (0.0055 mol) and tetrakis(triphenylphosphine)palladium(0) (0.29 g) were added under argon. The reaction mixture was degassed again and refluxed for 5-8 h until complete conversion (monitored by TLC). After cooling, the mixture was diluted twofold with ethanol, and the precipitated solid was collected by filtration, washed thoroughly with water and ethanol, and air-dried. The crude product was purified by column chromatography on silica gel using dichloromethane as the eluent.

Synthesis of 2-(thiophen-2-yl)-1-(4'-vinyl-[1,1'-biphenyl]-4-yl)-1H-phenanthro[9,10-d]imidazole ***Th-VPPI***

Beige powder; yield: 76%. ^{1}H NMR (500.13 MHz, CDCl$_3$), δ: 8.85-8.83 (d, $^{3}J_{H,H}$ = 7.81 Hz, 1H), 8.70-8.69 (d, $^{3}J_{H,H}$ = 8.20 Hz, 1H), 8.64-8.63 (d, $^{3}J_{H,H}$ = 8.20 Hz, 1H), 7.95-7.94 (d, $^{3}J_{H,H}$ = 8.20 Hz, 2H), 7.71-7.68 (m, 3H), 7.62-7.57 (m, 3H), 7.52-7.51 (d, $^{3}J_{H,H}$ = 8.20 Hz, 2H), 7.45-7.42 (m, 1H), 7.24-7.21 (m, 3H), 6.91-6.90 (d, $^{3}J_{H,H}$ = 3.12 Hz, 1H), 6.86 (t, $^{3}J_{H,H}$ = 4.29 Hz, 1H), 6.78-6.73 (dd, $^{3}J_{H,H}$ = 17.97, 10.94 Hz, 1H), 5.83-5.80 (d, $^{3}J_{H,H}$ = 17.85 Hz, 1H), 5.31-5.29 (d, $^{3}J_{H,H}$ = 10.98 Hz, 1H). ^{13}C NMR

(125.76 MHz, $CDCl_3$), *δ*: 145.98; 142.56; 138.49; 137.56; 137.52; 137.27; 136.12; 133.01; 130.52; 129.58; 129.26; 129.17; 128.64; 128.26; 128.14; 127.50; 127.43; 127.36; 127.27; 127.22; 127.01; 126.94; 126.91; 126.40; 126.31; 125.67; 124.93; 124.09; 123.05; 122.89; 122.81; 120.58; 120.53; 114.64. IR (ATR, cm^{-1}): 3121, 3000 (Ar-C-H), 1915, 1800 (overtones of aromatic and vinyl C=C), 1606 (C=N, imidazole), 1573, 1496 ($C=C_{arom}$), 1450, 1386 (ring skeletal and C-N), 1336 (δ_{CH}, imidazole), 1231 (C-N+C-H), 1095 ($C\text{-}C_{arom}$), 985 ($\nu_{C=C}$, vinyl group), 935, 897 (γ_{CH}, aromatic/vinyl), 830 (γ_{CH}, p-disubstituted phenyl), 750 (γ_{CH}, phenanthrene unit), 711, 678 ($\nu_{C\text{-}S}$, thiophene), 513, 429 (skeletal deformations).

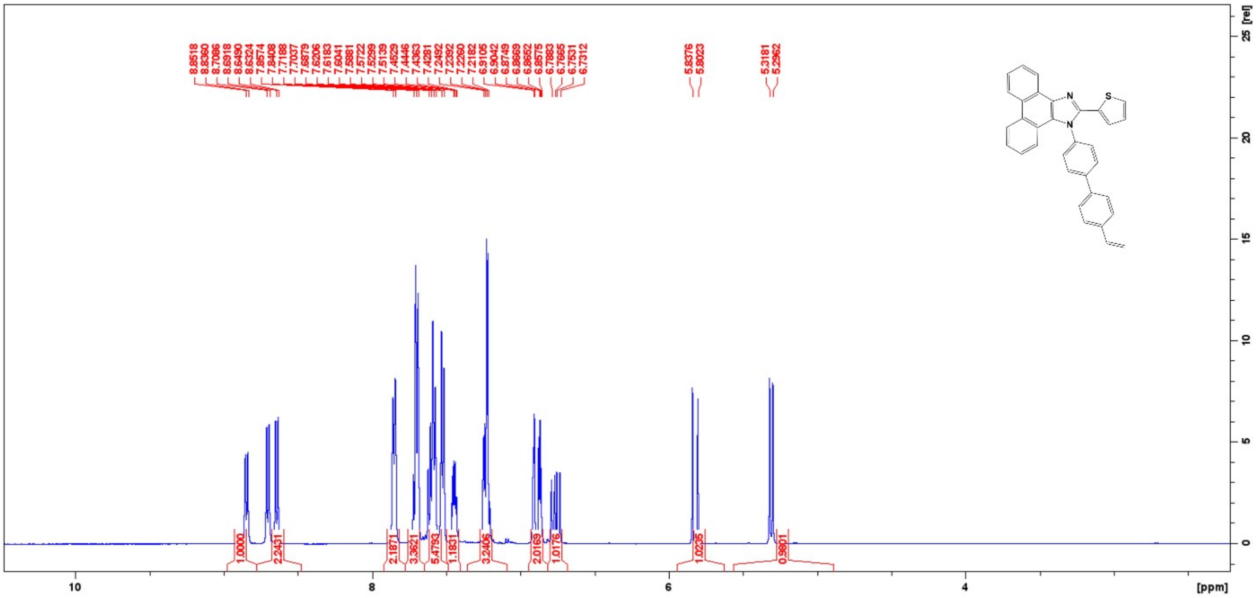


Figure S14. ^1H NMR spectrum of Th-VPPI in $CDCl_3$ at room temperature.

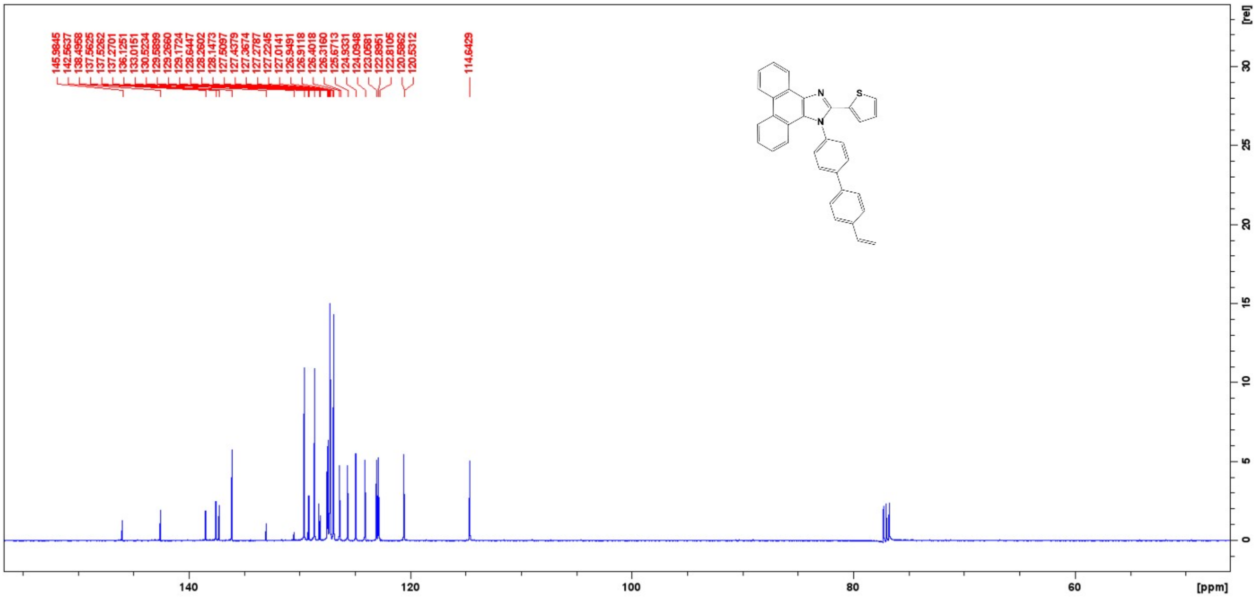


Figure S15. ^{13}C NMR spectrum of Th-VPPI in $CDCl_3$ at room temperature.

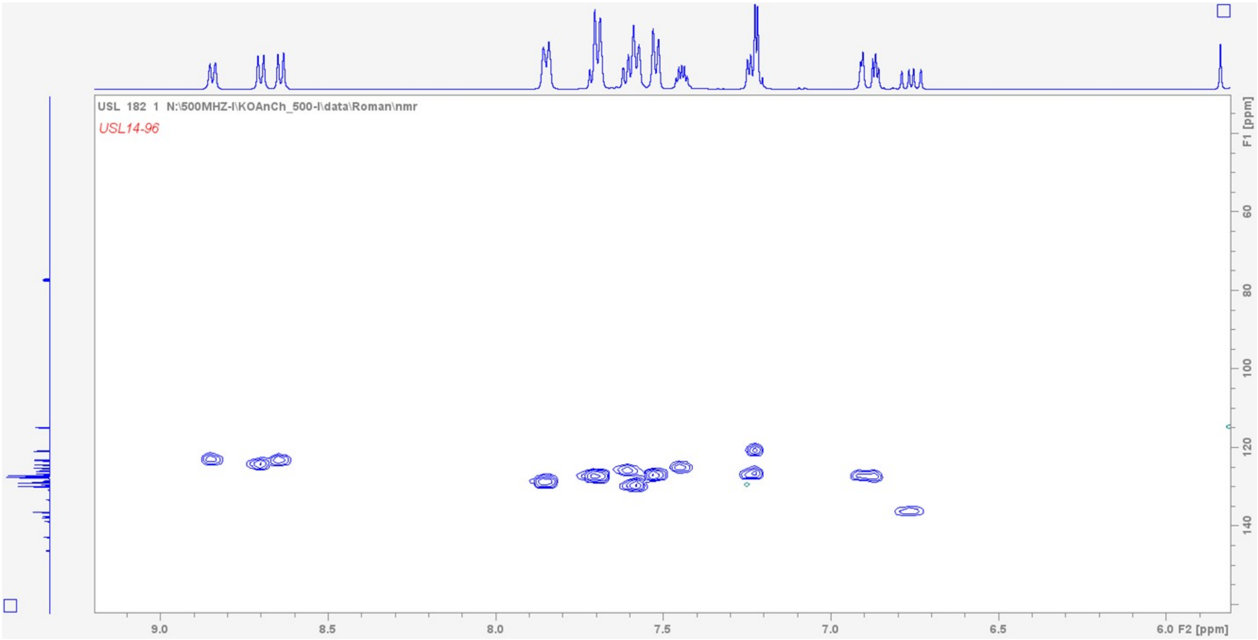


Figure S16. Partial ^{1}H-^{13}C-HSQC NMR spectrum of Th-VPPI in $CDCl_3$ at room temperature.

