Defying Strain in the Synthesis of an Electroactive Bilayer Helicene

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Figure S1. Resolution of the enantiomers of PPDH by chiral preparative HPLC. The enantiomers were resolved from 8 mg of racemate dissolved in 6 mL of 1:2 (v/v) dichloromethane/hexanes. This solution was injected in 1 mL aliquots onto a CHIRALPAK® IB-3 column (30 mm I.D. × 250 mm, 5 µm), with 20% dichloromethane/hexanes flowing at 28.5 mL/min at room temperature. The (-) and (+) correspond to the sign of the longest-wavelength Cotton effect observed for these enantiomers (Δε₅₄₀ nm = -80 and +82 M⁻¹ cm⁻¹).
Figure S2. To show that the large extent of aryl surface overlap in PPDH inhibits racemization, we heated (-)-PPDH (1.7 mg) in diphenyl ether (0.75 mL) at 250 °C for 1 h. These are the HPLC traces of the solution before (a) and after (b) 1 h at 250 °C. This solution was injected in 10 µL aliquots onto a CHIRALPAK® IB-3 column (4.6 mm I.D. × 250 mm, 3 µm), with 20% dichloromethane/hexanes flowing at 1 mL/min at room temperature. The small peak at ~6 min corresponds to the complete elution of diphenyl ether. There is no trace of (+)-PPDH, confirming that PPDH does not racemize under these conditions.
**Figure S3.** From SCXRD, racemic PPDH stacks into heterochiral columns (red, \(M\)-PPDH; blue, \(P\)-PPDH). Solvent, the CH(CH\(_3\))\(_2\) chains, and hydrogen atoms have been hidden to provide a clear view of the aryl surface.
**Figure S4.** From SCXRD, the intermolecular junction between two molecules of PPDH consists of 24 pairs of overlapping π-bonded carbon atoms (shown in pink). (a) The four closest pairs, which approach to within twice the van der Waals radius of the carbon atom (i.e., 3.4 Å), are designated with black arrows. (b) Top view of the same PPDH molecules as in (a), only the uppermost and bottommost PDI subunits have been removed for clarity. The distances between the overlapping atoms (in Å) are indicated to the right of each pair, and the four nearest neighbors are underlined in bold. Free solvent, the CH(C₅H₁₁)₂ chains, and hydrogen atoms have been hidden to provide a clear view of the aryl surface. Thermal ellipsoids are set at 30% probability.
Figure S5. We define the bend angle of each PDI subunit in PPDH as the dihedral of the least-squares-fit planes defined by the pink and blue naphthalene fragments. From SCXRD, the bend angle of one PDI subunit in PPDH measures 11°, whereas the bend angle of the other PDI subunit (planes not shown) measures 9°. Free solvent, the CH(C$_5$H$_{11}$)$_2$ chains, and hydrogen atoms have been hidden to provide a clear view of the aryl surface. Thermal ellipsoids are set at 30% probability.
Figure S6. Structure of PPDH-OPe from SCXRD. (a) α,α,α-Trifluorotoluene – the solvent used in this crystallization – occupies the cavity between the PDI faces. (b and c) Different views of M-PPDH-OPe, with the solvent hidden. (d) PPDH-OPe packs into heterochiral columns (red, M-PPDH-OPe; blue, P-PPDH-OPe). The CH(C₅H₁₁)₂ imide chains, C₆H₆ alkyl fragments of the pentoxy groups, and hydrogen atoms have been hidden to provide a clear view of the aryl surface.
II. General Experimental Details

**Synthesis and Materials:** All reactions were conducted in oven-dried glassware with magnetic stirring. Schlenk flasks were evacuated and backfilled with argon or nitrogen three times prior to use. Anhydrous tetrahydrofuran was obtained from a Glass Contour solvent system consisting of a Schlenk manifold with purification columns packed with activated alumina and supported copper catalyst. These solvents were dispensed from Pure-Pac™ containers purchased from Sigma-Aldrich. Anhydrous, Sure/Seal™ 1,4-dioxane was used as purchased from Sigma-Aldrich. Bis(pinacolato)diboron was used as purchased from Matrix Scientific. 1-Bromoperylene-3,4,9,10-tetracarboxylicdiimide (PDIBr) was prepared using a procedure developed by Rajasingh et al.¹ 3,6-Dibromophenanthrene was synthesized using a procedure by Scott et al.² 3,6-Dibromophenanthrene-9,10-quinone was synthesized using a procedure by Francke et al.³ Potassium acetate was stored in a 200 °C oven for at least 24 h prior to use. Phenanthrene-9,10-quinone, 1-bromopentane, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, and [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium were purchased from Sigma-Aldrich. All remaining reagents and solvents were purchased from commercial sources and used without additional purification. SATCO 55 W Bright White (3700 lumens) compact fluorescent lamps (CFLs) were used during the oxidative photocyclizations.

**Purification:** Automated flash chromatography was performed using a Teledyne Isco CombiFlash Rf200 and Redisep Rf Silica columns. Silica plugs consisted of Silicycle SiliaFlash® P60 40-63 μm silica gel. Preparative thin-layer chromatography (TLC) employed Silicycle SiliaPlate™ Glass Backed TLC silica gel plates, 60 Å, 20 × 20 cm, 2000 μm thickness, F-254 indicator. Analytical TLC plates were cut from Silicycle SiliaPlate™ Glass Backed TLC Extra Hard Layer silica gel plates, 60 Å, 20 × 20 cm, 250 μm thickness, F-254 indicator.

**NMR Spectroscopy:** ¹H-NMR spectra were recorded on Bruker 500 MHz or 400 MHz spectrometers. ¹³C-NMR spectra were recorded on Bruker 126 MHz or 100 MHz spectrometers with complete proton decoupling. Chemical shifts for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CHCl₃: δ 7.26; C₂H₂Cl₄: δ 6.00). Chemical shifts for carbon are reported in ppm downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl₃: δ 77.16, C₂D₂Cl₄: δ 73.78). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet, bm = broad multiplet), coupling constants in hertz, and integration.

**High-Resolution Mass Spectrometry (HRMS):** HRMS data were obtained at the Columbia University Mass Spectrometry facility using a Waters XEVO G2XS instrument equipped with a
UPC² SFC inlet, electrospray (ESI) and atmospheric pressure chemical (APCI) ionization, and a QToF mass spectrometer.

**UV-Visible-Near-Infrared Absorbance Spectroscopy:** The absorbance spectra in Figures 2b and S11 were obtained on a Jasco V-750 spectrophotometer.

**Fluorescence:** The fluorescence spectra in Figures 2b and S11 were recorded using a Jasco FP-8300 spectrofluorometer. Fluorescence quantum yields were measured with a Jobin Yvon FluoroMax4 spectrofluorometer equipped with a Horiba Scientific integrating sphere. Very dilute solutions of PPDH and PPDH-OPE in cyclohexane (absorbance of ~0.08 at the long wavelength peaks of 489 and 494 nm, respectively) were used in these quantum yield experiments. At room temperature, the solutions were excited from 395-405 nm, and their emissions were measured from 475-675 nm.

**Voltammetry:** Cyclic voltammograms in Figure 4 were recorded on a CHI600C electrochemical workstation using Ag/AgCl as the reference electrode, glassy carbon (3 mm diameter) as the working electrode, and a platinum wire as the counter electrode. Experiments were performed under argon in dichloromethane with [Bu₄N][PF₆] as the supporting electrolyte at a scan rate of 0.05 V/s.

**Chiral Resolution:** Racemic samples were analyzed by an Agilent 1200 Series analytical HPLC equipped with a diode array detector. Racemic samples were separated into their enantiomers by preparative HPLC using a Waters Prep150 LC System equipped with a UV-vis detector and an automated fraction collector. Further details are provided in the captions of Figures S1, S2, S9, and S10.

**Electronic Circular Dichroism:** The ECD spectra were recorded using a Jasco J-810 spectropolarimeter. A 10 mm path length high precision cell made of Quartz SUPRASIL® from Hellma Analytics was used in the collection of the spectra in Figure 2a.

**Single-crystal X-ray Diffraction:** Data for all compounds were collected on an Agilent SuperNova diffractometer using mirror monochromated Cu Kα radiation. Data collection, integration, scaling (ABSPACK), and absorption correction (face-indexed Gaussian integration or numeric analytical methods) were performed in CrysAlisPro (CrysAlisPro 1.171.38.41. Oxford Diffraction/Agilent Technologies UK Ltd, Yarnton, England). The structure was solved by intrinsic phasing/Agilent Technologies UK Ltd, Yarnton, England). The structure was solved by intrinsic phasing using SHELXT and refined with full-matrix least-squares on F² in SHELXL using the OLEX2 interface. Successive cycles of least-square refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms were added in idealized positions.
Crystallographic data for **PPDH** and **PPDH-OPe** are given in Section VIII. Slow vapor diffusion of acetonitrile into a solution of **PPDH** in anisole afforded bright red prisms. Slow vapor diffusion of acetonitrile into a solution of **PPDH-OPe** in α,α,α-trifluorotoluene afforded small orange rods. The crystals were mounted on MiTeGen Kapton loops (polyimide) using paratone oil. Data were collected at 100 K.

**Quantum Mechanical Calculations:** All quantum chemical calculations were performed using Jaguar, version 8.3, Schrodinger, Inc., New York, NY, 2014. The geometries were optimized in the gas phase using the B3LYP functional and the 6-31G** basis set. For the optimized geometries of **PPDH** and **PPDH-OPe**, the associated absorption spectra were calculated using the TD-DFT method that is included in the Jaguar package. The B3LYP functional and the 6-31G** basis set were used in these calculations. All alkyl chains (CH[C₅H₁₁]₂ and C₅H₁₁) were modeled as methyl groups.

The effects of dispersion were also assessed in the geometric optimizations of **PPDH** and **PPDH-OPe**. In their energy benchmark study of 47 density functionals, Goerigk and Grimme emphasized the efficacy of DFT-D3 in modeling noncovalent interactions. They regard Zhao and Truhlar’s PW6B95, coupled with the DFT-D3 correction, as “the most robust and very accurate general purpose hybrid-functional.” Therefore, the PW6B95-D3/6-31G** level of theory was also used to optimize the gas-phase geometries of **PPDH** and **PPDH-OPe**. These optimized geometries diverge substantially from the SCXRD structures of **PPDH** and **PPDH-OPe**, which closely resemble the geometries predicted by B3LYP/6-31G** (Figure S23). Steric repulsion between the PDI subunits evidently predominates in these systems, which makes the B3LYP functional an appropriate choice for the calculation of strain (see Section VII).
III. Synthesis and Characterization

Scheme S1. Synthesis of PPDH and 5PPD

Scheme S2. Synthesis of PPDH-OPe
3,6-Dibromophenanthrene (S1): *trans*-4,4’-Dibromostilbene (0.362 g, 1.07 mmol, 1 eq), iodine (0.603 g, 2.38 mmol, 2.22 eq), and propylene oxide (2.0 ml, 29 mmol, 27 eq) were combined with 310 mL of benzene in a 320-mL quartz round-bottom flask and sparged with nitrogen for 10 minutes. The flask was placed in a Rayonet photoreactor (The Southern New England Ultraviolet Company) with sixteen 300 nm lamps and stirred under UV light for 8 h. This reaction mixture was combined with another batch that started with 0.314 g of dibromostilbene. The solvent was removed under reduced pressure. The solid was purified by hot recrystallization from hexanes to yield 0.499 g of white needles (1.48 mmol, 74% over two batches). All spectra matched those reported in the literature.

S2: S1 (0.107 g, 0.318 mmol, 1 eq), bis(pinacolato)diboron (0.176 g, 0.692 mmol, 2.18 eq), potassium acetate that had been dried in a 200 °C oven (0.243 g, 2.48 mmol, 7.79 eq), and [1,1’-bis(diphenylphosphino)ferrocene]dichloropalladium (0.0163 g, 0.0223 mmol, 7.00 mol%) were placed in an oven-dried 10-mL Schlenk flask, then evacuated and back-filled with nitrogen three times. In a separate oven-dried 10-mL round-bottom flask, 2 mL of anhydrous 1,4-dioxane were sparged for 8 min, then transferred to the reaction mixture and sparged for 3 min. The Schlenk flask was sealed with a glass stopcock and heated to 80 °C overnight, at which point it was added to 50 mL of deionized water. The aqueous layer was extracted with 3 x 50 mL of ethyl acetate. The organic layer was dried with MgSO₄, filtered, and the solvent removed with a rotary evaporator. Purification by column chromatography (SiO₂, gradient from 100% hexanes to 100% dichloromethane) afforded the white solid S2 (0.0406 g, 0.0944 mmol, 30%). ¹H NMR (400 MHz, CDCl₃, 300 K) δ 9.30 (s, 2H), 8.02 (dd, J = 10.8, 0.9 Hz, 2H), 7.88 (d, J = 9.9 Hz, 2H), 7.77 (s, 2H), 1.45 (s, 24H). ¹³C NMR (100 MHz, CDCl₃, 300 K) δ 134.24, 132.17, 130.37, 130.05, 128.20, 127.88, 84.16, 25.10. HRMS (APCI+) calculated m/z for [C₂₆H₃₂B₂O₄+H]⁺ is 431.2560; found 431.2575.
S3: PDIBr (0.152 g, 0.196 mmol, 2.12 eq), S2 (0.0398 g, 0.0925 mmol, 1 eq), K₂CO₃ (0.300 g, 2.17 mmol, 24.4 eq), and [1,1’-bis(diphenylphosphino)ferrocene]dichloropalladium (0.0088 g, 0.012 mmol, 13 mol%) were placed in a 10-mL Schlenk flask, then evacuated and back-filled with nitrogen three times. In a separate 10-mL round-bottom flask, 3 mL of tetrahydrofuran and 1 mL of deionized H₂O were sparged with nitrogen for 10 min, then transferred to the reaction mixture and sparged for 4 min. The Schlenk flask was sealed with a glass stopcock and heated at 75 °C overnight, at which point it was added to 35 mL of deionized water. It was extracted with dichloromethane until the aqueous layer turned colorless. The organic layer was dried with Na₂SO₄, filtered, and the solvent removed with a rotary evaporator. Purification by column chromatography (SiO₂, gradient from 100% hexanes to 100% dichloromethane) afforded the dark red solid S3 (0.133 g, 0.0847 mmol, 92%). 

\[ ^{1}H \text{ NMR (500 MHz, } C₂D₂Cl₄, 403 K) \delta 9.12 (s, 2H), 8.77-8.65 (many overlapping signals, 10H), 8.13 (two overlapping doublets, 4H), 8.06 (s, 2H), 7.97 (d, } J = 8.3 \text{ Hz, 2H}, 7.69 (d, } J = 8.2 \text{ Hz, 2H}), 7.69 \text{ (d, } J = 8.2 \text{ Hz}, 2H), 5.17 \text{ (bm, 4H), 1.94 (bm, 8H), 1.34 (broad, overlapping signals, 55H), 0.88 (broad, overlapping signals, 25H).} \]

\[ ^{13}C \text{ NMR (126 MHz, } C₂D₂Cl₄, 403 K) \delta 163.73, 163.70, 163.45, 141.39, 141.32, 135.96, 134.77, 134.31, 134.19, 132.54, 132.28, 131.79, 130.66, 130.51, 130.00, 129.94, 129.07, 128.58, 128.08, 127.56, 127.44, 123.91, 123.57, 123.11, 122.98, 122.79, 122.52, 122.32, 74.03, 54.89, 54.70, 32.34, 31.39, 26.36, 22.06, 13.42. \]

HRMS (APCI+) calculated m/z for [C₁₀₆H₁₁₄N₄O₇+Na]⁺ is 1594.8562; found 1594.8595.

