Supporting Information

Pyrazinacene Conjugated Polymers:

A Breakthrough in Synthesis and Unraveling the Conjugation Continuum

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1.0 General Information

Unless otherwise stated, reactions were performed in oven-dried glassware fitted with rubber septa under nitrogen atmosphere and were stirred with Teflon-coated magnetic stirring bars. Reagents used for polymer synthesis were purchased from Fisher, Acros, Oakwood, Ambeed, Arctom, AK Scientific and Sigma Aldrich. All air or moisture-sensitive reactions were performed under nitrogen atmosphere using standard Schlenk techniques. The majority of organomercury(II) compounds pose no significant risks and typically do not require any specific precautions beyond those typically followed for potentially unsafe materials in a modern chemical lab. No toxic alkylmercury compounds were synthesized for this project. Necessary safety precautions were taken when handling mercuric chloride and any organomercury(II) compounds synthesized. Thin layer chromatography was performed using Silicagel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation, $KMnO_4$ stain and other stains. Silica gel of particle size 230-400 mesh was used for flash chromatography. Unless otherwise stated, all starting materials and reagents were used without further purification. ^1H and ^{13}C NMR spectra were recorded on Varian 400-MR NMR. Chemical shifts are reported in δ (ppm) relative to the residual solvent peak $CDCl_3$: 7.25 for ^1H; CD_2Cl_2: 5.33 for ^1H; and $CDCl_3$: 77.36 for ^{13}C; Coupling constants (J) are expressed in Hertz (Hz). Splitting patterns are designated as s(singlet), br(broad signal), d(doublet), t(triplet), dd(doublet of doublets), dt(doublet of triplets), dq(doublet of quartets), m(multiplet), and q(quartet). High-resolution ESI mass spectra were recorded on a Water Synapt G2-Si (University of Illinois). UV-vis absorption spectra were recorded on Agilent Technologies Cary Series 5000 UV-vis-NIR Spectrophotometer. Fluorescence absorption spectra were recorded on Horiba Scientific Fluoromax-4 Spectrophotometer. Cyclic voltammetry experiments were done using PGZ402, and data was analyzed by Voltamaster 4. Molecular weight measurements of polymers were performed by gel permeation chromatography (GPC) on Agilent Technologies 1260 Infinity. The column chromatography of UV active compounds was performed on Biotage Isolera one 3.0.

Cyclic voltammetry experiments were conducted as follows: A three-electrode cell was used, using a glassy carbon (3 mm) working electrode and a platinum wire counter electrode. Silver/silver ion (0.01 M $AgNO_3$, 0.1M $TBAPF_6$ solution in MeCN) was used as a reference electrode. For polymers, thin film cyclic voltammetry was performed using 0.1 M $TBAPF_6$ solution in MeCN as supporting electrolyte using a scan rate of 200 mVs^{-1}. Polymer solutions were prepared using 10 mg/mL concentration, and 50 µL volume was used to make the film. The films were prepared by drop-coating the electrode and dried under vacuum for 1h. Solution cyclic voltammetry of the TIPS azaacene monomers was performed in ca. 1 mM solution in THF containing 0.1M $TBAPF_6$ as supporting electrolyte at a scan rate of 200mV s^{-1}. For solution cyclic voltammetry of $HgCl_2$ and Bis-phenylethynylmercury, ca. 1 mM solution in MeCN containing 0.1M

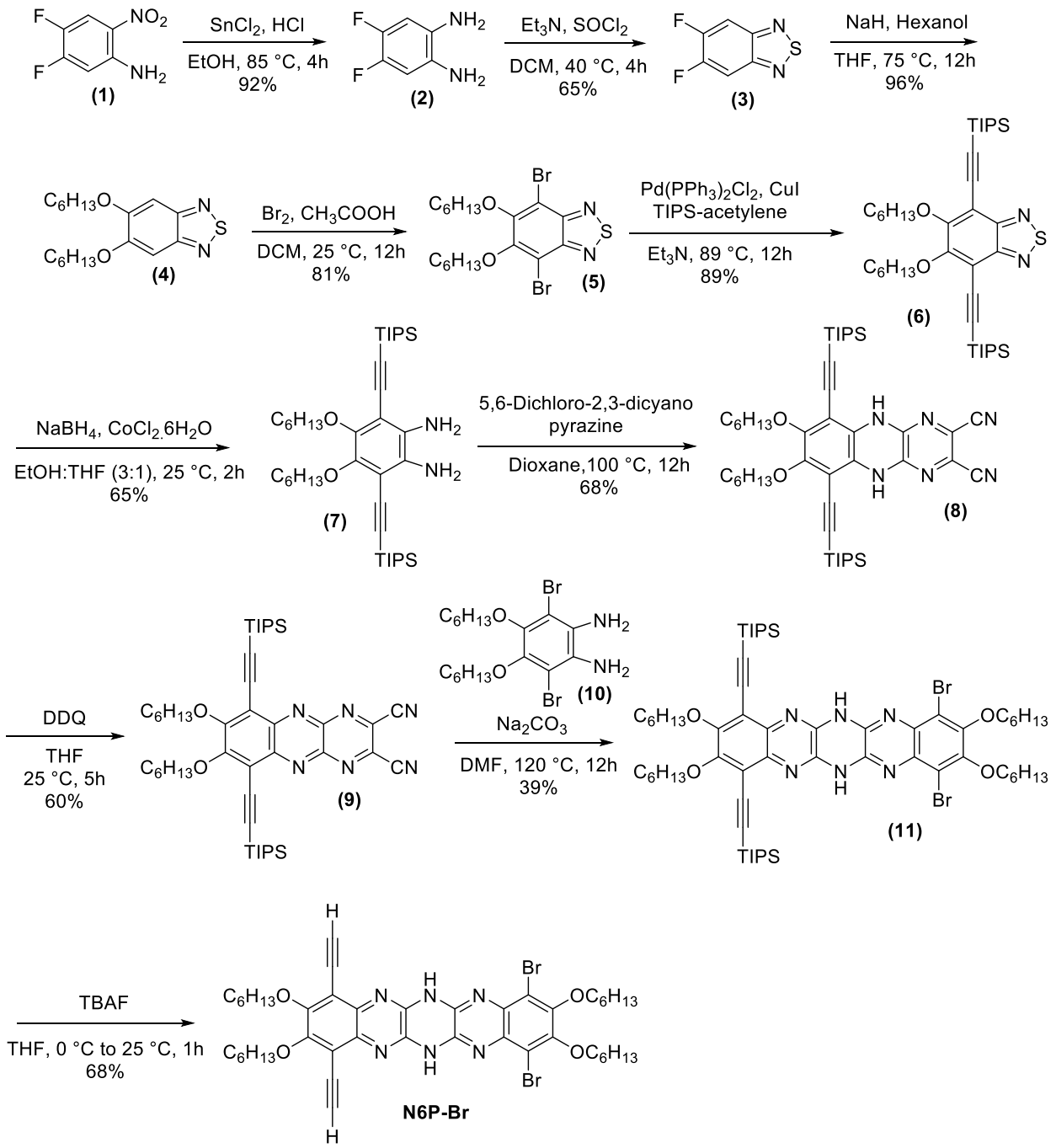
$TBAPF_6$ as supporting electrolyte at a scan rate of 200mV s^{-1} were performed. All solutions and films were prepared under a nitrogen atmosphere in a glove box. A blanket of N_2 was used over the solution during the experiment. The working electrode was polished with 0.05 μm alumina polish prior to each scan. All reduction potentials are reported with respect to $E_{1/2}$ of the Fc/Fc^+ redox couple. The energy level of the Fc/Fc^+ was presumed at -4.8 eV at vacuum. LUMO values were calculated using the formula:

$$E_{LUMO} = -[4.8 - E_{\frac{1}{2},FC,FC^+} + E_{Red,onset}]$$

Where $E_{Red,onset}$ is the onset of reduction and $E_{\frac{1}{2},FC,FC^+}$ is the half-wave potential of the ferrocene reference. LUMO values are determined from the onset of the second CV trace that is obtained when the potential was swept towards more negative potentials from the open circuit potential. Bad gap (E_g^{opt}) was calculated using the onset of thin-film UV-Vis absorption spectra (λ_{onset}) using the formula: (E_g^{opt}) = $1240/\lambda_{onset}$. $HOMO^{UV}$ was calculated from E_g^{opt} - $LUMO^{CV}$.[1-7]

Anion recognition studies were conducted as follows: Stock solutions of known concentrations of monomers, polymers (using repeat unit molecular weight for polymers), and anions were prepared in anhydrous Tetrahydrofuran in the glovebox. Samples with constant concentration (20 μM for polymers and N4A and 10 μM for all other monomers) were prepared by mixing 10 equivalents of anion solution, polymer solution, and THF. Any changes in UV-Vis absorbance and fluorescence spectra were recorded with the addition of 10 equivalents of anions. Tetra-n-butylammonium salts of F^- and OH^- were employed for anion studies.

2.0 General Reaction Scheme for the Synthesis of N6P-Br



Note: Compounds 2-5 were prepared by following a modified synthetic protocol from the reported procedures.[8-10] The substituted stannyl acetylenes and bis-phenylethynylmercury were synthesized following the literature.[11-13]

Synthesis of 5,6-bis(hexyloxy)-4,7-bis((triisopropylsilyl)ethynyl)benzo[c][1,2,5]thiadiazole (6): An oven dried round bottom flask was charged with compound **5** (2.00 g, 4.046 mmol, 1.0 eq.), $Pd(PPh_3)_2Cl_2$ (57 mg, 0.081 mmol, 2 mol%) and CuI (30 mg, 0.162 mmol, 4 mol%) under nitrogen and sealed. Deoxygenated triethylamine (15 ml) was added under nitrogen followed by triisopropylsilylacetylene (2.7 mL, 12.14 mmol, 3.0 eq.). The brownish solution was set to reflux for 12h. After 12h, solvent was removed under reduced pressure and the residue was passed through a short pad of celite eluting with dichloromethane (20 ml). The dichloromethane layer was washed with brine (10 ml), dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was further purified by flash column chromatography (using 1% EtOAc in hexane) to afford **6** as a yellow solid. (2.5 g, 89% yield). R_f = 0.75 (5% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.35-4.31 (m, 4H), 1.92 – 1.80 (m, 4H), 1.51-1.44 (m, 4H), 1.36-1.32 (m, 8H), 1.20 (d, *J* = 1.1 Hz, 42H), 0.93-0.89 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.69, 154.96, 110.67, 106.60, 101.42, 77.50, 34.39, 33.01, 28.25, 25.26, 21.41, 16.69, 14.10. **HRMS** (ESI) m/z 697.4615 $[M + H]^+$; calculated for $[C_{40}H_{68}N_2O_2SSi_2 + H]^+$: 697.4618.

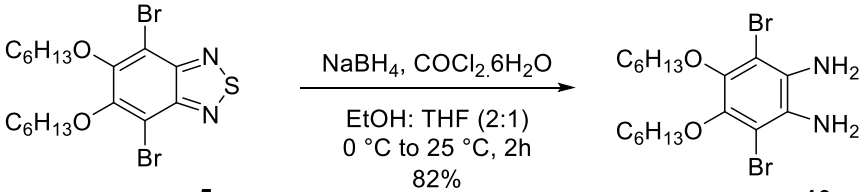
Synthesis of 4,5-bis(hexyloxy)-3,6-bis((triisopropylsilyl)ethynyl)benzene-1,2-diamine (7): Sodium borohydride (54 mg, 1.435 mmol, 10 eq.) and $CoCl_2.6H_2O$ (3 mg, 0.01435 mmol, 0.10 eq.) were added portion wise into a solution of **6** (100 mg, .1435 mmol, 1.0 eq.) in Ethanol: THF (3:1) at 25 ℃. The resulting black reaction mixture was stirred at room temperature for 2 h. After completion of the reaction, the reaction mixture was evaporated to dryness, quenched by adding 1 mL of sat. NH_4Cl solution and extracted with diethyl ether (4 mL). The combined organic layers were washed with water and brine successively, dried over anhydrous sodium sulfate. After removal the solvent under rotary evaporator, the crude product was purified by column chromatography using 3% EtOAc in hexane as an eluent to afford compound **8** as a brown liquid (62 mg, 65% yield). R_f = 0.35 (5% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.99 (t, *J* = 6.9 Hz, 4H), 3.83-3.80 (m, 4H), 1.80-1.72 (m, 4H), 1.45-1.38 (m, 4H), 1.32-1.28 (m, 8H), 1.14 (s, 42H), 0.90-0.87 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.11, 135.56, 109.35, 103.68, 102.85, 76.99, 34.50, 32.98, 28.36, 25.27, 21.40, 16.69, 13.98. **HRMS** (ESI) m/z 669.5205 $[M + H]^+$; calculated for $[C_{40}H_{72}N_2O_2Si_2 + H]^+$: 669.5211.

Synthesis of 7,8-bis(hexyloxy)-6,9-bis((triisopropylsilyl)ethynyl)-5,10-dihydropyrazino[2,3-b]quinoxaline-2,3-dicarbonitrile (8): A mixture of **7** (200 mg, 0.298 mmol, 1.0 eq.) and 2,3-dichloro-5,6-dicyanopyrazine (65 mg, 0.328 mmol, 1.1 eq.) in 1,4-dioxane (8 mL) was refluxed overnight. After cooled to room temperature, the resulting brownish solution was evaporated to dryness, washed by adding 2 mL of water, and extracted with ethyl acetate (4 mL). The combined organic layers were dried over

anhydrous sodium sulfate. After removal the solvent under rotary evaporator, the crude product was purified by column chromatography using 2% EtOAc in hexane as an eluent to afford compound **8** as a brown gel (162 mg, 68% yield). R_f = 0.32 (5% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.82 (s, 2H), 3.97 (t, *J* = 6.9 Hz, 4H), 1.75-1.68 (m, 4H), 1.40-1.37 (m, 4H), 1.31-1.28 (m, 8H), 1.12 (d, *J* = 4.7 Hz, 42H), 0.90-0.87 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.55, 147.77, 128.54, 127.59, 116.58, 108.63, 108.60, 98.49, 77.18, 34.34, 32.79, 28.21, 25.20, 21.33, 16.65, 13.81. **HRMS** (ESI) m/z 795.5144 $[M + H]^+$; calculated for $[C_{46}H_{70}N_6O_2Si_2 + H]^+$: 795.5177.

Synthesis of 7,8-bis(hexyloxy)-6,9-bis((triisopropylsilyl)ethynyl)pyrazino[2,3-b]quinoxaline-2,3-dicarbonitrile (9): A mixture of **8** (250 mg, 0.314 mmol, 1.0 eq.) and 2,3-dichloro-5,6-dicyanoquinone (DDQ) (85 mg, 0.377 mmol, 1.2 eq.) in anhydrous THF (10 mL) was stirred at room temperature overnight under N_2 atmosphere. After 5h, solvent was removed under reduced pressure and the residue was further purified by flash column chromatography (using 1% EtOAc in hexane) to afford **10** as a dark green solid. (149 mg, 60% yield). R_f = 0.30 (5% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.78 (t, *J* = 6.7 Hz, 4H), 1.94-1.86 (m, 4H), 1.55-1.49 (m, 4H), 1.38-1.34 (m, 8H), 1.23 (d, *J* = 4.2 Hz, 42H), 0.93-0.90 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.81, 151.21, 145.23, 135.68, 115.76, 113.93, 111.07, 100.24, 78.09, 34.19, 32.98, 28.11, 25.22, 21.41, 16.63, 14.13. **HRMS** (ESI) m/z 793.4988 $[M + H]^+$; calculated for $[C_{46}H_{68}N_6O_2Si_2+H]^+$: 793.5021.

Synthesis of 3,6-dibromo-4,5-bis(hexyloxy)benzene-1,2-diamine (10):



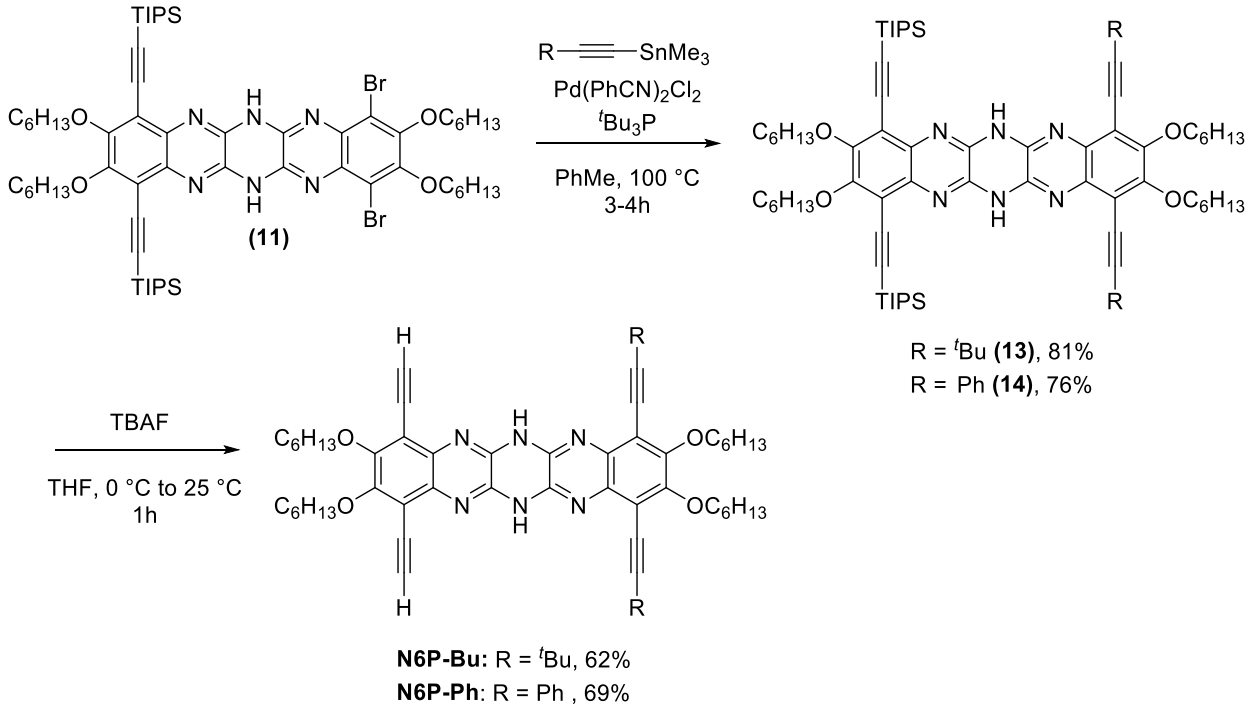
Sodium borohydride (229 mg, 6.07 mmol, 10 eq.) and $CoCl_2.6H_2O$ (14 mg, 0.061 mmol, 0.10 eq.) were added portion wise into a solution of **5** (300 mg, 0.607 mmol, 1.0 eq.) in Ethanol: THF (2:1) of total 12 mL at 0 ℃. The resulting black reaction mixture was stirred at room temperature for 2 h. After completion of the reaction, the reaction mixture was evaporated to dryness, quenched by adding 1 mL of sat. NH_4Cl solution and extracted with diethyl ether (4 mL). The combined organic layers were washed with water and brine successively, dried over anhydrous sodium sulfate. After removal the solvent under rotary evaporator, the crude product was purified by column chromatography using 10% EtOAc in hexane as an eluent to afford compound 10 as a brown liquid (232 mg, 82% yield). R_f = 0.45 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.93 (t, *J* = 6.7 Hz, 4H), 3.52 (s, 4H), 1.81 – 1.70 (m, 4H), 1.51 – 1.44 (m, 4H), 1.36

– 1.31 (m, 8H), 0.92 – 0.88 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.73, 132.37, 109.30, 76.82, 34.35, 32.81, 28.42, 25.29, 16.70.