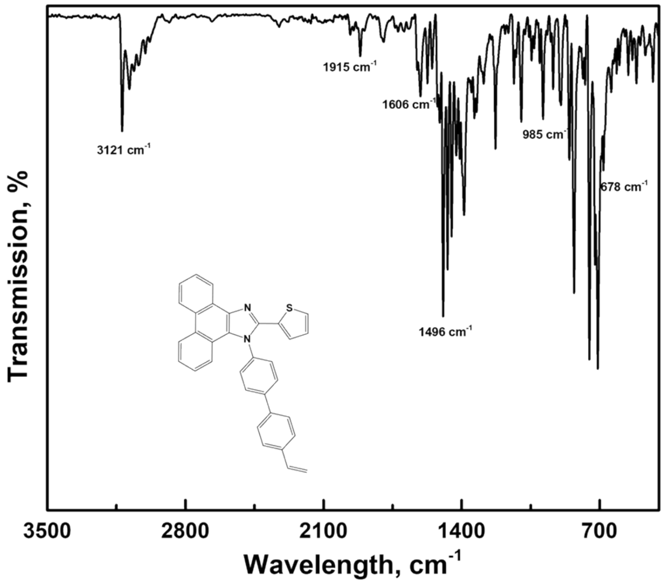


Figure S17. IR (ATR) spectrum of Th-VPPI .

Synthesis of 2-(benzo[b]thiophen-2-yl)-1-(4'-vinyl-[1,1'-biphenyl]-4-yl)-1H-phenanthro[9,10-d]imidazole ***BTh-VPPI***

Beige powder; yield: 81%. ^{1}H NMR (500.13 MHz, CDCl$_3$), δ: 8.84-8.83 (d, $^{3}J_{H,H}$ = 7.91 Hz, 1H), 8.71-8.69 (d, $^{3}J_{H,H}$ = 8.27 Hz, 1H), 8.64-8.63 (d, $^{3}J_{H,H}$ = 8.27 Hz, 1H), 7.92-7.91 (d, $^{3}J_{H,H}$ = 8.27 Hz, 2H), 7.75-7.74 (d, $^{3}J_{H,H}$ = 8.27 Hz, 2H), 7.72-7.69 (m, 2H), 7.66-7.64 (d, $^{3}J_{H,H}$ = 8.27 Hz, 2H), 7.61 (t, $^{3}J_{H,H}$ = 7.56 Hz, 1H), 7.56-7.53 (m, 3H), 7.47-7.45 (m, 1H), 7.25-7.20 (m, 4H), 7.04 (s, 1H), 6.80-6.74 (dd, $^{3}J_{H,H}$ = 17.59, 10.91 Hz, 1H), 5.84-5.81 (d, $^{3}J_{H,H}$ = 17.59 Hz, 1H), 5.32-5.30 (d, $^{3}J_{H,H}$ = 10.91 Hz, 1H). ^{13}C NMR (125.76 MHz, CDCl$_3$), *δ*: 145.61; 142.74; 140.18; 139.60; 138.49; 137.74; 137.64; 137.18; 136.09; 133.02; 129.57; 129.38; 128.74; 128.66; 128.31; 127.30; 127.28; 126.94; 126.88; 126.43; 125.80; 125.15; 125.11; 124.41; 124.12; 123.53; 123.04; 122.90; 122.72; 121.92; 120.70; 114.69. IR (ATR, cm^{-1}): 3054 (Ar-C-H), 1919, 1830 (overtones of aromatic and vinyl C=C), 1606 (C=N, imidazole), 1492, 1454 (C=C$_{arom}$), 1391 (C-N + ring skeletal), 1231, 1192, 1154 (δ_{CH+C-N}), 990 ($\nu_{C=C}$, vinyl group), 935, 910 (γ_{CH}, aromatic/vinyl), 830 (γ_{CH}, p-disubstituted phenyl), 737 (γ_{CH}, phenanthrene unit), 656 (ν_{C-S}, benzo[*b*]thiophene), 559, 433 (skeletal deformations).

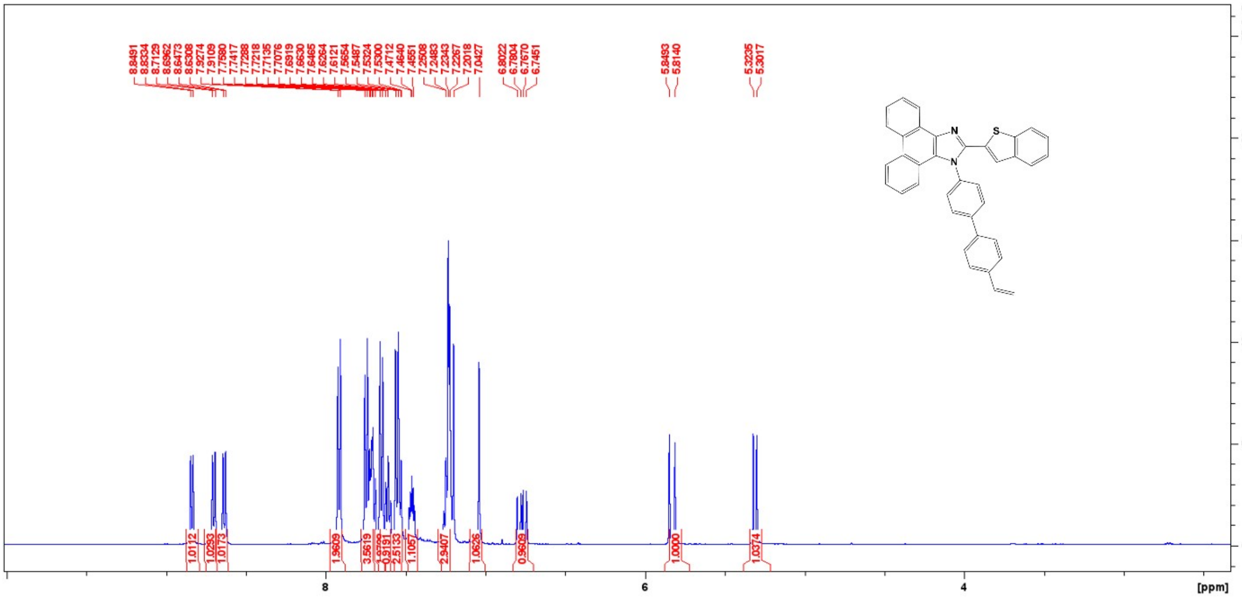


Figure S18. ^{1}H NMR spectrum of BTh-VPPI in CDCl$_3$ at room temperature.

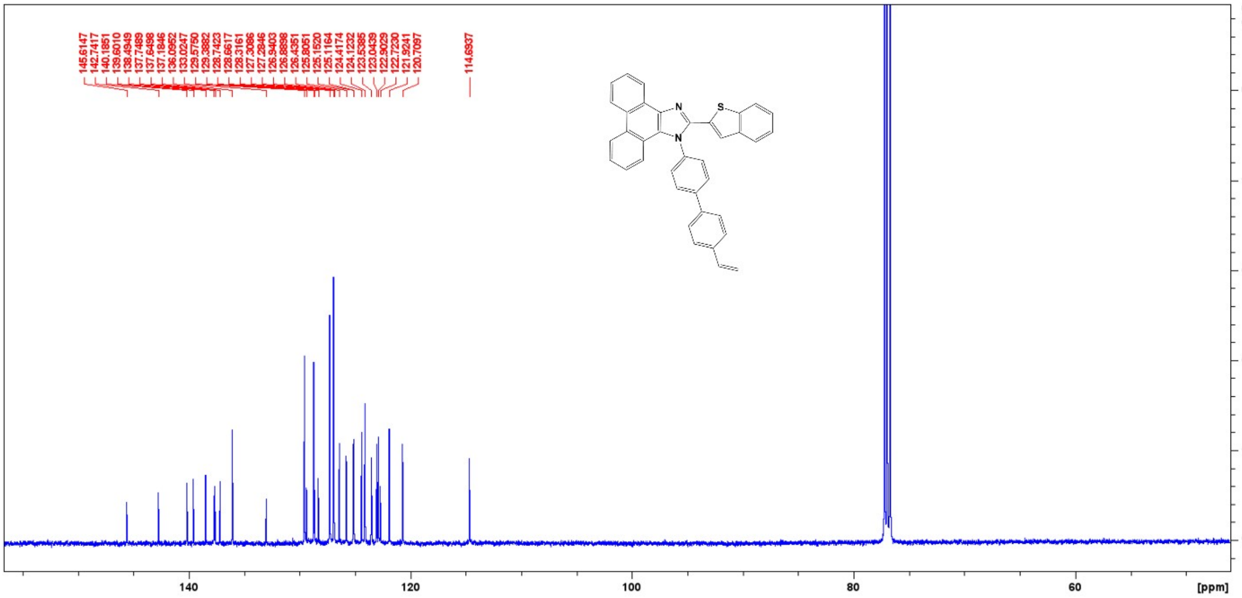


Figure S19. ^{13}C NMR spectrum of BTh-VPPI in $CDCl_3$ at room temperature.

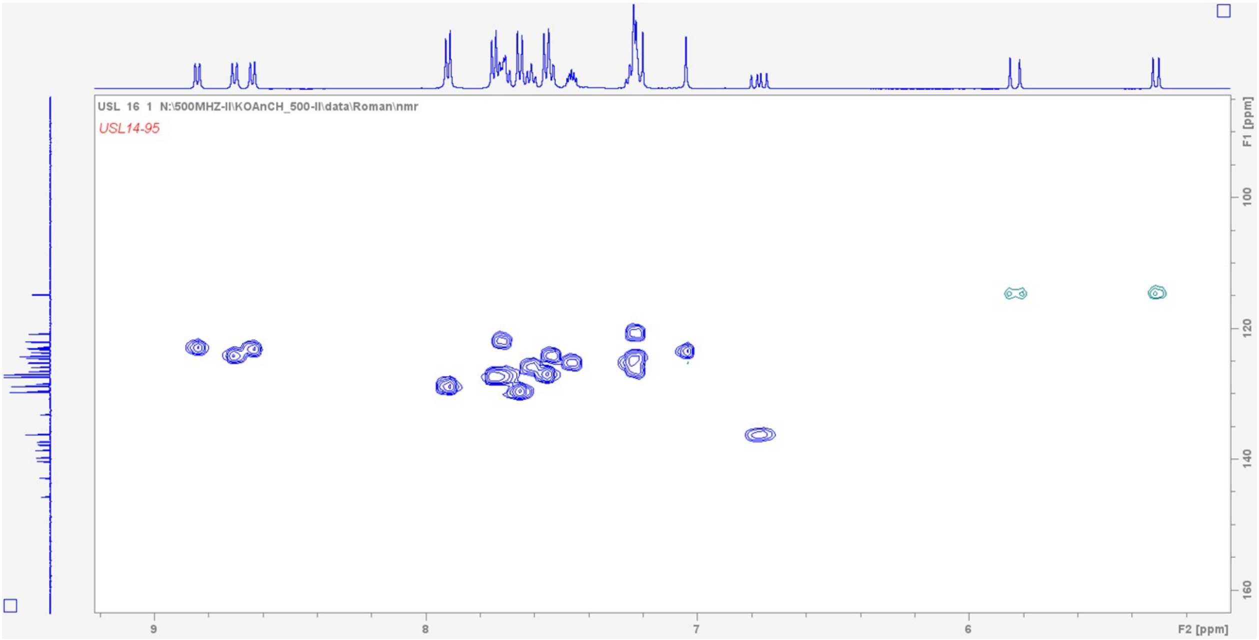


Figure S20. Partial ^{1}H-^{13}C-HSQC NMR spectrum of BTh-VPPI in $CDCl_3$ at room temperature.