PPDH and 5PPD: PPD (0.0308 g, 0.0196 mmol, 1 eq), iodine (0.0322 g, 0.127 mmol, 6.48 eq), and K₂CO₃ (0.545 g, 3.94 mmol, 201 eq) were dissolved in 98 mL of benzene in a 150-mL round-bottom flask. The solution was sparged with nitrogen for 30 min and left under positive pressure of nitrogen while being irradiated by two 55 W CFLs for 24 h at 30 °C (the temperature
to which the light bulbs heated the solution) in a pristine oil bath. The solvent was removed by rotary evaporation and the material was loaded onto a small silica plug and dried with air. The plug was flushed with acetonitrile (40 mL) to remove iodine and benzene (but not the products, which are insoluble in acetonitrile and stay on the baseline). The mixture of products was brought down with 9:1 (v/v) dichloromethane/ethyl acetate and the solvent was removed by rotary evaporation. $^1$H NMR was taken of this mixture in CD$_2$Cl$_4$ at 393 K (Figure S7). To isolate the products, the mixture was loaded onto a plug again and flushed with 9:1 (v/v) dichloromethane/hexanes, then dichloromethane. These dichloromethane washes contained only 5PPD (0.0108 g, 0.0689 mmol, 35% isolated yield). PPDH was brought down with 9:1 (v/v) dichloromethane/ethyl acetate and the solvent removed by rotary evaporation to give a red solid (0.0193 g, 0.0123 mmol, 63% isolated yield). PPDH: $^1$H NMR (500 MHz, CD$_2$Cl$_4$, 393 K) $\delta$ 10.27 (s, 2H), 9.48 (d, $J = 8.7$ Hz, 2H), 9.08 (d, $J = 8.1$ Hz, 2H), 8.97 (d, $J = 8.2$ Hz, 2H), 8.75 (two overlapping doublets, 4H), 8.61 (s, 2H), 8.39 (d, $J = 8.1$ Hz, 2H), 8.33 (s, 2H), 5.35 (bm, 2H), 4.50 (bm, 2H), 2.35-2.20 (several overlapped signals, 8H), 1.69-0.79 (many overlapped signals, 80H). $^{13}$C NMR (126 MHz, CD$_2$Cl$_4$, 393 K) $\delta$ 164.16, 163.97, 162.72, 162.25, 132.84, 131.82, 129.91, 129.68, 129.66, 129.01, 128.49, 127.84, 127.72, 127.17, 126.25, 125.44, 125.31, 125.09, 123.80, 123.76, 123.43, 123.01, 122.68, 122.54, 121.87, 121.48, 119.47, 74.03, 55.35, 53.55, 32.73, 32.57, 31.61, 31.55, 31.26, 30.91, 30.78, 30.65, 26.85, 26.73, 25.95, 25.85, 22.22, 22.06, 13.56, 13.45, 13.41. HRMS (APCI+) calculated m/z for [C$_{106}$H$_{110}$N$_4$O$_8$+H]$^+$ is 1568.8430; found 1568.8474. 5PPD: $^1$H NMR (500 MHz, CD$_2$Cl$_4$, 393 K) $\delta$ 10.58 (s, 1H), 10.43 (s, 1H), 10.32 (s, 1H), 10.17 (s, 1H), 10.00 (s, 1H), 9.44-9.41 (three overlapping doublets, 3H), 9.19 (d, $J = 8.2$ Hz, 1H), 9.14-9.09 (three overlapping doublets, 3H), 9.04 (s, 1H), 9.02 (d, $J = 8.0$ Hz, 1H), 8.92 (d, $J = 8.0$ Hz, 1H), 8.67 (d, $J = 8.7$ Hz, 1H), 8.54 (d, $J = 8.6$ Hz, 1H), 8.38 (d, $J = 8.7$ Hz, 1H), 5.43 (bm, 2H), 4.98 (bm, 1H), 4.66 (bm, 1H), 2.46 (bm, 4H), 2.11-1.90 (overlapping peaks, 8H), 1.58-1.36 (overlapping peaks, 44 H), 0.98-0.48 (overlapping peaks, 32H). $^{13}$C NMR (126 MHz, CD$_2$Cl$_4$, 393 K) $\delta$ 164.42, 164.35, 164.29, 164.10, 163.80, 163.76, 163.67, 162.96, 134.13, 133.77, 133.64, 133.59, 133.32, 133.23, 132.29, 130.14, 129.54, 129.48, 129.39, 128.86, 128.86, 128.57, 128.10, 127.95, 127.85, 127.73, 127.62, 127.40, 127.29, 126.58, 126.52, 125.02, 125.01, 124.94, 124.88, 124.83, 124.70, 124.50, 123.55, 123.52, 123.24, 123.01, 122.88, 122.81, 74.03, 55.14, 53.79, 32.52, 32.47, 32.07, 31.75, 31.53, 31.41, 30.83, 26.53, 26.42, 25.68, 25.62, 22.31, 22.23, 22.08, 21.63, 21.60, 13.65, 13.59, 13.24, 13.19. HRMS (APCI+) calculated m/z for [C$_{106}$H$_{110}$N$_4$O$_8$+H]$^+$ is 1568.8430; found 1568.8464.

This reaction was repeated with PPD (0.0331 g, 0.0211 mmol, 1 eq), iodine (0.0371 g, 0.146 mmol, 6.94 eq), and K$_2$CO$_3$ (0.634 g, 4.59 mmol, 218 eq) in 106 mL of benzene at 70 °C for 24 h in a pristine oil bath. Isolation and purification followed the same procedure as above to give 0.0274 g (0.0175 mmol, 83%) of PPDH.

This reaction was repeated with PPD (0.0268 g, 0.0171 mmol, 1 eq), iodine (0.0291 g, 0.115 mmol, 6.72 eq), and K$_2$CO$_3$ (0.476 g, 3.44 mmol, 202 eq) in 90 mL of chlorobenzene at 110 °C for 24 h in a pristine oil bath. Isolation and purification followed the same procedure as above to give 0.0242 g (0.0154 mmol, 91%) of PPDH.
Figure S7. $^1$H-NMR spectra (500 MHz, C$_2$D$_2$Cl$_4$, 393 K) of the product mixtures (after an acetonitrile plug to remove iodine and benzene) resulting from the oxidative photocyclization of PPD at different temperatures. The integral shown for PPDH corresponds to two protons and the integral shown for 5PPD corresponds to one proton.
3,6-Dibromophenanthrene-9,10-quinone (S3): This molecule was synthesized according to a published procedure. All spectra matched those previously reported.

S4: 3,6-Dibromophenanthrene-9,10-quinone S3 (5.45 g, 14.9 mmol, 1 eq), Na₂S₂O₄ (25.9 g, 149 mmol, 10.0 eq), and tetrabutylammonium bromide (4.82 g, 15.0 mmol, 1.00 eq) were placed in a 500-mL round-bottom flask. Tetrahydrofuran (110 mL) and deionized water (110 mL) were added. The flask was capped and shaken for 6 min. 1-Bromopentane (8.1 mL, 65 mmol, 4.4 eq) was added, followed by KOH (22.0 g, 392 mmol, 26.3 eq) in 110 mL of water. The mixture became dark. It was allowed to stir for 48 h, after which it was judged complete by TLC (95:5 [v/v] hexane/ethyl acetate). The aqueous layer was extracted with 3 x 200 mL of ethyl acetate. The organic layers were combined and washed with water (2 x 200 mL), brine (1 x 100 mL), dried with Na₂SO₄, decanted, and the solvent removed with a rotary evaporator to yield a brown oil. Ethanol was added to precipitate the product, which was further washed with ethanol, leaving 4.59 g (9.03 mmol, 61%) of a pale yellow solid. This product contained trace (<5% by NMR) S4-deO, a molecule that lacks one oxygen. S4-deO could not be removed from S4 by silica gel column chromatography or recrystallization, so the product was carried forward. The monodeoxygenated impurity was removed by preparative HPLC after the oxidative photocyclization of PPD-OPe. An analytically pure sample of S4 and (and S4-deO, whose ¹H-NMR spectrum is included in Section VI) were obtained by preparative TLC (cyclohexane). ¹H NMR (500 MHz, CDCl₃, 300 K) δ 8.64 (s, 2H), 8.09 (d, J = 8.7 Hz, 2H), 7.70 (d, J = 8.8 Hz, 2H), 4.18 (t, J = 6.7 Hz, 4H), 1.91 (m, 4H), 1.54 (m, 4H), 1.44 (m, 4H), 0.97 (t, J = 7.3, 6H). ¹³C NMR (125 MHz, CDCl₃, 300 K) δ 143.28, 130.58, 129.00, 128.88, 125.52, 124.33, 120.44, 73.87, 30.26, 28.51, 22.72, 14.22. HRMS (APCI⁺) calculated m/z for [C₂₄H₂₈Br₂O₂]⁺ is 508.0436; found 508.0456.
S5: A 50-ml Schlenk flask was charged with S4 (0.982 g, 1.93 mmol, 1 eq), tetrahydrofuran (36 mL), and N,N,N′,N′-tetramethylethylenediamine (0.64 mL, 4.3 mmol, 2.2 eq). The flask was immersed in an acetone/dry ice bath. After being cooled for 15 min, 1.59 M n-butyllithium in hexanes (2.7 mL, 4.3 mmol, 2.2 eq) was added dropwise over 9 min and the solution was allowed to stir for an hour. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.91 mL, 4.4 mmol, 2.3 eq) was added and the solution was stirred cold for 20 min, then warmed up to room temperature. The reaction was monitored by TLC (95:5 [v/v] hexanes:ethyl acetate) and judged complete after 1 h. The reaction mixture was poured into saturated aqueous NH₄Cl (100 mL) and extracted with ethyl acetate (3 x 100 mL). The organic layer was dried with MgSO₄, filtered, and the solvent removed with a rotary evaporator to yield a slowly solidifying brown solid. The solid was recrystallized twice from ethanol to give 0.62 g (1.04 mmol, 54%) of white crystals. ¹H NMR (500 MHz, CDCl₃, 323 K) δ 9.22 (s, 2H), 8.23 (d, J = 8.2 Hz), 8.02 (d, J = 8.2 Hz), 4.21 (t, J = 6.7 Hz, 4H), 1.91, (m, 4H), 1.55 (m, 4H), 1.44-1.40 (two overlapped peaks, 28H), 0.96 (t, J = 7.3 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃, 323 K) δ 144.27, 132.33, 131.77, 130.25, 128.40, 121.46, 84.12, 73.79, 30.30, 28.54, 25.09, 22.73, 14.24. HRMS (APCI+) calculated m/z for [C₃₆H₅₂B₂O₆+H]⁺ is 603.4035; found 603.4047.

PPD-OPe: PDIBr (0.498 g, 0.640 mmol, 2.17 eq), S5 (0.178 g, 0.295 mmol, 1 eq), K₂CO₃ (1.32 g, 9.53 mmol, 32.3 eq) and [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium (48.1 mg, 0.0657 mmol, 22.3 mol%) were placed in a two-neck 50-mL round-bottom flask fitted with a reflux condenser. The flask was evacuated and backfilled with nitrogen three times. In a separate flask, tetrahydrofuran (18 mL) and H₂O (2 mL) were sparged for 30 min with nitrogen. The solvents were transferred into the flask with the solids by syringe and sparged for 15 min. The reaction mixture was heated to reflux for 16 h, at the end of which it was added to 50 mL of deionized water. The aqueous layer was extracted with dichloromethane until it became clear
(≈100 mL). The organic layer was dried with MgSO₄, filtered, and the solvent removed with a rotary evaporator. Purification by column chromatography (SiO₂, gradient from 100% hexanes to 90% dichloromethane) afforded a red solid (0.348 g, 0.200 mmol, 68%). ¹H NMR (500 MHz, C₂D₂Cl₄, 403 K) δ 9.06 (s, 2H), 8.76-8.65 (several overlapped peaks, 10H), 8.51 (d, J = 8.3 Hz, 2H), 8.16 (d, J = 8.1 Hz, 2H), 8.01 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 5.18 (bm, 4H), 4.51 (bm, 4H), 2.25 (bm, 8H), 2.11 (m, 4H), 1.94 (bm, 8H), 1.73 (m, 4H), 1.61 (m, 4H), 1.35 (bm, 48H), 1.09 (t, J = 7.1 Hz, 6H), 0.89 (bm, 24H).

¹³C NMR (126 MHz, C₂D₂Cl₄, 403 K) δ 163.72, 163.47, 143.90, 141.48, 140.25, 136.06, 134.75, 134.42, 134.22, 132.49, 130.65, 130.61, 130.16, 130.03, 129.94, 129.88, 129.08, 128.53, 128.08, 127.45, 127.41, 124.62, 123.87, 123.56, 123.10, 122.91, 122.71, 122.36, 122.29, 73.95, 54.84, 54.67, 32.34, 31.40, 29.99, 28.26, 26.35, 22.24, 22.08, 13.54, 13.44. HRMS (APCI⁺) calculated m/z for [C₁₁₆H₁₃₄N₄O₁₀+H]⁺ is 1745.0206; found 1745.0222.

