The Importance of Intramolecular Conductivity in Three-Dimensional Molecular Solids

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Supplementary Table S1 : OFET characteristics for the two macrocycles and acyclic controls

	cis-**cPBPB** Highest/average	*trans*-**cPBPB** Highest/average	*cis*-**AC** Highest/average	*trans*-**AC** Highest/average
Mobility (cm^2V^{-1})	0.4×10^{-3}/ $0.4 \pm 0.1 \times 10^{-3}$	1.3×10^{-3}/ $1.2 \pm 0.1 \times 10^{-3}$	2.1×10^{-4}/ $1.9 \pm 0.3 \times 10^{-4}$	1.8×10^{-4}/ $1.5 \pm 0.3 \times 10^{-4}$

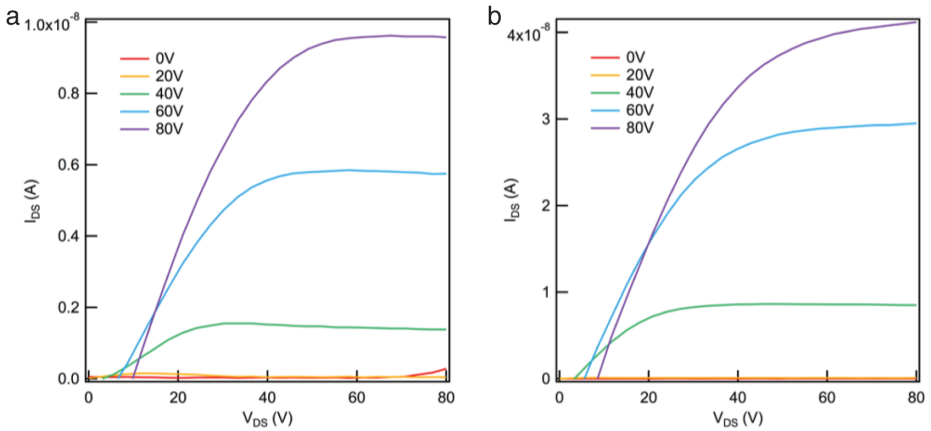


Figure S1. Output curves for a) *cis*-**cPBPB** and b) *trans*-**cPBPB** films from OFETs.

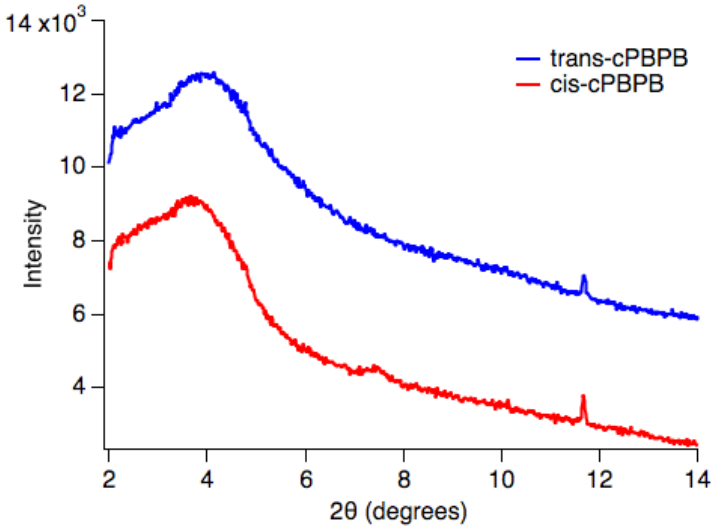


Figure S2. PXRD for a) *cis*-**cPBPB** and b) *trans*-**cPBPB** drop cast from chloroform.

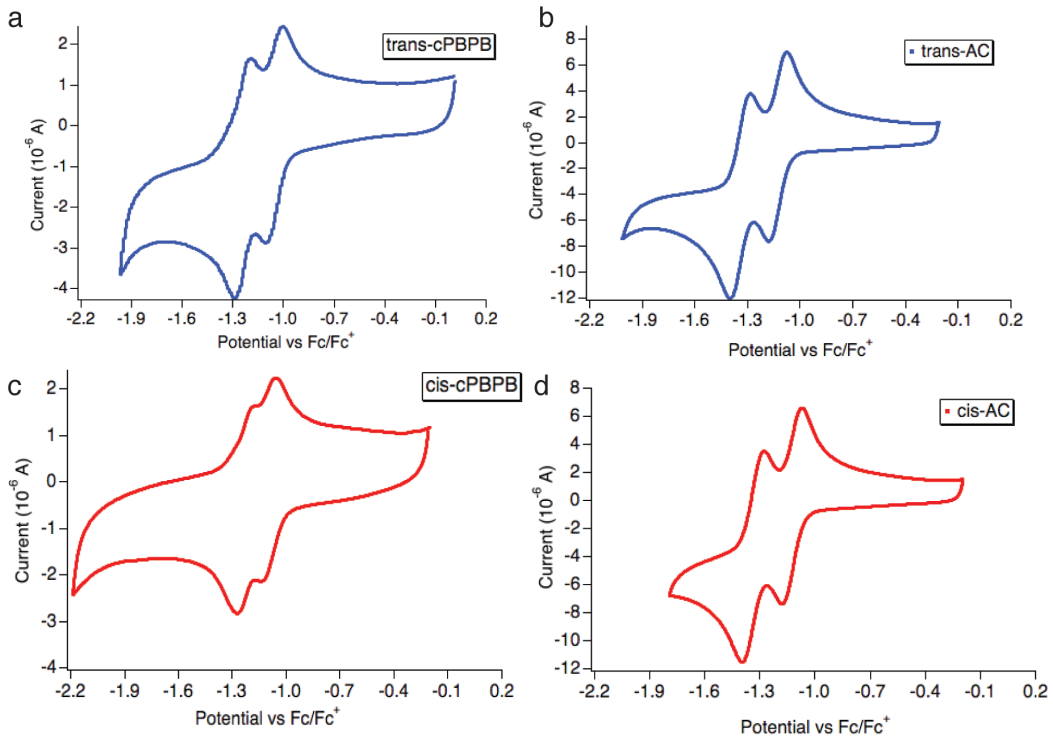


Figure S3. CV of a) *trans*-**cPBPB**; b) *trans*-**AC**; (c) *cis*-**cPBPB**; and d) *cis*-**AC**. CVs taken in CH_2Cl_2 containing 0.1 M NBu_4PF_6 as the electrolyte.

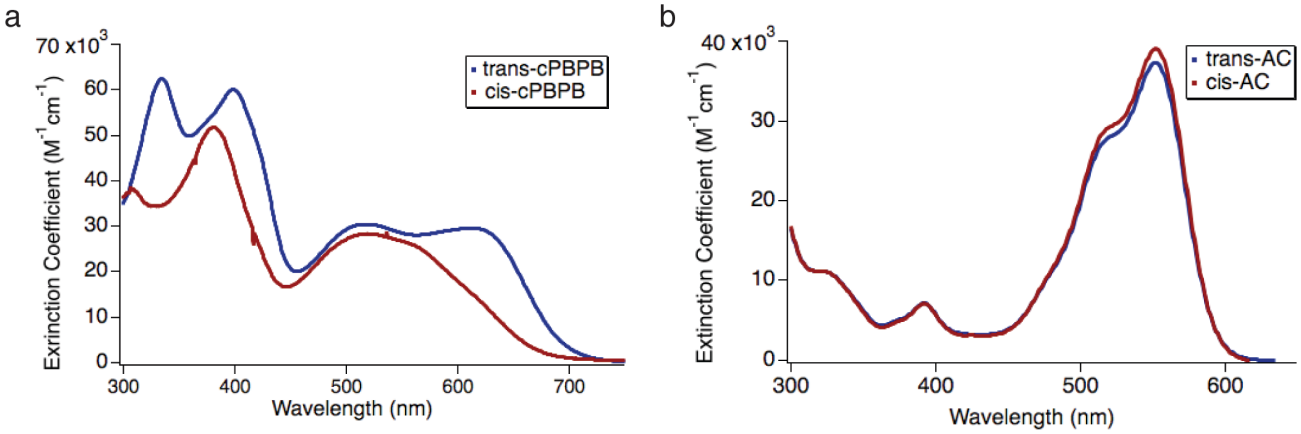


Figure S4. UV-vis spectrum of a) *cis*-**cPBPB** and *trans*-**cPBPB** and b) *cis*-**AC** and *trans*-**AC**.

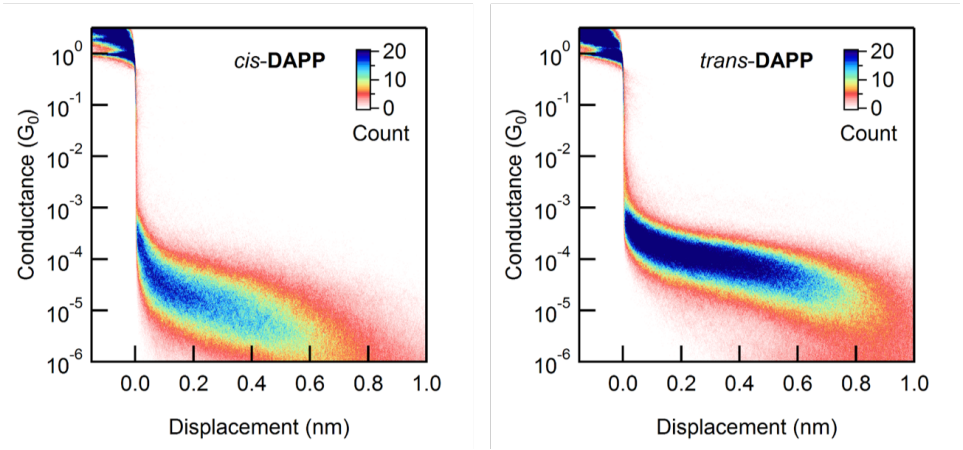


Figure S5. The two-dimensional conductance-displacement histograms of *cis*-**DAPP** and *trans*-**DAPP**.

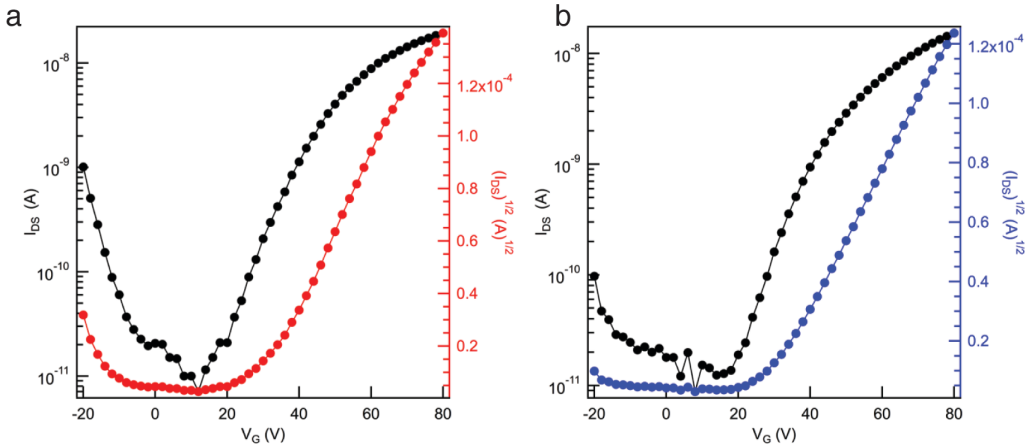


Figure S6. Transfer characteristics for a) *cis*--**AC** and b) *trans*-**AC**. The mobilities are similar: 2.1 × 10^{-4} $cm^2V^{-1}s^{-1}$ and 1.8 × 10^{-4} $cm^2V^{-1}s^{-1}$ for *cis*-**AC** and *trans*-**AC**, respectively.

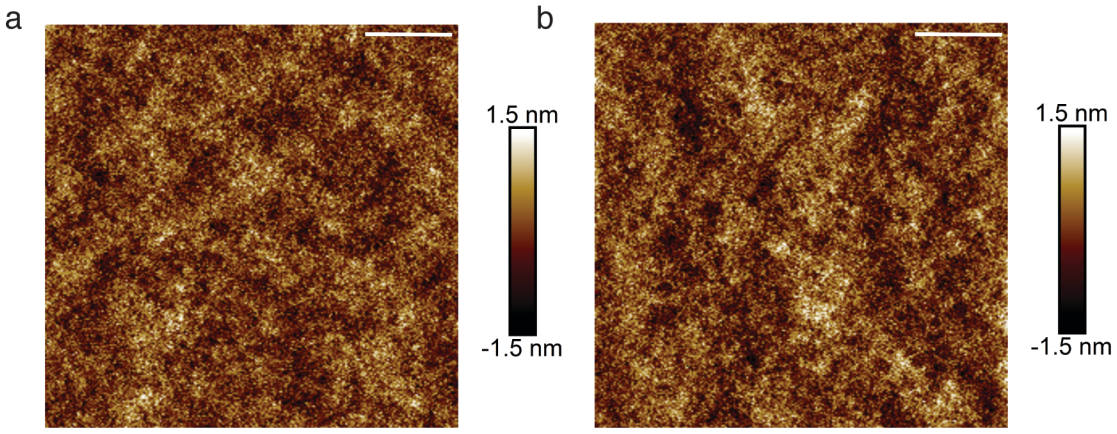


Figure S7: AFM micrograph height image for *cis*-**AC** and (b) *trans*-**AC**. Both films are continuous and smooth and have a root mean square roughness of 0.43 and 0.45 nm for the *cis* and *trans*-based films, respectively. The scale bar is 1.0 μm.

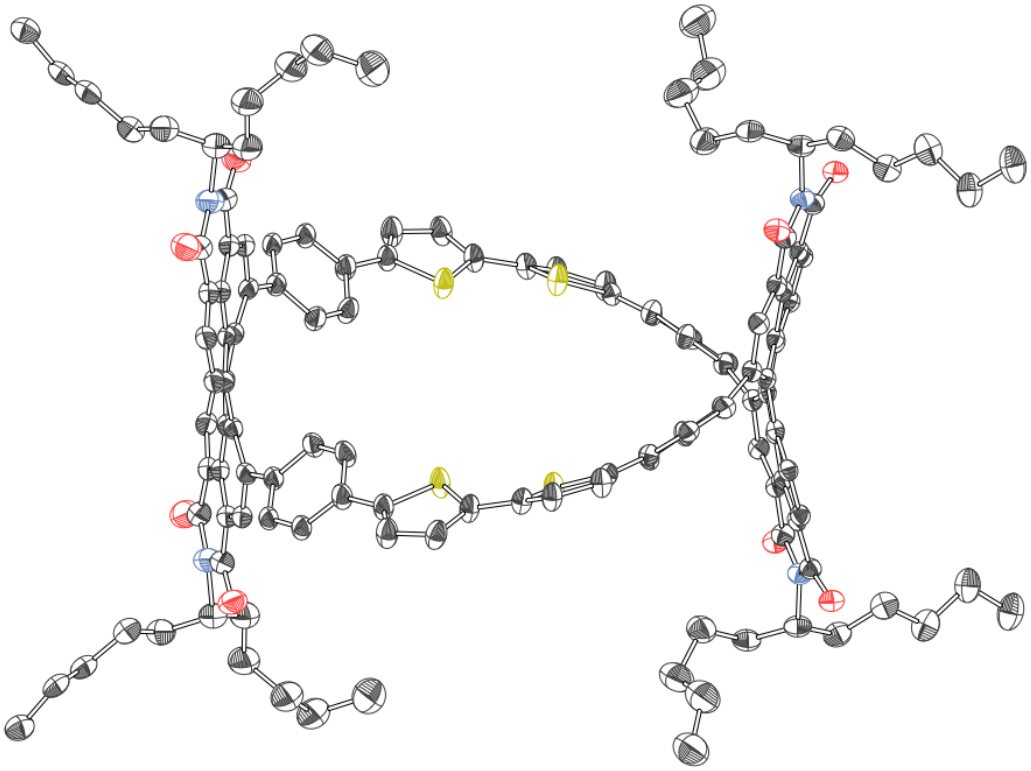


Figure S8. Molecular structure of *trans*-**cPBPB**. One of the two independent molecules is shown. Thermal ellipsoids are rendered at the 20% probability level. Black, carbon; red, oxygen; blue, nitrogen; yellow, sulfur. Hydrogen atoms and the minor positions of disordered atoms are omitted.

II. General Experimental Information

Synthesis. All reactions were performed in oven-dried or flame-dried round bottom flasks, unless otherwise noted. The flasks were fitted with rubber septa and reactions were conducted under a positive pressure of nitrogen or argon, unless otherwise noted. Anhydrous and anaerobic solvents were obtained from a Glass Contour solvent system consisting of a Schlenk manifold with purification columns packed with activated alumina and supported copper catalyst. Reaction monitoring by thin layer chromatography (TLC) was performed on J.T. Baker Baker-flex Silica Gel IB2-F (25 mm x 75 mm) TLC plates. TLC visualization was accomplished by visible observation and irradiation with a UV lamp.

Purification. Automated flash chromatography was performed using a Teledyne Isco Combiflash Rf200 and Redisep Rf Silica columns. The 1,6- and 1,7-regioisomers of *N,N'*-di(6-undecyl)-dibromoperylene-3,4:9,10-tetracarboxylic diimide were separated using prep HPLC on a COSMOSIL Buckyprep 20 x 250 mm, 18.9 mL/min and 12:88 CH2Cl2:hexanes.

Reagents. Commercial reagents were used without further purification. Chemicals, and all other reagents were purchased from Sigma-Aldrich.

Spectrometers. ^{1}H NMR spectra were recorded on a Bruker 500 MHz spectrometer. ^{13}C NMR spectra were recorded on a Bruker 125 MHz spectrometer with complete proton decoupling. NMR spectra were recorded at 300 K unless otherwise noted. Chemical shifts for protons are reported in parts per million (ppm) and chemical shifts for carbon are reported in ppm downfield. Data are represented as follows: chemical shift, multiplicity (b = broad, s = singlet, d = doublet, dd= doublet of doublets, t = triplet, m = multiplet), coupling constants in Hz, and integration.

High-resolution mass spectrometry (HRMS) was performed on a Waters XEVO G2XS instrument equipped with a UPC SFC inlet, electrospray (ESI) and atmospheric pressure chemical (APCI) ionization, and a QToF mass spectrometer.

UV-vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum400 FTIR spectrometer using a PIKE ATR attachment.