Synthesis of 1,4-dibromo-2,3,9,10-tetrakis(hexyloxy)-8,11-bis((triisopropylsilyl)ethynyl)-6,13-dihydropyrazino[2,3-b:5,6-b']diquinoxaline (11): A mixture of **9** (1.900 gm, 2.395 mmol, 1 eq.), **10** (synthesized by same protocol for making **7**) (2.2 gm, 4.790 mmol, 2.0 eq.), and sodium carbonate (1.5 gm, 14.371 mmol, 6.0 eq.) in *N,N*-dimethylformamide (20 mL) was heated at 120 ℃ for 12 h. After completion of the reaction, the mixture was allowed to cool to room temperature and diluted by water (10 ml). The resulting solution is treated with dichloromethane (25 mL) for several times. The combined organic layers was treated with brine successively and dried over anhydrous sodium sulfate. Removing the solvent under rotary evaporator, the crude product was purified by column chromatography using 1% EtOAc in hexane as an eluent to afford compound **11** as a yellow orange solid (1.1 g, 39% yield). R_f = 0.80 (1% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (s, 2H), 4.17 (t, *J* = 7.0 Hz, 4H), 4.07 (t, *J* = 6.7 Hz, 4H), 1.88-1.81 (m, 8H), 1.53-1.50 (m, 4H), 1.46-1.42 (m, 4H), 1.37-1.32 (m, 16H), 1.18 (s, 42H), 0.93-0.90 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.94, 153.81, 143.11, 141.85, 139.52, 137.21, 117.64, 117.53, 105.65, 102.00, 77.21, 77.14, 34.46, 34.30, 33.02, 32.83, 28.34, 28.26, 25.26, 25.25, 21.47, 16.68, 14.17. **HRMS** (ESI) m/z 1203.5508 $[M + H]^+$; calculated for $[C_{62}H_{96}N_6O_4Si_2Br_2 + H]^+$: 1203.5477.

Synthesis of 1,4-dibromo-8,11-diethynyl-2,3,9,10-tetrakis(hexyloxy)-6,13-dihydropyrazino [2,3-b:5,6-b']diquinoxaline (N6P-Br): In a clean and dry 25 mL round-bottom flask equipped with a stirring bar, **11** (100 mg, 0.0828 mmol, 1 eq.) was dissolved in anhydrous THF (6 mL) with stirring. A 1(M) solution of n-Bu_4N^+ F^- in THF (.182 mL, 0.182 mmol, 2.2 eq.) was added at 0 ℃ and the mixture was stirred for 1h. After completion of the reaction, the mixture was diluted by water (3 ml). The resulting solution is treated with dichloromethane (3 mL) for several times. The combined organic layers was treated with brine successively and dried over anhydrous sodium sulfate. Removing the solvent under rotary evaporator, the crude product was purified by column chromatography using 10% EtOAc in hexane as an eluent to afford compound **N6P-Br** as a yellow solid (26 mg, 68% yield). R_f = 0.50 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (s, 2H), 4.15 (t, *J* = 6.6 Hz, 4H), 4.06 (t, *J* = 6.7 Hz, 4H), 3.64 (s, 2H), 1.87-1.77 (s, 8H), 1.53-1.46 (m, 8H), 1.37-1.31 (m, 16H), 0.93-0.89 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.91, 153.93, 142.88, 142.61, 139.29, 137.17, 117.67, 116.64, 90.73, 79.21, 77.48, 77.17, 34.31, 34.29, 32.90, 32.85, 28.35, 28.31, 25.27, 16.69. **HRMS** (ESI) m/z 891.2800 $[M + H]^+$; calculated for $[C_{44}H_{56}N_6O_4Br_2 + H]^+$: 891.2808.

3.0 General Reaction Scheme for the Synthesis of N6P-Ph and N6P-Bu



Synthesis of 1,4-bis(3,3-dimethylbut-1-yn-1-yl)-2,3,9,10-tetrakis(hexyloxy)-8,11-bis((triiso propylsilyl)ethynyl)-6,13-dihydropyrazino[2,3-b:5,6-b']diquinoxaline (13)

Bis(benzonitrile)palladium (II) dichloride (3 mg, 0.0083 mmol, 0.1 equiv.) was placed in an oven dried round bottom flask inside of a glovebox under nitrogen atmosphere. Anhydrous toluene (3 mL) was added followed by P(t-Bu)$_3$ (3 mg, 0.0166 mmol, 0.2 equiv.). Compound **11** (100 mg, 0.083mmol, 1 equiv.) and trimethyl(tert-butylethynyl)stannane[11, 14] (131 mg, 0.497 mmol, 6 equiv.) in 1 mL of toluene, were added and the reaction mixture stirred at reflux for 4 h. After completion of the reaction, the crude reaction mixture was evaporated, and water added. Then the organic layer separated, and the crude reaction mixture was extracted with DCM (5 mL). The organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography using 6% EtOAc in hexane as an eluent to afford compound **13** as a brown solid (82 mg, 81% yield). R_f= 0.50 (10% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (s, 2H), 4.20-4.13 (m, 8H), 1.88-1.80 (m, 8H), 1.56 - 1.45 (m, 8H), 1.44 (s, 18H), 1.38-1.31 (m, 16H), 1.20 (s, 42H), 0.94-0.89 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.25, 156.92, 142.03, 141.90, 139.94, 139.00, 117.36, 117.09, 112.27, 105.57, 102.31, 77.23, 77.00, 74.75, 34.43, 33.65, 33.08, 33.01, 31.37, 28.46, 28.29, 25.27, 25.25, 21.44, 21.41, 16.69, 16.68, 14.19. **HRMS** (ESI) m/z 1207.8470 $[M + H]^+$; calculated for $[C_{74}H_{114}N_6O_4Si_2 + H]^+$: 1207.8518.

Synthesis of 2,3,9,10-tetrakis(hexyloxy)-1,4-bis(phenylethynyl)-8,11-bis((triisopropylsilyl) ethynyl)-6,13-dihydropyrazino[2,3-b:5,6-b']diquinoxaline (14)

Compound **14** was synthesized following the same procedure used for compound **13** from compound **11** with 0.083 mmol of **11** and trimethyl(phenylethynyl)stannane[11, 13, 14]**.** The compound **14** was obtained as a brown solid (79 mg, 76% yield). R_f = 0.55 (10% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (s, 2H), 7.67-7.64 (m, 4H), 7.42-7.39 (m, 6H), 4.26 (t, *J* = 6.6 Hz, 4H), 4.18 (t, *J* = 7.0 Hz, 4H), 1.90-1.80 (m, 8H), 1.58-1.53 (m, 4H), 1.46-1.44 (m, 4H), 1.37-1.31 (m, 16H), 1.21 (s, 42H), 0.93-0.86 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.52, 156.96, 142.66, 141.77, 139.96, 139.00, 134.38, 131.24, 130.98, 126.02, 117.25, 105.57, 103.03, 102.21, 85.63, 77.46, 77.21, 34.44, 34.38, 33.12, 33.01, 28.54, 28.28, 25.25, 21.50, 21.47, 21.46, 16.67, 14.16. **HRMS** (ESI) m/z 1247.7872 $[M + H]^+$; calculated for $[C_{78}H_{106}N_6O_4Si_2 + H]^+$: 1247.7892.

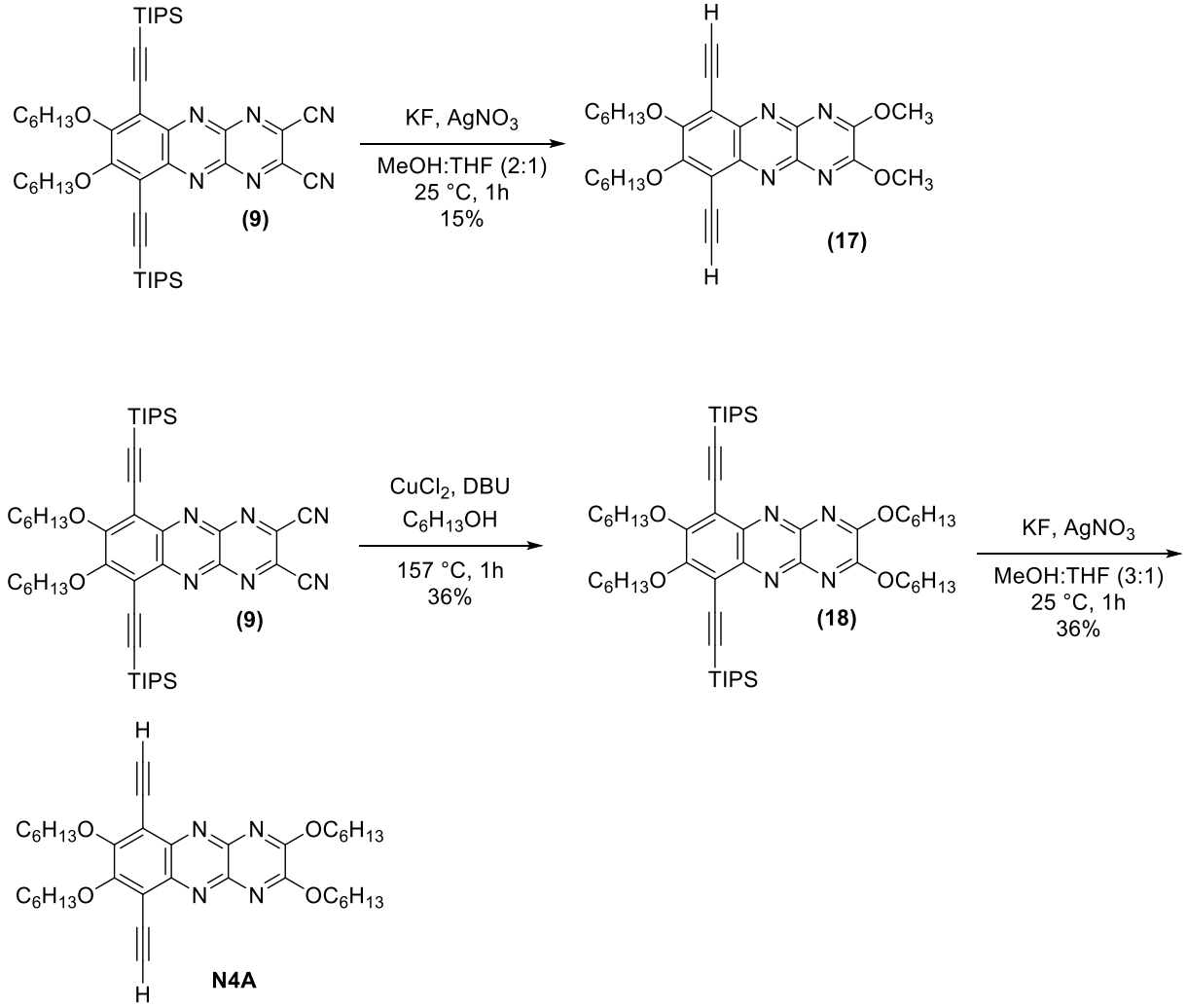
Synthesis of 1,4-bis(3,3-dimethylbut-1-yn-1-yl)-8,11-diethynyl-2,3,9,10-tetrakis(hexyloxy)-6,13-dihydropyrazino[2,3-b:5,6-b']diquinoxaline (N6P-Bu):

N6P-Bu was synthesized following the same procedure used for compound **N6P-Br** from compound **11 (**with 0.083 mmol of **13).** The compound **N6P-Bu** was obtained as a brown solid (37 mg, 69% yield). R_f = 0.15 (10% EtOAc in hexane). **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 8.32 (s, 2H), 4.17-4.11 (m, 8H), 3.67 (s, 2H), 1.87-1.78 (m, 8H), 1.56 – 1.48 (m, 8H), 1.40 – 1.35 (m, 34H), 0.94 – 0.91 (m, 12H). **^{13}C NMR** (100 MHz, CD_2Cl_2) δ 157.86, 156.96, 143.02, 142.04, 139.59, 138.81, 116.98, 116.56, 112.03, 90.28, 79.53, 77.33, 76.95, 74.77, 34.42, 34.28, 33.41, 33.06, 32.89, 32.31, 31.21, 28.45, 28.30, 25.26, 16.44. **HRMS** (ESI) m/z 895.5819 $[M + H]^+$; calculated for $[C_{56}H_{74}N_6O_4 + H]^+$: 895.5850.

Synthesis of 1,4-diethynyl-2,3,9,10-tetrakis(hexyloxy)-8,11-bis(phenylethynyl)-6,13-dihydropyrazino[2,3-b:5,6-b']diquinoxaline (N6P-Ph)

N6P-Ph was synthesized following the same procedure used for compound **N6P-Br** from compound **11 (**with 0.058 mmol of **14).** The compound **N6P-Ph** was obtained as a brown solid (37 mg, 69% yield). R_f = 0.15 (10% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (s, 2H), 7.56-7.53 (m, 4H), 7.34-7.26 (s, 6H), 4.24 (t, *J* = 6.5 Hz, 4H), 4.15 (t, *J* = 6.6 Hz, 4H), 3.60 (s, 2H), 1.86 - 1.79 (m, 8H), 1.56-1.48 (m, 8H), 1.37-1.30 (m, 16H), 0.92-0.87 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.78, 156.91, 142.66, 142.37, 139.52, 139.04, 134.25, 131.16, 130.96, 126.12, 117.25, 116.69, 103.07, 90.43, 85.65, 77.48, 77.45, 34.40, 34.28, 33.14, 32.89, 28.55, 28.32, 25.27, 25.26, 16.68. **HRMS** (ESI) m/z 935.5197 $[M + H]^+$; calculated for $[C_{60}H_{66}N_6O_4 + H]^+$: 935.5224.

4.0 General Reaction Scheme for the Synthesis of N4A



Synthesis of 6,9-diethynyl-2,3,7,8-tetrakis(hexyloxy)pyrazino[2,3-b]quinoxaline (17)

To an oven dried 25 mL round bottom flask, compound **9** (100 mg, 0.12 mmol, 1.0 eq.) was added. This was followed by the addition of KF (29.2 mg, 0.48 mmol, 4.0 eq.) and $AgNO_3$ (85.0 mg, 0.48 mmol, 4.0 eq.). 4 mL of Methanol: THF (2:1) was added to dissolve the reaction content and the mixture was left to stir at room temperature. After 1h, 1(N) HCl was slowly added until the red colored reaction mixture turned yellow with the precipitation of AgCl. DCM was added to the mixture and the soluble fraction decanted into a separatory funnel and subjected to a liquid-liquid extraction over water. This was then further purified by flash column chromatography (15% EtOAc in Hexane) to afford the yellow-orange solid as product (9 mg, 15% yield). R_f = 0.5 (30% EtOAc/Hex). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.38 – 4.32 (m, 11H), 3.89 (s, 2H), 1.92 – 1.82 (m, 5H), 1.58 – 1.49 (m, 8H), 1.40 – 1.30 (m, 10H), 0.95 – 0.86 (m, 7H).

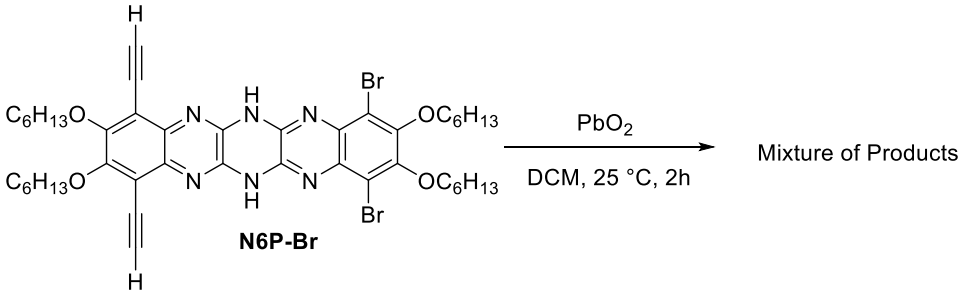
Synthesis of 2,3,7,8-tetrakis(hexyloxy)-6,9-bis((triisopropylsilyl)ethynyl)pyrazino[2,3-b]quinoxaline (18)

An oven dried 50 mL round bottom flask was charged with the compound **9** (1.0 g, 12.61 mmol, 1.0 eq.), $CuCl_2$ (67.8 mg, 0.504 mmol, 40 mol%) in excess hexanol (20 mL). This was followed by the addition of 1.2 ml of DBU, and the reaction was set to reflux for an hour and monitored by TLC. Upon completion, the reaction mixture was taken in a separatory funnel and subjected to liquid-liquid extraction using DCM (10 mL) and water. The DCM layer was collected and dried over Na_2SO_4 and subsequently passed over a silica pad and washed by DCM (500 mL) to remove excess hexanol and was then further purified by gravity column chromatography (6% EtOAc/Hex), affording the brownish gel-like tetrahexyloxy compound (423 mg, 36% yield). R_f = 0.80 (15% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.67 (t, *J* = 6.9 Hz, 4H), 4.40 (t, *J* = 6.9 Hz, 4H), 1.97 – 1.87 (m, 8H), 1.54 – 1.46 (m, 8H), 1.40 – 1.33 (m, 16H), 1.25 (d, *J* = 2.3 Hz, 42H), 0.93 – 0.89 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.23, 156.52, 144.95, 143.80, 117.45, 107.41, 102.38, 77.42, 71.29, 34.40, 34.12, 33.08, 31.00, 28.28, 28.24, 25.26, 25.24, 21.51, 21.48, 16.67, 16.63, 14.26. **HRMS** (ESI) m/z 943.6856 $[M + H]^+$; calculated for $[C_{56}H_{94}N_4O_4Si_2 + H]^+$: 943.6852.

Synthesis of 6,9-diethynyl-2,3,7,8-tetrakis(hexyloxy)pyrazino[2,3-b]quinoxaline (N4A)

To an oven dried 25 mL round bottom flask, compound **18** (50 mg, 0.053 mmol, 1.0 eq.) was added. This was followed by the addition of KF (12.3 mg, 0.2120, 4.0 eq.) and $AgNO_3$ (36.0 mg, 0.2120 mmol, 4.0 eq.). 4 mL of Methanol: THF (3:1) was added to dissolve the reaction content and the mixture was left to stir at room temperature. After 1h, 1(N) HCl was slowly added until the red colored reaction mixture turned yellow with the precipitation of AgCl. DCM was added to the mixture and the soluble fraction decanted into a separatory funnel and subjected to a liquid-liquid extraction over water. This was then further purified by flash column chromatography (15% EtOAc in Hexane) to afford the yellow-orange solid as product (12 mg, 36% yield). R_f = 0.6 (30% EtOAc/Hex). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.72 (t, *J* = 6.8 Hz, 4H), 4.34 (t, *J* = 6.6 Hz, 4H), 3.88 (s, 2H), 1.95 – 1.83 (m, 8H), 1.58 – 1.47 (m, 8H), 1.38 – 1.34 (m, 16H), 0.93 – 0.89 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.06, 157.14, 145.41, 143.14, 117.25, 92.39, 79.12, 77.84, 71.87, 34.26, 34.07, 32.96, 31.05, 28.29, 28.23, 25.26, 25.18, 16.68, 16.61. **HRMS** (ESI) m/z 631.4208 $[M + H]^+$; calculated for $[C_{38}H_{54}N_4O_4 + H]^+$: 631.4223.

5.0 Failed attempt at oxidation



A mixture of **N6P-Br** (25 mg, 0.028 mmol, 1.0 eq.) and PbO_2 (10 eq.) in anhydrous DCM (15 mL) was stirred at room temperature for 2h under N_2 atmosphere. After 2h, solvent was passed through a short pad of celite eluting with dichloromethane (20 ml). The dichloromethane layer was washed with brine (10 ml), dried over anhydrous Na_2SO_4 and concentrated under vacuum. A mixture of products were obtained in each case and were not isolated.