PPDH-OPe: PPD-OPe (0.0291 g, 0.0167 mmol, 1 eq), iodine (0.0285 g, 0.112 mmol, 6.73 eq), and K₂CO₃ (0.460 g, 3.33 mmol, 200 eq) were dissolved in 78 mL of benzene in a 150-mL round-bottom flask. The solution was sparged with nitrogen for 30 min and left under positive pressure of nitrogen while being irradiated by two 55 W CFL light bulbs for 76 h in a pristine oil bath. The amount of mono-cyclized intermediate decreased over this time, as observed by TLC (4:1 [v/v] dichloromethane/hexanes). However, the amount of decomposition also increased, so the reaction was halted. The solvent was removed by rotary evaporation and the material was loaded onto a small silica plug and dried with air. The plug was flushed with acetonitrile (40 mL), followed by 9:1 (v/v) dichloromethane/hexanes, then dichloromethane. These dichloromethane washes contained the mono-cyclized intermediate and decomposition (which have a combined mass of 4 mg. The decomposition product has broad, unidentifiable peaks in its ¹H-NMR spectrum and a mass that corresponds to loss of the pentyl groups). PPDH-OPe was brought down with 9:1 (v/v) dichloromethane/ethyl acetate and the solvent removed by rotary evaporation to give a red solid (0.0256 g, 88%). Due to the difficulty of separating S₄ from S₄-deO on a large scale, PPDH-OPe contains a small amount of the [7]helicene PPDH-OPe-deO (<5% of the product by NMR [Figure S8]). The separation between such similar molecules by HPLC is poor and the recovery is 76%, with the rest remaining in mixed fractions (Figure S9). ¹H NMR (500 MHz, C₂D₂Cl₄, 393 K) δ 10.26 (s, 2H), 9.47 (d, J = 9.0 Hz, 2H), 9.14 (d, J = 8.9
Hz, 2H), 9.08 (d, $J = 8.1$ Hz, 2H), 8.97 (d, $J = 8.2$ Hz, 2H), 8.74 (d, $J = 8.2$ Hz, 2H), 8.37 (d, $J = 8.1$ Hz, 2H), 8.29 (s, 2H), 5.35 (m, 2H), 4.84 (m, 2H), 4.69 (m, 2H), 4.49 (m, 2H), ~2.35-2.20 (bm, 12H), 1.89 (m, 4H), ~1.76-0.79 (several overlapping signals, 90H). $^{13}$C NMR (126 MHz, C$_2$D$_2$Cl$_4$, 363 K) $\delta$ 164.17, 164.01, 162.71, 162.35, 145.67, 132.79, 131.72, 130.19, 129.56, 129.28, 128.42, 127.88, 127.61, 127.10, 126.36, 125.44, 125.01, 124.15, 123.70, 123.50, 123.40, 123.00, 122.98, 122.59, 122.50, 122.43, 121.78, 121.37, 119.33, 74.76, 55.31, 53.53, 32.74, 32.55, 31.62, 31.55, 31.28, 30.81, 30.64, 30.15, 28.38, 26.87, 26.73, 25.98, 25.91, 22.39, 22.23, 22.10, 22.06, 13.70, 13.57, 13.48, 13.42. HRMS (ESI+) calculated m/z for [C$_{116}$H$_{130}$N$_4$O$_9$+Na]$^+$ is 1762.9712; found 1762.9644. For PPDH-OPe-deO, HRMS (APCI+) calculated m/z for [C$_{116}$H$_{130}$N$_4$O$_9$+H]$^+$ is 1724.9944; found 1724.9944.

Figure S8. $^1$H-NMR spectrum (CDCl$_3$, 323 K) of the mixture of PPDH-OPe and PPDH-OPe-DeO after a dichloromethane wash to remove the mono-cyclized intermediate and decomposition byproducts.
Figure S9. Separation of PPDH-OPe from the mono-deoxygenated impurity, PPDH-OPe-deO, by preparative HPLC. PPDH-OPe (~80 mg) was dissolved in 8 mL of 1:3 (v/v) dichloromethane/hexanes and injected in 1000 µL aliquots onto a CHIRALPAK® IA-3 column (21 mm I.D. × 250 mm, 5 µm), with 18% dichloromethane/hexanes flowing at 18 mL/min at room temperature. PPDH-OPe-deO is the small peak at 22 min. The splitting of the major peak is due to minimal separation of the enantiomers of PPDH-OPe on this chiral column.
Figure S10. Resolution of the enantiomers of PPDH-OPe by chiral preparative HPLC. The enantiomers of PPDH-OPe were resolved from 13 mg of racemic material dissolved in 9 mL of 1:8 [v/v] dichloromethane/hexanes. This solution was injected in 1000 µL aliquots onto a CHIRALPAK® IB-3 column (30 mm I.D. × 250 mm, 5 µm), with 16% polar eluent/hexanes (where the polar eluent was a mixture of 99:1 [v/v] dichloromethane/ethyl acetate) flowing at 19 mL/min at room temperature. The (-) and (+) correspond to the sign of the longest-wavelength Cotton effect observed for these enantiomers (Δε_{555 nm} = -68 and +65 M⁻¹ cm⁻¹).
V. Absorbance and Fluorescence of PPDH, PPDH-OPe, and NPDH in Cyclohexane

![Graph showing UV-visible absorbance spectra of PPDH, PPDH-OPe, and NPDH in cyclohexane (10 µM, 1 cm path length) and fluorescence spectra of PPDH and PPDH-OPe in cyclohexane (3 µM, λ<sub>ex</sub> = 410 nm). Inset shows PPDH (left vial) and PPDH-OPe (right vial) in cyclohexane under a UV lamp emitting ~254 and ~365 nm light.](image)

**Figure S11.** UV-visible absorbance spectra of PPDH, PPDH-OPe, and NPDH in cyclohexane (10 µM, 1 cm path length) and fluorescence spectra of PPDH and PPDH-OPe in cyclohexane (3 µM, λ<sub>ex</sub> = 410 nm). Inset shows PPDH (left vial) and PPDH-OPe (right vial) in cyclohexane under a UV lamp emitting ~254 and ~365 nm light.
VI. $^1$H-NMR and $^{13}$C-NMR Spectra
Part A: Calculating Strain Energy

We minimized the geometries of PPDH, 5PPD, and PPPD by DFT at the B3LYP/6-31G** level of theory. We calculated the strain energy of the helicenes by the formula:

\[ E_{PPDH \text{ or } 5PPD} - E_{PPPD} = \text{Strain Energy} \]  

The total energies (in hartrees) of the six phenanthrene-bridged PDI-dimers are provided on pages 34, 43, 46, 50, 58, and 61. As an isomer of PPDH and 5PPD, PPPD is a good reference because it is nearly planar and, therefore, virtually unstrained. The CH(C5H11)2 and C5H11 chains were modeled as methyl groups to simplify the calculations.

Figure S12. The strain energies of PPDH, PPDH-OPe, and their isomers calculated using Equation 1.
Part B: Molecular Orbitals, DFT-Optimized Molecular Structure, and TD-DFT Excited State Calculations of PPDH

Figure S13. Highest- and lowest-unoccupied molecular orbitals of PPDH from DFT (B3LYP/6-31G**). Orbital isosurfaces are illustrated at 0.05 electrons Bohr$^{-3}$. Methyl groups are used in place of CH(C$_3$H$_{11}$)$_2$ chains to simplify the calculations.
Figure S14. DFT-optimized model of M-PPDH (B3LYP/6-31G**) from different perspectives. Methyl groups substitute for the CH(C\textsubscript{5}H\textsubscript{11})\textsubscript{2} chains to simplify the calculation.

Methyl groups substitute for the CH(C\textsubscript{5}H\textsubscript{11})\textsubscript{2} chains to simplify the calculation.

Total energy = -3354.306915 hartrees

| atom | x       | y       | z       |
|------|---------|---------|---------|
| C1   | -2.1825497627 | 2.3646560901 | 0.5642590288 |
| C2   | -2.331990342  | 0.9473396360 | 0.6142325285 |
| C3   | -3.6326258133 | 0.3828062069 | 0.713625847  |
| C4   | -4.7698597722 | 1.2114987737 | 0.7198552691 |
| C5   | -4.6130520846 | 2.5914442904 | 0.6393076515 |
| C6   | -3.3411544063 | 3.1562672986 | 0.5694617036 |
| C7   | -1.1944491725 | 0.0789899441 | 0.5685160729 |
| C8   | -1.3572951154 | -1.3182444480 | 0.7087202744 |
| C9   | -2.6726642468 | -1.8443531697 | 0.8362093940 |
| C10  | -3.7762523313 | -1.0299459981 | 0.8200673835 |
| C11  | -5.1262558308 | -1.6429916531 | 0.9040079896 |
| N12  | -6.2185285434 | -0.7690334209 | 0.8696219768 |
| C13  | -6.1345020186 | 0.6325351371 | 0.7985908192 |
| C14  | -0.8309694905 | 2.9298789953 | 0.5413201136 |
| C15  | 0.2913216198  | 2.0491575481 | 0.4755506099 |
| C16  | 0.1196271254  | 0.6280881949 | 0.4300483123 |
| C17  | -0.5870339442 | 4.3106135527 | 0.6027554415 |
| C18  | 0.7053809046  | 4.8298245361 | 0.6163868064 |
| C19  | 1.8053602630  | 3.9804088846 | 0.5592726976 |
| C20  | 1.6064187463  | 2.5907367724 | 0.4750537014 |
| C21  | 2.7243552835  | 1.7098411410 | 0.4306898059 |
| C22  | 2.5379788605  | 0.3551211655 | 0.3357614853 |
| C23  | 1.2390650937  | -0.2300358563 | 0.2842089163 |
| C24  | 3.1756387790  | 4.5436994595 | 0.6178125216 |
| N25  | 4.2405298814  | 3.6298581940 | 0.6137277191 |
| C26  | 4.1124669790  | 2.2378878000 | 0.4991329208 |
| C27  | -7.5446775066 | -1.3922604035 | 0.9305253111 |
| C28  | 5.5875267511  | 4.2022707797 | 0.7071227562 |
| O29  | 3.3978486391  | 5.7456100477 | 0.6814394228 |
| Atom | x         | y         | z         |
|------|-----------|-----------|-----------|
| O30  | 5.0967158642 | 1.5102796891 | 0.4568807883 |
| O31  | -5.3061262985 | -2.8507213894 | 0.9944672970 |
| O32  | -7.1408417845 | 1.3283745218 | 0.7962132003 |
| C33  | 1.0504631032 | -1.6688510699 | 0.2542451371 |
| C34  | -0.2016192432 | -2.1870125774 | 0.6688503614 |
| C35  | 2.1147882900 | -2.6084352431 | -0.0459346356 |
| C36  | 2.0605833275 | -3.8837590586 | 0.5795990208 |
| C37  | 0.8290756377 | -4.3322150309 | 1.1359253988 |
| C38  | -0.2874640679 | -3.5508115651 | -0.6378786769 |
| C39  | 3.2316062280 | -4.6925557819 | 0.6436855706 |
| C40  | -0.2016192432 | -2.1870125774 | 0.6688503614 |
| C41  | 4.4095939755 | -4.2427410480 | 0.1181839858 |
| C42  | 3.2316062280 | -4.6925557819 | 0.6436855706 |
| C43  | -0.2016192432 | -2.1870125774 | 0.6688503614 |
| C44  | 4.4562454166 | -0.8842839981 | -2.4888289404 |
| C45  | 5.6730919082 | -1.4911766621 | -2.0512490310 |
| C46  | 5.6527944926 | -2.6044301366 | -1.2629863170 |
| H47  | -5.5012172675 | 3.2134590926 | 0.6378786769 |
| H48  | -3.2612557279 | 4.2353351397 | 0.5187355932 |
| H49  | -2.8461623198 | -2.9105468656 | 0.9007977274 |
| H50  | -1.4172533864 | 5.0042253146 | 0.6591381071 |
| H51  | 0.8782319326 | 5.8983715752 | 0.6822286368 |
| H52  | 3.4218322258 | -0.2646038930 | 0.3497466782 |
| H53  | -8.2869805505 | -0.6033075839 | 0.9007977274 |
| H54  | -7.6464833186 | -2.1150326982 | 0.1186354263 |
| H55  | -7.6639547653 | -1.9245922737 | 1.8769948257 |
| H56  | 5.6233361272 | 4.9050438804 | 1.5404710353 |
| H57  | 6.2877954596 | 3.8388777751 | 0.8534219337 |
| H58  | 5.8332390211 | 4.7448190481 | -0.2092152517 |
| H59  | 0.7845201090 | -5.3279303726 | 1.5675264899 |
| H60  | -1.2285099785 | -3.9451460266 | 1.4441862417 |
| H61  | 5.3309123218 | -4.8019782664 | 0.2534809292 |
| H62  | -3.1794213551 | -5.6452349990 | 1.1625913616 |
| H63  | 6.6212020488 | -1.1229893970 | -2.4209816134 |
| H64  | 6.5723791109 | -3.1355276428 | -1.0352954500 |
| C65  | 3.2604164895 | 0.6383396320 | -4.0354250978 |
| C66  | 4.4637141670 | 0.2266307582 | -3.4169170019 |
| C67  | 5.6556159657 | 0.9518928244 | -3.6939510218 |
| C68  | 5.6588053411 | 2.0381135448 | -4.5311633214 |
| C69  | 6.5928043919 | 0.6952183933 | -3.2183904005 |
| C70  | 4.4630536306 | 2.4552435848 | -5.1813350566 |
| C71  | 3.2566033430 | 1.7375126800 | -4.9524736186 |
| C72  | 2.0699493214 | 2.1201950906 | -5.6458725487 |
| C73  | 2.1264883846 | 3.2380560477 | -6.4924974214 |
| C74  | 3.3058578959 | 3.9542506567 | -6.6845119758 |
| C75  | 4.4784016110 | 3.566886351 | -6.0445753467 |
|   |   |   |   |   |
|---|---|---|---|---|
| H76 | 1.2390505982 | 3.5649090161 | -7.0193472247 |
| H77 | 3.3348599879 | 4.8179725819 | -7.3395115298 |
| C78 | 2.0509074959 | -0.0831934301 | -3.7825561976 |
| C79 | 2.0285352735 | -1.1150846980 | -2.8099359895 |
| C80 | 0.8610205602 | -1.9295666437 | -2.7320309875 |
| C81 | -0.2535818755 | -1.6804271253 | -3.4917943635 |
| H82 | 0.8405889980 | -2.8051399604 | 0.040404 |
| C83 | 2.0509074959 | -0.0831934301 | -3.7825561976 |
| C84 | 0.8610205602 | -1.9295666437 | -2.7320309875 |
| C85 | -0.2535818755 | -1.6804271253 | -3.4917943635 |
| H86 | 0.8405889980 | -2.8051399604 | 0.040404 |
| H87 | 0.8599076066 | 1.3143768338 | -5.4708942969 |
| H88 | -0.3184468351 | 1.551863735 | -6.1963723828 |
| H89 | -1.4452481133 | 0.7466147772 | -6.052693403 |
| C90 | -1.4355802785 | -0.3215442761 | -5.1594534320 |
| H91 | -0.3610942013 | 2.3668230175 | -6.070202725 |
| H92 | -2.3419002007 | 0.9283945762 | -6.323847345 |
| C93 | 6.9293448876 | 2.7765155213 | -4.7506367231 |
| N94 | 6.8769933132 | 3.8812449870 | -5.6089106918 |
| C95 | 5.7266086537 | 4.3357428133 | -6.277256058 |
| C96 | 8.1371532357 | 4.6053953265 | -5.8068486462 |
| O97 | 5.7638582965 | 5.3146652177 | -7.0106267156 |
| O98 | 7.9860424153 | 2.4579116491 | -4.2211394241 |
| C99 | -2.6259317065 | -1.1974838740 | -5.0466079035 |
| C100 | -2.5408127169 | -2.270477317 | -4.152370417 |
| C101 | -1.4243602201 | -2.5860440902 | -3.3623605423 |
| C102 | -3.7227296647 | -3.1386736675 | -4.0647913075 |
| O103 | -3.6470358155 | -1.0187218090 | -5.6971455369 |
| O104 | -1.4292476141 | -3.5473689031 | -2.6041389457 |
| H105 | 7.9449957691 | 5.4235811799 | -6.4961955111 |
| H106 | 8.4994534768 | 4.9861273318 | -4.8494268788 |
| H107 | 8.8923837103 | 3.9284903235 | -6.2116497072 |
| H108 | -3.5517541522 | -3.8561008361 | -3.2662802860 |
| H109 | -4.6048469060 | -2.5304416711 | -3.8596050394 |
| H110 | -3.8779070215 | -3.6573552991 | -5.0140533031 |
### PPDH Frontier Molecular Orbital Energies (eV):