Cyclic Voltammetry. Cyclic voltammograms (CVs) were recorded on a CH166 electrochemical workstation using a Platinum wire, Platinum wire, and Glassy Carbon as the counter, reference, and working electrode, respectively, at room temperature. Experiments were performed in CH_2Cl_2 with NBu_4PF_6 as the supporting electrolyte at a scan rate of 0.1 V/s. For calibration, the redox potential of ferrocene/ferrocenium was measured under the same conditions. It was found to be 0.188 V for *cis*-**cPBPB**. It is assumed that the redox potential of Fc/Fc^+ has an absolute energy level of -4.80 eV to vacuum, and we calculated the LUMO energy levels according to the following paper DOI: 10.1038/ncomms2411.[1]

Thin film transistors. To create the devices, we first silanize the substrate (300 nm of SiO_2 on a Si wafer) with octadecyltrichlorosilane (OTS). Au is deposited onto the substrate as bottom-contact source and drain electrodes (40 nm) with a width of 105 μm and length of 20 μm. Next, we spin-cast organic films onto the surface at 1,000 r.p.m. for 1 min, to form transistors using the silicon wafer as the global back gate for the device. Finally, the samples were annealed under inert atmosphere at 160℃ for 10 minutes to optimize device. The thin film transistors were tested on the Agilent 4155C semiconductor parameter analyzer.

Single crystal X-ray diffraction. Data for *trans*-**cPBPB** was collected on an Agilent SuperNova diffractometer using mirror-monochromated Cu Kα radiation. Data integration, scaling (ABSPACK) and absorption correction (face-indexed Gaussian integration[2] or numeric analytical methods[3]) were performed in CrysAlisPro.[4] Structure solution was performed using ShelXT.[5] Subsequent refinement was performed by full-matrix least-squares on F^2 in ShelXL.[6] Olex2[6] was used for viewing and to prepare CIF files. PLATON[7] was used extensively for SQUEEZE.[8] ORTEP graphics were prepared in CrystalMaker.[9] Thermal ellipsoids are rendered at the 20% probability level.

We grew crystals of **cPBPB** for crystallography from a solution of toluene vapor diffused with methanol. A natural crystal (0.10 x 0.07 x 0.05 mm) was mounted with STP oil treatment and cooled to 100 K on the diffractometer. The diffraction was extremely weak and extended to low resolution, with no detectable intensity beyond 1 Å resolution. Complete data (99.3%) were collected to 0.985 Å. 116722 reflections were collected (15869 unique, 8603 observed) with R(int) 10.0% and R(sigma) 6.3% after analytical absorption correction (Tmax .979, Tmin .965).

According to the systematic absences, the space group was Cc or C2/c. Using ShelXT, the structure was solved readily in C2/c with two half-molecules in the asymmetric unit. Each molecule lies on a twofold axis with the PDI fragments normal to the axis. (Most non-H atoms appeared in the initial solution, but all four independent C_{11} side chains were disordered over two or three positions. These disorders were modeled with the aid of absolute (DFIX) restraints on all 1,2 and 1,3 distances, SAME similarity restraints for the two (three) components of each disordered chain, and SIMU restraints on the ADPs of all

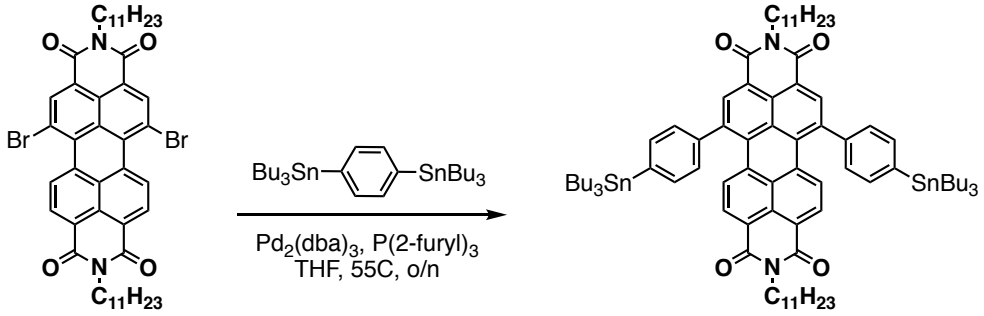
disordered atoms. In view of the poor data-to-parameters ratio, a global RIGU restraint was applied. C-H hydrogens were placed in calculated positions and refined with riding coordinates and ADPs.

The structure contained large voids with no Fourier peak larger than 1.1 $e^- Å^{-3}$. Since there were no recognizable solvent molecules in the Fourier maps, the voids were treated with PLATON SQUEEZE. The unit cell contains 8853 $Å^3$ of solvent-accessible volume with 2555 e^- (equivalent to 51 toluene molecules) in the void space, giving 1 toluene per 174 $Å^3$ of void space. Since crystalline toluene packs with 1 molecule per 145 $Å^3$, the results of the SQUEEZE analysis are reasonable. When the solvent in void space had been included as a diffuse contribution to the scattering, R_1 improved from 15.0% to 9.6%.

The final refinement (15869 data, 3138 restraints, 1789 parameters) converged with R_1 ($F_o > 4\sigma(F_o)$) = 9.7%, wR_2 = 33.4%, S = 1.08. The largest Fourier features were 0.54 and -0.31 $e^- A^{-3}$.

STM-Break Junction Measurements. We measure the single-molecule conductance using the STM-BJ technique with a custom-built setup described previously.[10] Briefly, we drive a Au tip in and out of contact with a Au-on-mica substrate and record the conductance (current/voltage) of the junction as the tip is withdrawn. Upon rupture of the Au contact, a molecule may bridge the gap as evidenced by an additional plateau in the conductance versus displacement trace. We collect 10,000 such traces, which contain 2000 data points per nanometer of extension (40 kHz sampling rate) and construct the 1D and 2D conductance histograms without data selection from these data. The conductance histogram is binned logarithmically, with 100 bins per decade along the conductance axis. For two-dimensional histograms, traces are aligned along the displacement axis at the point when the conductance crosses 0.5 G_0 and then overlaid in 2D (see Figure S4). The histograms are normalized by the number of traces used to construct them. The PDIs studied here were introduced into the setup in a 1,2,4-trichlorobenzene solution with 0.1~1 mM concentration.

III. Synthetic Procedures and Characterization Data



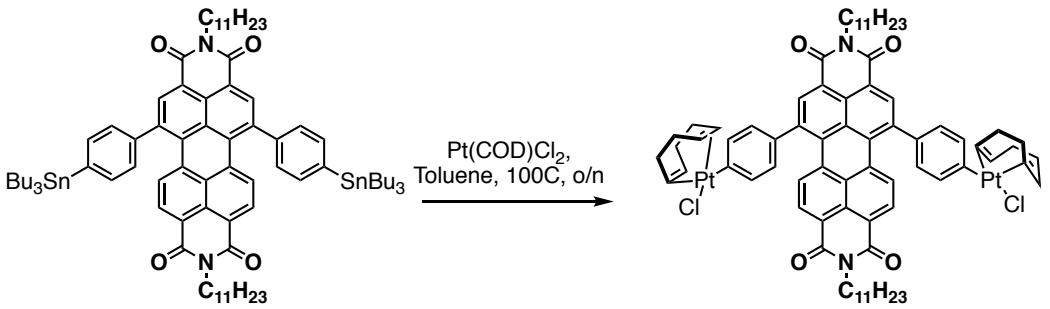
1,6-**PDI**
cis-**PDI**

SI-I

Synthesis of 1,6-Bis[4-(tributylstannyl)-phenyl]-PDI (SI-I). Pure 1,6-dibromo PDI (1.00 equiv, 0.199 mMol, 0.171 g), 1,4-bis(tributylstannyl)benzene (4.00 equiv, 0.799 mMol, 0.524 g), THF (9.95 mL), and tri(2-furyl)phosphine (0.400 equiv, 0.0796 mMol, 0.0180 g) were added to an oven-dried 25.0 mL round bottom flask under nitrogen and equipped with a stir bar. Solution was sparged with N_2 for 30 minutes. Tris(dibenzylidenacetone)dipalladium (0.100 equiv, 0.018 mMol, 0.0199 g) was added to the solution which was then degassed for an additional 30 minutes. Mixture was then placed in a 55ºC oil bath overnight. The crude mixture was concentrated and purified by column chromatography (40 g Redisep Rf Silica) with a gradient of 0% to 80% CH_2Cl_2/Hexanes flow to yield the 1,6-isomer as a magenta pink solid (0.083 mMol, 0.071 g). By-products were resubmitted to the same conditions described above to yield 0.119 g for a combined total yield of 42%. **^{1}H NMR** (400 MHz, 300K, $CDCl_3$) δ 8.59 (br s, 2H), 8.09 (br d, 2H), 7.84 (d, J = 8.1 Hz, 2H), 7.57* (d, J = 7.7 Hz, 4H), 7.39 (d, J = 7.9 Hz, 4H), 5.20 (br m, 1H), 5.11 (br m, 1H), 2.25 (br m, 2H), 2.16 (br m, 2H), 1.82 (br m, 4H), 1.61* (m, 12H), 1.40 (m, 12H), 1.26 (br m, 24H), 1.14* (m, 12H), 0.94 (t, 18H), 0.83 (br t, 12H). **^{13}C NMR** (100 MHz, 300K, $CDCl_3$) δ 164.78 (br), 163.73 (br), 142.83, 142.22, 142.18, 142.13, 138.05*, 135.97**, 135.32**, 134.34, 132.70, 130.00**, 129.70, 129.50, 129.25**, 128.70, 128.47, 128.06*, 127.25, 122.87**, 122.03**, 121.84**, 54.68, 54.55, 32.34, 31.78, 31.76, 31.59, 29.13*, 27.35*, 26.65, 26.56, 22.65, 22.57, 22.54, 14.11, 14.04, 13.72, 13.75, 9.74*. **IR** (cm^{-1}) 2954, 2928, 2870, 2856, 1697, 1658, 1589, 1587, 1465, 1459, 1421, 1414, 1344, 1325, 1262, 1250, 813. **HRMS** (APCI+) calculated m/z for $[C_{82}H_{114}N_2O_4Sn_2+H]^+$ is 1431.6924, found 1431.6901.

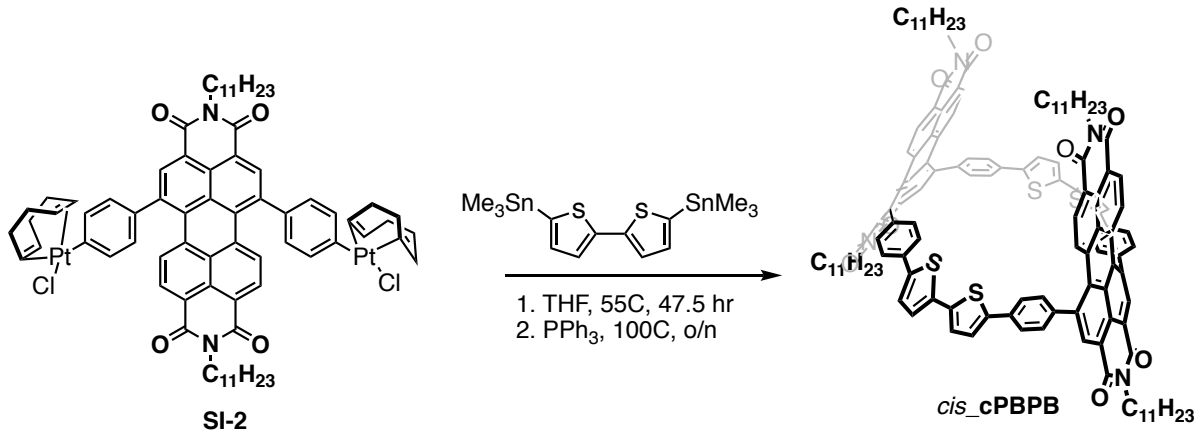
**Broadening (br) of peaks in the ^{1}H NMR spectrum is due to rotational isomers about the imide side chains.[11,12]

*Tin satellite peaks visible.



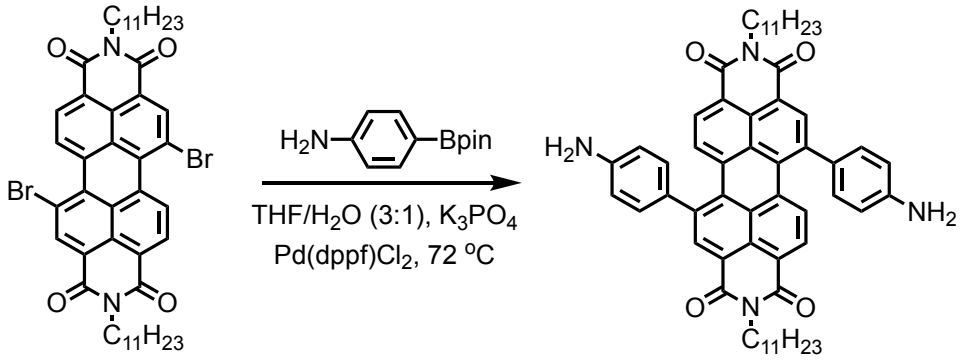
Synthesis of 1,6-Bis[4-(Pt(COD)Cl)-phenyl]-PDI (SI-2). 1,6-Bis[4-(tributylstannyl)-phenyl]-PDI (**SI-1**) (0.206 mMol, 0.295 g, 1 eq), Dichloro(1,5-cyclooctadiene)platinum(II) (0.433 mmol, 0.162 g, 2.1 eq) and toluene (21 mL) were added to an oven-dried two-neck, 50-mL round bottom flask equipped with a stir bar. The mixture was degassed for 30 minutes then placed in a 100 ºC oil bath and allowed to stir for 24 hours. The crude mixture was then concentrated and purified by column chromatography (24 g Redisep RF Silica) using a gradient from 0% to 80% CH_2Cl_2/hexanes at 60 mL/min. Product was collected and concentrated as a purple solid (0.123 g, 0.0771 mMol, 38% yield). **^{1}H NMR** (500 MHz, 300K, $CDCl_3$) δ 8.56 (br s, 1H), 8.54 (br s,1H), 8.09 (br d, 1H), 8.06 (br d, 1H), 7.85 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 7.8 Hz, 4H), 7.16 (d, J = 8.2 Hz, 4H), 5.88 (s, 4H), 5.17 (br m, 1H), 5.11 (br m, 1H), 4.71 (s, 4H), 2.74 (br m, 4H), 2.60 (br m, 4H), 2.44 (br m, 8H), 2.24 (br m, 2H), 2.15 (br m, 2H), 1.82 (br m, 4H), 1.25 (br m, 24H), 0.85 (br t, 12H). **^{13}C NMR** (100 MHz, 300K, $CDCl_3$) δ 164.80, 163.84, 145.29, 142.26, 138.67, 135.92**, 135.58, 135.21**, 134.65, 129.99**, 129.51, 129.45, 129.25**, 128.75, 128.50, 128.39, 126.98, 122.80**, 122.29**, 121.94**, 121.43**, 115.91, 87.78, 54.58, 54.48, 32.41, 32.32, 32.28, 31.81, 31.76, 28.01, 26.68, 26.55, 22.57, 14.09, 14.05. **IR** (cm^{-1}) 2958, 2925, 2857, 1695, 1656, 1583, 1410, 1325, 1275, 1262, 763, 749. **HRMS** (ESI+) calculated m/z for $[C_{74}H_{84}Cl_2N_2O_4Pt_2+Na]^+$ is 1546.4923, found 1546.4922.

**Broadening (br) of peaks in the ^{1}H NMR spectrum is due to rotational isomers about the imide side chains.[11,12]



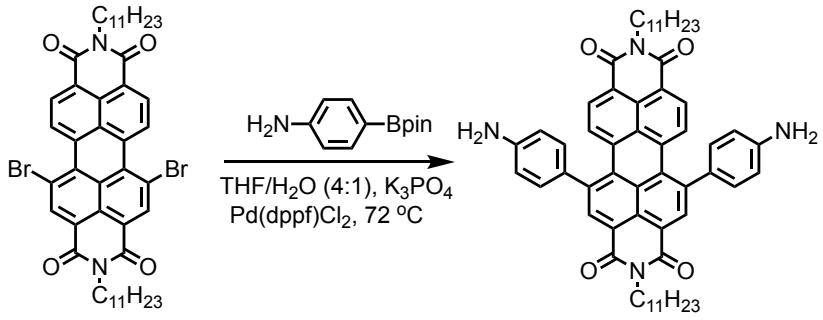
***Synthesis of cis-cPBPB*:** 1,6-Bis[4-(Pt(COD)Cl)-phenyl]-PDI (0.105 mMol, 0.160 g)), commercially available 5,5'-(bistrimethylstannyl)-2,2'-bithiophene (0.105 mMol, 0.0516 g), and THF were added to a 250 mL oven dried round bottom flask equipped with a stir bar. The mixture was sparged with nitrogen for 30 min then added to an oil bath at 55 ºC and allowed to stir for 47.5 h. Crude mixture was then removed from oil bath and concentrated. Triphenylphosphine (2.10 mMol, 0.613 g) and toluene (40.0 mL) were added to the flask. Mixture was sparged with nitrogen for 15 min then placed in a 100 ºC oil bath and allowed to stir overnight. The crude mixture was first washed with hexanes, followed by methanol and then purified by column chromatography (24 g Redisep Rf Silica) using a gradient from 0% to 85% CH_2Cl_2/hexanes at 35 mL/min. The polar fractions were further purified with prepatory TLC. Product was a dark purple solid (0.009 g, 8.5%). **^{1}H NMR** (400 MHz, 360 K, $C_2D_2Cl_4$) δ 8.75 (s, 4H), 8.18 (d, J = 8.3 Hz, 4H), 7.81 (d, J = 8.2 Hz, 8H), 7.57 (d, J = 8.2 Hz, 8H), 7.47 (d, J = 8.2 Hz, 4H), 7.41 (d, J = 3.7 Hz, 4H), 7.28 (d, J = 3.7 Hz, 4H), 5.23 (br m, 2H), 5.05 (br m, 2H), 2.30 (br m, 4H), 2.09 (br m, 4H), 1.95 (br m, 4H), 1.36 (br m, 28H)*, 1.05 (br m, 8H), 0.90 (br m, 28H), 0.58 (br m, 12H). **^{13}C NMR** (100 MHz, 328 K, $CDCl_3$) δ 166.17, 165.49, 165.07, 164.43, 144.44, 142.15, 141.98, 140.08, 136.12, 134.71**, 134.16**, 132.63, 131.73, 131.44, 130.73, 130.03, 129.62, 129.45, 128.57, 124.85, 124.44, 124.21**, 123.96**, 123.27**, 56.23, 55.16, 33.74, 33.56, 33.10, 32.56, 31.05, 27.97, 27.58, 23.90, 23.49, 15.46, 15.15. **IR** (cm^{-1}) 2972, 2954, 2926, 2855, 1695, 1655, 1586, 1426, 1405, 1322, 1260, 1250, 1103, 1126, 811, 794, 751. **HRMS** (ESI+) calculated m/z for $[C_{132}H_{128}N_4O_8S_4+H]^+$ is 2025.8693, found 2025.8676. *There is a peak underneath that corresponds to four protons that are one of the methylenes of the side chains.