6.0 Attempted reaction conditions for Sonogashira Reactions:

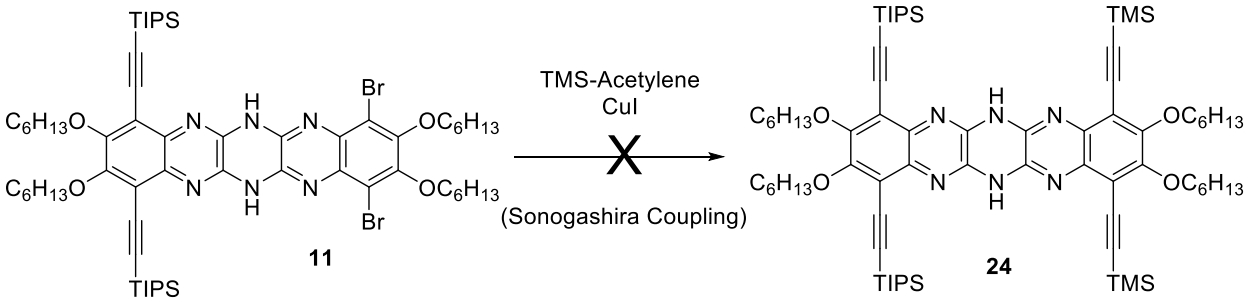


Table S1: Conditions for Sonogashira coupling

Entry	Pd-Source	Ligand	Solvent	Temp.	Time	Result
1	$Pd(PPh_3)_4$	PPh_3	PhMe:Et_3N (4:1)	100 °C	14h	SM isolated
2	$Pd[P(^tBu)_3]_2$	---	PhMe:Et_3N (1:1)	89 °C	14h	SM isolated
3	$Pd(PPh_3)_2Cl_2$	---	Et_3N	89 °C	14h	Product not formed
4	$Pd(OAc)_2$	PPh_3	THF: Diisopropylamine(4:1)	65 °C	20h	SM isolated

Note: All reactions were performed with **11** (100 mg, 0.083 mmol., 1 eq.), Pd-Source (0.0083 mmol, .1 eq.), Ligand (0.0083 mmol, .1 eq.) and CuI (0.0166 mmol, .2 eq.) in 4 mL of total solvent. (SM is starting material)

7.0 Synthetic Approaches Towards Polymerization

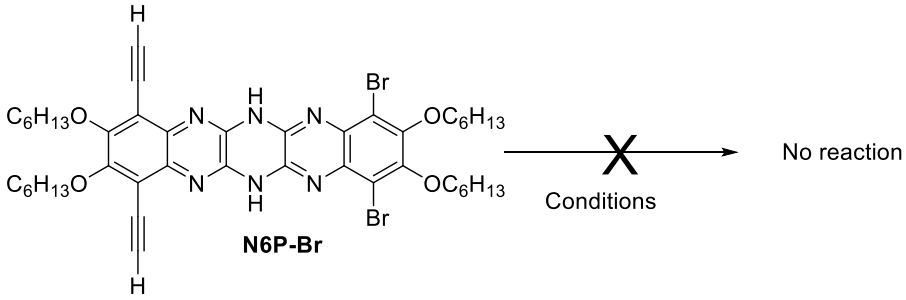


Table S2: Conditions for polymerization

Entry	Catalyst	Additive	Solvent	Temp	Time	Result
1	$Pd(PPh_3)_2Cl_2$, CuI	1,4-diiodobenzene (1 equiv)	PhMe:Piperidine (1:1)	35 ℃	24h	SM isolated
2	$Pd(PPh_3)_4$, CuI	Hydroquinone (2.5 equiv)	PhMe:DIPA (4:1)	60 ℃	12h	SM isolated

Note: All reactions were performed with **N6P-Br** (10 mg, 0.0103 mmol., 1 eq.), Pd-catalyst (0.05 eq.), Cu-catalyst (0.2 eq.) and additive in 2 mL of solvent. (SM is starting material)

8.0 Synthetic Approaches Towards Stille Polymerization

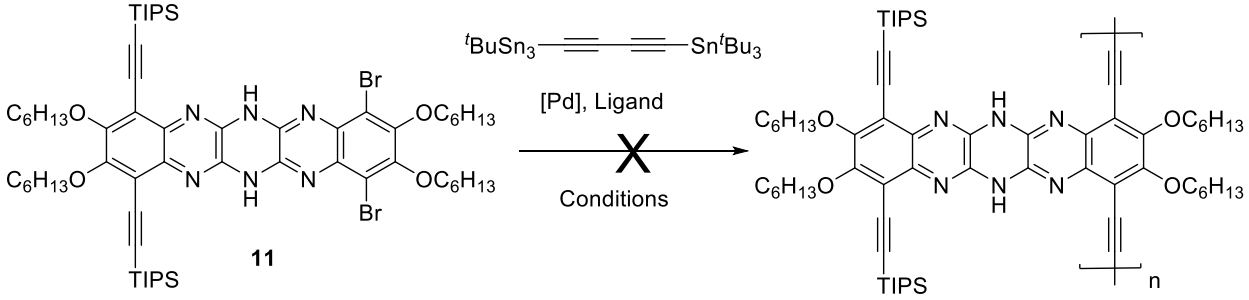
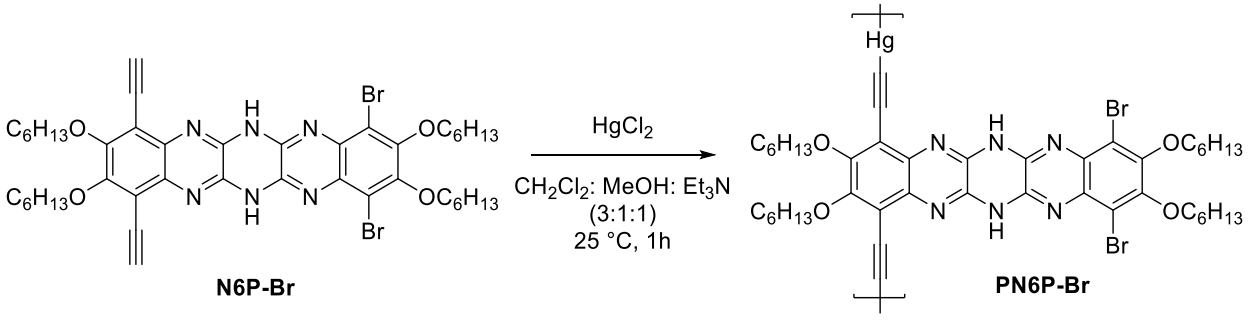


Table S3: Conditions for Stille polymerization

Entry	Pd-Source	Ligand	Additive	Solvent	Temp	Time	Result
1	$Pd_2(dba)_3$	PPh_3	---	PhMe	100 ℃	96h	SM isolated
2	$Pd(C_6H_5)_2Cl_2$	$P(^tBu)_3$	---	PhMe	100 ℃	120h	SM isolated
3	$Pd(PPh_3)_4$	---	---	PhMe	110 ℃	96h	SM isolated
4	$Pd(PPh_3)_2Cl_2$	PPh_3	CuI	DMF	80 ℃	19h	Insol. ppt. found
5	$Pd(PPh_3)_4$	---	---	DMF	80 ℃	24h	SM isolated
6	$Pd(^tBu_3P)_2$	---	K_3PO_4	PhMe	100 ℃	48h	SM isolated

Note: All reactions were performed with **11** (25 mg, 0.0207 mmol., 1 eq.), Pd-Source (0.002 mmol, .1 eq.), Ligand (0.0041 mmol, .2 eq.) and bis(tributylstannyl) butadiyne[15] (0.0207 mmol, 1 eq.) in 1.5 mL of solvent. (SM is starting material)

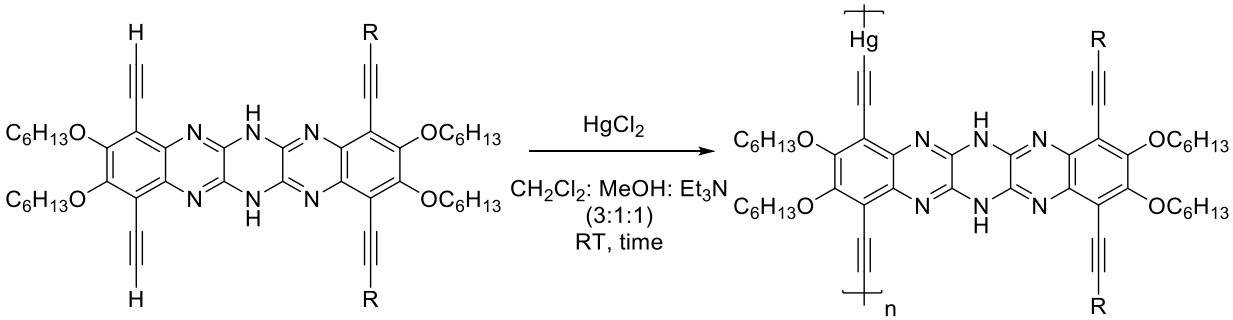
9.0 Synthesis of Organometallic Pyrazinacene Conjugated Polymers



N6P-Br **PN6P-Br**

Synthesis of PN6P-Br:

A dry and clean flask was charged with **N6P-Br** (100 mg, 0.112 mmol, 1.0 eq.), $HgCl_2$ (30 mg, 0.112 mmol, 1.0 eq.), and then deoxygenated dichloromethane: methanol (30 mL: 10 mL) was added to the mixture. After the solids are fully dissolved, deoxygenated triethylamine (10 ml) was added under nitrogen to the mixture. The mixture was stirred at room temperature for 1h. The suspension was concentrated, precipitated in methanol (20 mL) and filtered. The solid was further washed with diethyl ether. The crude polymer was purified by Soxhlet with MeOH for 6 hours and then with diethyl ether for another 2 hours to give **PN6P-Br** as a black solid (89 mg, 89% yield) with an of Mn 15 kDa and Mw 37 kDa. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.12 (brs, 4H), 1.82 (brs, 8H), 1.58 – 1.21 (m, 24H), 0.97 (brs, 12H).



N6P-Ph: R = Ph
N6P-Bu: R = ^{t}Bu

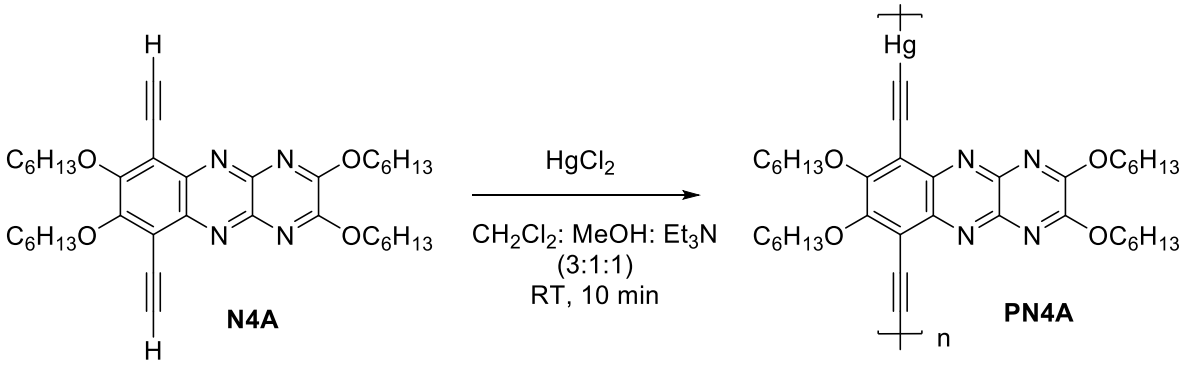
PN6P-Ph: R = Ph, 90%
PN6P-Bu: R = ^{t}Bu, 93%

Synthesis of PN6P-Ph:

PN6P-Ph was synthesized following the same procedure used for synthesis of polymer **PN6P-Br** with 0.106 mmol of **N6P-Ph** and the polymerization was run for 30 min**.** The crude polymer was purified by Soxhlet with MeOH for 6 hours then with acetonitrile for another 8h. The polymer **PN6P-Ph** was obtained as a black solid (90 mg, 90% yield) with an Mn 20 kDa and Mw 36 kDa. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 8.62 – 6.73 (m, 10H), 4.55 – 3.95 (m, 8H), 1.84 (s, 8H), 1.74 – 1.20 (m, 24H), 0.92 (s, 12H).

Synthesis of PN6P-Bu:

PN6P-Bu was synthesized following the same procedure used for synthesis of polymer **PN6P-Br** with 0.103 mmol of **N6P-Bu** and the polymerization was run for 90 min**.** The crude polymer was purified by Soxhlet with MeOH for 6 hours then with acetonitrile for another 8h. The polymer **PN6P-Bu** was obtained as a black solid (93 mg, 93% yield) with an Mn 21 kDa and Mw 36 kDa. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.11 (brs, 8H), 1.87 (brs, 8H), 1.61 – 1.10 (m, 42H), 1.00 – 0.81 (m, 12H).



Synthesis of PN4A:

PN4A was synthesized following the same procedure used for synthesis of polymer **PN6P-Br** with 0.158 mmol of **N4A** and the polymerization was run for 10 min**.** The crude polymer was purified by Soxhlet with MeOH for 6 hours then with diethyl ether for another 8h. The polymer **PN4A** was obtained as a dark brown solid (94 mg, 94% yield) with an Mn 15 kDa and Mw 37 kDa. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.12 – 3.91 (m, 8H), 2.12 – 1.89 (m, 8H), 1.33 (d, 24H), 0.95 (s, 12H).

10.0 GEL PERMEATION CHROMATOGRAPHY TRACES OF THE POLYMERS

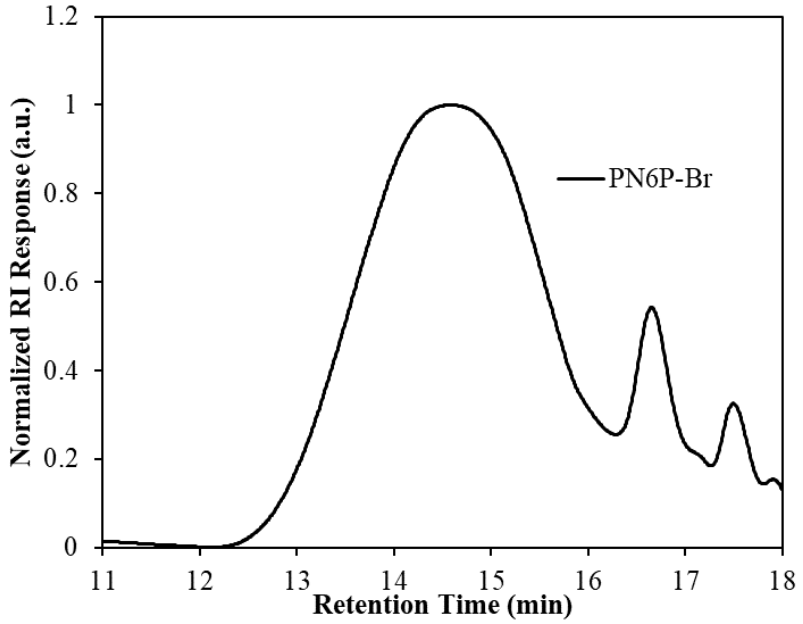


Figure S1: PN6P-Br

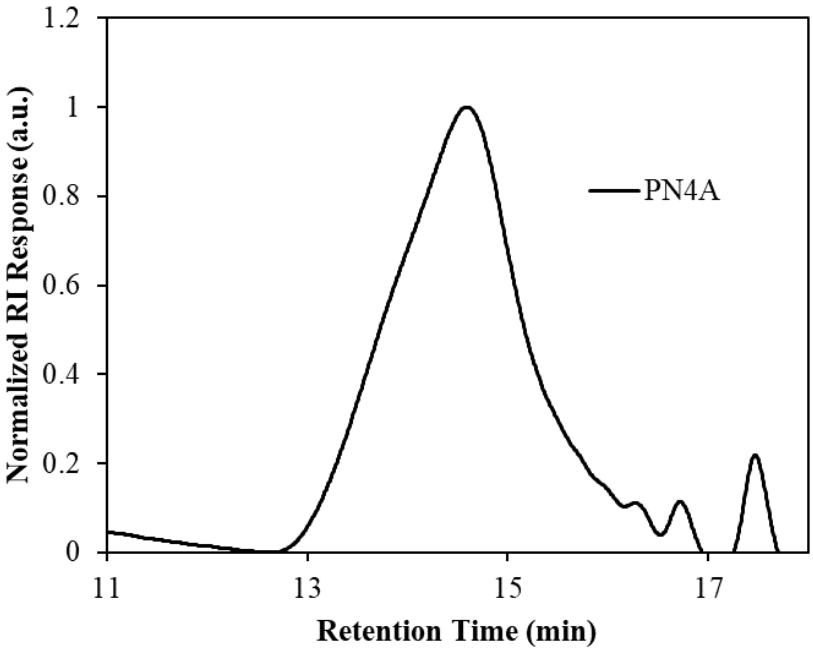


Figure S2: PN4A

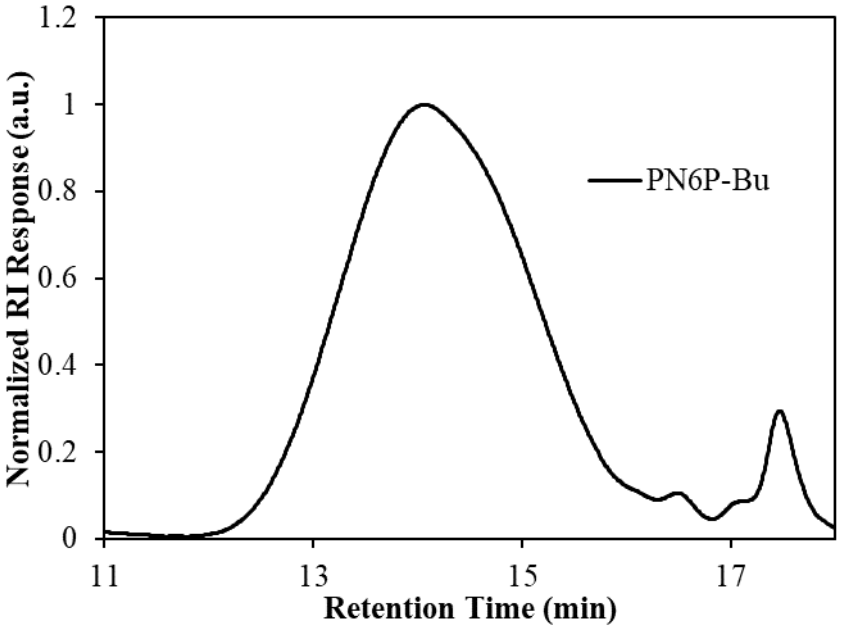


Figure S3: PN6P-Bu

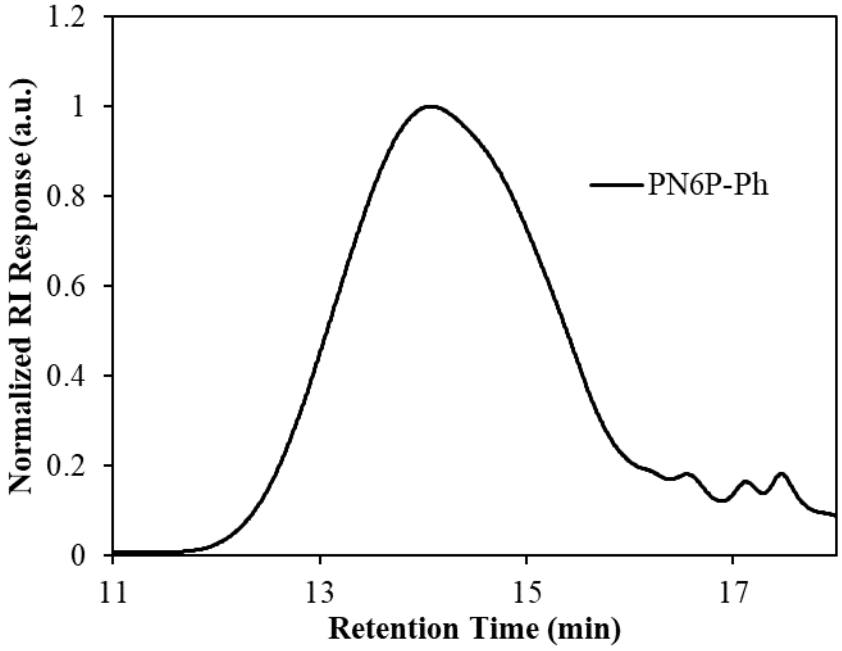


Figure S4: PN6P-Ph

11.0 SINGLE CRYSTAL X-RAY DIFFRACTION

Single crystal of compound 11 (N6P-Br TIPS; CCDC 2280176) was mounted under mineral oil on a Mitegen micromount and immediately placed in a cold nitrogen stream at 100(2) K prior to data 6 collection. Data for compound 11 was collected on a Bruker D8 Quest equipped with a Photon100 CMOS detector and a Mo ImS source. A series of phi and omega scans were collected using monochromatic Mo Kα radiation, (λ = 0.71073 Å), and integrated with the Bruker SAINT[16] program. Structure solutions and refinements were performed using the SHELX suite[17] and SHELXLE[18]. Further comments on structural models: $C_{58}H_{94}N_6O_4Si_2Br_2$ (N6P-Br TIPS; CCDC 2280176). A structural model consisting of two of the target molecules, one water molecule, and two partially occupied ethanol molecules was developed. All of the triisopropyl silyl groups are disordered over two orientations. The like C-C and Si-C distances were restrained to be similar (esd 0.01 Å). All of the hexyl groups are disordered over two orientations. The like C-C and O-C distances were restrained to be similar (esd 0.01 Å). The water solvent molecule is disordered over two positions. Both partially occupied ethanol solvent molecules are disordered over two positions. The like C-C and O-C distances were restrained to be similar (esd 0.01 Å). Similar displacement amplitudes (esd 0.01) were imposed on disordered sites overlapping by less than the sum of van der Waals radii. The disordered atoms were restrained to behave relatively isotropic. The amine H atoms were located in the difference map. The N-H distances were restrained to be 0.88 (esd 0.01 Å). Remaining H atoms were included as riding idealized contributors. Methyl, hydroxyl and amine H atom U's were assigned as 1.5 times Ueq of the carrier atom; remaining H atom U's were assigned as 1.2 times carrier Ueq.