| LUMO+9  | LUMO+8  | LUMO+7  | LUMO+6  | LUMO+5  |
|---------|---------|---------|---------|---------|
| -1.27349 | -1.38669 | -1.63296 | -1.63813 | -1.76983 |
| LUMO+4  | LUMO+3  | LUMO+2  | LUMO+1  | LUMO    |
| -1.81963 | -2.16793 | -2.27134 | -3.2602  | -3.28605 |
| HOMO    | HOMO-1  | HOMO-2  | HOMO-3  | HOMO-4  |
| -5.88855 | -6.00528 | -6.24093 | -6.39033 | -6.86163 |
| HOMO-5  | HOMO-6  | HOMO-7  | HOMO-8  | HOMO-9  |
| -7.28585 | -7.28912 | -7.29266 | -7.29783 | -7.3166 |

### Restricted Singlet Excited State 1:
2.2136 eV  560.11 nm

| excitation | X coeff. |
|------------|----------|
| HOMO-3 => LUMO | 0.13047 |
| HOMO-1 => LUMO+1 | -0.36785 |
| HOMO => LUMO | -0.91680 |

Transition dipole moment (debye):
X = -2.5697  Y = -0.8561  Z = 1.4840
Tot = 3.0884

Oscillator strength, f = 0.0801

### Restricted Singlet Excited State 3:
2.3857 eV  519.70 nm

| excitation | X coeff. |
|------------|----------|
| HOMO-3 => LUMO+1 | -0.17611 |
| HOMO-2 => LUMO | 0.31161 |
| HOMO-1 => LUMO | -0.86374 |
| HOMO => LUMO+1 | 0.32718 |

Transition dipole moment (debye):
X = -0.3208  Y = 0.0556  Z = 0.0341
Tot = 0.3274

Oscillator strength, f = 0.0010

### Restricted Singlet Excited State 2:
2.2312 eV  555.69 nm

| excitation | X coeff. |
|------------|----------|
| HOMO-1 => LUMO | -0.37572 |
| HOMO => LUMO+1 | -0.91712 |

Transition dipole moment (debye):
X = -0.5835  Y = 0.8871  Z = -0.3855
Tot = 1.1296

Oscillator strength, f = 0.0108

### Restricted Singlet Excited State 4:
2.4107 eV  514.30 nm

| excitation | X coeff. |
|------------|----------|
| HOMO-3 => LUMO | 0.25271 |
| HOMO-2 => LUMO+1 | -0.40311 |
| HOMO-1 => LUMO+1 | 0.81908 |
| HOMO => LUMO | -0.28766 |

Transition dipole moment (debye):
X = -4.2084  Y = -2.3244  Z = 0.1421
Tot= 4.8097
Oscillator strength, f= 0.2115

Restricted Singlet Excited State 5:
2.5447 eV   487.23 nm

excitation   X coeff.
-------------
HOMO-3 => LUMO  -0.36853
HOMO-2 => LUMO+1 -0.85960
HOMO-1 => LUMO+1 -0.29278
HOMO-1 => LUMO+3  0.10909

Transition dipole moment (debye):
X= 3.0354   Y= 0.4303   Z= -2.2792
Tot= 3.8201

Oscillator strength, f= 0.1408

Restricted Singlet Excited State 6:
2.5508 eV   486.06 nm

excitation   X coeff.
-------------
HOMO-3 => LUMO+1 -0.14627
HOMO-2 => LUMO  -0.90971
HOMO-1 => LUMO  -0.26449
HOMO-1 => LUMO+2  0.13558
HOMO => LUMO+1  0.11117
HOMO => LUMO+3 -0.16955

Transition dipole moment (debye):
X= 0.8624   Y= -2.2525   Z= 1.1692
Tot= 2.6806

Oscillator strength, f= 0.0695

Restricted Singlet Excited State 7:
2.7162 eV   456.47 nm

excitation   X coeff.
-------------
HOMO-3 => LUMO  0.11614
HOMO-3 => LUMO+1 -0.92730
HOMO-2 => LUMO  0.13272
HOMO-1 => LUMO  0.16736
HOMO-1 => LUMO+2  0.16659
HOMO => LUMO+1 -0.15063
HOMO => LUMO+3 -0.11268

Transition dipole moment (debye):
X= 0.8625   Y= -0.2002   Z= 0.2345
Tot= 0.9160

Oscillator strength, f= 0.0086

Restricted Singlet Excited State 8:
2.7302 eV   454.13 nm

excitation   X coeff.
-------------
HOMO-3 => LUMO  0.85153
HOMO-3 => LUMO+1  0.12604
HOMO-2 => LUMO+1 -0.26610
HOMO-1 => LUMO+1 -0.29203
HOMO => LUMO  0.23787
HOMO => LUMO+2  0.13932

Transition dipole moment (debye):
X= 5.2292   Y= 3.2302   Z= 0.5136
Tot= 6.1679

Oscillator strength, f= 0.3939

Restricted Singlet Excited State 9:
3.0560 eV   405.71 nm

excitation   X coeff.
-------------
HOMO-4 => LUMO -0.21411
HOMO-3 => LUMO -0.16221
HOMO-3 => LUMO+2 -0.11509
HOMO => LUMO+2  0.93945

Transition dipole moment (debye):
X= 0.1461   Y= -1.2442   Z= -3.0535
Tot= 3.3005
Oscillator strength, f= 0.1262

Restricted Singlet Excited State 10:
3.0980 eV    400.21 nm

excitation    X coeff.
--------------
HOMO-4 => LUMO+1  0.75396
HOMO-3 => LUMO+1  0.14918
HOMO-2 => LUMO    0.11780
HOMO-2 => LUMO+2  -0.21848
HOMO => LUMO+2   0.26659
HOMO => LUMO+3   -0.49329

Transition dipole moment (debye):
X= -0.3509  Y= 0.4947  Z= -0.0646
Tot= 0.6099

Oscillator strength, f= 0.0044

Restricted Singlet Excited State 11:
3.1223 eV    397.09 nm

excitation    X coeff.
--------------
HOMO-4 => LUMO  0.90768
HOMO-1 => LUMO+3 0.26559
HOMO => LUMO+2  0.24154
HOMO => LUMO+8  0.10068

Transition dipole moment (debye):
X= 1.1601  Y= -2.0057  Z= 0.9037
Tot= 2.4870

Oscillator strength, f= 0.0753

Restricted Singlet Excited State 12:
3.2095 eV    386.30 nm

excitation    X coeff.
--------------
HOMO-4 => LUMO+1  0.57124
HOMO-3 => LUMO+3  -0.24053
HOMO-2 => LUMO+2  0.53001
HOMO-1 => LUMO+2  -0.14452
HOMO => LUMO+3   0.49289

Transition dipole moment (debye):
X= 1.0936  Y= -2.0057  Z= 0.9037
Tot= 2.4870

Oscillator strength, f= 0.0044

Restricted Singlet Excited State 13:
3.2819 eV    377.78 nm

excitation    X coeff.
--------------
HOMO-9 => LUMO  -0.14136
HOMO-5 => LUMO+1 0.11636
HOMO-3 => LUMO+2  -0.12191
HOMO-1 => LUMO+2  -0.87206
HOMO => LUMO+3  -0.36694

Transition dipole moment (debye):
X= 0.3332  Y= -0.4694  Z= 0.1413
Tot= 0.5927

Oscillator strength, f= 0.0044

Restricted Singlet Excited State 14:
3.2998 eV    375.74 nm

excitation    X coeff.
--------------
HOMO-8 => LUMO  0.57376
HOMO-8 => LUMO+1 -0.52210
HOMO-8 => LUMO+4 -0.14112
HOMO-8 => LUMO+5  -0.14075
HOMO-7 => LUMO  -0.11002
HOMO-6 => LUMO  -0.25775
HOMO-6 => LUMO+1  0.15197
HOMO-5 => LUMO  0.29499
HOMO-5 => LUMO+1  -0.34221
Transition dipole moment (debye):
X = 0.0437    Y = 0.0078    Z = -0.0314
Tot = 0.0543

Oscillator strength, f = 0.0000

Restricted Singlet Excited State 15:
3.3003 eV    375.68 nm

| excitation | X coeff. |
|------------|----------|
| HOMO-8 => LUMO+1 | -0.13728 |
| HOMO-7 => LUMO   | 0.61064  |
| HOMO-7 => LUMO+1 | 0.62574  |
| HOMO-7 => LUMO+4 | -0.14990 |
| HOMO-7 => LUMO+5 | 0.13082  |
| HOMO-6 => LUMO   | 0.14907  |
| HOMO-6 => LUMO+1 | 0.19854  |
| HOMO-5 => LUMO   | 0.23658  |
| HOMO-5 => LUMO+1 | 0.14604  |

Transition dipole moment (debye):
X = -0.0008    Y = -0.0194    Z = 0.0077
Tot = 0.0209

Oscillator strength, f = 0.0000

Restrict
ed Singlet Excited State 16:
3.3051 eV    375.14 nm

| excitation | X coeff. |
|------------|----------|
| HOMO-9 => LUMO   | -0.19346 |
| HOMO-9 => LUMO+1 | 0.24490  |
| HOMO-8 => LUMO   | 0.39086  |
| HOMO-8 => LUMO+1 | -0.35373 |
| HOMO-7 => LUMO+1 | -0.10065 |
| HOMO-6 => LUMO   | 0.52238  |
| HOMO-6 => LUMO+1 | -0.24968 |
| HOMO-6 => LUMO+4 | 0.10091  |
| HOMO-5 => LUMO   | -0.28908 |
| HOMO-5 => LUMO+1 | 0.34856  |

HOMO-5 => LUMO+5 -0.10747

Transition dipole moment (debye):
X = -0.1122    Y = 0.0691    Z = 0.2005
Tot = 0.2399

Oscillator strength, f = 0.0007

Restricted Singlet Excited State 17:
3.3066 eV    374.96 nm

| excitation | X coeff. |
|------------|----------|
| HOMO-9 => LUMO   | 0.29690  |
| HOMO-9 => LUMO+1 | 0.17003  |
| HOMO-8 => LUMO   | -0.12352 |
| HOMO-7 => LUMO+1 | -0.27316 |
| HOMO-7 => LUMO+5 | -0.23739 |
| HOMO-6 => LUMO   | 0.40322  |
| HOMO-6 => LUMO+1 | 0.53161  |
| HOMO-6 => LUMO+5 | -0.12477 |
| HOMO-5 => LUMO+1 | 0.41062  |
| HOMO-5 => LUMO+1 | 0.22268  |

Transition dipole moment (debye):
X = -0.0085    Y = -0.0292    Z = 0.1554
Tot = 0.1583

Oscillator strength, f = 0.0003

Restricted Singlet Excited State 18:
3.3541 eV    369.65 nm

| excitation | X coeff. |
|------------|----------|
| HOMO-4 => LUMO   | 0.27739  |
| HOMO-2 => LUMO+3 | 0.15924  |
| HOMO-1 => LUMO+3 | -0.91730 |

Transition dipole moment (debye):
X = 3.3030    Y = 0.5397    Z = -3.1973
Tot = 4.6286

Oscillator strength, f = 0.0003
Oscillator strength, $f = 0.2725$

Restricted Singlet Excited State 19:
3.5138 eV 352.85 nm

| excitation | X coeff. |
|------------|----------|
| HOMO-14 => LUMO | -0.13882 |
| HOMO-14 => LUMO+1 | 0.24200 |
| HOMO-12 => LUMO | 0.44063 |
| HOMO-12 => LUMO+1 | -0.23780 |
| HOMO-11 => LUMO | -0.22887 |
| HOMO-10 => LUMO | 0.37037 |
| HOMO-10 => LUMO+1 | -0.48523 |
| HOMO-9 => LUMO | -0.27289 |
| HOMO-5 => LUMO | 0.19775 |
| HOMO-2 => LUMO+2 | -0.20486 |
| HOMO => LUMO+3 | 0.16180 |

Transition dipole moment (debye):
X = 0.7011  Y = -1.0255  Z = 0.3112
Tot = 1.2807

Oscillator strength, $f = 0.0219$

Restricted Singlet Excited State 20:
3.5194 eV 352.29 nm

| excitation | X coeff. |
|------------|----------|
| HOMO-14 => LUMO | -0.31622 |
| HOMO-14 => LUMO+1 | -0.15302 |
| HOMO-12 => LUMO | -0.17282 |
| HOMO-12 => LUMO+1 | -0.44696 |
| HOMO-11 => LUMO | 0.30640 |
| HOMO-11 => LUMO+1 | 0.41568 |
| HOMO-10 => LUMO | 0.44651 |
| HOMO-10 => LUMO+1 | 0.11264 |
| HOMO-9 => LUMO | 0.13533 |
| HOMO-5 => LUMO | -0.10344 |

HOMO-3 => LUMO+2  0.19620
HOMO-2 => LUMO+2  0.13555
HOMO => LUMO+3  0.17698
HOMO => LUMO+3  -0.10381

Transition dipole moment (debye):
X = -0.0603  Y = 0.7066  Z = -0.5898
Tot = 0.9223

Oscillator strength, $f = 0.0114$
Figure S15. The simulated UV-visible absorbance spectrum of PPDH from TD-DFT (B3LYP/6-31G**), with (a) 35-nm-full-width-at-half-maximum electronic transitions and (b) zero-bandwidth. The energies of these transitions have not been scaled to match the experimental spectrum; instead, their wavelengths correspond to the singlet excited states listed above.
Part C: DFT-Optimized Molecular Structure of 5PPD

Figure S16. DFT-optimized model of \textbf{M-5PPD} (B3LYP/6-31G**) from different perspectives. Methyl groups substitute for the CH(C\textsubscript{5}H\textsubscript{11})\textsubscript{2} chains to simplify the calculation.