**Broadening (br) of peaks in the ^{1}H NMR spectrum is due to rotational isomers about the imide side chains.[11,12]



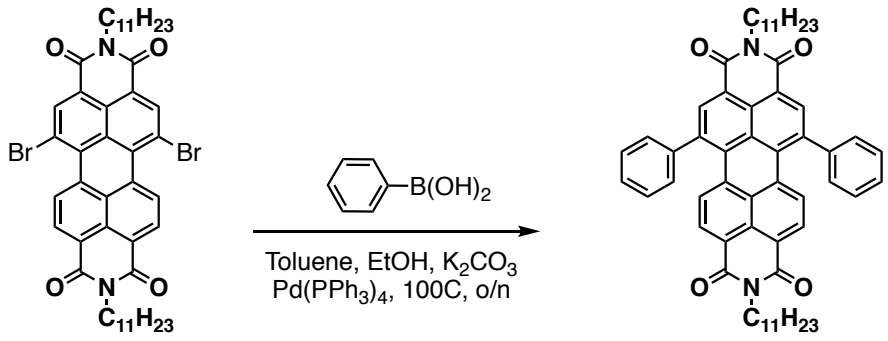
1,7 - **PDI** *trans*-**DAPP**

A solution of 1,7-dibromoPDI (100 mg, 0.117 mmol, 1.00 equiv) and 4-aminophenylboronic acid pinacol ester (150 mg, 0.685 mmol, 5.85 equiv) in THF (6 mL) was degassed under nitrogen for 30 mins. In a separate reaction vial, an aqueous solution of potassium phosphate (500 mg, 2.355 mmol, 20.13 equiv) in 2 mL water was degassed under nitrogen for 30 mins, and syringed into the degassing orange THF solution. The resultant reaction mixture was degassed for another 15 mins followed by addition of solid [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium (II) (10 mg, 0.012 mmol, 10 mol%). The orange solution was degassed for an additional 15 mins. It was placed in oil bath set at 72 °C under refluxing conditions for overnight. The blue solution was concentrated under reduced pressure to remove THF. The blue solution was diluted with brine (30 mL) and extracted with CH_2Cl_2 (50 mL) twice. The combined organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure to a blue powdery residue. The solid was washed with methanol, and the residual solid was purified by silica gel chromatography (24 g Redisep Rf Silica) using a gradient from 100% CH_2Cl_2 to 5% ethyl acetate/CH_2Cl_2 to yield 1,7-bis-coupled 4-aminophenylPDI compound as dark blue solid (92 mg, 0.104 mmol, 89% yield). **^{1}H NMR** (500 MHz, $C_2D_2Cl_4$, 350K): δ 8.61 (s, 2H), 8.16 (d, J=8.2 Hz, 2H), 8.04 (d, J=8.2 Hz, 2H), 7.40 (d, J=8.5 Hz, 4H), 6.82 (d, J=8.5 Hz, 4H), 5.19-5.13 (m, 2H), 3.92 (br s, 4H), 2.27-2.20 (m, 4H), 1.94-1.88 (m, 4H), 1.40-1.31 (m, 24H), 0.90 (t, J=6.8 Hz, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$, 323K): δ 163.92, 147.03, 141.21, 135.44, 132.29, 132.16, 130.33, 129.60, 129.42, 127.74, 122.34, 116.42, 54.59, 32.43, 31.75, 26.60, 22.50, 13.94. **IR** (ATR-ZnSe) [cm^{-1}] 3371, 2925, 2857, 1688, 1648, 1622, 1607, 1582, 1519, 1406, 1324, 1265, 1240, 1180. **HRMS** (ESI+) calculated m/z for $[C_{58}H_{64}N_4O_4+H]^+$ 881.5006; found 881.5009.



1,6 - **PDI** *cis*-**DAPP**

A solution of 1,6-dibromoPDI (90 mg, 0.105 mmol, 1.00 equiv) and 4-aminophenylboronic acid pinacol ester (90 mg, 0.411 mmol, 3.91 equiv) in THF (8 mL) was degassed under nitrogen for 30 mins. In a separate reaction vial, an aqueous solution of potassium phosphate (250 mg, 1.178 mmol, 11.22 equiv) in 2 mL water was degassed under nitrogen for 30 mins, and syringed into the orange THF solution. The resultant reaction mixture was degassed for another 15 mins followed by addition of solid [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium (II) (10 mg, 0.012 mmol, 11 mol%). The orange solution was degassed for another 15 mins. It was placed in oil bath set at 72 °C under refluxing conditions for overnight. The blue solution was concentrated under reduced pressure to remove THF. The blue solution was diluted with brine (30 mL) and extracted with CH_2Cl_2 (50 mL) twice. The combined organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure to a blue powdery residue. The solid was washed with methanol, and the residual solid was purified by silica gel chromatography (24 g Redisep Rf Silica) using a gradient from 100% CH_2Cl_2 to 5% ethyl acetate/CH_2Cl_2 to yield 1,6-bis-coupled 4-aminophenylPDI compound as dark blue solid (77 mg, 0.087 mmol, 83% yield). **^{1}H NMR** (500 MHz, $C_2D_2Cl_4$, 350K): δ 8.56 (s, 2H), 8.17 (d, J=8.2 Hz, 2H), 8.00 (d, J=8.2 Hz, 2H), 7.26 (d, J=8.4 Hz, 4H), 6.80 (d, J=8.4 Hz, 4H), 5.20-5.11 (m, 2H), 3.90 (br s, 4H), 2.28-2.16 (m, 4H), 1.93-1.89 (m, 4H), 1.36-1.32 (m, 24H), 0.91-0.88 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$, 323K): δ 164.90, 164.80, 163.75, 146.79, 142.35, 135.59, 134.85, 132.27, 129.97, 129.57, 128.96, 128.85, 128.42, 126.66, 122.63, 121.97, 121.20, 116.29, 54.53, 54.42, 32.29, 31.73, 31.69, 26.58, 26.50, 22.51, 22.49, 14.01, 13.99. **IR** (ATR-ZnSe) [cm $^{-1}$] 3360, 2953, 2924, 2856, 1691, 1642, 1604, 1583, 1504, 1436, 1325, 1247, 1181. **HRMS** (ESI+) calculated m/z for $[C_{58}H_{64}N_4O_4+H]^+$ 881.5006; found 881.4988.

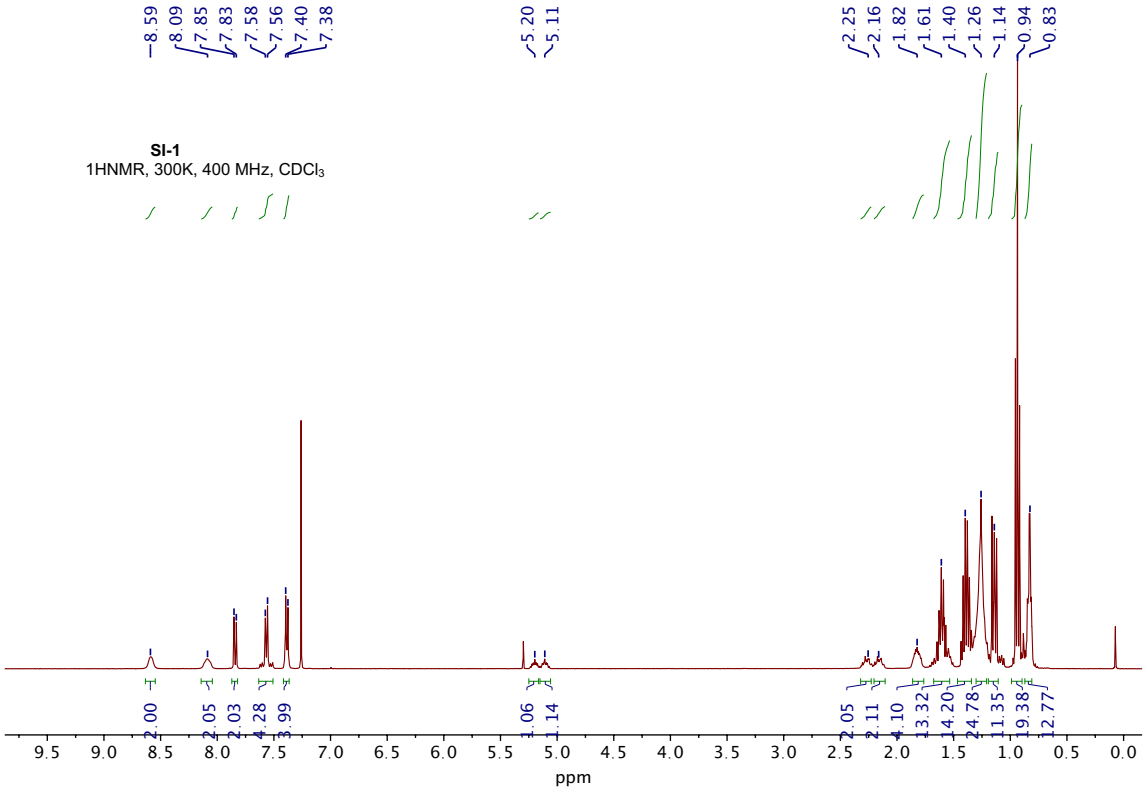


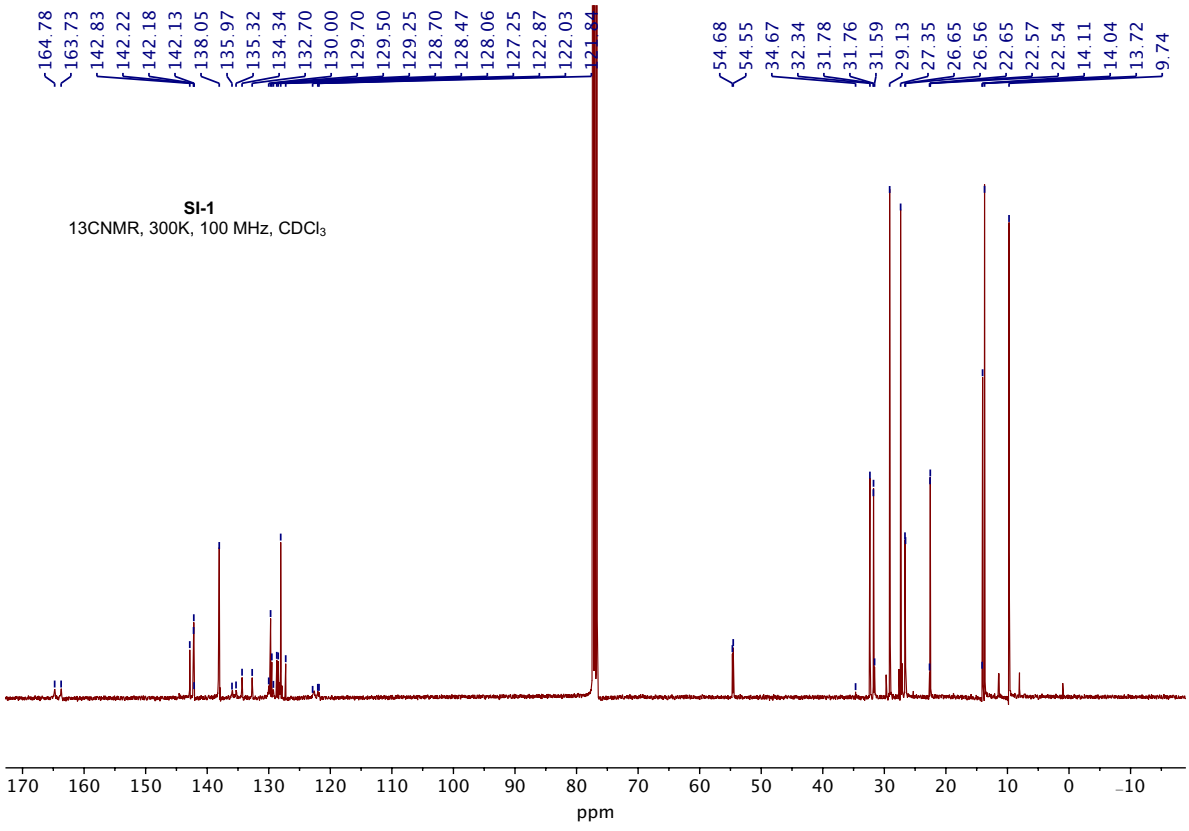
1,6-**PDI**
cis-**PDI**

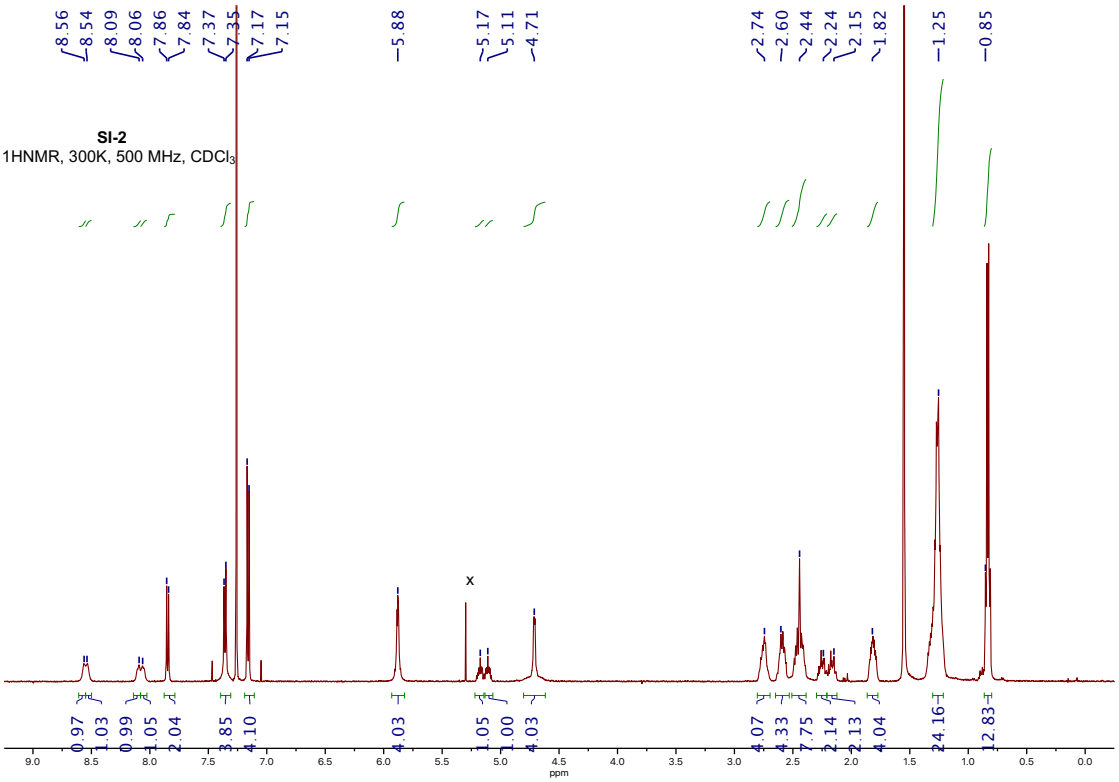
cis-**AC**

Synthesis of cis-AC: *N,N'*-Di(6-undecyl)-1,6-dibromoperylene-3,4:9,10-tetracarboxylic diimide (0.0500 g, 0.0584 mmol, 1.00 equiv), phenyl boronic acid (0.0290 g, 0.234 mmol, 4.00 equiv), aqueous K_2CO_3 (2 M, 1.00 mL), EtOH (0.200 mL) and toluene (3.00 mL) were added to a 20 ml scintillation vial equipped with a stir bar. The mixture was sparged with N_2 for thirty minutes. While under N_2, a spatula tip of tetrakis(triphenylphosphine)palladium(0) was added. The mixture was further sparged for ten minutes before placed in a 100 °C oil bath under N_2 for overnight. The crude mixture was extracted with ethyl acetate and brine, concentrated, and purified by column chromatography (24 g Redisep Rf Silica) using a gradient from 0% to 100% CH_2Cl_2/hexanes to yield *cis*-**AC** (0.0480 g, 0.0565 mmol, 97%). **^{1}H NMR** (400 MHz, CDCl3, 300K): δ 8.61 (br s, 2H), 8.12 (br s, 2H), 7.83 (d, 2H), 7.59 – 7.55 (m, 4H), 7.54 – 7.47 (br d, 6H), 5.15 (br, 2H), 2.20 (m, 4H), 1.83 (m, 4H), 1.34 (m, 24H), 0.81 (t, 12H). **^{13}C NMR** (100 MHz,$CDCl_3$) δ 164.70, 163.60, 142.26, 141.10, 135.82, 135.19, 134.84, 132.50, 130.24, 130.17, 129.92, 129.25, 129.05, 128.61, 127.92, 122.86, 122.52, 122.16, 122.81, 54.65, 32.33, 31.76, 26.59, 22.56, 14.04. **IR** (cm^{-1}) 2953, 2928, 2868, 2861, 2856, 1697, 1659, 1598, 1589, 1408, 1326, 1240, 814. **HRMS** (ESI+) calculated m/z for $[C_{58}H_{62}N_2O_4+H]^+$ 851.4788, found 851.4780. Broadening (br) of peaks in the ^{1}H NMR spectrum is due to rotational isomers about the imide side chains.[11,12]