Table S4: Crystal data and structure refinement for **Compound 11**.

Identification code	B22151_a	
Empirical formula	C127 H201 Br4 N12 O10 Si4	
Formula weight	2500.59	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 18.459(2) Å	a= 69.636(3)°.
	b = 19.931(3) Å	b= 88.799(4)°.
	c = 20.926(3) Å	g = 70.200(3)°.
Volume	6749.5(15) $Å^3$	
Z	2	
Density (calculated)	1.230 Mg/m^3	

Absorption coefficient	1.286 mm^{-1}
F(000)	2659
Crystal size	0.616 x 0.270 x 0.124 mm^3
Theta range for data collection	1.487 to 25.479°.
Index ranges	-21<=h<=22, -24<=k<=24, -25<=l<=25
Reflections collected	327470
Independent reflections	24821 [R(int) = 0.2262]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.86351 and 0.59327
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	24821 / 4650 / 2316
Goodness-of-fit on F^2	1.065
Final R indices [I>2sigma(I)]	R1 = 0.1000, wR2 = 0.2306
R indices (all data)	R1 = 0.1754, wR2 = 0.2818
Extinction coefficient	n/a
Largest diff. peak and hole	1.873 and -1.268 e.$Å^{-3}$

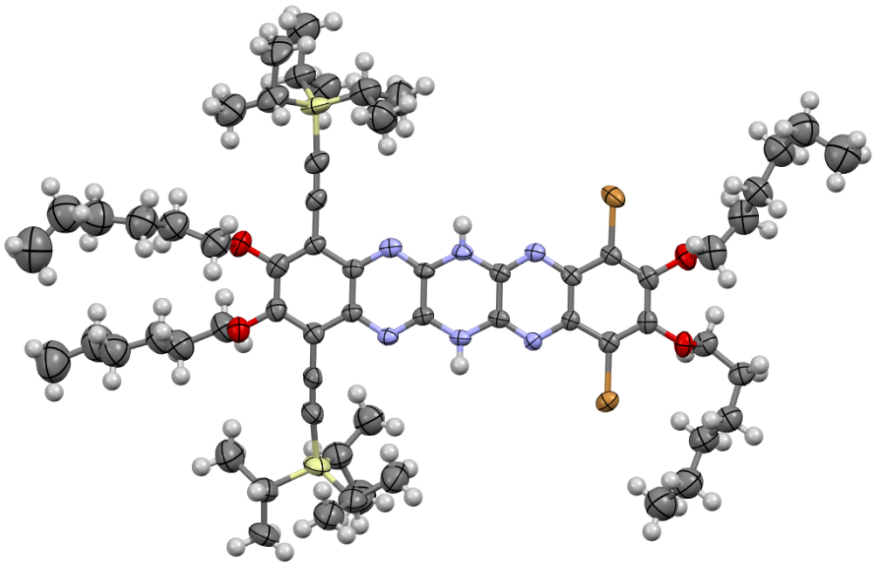


Figure S5: Single Crystal X-Ray thermal ellipsoid plots of Compound **11**

12.0 UV-Vis and Fluorescence spectra

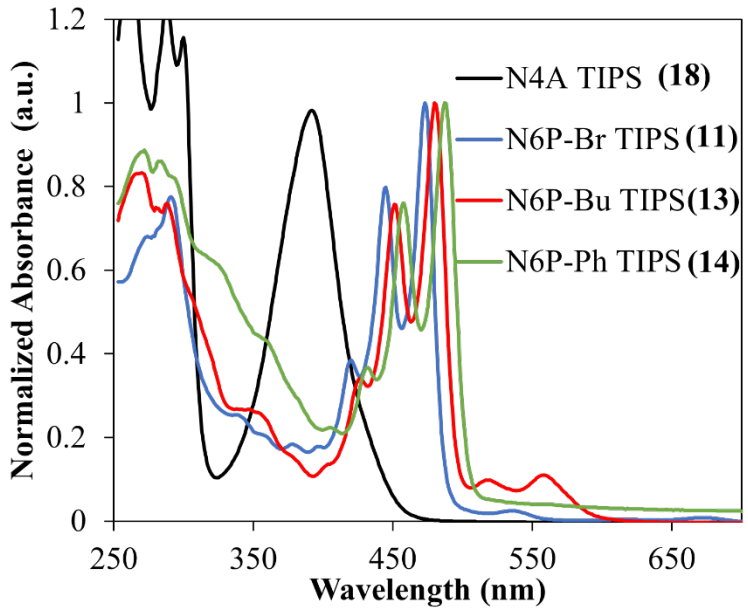


Figure S6: UV-Vis spectra of TIPS precursors

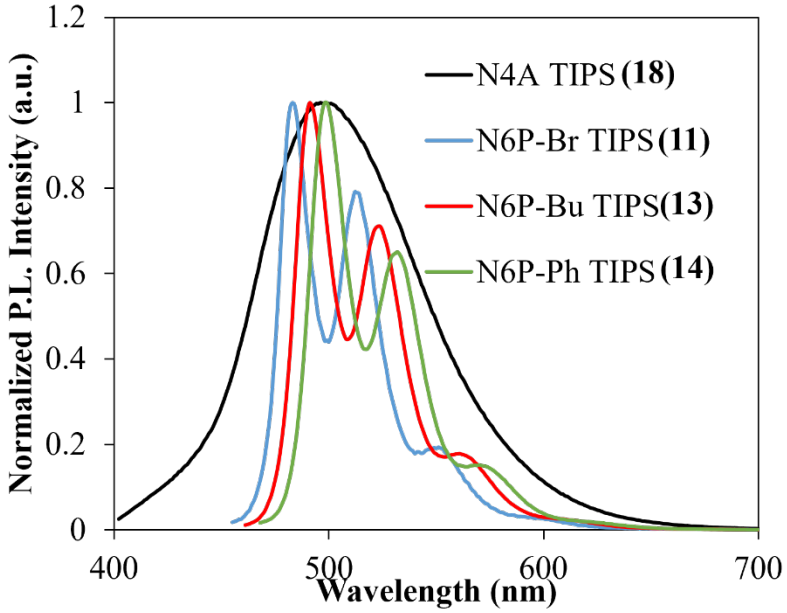


Figure S7: Fluorescence spectra of TIPS precursors

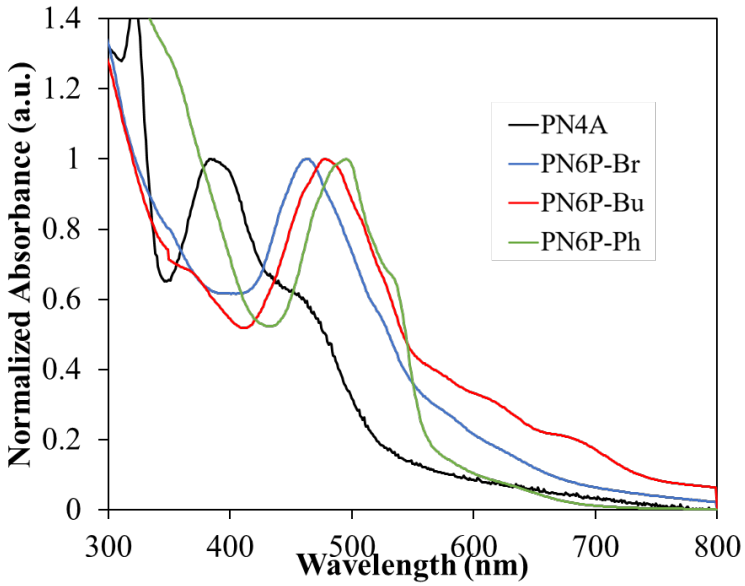


Figure S8: Thin film UV-Vis spectra of polymers

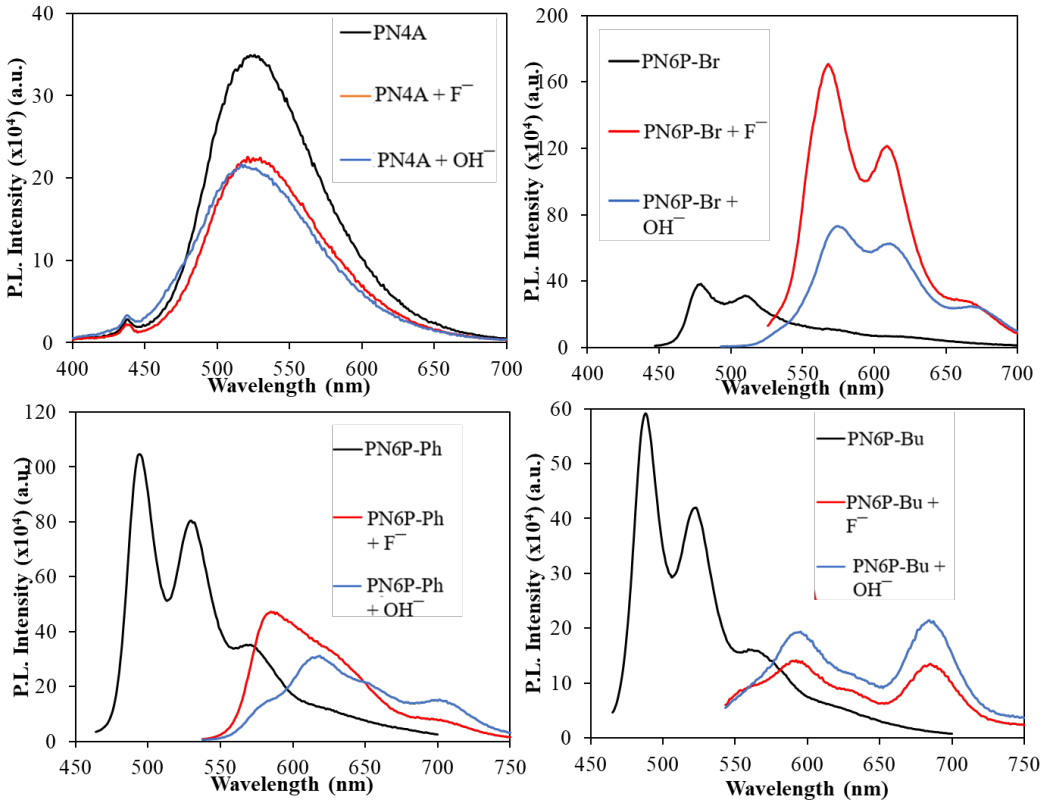


Figure S9: Fluorescence spectra of polymers in the presence of 10 equivalents of fluoride and hydroxide anions recorded after 30 mins of anion addition, respectively

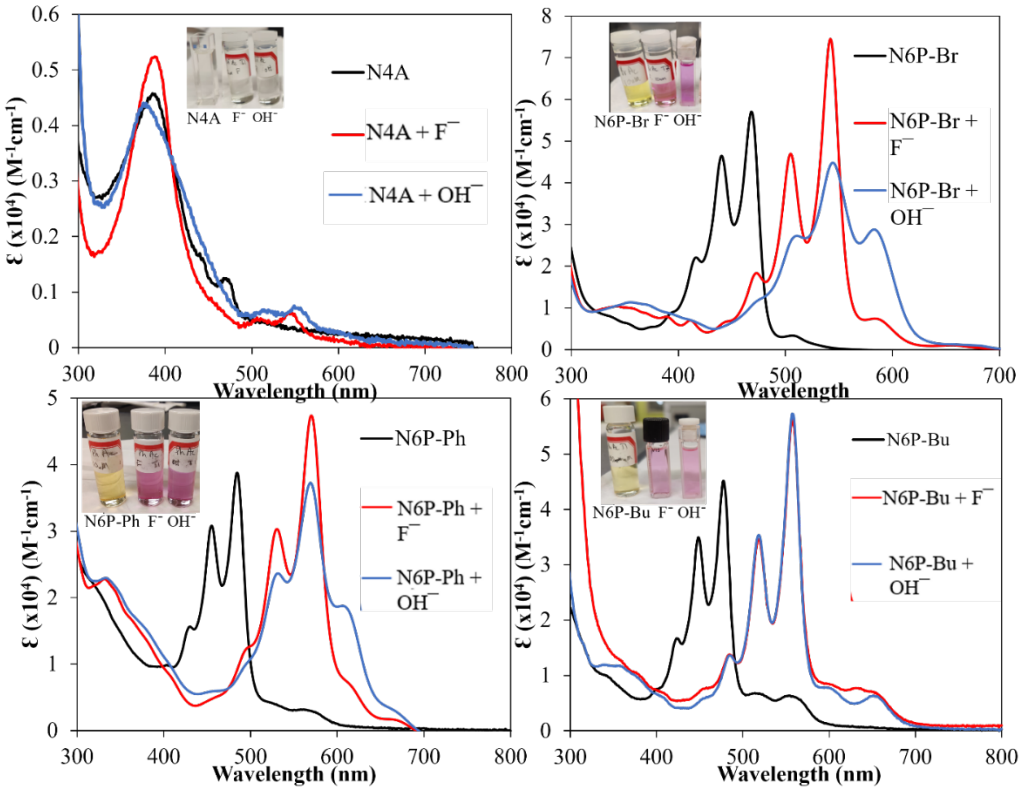


Figure S10: UV-Vis absorbance spectra of monomers in the presence of 10 equivalents of fluoride and hydroxide anions recorded after 30 mins of anion addition, respectively

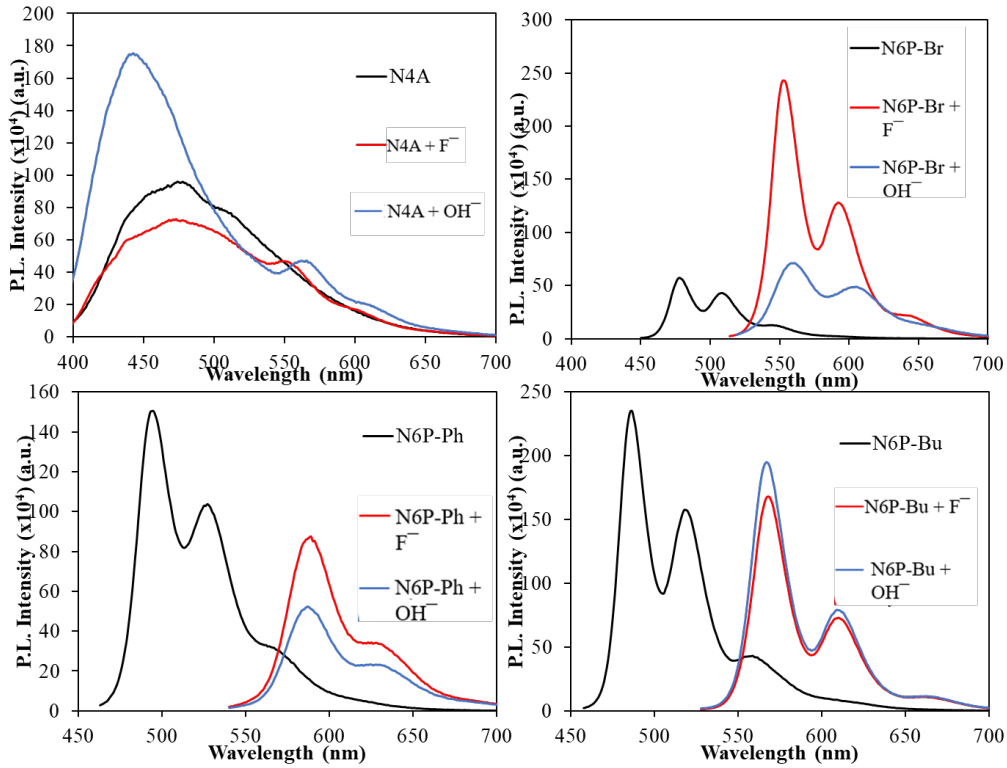
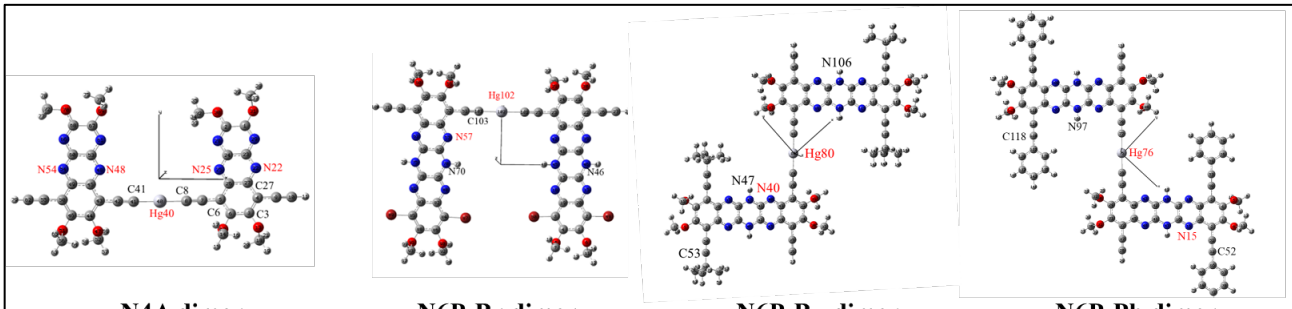


Figure S11: Fluorescence spectra of monomers in the presence of 10 equivalents of fluoride and hydroxide anions recorded after 30 mins of anion addition, respectively

13.0 DFT SIMULATIONS

The molecular geometries were optimized using density functional theory DFT at B3LYP/genecp level for neutral molecules and UB3LYP/genecp for radical anions, Stuttgart RSC 1997 ECP was used for Hg, and 6-311G** was used for all other atoms. Isovalue surface of HOMO and LUMO were computed using the same basis set (isovalue was set at 0.02 for all MOs). Mullikan population analysis was conducted using Population keyword in Gaussian.