Total energy = -3354.322628 hartrees

| atom | x (angstroms) | y (angstroms) | z (angstroms) |
|------|---------------|---------------|---------------|
| C1   | 0.1469196515  | 3.4161950451  | 3.3037084652  |
| C2   | -0.7260532238 | 2.2957728989  | 3.4361563417  |
| C3   | -1.8305777977 | 2.3684355978  | 4.3290863537  |
| C4   | -2.0940603206 | 3.5523880971  | 5.0430088841  |
| C5   | -1.2559904971 | 4.6500002093  | 4.8800168198  |
| C6   | -0.1528040808 | 4.5769886424  | 4.0319355190  |
| C7   | -0.5042164416 | 1.0901466897  | 2.6998704525  |
| C8   | -1.3331067240 | -0.0371710657 | 2.9018172153  |
| C9   | -2.4098078035 | 0.0646332229  | 3.8248041957  |
| C10  | -2.6651439453 | 1.2291433196  | 4.5036923367  |
| C11  | -3.8270962012 | 1.2835941700  | 5.4264904555  |
| N12  | -4.0456099466 | 2.4917869192  | 6.0965045891  |
| C13  | -3.2501733044 | 3.6440630435  | 5.9676995517  |
| C14  | 1.3342293647  | 3.2912957748  | 2.4548258065  |
| C15  | 1.5498722251  | 2.0747711117  | 1.7423927041  |
| C16  | 0.6065402524  | 0.9980251040  | 1.8020400751  |
| C17  | 2.2865700585  | 4.3136554049  | 2.3310353959  |
| C18  | 3.4391483971  | 4.1553959045  | 1.5665134796  |
| C19  | 3.6782190797  | 2.9596363974  | 0.8983957447  |
| C20  | 2.7316690102  | 1.9212721651  | 0.9684885797  |
| C21  | 2.9743251240  | 0.6847177581  | 0.3049581123  |
| C22  | 2.0335561527  | -0.3131659269 | 0.328398440  |
| C23  | 0.7922618961  | -0.1655626631 | 1.0157074849  |
| C24  | 4.9351693092  | 2.7830882993  | 0.1349492240  |
| N25 | 5.1531001419 | 1.5272099086 | -0.4499741530 |
| C26 | 4.2519301260 | 0.4522418689 | -0.4193693180 |
| C27 | -5.2004844984 | 2.5309367293 | 6.9996786162 |
| C28 | 6.4263818598 | 1.3559947242 | -1.1562732091 |
| O29 | 5.773536724 | 3.6674739685 | 0.2099905556 |
| C30 | 4.5130814128 | -0.6105891902 | -0.9662535939 |
| O31 | -4.5742752756 | 0.3314500607 | 5.6107798095 |
| C32 | -3.5075336367 | 4.6646921715 | 6.5911032031 |
| C33 | -0.1880473155 | -1.2413876421 | 1.0562725297 |
| C34 | -1.1088273683 | -1.2480685376 | 2.1390349909 |
| C35 | -0.1933512249 | -2.3618359634 | 0.1410693830 |
| C36 | -0.7520024225 | -3.5825648413 | 0.5875724427 |
| C37 | -1.5214064966 | -3.6102008977 | 1.7804429705 |
| C38 | -1.7698925134 | -2.4624791841 | 2.4791192749 |
| C39 | 0.2605202580 | -2.3151254462 | -1.2459263552 |
| C40 | 0.4669962347 | -3.5393702589 | -1.9610931241 |
| C41 | 0.0909439189 | -4.7832571410 | -1.3570536499 |
| C42 | -0.5564138216 | -4.7903637274 | -0.1638107521 |
| C43 | 0.3805819714 | -1.1246592529 | -1.9733082485 |
| C44 | 0.8109573243 | -1.0787616838 | -3.3041764951 |
| C45 | 1.1614485575 | -2.3016113302 | -3.9610962692 |
| C46 | 0.9466393967 | -3.4991859453 | -3.2744019370 |
| H47 | -1.4741985096 | 5.5553303056 | 5.4356932745 |
| H48 | 0.4846873566 | 5.4484468284 | 3.9500549959 |
| H49 | -3.0887927586 | -0.7601237854 | 3.9968324970 |
| H50 | 2.1417239317 | 5.2534596121 | 2.8485345585 |
| H51 | 4.1732675986 | 4.9498470880 | 1.4893805390 |
| H52 | 2.2793397502 | -1.2395242329 | -0.1701606787 |
| H53 | -5.248205199 | 3.5258779481 | 7.4349205490 |
| H54 | -6.1127814500 | 2.3098583507 | 6.4417168687 |
| H55 | -5.0861087748 | 1.7749900705 | 7.7796213650 |
| H56 | 7.2540899441 | 1.5640855375 | -0.4752999594 |
| H57 | 6.4710945887 | 0.3304507318 | -1.5140695396 |
| H58 | 6.4869755031 | 2.0564918021 | -1.9920671585 |
| H59 | -1.9539352028 | -4.5533898268 | 2.1014942958 |
| H60 | -2.4184961164 | -2.5019367947 | 3.3449853680 |
| H61 | 0.2694204627 | -5.7061257359 | -1.9012126743 |
| H62 | -0.9309247690 | -5.7188103898 | 0.2579914214 |
| H63 | 1.1138030062 | -4.4492795042 | -3.7666387802 |
| C64 | 1.3515116428 | 0.1869524914 | -5.3749306979 |
| C65 | 0.9113033634 | 0.1790496990 | -4.0312187954 |
| C66 | 0.5886589887 | 1.4150052941 | -3.4122023605 |
| C67 | 0.6634117656 | 2.6043255730 | -4.0927874232 |
| H68 | 0.2789166783 | 1.4691517700 | -2.3770442993 |
| C69 | 1.0740372771 | 2.6343265357 | -5.4533288990 |
| C70 | 1.4337537858 | 1.4194190236 | -6.1014398558 |
Part D: DFT-Optimized Molecular Structure of PPPD

![DFT-optimized model of PPPD](image_url)

**Figure S17.** DFT-optimized model of **PPPD** (B3LYP/6-31G**) from different perspectives. Methyl groups substitute for the CH(C_5H_11)_2 chains to simplify the calculation.

Total energy = -3354.339834 hartrees

| atom | x          | y          | z          |
|------|------------|------------|------------|
| C1   | 2.2393104037 | 1.3695645337 | 0.1298593516 |
| C2   | 3.3905808018  | 0.5812658660  | 0.0858623426  |
| C3   | 4.6541732192  | 1.253642053  | 0.0800503198  |
| C4   | 4.6939876124  | 2.6467550378  | 0.0764406851  |
| C5   | 3.5382079681  | 3.4380577513  | 0.0985790450  |
| C6   | 2.2708322392  | 2.7772207944  | 0.1504586052  |
| C7   | 3.3745988638  | -0.8879454743 | 0.0544182241  |
| C8   | 4.6221162482  | -1.5890307264 | 0.0778193147  |
| C9   | 5.8625673954  | -0.8580623608 | 0.0941979397  |
| C10  | 5.8778815086  | 0.4944709057  | 0.0833757129  |
| C11  | 3.6000114661  | 4.8920927198  | 0.0707157385  |
| C12  | 2.408345975  | 5.6516311901  | 0.1070743265  |
| C13  | 1.1317144036  | 4.9920060128  | 0.1921057489  |
| C14  | 1.0547819105  | 3.5772121370  | 0.2262404904  |
| C15  | 4.8417213631  | 5.5769160353  | -0.022806059  |
| C16  | 4.9145354134  | 6.9458687760  | -0.0405448313 |
| C17  | 3.7306090145  | 7.7308977932  | -0.0074076972 |
| C18  | 2.4648786449  | 7.0840263559  | 0.0688831931  |
| C19  | 1.2810316908  | 7.8797894341  | 0.1066840524  |
| C20  | -0.0194403366 | 7.2109476909 | 0.1990390723  |
| C21  | -0.0624457142 | 5.7837442363 | 0.2474785922  |
| C22  | -1.3237390941 | 5.1336558411 | 0.3547854191  |
| C23  | -1.3754759287 | 3.7146271627 | 0.4198934615  |
| C24  | -0.2235761942 | 2.9710181397 | 0.3527780664  |
| C25  | -1.2275934136 | 7.9203987987 | 0.2467620221  |
| C26  | -2.4569354334 | 7.2714909780 | 0.3459986730  |
| C27  | -2.5144734553 | 5.8852177412 | 0.4036351670  |
| C28  | 3.8190611465 | 9.1364815682 | -0.0495407481 |
| C29  | 2.6568249437 | 9.8964445518 | -0.0166763016 |
| C30  | 1.4120151161 | 9.2749925733 | 0.0605498303 |
| C31  | -3.8302454392 | 5.2106406661 | 0.5155705142 |
| N32  | -3.8238213616 | 3.8115314908 | 0.5876665200 |
| C33  | -2.6748172553 | 3.0061982488 | 0.5717750038 |
| C34  | 6.2495143334 | 7.5935956428 | -0.1179844801 |
| C35  | -2.7465622732 | 1.7898436671 | 0.6757344479 |
| O36  | -4.8890502624 | 5.8238322806 | 0.5497274523 |
| C37  | 7.2960548096 | 6.9586530434 | -0.1553416067 |
| O38  | -2.7465622732 | 1.7898436671 | 0.6757344479 |
| O39  | 7.2960548096 | 6.9586530434 | -0.1553416067 |
| C40  | 5.2370933917 | 11.0378080042 | 0.5497274523 |
| C41  | 2.2069167597 | -1.6500804130 | -0.0067730857 |
| C42  | 2.2054582421 | -3.0578067793 | -0.0283948164 |
| C43  | 3.4569184403 | -3.7477665213 | 0.0363735344 |
| C44  | 4.6299057540 | -2.9827351825 | 0.0774031833 |
| C45  | 0.9717352744 | -3.8292063621 | -0.1190841919 |
| C46  | -0.2925844627 | -3.1939360247 | 0.0452979023 |
| C47  | 1.0166670964 | -5.2453000721 | -0.1004216079 |
| C48  | 2.2769483336 | -5.9346858906 | -0.0067682123 |
| C49  | 3.4850499284 | -5.2032813564 | 0.0552979023 |
| C50  | -2.7414431691 | -3.1670236295 | -0.4757927300 |
| C51  | 1.1964913756 | -9.5341900124 | -0.2017447480 |
| C52  | 2.4249039046 | -10.1854849399 | 0.0686665787 |
| C53  | 3.6035264336 | -9.4530414542 | 0.1306728308 |
| C54  | -2.6478486848 | -6.0512428888 | -0.361202116 |
| C55  | -2.6213124717 | -7.4389310620 | -0.3261372007 |
| C56  | -1.4072659322 | -8.1156518831 | -0.2237421950 |
| C57  | -2.7414431691 | -3.1670236295 | -0.4757927300 |
| C58  | -3.9084591508 | -3.9446034657 | -0.5182046534 |
| C59  | -3.9470997715 | -5.3445650327 | -0.4739546262 |
| C60  | 4.9014816055 | -10.1673597135 | 0.2220196743 |
| C61  | 6.0559725243 | -9.3672087918 | 0.2808037298 |
| C62  | 6.0675333158 | -7.9683985140 | 0.2615818930 |
| C63  | -5.0190008640 | -5.9326926430 | -0.5304376069 |
|   | x   | y   | z   |
|---|-----|-----|-----|
| O74 | -2.7840228353 | -1.9473104728 | -0.5543075370 |
| O75 | 7.1278727002 | -7.3588389715 | 0.3199472360 |
| O76 | 4.9745218708 | -11.3885218640 | -0.2451556123 |
| C77 | 7.3633850844 | -10.0255855535 | 0.3713133396 |
| C78 | -5.2010746951 | -3.262539069 | -0.6378133148 |
| H79 | 1.2786251550 | 0.8756614303 | 0.1507783198 |
| H80 | 5.6716179869 | 3.1116977176 | 0.3199472360 |
| H81 | 7.3633850844 | 10.3885218640 | 0.2451556123 |
| H82 | -3.848010940 | 7.8314866420 | 0.3823725507 |
| H83 | 2.7420066612 | 10.9769024336 | -0.0505311360 |
| H84 | 0.5307702023 | 9.9039185779 | 0.0867436679 |
| H85 | -4.9699618428 | 2.0879901417 | 0.7185268675 |
| H86 | -5.6240109822 | 3.4840055441 | 1.6300831929 |
| H87 | -5.7645190309 | 3.4516926896 | -0.1336974451 |
| H88 | 7.4525782710 | 10.6953276411 | -0.2498397397 |
| H89 | 8.1926719220 | 9.3243050820 | 0.6357196024 |
| H90 | 2.7420066612 | 10.9769024336 | -0.0505311360 |
| H91 | 7.1944002715 | -11.0993877208 | 0.3692209489 |
| H92 | 7.9642446486 | -9.7312739070 | -0.4773707102 |
| H93 | 8.1132304421 | 9.2819488130 | -1.1312675475 |
| H94 | 1.2581882233 | -1.134209568 | -0.0426633088 |
| H95 | 5.9562675705 | -3.4701333295 | 0.1052416102 |
| H96 | -0.3836477607 | -2.1162653949 | -0.284352767 |
| H97 | 5.6598739591 | 3.4516926896 | 0.1974828525 |
| H98 | 0.3012149851 | 10.1414993185 | -0.0683772535 |
| H99 | 7.1944002715 | 9.2819488130 | -1.1312675475 |
| H100 | -1.4285106207 | -9.1975308261 | -0.2024636214 |
| H101 | 7.1944002715 | -11.0993877208 | 0.3692209489 |
| H102 | 7.9642446486 | -9.7312739070 | -0.4773707102 |
| H103 | 8.1132304421 | 9.2819488130 | -1.1312675475 |
| H104 | 5.9562675705 | -3.4701333295 | 0.1052416102 |
| H105 | -0.3836477607 | -2.1162653949 | -0.284352767 |
| H106 | 5.6598739591 | 3.4516926896 | 0.1974828525 |
| H107 | 0.3012149851 | 10.1414993185 | -0.0683772535 |
| H108 | 7.1944002715 | 9.2819488130 | -1.1312675475 |
Part E: Molecular Orbitals, DFT-Optimized Molecular Structure, and TD-DFT Excited State Calculations of PPDH-OPe