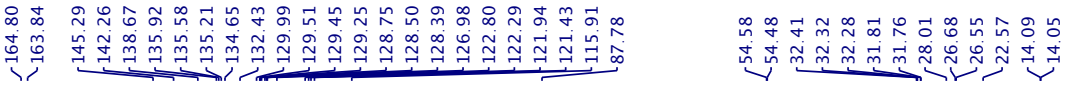
IV. ^{1}H NMR and ^{13}C NMR Spectra



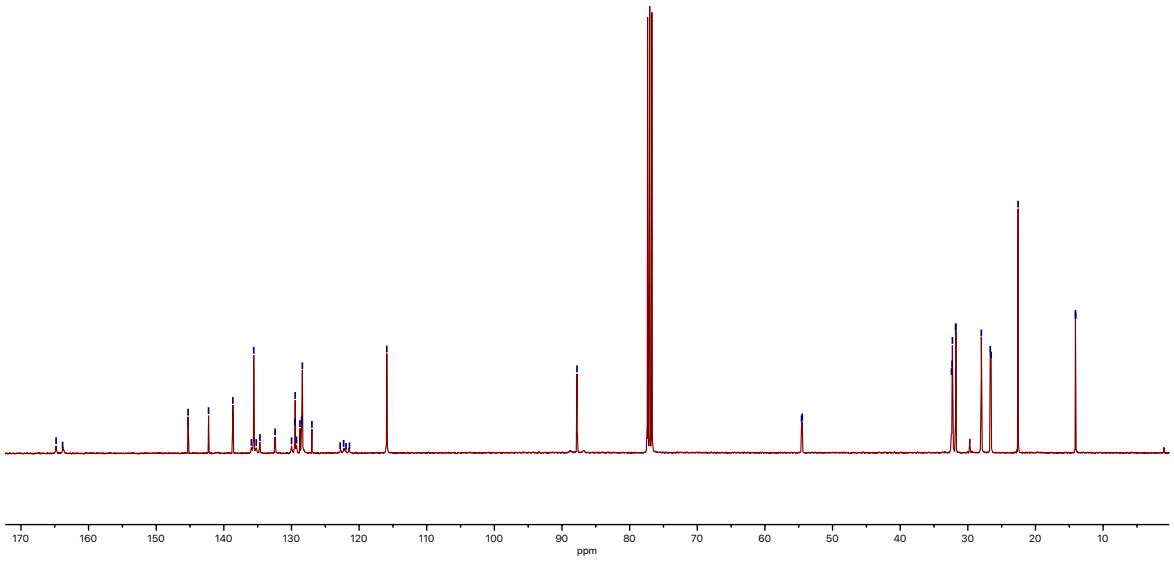


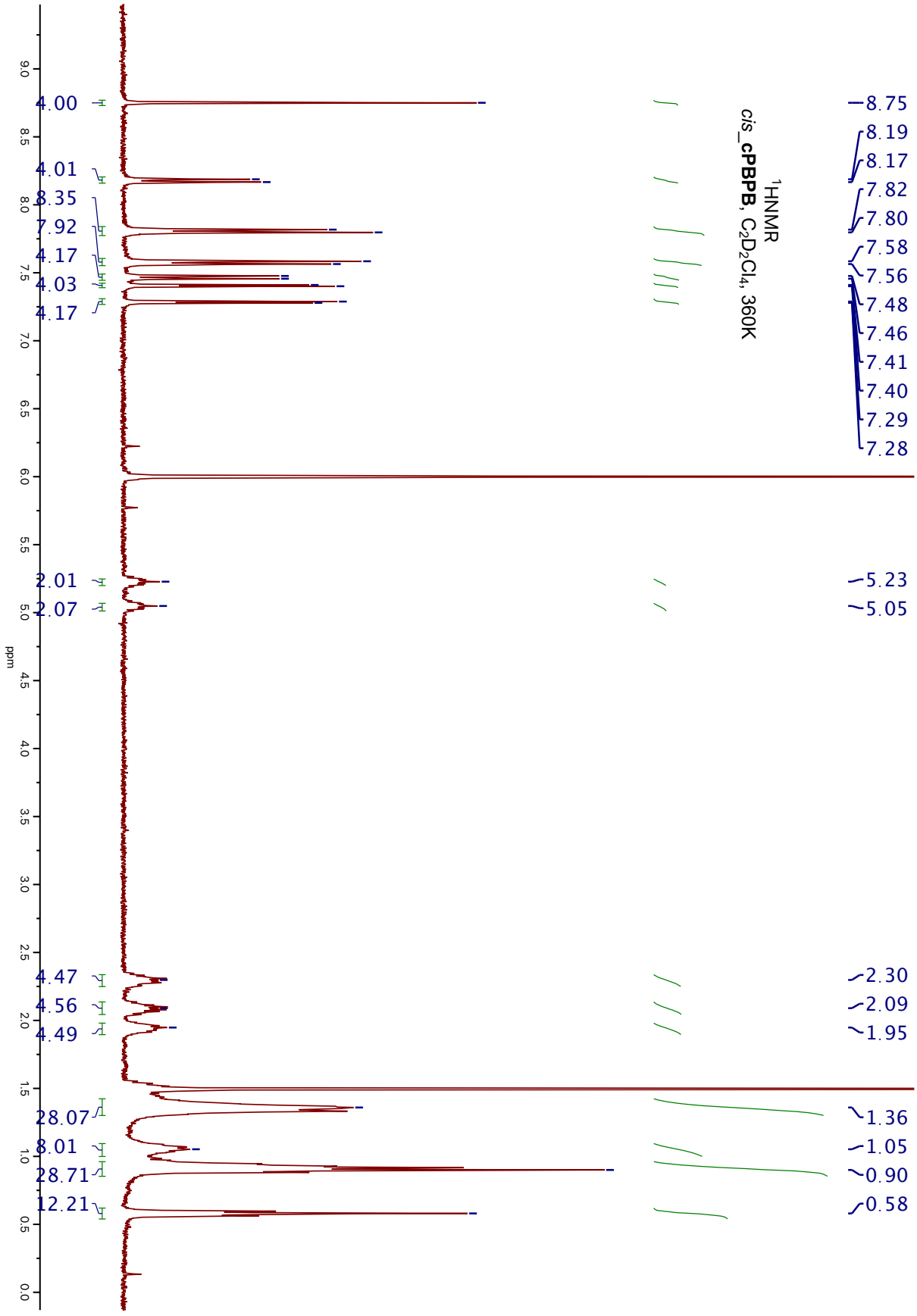


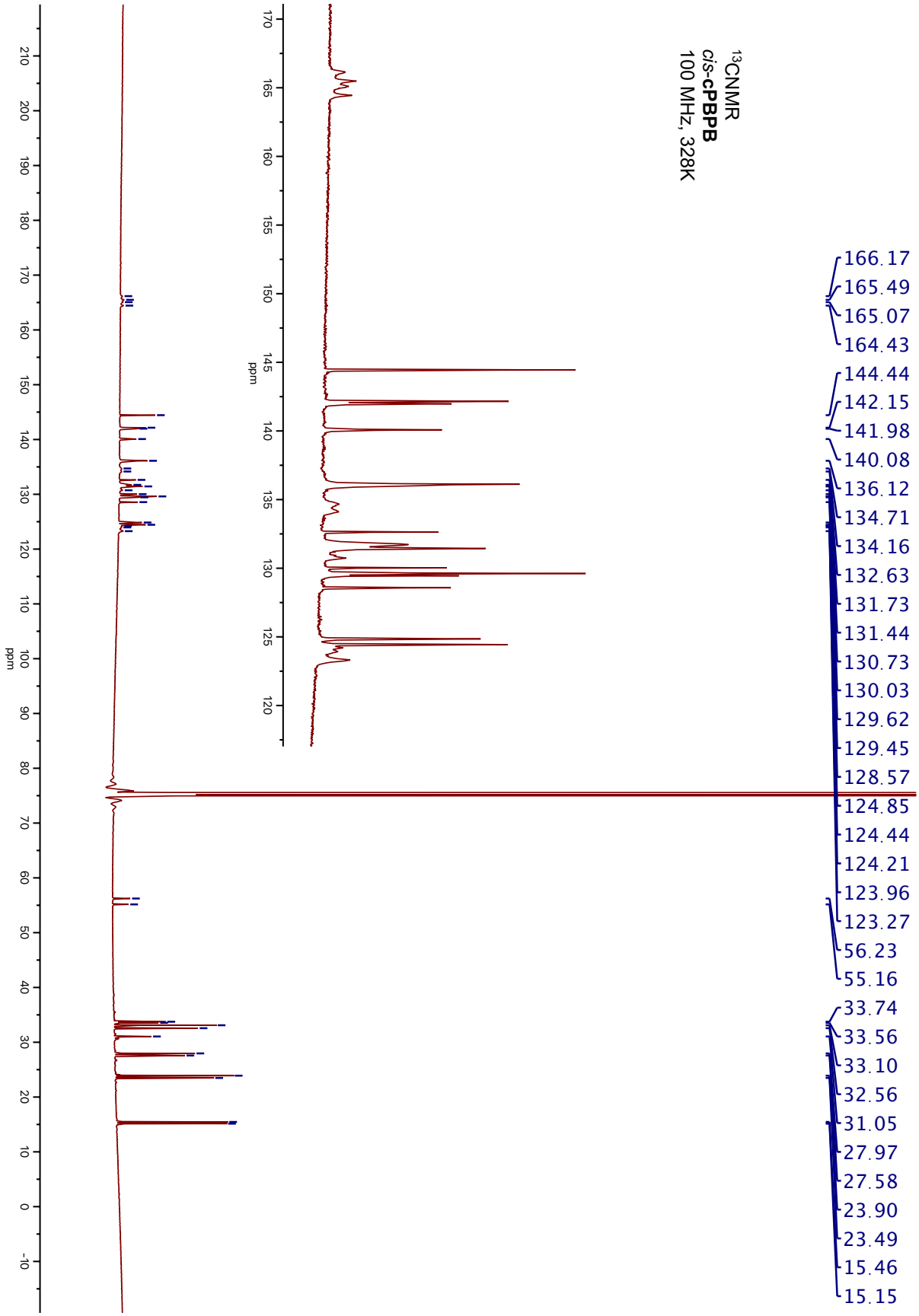
SI-2
1HNMR, 300K, 500 MHz, $CDCl_3$

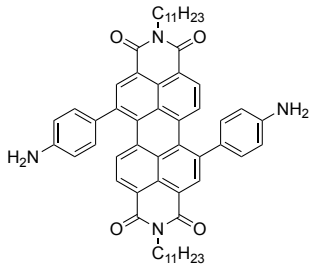


SI-2
13CNMR, 300K, 100 MHz, $CDCl_3$

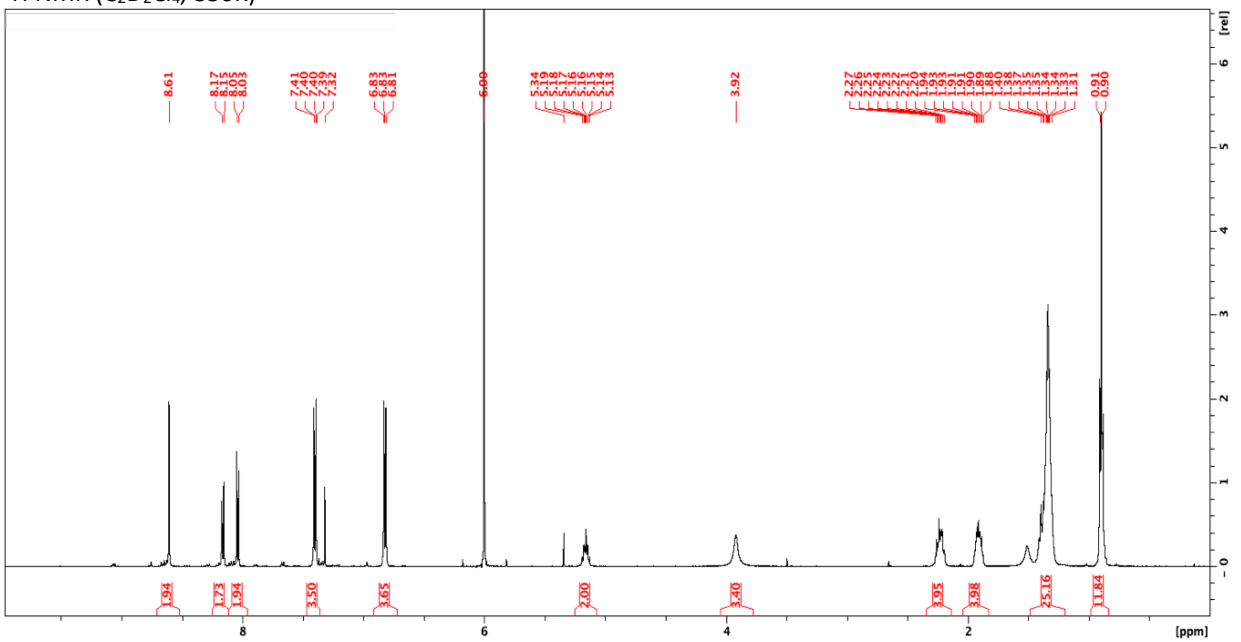



^{1}HNMR
*cis*_**cPBPB**, $C_2D_2Cl_4$, 360K
ppm
4.00
4.01
8.35
7.92
4.17
4.03
4.17
2.01
2.07
4.47
4.56
4.49
28.07
8.01
28.71
12.21
8.75
8.19
8.17
7.82
7.80
7.58
7.56
7.48
7.46
7.41
7.40
7.29
7.28
5.23
5.05
2.30
2.09
1.95
1.36
1.05
0.90
0.58

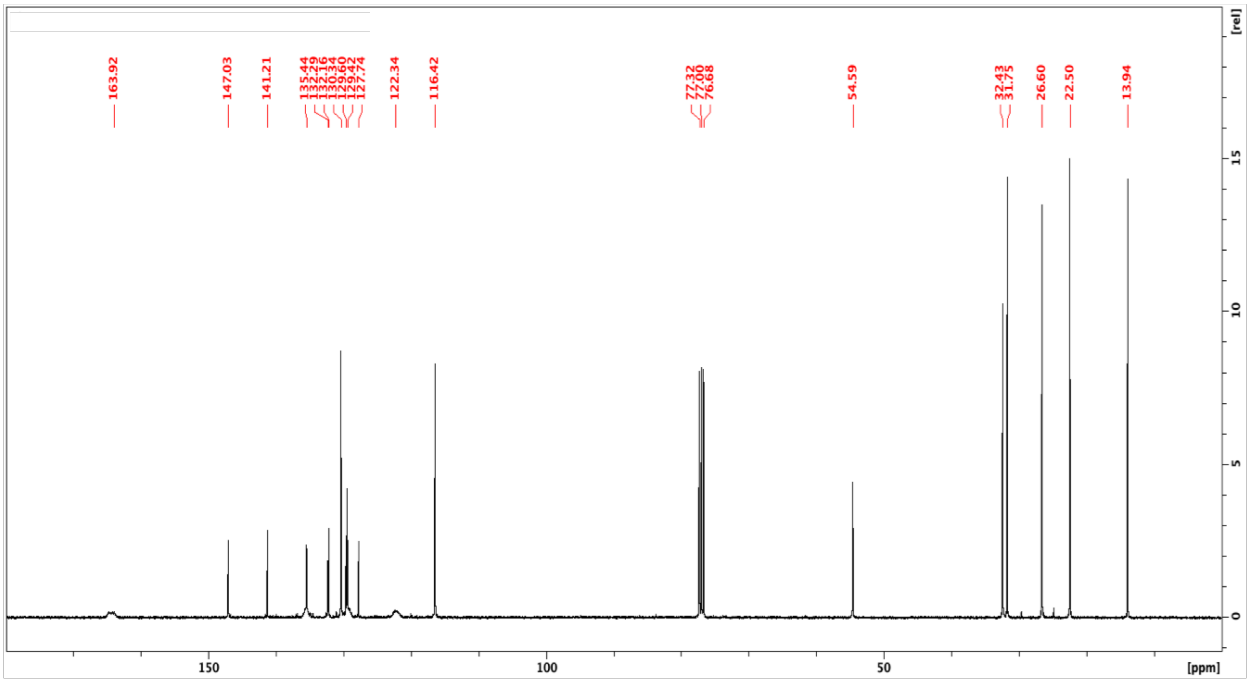

^{13}CNMR
cis-**cPBPB**
100 MHz, 328K
166.17
165.49
165.07
164.43
144.44
142.15
141.98
140.08
136.12
134.71
134.16
132.63
131.73
131.44
130.73
130.03
129.62
129.45
128.57
124.85
124.44
124.21
123.96
123.27
56.23
55.16
33.74
33.56
33.10
32.56
31.05
27.97
27.58
23.90
23.49
15.46
15.15
ppm

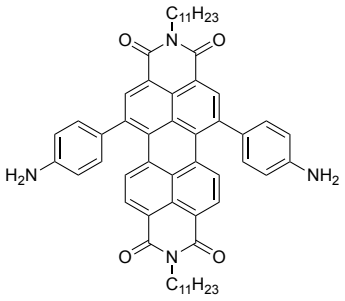


^{1}H NMR ($C_2D_2Cl_4$, 350K)

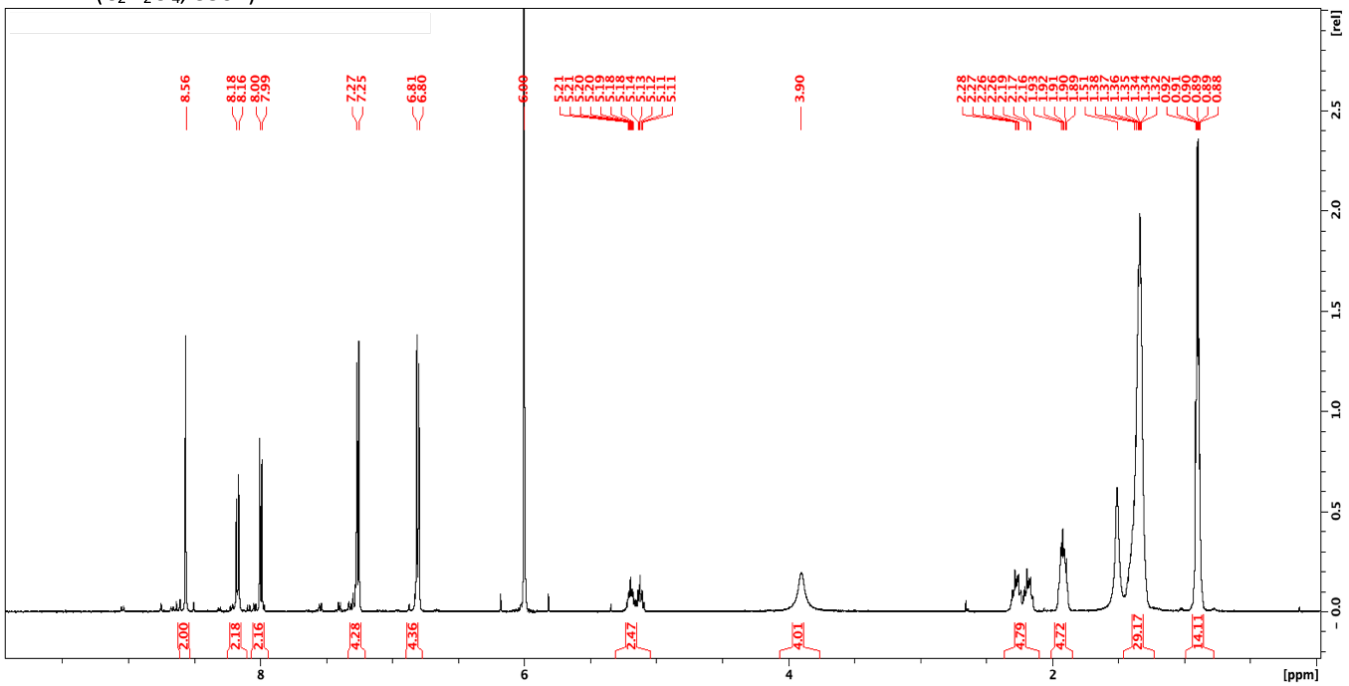


^{13}C NMR ($CDCl_3$, 323K)