N4A dimer **N6P-Br dimer** **N6P-Bu dimer** **N6P-Ph dimer**

Dimer	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2
N4A	C27-p=0.1036 C6-p=0.1029 C3-p=0.1024	C41-p=0.1077	C8-p=0.1128	N48-p=0.1125 N54-p=0.1050	N22-p=0.1172 N25-p=0.1066	Hg40-p=0.2288
N6P-Br	C103-p=0.0750	N46-p=0.0775	N70-p=0.0785	Hg102-p=0.0498	N57-p=0.0446	Hg102-p=0.1449
N6P-Bu	C53-p=0.0641	N106-p=0.0609	N47-p=0.0619	Hg80-p=0.0608	N40-p=0.0409	Hg80-p=0.1063
N6P-Ph	N97-p=0.0607	C52-p=0.0512	C118-p=0.0509	Hg76-p=0.0393	N15-p=0.0328	Hg76-p=0.0864

Figure S12: Mulliken population analysis of the Hg dimers

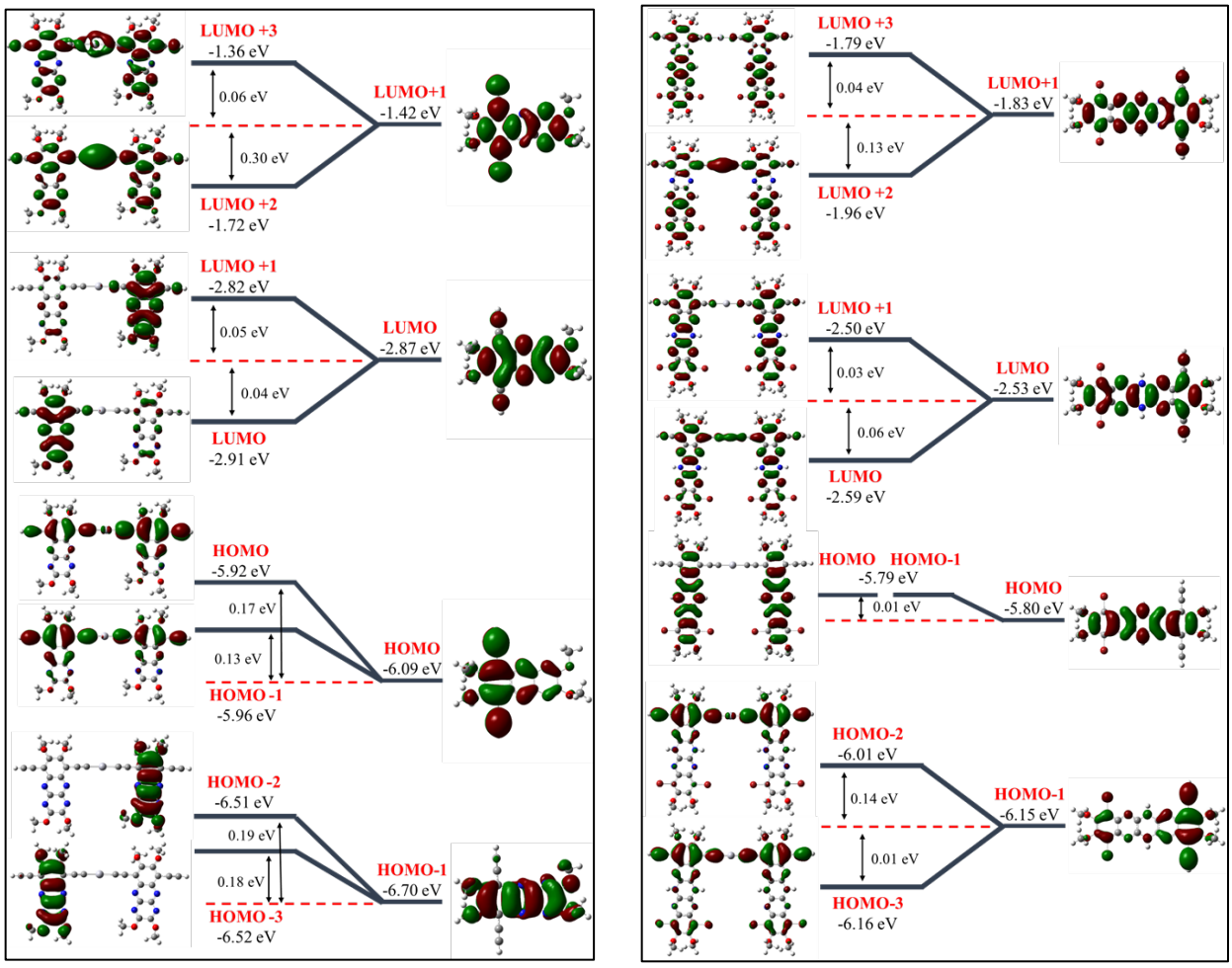


Figure S13: HOMO and LUMO of monomer and dimer of N4A (left) and N6P-Br (right)

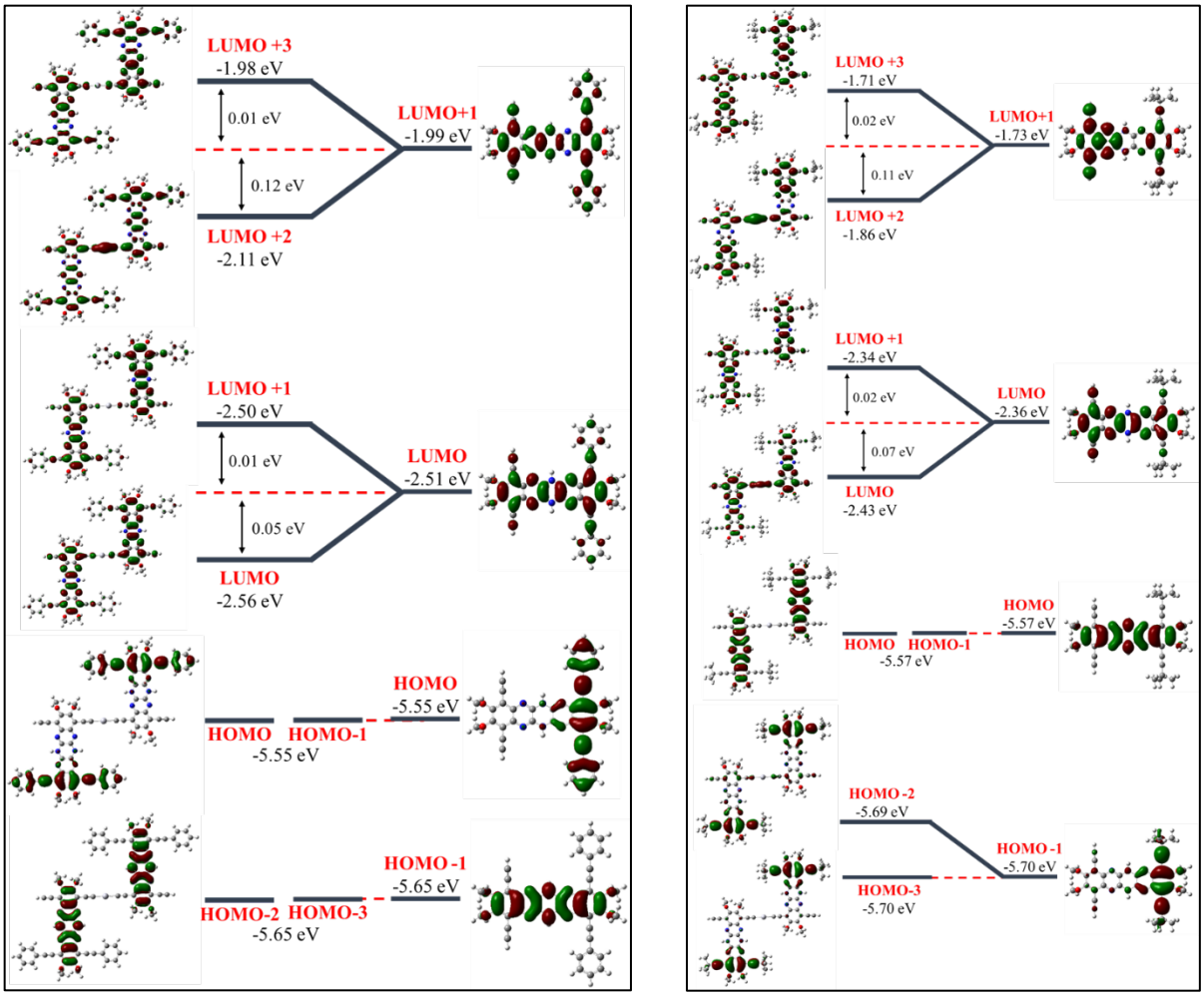


Figure S14: HOMO and LUMO of monomer and dimer of N6P-Ph (left) and N6P-Bu (right)

