

Impact of Pyrene Orientation on the Electronic Properties and Stability of Graphene Ribbons

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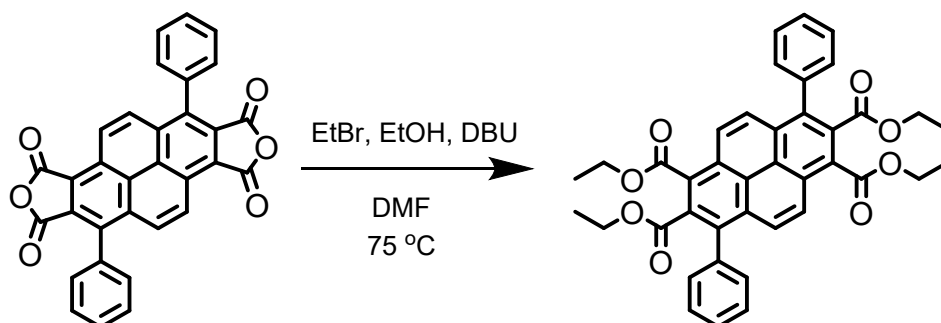
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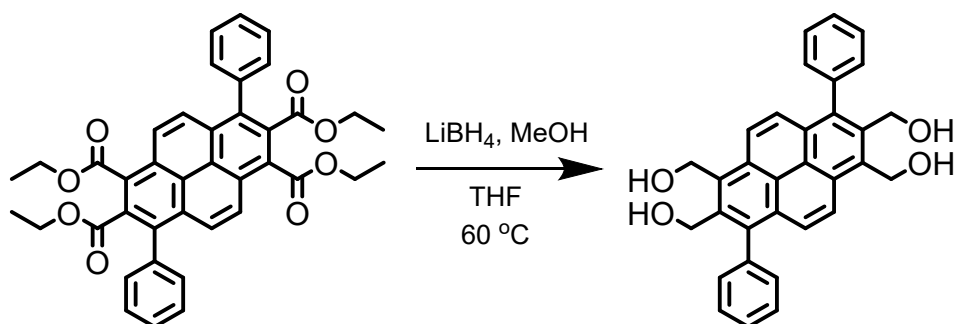
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Synthetic and Experimental Procedures

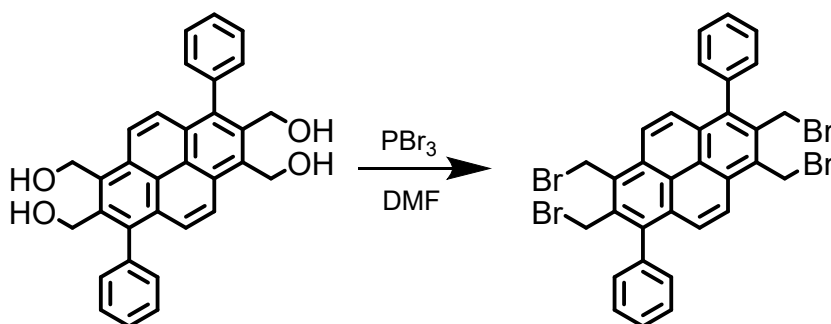
All reagents and solvents were obtained from Sigma Aldrich, Oakwood Chemicals, Gelest, or VWR and used without further purification. ^1H and ^{13}C NMR spectra were measured on a 400 MHz Bruker NMR spectrometer in CDCl_3 (7.26 ppm for ^1H NMR, 77.16 ppm for ^{13}C NMR). MALDI TOF MS was analyzed on a Bruker Microflex LRF with no matrix. High resolution mass spectra (HRMS) were recorded using ESI as the ionization method. Solution UV-Vis was recorded on an Agilent Carey 60 UV-Vis spectrophotometer. Cyclic voltammetry (CV) measurements were performed in DCM on a BASi Epsilon Potentiostat with a three-electrode cell, using 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as supporting electrolyte, AgCl/Ag^+ as reference electrode, glassy carbon as working electrode, Pt wire as counter electrode, with scan rate at 100 mV/s. EPR measurements were done using a Bruker EMX Plus x-band instrument with a working microwave frequency of 9.7 GHz. Compound **1**, 1,4-antraquinone, and NODIPS-acetylene were synthesized according to literature procedures.¹⁻³