![Diagram of molecular orbitals](image)

**Figure S18.** Highest- and lowest-unoccupied molecular orbitals of PPDH-OPe by DFT (B3LYP/6-31G**). Orbital isosurfaces are illustrated at 0.05 electrons Bohr$^{-3}$. We substitute methyl groups for the CH(C$_5$H$_{11}$)$_2$ and C$_5$H$_{11}$ chains to simplify the calculations.
**Figure S19.** DFT-optimized model of *M-PPDH-OPe* (B3LYP/6-31G**) from different perspectives. Methyl groups substitute for the CH(C₅H₁₁)₂ and C₅H₁₁ chains to simplify the calculation.

Total energy = -3583.346743 hartrees

| Atom | x (Å)       | y (Å)       | z (Å)       |
|------|-------------|-------------|-------------|
| C1   | -2.2733393585 | 2.3430114030 | 0.4296357562 |
| C2   | -2.4072544101 | 0.9255901905 | 0.5238128084 |
| C3   | -3.7016047842 | 0.3521714363 | 0.6660156968 |
| C4   | -4.847318783  | 1.1695465076 | 0.6653322870 |
| C5   | -4.705673021  | 2.5475708611 | 0.5350910721 |
| C6   | -3.4412920582 | 3.1219446442 | 0.4252128530 |
| C7   | -1.2628117011 | 0.0664563982 | 0.4914387514 |
| C8   | -1.411056674  | -1.3298374598 | 0.6619526493 |
| C9   | -2.7200317874 | -1.8616995796 | 0.8261298560 |
| C10  | -3.8303376161 | -1.0577030612 | 0.8148351905 |
| C11  | -5.1713995617 | -1.6791654167 | 0.9613868674 |
| N12  | -6.2721768412 | -0.8154401972 | 0.938063229  |
| C13  | -6.2039048715 | 0.5822707877  | 0.8018175560 |
| C14  | -0.9297005362 | 2.9230068222  | 0.3812699269 |
| C15  | 0.2011857869  | 2.0519437553  | 0.354597477  |
| C16  | 0.0456297687 | 0.6267900865  | 0.3481600565 |
| C17  | -0.7025884139 | 4.3089191108  | 0.387447860  |
| C18  | 0.5842348029  | 4.8418060431  | 0.3947653642 |
| C19  | 1.6937160465  | 4.0023236433  | 0.3855314787 |
| C20  | 1.5100593592  | 2.6081610655  | 0.3510846585 |
| C21  | 2.6359724760  | 1.7361613242  | 0.3566354988 |
| C22  | 2.4652162789  | 0.3765392410  | 0.305553316  |
| C23  | 1.1748457979  | -0.2246170570 | 0.2402794229 |
| C24  | 3.0577482297  | 4.5806536072  | 0.4423830487 |
| N25  | 4.1317333871  | 3.6780717161  | 0.4734999217 |
| C26  | 4.0181683265  | 2.2801275244  | 0.4250797652 |
| C27  | -7.5888709605 | -1.4459613023 | 1.0770016017 |
| C28  | 5.4708688814  | 4.2705185753  | 0.5524465120 |
| O29  | 3.2682777530  | 5.785902271  | 0.4735417993 |
|   |        |        |        |        |
|---|--------|--------|--------|--------|
| O30 | 5.0088373687 | 1.5602918161 | 0.4320052348 |  
| O31 | -5.3369717530 | -2.8845680964 | 1.0979008283 |  
| O32 | -7.2166207371 | 1.2691742567 | 0.7966380082 |  
| C33 | 1.0026470111 | -1.6667312890 | 0.2232594489 |  
| C34 | -0.2502441153 | -2.1923859496 | 0.6255221960 |  
| C35 | 2.0803839585 | -2.5982634721 | -0.0620498475 |  
| C36 | 2.0216628332 | -3.8749746585 | 0.5579837889 |  
| C37 | 0.7852005094 | -4.3395224417 | 1.0892312563 |  
| C38 | -0.3329874941 | -3.5608545296 | 1.0265736002 |  
| C39 | 3.2206802830 | 1.2691742567 | 0.7966380082 |  
| C40 | -0.2502441153 | -2.1923859496 | 0.6255221960 |  
| C41 | 2.0803839585 | -2.5982634721 | -0.0620498475 |  
| C42 | 2.0216628332 | -3.8749746585 | 0.5579837889 |  
| C43 | 0.7852005094 | -4.3395224417 | 1.0892312563 |  
| C44 | -0.3329874941 | -3.5608545296 | 1.0265736002 |  
| H47 | -5.600245705  | 3.1608975706 | 0.5307004891 |  
| H48 | -3.3744691208 | 4.1997364034 | 0.3407548363 |  
| H49 | -2.886047187  | -2.9256810049 | 0.9275268445 |  
| H50 | -1.5406626697 | 4.9946925188 | 0.4066366109 |  
| H51 | 0.7460606878  | 5.9138133036 | 0.4199845836 |  
| H52 | 3.3548317394  | -0.2330029098 | 0.3568951647 |  
| H53 | -8.3396625979 | -0.6614872630 | 1.028711474 |  
| H54 | -7.7363833518 | -2.171692235 | 0.2745486086 |  
| H55 | -7.6467818443 | -1.9761654447 | 2.0300956719 |  
| H56 | 5.5511769926  | 4.8802886168 | 1.4548132249 |  
| H57 | 6.1922790909  | 3.4575849137 | 0.5729461443 |  
| H58 | 5.643544891   | 4.9151742924 | -0.3117780204 |  
| H59 | 0.7479251444  | -5.3431173295 | 1.4954439782 |  
| H60 | -1.2756517279 | -3.9680158553 | 1.3672932829 |  
| O61 | 5.5568913441  | -4.936333176 | 0.3035326814 |  
| O62 | 3.093470132   | -5.9164534513 | 1.2603472635 |  
| H63 | 6.6355550831  | -1.0732045361 | -2.3106399598 |  
| H64 | 6.5530808061  | -3.1100183080 | -0.9491677665 |  
| C65 | 3.3134216966  | 0.7057471498 | -3.9806318121 |  
| C66 | 4.5018883440  | 0.2848259841 | -3.3402578649 |  
| C67 | 5.7011696742  | 1.0117573295 | -3.5805112936 |  
| C68 | 5.7261767093  | 2.1021170374 | -4.4122633989 |  
| H69 | 6.6256852121  | 0.7521209461 | -3.081469333 |  
| C70 | 4.5479697991  | 2.5226757550 | -5.0917288832 |  
| C71 | 3.3336614175  | 1.8100802830 | -4.8908389150 |  
| C72 | 2.1649337045  | 2.2011852319 | -5.6081804780 |  
| C73 | 2.2476718879  | 3.3139519171 | -6.4586423041 |  
| C74 | 3.4344789229  | 4.0226722432 | -6.6269072292 |  
| C75 | 4.5886550475  | 3.6323679244 | -5.9561512117 |  

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PPDH-OPe Frontier Molecular Orbital Energies (eV):

LUMO+9    LUMO+8    LUMO+7    LUMO+6    LUMO+5
-1.22261  -1.35322  -1.60057  -1.6033   -1.73146

LUMO+4    LUMO+3    LUMO+2    LUMO+1    LUMO
-1.78806  -2.08521  -2.25637  -3.23108  -3.24768

HOMO      HOMO-1    HOMO-2    HOMO-3    HOMO-4
-5.84555  -5.92066  -6.07848  -6.34978  -6.79387

HOMO-5    HOMO-6    HOMO-7    HOMO-8    HOMO-9
-7.20884  -7.26136  -7.26191  -7.26953  -7.2698

Restricted Singlet Excited State 1:
2.1994 eV    563.71 nm

excitation  X coeff.
-----------  ----------
HOMO-3 => LUMO  -0.10911
HOMO-1 => LUMO+1 -0.49546
HOMO => LUMO    -0.85248

Transition dipole moment (debye):
X= 2.1911     Y= 0.4411     Z= -1.4716
Tot= 2.6760

Oscillator strength, f= 0.0597

-----------------------------------------

Restricted Singlet Excited State 3:
2.2955 eV    540.12 nm

excitation  X coeff.
-----------  ----------
HOMO-3 => LUMO  -0.13048
HOMO-2 => LUMO  -0.13009
HOMO-2 => LUMO+1 0.38241
HOMO-1 => LUMO  -0.35829
HOMO-1 => LUMO+1 0.70703
HOMO => LUMO    -0.37567
HOMO => LUMO+1  0.17696

Transition dipole moment (debye):
X= 2.7541     Y= 1.1239     Z= 0.7256
Tot= 3.0618

Oscillator strength, f= 0.0816

-----------------------------------------

Restricted Singlet Excited State 2:
2.2144 eV    559.90 nm

excitation  X coeff.
-----------  ----------
HOMO-2 => LUMO  0.10531
HOMO-1 => LUMO  -0.42892
HOMO => LUMO+1 -0.88307

Transition dipole moment (debye):
X= 0.4612     Y= -1.2410     Z= 0.6630
Tot= 1.4806

Oscillator strength, f= 0.0184

-----------------------------------------

Restricted Singlet Excited State 4:
2.2983 eV    539.47 nm

excitation  X coeff.
-----------  ----------
HOMO-3 => LUMO+1 0.11806
HOMO-2 => LUMO  -0.28694
HOMO-2 => LUMO+1 -0.18368
HOMO-1 => LUMO  -0.77348
HOMO-1 => LUMO+1 -0.33324

-----------------------------------------
HOMO => LUMO 0.17650
HOMO => LUMO+1 0.32817

Transition dipole moment (debye):
X= -0.5787 Y= -1.8561 Z= 0.1862
Tot= 1.9532

Oscillator strength, f= 0.0332

Restricted Singlet Excited State 5:
2.4940 eV 497.14 nm

excitation X coeff.
-------- --------
HOMO-3 => LUMO+1 0.20489
HOMO-2 => LUMO 0.90594
HOMO-1 => LUMO -0.23055
HOMO-1 => LUMO+2 0.12595
HOMO => LUMO+1 0.18552
HOMO => LUMO+3 -0.10745

Transition dipole moment (debye):
X= -0.8142 Y= 2.1419 Z= -1.0870
Tot= 2.5361

Oscillator strength, f= 0.0608

Restricted Singlet Excited State 6:
2.5010 eV 495.73 nm

excitation X coeff.
-------- --------
HOMO-3 => LUMO -0.40388
HOMO-2 => LUMO+1 -0.83391
HOMO-1 => LUMO+1 0.29490
HOMO => LUMO -0.15501

Transition dipole moment (debye):
X= 4.6828 Y= 1.5194 Z= -2.1029
Tot= 5.3534

Oscillator strength, f= 0.2718

Restricted Singlet Excited State 7:
2.7070 eV 458.01 nm

excitation X coeff.
-------- --------
HOMO-3 => LUMO+1 0.92809
HOMO-2 => LUMO -0.18354
HOMO-1 => LUMO 0.12435
HOMO-1 => LUMO+2 0.17491
HOMO => LUMO+1 -0.15612
HOMO => LUMO+3 -0.11575

Transition dipole moment (debye):
X= -0.2535 Y= 0.7636 Z= -0.2444
Tot= 0.8409

Oscillator strength, f= 0.0073

Restricted Singlet Excited State 8:
2.7263 eV 454.77 nm

excitation X coeff.
-------- --------
HOMO-3 => LUMO -0.86865
HOMO-2 => LUMO+1 0.31278
HOMO-1 => LUMO+1 -0.18374
HOMO => LUMO 0.23897
HOMO => LUMO+2 0.15343

Transition dipole moment (debye):
X= -5.1380 Y= -3.2027 Z= -0.6309
Tot= 6.0872

Oscillator strength, f= 0.3831

Restricted Singlet Excited State 9:
3.0251 eV 409.86 nm

excitation X coeff.
-------- --------
HOMO-4 => LUMO -0.17602
HOMO-3 => LUMO 0.17070
HOMO-3 => LUMO+2 0.11572
HOMO => LUMO+2 0.94588
Transition dipole moment (debye):
X= -0.0874 Y= 1.1406 Z= 2.9201
Tot= 3.1362
Oscillator strength, f= 0.1128

Restricted Singlet Excited State 10:
3.0452 eV  407.15 nm

excitation   X coeff.
------------  ---------
HOMO-4 => LUMO+1  0.52857
HOMO-3 => LUMO+1  -0.19286
HOMO-3 => LUMO+3  -0.12062
HOMO-2 => LUMO+2  0.26617
HOMO-1 => LUMO+2  0.60270
HOMO => LUMO+3  -0.44421

Transition dipole moment (debye):
X= 0.1619 Y= -0.4630 Z= -0.0100
Tot= 0.4906
Oscillator strength, f= 0.0028