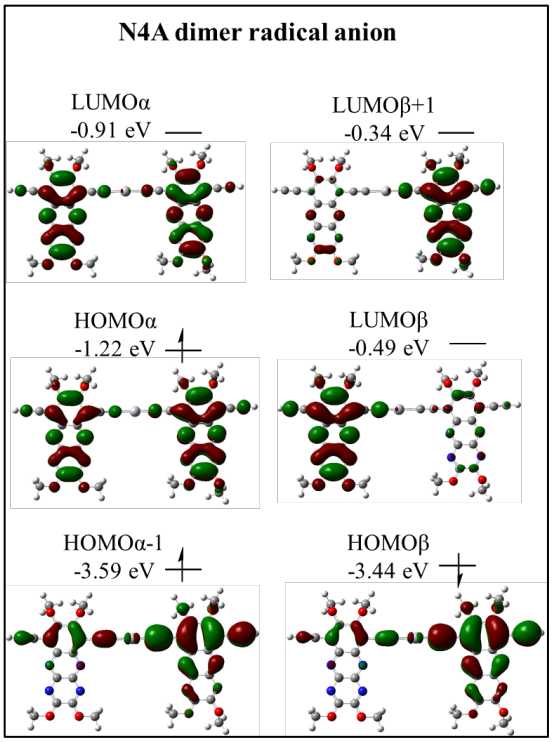


Figure S15: HOMO and LUMO of radical anions of N4A dimer

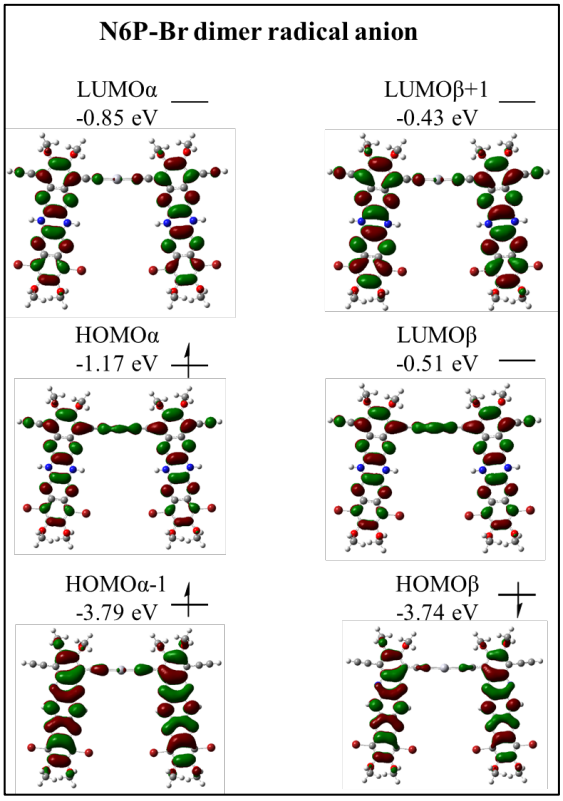


Figure S16: HOMO and LUMO of radical anions of N6P-Br dimer

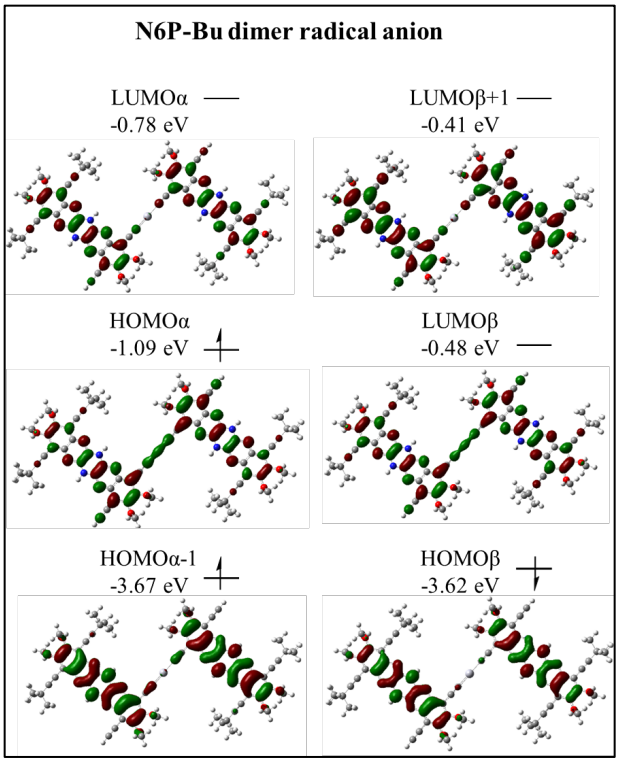


Figure S17: HOMO and LUMO of radical anions of N6P-Bu dimer

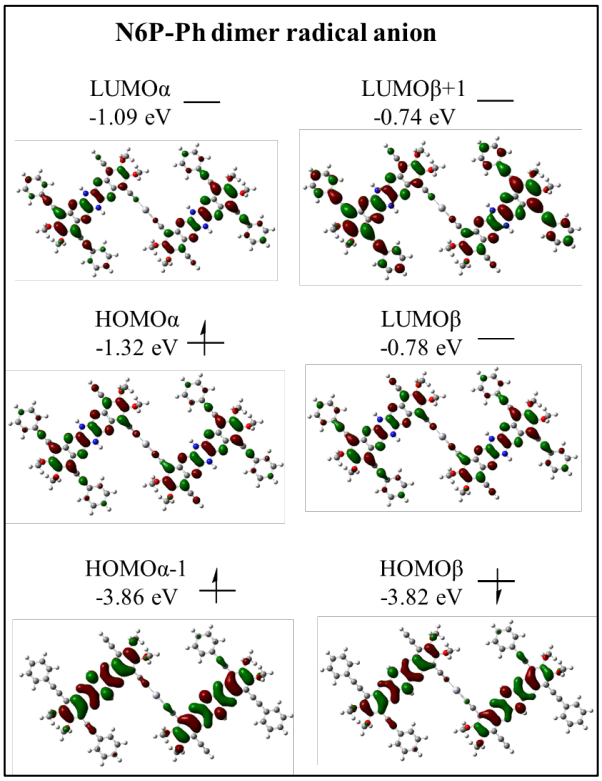


Figure S18: HOMO and LUMO of radical anions of N6P-Ph dimer

14.0 CYCLIC VOLTAMMETRY

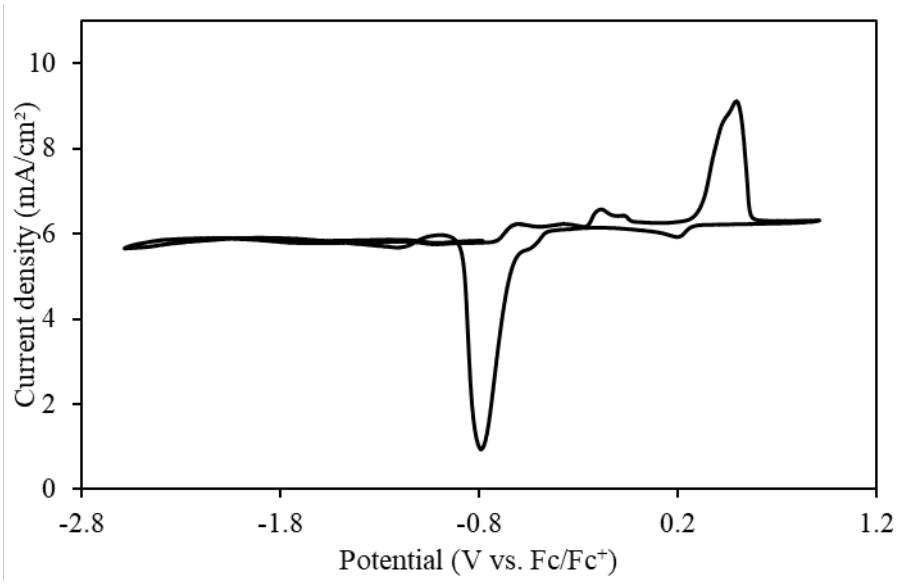


Figure S19: Cyclic Voltammogram of $HgCl_2$

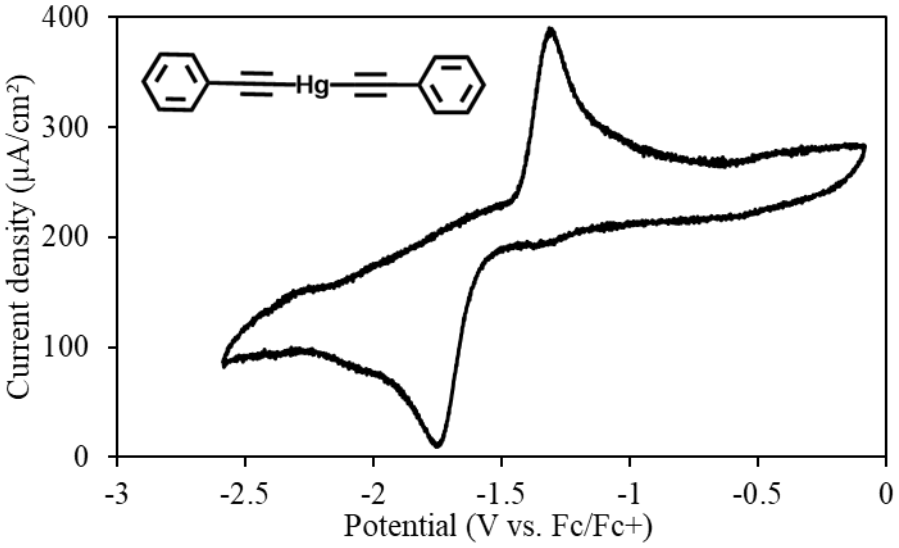


Figure S20: Cyclic Voltammogram of Bis-phenylethynylmercury

15.0 NMRs

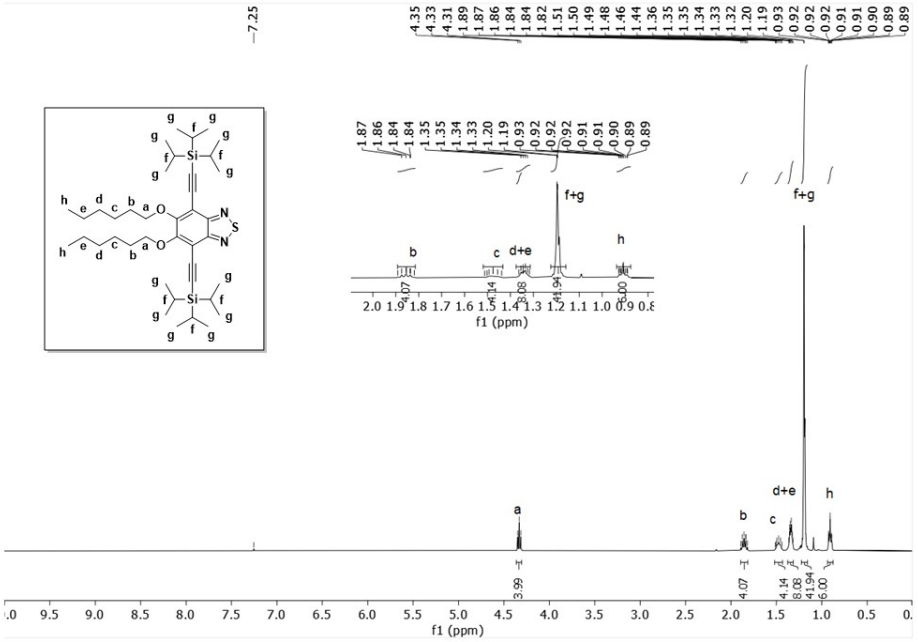


Figure S21: ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **6**

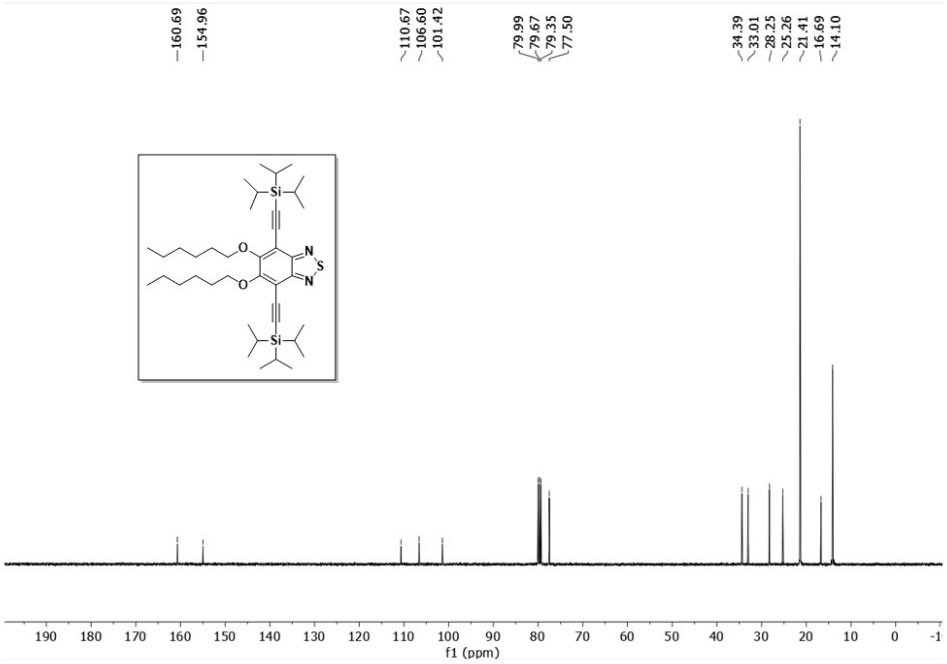


Figure S22: ^{13}C NMR (100 MHz, $CDCl_3$) of compound **6**

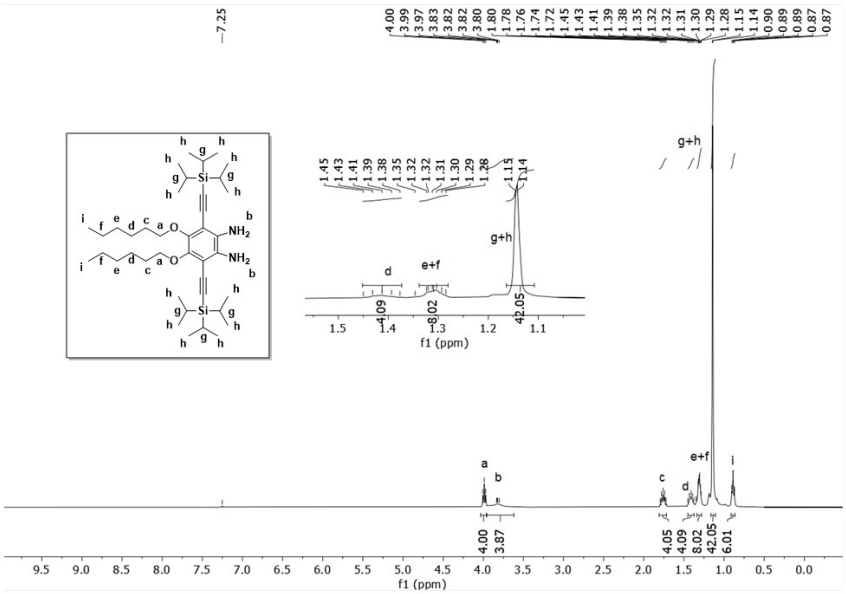


Figure S23: 1H (400 MHz, $CDCl_3$) of Compound **7**

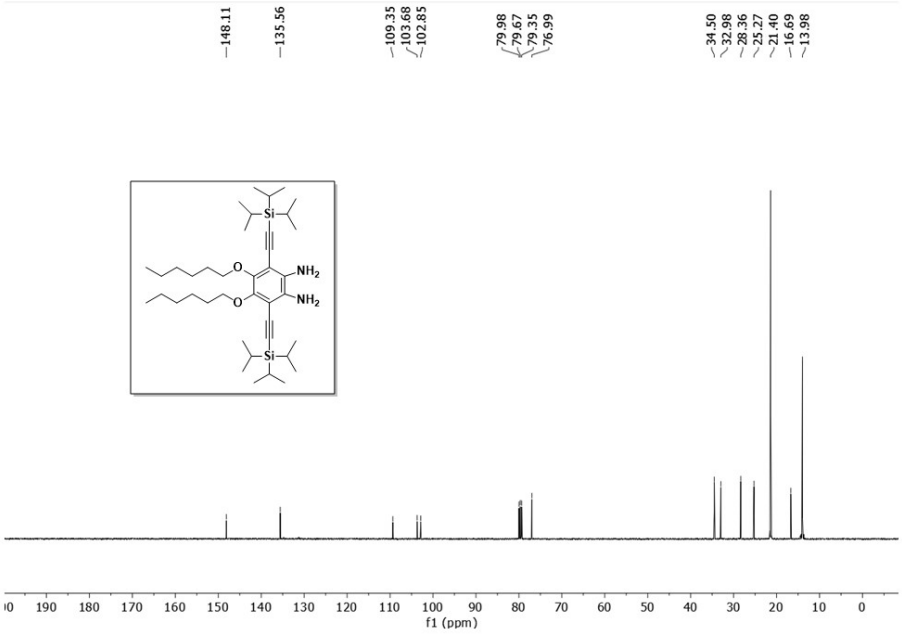


Figure S24: ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **7**

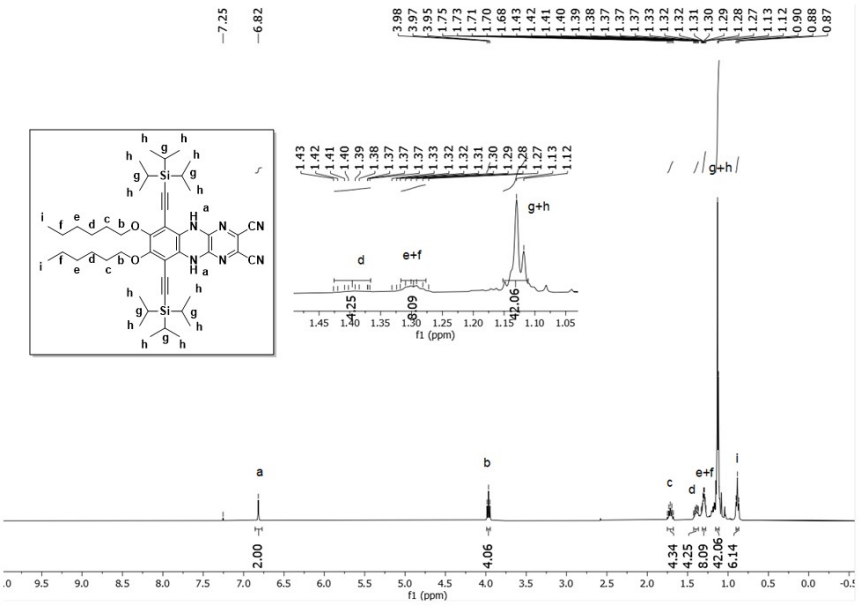


Figure S25: ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **8**

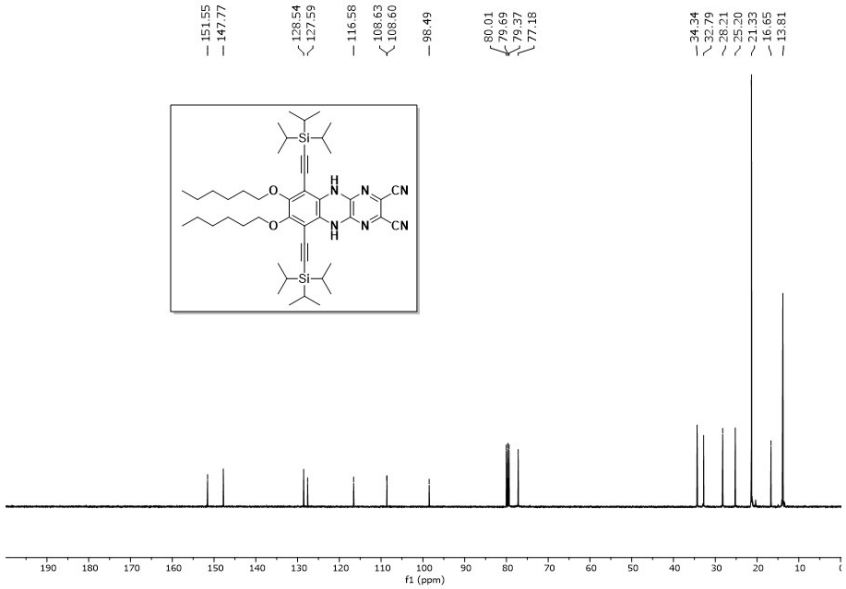


Figure S26: ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **8**

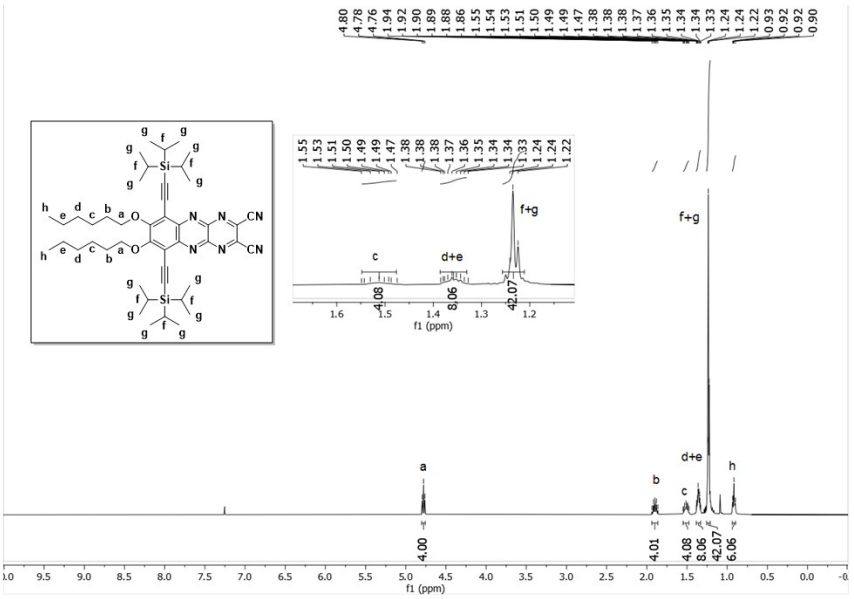