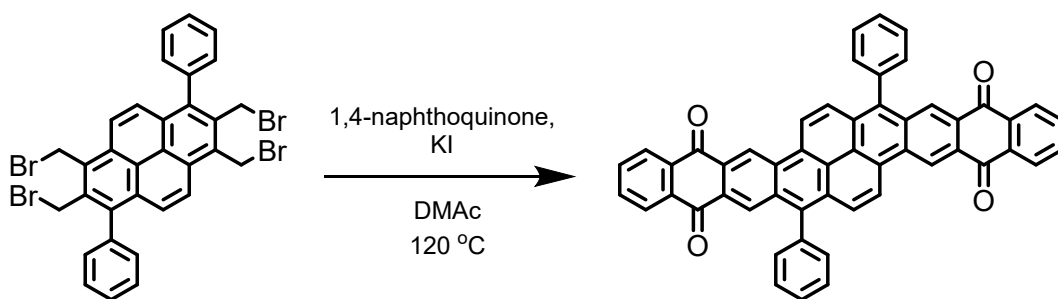
1,6-Diphenylpyrene-2,3,7,8-tetraethyloate (2): A 250 ml RB flask was charged with **3** (4.50 g, 9.11 mmol), bromoethane (19.8 g, 182 mmol, 20 eq.), ethanol (15.9 ml, 273 mmol, 30 eq.), DBU (13.6 ml, 91.1 mmol, 10 eq.), and DMF (70 ml). The flask was outfitted with a condenser, and the mixture was stirred at 75 °C for 16 hours. The mixture was poured into water (200 ml), extracted into ethyl acetate, and washed again with water (100 ml). The organic layer was dried with magnesium sulfate, and then flushed through a silica plug (ethyl acetate). The solvent was removed to give the product as a yellow solid. Yield: 5.44 g, 93%. m.p. 295 °C. ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS, ppm): δ 8.49 (d, $J = 9.6$ Hz, 2H), 8.01 (d, $J = 9.6$ Hz, 2H), 7.55 (m, 6H), 7.49 (m, 4H), 4.52 (q, $J = 7.2$ Hz, 4H), 4.06 (q, $J = 7.2$ Hz, 4H), 1.44 (t, $J = 7.2$ Hz, 6H), 0.98 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3 , 25 °C, TMS, ppm): 168.5, 167.7, 137.7, 136.4, 132.4, 131.1, 130.6, 128.3, 128.1, 127.5, 126.7, 126.3, 124.4, 62.3, 61.6, 14.1, 13.6. HRMS (TOF MS ESI⁻) for $[\text{M}]^-$: calc. for $\text{C}_{40}\text{H}_{34}\text{O}_8$: 642.2254, found: 642.2247.



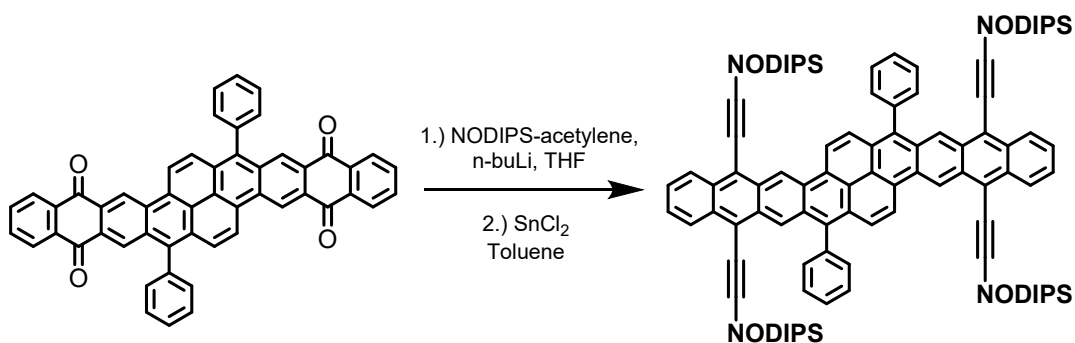
1,6-Diphenylpyrene-2,3,7,8-tetramethanol (3): A flame-dried 250 ml RB flask under N_2 was charged with **4** (4.00 g, 6.23 mmol), anhydrous THF (40 ml), and methanol (4.03 ml, 99.8 mmol, 16 eq.). 4M lithium borohydride in THF (24.9 ml, 99.8 mmol, 16 eq.) was added slowly at room temperature, and the mixture was then heated to $60\text{ }^\circ\text{C}$ and stirred for 16 hours. The flask was allowed to cool to room temperature, at which point the mixture was quenched with dropwise additions of water (10 ml) and 10% HCl (10 ml) until foaming ceased. The mixture was then poured into 100 ml of water and then filtered. The crude product was taken up in acetone (150 ml), triturated, and then filtered to give the product as a pale-yellow powder. The crude product was taken to the next step without further purification. Yield: 2.40 g, 81%. MS (MALDI TOF) calc. for $\text{C}_{32}\text{H}_{22}\text{O}_4$: 474.1833 $[\text{M}]^+$, found: 474.2643.



1,6-Diphenylpyrene-2,3,7,8-tetrabromomethyl (4): To a 250 ml flame-dried RB flask under N_2 was added anhydrous DMF (40 ml) and **3** (2.40 g, 5.05 mmol). 1M PBr_3 (30.3 ml, 30.3 mmol, 6 eq.) in DCM was then added, and the mixture was stirred for 14 hours, during which time a precipitate formed. The reaction was quenched slowly with water (20 ml) and 10% HCl (20 ml), and the mixture was then poured in 100 ml MeOH, triturated, and then filtered. The filtrate was then taken up in acetone, triturated, and then filtered, and the product was recovered as a yellow solid. The crude product was taken to the next step without further purification. Yield: 2.70 g, 77%. MS (MALDI TOF) calc. for $\text{C}_{32}\text{H}_{22}\text{Br}_4$: 642.927 $[\text{M}-\text{Br}]^+$, found: 642.822.