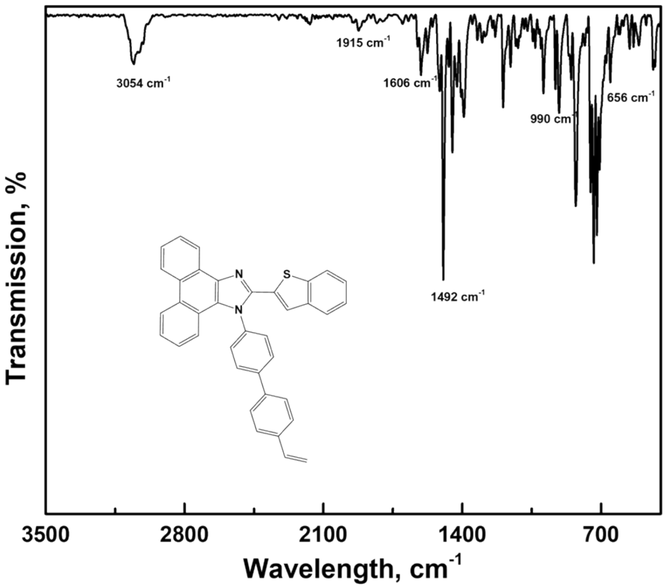


Figure S21. IR (ATR) spectrum of BTh-VPPI .

Synthesis of 2-(thieno[3,2-b]thiophen-2-yl)-1-(4'-vinyl-[1,1'-biphenyl]-4-yl)-1H-phenanthro[9,10-d]imidazole ***TTh-VPPI***

Beige powder; yield: 79%. ^{1}H NMR (500.13 MHz, CDCl3), δ: 8.84-8.83 (d, $^3J_{H,H}$ = 7.58 Hz, 1H), 8.69-8.68 (d, $^3J_{H,H}$ = 8.31 Hz, 1H), 8.63-8.61 (d, $^3J_{H,H}$ = 8.31 Hz, 1H), 7.90-7.89 (d, $^3J_{H,H}$ = 8.31 Hz, 2H), 7.74-7.73 (d, $^3J_{H,H}$ = 8.31 Hz, 2H), 7.69 (t, $^3J_{H,H}$ = 7.54 Hz, 1H), 7.63-7.58 (m, 3H), 7.55-7.53 (d, $^3J_{H,H}$ = 8.31 Hz, 2H), 7.44 (t, $^3J_{H,H}$ = 7.58 Hz, 1H), 7.31-7.30 (d, $^3J_{H,H}$ = 5.41 Hz, 1H), 7.23-7.17 (m, 2H), 7.14-7.13 (d, $^3J_{H,H}$ = 5.41 Hz, 1H), 7.06 (br.s, 1H), 6.79-6.73 (dd, $^3J_{H,H}$ = 17.34, 10.83 Hz, 1H), 5.84 (d, $^3J_{H,H}$ = 17.69 Hz, 1H), 5.31-5.29 (d, $^3J_{H,H}$ = 10.83 Hz, 1H). ^{13}C NMR (125.76 MHz, $CDCl_3$), *δ*: 145.75; 142.75; 140.63; 139.37; 138.39; 137.65; 137.02; 136.09; 129.25; 128.37; 128.29; 127.31; 127.27; 126.93; 126.43; 124.09; 123.03; 122.93; 122.65; 120.58; 119.37; 114.68. IR (ATR, cm^{-1}): 3067 (Ar-C-H), 1906, 1796 (overtones of aromatic and vinyl C=C), 1606 (C=N, imidazole), 1496, 1454 (C-C_{arom}), 1391 (ring skeletal and C-N), 1200, 1171 ($\delta_{CH+C\text{-}N}$), 985 ($\nu_{C=C}$, vinyl group), 944, 897 (γ_{CH}, aromatic/vinyl), 830 [(γ_{CH}, p-disubstituted phenyl), 749 (γ_{CH}, phenanthrene unit), 720, 690 ($\nu_{C\text{-}S}$, thieno[3,2-*b*]thiophene), 631 (ring deformation), 517, 471 (skeletal modes).

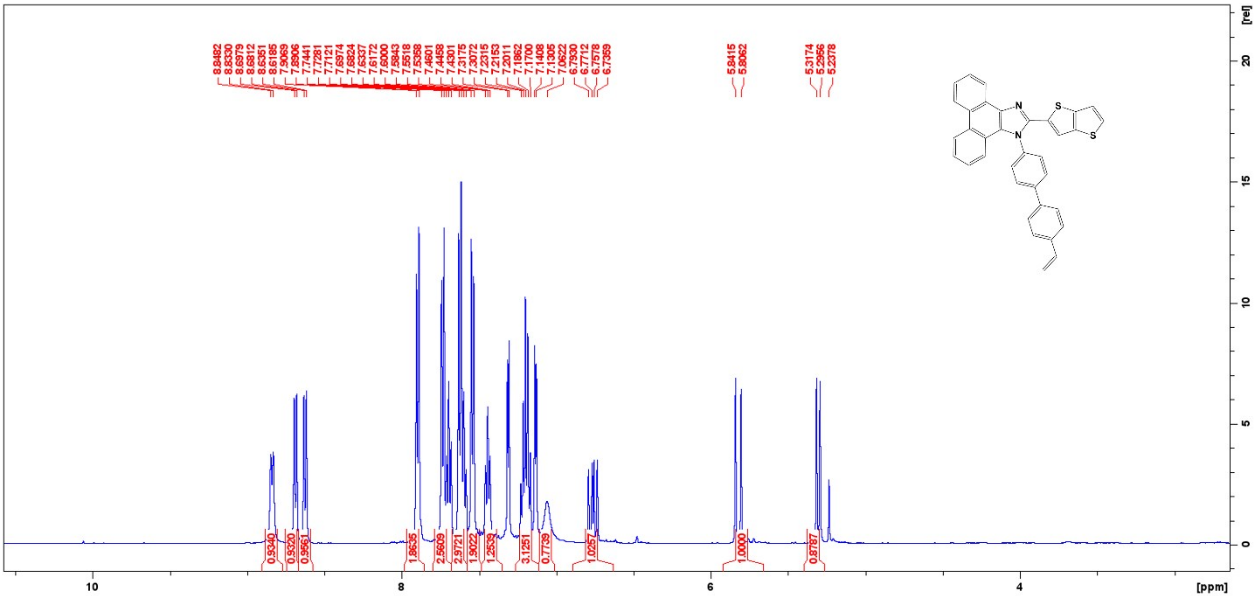


Figure S22. ^{1}H NMR spectrum of TTh-VPPI in $CDCl_3$ at room temperature.

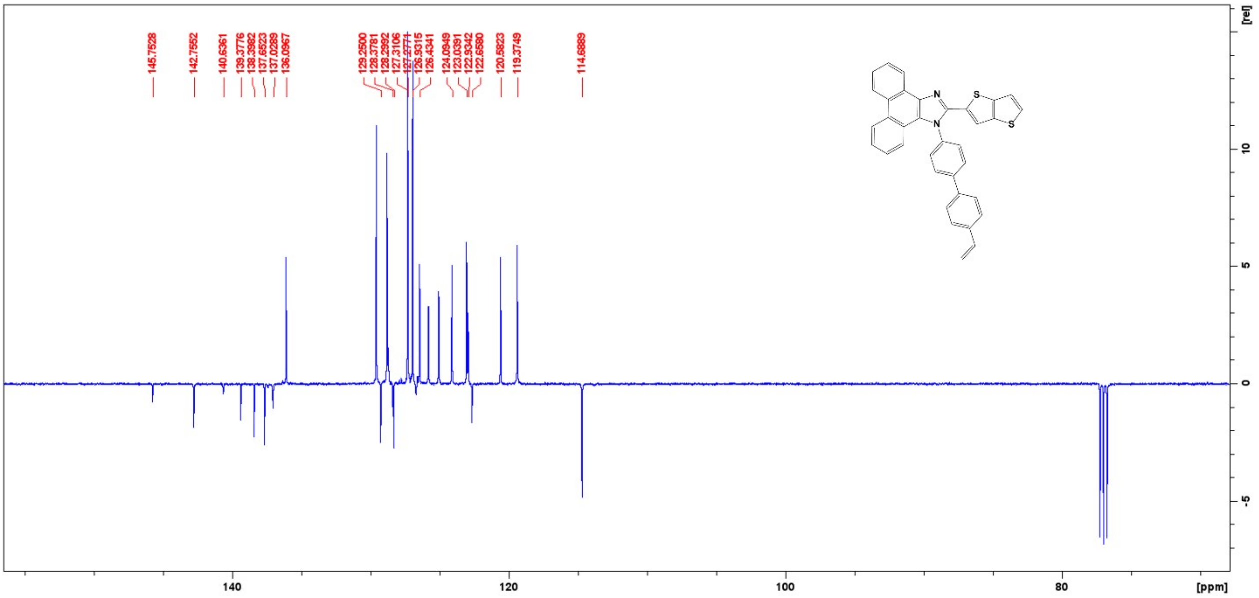


Figure S23. ^{13}C NMR spectrum of TTh-VPPI in $CDCl_3$ at room temperature.