Figure S27: ^{1}H NMR (400 MHz, $CDCl_3$) of compound **9**

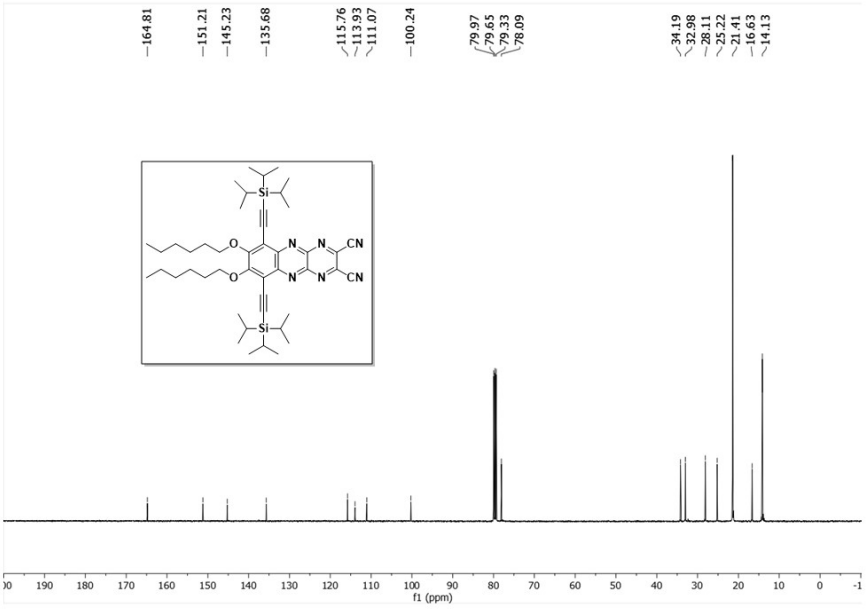


Figure S28: ^{13}C NMR (100 MHz, $CDCl_3$) of compound **9**

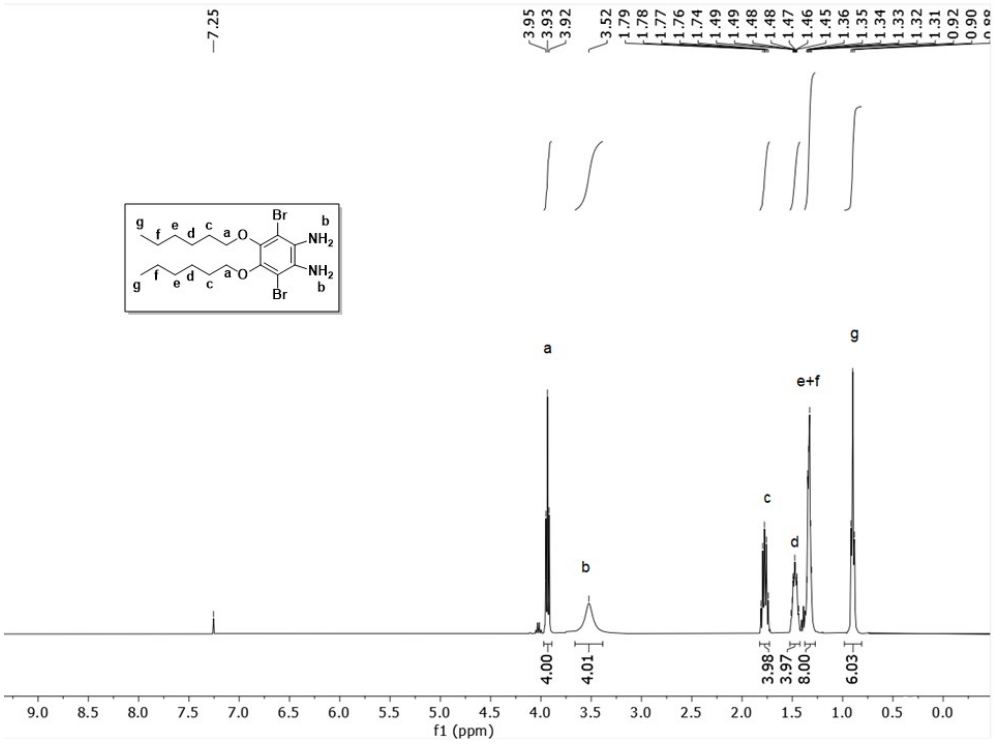


Figure S29: 1H NMR (400 MHz, $CDCl_3$) of **10**

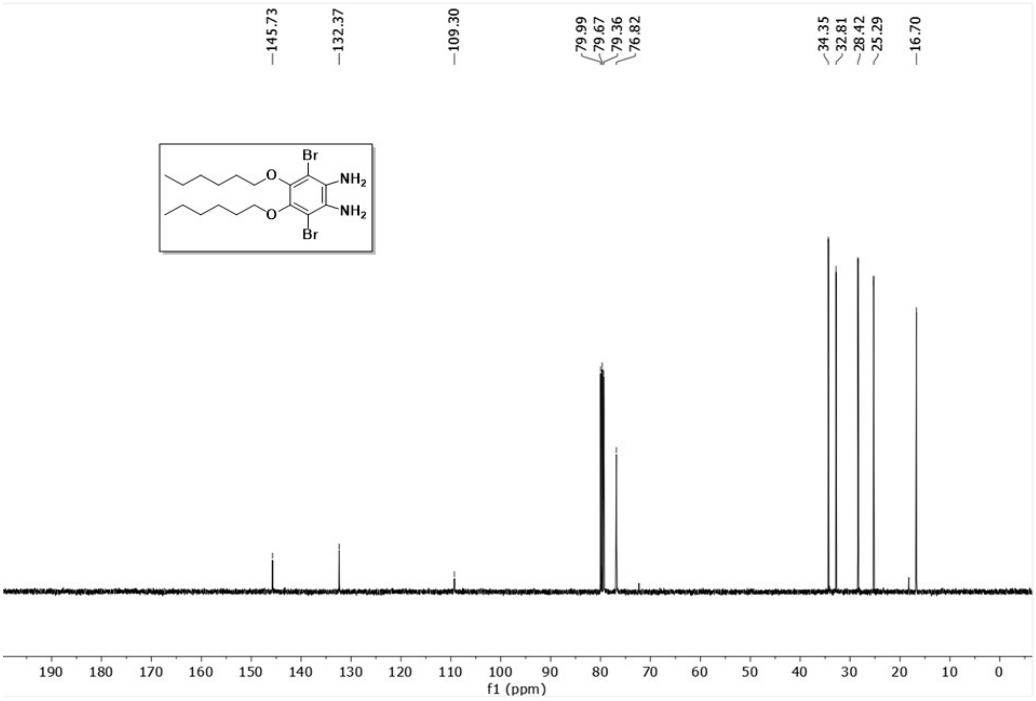


Figure S30: 13C NMR (400 MHz, $CDCl_3$) of **10**

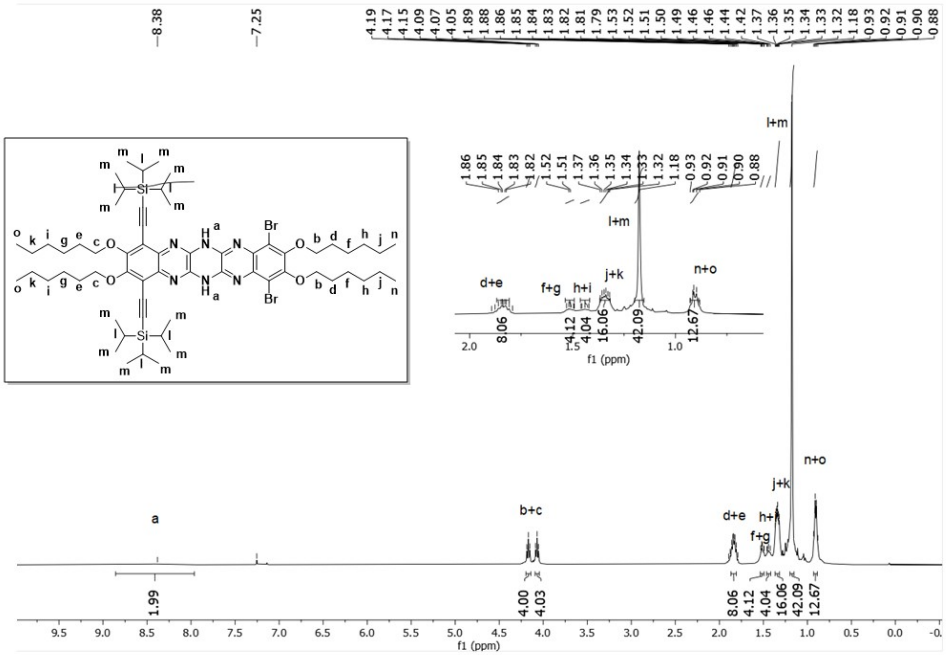


Figure S31: ^{1}H NMR (400 MHz, $CDCl_3$) of compound **11**

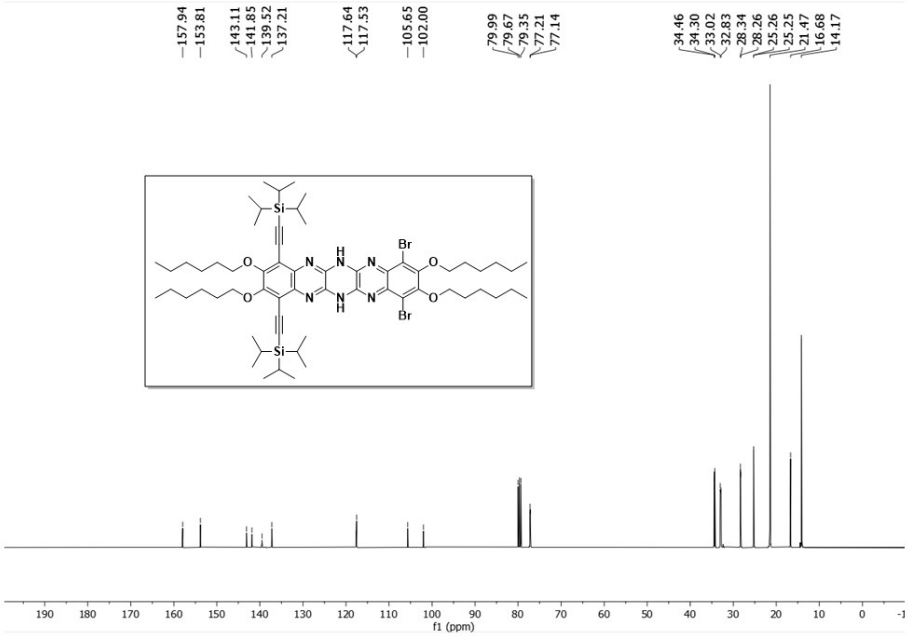


Figure S32: ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **11**

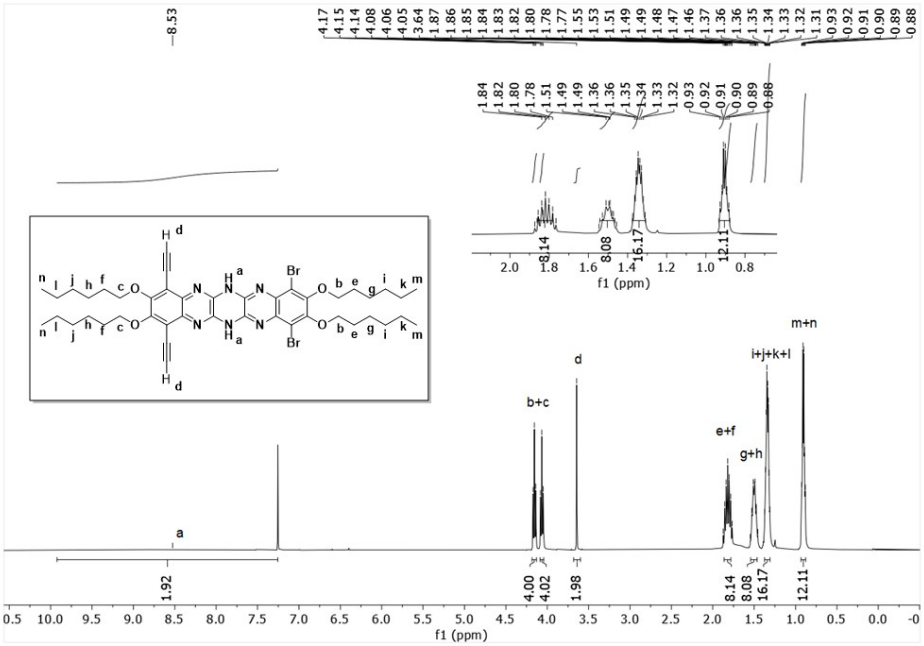


Figure S33: H NMR (400 MHz, $CDCl_3$) of compound **N6P-Br**

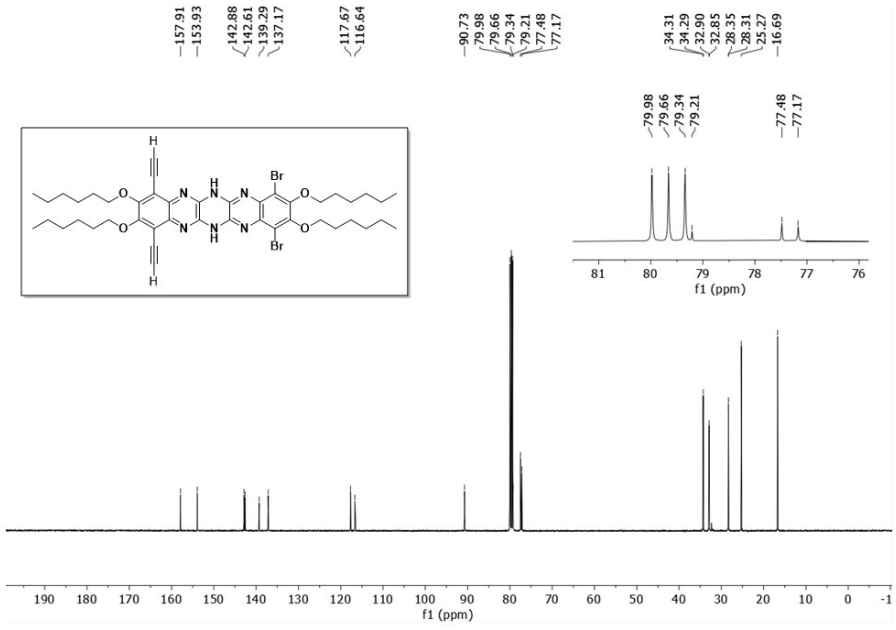


Figure S34: ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **N6P-Br**

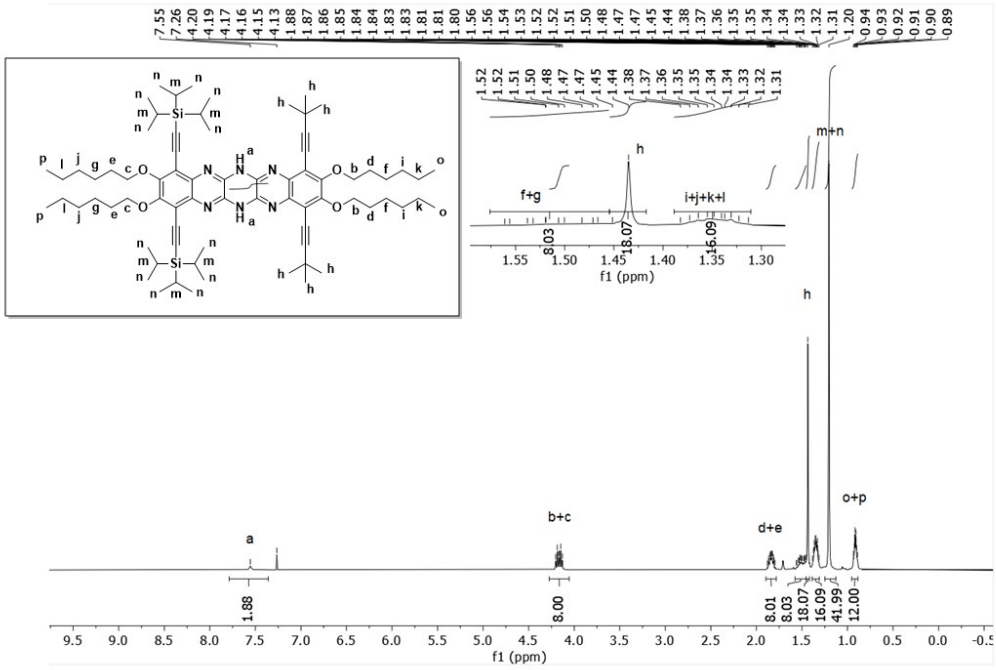


Figure S35: ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **13**

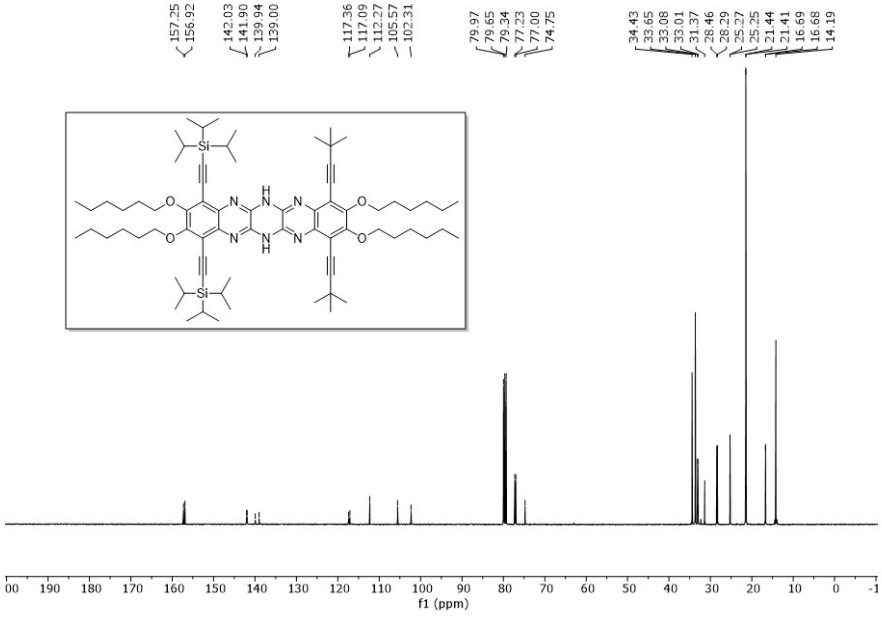


Figure S36: ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **13**

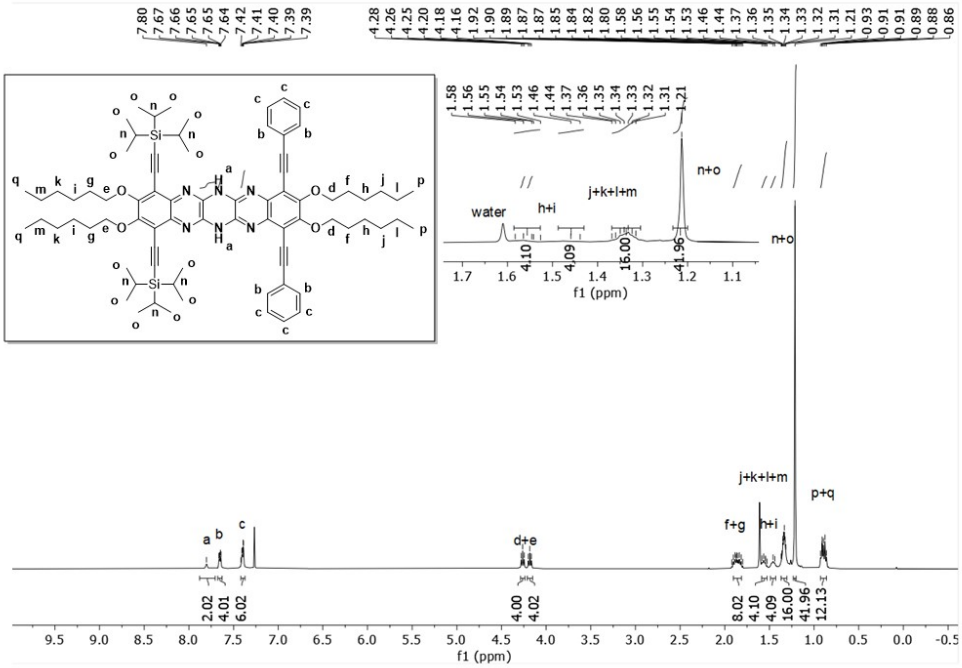


Figure S37: ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **14**

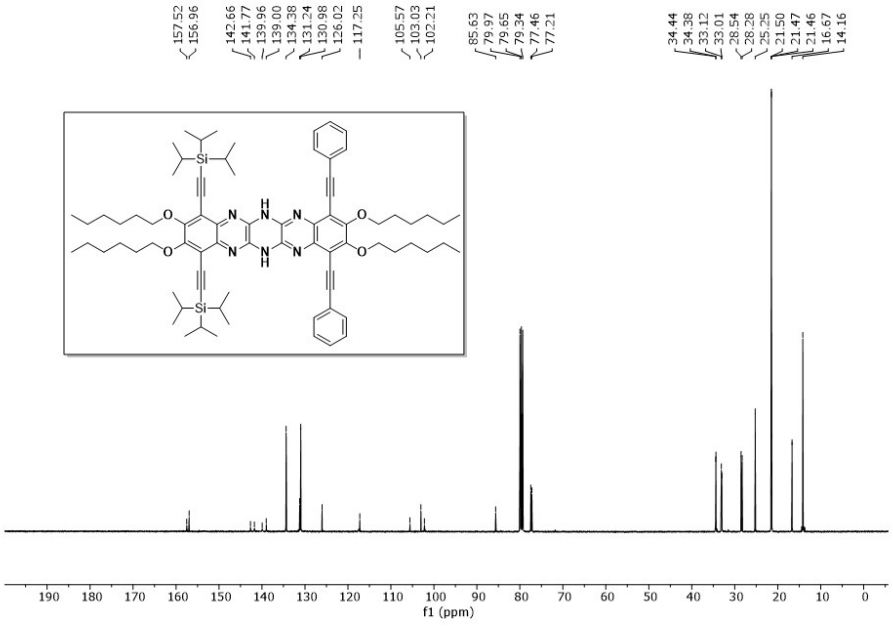


Figure S38: ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **14**

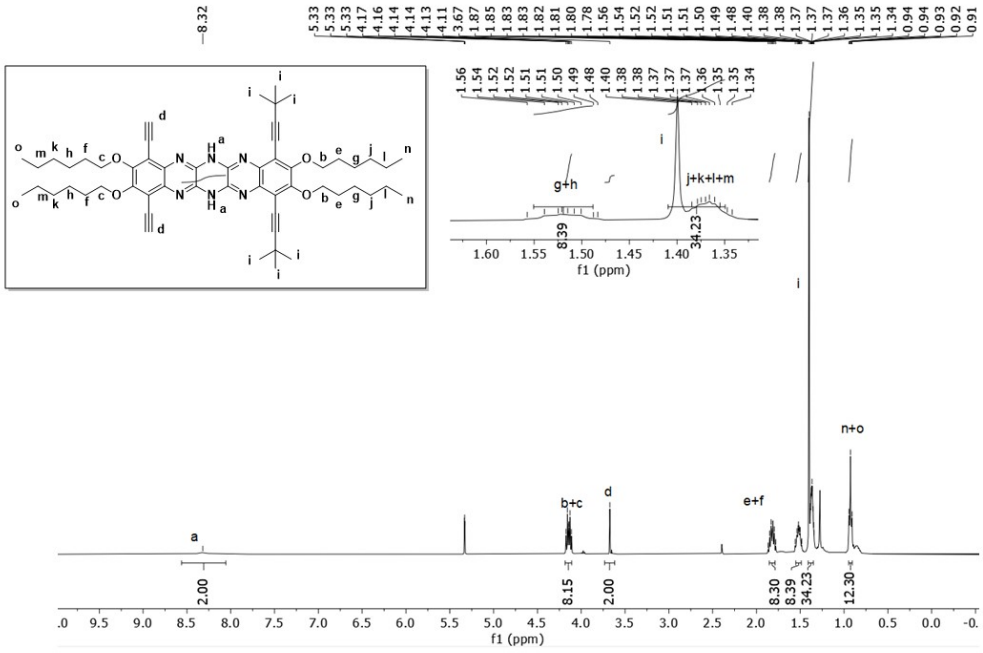


Figure S39: ^{1}H NMR (400 MHz, CD_2Cl_2) of Compound **N6P-Bu**