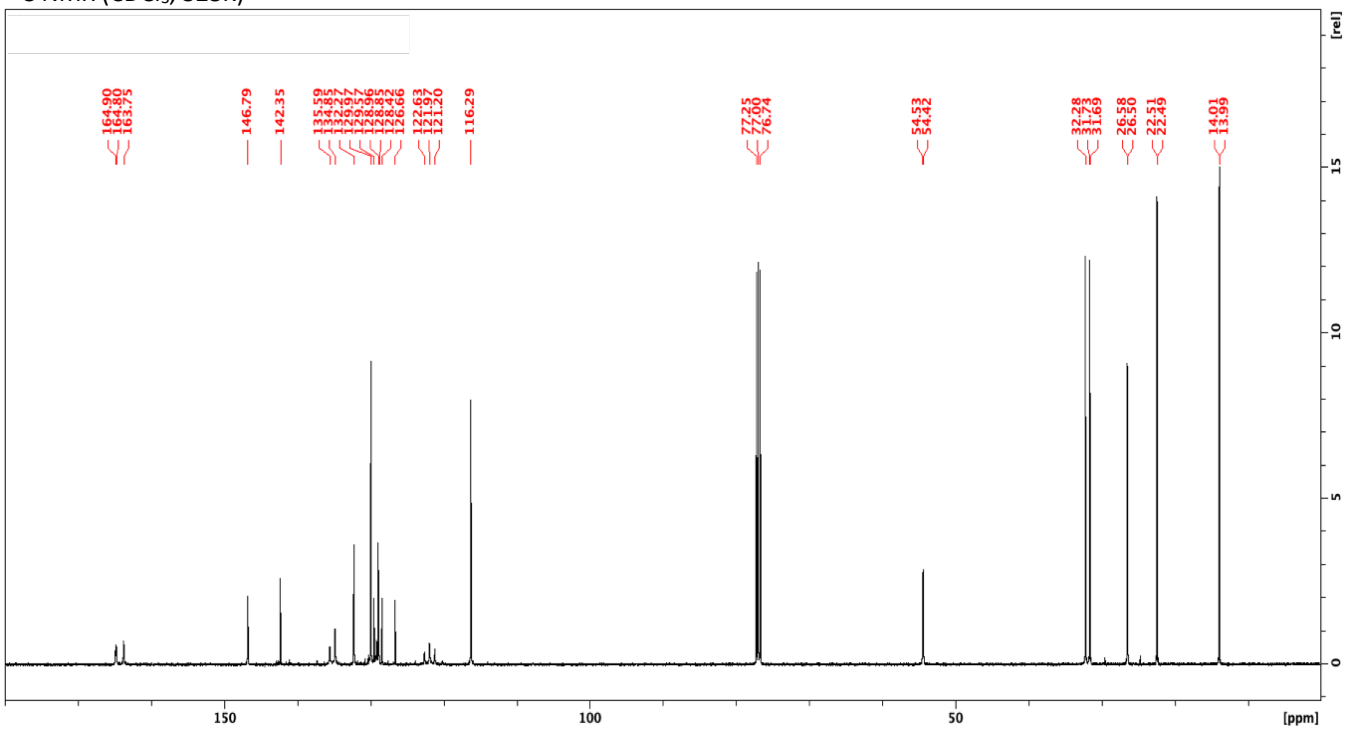


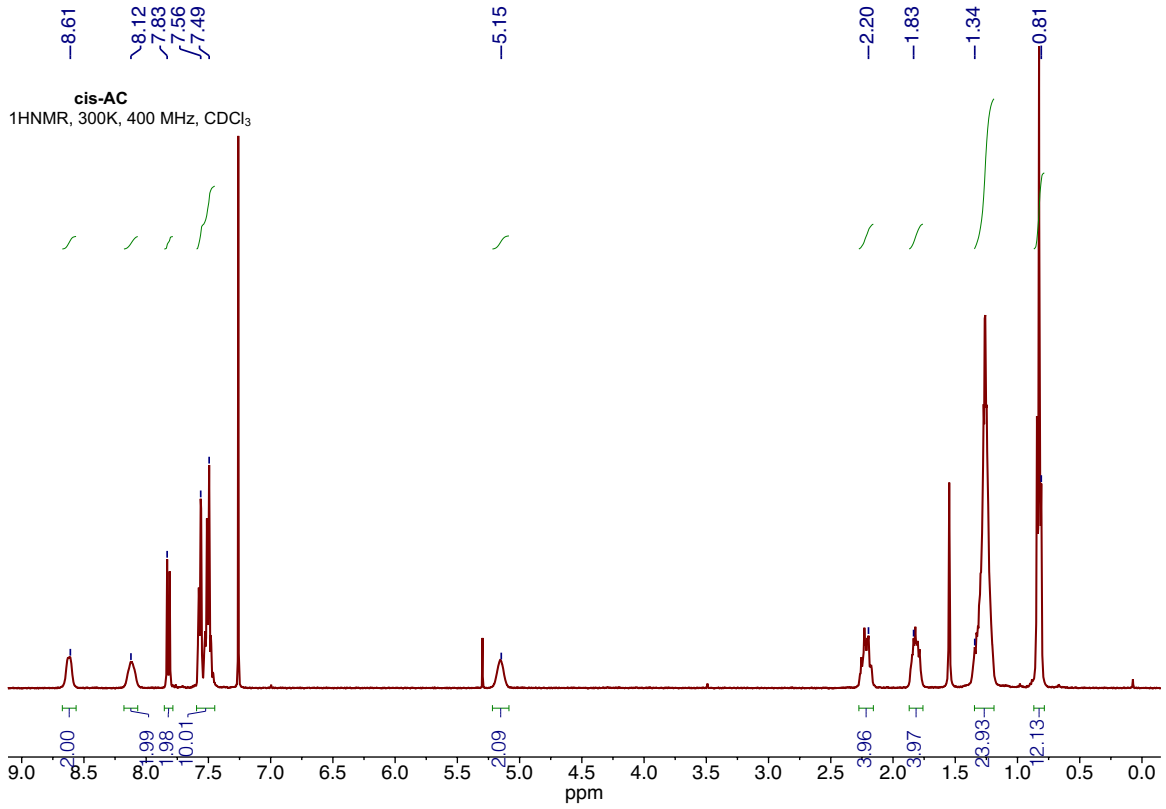


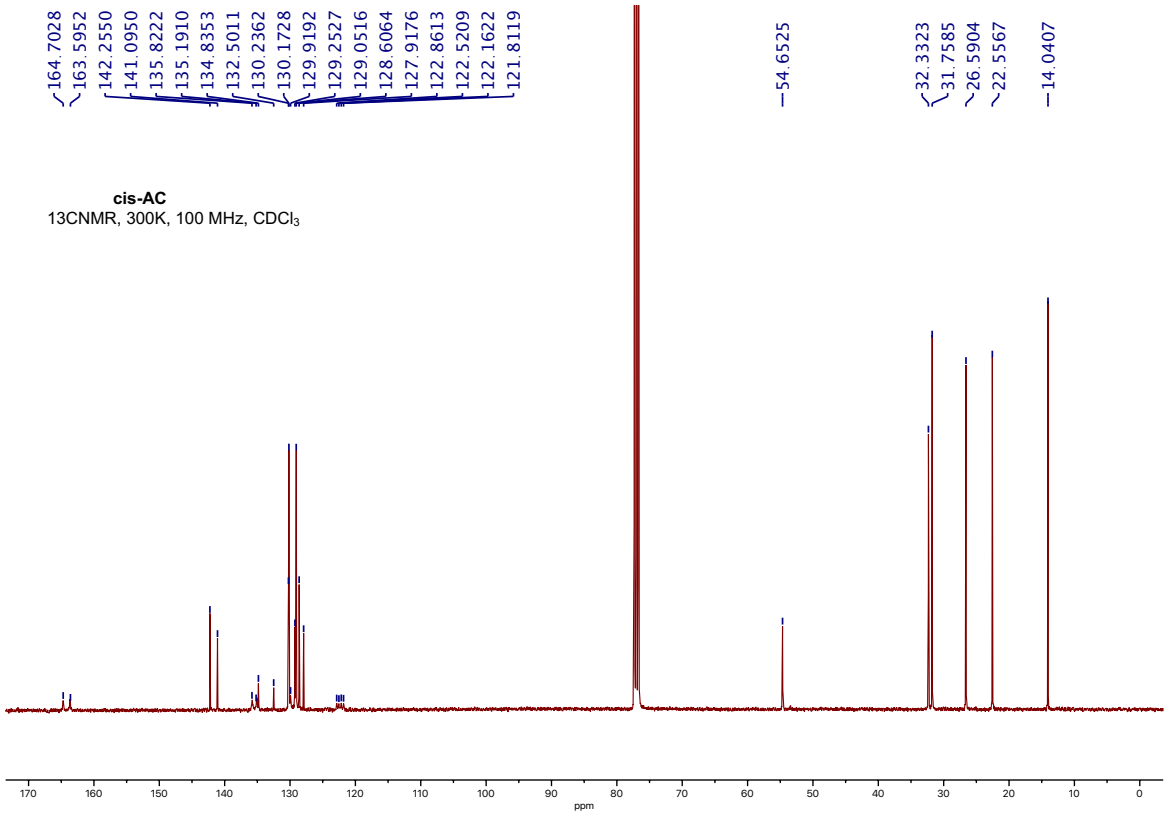
^{1}H NMR ($C_2D_2Cl_4$, 350K)



^{13}C NMR ($CDCl_3$, 323K)




8.61
8.12
7.83
7.56
7.49
5.15
2.20
1.83
1.34
0.81
cis-AC
1HNMR, 300K, 400 MHz, CDCl3
2.00
1.99
1.98
10.01
2.09
3.96
3.97
23.93
12.13
ppm

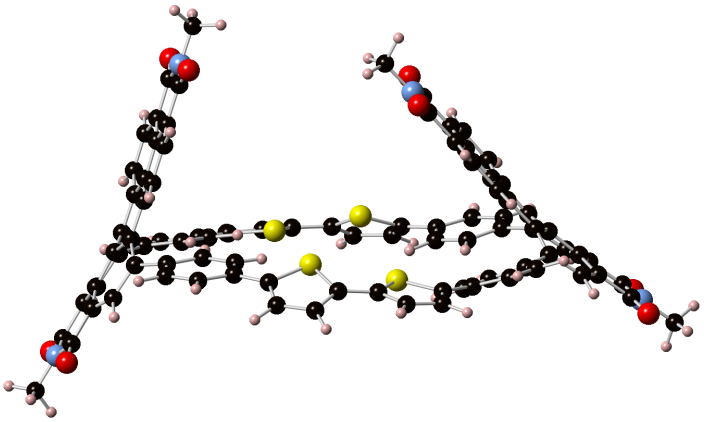

164.7028
163.5952
142.2550
141.0950
135.8222
135.1910
134.8353
132.5011
130.2362
130.1728
129.9192
129.2527
129.0516
128.6064
127.9176
122.8613
122.5209
122.1622
121.8119
54.6525
32.3323
31.7585
26.5904
22.5567
14.0407
cis-AC
13CNMR, 300K, 100 MHz, CDCl3
ppm

V. Density Functional Theory (DFT) calculations

All quantum chemical calculations were performed using Jaguar, version 8.3, Schrodinger, Inc., New York, NY, 2013. (See A. D. Bochevarov, E. Harder, T. F. Hughes, J. R. Greenwood, D. A. Braden, D. M. Philipp, D. Rinaldo, M. D. Halls, J. Zhang, R. A. Friesner, "Jaguar: A High Performance Quantum Chemistry Software Program with Strengths in Life and Materials Sciences", Int. J. Quantum Chem., 2013, 113(18), 2110-2142). All geometries were optimized using the B3LYP functional and the 6-31G** basis set. In the following pages, we include for each molecule its optimized geometry and total energy. The TD-DFT excited state calculations for *cis*-**cPBPB** present the fifteen lowest energy roots. We also provide the results of the homodesmotic reaction employed in order to calculate strain within the two macrocycles. Computations for *trans*-**cPBPB** were previously published.[13]

Lowest Energy Geometries – xyz coordinates

***cis*_cPBPB**
Final Heat of Formation = -5948.571806



H	7.658252	-4.281555	1.179927
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H	-8.107008	3.709119	1.433691
H	7.719802	3.217096	2.202196
H	8.368280	0.696616	2.148717
H	8.550660	-1.838906	1.345177
H	1.503125	-5.313964	0.283514
H	4.795645	-8.075281	0.283243
H	6.359200	-6.194807	0.420670
H	3.043003	-3.451240	0.470003
H	-3.638890	-3.432346	0.980818
H	-8.959234	1.245785	1.345451
H	-8.210788	-3.931177	1.961736
H	-2.218948	-5.371265	0.671971
C	-1.305559	7.002332	-0.723196
C	-1.205260	7.406919	0.685651
C	0.079868	7.800864	1.186450
C	1.182332	7.012197	-0.898534
C	-2.289907	7.361151	1.600278
C	-0.999494	8.658602	3.215250
C	1.279853	7.405193	0.510582
C	-2.531978	6.907945	-1.389466
C	1.448254	8.655972	3.033108
C	-0.107704	6.816847	-1.481284
C	2.568696	8.077202	2.462638
C	0.893525	5.945135	-5.072414
C	-2.193082	8.087792	2.807701
C	2.482293	7.339931	1.262452
N	-0.386656	5.746760	-5.604420
C	2.208748	6.585116	-3.074341
C	2.306426	6.938609	-1.726755
C	0.973025	6.331054	-3.644307
C	-1.589110	5.923408	-4.901802
C	0.174657	8.407934	2.468801
C	-0.918883	9.373541	4.511688
C	-0.375440	-9.154493	1.211280
C	0.883319	-9.536258	1.732544
C	1.768974	-6.300892	-3.830104
C	5.218650	4.000800	0.897116
C	3.502771	6.283649	1.007915

C	**3.833214**	**3.893761**	**0.668207**
C	**5.727861**	**-3.501620**	**0.570742**
C	**2.568147**	**-5.514289**	**0.287450**
C	**-0.201388**	**6.474688**	**-2.866895**
C	**-1.469358**	**6.309079**	**-3.474389**
C	**-1.902303**	**-5.934256**	**-4.229267**
C	**0.427694**	**10.440903**	**6.235532**
O	**2.653543**	**9.631303**	**4.831849**
C	**-2.617401**	**6.547637**	**-2.736937**
N	**-0.781901**	**-5.029181**	**-6.218563**
C	**-1.995878**	**-5.318033**	**-5.576284**
C	**6.654462**	**0.320731**	**0.873814**
S	**5.076212**	**-1.890935**	**0.324010**
H	**3.093576**	**6.510555**	**-3.696890**
C	**1.570393**	**9.365553**	**4.328839**
O	**-2.674023**	**5.760384**	**-5.444848**
C	**-3.370846**	**6.340768**	**1.474631**
H	**-1.906334**	**4.848630**	**0.948443**
O	**1.883810**	**5.794630**	**-5.776665**
C	**0.488318**	**-5.340402**	**-5.716353**
C	**0.776400**	**-7.781146**	**-0.480687**
C	**-0.446169**	**5.344275**	**-7.012413**
C	**-5.194214**	**4.143599**	**1.468332**
C	**-3.000729**	**-6.857083**	**-2.285204**
C	**-5.622602**	**5.447946**	**1.784473**
C	**1.964397**	**-7.900069**	**0.283013**
C	**-0.644559**	**-6.216849**	**-3.643449**
C	**-1.521941**	**-10.508172**	**2.984176**
C	**-2.951353**	**5.033259**	**1.166563**
C	**2.020994**	**-8.869701**	**1.308037**
C	**-3.063835**	**-6.268119**	**-3.551605**
C	**5.726553**	**5.287163**	**1.162811**
C	**5.294199**	**-5.989962**	**0.393320**
C	**-4.728630**	**6.523938**	**1.789638**
C	**4.886199**	**6.402668**	**1.226586**
C	**-1.782790**	**-7.101317**	**-1.641316**
C	**-3.832805**	**3.973275**	**1.151774**
C	**1.845697**	**-6.883040**	**-2.562814**
C	**0.542114**	**-5.952118**	**-4.368276**
C	**7.051956**	**-3.413092**	**0.948177**
O	**-3.068592**	**-5.065339**	**-6.109513**
O	**-1.903758**	**9.660457**	**5.179128**
N	**0.364420**	**9.721998**	**4.958961**
O	**-2.523601**	**-10.913284**	**3.558502**
C	**-3.292524**	**-5.511009**	**0.712508**
C	**4.838798**	**-4.658568**	**0.437958**
C	**0.971127**	**-10.510281**	**2.846555**
C	**-6.035450**	**-5.834770**	**0.911591**
N	**-0.252371**	**-10.968387**	**3.367876**
C	**-5.211306**	**-6.954784**	**0.760532**
O	**1.492168**	**-5.105095**	**-6.376516**
C	**3.017999**	**-6.847427**	**0.237567**
C	**6.588276**	**-1.122499**	**0.759394**
C	**-5.501135**	**-4.532660**	**0.968587**
C	**-0.224226**	**-11.948354**	**4.458249**
S	**5.406629**	**1.322323**	**0.162377**
C	**3.006959**	**4.995797**	**0.725719**
C	**7.178730**	**2.480114**	**1.620838**
O	**2.040622**	**-10.901788**	**3.293723**

C	**-7.443537**	**2.851734**	**1.452753**
C	**-3.820520**	**-6.813260**	**0.629770**
C	**-4.102038**	**-4.408236**	**0.881662**
C	**-7.910592**	**1.511426**	**1.404891**
C	**-6.899136**	**0.572415**	**1.390859**
C	**3.446615**	**-4.455191**	**0.388945**
C	**4.403172**	**-7.062239**	**0.308503**
C	**-6.951369**	**-0.875926**	**1.350626**
C	**-0.437671**	**-8.294152**	**0.081154**
C	**-6.069899**	**2.968447**	**1.473906**
C	**-7.571590**	**-3.118190**	**1.637747**
C	**7.537005**	**-2.083391**	**1.050288**
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C	**-7.937156**	**-1.751425**	**1.760341**
S	**-5.570612**	**-1.769266**	**0.752528**
C	**6.022098**	**2.776321**	**0.931282**
C	**7.532878**	**1.106599**	**1.593919**
C	**-2.801981**	**-7.900316**	**0.550778**
H	**-3.039400**	**8.131272**	**3.484953**
H	**-3.579244**	**6.458282**	**-3.229476**
H	**3.500220**	**8.112865**	**3.017692**
H	**5.317294**	**7.374627**	**1.450509**
C	**-1.706184**	**-7.782101**	**-0.341750**
C	**-2.744277**	**-8.863372**	**1.579379**
C	**-0.572765**	**-6.799340**	**-2.339454**
H	**-3.456721**	**2.989719**	**0.889833**
C	**-1.567441**	**-9.533439**	**1.870359**
H	**3.387626**	**2.918008**	**0.507693**
C	**0.707076**	**-7.108457**	**-1.782836**
H	**1.940693**	**4.852003**	**0.603421**
H	**-3.603515**	**-9.028916**	**2.221487**
H	**-6.659573**	**5.624485**	**2.050845**
H	**-4.017604**	**-6.076529**	**-4.030443**
H	**-5.096504**	**7.514470**	**2.043058**
H	**6.791817**	**5.420894**	**1.326745**
H	**2.947168**	**-9.038798**	**1.847549**
H	**2.663372**	**-6.124508**	**-4.417474**
H	**-5.661690**	**-7.942575**	**0.715813**
H	**-7.110383**	**-5.978125**	**0.970364**
C	**-0.830307**	**-4.412392**	**-7.547028**
H	**-1.492304**	**5.205793**	**-7.273610**
H	**0.007225**	**6.115406**	**-7.639107**
H	**0.114290**	**4.417737**	**-7.153124**
H	**1.465188**	**10.711586**	**6.414402**
H	**-0.204846**	**11.328638**	**6.184236**
H	**0.058753**	**9.805052**	**7.044161**
H	**-0.035905**	**-3.670462**	**-7.619416**
H	**0.809094**	**-12.252754**	**4.604714**
H	**-0.621028**	**-11.503225**	**5.373909**
H	**-0.849022**	**-12.804142**	**4.196444**
H	**-1.810680**	**-3.959678**	**-7.672299**
H	**3.283413**	**7.158074**	**-1.318685**
H	**-0.672982**	**-5.165758**	**-8.324581**
H	**-3.447393**	**7.118635**	**-0.854660**
H	**-3.925618**	**-7.137801**	**-1.799848**
H	**2.816461**	**-7.173473**	**-2.186557**

First fifteen roots from TD-DFT for *cis*-cPBPB.