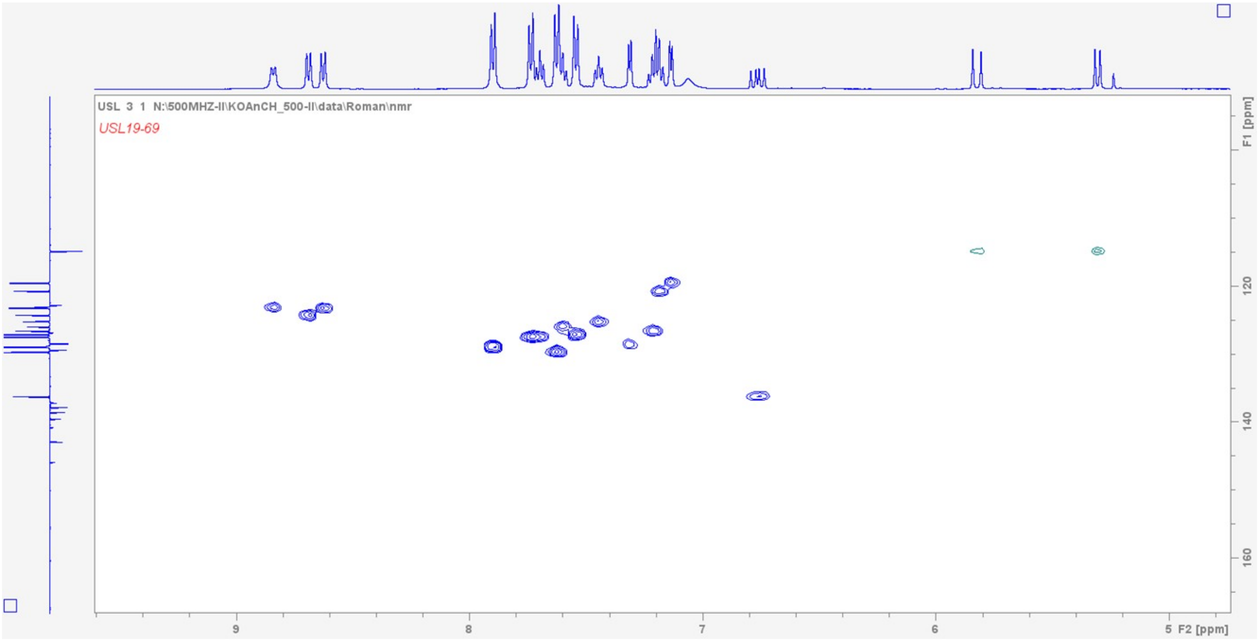


Figure S24. Partial ^{1}H-^{13}C-HSQC NMR spectrum of TTh-VPPI in $CDCl_3$ at room temperature.

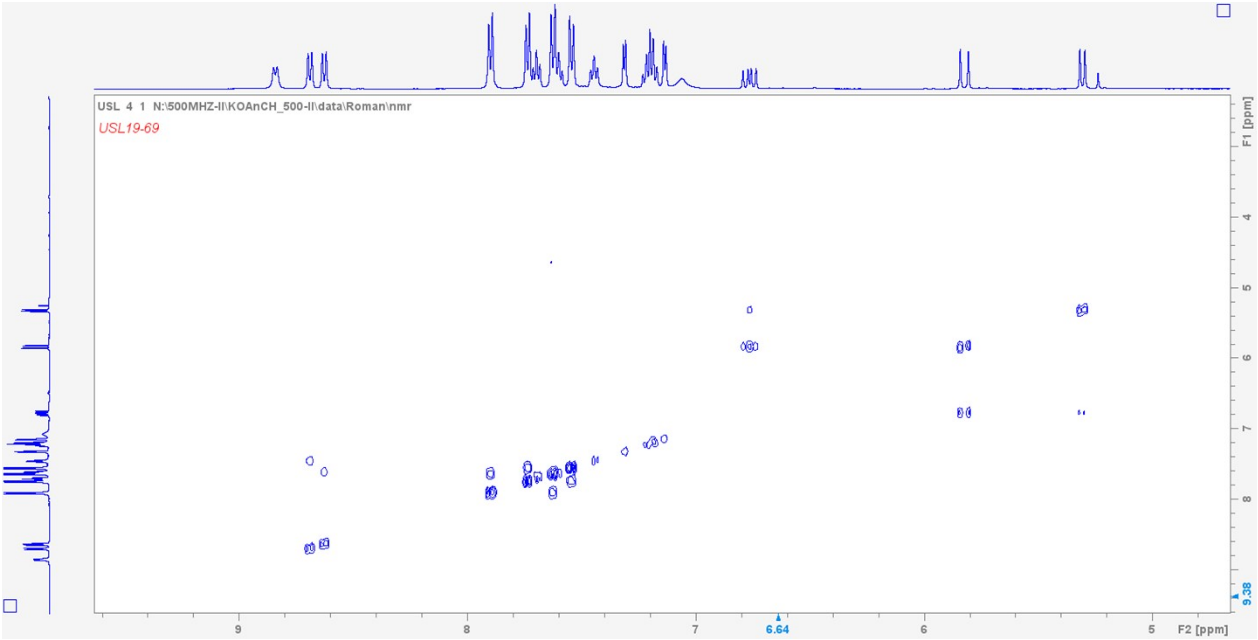


Figure S25. ^{1}H-^{1}H-COSY NMR spectrum of TTh-VPPI in $CDCl_3$ at room temperature.

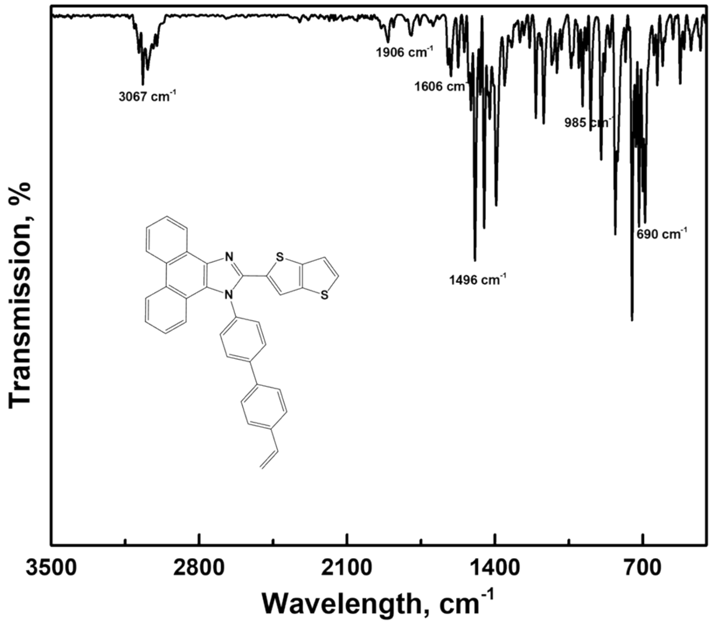


Figure S26. IR (ATR) spectrum of TTh-PPI-Br.

Radical Copolymerization

Radical copolymerization of the three phenanthroimidazole-based vinyl monomers was performed under identical conditions. Each monomer (0.10 g, 5 wt%) was reacted with N-vinylcarbazole (2.0 g, 10.6 mmol) in dry 1,2-dichlorobenzene (12 ml) using azobisisobutyronitrile (AIBN, 0.03 g, 0.18 mmol) as a radical initiator. The mixture was degassed, backfilled with argon, sealed, and stirred at 75 °C for 48 hours. After cooling to room temperature, the reaction mixture was poured into hexane (100 ml). The resulting precipitate was filtered, thoroughly washed with hexane, and dried under vacuum. The copolymers obtained appeared as white-off powders: P(Th-VPPI-*co*-VK): yield 1.9 g; P(BTh-VPPI-*co*-VK): yield 2.0 g; P(TTh-VPPI-*co*-VK): yield 1.8 g.

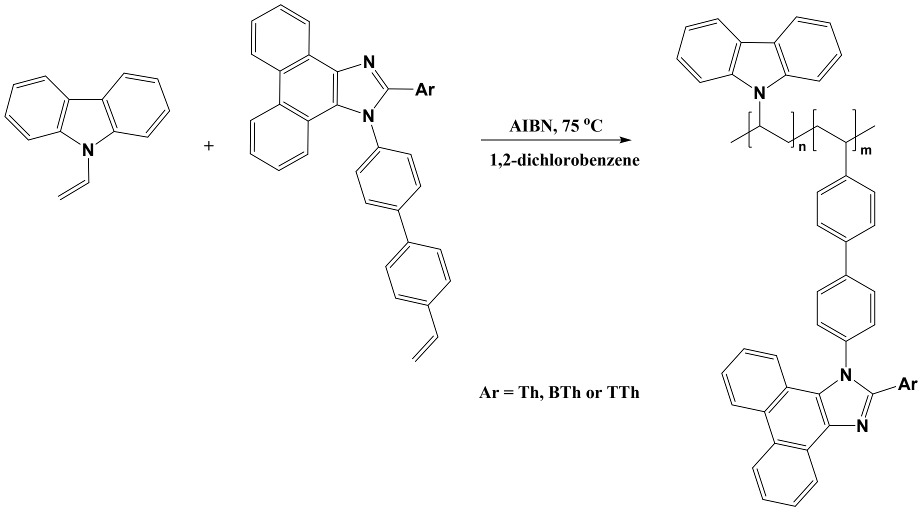


Figure S27. Schematic representation of the radical copolymerization of N-vinylcarbazole with vinyl-functionalized phenanthroimidazole monomers (VPPI; Ar = Th, BTh or TTh) to give statistical P(VK-*co*-VPPI) copolymers. Indices n and m indicate the relative numbers of repeating units and do not imply a defined sequence distribution.