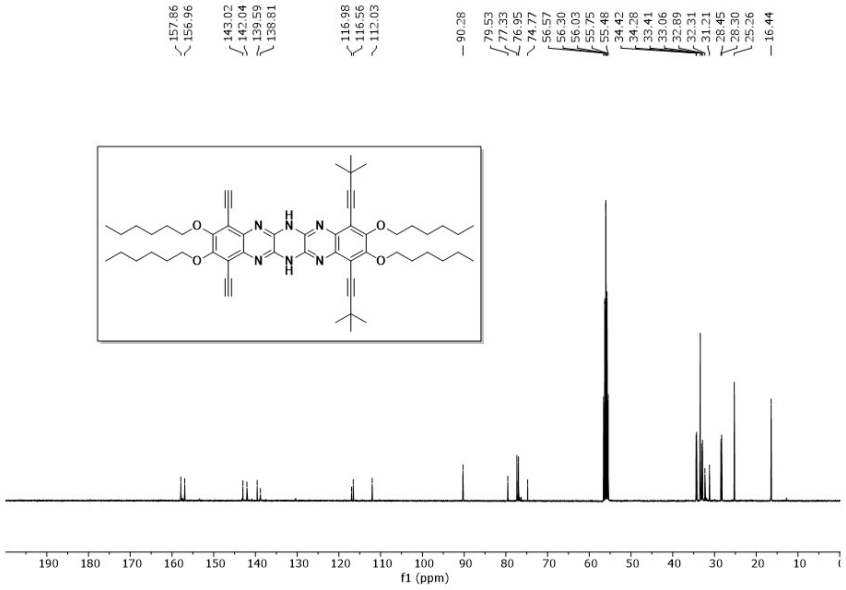


Figure S40: ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **N6P-Bu**

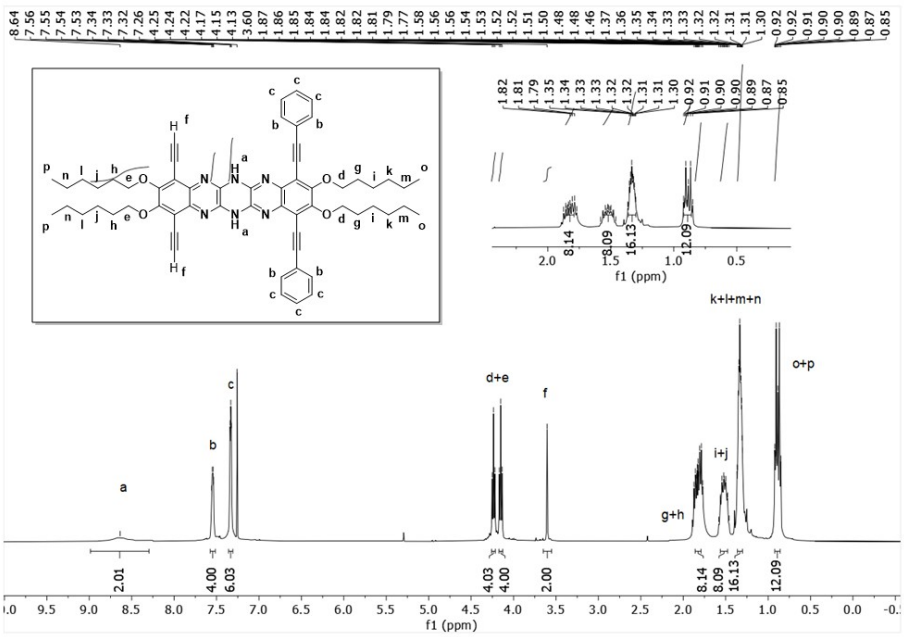


Figure S41: H NMR (400 MHz, $CDCl_3$) of Compound **N6P-Ph**

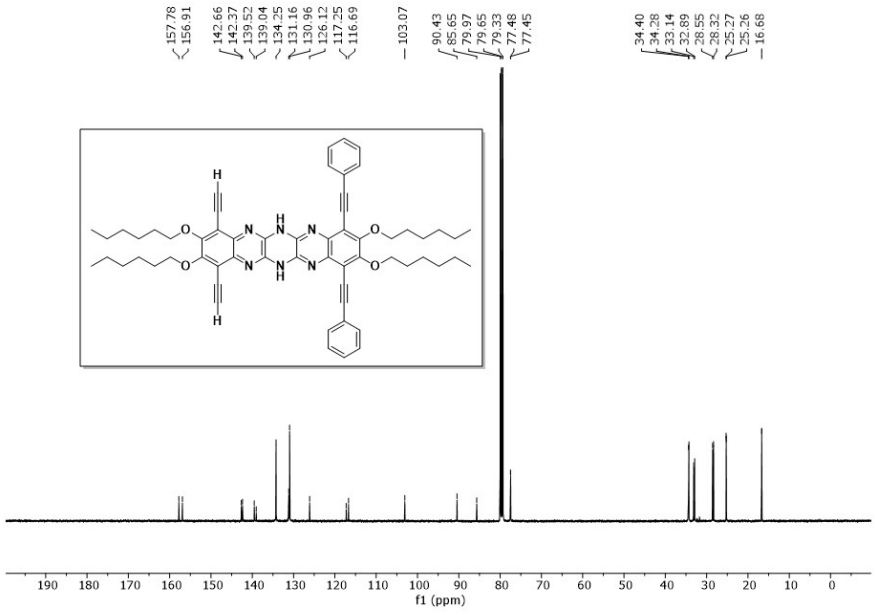


Figure S42: ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **N6P-Ph**

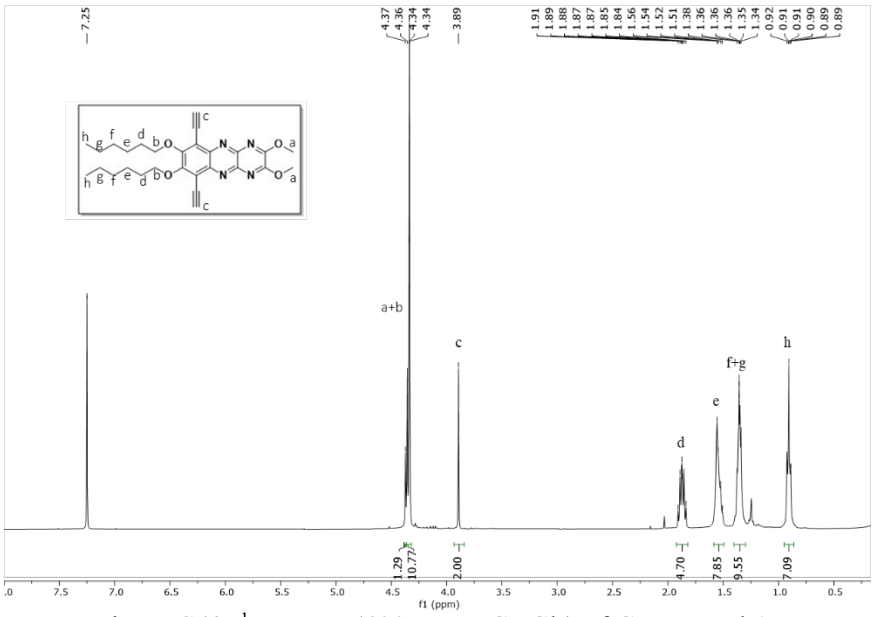


Figure S43: ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **17**

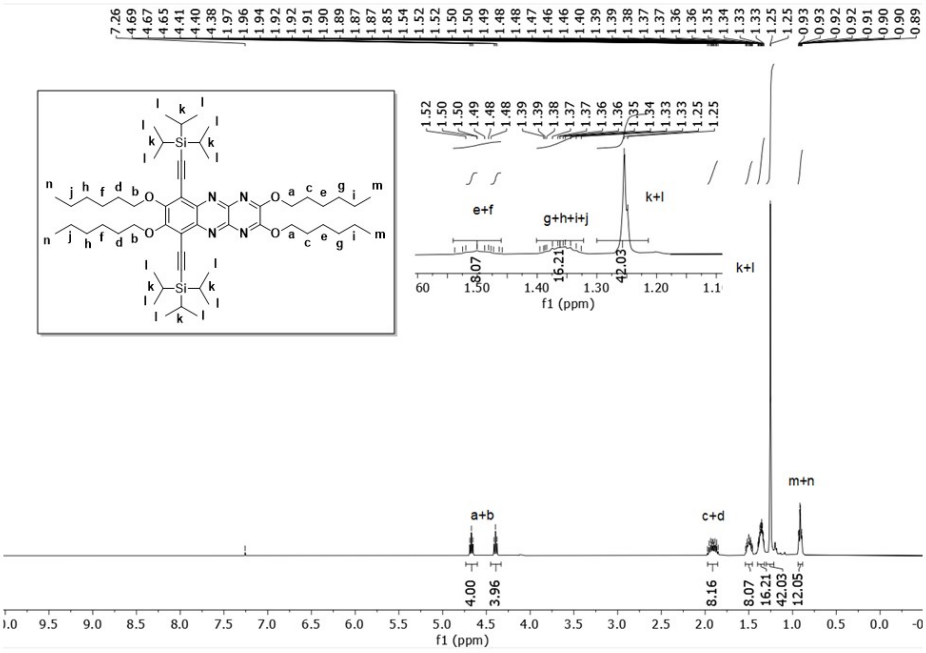


Figure S44: ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **18**

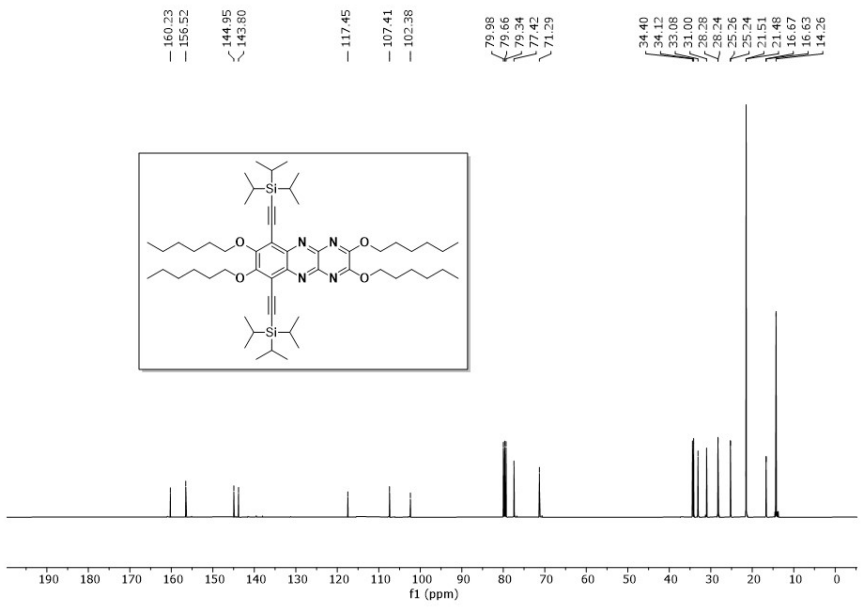


Figure S45: ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **18**

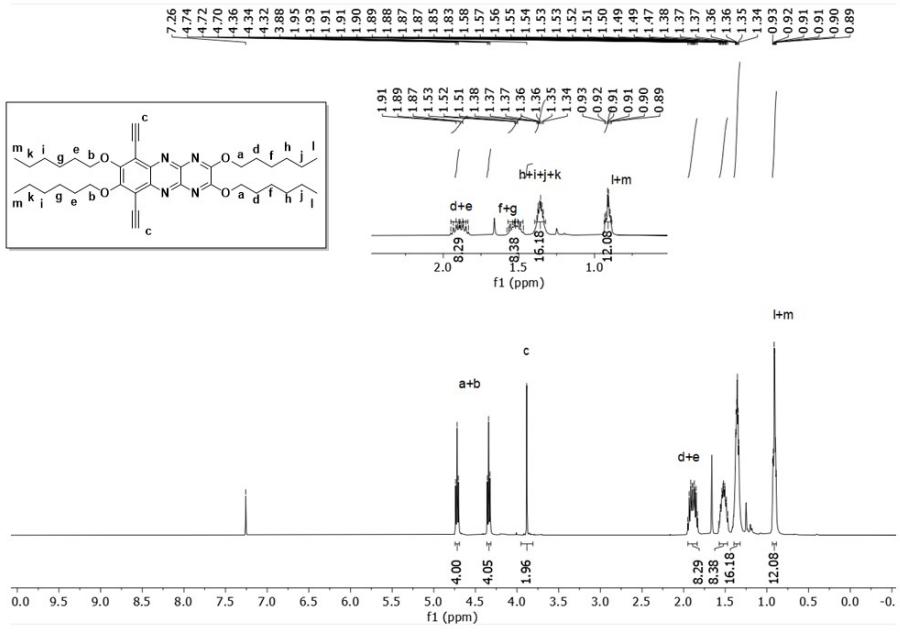


Figure S46: ^{1}H NMR (400 MHz, $CDCl_3$) of Compound **N4A**

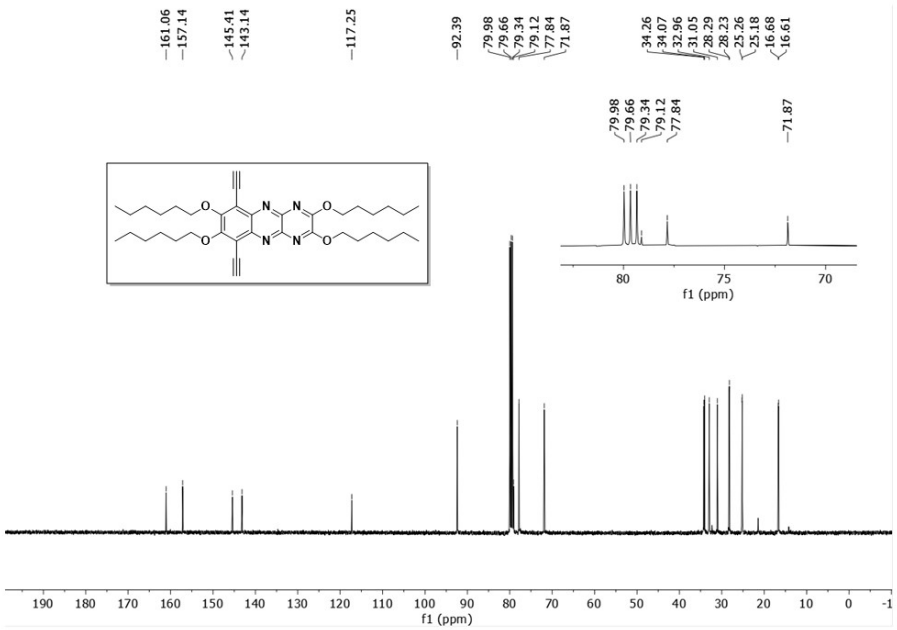


Figure S47: ^{13}C NMR (100 MHz, $CDCl_3$) of Compound **N4A**

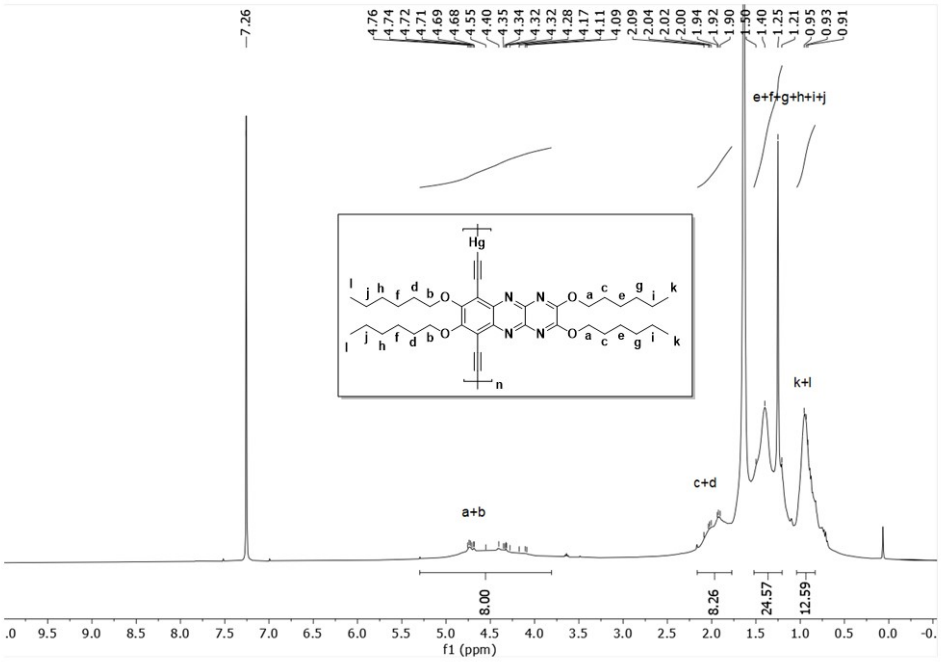


Figure S48: ^{1}H NMR (400 MHz, $CDCl_3$) of **PN4A**

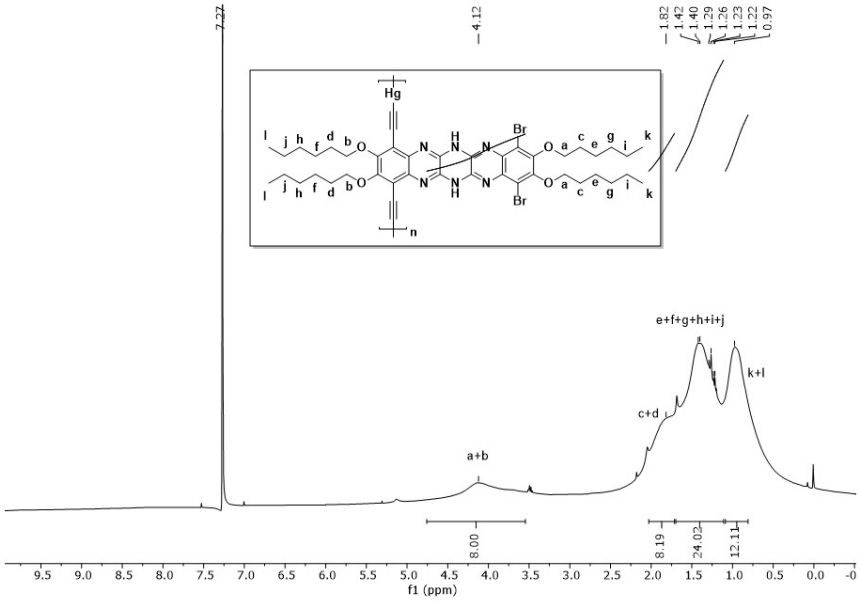


Figure S49: ^{1}H NMR (400 MHz, $CDCl_3$) of **PN6P-Br**

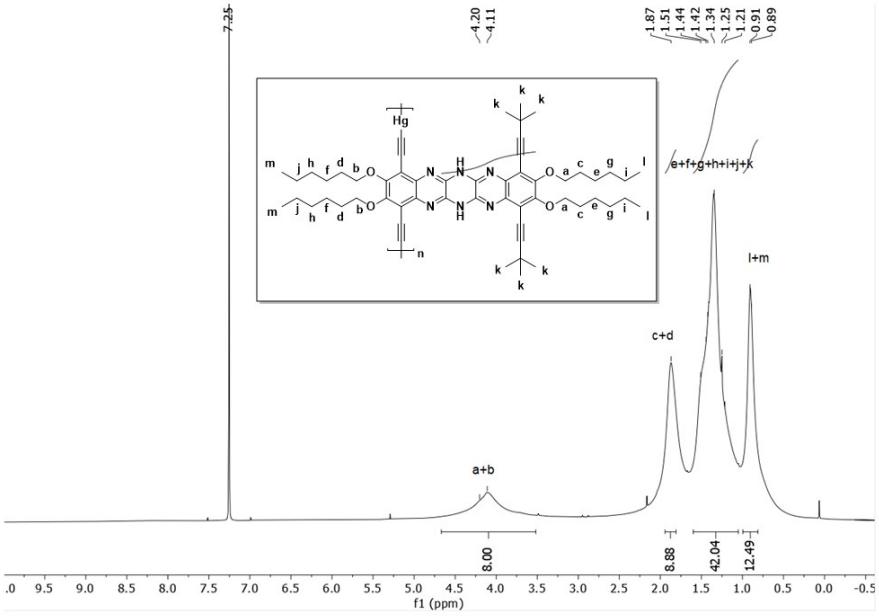


Figure S50: ^{1}H NMR (400 MHz, $CDCl_3$) of **PN6P-Bu**

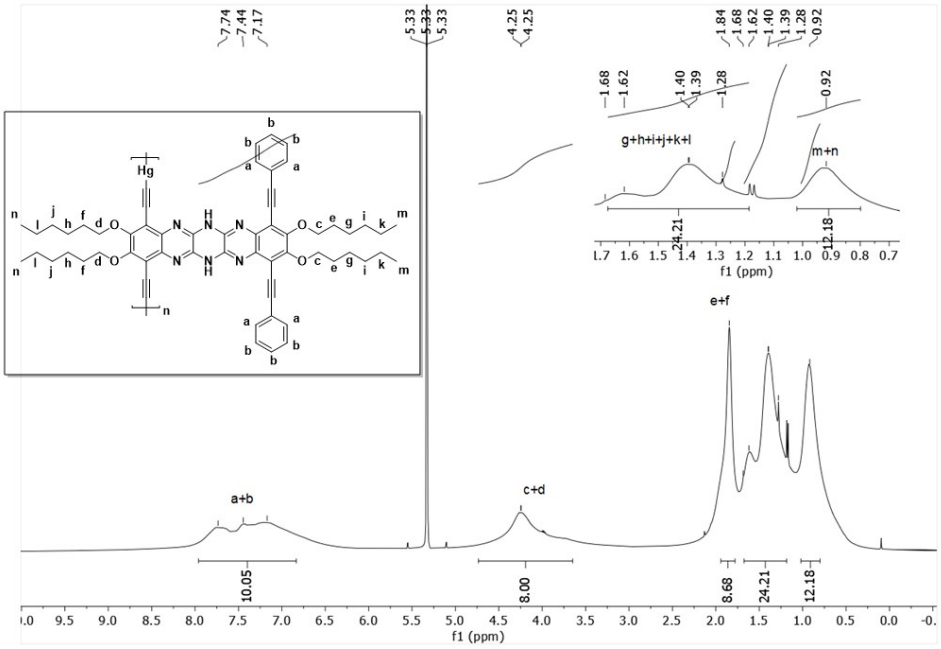


Figure S51: ^{1}H NMR (400 MHz, CD_2Cl_2) of **PN6P-Ph**

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