Restricted Singlet Excited State 1:

Excitation energy = 0.0610906005 hartrees 1.66235982 eV 745.83 nm

excitation	X coeff.
377 => 379	0.33699
378 => 379	-0.92552
378 => 380	-0.11201

Transition dipole moment (debye):
X= -0.7055 Y= 3.6338 Z= -1.2782 Tot= 3.9161

Oscillator strength, f= 0.0967

Restricted Singlet Excited State 2:

Excitation energy = 0.0625676576 hartrees 1.70255259 eV 728.23 nm

excitation	X coeff.
377 => 379	-0.90608
377 => 380	-0.17843
378 => 379	-0.35791

Transition dipole moment (debye):
X= 1.0060 Y= 1.8391 Z= -1.2889 Tot= 2.4608

Oscillator strength, f= 0.0391

Restricted Singlet Excited State 3:

Excitation energy = 0.0638476678 hartrees 1.73738344 eV 713.63 nm

excitation	X coeff.
377 => 379	0.11622
378 => 380	0.98095

Transition dipole moment (debye):
X= -1.6218 Y= -1.3297 Z= -3.3019 Tot= 3.9116

Oscillator strength, f= 0.1008

Restricted Singlet Excited State 4:

Excitation energy = 0.0659836862 hartrees 1.79550746 eV 690.52 nm

excitation	X coeff.

377 => 379 0.18899
377 => 380 -0.97047
378 => 380 -0.11217

Transition dipole moment (debye):
X= -3.5429 Y= 0.4476 Z= 1.2379 Tot= 3.7795

Oscillator strength, f= 0.0973

Restricted Singlet Excited State 5:

Excitation energy = 0.0759310259 hartrees 2.06618834 eV 600.06 nm

excitation X coeff.
---------- ---------
376 => 379 -0.99402

Transition dipole moment (debye):
X= -0.5525 Y= -0.2414 Z= -5.4369 Tot= 5.4702

Oscillator strength, f= 0.2345

Restricted Singlet Excited State 6:

Excitation energy = 0.0777532387 hartrees 2.11577327 eV 586.00 nm

excitation X coeff.
---------- ---------
376 => 380 -0.98776

Transition dipole moment (debye):
X= -0.2331 Y= 0.6236 Z= -3.2380 Tot= 3.3057

Oscillator strength, f= 0.0877

Restricted Singlet Excited State 7:

Excitation energy = 0.0839091082 hartrees 2.28328301 eV 543.01 nm

excitation X coeff.
---------- ---------
375 => 379 -0.99157

Transition dipole moment (debye):
X= -0.2253 Y= -2.1072 Z= -2.3713 Tot= 3.1803

Oscillator strength, f= 0.0876

Restricted Singlet Excited State 8:

Excitation energy = 0.0864608397 hartrees 2.35271915 eV 526.98 nm

```
 excitation     X coeff.
------------   ---------
 375 =>  380     0.98990

 Transition dipole moment (debye):
   X=    -0.3522     Y=     1.7551     Z=    -5.4193  Tot=     5.7073

 Oscillator strength, f=     0.2906

--------------------------------------------------------------------------------
 Restricted Singlet Excited State   9:
----------------------------------------

 Excitation energy =  0.0948538603 hartrees      2.58110486 eV      480.35 nm

 excitation     X coeff.
------------   ---------
 372 =>  379     0.16804
 374 =>  379    -0.85580
 374 =>  380     0.25715
 377 =>  379     0.11098
 377 =>  382     0.15426
 378 =>  381    -0.33998

 Transition dipole moment (debye):
   X=     2.2358     Y=    -0.6118     Z=    -0.2839  Tot=     2.3353

 Oscillator strength, f=     0.0534

--------------------------------------------------------------------------------
 Restricted Singlet Excited State  10:
----------------------------------------

 Excitation energy =  0.0963328717 hartrees      2.62135081 eV      472.98 nm

 excitation     X coeff.
------------   ---------
 372 =>  380    -0.14821
 374 =>  379    -0.44565
 374 =>  380    -0.58636
 377 =>  382    -0.18366
 378 =>  381     0.60161

 Transition dipole moment (debye):
   X=     1.8757     Y=     0.9499     Z=    -0.1500  Tot=     2.1079

 Oscillator strength, f=     0.0442

--------------------------------------------------------------------------------
 Restricted Singlet Excited State  11:
----------------------------------------

 Excitation energy =  0.0988396557 hartrees      2.68956388 eV      460.98 nm

 excitation     X coeff.
------------   ---------
 374 =>  380     0.71487
 375 =>  381     0.10446
```

376 => 383 -0.15476
378 => 381 0.63986

Transition dipole moment (debye):
X= -1.4208 Y= 1.2562 Z= 0.2145 Tot= 1.9086

Oscillator strength, f= 0.0372

Restricted Singlet Excited State 12:

Excitation energy = 0.1056867332 hartrees 2.87588233 eV 431.12 nm

excitation X coeff.
---
377 => 381 0.97270

Transition dipole moment (debye):
X= -0.7305 Y= -10.9434 Z= -0.5560 Tot= 10.9818

Oscillator strength, f= 1.3153

Restricted Singlet Excited State 13:

Excitation energy = 0.1097775026 hartrees 2.98719783 eV 415.05 nm

excitation X coeff.
---
373 => 379 -0.11909
378 => 382 -0.97130

Transition dipole moment (debye):
X= 0.0965 Y= -7.8524 Z= -0.3643 Tot= 7.8615

Oscillator strength, f= 0.7001

Restricted Singlet Excited State 14:

Excitation energy = 0.1099973014 hartrees 2.99317886 eV 414.22 nm

excitation X coeff.
---
372 => 379 0.11890
374 => 379 0.13804
375 => 383 -0.17290
376 => 381 0.73838
376 => 386 0.15620
377 => 382 0.12515
378 => 383 -0.54733

Transition dipole moment (debye):
X= -4.6623 Y= -0.0028 Z= 0.0219 Tot= 4.6624

Oscillator strength, f= 0.2467

Restricted Singlet Excited State 15:

Excitation energy = 0.1117001572 hartrees 3.03951593 eV 407.91 nm

excitation	X coeff.
368 => 379	0.11729
373 => 379	0.94633
376 => 382	0.12027
378 => 382	-0.11004

Transition dipole moment (debye):

X= 0.4579 Y= -1.1293 Z= -1.7251 Tot= 2.1121

Oscillator strength, f= 0.0514

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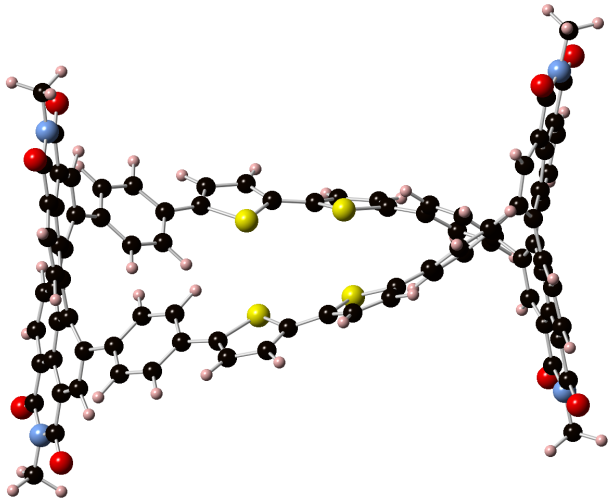
*trans*_**cPBPB**

Final Heat of Formation = -5948.582452



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H	-8.552342	-1.130130	0.960989
H	-7.808430	3.698092	-0.499800
H	7.723016	3.176686	0.618561
H	8.257131	0.651206	0.244544
H	8.121079	-1.589498	-1.014161
H	1.549809	-5.996235	-0.110919
H	4.264289	-7.363391	-3.155524
H	5.796426	-5.538855	-2.596380
H	3.101928	-4.215162	0.485313
H	-3.557266	-3.764780	-0.518083
H	-8.545919	1.229471	-0.107770
H	-7.951011	-3.655420	1.212110
H	-2.189449	-5.752749	-0.237154
C	-1.156063	7.863026	-0.595819
C	-1.240975	7.962287	0.863294
C	-0.035351	7.873851	1.625341
C	1.311428	8.099306	-0.421930
C	-2.443363	8.199950	1.535777
C	-1.345102	8.135796	3.686849
C	1.225487	7.683485	0.981719
C	-2.221768	7.496082	-1.450187
C	1.053574	7.613966	3.800389
C	0.101314	8.198406	-1.178366
C	2.197979	7.189738	3.152480
C	1.421477	9.480075	-4.509042
C	-2.493746	8.310023	2.929405
C	2.290310	7.148587	1.741085
N	0.210341	9.461060	-5.219887
C	2.545462	8.936712	-2.355348
C	2.513136	8.466821	-1.036156
C	1.384550	8.981980	-3.115281
C	-1.007695	8.944574	-4.744943
C	-0.111891	7.887293	3.044701
C	-1.415547	8.196847	5.163853
C	-0.165691	-9.052789	2.175949
C	1.089090	-9.526138	2.621649

C	**1.414272**	**-7.558929**	**-3.635819**
C	**4.929477**	**4.016460**	**0.462769**
C	**3.335836**	**6.268971**	**1.153821**
C	**3.696590**	**4.257347**	**-0.169802**
C	**5.367256**	**-3.506402**	**-0.824260**
C	**2.495495**	**-5.927797**	**-0.636083**
C	**0.158635**	**8.565944**	**-2.548963**
C	**-1.017600**	**8.486300**	**-3.334723**
C	**-2.208465**	**-8.299149**	**-3.901923**
C	**-0.307612**	**8.029891**	**7.327945**
O	**2.001625**	**7.410603**	**5.969473**
C	**-2.149391**	**7.888691**	**-2.807137**
N	**-1.278891**	**-8.012767**	**-6.158693**
C	**-2.413230**	**-8.274304**	**-5.369769**
C	**6.150159**	**0.300998**	**-0.126483**
S	**4.597653**	**-2.021262**	**-0.293849**
H	**3.474185**	**9.266054**	**-2.808193**
C	**1.016225**	**7.647524**	**5.283179**
O	**-2.001069**	**8.896858**	**-5.458539**
C	**-3.247528**	**6.511953**	**-1.020909**
H	**-1.782595**	**5.406030**	**0.114289**
O	**2.437735**	**9.910639**	**-5.037677**
C	**0.023518**	**-7.821747**	**-5.672234**
C	**0.793222**	**-8.624118**	**-0.049522**
C	**0.257672**	**9.990555**	**-6.586232**
C	**-4.942190**	**4.288860**	**-0.461791**
C	**-3.115921**	**-8.425502**	**-1.663325**
C	**-5.403865**	**5.390176**	**-1.208318**
C	**2.022814**	**-9.080113**	**0.434201**
C	**-0.912883**	**-8.147992**	**-3.360556**
C	**-1.103828**	**-9.344304**	**4.486025**
C	**-2.805736**	**5.424842**	**-0.242497**
C	**2.164114**	**-9.551533**	**1.744678**
C	**-3.292850**	**-8.460161**	**-3.051526**
C	**5.396772**	**4.987581**	**1.368983**
C	**4.883721**	**-5.655206**	**-2.021698**
C	**-4.573671**	**6.475576**	**-1.484108**
C	**4.615365**	**6.089893**	**1.707630**
C	**-1.847975**	**-8.290602**	**-1.089375**
C	**-3.627804**	**4.351201**	**0.036349**
C	**1.631272**	**-7.607001**	**-2.237784**
C	**0.196457**	**-7.885452**	**-4.200579**
C	**6.703100**	**-3.280454**	**-1.073855**
O	**-3.505799**	**-8.463497**	**-5.887416**
O	**-2.450340**	**8.433582**	**5.772644**
N	**-0.220570**	**7.969656**	**5.865575**
O	**-2.006866**	**-9.257013**	**5.307671**
C	**-3.164273**	**-5.716718**	**0.235768**
C	**4.558964**	**-4.708104**	**-1.032247**
C	**1.264616**	**-9.984786**	**4.020392**
C	**-5.626425**	**-5.551667**	**1.497230**
N	**0.138628**	**-9.879192**	**4.856682**
C	**-4.852566**	**-6.703664**	**1.632534**
O	**0.954344**	**-7.610082**	**-6.438267**
C	**2.767541**	**-6.816409**	**-1.694561**
C	**6.088271**	**-1.113025**	**-0.432636**
C	**-5.173608**	**-4.449899**	**0.745960**
C	**0.256890**	**-10.330985**	**6.246681**
S	**4.715326**	**1.304978**	**-0.143918**

C	**2.920369**	**5.350298**	**0.170896**
C	**6.966703**	**2.436251**	**0.384513**
O	**2.323786**	**-10.437650**	**4.433455**
C	**-7.109242**	**2.893145**	**-0.305326**
C	**-3.591687**	**-6.804242**	**1.021345**
C	**-3.934139**	**-4.579377**	**0.092850**
C	**-7.512859**	**1.553862**	**-0.078528**
C	**-6.462093**	**0.688919**	**0.154610**
C	**3.366802**	**-4.902632**	**-0.312663**
C	**4.005942**	**-6.685420**	**-2.346945**
C	**-6.492063**	**-0.735925**	**0.410182**
C	**-0.342396**	**-8.673790**	**0.818154**
C	**-5.745970**	**3.085545**	**-0.245398**
C	**-7.228508**	**-2.897764**	**0.932056**
C	**7.110144**	**-1.942289**	**-0.850733**
C	**-5.905096**	**-3.184982**	**0.675235**
S	**-4.946352**	**1.563098**	**0.108522**
C	**-7.560627**	**-1.528190**	**0.781948**
S	**-5.050567**	**-1.713822**	**0.243775**
C	**5.632654**	**2.750703**	**0.250552**
C	**7.259848**	**1.067242**	**0.170126**
C	**-2.586073**	**-7.857098**	**1.320055**
H	**-3.428076**	**8.509312**	**3.442435**
H	**-2.980052**	**7.690456**	**-3.476168**
H	**3.022092**	**6.830193**	**3.758593**
H	**4.983361**	**6.788306**	**2.453730**
C	**-1.628147**	**-8.258887**	**0.360921**
C	**-2.398289**	**-8.259977**	**2.663276**
C	**-0.711874**	**-8.224294**	**-1.954879**
H	**-3.237357**	**3.534143**	**0.635062**
C	**-1.249508**	**-8.911113**	**3.076065**
H	**3.323487**	**3.552430**	**-0.906718**
C	**0.608421**	**-8.137935**	**-1.419943**
H	**1.940504**	**5.460379**	**-0.280465**
H	**-3.143673**	**-8.015725**	**3.412958**
H	**2.887520**	**-9.068311**	**-0.218566**
H	**-6.410104**	**5.379493**	**-1.615123**
H	**-4.278303**	**-8.585496**	**-3.486358**
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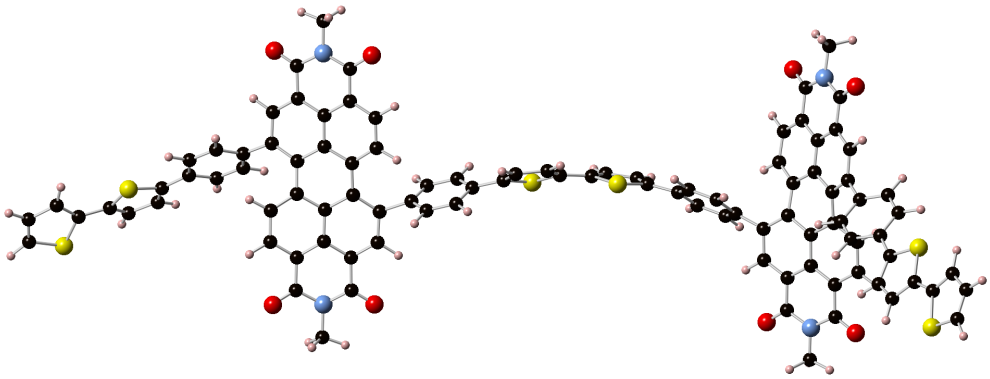
H	**6.348009**	**4.840491**	**1.870574**
H	**3.117400**	**-9.922927**	**2.103997**
H	**2.198226**	**-7.200088**	**-4.293774**
H	**-3.983376**	**-8.501508**	**-1.020115**
H	**-5.224000**	**-7.521995**	**2.243050**
H	**-6.575282**	**-5.491669**	**2.020933**
C	**-1.465338**	**-7.952602**	**-7.612388**
H	**-0.757612**	**9.998668**	**-6.974604**
H	**0.678198**	**10.997504**	**-6.569986**
H	**0.896112**	**9.363261**	**-7.212833**
H	**0.702342**	**7.963657**	**7.724491**
H	**-0.785249**	**8.964626**	**7.624361**
H	**-0.913098**	**7.201230**	**7.704026**
H	**-0.751046**	**-7.241437**	**-8.023064**
H	**1.251676**	**-10.750354**	**6.374781**
H	**0.106132**	**-9.489760**	**6.926877**
H	**-0.509098**	**-11.080434**	**6.455336**
H	**-2.490520**	**-7.648993**	**-7.813184**
H	**-3.358636**	**8.297589**	**0.965425**
H	**3.436168**	**8.414110**	**-0.471374**