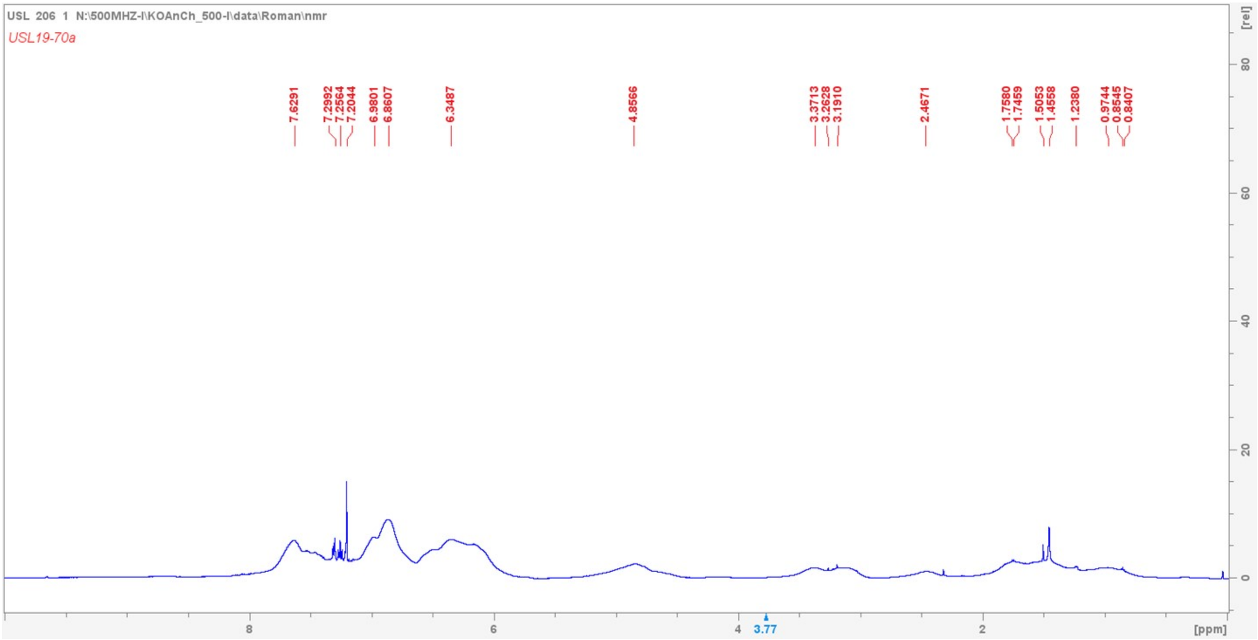


Figure S27. ^{1}H NMR spectrum of PVK pure in $CDCl_3$ at room temperature.

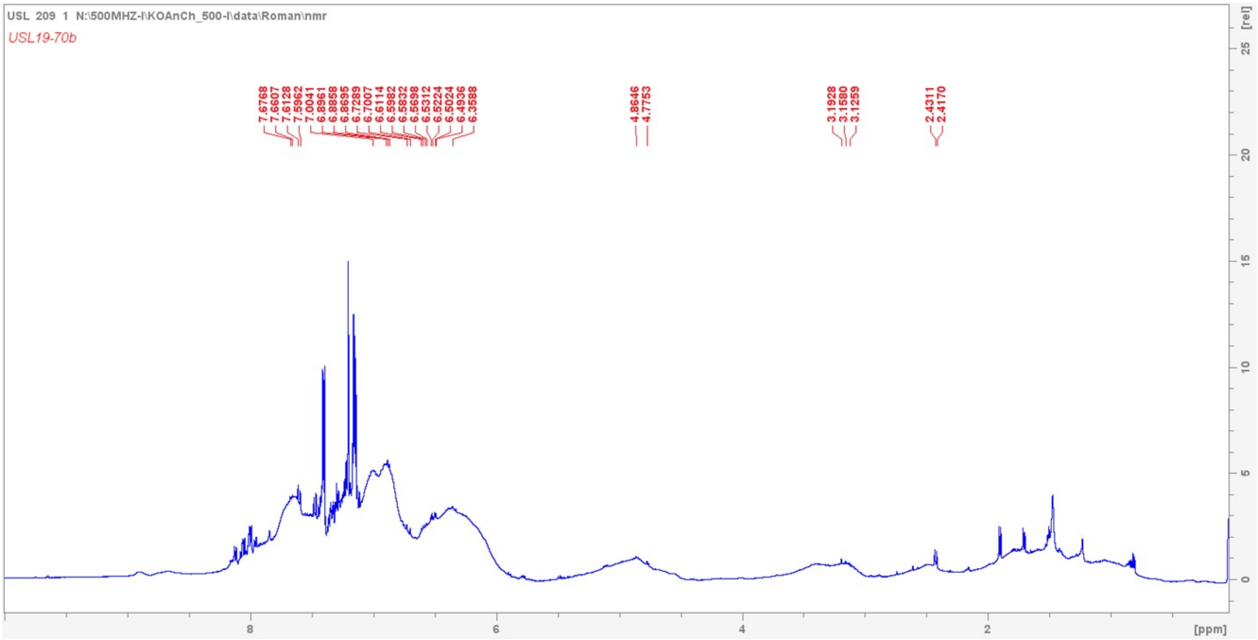


Figure S28. ^{1}H NMR spectrum of P(Th-VPPI-*co*-VK) in $CDCl_3$ at room temperature.

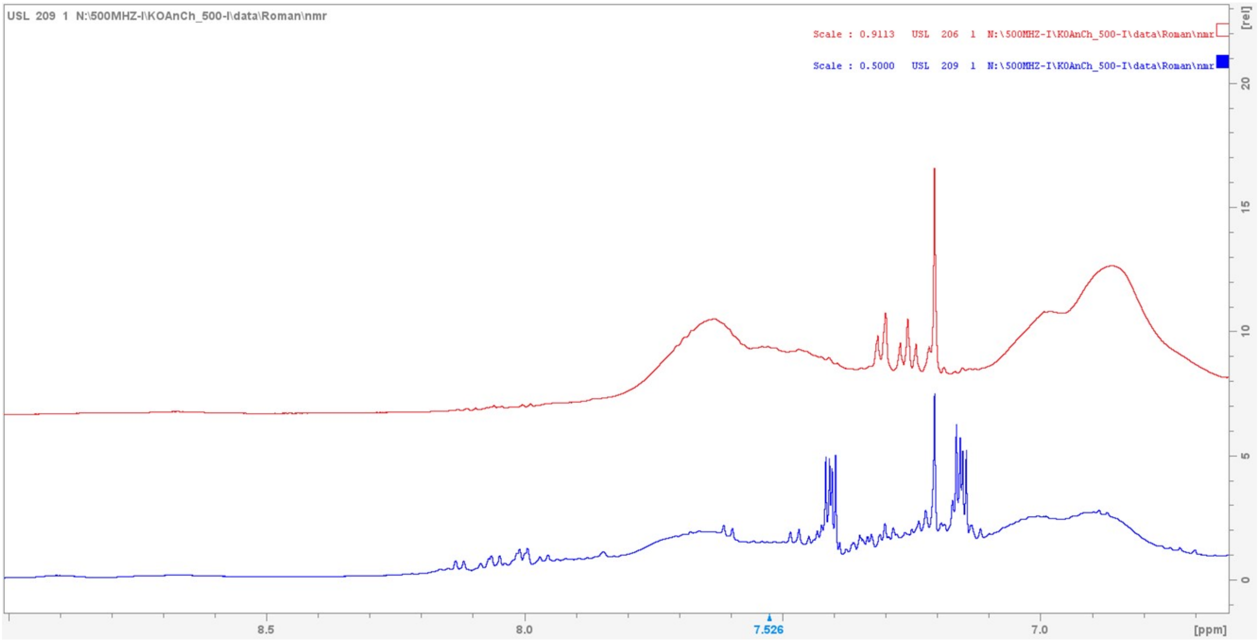


Figure S29. ^{1}H NMR spectrum of P(Th-VPPI-*co*-VK) in $CDCl_3$ at room temperature in comparison with PVK pure (aromatic part of the spectra).

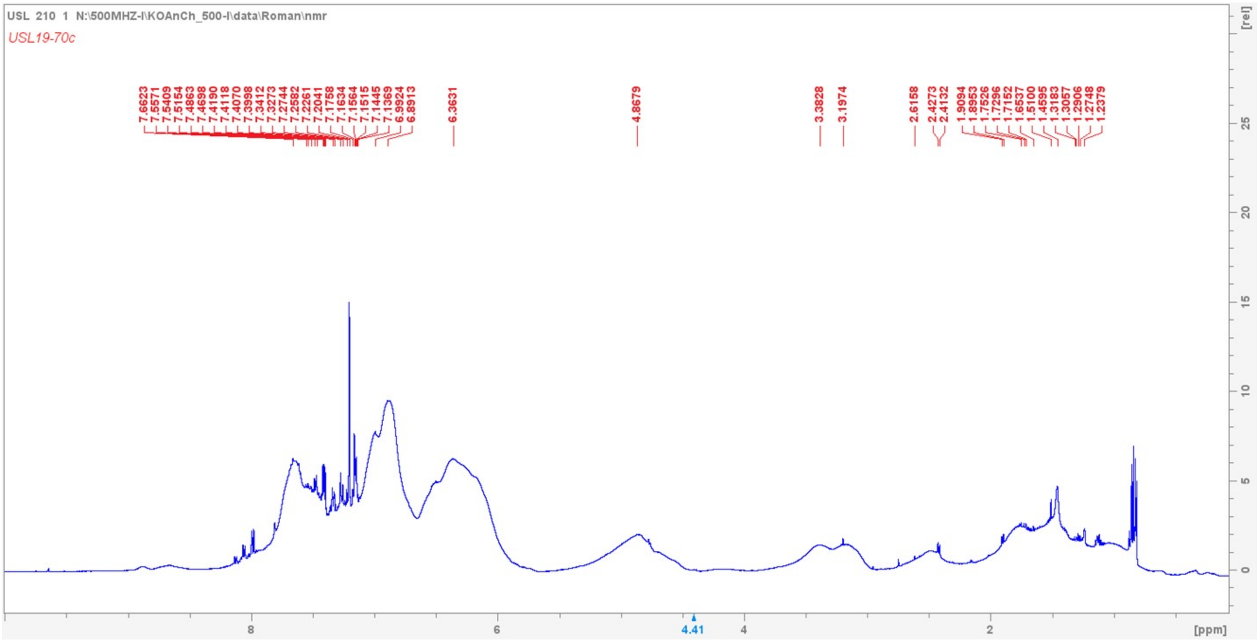


Figure S30. ^{1}H NMR spectrum of P(BTh-VPPI-*co*-VK) in $CDCl_3$ at room temperature.