Restricted Singlet Excited State 11:
3.0981 eV  400.19 nm

excitation   X coeff.
------------  ---------
HOMO-4 => LUMO  0.92761
HOMO-2 => LUMO+3 -0.11865
HOMO-1 => LUMO+3  0.20517
HOMO => LUMO+2  0.20068
HOMO => LUMO+8  0.10152

Transition dipole moment (debye):
X= -1.4040 Y= -0.2670 Z= 1.1252
Tot= 3.1236 eV  396.93 nm

Oscillator strength, f= 0.0002

Restricted Singlet Excited State 12:
3.1236 eV  396.93 nm

excitation   X coeff.
------------  ---------
HOMO-4 => LUMO+1  -0.77321
HOMO-3 => LUMO+3  -0.17299
HOMO-2 => LUMO+2  0.39945
HOMO-1 => LUMO+2  0.39257
HOMO-1 => LUMO+8  0.10120

Transition dipole moment (debye):
X= 0.5488 Y= -1.0852 Z= 0.5105
Tot= 1.3189
Oscillator strength, f= 0.0206

Restricted Singlet Excited State 13:
3.2659 eV  379.63 nm

excitation   X coeff.
------------  ---------
HOMO-5 => LUMO  -0.19165
HOMO-2 => LUMO+2  -0.56082
HOMO-1 => LUMO+2  0.59300
HOMO => LUMO+3  0.50791

Transition dipole moment (debye):
X= -0.0424 Y= -0.0329 Z= 0.0657
Tot= 0.0849
Oscillator strength, f= 0.0001

Restricted Singlet Excited State 14:
3.3023 eV  375.44 nm

excitation   X coeff.
------------  ---------
HOMO-9 => LUMO  0.15460
HOMO-9 => LUMO+1 -0.18845
HOMO-9 => LUMO+4  0.10635
HOMO-9 => LUMO+5  -0.11989
HOMO-7 => LUMO  0.14153
HOMO-7 => LUMO+1  -0.39011
HOMO-6 => LUMO  -0.64551
HOMO-6 => LUMO+1  0.53091

Transaction dipole moment (debye):
X= -0.0540  Y= -0.0281  Z= 0.0060
Tot= 0.0612

Oscillator strength, f= 0.0000

-------------------------------------------

Restricted Singlet Excited State 15:
3.3025 eV  375.43 nm

excitation    X coeff.
-------------  ---------
HOMO-8 => LUMO -0.15502
HOMO-8 => LUMO+1 -0.19297
HOMO-8 => LUMO+4 -0.11016
HOMO-8 => LUMO+5 -0.11523
HOMO-7 => LUMO  0.65526
HOMO-7 => LUMO+1 0.51639
HOMO-6 => LUMO  0.15859
HOMO-6 => LUMO+1 0.37967

Transaction dipole moment (debye):
X= -0.0733  Y= -0.0450  Z= -0.0056
Tot= 0.0862

Oscillator strength, f= 0.0001

-------------------------------------------

Restricted Singlet Excited State 16:
3.3107 eV  374.50 nm

excitation    X coeff.
-------------  ---------
HOMO-9 => LUMO+1 -0.32565
HOMO-8 => LUMO  0.68351
HOMO-8 => LUMO+1 0.52261
HOMO-7 => LUMO  0.14764
HOMO-7 => LUMO+1 0.14044
HOMO-7 => LUMO+5 -0.11931
HOMO-6 => LUMO  0.11695
HOMO-5 => LUMO  0.13704

Transaction dipole moment (debye):
X= 0.2030  Y= -0.0529  Z= -0.1712

Oscillator strength, f= 0.0009

-------------------------------------------

Restricted Singlet Excited State 17:
3.3110 eV  374.46 nm

excitation    X coeff.
-------------  ---------
HOMO-9 => LUMO -0.66302
HOMO-9 => LUMO+1 0.53541
HOMO-8 => LUMO+1 0.30119
HOMO-7 => LUMO  0.14936
HOMO-6 => LUMO -0.14137
HOMO-6 => LUMO+1 0.16417
HOMO-5 => LUMO+1 0.12645
HOMO-1 => LUMO+3 0.13832

Transaction dipole moment (debye):
X= 0.3953  Y= 0.0800  Z= -0.4888
Tot= 0.6337

Oscillator strength, f= 0.0050

-------------------------------------------

Restricted Singlet Excited State 18:
3.3286 eV  372.48 nm

excitation    X coeff.
-------------  ---------
HOMO-4 => LUMO  0.21604
HOMO-1 => LUMO+3 -0.93422

Transition dipole moment (debye):
X= -4.0268  Y= -0.8034  Z= 3.4747
Tot= 5.3790

Oscillator strength, f= 0.3652

-------------------------------------------

Restricted Singlet Excited State 19:
3.4495 eV  359.43 nm
**Excitation X coeff.**

| HOMO-X => LUMO+Y | X coeff. |
|------------------|----------|
| HOMO-15 => LUMO+1 | -0.11213 |
| HOMO-12 => LUMO   | -0.14599 |
| HOMO-11 => LUMO+1 |  0.14764 |
| HOMO-5  => LUMO   |  0.45510 |
| HOMO-4  => LUMO+1 |  0.25132 |
| HOMO-2  => LUMO+2 |  0.48036 |
| HOMO   => LUMO+3  |  0.59245 |

**Transition dipole moment (debye):**

X = -2.1021  Y = 3.5609  Z = -1.4997  
Tot = 4.3986

**Oscillator strength, f = 0.2531**

**Restricted Singlet Excited State 20:**

| Excitation X coeff. |
|----------------------|
| HOMO-11 => LUMO   |  0.15455 |
| HOMO-5  => LUMO+1 |  0.78115 |
| HOMO-3  => LUMO+2 | -0.48436 |
| HOMO-2  => LUMO+3 |  0.22547 |
| HOMO   => LUMO+4  | -0.12282 |

**Transition dipole moment (debye):**

X = -0.1367  Y = -0.0575  Z = -0.2912  
Tot = 0.3268

**Oscillator strength, f = 0.0014**

---

**Figure S20.** The simulated UV-visible absorbance spectrum of PPDH-OPe from TD-DFT (B3LYP/6-31G**) with (a) 35-nm-full-width-at-half-maximum electronic transitions and (b) zero-bandwidth. The energies of these transitions have not been scaled to match the experimental spectrum; instead, their wavelengths correspond to the singlet excited states listed above.
Part F: DFT-Optimized Molecular Structure of 5PPD-OPe

Figure S21. DFT-optimized model of \textit{M-5PPD-OPe} (B3LYP/6-31G**) from different perspectives. Methyl groups substitute for the CH(C$_{3}$H$_{11}$)$_{2}$ and C$_{5}$H$_{11}$ chains to simplify the calculation.

Total energy = -3583.364068 hartrees

| atom | $x$ | $y$ | $z$ |
|------|----|----|----|
| C1   | 0.2230794379 | 3.4575002304 | 3.3252731050 |
| C2   | -0.7074600619 | 2.3803165053 | 3.4137239584 |
| C3   | -1.8425784290 | 2.5041421581 | 4.2611978348 |
| C4   | -2.0788959710 | 3.6987486123 | 4.9670207894 |
| C5   | -1.1880769068 | 4.7585871742 | 4.8375895284 |
| C6   | -0.0550967434 | 4.6339039835 | 4.0366300681 |
| C7   | -0.5166206706 | 1.1706623001 | 2.6747686431 |
| C8   | -1.4107361173 | 0.0868283765 | 2.8308097745 |
| C9   | -2.5135561233 | 0.2362913540 | 3.7159087352 |
| C10  | -2.7366757665 | 1.4056911315 | 4.3970124116 |
| C11  | -3.9258990856 | 1.5103104366 | 5.2804757568 |
| N12  | -4.1114507346 | 2.7256753982 | 5.9482766376 |
| C13  | -3.2639607995 | 3.8431320253 | 5.8473400876 |
| C14  | 1.4419361912 | 3.2730766145 | 2.5350454110 |
| C15  | 1.6243759289 | 2.0544318103 | 1.8169820508 |
| C16  | 0.6232058073 | 1.0293788731 | 1.8212443149 |
| C17  | 2.4599678948 | 4.2367869919 | 2.4776292034 |
| C18  | 3.6378098777 | 4.0215763363 | 1.7667320135 |
| C19  | 3.8365555309 | 2.8269571804 | 1.0835337337 |
| C20  | 2.8301474127 | 1.8443284288 | 1.0944949157 |
| C21  | 3.0257131794 | 0.6090331413 | 0.4137350819 |
| C22  | 2.0314730359 | -0.3347122588 | 0.3770411431 |
| C23  | 0.7771374161 | -0.1322754747 | 1.0245514449 |
| C24  | 5.1133448328 | 2.5903550136 | 0.3698988179 |
| N25  | 5.2730274894 | 1.3413195300 | -0.2474592880 |
| C26  | 4.3145802010 | 0.3154002691 | -0.2633614528 |
|    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|
| C27 | -5.2910689567 | 2.8143146164 | 6.8151628247 |
| C28 | 6.5566456836 | 1.1129737333 | -0.9179040192 |
| O29 | 6.0107357959 | 3.4211490273 | 0.3168287135 |
| O30 | 4.5385792204 | -0.7534796650 | -0.8152290754 |
| O31 | -4.7216266773 | 0.5931926490 | 5.4365382827 |
| O32 | -3.5002369787 | 4.8754823228 | 6.4596991706 |
| C33 | -0.2577689789 | -1.1554509390 | 1.0170241100 |
| C34 | -1.2195102164 | -1.1263910965 | 2.0631970949 |
| C35 | -0.2838963026 | -2.2620920320 | 0.0863737488 |
| C36 | -0.9168494244 | -3.4587420674 | 0.4967389044 |
| C37 | -1.7351185768 | -3.4630370151 | 1.6568677535 |
| C38 | -1.9555026567 | -2.3091424797 | 2.3557365083 |
| C39 | 0.2053267217 | -2.2128039074 | -1.2856235310 |
| C40 | 0.3766400820 | -3.4325137480 | -2.0169939294 |
| C41 | -0.0354779058 | -4.6792119510 | -1.4300286445 |
| C42 | -0.7539849518 | -4.6739273251 | -0.2639191586 |
| C43 | 0.3900301006 | -1.0149645272 | -1.9865467015 |
| C44 | 0.8102044855 | -0.9648107508 | -3.3203672617 |
| C45 | 1.1101653498 | -2.1915324724 | -3.9951732629 |
| C46 | 0.8667104910 | -3.3944138538 | -3.3260169686 |
| H47 | -1.3901398940 | 5.6747120984 | 5.3814297092 |
| H48 | 0.6217708412 | 5.4766992303 | 3.9760603481 |
| H49 | -3.2366637964 | -0.5563823862 | 3.8547609334 |
| H50 | 2.3485732119 | 5.1732282835 | 3.0093741895 |
| H51 | 4.4220503844 | 4.7701471832 | 1.7425383698 |
| H52 | 2.2443380275 | -1.2624259094 | -0.1346174790 |
| H53 | -5.2957728946 | 3.8022673133 | 7.2685676492 |
| H54 | -6.1968583822 | 2.6575081796 | 6.2255209464 |
| H55 | -5.2446373868 | 2.0380345957 | 7.581813719 |
| H56 | 7.3718604430 | 1.2012658293 | -0.1964573189 |
| H57 | 6.5328760980 | 0.1148055019 | -1.3477125574 |
| H58 | 6.7063671790 | 1.8650439603 | -1.6952541342 |
| H59 | -2.2142416012 | -4.3902790602 | 1.9459009870 |
| H60 | -2.6446059234 | -2.3244626547 | 3.1907031215 |
| H61 | 0.9934617097 | -4.3440964736 | -3.8258990774 |
| C62 | 1.3297371827 | 0.3052162356 | -5.3949310899 |
| C63 | 0.9139952488 | 0.2958358083 | -4.0430079112 |
| C64 | 0.5783818614 | 1.5288653923 | -3.4254533148 |
| C65 | 0.6260736311 | 2.7175616315 | -4.1092597968 |
| H66 | 0.2614818044 | 1.5778318025 | -2.3927281630 |
| C67 | 1.0308092125 | 2.7507446091 | -5.4707443896 |
| C68 | 1.3976180743 | 1.5386597996 | -6.1210908936 |
| C69 | 1.8171749081 | 1.5811087346 | -7.4853529480 |
| C70 | 1.8357398562 | 2.8204035038 | -8.1395836801 |
| C71 | 1.4649639176 | 3.9995695970 | -7.4952554129 |
| C72 | 1.0650030429 | 3.9765933409 | -6.1652506612 |
| H73 | 2.1426858497 | 2.8812515225 | -9.1765289736 |
| H74 | 1.4823130554 | 4.9507058805 | -8.0157601313 |
| C75 | 1.6902686883 | -0.9245738192 | -6.0527917128 |
|  C76  |  1.6022612127 |  -2.1555324734 |  -5.3645141397 |
|-------|---------------|-----------------|----------------|
|  C77  |  2.0027408269 |  -3.3413214850 |  -6.0326231531 |
|  C78  |  2.4504144578 |  -3.3269133377 |  -7.3300192613 |
|  H79  |  1.9799274453 |  -4.3001735249 |  -5.5322894898 |
|  C80  |  2.5207636154 |  -2.1041215626 |  -8.0515336844 |
|  C81  |  2.1397234318 |  -0.8903140156 |  -7.4172444605 |
|  C82  |  2.2124423814 |  0.3328821892  |  -8.1456232605 |
|  C83  |  2.6611456058 |  0.2903524930  |  -9.4724137602 |
|  C84  |  3.0345387070 |  -0.9036736367 |  -10.086875548 |
|  C85  |  2.9691390950 |  -2.1009600987 |  -9.3872029209 |
|  H86  |  2.7287845643 |  1.2029432055  |  -10.0507407589|
|  H87  |  3.3815111434 |  -0.9206499848 |  -5.5322894898 |
|  C88  |  0.2410979113 |  3.9671870676  |  -3.4048435316 |
|  N89  |  0.2849633982 |  5.1499427665  |  -4.1504365547 |
|  C90  |  0.6750418768 |  5.2438920300  |  -5.4982284930 |
|  C91  |  -0.1104227416|  6.3738678580  |  -3.4464089866 |
|  O92  |  0.6876078546 |  6.3200252339  |  -6.086621040 |
|  O93  |  -0.1053394445|  3.9900516912  |  -2.2301705770 |
|  C94  |  3.3745925138 |  -3.3623824878 |  -10.0521890312|
|  N95  |  3.2952595359 |  -4.5375424640 |  -9.2916078167 |
|  C96  |  2.8585266020 |  -4.6104092348 |  -7.9607471518 |
|  C97  |  3.7087332287 |  -5.7730733334 |  -9.9648007081 |
|  O98  |  3.7667638493 |  -3.4063484248 |  -11.2108173668|
|  O99  |  2.8777985481 |  -5.6770770299 |  -7.3612404459 |
|  H100 |  -0.0408284128|  7.1988970301  |  -4.1508578697 |
|  H101 |  -1.1313128187|  6.2706465632  |  -3.0726296767 |
|  H102 |  0.5504323302 |  6.5402934840  |  -2.5929744612 |
|  H103 |  3.5960501292 |  -6.5897159163 |  -9.2562593597 |
|  H104 |  3.0868689170 |  -5.9397418530 |  -10.8467958569|
|  H105 |  4.7473987360 |  -5.6865566722 |  -10.2906736266|
|  H106 |  0.1579933337 |  -0.0957200376 |  -1.4722493786 |
|  O107 |  -1.2839211423|  -5.8220638318 |  0.2735656863 |
|  C108 |  -2.3026207952|  -6.4648995882 |  -0.5115526792 |
|  O109 |  0.1932248527 |  -5.8291659345 |  -2.1449723171 |
|  C110 |  1.0679812265 |  -6.7765217467 |  -1.5076171191 |
|  H111 |  -3.1500087886|  -5.7887103399 |  -0.6689387054 |
|  H112 |  -1.9121486703|  -6.7938820201 |  -1.4779591466 |
|  H113 |  -2.6298058194|  -7.3271389560 |  0.0719667542 |
|  H114 |  0.6450925066 |  -7.1317006273 |  -0.5635910986 |
|  H115 |  1.1709669324 |  -7.6076337928 |  -2.2068208897 |
|  H116 |  2.0509261432 |  -6.3282464394 |  -1.3254584339 |
**Part G: DFT-Optimized Molecular Structure of PPPD-Ope**