H -1.288423 -8.933121 -8.065543

*trans*_cPBPB_Acyclic for Homodesmotic Calculations
Final Heat of Formation = -7053.442019



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H	-2.058853	0.684038	-18.424512
H	-3.776636	-1.236636	-17.972620
H	-1.775695	-4.273604	-14.788876
H	-8.024836	-7.371139	-18.749207
H	-5.305647	-10.121626	-16.880256
H	-3.946001	-8.246249	-16.082889
H	-6.668862	-5.489172	-17.956364
H	-13.087586	-10.481150	-23.675002
H	-12.127208	-9.956352	-21.492947
C	5.143194	6.940450	-17.056760
C	5.884552	6.228233	-18.113325
C	5.492925	4.894972	-18.464409
C	3.349923	5.188678	-17.229018
C	6.929674	6.821555	-18.827061
C	7.429917	4.785823	-20.005890
C	4.275089	4.303227	-17.970355
C	5.620588	8.096059	-16.392319
C	6.031192	2.819424	-19.665553
C	3.832739	6.450572	-16.733042
C	4.921123	2.232647	-19.105361
C	0.732859	7.667324	-14.827264
C	7.690846	6.119120	-19.764944
C	4.021882	2.946163	-18.288108
N	1.272043	8.836722	-14.276367
C	1.160672	5.677884	-16.237118
C	2.009082	4.864450	-16.994992
C	1.635865	6.841485	-15.664527
C	2.588477	9.282185	-14.465736
C	6.326323	4.167719	-19.372049
C	8.282043	4.033311	-20.957340
C	-12.074580	-9.280565	-16.711511
C	-11.577682	-8.637659	-15.554208
C	-6.640533	-10.832438	-19.354676
C	0.594746	0.432678	-17.449397
C	2.818440	2.127554	-17.925458
C	1.541474	0.683750	-16.441317
C	-4.301763	-5.620524	-16.558499
C	-7.138023	-7.568038	-18.154061
C	2.971242	7.239758	-15.906411
C	3.451731	8.436162	-15.329428
C	-9.018513	-13.212032	-20.898969

C	**8.819443**	**1.954878**	**-22.106506**
O	**6.652153**	**0.837853**	**-20.818110**
C	**4.754887**	**8.820633**	**-15.551556**
N	**-6.750433**	**-13.713256**	**-21.696851**
C	**-8.114489**	**-14.048233**	**-21.726660**
C	**-2.254004**	**-2.263606**	**-16.825720**
S	**-4.204908**	**-4.129654**	**-17.480170**
H	**0.125489**	**5.399831**	**-16.072229**
C	**6.878069**	**2.017080**	**-20.580885**
O	**2.992506**	**10.313757**	**-13.945710**
C	**7.012504**	**8.624026**	**-16.468127**
H	**6.430207**	**10.565371**	**-17.197500**
O	**-0.434022**	**7.366677**	**-14.609444**
C	**-6.193213**	**-12.677340**	**-20.938007**
C	**-9.770436**	**-9.791292**	**-17.423250**
C	**0.370007**	**9.635942**	**-13.441799**
C	**9.664700**	**9.623582**	**-16.639091**
C	**-11.248054**	**-12.666747**	**-20.161310**
C	**9.402377**	**8.330954**	**-16.137468**
C	**-9.328077**	**-9.170576**	**-16.250845**
C	**-8.515176**	**-12.148845**	**-20.112826**
C	**-14.416568**	**-8.651215**	**-16.026969**
C	**7.261696**	**9.933408**	**-16.898667**
C	**-10.213673**	**-8.614179**	**-15.321823**
C	**-10.374508**	**-13.485888**	**-20.881304**
C	**0.800240**	**1.023728**	**-18.708554**
C	**-4.852033**	**-8.041706**	**-16.644185**
C	**8.106101**	**7.844366**	**-16.056998**
C	**1.890535**	**1.848328**	**-18.940403**
C	**-10.801094**	**-11.563044**	**-19.428367**
C	**8.561541**	**10.419918**	**-16.992783**
C	**-7.468744**	**-10.047963**	**-18.522078**
C	**-7.128616**	**-11.877891**	**-20.107733**
C	**-3.355320**	**-5.612965**	**-15.556905**
O	**-8.524707**	**-14.980112**	**-22.406298**
O	**9.232857**	**4.537687**	**-21.540542**
N	**7.958248**	**2.687707**	**-21.173552**
O	**-15.626919**	**-8.633649**	**-16.210995**
C	**-13.049704**	**-10.526006**	**-21.544543**
C	**-5.195437**	**-6.712889**	**-16.953446**
C	**-12.497823**	**-8.000937**	**-14.579116**
C	**-15.446708**	**-11.926922**	**-21.709548**
N	**-13.867466**	**-8.048558**	**-14.888736**
C	**-14.911334**	**-11.598454**	**-20.464091**
O	**-4.988410**	**-12.462879**	**-20.979185**
C	**-6.774221**	**-8.895046**	**-17.872623**
C	**-2.889284**	**-3.518990**	**-16.486858**
C	**-14.789265**	**-11.565744**	**-22.897308**
C	**-14.819465**	**-7.425670**	**-13.964311**
S	**-0.586799**	**-1.921334**	**-16.385091**
C	**2.636147**	**1.519266**	**-16.676236**
C	**-1.825681**	**-0.207032**	**-17.853206**
O	**-12.095833**	**-7.461282**	**-13.556754**
C	**-13.689460**	**-10.917339**	**-20.354153**
C	**-13.589692**	**-10.831630**	**-22.781083**
C	**-6.365956**	**-6.502038**	**-17.705945**
C	**-5.619681**	**-9.105446**	**-17.101649**
C	**-11.186290**	**-9.917448**	**-17.627051**
C	**-2.563809**	**-4.439620**	**-15.514879**

C	**-0.593469**	**-0.410086**	**-17.274378**
C	**-2.759601**	**-1.239152**	**-17.597431**
C	**-13.097361**	**-10.519150**	**-19.046735**
H	**8.501506**	**6.602018**	**-20.299187**
H	**5.116606**	**9.714331**	**-15.054369**
H	**4.719112**	**1.192776**	**-19.336400**
H	**2.031556**	**2.286950**	**-19.924127**
C	**-11.725150**	**-10.655689**	**-18.729726**
C	**-13.946428**	**-9.860130**	**-18.131282**
C	**-9.389290**	**-11.346354**	**-19.317099**
H	**8.715936**	**11.430415**	**-17.359321**
C	**-13.467143**	**-9.295062**	**-16.967251**
H	**1.410826**	**0.238987**	**-15.458636**
C	**-8.847174**	**-10.354992**	**-18.429175**
H	**3.349067**	**1.706438**	**-15.878350**
H	**-15.005371**	**-9.769872**	**-18.346998**
H	**-8.271392**	**-9.112091**	**-16.043419**
H	**10.220599**	**7.693628**	**-15.825425**
H	**-10.745515**	**-14.329644**	**-21.452266**
H	**7.936256**	**6.837203**	**-15.687988**
H	**0.110797**	**0.804154**	**-19.517140**
H	**-9.846430**	**-8.142161**	**-14.417545**
H	**-5.582111**	**-10.606240**	**-19.419771**
H	**-12.305081**	**-12.893407**	**-20.188982**
H	**-15.435347**	**-11.908580**	**-19.564404**
H	**-16.372090**	**-12.493649**	**-21.754443**
C	**-5.816329**	**-14.491842**	**-22.516572**
H	**0.925256**	**10.501424**	**-13.089299**
H	**-0.497763**	**9.946419**	**-14.027586**
H	**0.016630**	**9.036247**	**-12.600264**
H	**8.449619**	**0.934420**	**-22.167438**
H	**8.793066**	**2.433237**	**-23.087939**
H	**9.850643**	**1.970492**	**-21.747498**
H	**-5.312220**	**-13.834470**	**-23.228329**
H	**-14.250864**	**-6.995900**	**-13.143554**
H	**-15.388833**	**-6.653726**	**-14.486091**
H	**-15.521410**	**-8.175998**	**-13.594369**
H	**-6.389517**	**-15.253876**	**-23.038713**
H	**7.170860**	**7.858140**	**-18.662184**
H	**1.594026**	**3.961550**	**-17.407899**
H	**-5.057059**	**-14.950241**	**-21.879594**
C	**-15.265772**	**-11.931290**	**-24.234574**
C	**-14.501453**	**-12.038111**	**-25.376890**
C	**-15.229742**	**-12.405567**	**-26.529472**
C	**-16.574803**	**-12.595063**	**-26.300577**
S	**-16.943360**	**-12.310567**	**-24.604618**
H	**-13.429975**	**-11.879955**	**-25.383939**
H	**-14.778035**	**-12.528283**	**-27.507372**
C	**-17.590847**	**-12.973175**	**-27.260133**
C	**-18.961639**	**-13.010824**	**-27.127594**
C	**-19.636894**	**-13.425681**	**-28.310068**
C	**-18.782956**	**-13.704403**	**-29.338830**
S	**-17.126249**	**-13.476729**	**-28.880570**
H	**-19.471608**	**-12.734404**	**-26.211814**
H	**-20.714586**	**-13.507354**	**-28.390304**
C	**11.043176**	**10.088055**	**-16.806316**
C	**12.213975**	**9.454434**	**-16.449800**
C	**13.386538**	**10.158255**	**-16.805777**
C	**13.139325**	**11.348257**	**-17.451992**

S	**11.412620**	**11.598582**	**-17.622670**
H	**12.239505**	**8.501847**	**-15.938141**
H	**14.387755**	**9.808455**	**-16.582166**
C	**14.095592**	**12.299548**	**-17.972307**
C	**13.929660**	**13.634723**	**-18.262454**
C	**15.109959**	**14.258654**	**-18.749761**
C	**16.170845**	**13.399446**	**-18.833180**
S	**15.742411**	**11.797992**	**-18.325320**
H	**12.991952**	**14.155616**	**-18.104750**
H	**15.168047**	**15.306800**	**-19.017837**
H	**17.179502**	**13.606874**	**-19.161314**
H	**-19.022186**	**-14.029030**	**-30.341418**

*cis*_cPBPB_Acyclic for Homodesmotic Calculations
Final Heat of Formation = -7053.435400

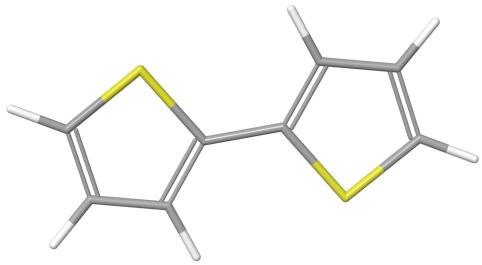
H	-1.834122	-7.849178	-15.386708
H	0.585078	-2.296806	-20.657102
H	-1.203638	-4.109005	-20.081153
H	0.032051	-6.075792	-15.801352
H	-6.716251	-8.403724	-19.252300
H	-5.384920	-10.947647	-16.057199
H	-3.303308	-9.656397	-15.896592
H	-4.649469	-7.115692	-19.100859
H	-13.650605	-8.662737	-23.571423
H	-11.832841	-9.157944	-21.991861
C	5.184765	5.150000	-17.279303
C	6.384775	4.873091	-18.091168
C	6.476311	3.581346	-18.723017
C	4.054602	3.169999	-18.298256
C	7.450856	5.783429	-18.257328
C	8.761521	4.118088	-19.470327
C	5.368750	2.662793	-18.733857
C	5.121259	6.163265	-16.319804
C	7.852765	1.900306	-19.891748
C	4.017512	4.350963	-17.494047
C	6.825900	0.992858	-19.766042
C	0.295540	4.469725	-16.608928
C	8.612994	5.384702	-18.954948
C	5.591631	1.341826	-19.181767
N	0.331967	5.533863	-15.698172
C	1.621575	3.008471	-18.110790
C	2.840697	2.562884	-18.635836
C	1.587250	4.055848	-17.207503
C	1.487878	6.236659	-15.320929
C	7.696681	3.199154	-19.359493
C	10.022948	3.754300	-20.163558
C	-10.567710	-6.646406	-17.405416
C	-9.689138	-6.001871	-16.499859
C	-7.332012	-11.930861	-18.015977
C	2.785555	-1.927669	-18.933712
C	4.622606	0.215598	-19.075930
C	3.280766	-1.325949	-17.763988
C	-2.603969	-7.453500	-17.372487
C	-5.969983	-8.682193	-18.516351
C	2.783230	4.740896	-16.887640
C	2.755707	5.819241	-15.971028
C	-10.633270	-12.872562	-19.369603
C	11.372758	2.096795	-21.331978

O	**9.262822**	**0.352228**	**-21.014658**
C	**3.928096**	**6.484370**	**-15.662178**
N	**-9.282591**	**-14.900990**	**-19.103070**
C	**-10.503840**	**-14.344090**	**-19.509726**
C	**-0.017443**	**-4.664935**	**-18.354864**
S	**-2.127713**	**-6.403790**	**-18.693989**
H	**0.690218**	**2.522599**	**-18.380282**
C	**9.108570**	**1.480081**	**-20.564831**
O	**1.440999**	**7.146828**	**-14.503609**
C	**7.523600**	**7.203878**	**-17.794913**
H	**5.966205**	**7.995279**	**-19.059764**
O	**-0.767899**	**3.925813**	**-16.878061**
C	**-8.202585**	**-14.173278**	**-18.588426**
C	**-9.068398**	**-8.598456**	**-17.465697**
C	**-0.951677**	**5.923567**	**-15.107074**
C	**8.007721**	**9.914547**	**-17.105107**
C	**-11.920401**	**-10.845043**	**-19.819211**
C	**8.761562**	**8.872812**	**-16.534668**
C	**-8.274651**	**-7.953230**	**-16.509242**
C	**-9.611009**	**-12.093513**	**-18.788301**
C	**-12.049287**	**-4.602380**	**-17.349511**
C	**6.739220**	**8.233262**	**-18.334905**
C	**-8.572387**	**-6.674105**	**-16.035693**
C	**-11.746339**	**-12.244643**	**-19.880366**
C	**3.288590**	**-1.489007**	**-20.170759**
C	**-4.046741**	**-9.372808**	**-16.634185**
C	**8.531747**	**7.550321**	**-16.882241**
C	**4.194679**	**-0.439992**	**-20.239009**
C	**-11.008126**	**-10.057842**	**-19.074383**
C	**6.976653**	**9.564103**	**-17.995954**
C	**-7.473431**	**-10.542383**	**-17.832568**
C	**-8.392041**	**-12.711034**	**-18.427853**
C	**-1.728623**	**-7.306896**	**-16.318620**
O	**-11.405422**	**-15.039530**	**-19.957630**
O	**10.954524**	**4.535657**	**-20.303349**
N	**10.117490**	**2.449379**	**-20.661465**
O	**-13.046343**	**-3.985674**	**-17.703726**
C	**-12.824336**	**-9.562094**	**-21.809557**
C	**-3.810105**	**-8.272501**	**-17.476310**
C	**-9.964756**	**-4.632120**	**-15.997589**
C	**-15.361243**	**-10.612856**	**-21.377020**
N	**-11.129475**	**-4.012055**	**-16.475513**
C	**-14.335680**	**-10.881397**	**-20.481239**
O	**-7.163046**	**-14.744683**	**-18.287365**
C	**-6.223901**	**-9.757770**	**-17.649450**
C	**-0.799487**	**-5.729253**	**-17.773487**
C	**-15.143549**	**-9.811957**	**-22.511698**
C	**-11.438057**	**-2.650100**	**-16.030048**
S	**1.499789**	**-4.118595**	**-17.660966**
C	**4.179241**	**-0.267258**	**-17.836145**
C	**0.675937**	**-2.986114**	**-19.826260**
O	**-9.219679**	**-4.063956**	**-15.209302**
C	**-13.045084**	**-10.368942**	**-20.681240**
C	**-13.852298**	**-9.288104**	**-22.706283**
C	**-4.796956**	**-7.956171**	**-18.430224**
C	**-5.228502**	**-10.104522**	**-16.724324**
C	**-10.284419**	**-7.970390**	**-17.877298**
C	**-0.716467**	**-6.339646**	**-16.540022**
C	**1.709898**	**-2.919059**	**-18.920169**

C	**-0.301489**	**-3.951870**	**-19.501480**
C	**-12.417696**	**-7.954398**	**-19.028991**
H	**9.422303**	**6.092848**	**-19.091020**
H	**3.897468**	**7.280609**	**-14.926725**
H	**6.981896**	**-0.017260**	**-20.127645**
H	**4.565218**	**-0.110829**	**-21.205599**
C	**-11.241930**	**-8.643778**	**-18.707927**
C	**-12.661574**	**-6.643716**	**-18.607065**
C	**-9.805434**	**-10.692836**	**-18.587957**
H	**6.389333**	**10.345057**	**-18.470712**
C	**-11.752213**	**-5.981919**	**-17.805423**
H	**2.920705**	**-1.658817**	**-16.794874**
C	**-8.752331**	**-9.944143**	**-17.965046**
H	**4.529997**	**0.203550**	**-16.922665**
H	**-13.578489**	**-6.135680**	**-18.885592**
H	**-7.404395**	**-8.451619**	**-16.111450**
H	**9.536804**	**9.107323**	**-15.813081**
H	**-12.480295**	**-12.850065**	**-20.399710**
H	**9.153122**	**6.768846**	**-16.454363**
H	**2.964323**	**-1.980020**	**-21.081912**
H	**-7.936979**	**-6.187466**	**-15.304328**
H	**-6.366963**	**-12.403796**	**-17.870589**
H	**-14.529558**	**-11.518529**	**-19.623235**
H	**-16.337064**	**-11.060093**	**-21.218628**
C	**-9.089729**	**-16.348093**	**-19.235164**
H	**-0.765619**	**6.752007**	**-14.428143**
H	**-1.646841**	**6.219527**	**-15.895619**
H	**-1.385030**	**5.076604**	**-14.570894**
H	**11.296563**	**1.060949**	**-21.653227**
H	**11.532335**	**2.754916**	**-22.188746**
H	**12.209300**	**2.225239**	**-20.641995**
H	**-8.244844**	**-16.549913**	**-19.896938**
H	**-10.633168**	**-2.325210**	**-15.375494**
H	**-11.523095**	**-1.989809**	**-16.895629**
H	**-12.392353**	**-2.640254**	**-15.498787**
H	**-10.005731**	**-16.767521**	**-19.643907**
H	**2.827812**	**1.722332**	**-19.312284**
H	**-8.869843**	**-16.782619**	**-18.257759**
C	**-16.237349**	**-9.626155**	**-23.470185**
C	**-17.592301**	**-9.650874**	**-23.220557**
C	**-18.391200**	**-9.538525**	**-24.386580**
C	**-17.659044**	**-9.412686**	**-25.544526**
S	**-15.942209**	**-9.442812**	**-25.187318**
H	**-18.002136**	**-9.733576**	**-22.220623**
H	**-19.475189**	**-9.532744**	**-24.381177**
C	**-18.134743**	**-9.352472**	**-26.917683**
C	**-17.747531**	**-8.521885**	**-27.942625**
C	**-18.428127**	**-8.779503**	**-29.166907**
C	**-19.312763**	**-9.818528**	**-29.076828**
S	**-19.356947**	**-10.482731**	**-27.476143**
H	**-17.004663**	**-7.743168**	**-27.812392**
H	**-18.258937**	**-8.219726**	**-30.079514**
C	**8.375129**	**11.296850**	**-16.790046**
C	**9.629450**	**11.746143**	**-16.441798**
C	**9.692895**	**13.134325**	**-16.184319**
C	**8.486360**	**13.781805**	**-16.334189**
S	**7.238944**	**12.634305**	**-16.802332**
H	**10.495107**	**11.095526**	**-16.407888**
H	**10.605623**	**13.649539**	**-15.908999**