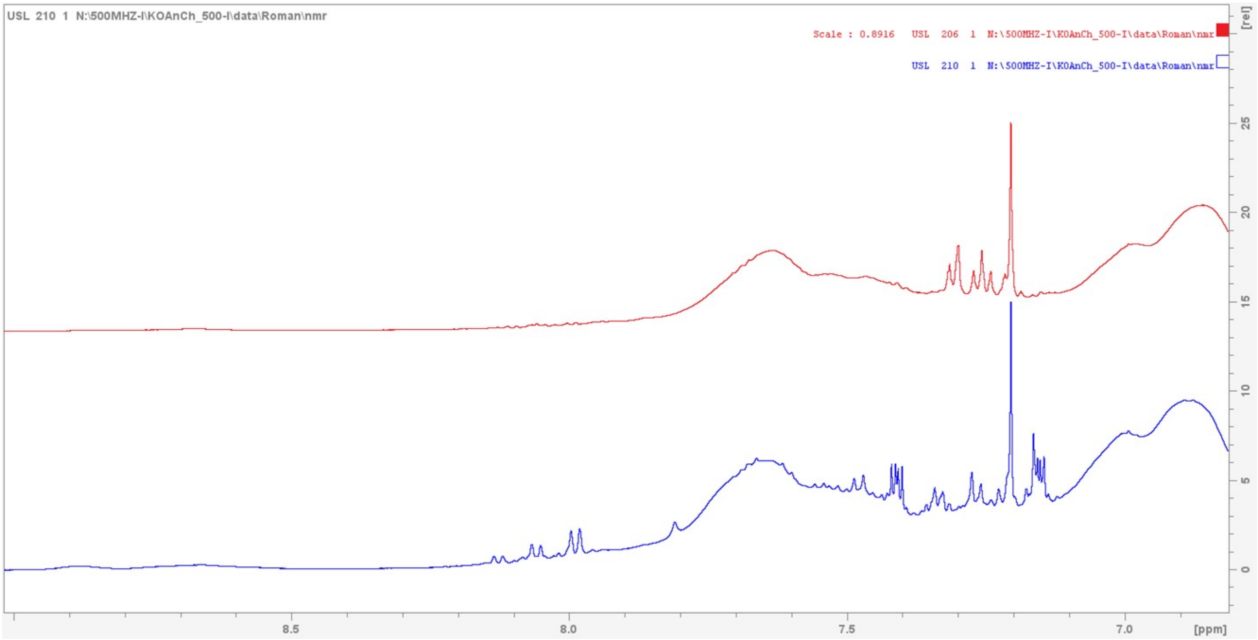


Figure S31. ^{1}H NMR spectrum of P(BTh-VPPI-*co*-VK) in $CDCl_3$ at room temperature in comparison with PVK pure (aromatic part of the spectra).

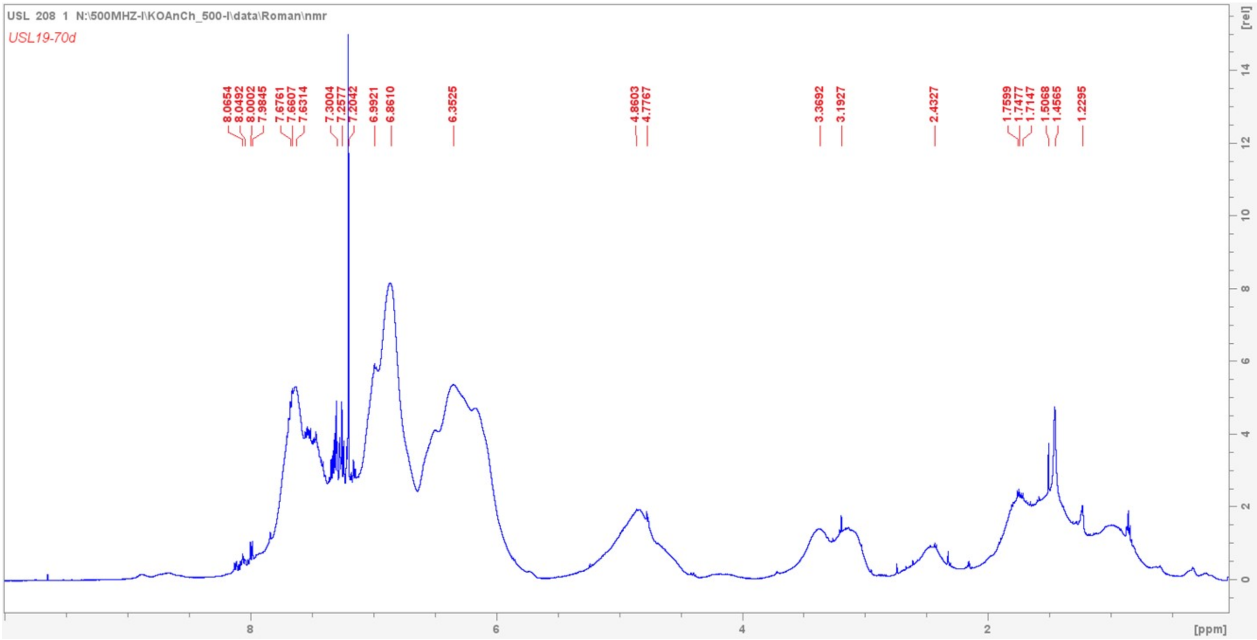


Figure S32. ^{1}H NMR spectrum of P(TTh-VPPI-*co*-VK) in $CDCl_3$ at room temperature.

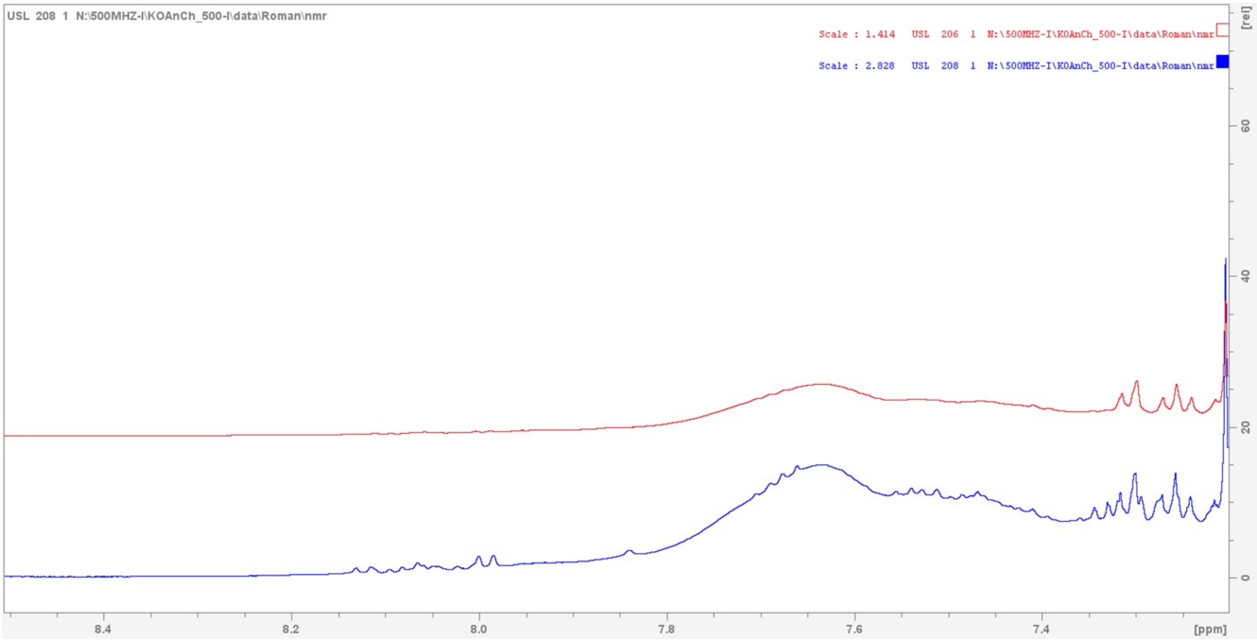


Figure S33. ^{1}H NMR spectrum of P(TTh-VPPI-*co*-VK) in $CDCl_3$ at room temperature in comparison with PVK pure (aromatic part of the spectra).

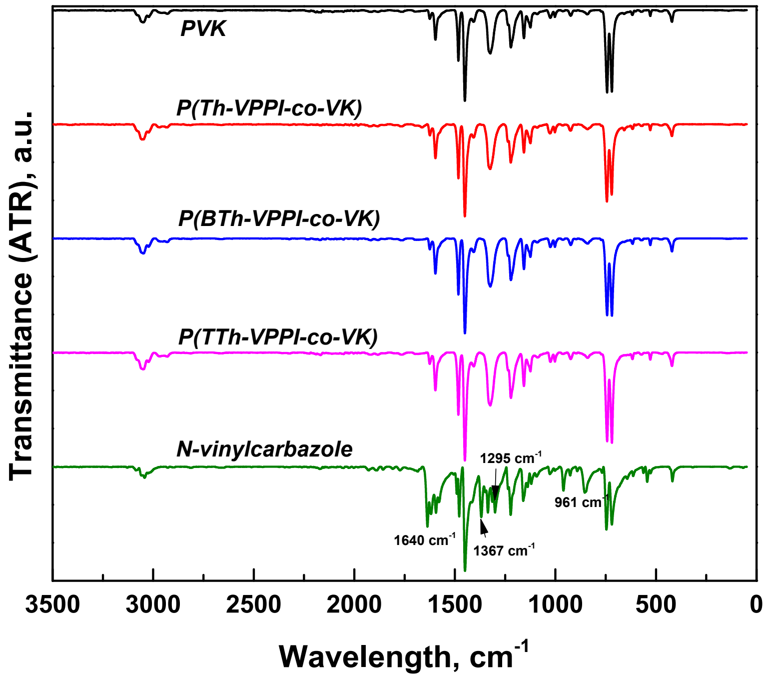


Figure S34. FTIR (ATR) spectra of copolymers.

Crystallography

Single crystals of **BTh-PPI-I, TTh-PPI-Br** and **TTh-VPPI** were grown from CH_2Cl_2/petrol ether (5:1).

Table S1. Selected parameters for compounds with the deposition numbers 2528847-2528849.

Unit Cell Parameters	TTh-PPI-Br	_BTh-PPI-I	TTh-VPPI
a	29.0625(6)	19.1835(4)	9.4257(3)
b	7.21410(10)	15.9078(4)	11.6997(3)
c	23.2557(5)	14.7232(4)	12.6281(4)
alpha	90	90	106.5550(10)
beta	120.7400(10)	95.9050(10)	107.1420(10)
gamma	90	90	93.3040(10)
volume	4190.71(14)	4469.20(19)	1260.23(7)
space_group	C2/c	P21/c	P-1

Thermal analysis

All STA plots show TGA (black) and DTG (blue, first derivative of TGA) curves with evaluation of T_{ons_1}, T_{onsMD}, T_{max}, mass-loss intervals, and residual mass.