![Molecular Structure Diagram]

**Figure S22.** DFT-optimized model of PPPD-Ope (B3LYP/6-31G**) from different perspectives. Methyl groups substitute for the CH(C$_5$H$_{11}$)$_2$ chains and C$_5$H$_{11}$ chains to simplify the calculation.

Total energy = -3583.381789 hartrees

| atom | x (angstroms) | y (angstroms) | z (angstroms) |
|------|--------------|--------------|--------------|
| C1   | 2.2598805513 | 1.3603290604 | 0.1812935206 |
| C2   | 3.4122529676 | 0.5789790315 | 0.0945306698 |
| C3   | 4.6720296636 | 1.255681675  | 0.0586297546 |
| C4   | 4.7077704088 | 2.6487375438 | 0.0380361469 |
| C5   | 3.5452071677 | 3.4306326167 | 0.0873434689 |
| C6   | 2.2844019426 | 2.7669877221 | 0.2016791977 |
| C7   | 3.3958810283 | -0.8866885057| 0.0488671190 |
| C8   | 4.6386700195 | -1.5926674887| 0.1052300813 |
| C9   | 5.8888567960 | -0.8643524407| 0.1356623332 |
| C10  | 5.9059378272 | 0.4980596755 | 0.0540292277 |
| C11  | 3.5941916041 | 4.8846156191 | 0.0307814001 |
| C12  | 2.4011968376 | 5.6380971944 | 0.1261047196 |
| C13  | 1.1364305317 | 4.9735402866 | 0.2974148909 |
| C14  | 1.0706665036 | 3.5596228206 | 0.3453175462 |
| C15  | 4.8236278295 | 5.5750513947 | -0.1363859946 |
| C16  | 4.8830232919 | 6.9437786916 | -0.2075156012 |
| C17  | 3.6980530854 | 7.7225114547 | -0.1092835337 |
| C18  | 2.4445183278 | 7.0699651544 | 0.0619699433 |
| C19  | 1.2596962131 | 7.8592531241 | 0.1660315770 |
| C20  | -0.0267141504| 7.1842087052 | 0.3598647897 |
| C21  | -0.0569218004| 5.7576254469 | 0.4253265271 |
| C22  | -1.3038376004| 5.1013148573 | 0.6266292120 |
| C23  | -1.3417035271| 3.6829908278 | 0.7068061160 |
| C24  | -0.1922205935| 2.9481546224 | 0.5630426955 |
| C25  | -1.2334693086| 7.8856986213 | 0.4891641585 |
| C26  | -2.4486093606| 7.2314422836 | 0.6824863503 |
| C27  | -2.4932570419| 5.8453811663 | 0.7550677640 |
| C28  | 3.7725693164 | 9.1276752876 | -0.1830133307 |
|   | C29       | C30       | C31       | C32       | C33       | C34       | C35       | C36       | C37       | C38       | C39       | C40       | C41       | C42       | C43       | C44       | C45       | C46       | C47       | C48       | C49       | C50       | C51       | C52       | C53       | C54       | C55       | C56       | C57       | C58       | C59       | C60       | C61       | C62       | C63       | C64       | C65       | C66       | C67       | C68       | C69       | C70       | C71       | C72       | C73       | C74       | C75       | C76       | C77       |
|---|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
|   | 2.6093657355 | 9.8811977430 | -0.0865548263 | 1.3767245162 | 9.2543167451 | 0.0854222252 | -3.7926907666 | 5.1631592842 | 0.9688730295 | 2.6204180118 | 9.6660479900 | 0.9605544444 | 6.2038133865 | 7.5982387520 | -0.3925175700 | 6.2123009218 | 8.9959236997 | -0.4546067816 | 5.0748442494 | 9.8167428876 | -0.3628273931 | 6.2576787429 | 8.0167428876 | -0.3657456931 | 5.1653897523 | 11.035279237 | -0.4295984493 | 6.0629792462 | 3.1077253354 | 1.2758604519 | 7.5233924047 | 9.6284724129 | -0.6333324946 | 2.2227989162 | -1.6410279930 | -0.0586912522 | 2.2210718958 | -3.0475403730 | -0.833149626 |
|   | 2.3762002134 | 1.0003279439 | 1.0234605432 | 3.9004012039 | 2.6093657355 | 9.8811977430 | -0.0865548263 | 1.3767245162 | 9.2543167451 | 0.0854222252 | 2.6204180118 | 9.6660479900 | 0.9605544444 | 6.2038133865 | 7.5982387520 | -0.3925175700 | 6.2123009218 | 8.9959236997 | -0.4546067816 | 5.0748442494 | 9.8167428876 | -0.3628273931 | 6.2576787429 | 8.0167428876 | -0.3657456931 | 5.1653897523 | 11.035279237 | -0.4295984493 | 6.0629792462 | 3.1077253354 | 1.2758604519 | 7.5233924047 | 9.6284724129 | -0.6333324946 | 2.2227989162 | -1.6410279930 | -0.0586912522 | 2.2210718958 | -3.0475403730 | -0.833149626 |
| Atom | X           | Y           | Z           | Coordinates |
|------|-------------|-------------|-------------|-------------|
| C78  | -5.1185902700 | -3.2129100906 | -1.2476083917 |             |
| C79  | 7.0446986223  | -1.6077013047 | 0.1725264146  |             |
| O80  | 7.0785010605  | 1.2140929325  | 0.0404502641  |             |
| C81  | 7.8991104229  | 1.0326987215  | -1.1268287994 |             |
| C82  | 7.8324466932  | -1.4606462286 | 1.3669980930  |             |
| C83  | 1.3048370253  | 0.8592102899  | 0.2435838444  |             |
| O84  | 5.6842806668  | 3.1091257574  | 0.0011642720  |             |
| C85  | 7.8991104229  | 1.0326987215  | -1.1268287994 |             |
| C86  | 7.8324466932  | -1.4606462286 | 1.3669980930  |             |
| O87  | 7.0446986223  | -1.6077013047 | 0.1725264146  |             |
| O88  | 7.0785010605  | 1.2140929325  | 0.0404502641  |             |
| C89  | 7.9624635533  | -9.7661461160 | -0.0637432961 |             |
| C90  | 7.8991104229  | 1.0326987215  | -1.1268287994 |             |
| O91  | 7.8324466932  | -1.4606462286 | 1.3669980930  |             |
| C92  | 1.3048370253  | 0.8592102899  | 0.2435838444  |             |
| O93  | 5.6842806668  | 3.1091257574  | 0.0011642720  |             |
| C94  | 7.9624635533  | -9.7661461160 | -0.0637432961 |             |
| C95  | 7.8991104229  | 1.0326987215  | -1.1268287994 |             |
| O96  | 7.8324466932  | -1.4606462286 | 1.3669980930  |             |
| C97  | 1.3048370253  | 0.8592102899  | 0.2435838444  |             |
| O98  | 5.6842806668  | 3.1091257574  | 0.0011642720  |             |
| C99  | 7.9624635533  | -9.7661461160 | -0.0637432961 |             |
| O100 | 7.8991104229  | 1.0326987215  | -1.1268287994 |             |
| O101 | 7.8324466932  | -1.4606462286 | 1.3669980930  |             |
| C102 | 1.3048370253  | 0.8592102899  | 0.2435838444  |             |
| O103 | 5.6842806668  | 3.1091257574  | 0.0011642720  |             |
| C104 | 7.9624635533  | -9.7661461160 | -0.0637432961 |             |
| O105 | 7.8991104229  | 1.0326987215  | -1.1268287994 |             |
| O106 | 7.8324466932  | -1.4606462286 | 1.3669980930  |             |
| C107 | 1.3048370253  | 0.8592102899  | 0.2435838444  |             |
| O108 | 5.6842806668  | 3.1091257574  | 0.0011642720  |             |
| O109 | 7.9624635533  | -9.7661461160 | -0.0637432961 |             |
| O110 | 7.8991104229  | 1.0326987215  | -1.1268287994 |             |
| O111 | 7.8324466932  | -1.4606462286 | 1.3669980930  |             |
| O112 | 1.3048370253  | 0.8592102899  | 0.2435838444  |             |
| O113 | 5.6842806668  | 3.1091257574  | 0.0011642720  |             |
| O114 | 7.9624635533  | -9.7661461160 | -0.0637432961 |             |
| O115 | 7.8991104229  | 1.0326987215  | -1.1268287994 |             |
| O116 | 7.8324466932  | -1.4606462286 | 1.3669980930  |             |
Part H: Superimposition of the SCXRD Structures and DFT-Optimized Geometries

Figure S23. Optimization in the gas phase at the B3LYP/6-31G** level of theory returns geometries of PPDH and PPDH-OPe (depicted in red) that resemble the corresponding structures from SCXRD (orange). In contrast, optimization at the PW6B95-D3/6-31G** level of theory gives highly compressed bilayers (blue). We substituted methyl groups for the CH(C₆H₁₁)₂ and C₆H₁₁ chains to simplify the DFT calculations. These alkyl groups have been hidden in the structures above to provide an unobstructed view of the aryl surfaces.
VIII. Single-crystal X-ray Diffraction Data

Crystallographic data corresponding to PPDH have been deposited with the Cambridge Crystallographic Data Centre (CCDC #1864290).

| PPDH·Anisole |
|--------------|
| **Formula**  | *C*_{113}H_{118}N_{4}O_{9} |
| **MW**       | 1676.11 |
| **Space group** | P-1 |
| **a (Å)**    | 15.2191(5) |
| **b (Å)**    | 16.2207(6) |
| **c (Å)**    | 19.6692(8) |
| **α (°)**    | 75.736(3) |
| **β (°)**    | 74.285(3) |
| **γ (°)**    | 76.470(3) |
| **V (Å³)**   | 4456.7(3) |
| **Z**        | 2 |
| **ρ_{calc} (g cm⁻³)** | 1.249 |
| **T (K)**    | 100 |
| **λ (Å)**    | 1.54184 |
| **2θ_{min}, 2θ_{max}** | 7, 147 |
| **Nref**     | 65476 |
| **R(int), R(σ)** | .0667, .0662 |
| **μ(mm⁻¹)**  | 0.613 |
| **Size (mm)** | .20 x .10 x .05 |
| **T_{min} / T_{max}** | .795 |
| **Data**     | 17715 |
| **Restraints** | 730 |
| **Parameters** | 1333 |
| **R₁(obs)**  | 0.0947 |
| **wR₂(all)** | 0.3043 |
| **S**        | 1.047 |
| **Peak, hole (e⁻ Å⁻³)** | 0.83, -0.53 |
Crystallographic data corresponding to PPDH-OPe have been deposited with the Cambridge Crystallographic Data Centre (CCDC #1864289).

**PPDH-OPe·CF₃Ph**

| Property            | Value                        |
|---------------------|------------------------------|
| Formula             | C₁₂₃H₁₃₅F₃N₄O₁₀              |
| MW                  | 1886.34                      |
| Space group         | P-1                          |
| a (Å)               | 16.011(3)                    |
| b (Å)               | 17.232(3)                    |
| c (Å)               | 19.864(3)                    |
| α (°)               | 68.468(15)                   |
| β (°)               | 77.568(14)                   |
| γ (°)               | 82.152(13)                   |
| V (Å³)              | 4968.3(15)                   |
| Z                   | 2                            |
| ρ calc (g cm⁻³)     | 1.261                        |
| T (K)               | 100                          |
| λ (Å)               | 1.54184                      |
| 2θ min, 2θ max      | 7, 78                        |
| N ref               | 13770                        |
| R(int), R(σ)        | .0894, .1413                 |
| μ(mm⁻¹)             | 0.659                        |
| Size (mm)           | .16 x .03 x .02              |
| T min / T max       | .760                         |
| Data                | 5376                         |
| Restraints          | 101                          |
| Parameters          | 687                          |
| R₁(obs)             | 0.0960                       |
| wR₂(all)            | 0.2985                       |
| S                   | 1.019                        |
| Peak, hole (e⁻ Å³)  | 0.46, -0.38                  |

*R₁ = \left[ \sum (F_o - F_c)^2 / \sum F_o^2 \right]^{1/2}; wR2 = \left[ \sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2) \right]^{1/2}, w = 1/[σ²(F_o^2) + (aP)^2 + bP], where P = [max(F_o^2,0) + 2(F_c^2)]/3*
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