C	**8.194712**	**15.180950**	**-16.108235**
C	**7.046902**	**15.892950**	**-16.376437**
C	**7.106161**	**17.250093**	**-15.952368**
C	**8.291357**	**17.569772**	**-15.351598**
S	**9.373735**	**16.214711**	**-15.308595**
H	**6.186834**	**15.455380**	**-16.871055**
H	**6.294520**	**17.956560**	**-16.081422**
H	**8.611831**	**18.523589**	**-14.957023**
H	**-13.185418**	**-8.437356**	**-19.608203**
H	**6.005956**	**6.732670**	**-16.079736**
H	**-19.962993**	**-10.213751**	**-29.844783**

Bithiophene



Total Energy: -1104.826802 hartrees

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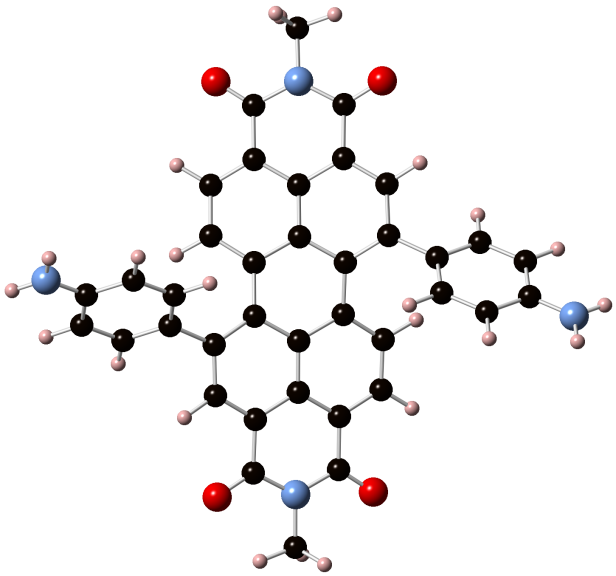
C3	1.7098905419	0.8694103010	0.0122565205
C4	2.0501584230	2.2514544128	0.0246320264
C5	0.9547258678	3.0684516605	0.0281022419
C6	-0.3530028893	-0.6332102763	-0.0062644825
S7	0.5229025548	-2.1569531073	-0.0161859979
C8	-0.9547258678	-3.0684516605	-0.0281022419
C9	-2.0501584230	-2.2514544128	-0.0246320264
C10	-1.7098905419	-0.8694103010	-0.0122565205
H11	2.4448343075	0.0724557652	0.0078978216
H12	3.0698389079	2.6188720882	0.0306528745
H13	0.9193525791	4.1486289730	0.0368265795
H14	-0.9193525791	-4.1486289730	-0.0368265795
H15	-3.0698389079	-2.6188720882	-0.0306528745
H16	-2.4448343075	-0.0724557652	-0.0078978216

*trans*_**DAPP**

Final Heat of Formation = -1982.587675



C	**5.032948**	**6.225155**	**-17.363312**
C	**5.682306**	**5.606906**	**-18.530798**
C	**5.252986**	**4.309444**	**-18.962953**
C	**3.237958**	**4.492861**	**-17.547763**
C	**6.663181**	**6.267517**	**-19.280581**
C	**6.976855**	**4.363053**	**-20.729424**
C	**4.132175**	**3.648390**	**-18.358431**
C	**5.571421**	**7.303917**	**-16.622909**
C	**5.629027**	**2.346437**	**-20.386541**
C	**3.729112**	**5.735657**	**-17.027782**
C	**4.663695**	**1.669432**	**-19.672272**
C	**0.672628**	**6.915148**	**-15.054415**
C	**7.291259**	**5.665129**	**-20.374295**
C	**3.911139**	**2.279609**	**-18.642108**
N	**1.234109**	**8.060289**	**-14.471619**
C	**1.062691**	**4.960849**	**-16.529560**
C	**1.898623**	**4.162757**	**-17.314924**
C	**1.554128**	**6.105671**	**-15.924910**
C	**2.557698**	**8.493394**	**-14.651381**
C	**5.960359**	**3.675106**	**-20.027806**
C	**7.690130**	**3.711318**	**-21.851673**
C	**1.366067**	**-0.479560**	**-16.480631**
C	**2.990730**	**1.381389**	**-17.894329**
C	**2.235855**	**0.393218**	**-15.796298**
C	**2.890370**	**6.500394**	**-16.163671**
C	**3.403477**	**7.668334**	**-15.549180**
C	**8.053023**	**1.756796**	**-23.259937**
O	**6.086214**	**0.494932**	**-21.806638**
C	**4.723826**	**8.017535**	**-15.744976**
H	**0.026088**	**4.687647**	**-16.365759**
C	**6.339673**	**1.649939**	**-21.487226**
O	**2.977790**	**9.500133**	**-14.094419**
C	**7.002732**	**7.702084**	**-16.635959**
H	**6.634024**	**9.814248**	**-16.871875**
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C	**9.740709**	**8.464511**	**-16.518030**
C	**9.357070**	**7.113290**	**-16.395816**
C	**7.391572**	**9.047747**	**-16.733486**
C	**1.329505**	**-0.407171**	**-17.885380**
C	**8.021488**	**6.748987**	**-16.455799**
C	**2.131755**	**0.497683**	**-18.569045**
C	**8.727586**	**9.426406**	**-16.686255**
O	**8.562403**	**4.271347**	**-22.504581**
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H	**8.045957**	**6.194203**	**-20.945541**
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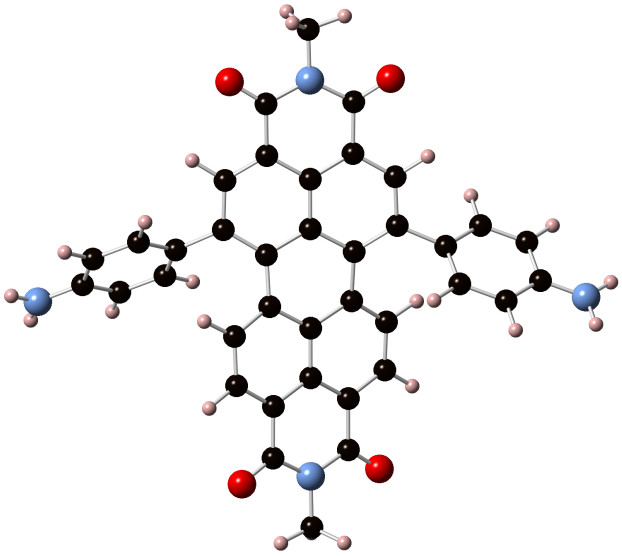
H	**4.491123**	**0.626203**	**-19.912058**
H	**2.076760**	**0.529741**	**-19.653740**
H	**8.995080**	**10.475625**	**-16.780836**
H	**2.296104**	**0.346795**	**-14.711873**
H	**3.690640**	**1.948406**	**-15.934685**
H	**10.118396**	**6.351931**	**-16.245429**
H	**7.756851**	**5.701079**	**-16.352040**
H	**0.668303**	**-1.068415**	**-18.439677**
H	**0.914920**	**9.696799**	**-13.238721**
H	**-0.521409**	**9.181358**	**-14.180010**
H	**-0.006954**	**8.229938**	**-12.780725**
H	**7.670499**	**0.745039**	**-23.369271**
H	**7.901176**	**2.327457**	**-24.178676**
H	**9.122932**	**1.742354**	**-23.041207**
H	**6.952601**	**7.272600**	**-19.007703**
H	**1.491733**	**3.260078**	**-17.747457**
N	**11.063884**	**8.828903**	**-16.469162**
N	**0.581945**	**-1.376527**	**-15.797400**
H	**11.786475**	**8.140303**	**-16.353334**
H	**11.339296**	**9.792017**	**-16.548012**
H	**0.607789**	**-1.430199**	**-14.794383**
H	**-0.028594**	**-2.007096**	**-16.286587**

*cis*_DAPP
Final Heat of Formation = -1982.586248



C	4.546200	3.491118	-17.334244
C	5.817619	3.993776	-17.881884
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C	4.815958	1.416413	-18.691877
C	6.220906	5.349039	-17.803832
C	8.448688	4.755158	-18.605100
C	6.257258	1.699163	-18.817767
C	3.820463	4.145600	-16.332963
C	8.929450	2.483281	-19.367294
C	4.030549	2.262541	-17.848753
C	8.526233	1.177541	-19.545626
C	0.714066	0.367041	-17.853819
C	7.549205	5.690880	-18.140277
C	7.210895	0.749749	-19.258845
N	0.047617	1.111575	-16.870666
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C	4.169615	0.370365	-19.357602
C	2.103520	0.765493	-18.166551
C	0.589991	2.206815	-16.176132
C	8.026356	3.424542	-18.823728
C	9.832934	5.174420	-18.931893
C	6.722522	-3.543002	-19.572266
C	6.979402	-0.716402	-19.384030
C	6.367418	-2.857321	-18.392854
C	2.696063	1.875632	-17.518909
C	1.968168	2.603885	-16.547355
C	12.051007	4.625089	-19.774654
O	11.125652	2.063811	-20.175190
C	2.559531	3.694225	-15.927631
H	2.343021	-0.757282	-19.635663
C	10.324175	2.862066	-19.706697
O	-0.055435	2.794716	-15.316460
C	5.316661	6.488383	-17.486500
H	3.814363	5.944319	-18.934826
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C	-1.322268	0.692115	-16.562162

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H	**6.602664**	**7.372679**	**-15.998010**
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H	**-1.705737**	**1.355121**	**-15.790766**
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H	**-1.323958**	**-0.343571**	**-16.215285**
H	**12.589086**	**3.761450**	**-20.157304**
H	**12.026637**	**5.423638**	**-20.519409**
H	**12.533321**	**5.012851**	**-18.874991**
H	**4.719046**	**-0.235670**	**-20.063061**
H	**4.226303**	**5.034943**	**-15.871474**
N	**6.592868**	**-4.907601**	**-19.663347**
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H	**6.855294**	**-5.397410**	**-20.500525**
H	**6.239814**	**-5.447817**	**-18.893298**
H	**3.105590**	**10.539386**	**-16.108998**
H	**1.984343**	**9.955241**	**-17.278311**

Homodesmotic Calculations:

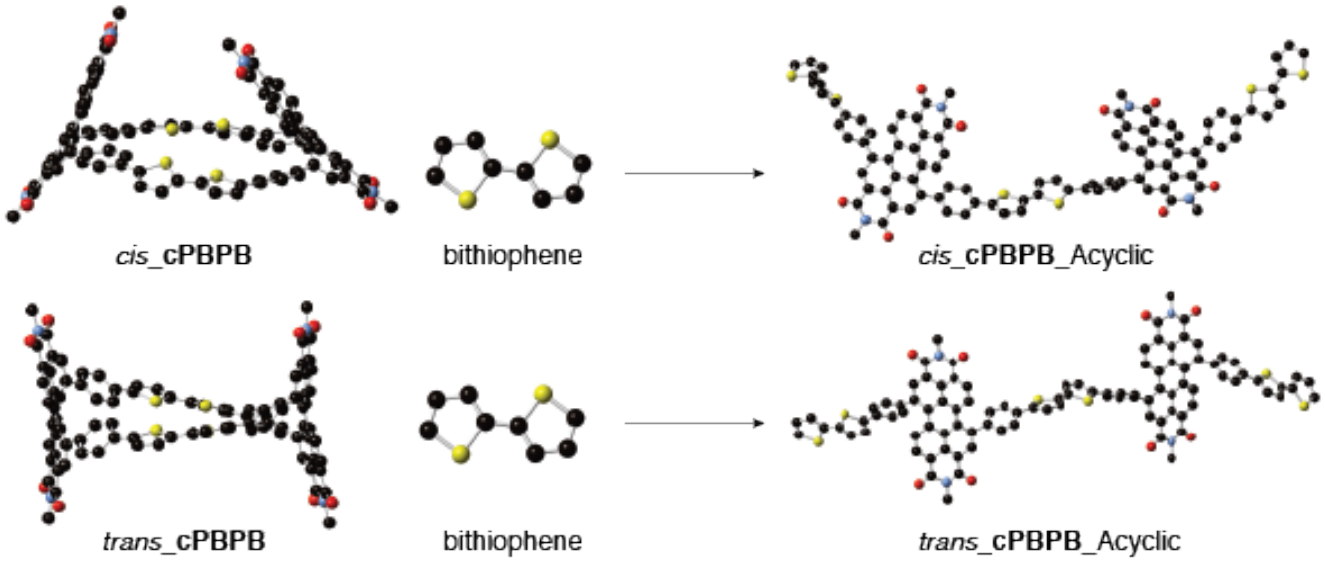

Table of energies for the Homodesmotic Reaction (enthalpy)

Compound	Total energy (hartree)	Strain energy (hartree)	Strain energy (kcal/mol)
trans-**cPBPB**	-5948.58245	0.033	21
cis-**cPBPB**	-5948.57180	0.037	23
Bithiophene	-1104.82680	-	-
*trans*_**cPBPB**_Acyclic	-7053.44201	-	-
*cis*_**cPBPB**_Acyclic	-7053.43540		

VI. Crystal and Refinement Data for *trans-cPBPB*

Table SI. Crystallographic data of *trans*-**cPBPB.**

Compound	**cPBPB**
Formula	$C_{132}H_{128}N_4O_8S_4$
MW	2026.62
Space group	*C2/c*
***a* (Å)**	27.9712(10)
***b* (Å)**	36.8383(9)
***c* (Å)**	28.3471(9)
***α* (°)**	90
***β* (°)**	92.641(3)
***γ* (°)**	90
V (Å^3)	29178.1(16)
Z	8
ρ_{calc} (g cm^{-3})	0.923
T (K)	100
λ (Å)	1.54184
$2\theta_{min}$, $2\theta_{max}$	7.276, 102.9
Nref	116722
R(int), R(σ)	0.1005, 0.0634
μ(mm^{-1})	0.958
Size (mm)	0.10 x 0.07 x 0.05
T_{max}, T_{min}	0.979, 0.965
Data	15869
Restraints	3138
Parameters	1789
R_1(obs)	0.0968
wR_2(all)	0.3343
S	1.081
Peak, hole (e$^-$ Å^{-3})	0.54, -0.31
Flack	

CCDC 1581857 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

1 You, J. B.; Dou, L. T.; Yoshimura, K.; Kato, T.; Ohya, K.; Moriarty, T.; Emery, K.; Chen, C. C.; Gao, J.; Li, G.; et al. A Polymer Tandem Solar Cell with 10.6% Power Conversion Efficiency. Nat. Commun. 2013, 4, 10.

2 Blanc, E.; Schwarzenbach, D.; Flack, H. D. The Evaluation of Transmission Factors and Their First Derivatives with Respect to Crystal Shape Parameters. J. Appl. Crystallogr. 1991, 24 (6), 1035–1041.

3 Clark, R. C.; Reid, J. S. The Analytical Calculation of Absorption in Multifaceted Crystals. Acta Crystallogr. Sect. A 1995, 51 (6), 887–897.

4 Version 1.171.37.35 (2014). Oxford Diffraction /Agilent Technologies UK Ltd, Yarnton, England.

5 Sheldrick, G. M. Crystal Structure Refinement with {\it SHELXL}. Acta Crystallogr. Sect. C 2015, 71 (1), 3–8.

6 Dolomanov, O. V; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. {\it OLEX2}: A Complete Structure Solution, Refinement and Analysis Program. J. Appl. Crystallogr. 2009, 42 (2), 339–341.

7 Spek, A. L. Structure Validation in Chemical Crystallography. Acta Crystallogr. Sect. D 2009, 65 (2), 148–155.

8 van der Sluis, P.; Spek, A. L. BYPASS: An Effective Method for the Refinement of Crystal Structures Containing Disordered Solvent Regions. Acta Crystallogr. Sect. A 1990, 46 (3), 194–201.

9 CrystalMaker Software Ltd, Oxford, England (www.crystalmaker.com).

10 Venkataraman, L., Klare, J. E., Nuckolls, C., Hybertsen, M. S. & Steigerwald, M. L. Dependence of single-molecule junction conductance on molecular conformation. *Nature* **442,** 904 (2006).

11 Rajasingh, P.; Cohen, R.; Shirman, E.; Shimon, L. J. W.; Rybtchinski, B. Selective Bromination of Perylene Diimides under Mild Conditions. *J. Org. Chem.* **2007**, *72* (16), 5973–5979

12 Ball, M.; Zhong, Y.; Fowler, B.; Zhang, B.; Li, P.; Etkin, G.; Paley, D. W.; Decatur, J.; Dalsania, A. K.; Li, H.; et al. Macrocyclization in the Design of Organic N-Type Electronic Materials. *J. Am. Chem. Soc.* **2016**, *138* (39), 12861–12867.

13 Ball, M.; Fowler, B.; Li, P.; Joyce, L. A.; Li, F.; Liu, T.; Paley, D.; Zhong, Y.; Li, H.; Xiao, S.; et al. Chiral Conjugated Corrals. *J. Am. Chem. Soc.* **2015**, *137* (31), 9982–9987