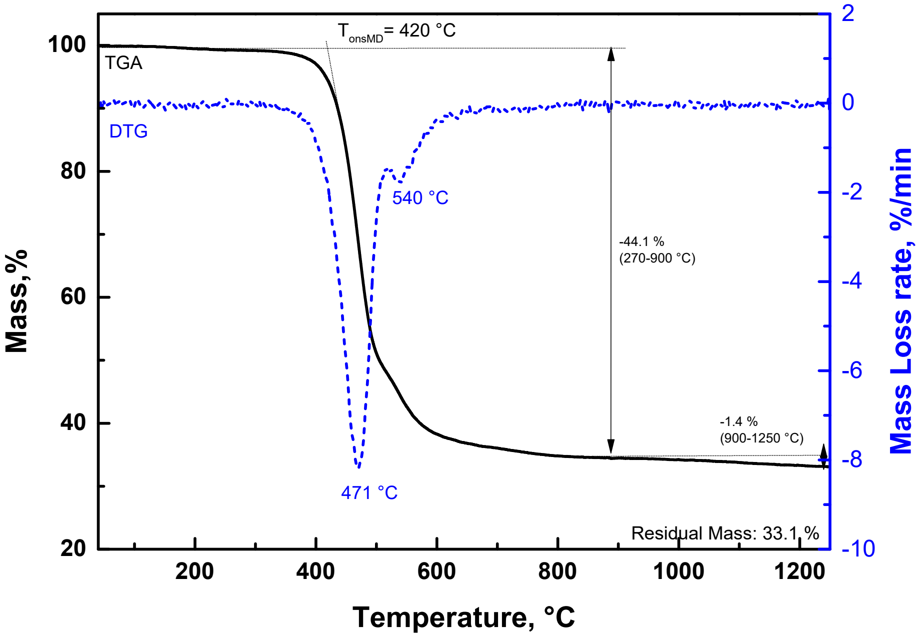


Figure S35. STA analysis of monomer Th-VPPI.

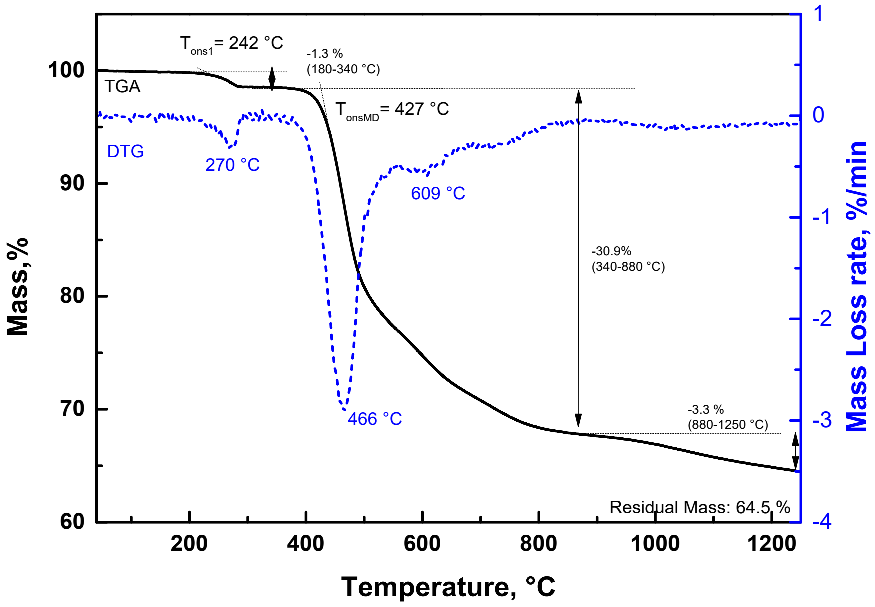


Figure S35. STA analysis of monomer BTh-VPPI.

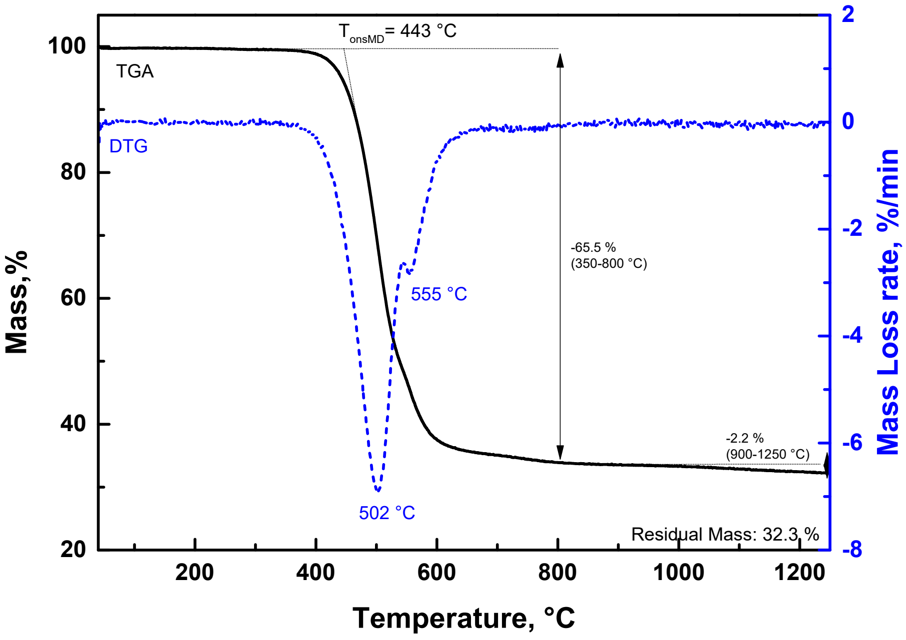


Figure S37. STA analysis of monomer TTh-VPPI.

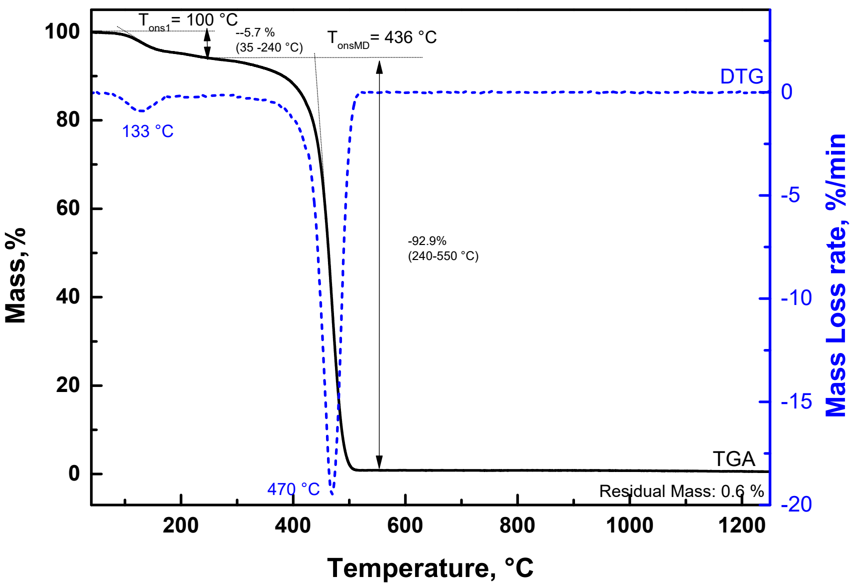


Figure S38. STA analysis of PVK pure.

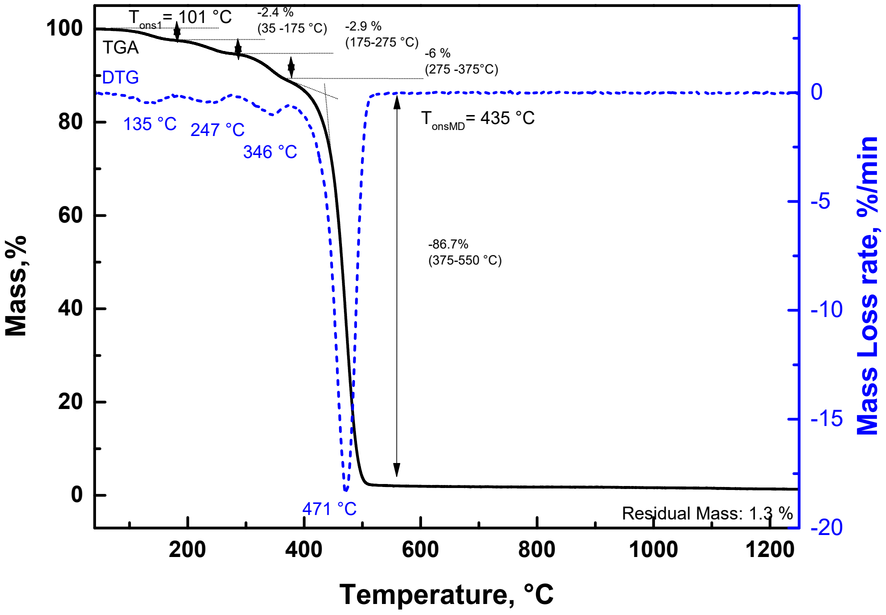


Figure S39. STA analysis of copolymer P(BTh-VPPI-*co*-VK).

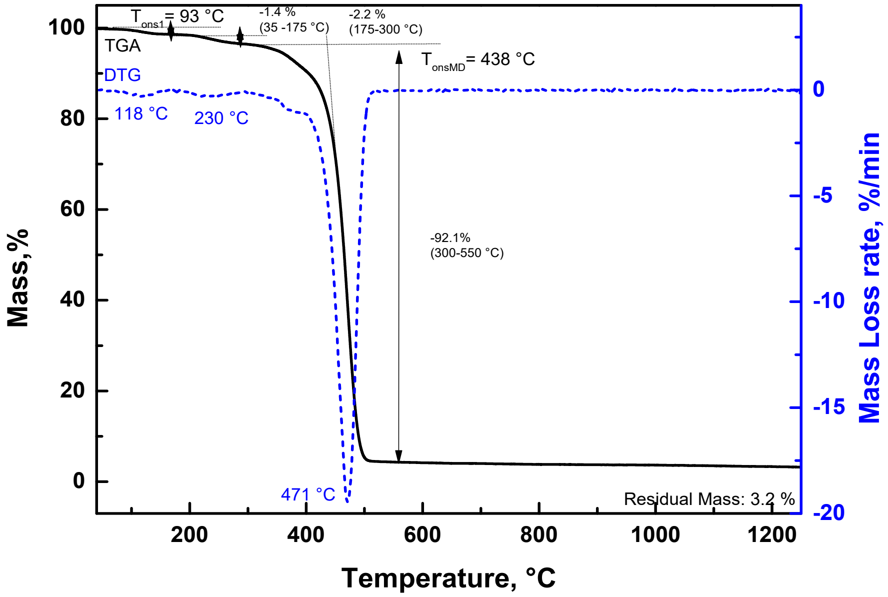


Figure S40. STA analysis of copolymer P(TTh-VPPI-*co*-VK).

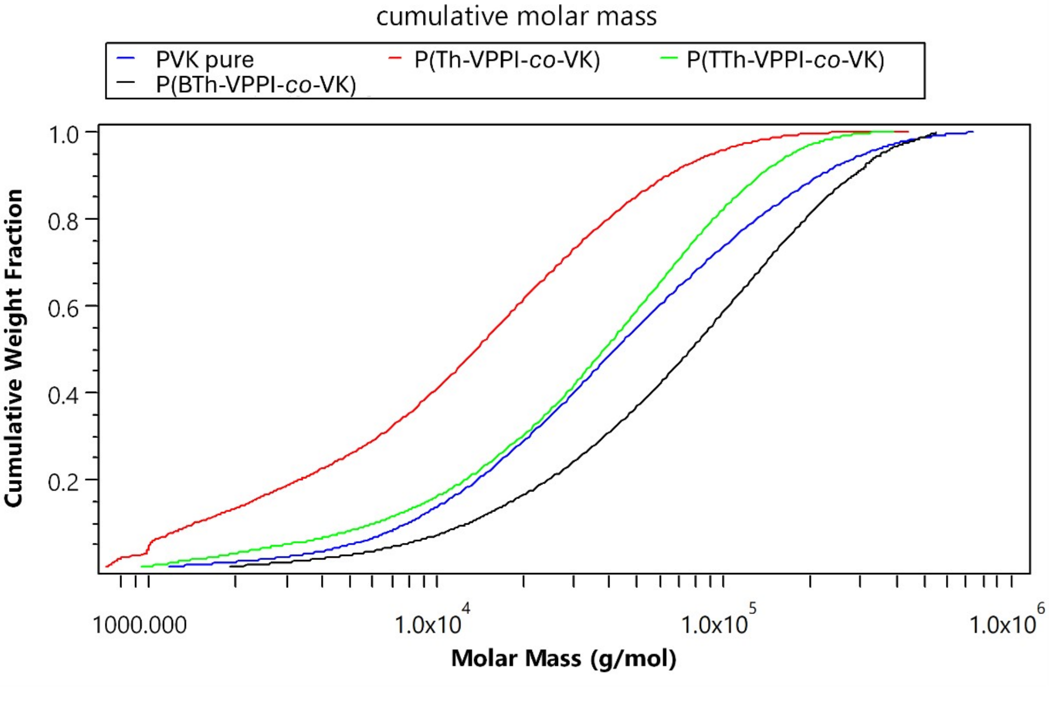


Figure S41. Overlay of cumulative molar mass distribution curves of the analysed polymers (sample identification is in the heading).

Table S2. Electrochemical and optical energy levels of the monomers

Compound	$E_{ox,onset}$ (vs Ag/AgCl)	HOMO, eV	$E_g$opt, eV	LUMO, eV
Th-VPPI	0.709	-5.32	3.18	-2.14
BTh-VPPI	0.732	-5.34	3.08	-2.26
TTh-VPPI	0.711	-5.32	3.09	-2.23

HOMO energy levels were calculated from the oxidation onset potentials using the relation HOMO=−($E_{ox,onset}$ (vs Fc/Fc$^+$)+4.8). The optical band gap $E_g$opt was determined from the absorption onset. LUMO energy levels were estimated using the relation LUMO=HOMO+$E_g$opt.

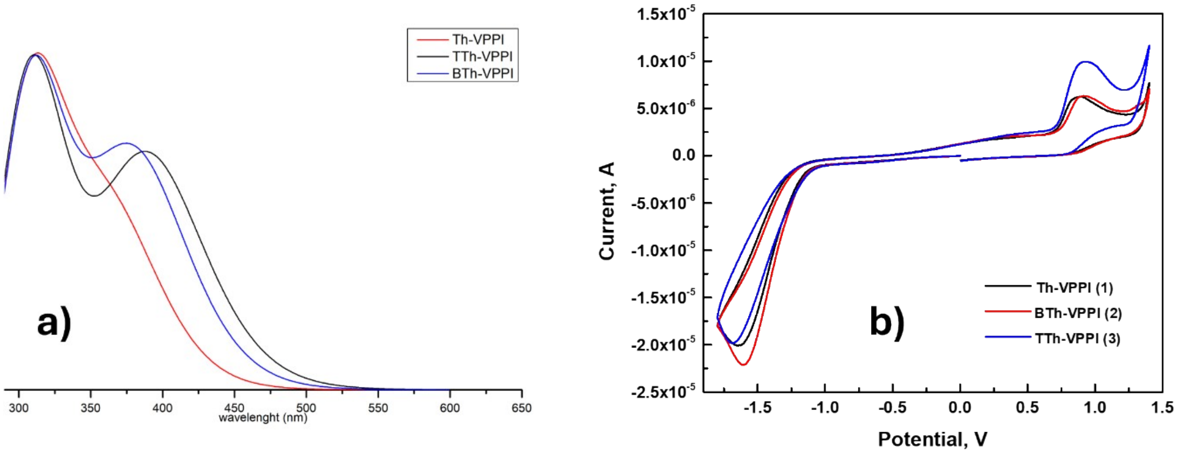


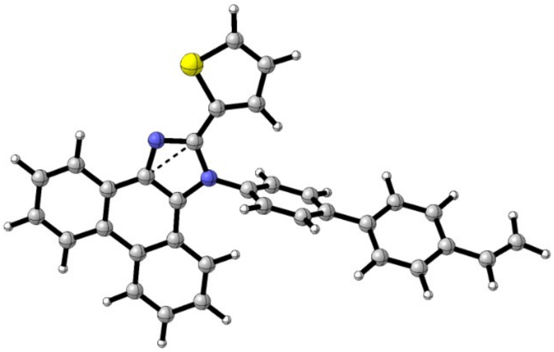
Figure S42. Simulated absorption spectra of Th-VPPI, BTh-VPPI, and TTh-VPPI obtained from TD-DFT calculations (B3LYP/6-311+G(d,p), CPCM ($CHCl_3$)). The spectra are dominated by the lowest-energy $S_0 \rightarrow S_1$ transition, corresponding predominantly to HOMO → LUMO excitation (a). Cyclic voltammograms of Th-VPPI, BTh-VPPI and TTh-VPPI monomers recorded in CH_2Cl_2 containing 0.1 M $TBAPF_6$ at a scan rate of 100 mV/s using a Pt working electrode, Pt counter electrode, and Ag/AgCl reference electrode.

Table S3. TD-DFT calculated excitation energies (λ_{calc}), oscillator strengths (f), and main orbital contributions for the lowest-energy electronic transitions of Th-VPPI, BTh-VPPI, and TTh-VPPI (B3LYP/6-311+G(d,p), CPCM ($CHCl_3$)).

Compound	**λ_{max}, (nm)**	**$\lambda_{A(max)}$ calc, (nm)**	**f**	**Transition**	**Main orbital transition**
Th-VPPI	370	382	0.0007	$S_0 \rightarrow S_1$	HOMO→LUMO
TTh-VPPI	379	391	0.84	$S_0 \rightarrow S_1$	HOMO→LUMO
BTh-VPPI	380	381	1.02	$S_0 \rightarrow S_1$	HOMO→LUMO

Coordinates

Th-VPPI



58
0 1 -1779.000550

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C	-7.1157460	-1.6103350	-0.0965190
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C	-3.4322850	-2.5089620	-0.0631490
C	-2.1587540	-1.8529930	-0.0342810
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C	-0.9780650	-2.6288420	-0.0340130

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H	2.7912530	-0.1985320	2.2092350
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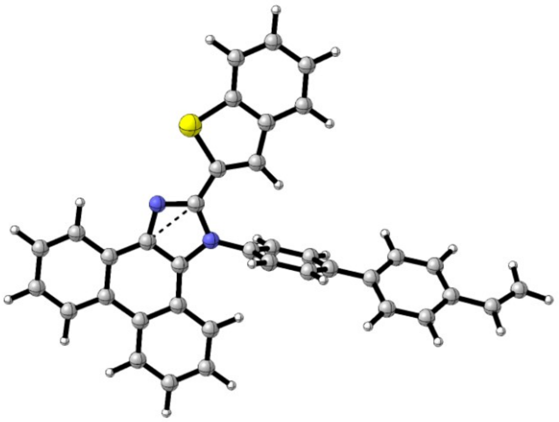
BTh-VPPI



64

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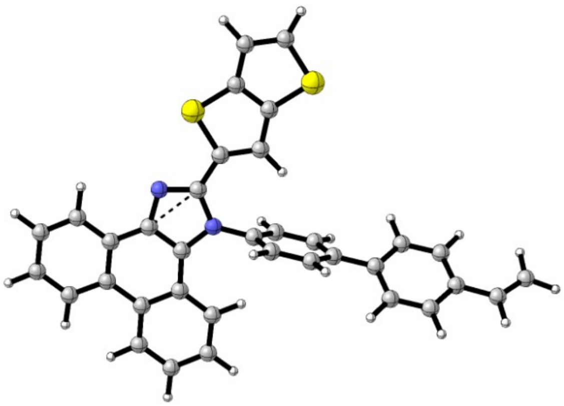
TTh-VPPI



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C	-2.3737410	-0.9038810	-0.0115920
C	-1.3534550	-3.2025900	-0.0170440
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C	-1.5194450	-4.5729820	-0.0295940
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H	-5.7924240	1.3149570	-0.0455700
H	-6.4566860	-3.5903680	-0.0829820
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H	-0.6509830	-5.2209390	-0.0243410
H	-2.9459580	-6.1952130	-0.0595250
H	-4.8945540	-4.7397500	-0.0732480
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C	-1.0030620	2.4644440	0.0275340
C	0.3581630	2.6786430	0.0660940
S	-1.9192020	3.9819630	-0.0054910
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H	1.0962690	1.8948800	0.0923810
C	-0.4413370	4.9014120	0.0325290
C	0.1050210	-0.4031950	0.0241970
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C	0.7560850	-0.5901480	1.2398540
C	2.1425280	-0.8766210	-1.1586620
H	0.2687130	-0.4041380	-2.1134430
C	2.1059120	-0.9192740	1.2510150
H	0.2074360	-0.4643660	2.1648170
C	2.8230850	-1.0670850	0.0537970
H	2.6683080	-1.0071880	-2.0960880
H	2.6139530	-1.0389290	2.1996150
C	4.2613200	-1.4138230	0.0693920
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C	6.1340940	-2.6202200	1.0299080
H	4.1222960	-2.7577000	1.7480960
C	6.4955180	-1.1839310	-0.8611590
H	4.7764300	-0.1589620	-1.6068440
C	7.0210270	-2.0720050	0.0918810
H	6.5116400	-3.3158410	1.7713820
H	7.1471300	-0.7303770	-1.5978500
C	8.4406900	-2.4460000	0.1476950
H	8.6939800	-3.1447120	0.9414510
C	9.4196940	-2.0217740	-0.6585630
H	9.2493120	-1.3257540	-1.4721900
H	10.4372340	-2.3669940	-0.5220210
C	-0.1197750	6.2881790	0.0350710
C	1.2328370	6.4808450	0.0727450
H	1.7662040	7.4188950	0.0835520
H	-0.8395220	7.0938270	0.0106400
S	2.1456100	4.9873800	0.1062330