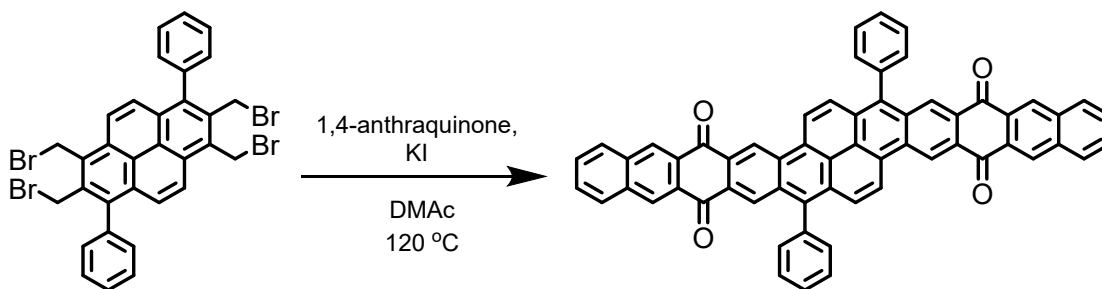


Diphenylbis(pentacene)quinone (BP-Q): A 150 ml sealed tube reactor was charged with N,N-dimethylacetamide (50 ml), **6** (1.00 g, 1.38 mmol), 1,4-naphthoquinone (0.872 g, 5.52 mmol, 4 eq.), and potassium iodide (1.74 g, 10.5 mmol, 8 eq.). The tube was sealed, and the mixture was then stirred at 120 °C for 2 days. The tube was allowed to cool to room temperature, unsealed, and the mixture was stirred open to air for 2 hours. The mixture was then poured into 500 ml of water and filtered. The crude filtrate was taken up in 250 ml acetone, sonicated for 10 minutes, and then filtered. The filtrate was then added to 250 ml THF, sonicated for 10 minutes, and then filtered. The crude product was collected as a black solid and was used without further purification. Yield: 0.611 g, 64%.

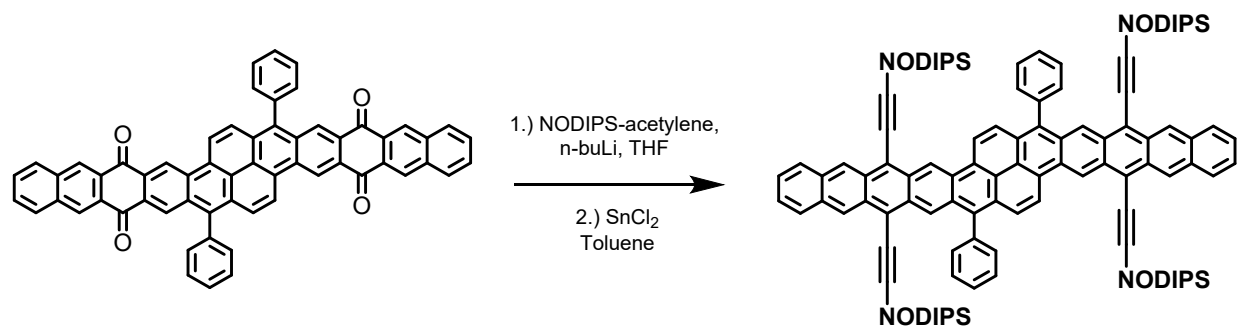


NODIPS-BP: A flame-dried 100 ml RB flask under N₂ was charged with 20 ml anhydrous THF and NODIPS-acetylene (1.37 g, 5.40 mmol, 13 eq.). The flask was cooled to 0 °C, and then 2.5 M n-butyllithium in hexanes (1.99 ml, 4.98 mmol, 12 eq.) was added slowly and the mixture was stirred for 30 minutes. **BP-Q** (0.300 g, 0.415 mmol) was then added, and the mixture was stirred for 16 hours. The reaction was quenched with water (20 ml) and 10% HCl (5 ml), and the organic layer was extracted into diethyl ether, dried with magnesium sulfate, and the solvent removed. The crude, viscous oil was purified on a silica plug in 5:1 hexanes:ethyl acetate to give a red oil, which was carried directly to the next step. The oil was dissolved in toluene (20 ml) and added to a 100 ml RB flask along with 0.750 g tin (II) chloride hydrate and the mixture was stirred for 30 minutes. The

reaction was quenched with water (20 ml) and the organic layer was extracted into diethyl ether, dried with magnesium sulfate, and the solvent removed. The crude product was purified by column chromatography in 6:1 hexanes:DCM to give the product as a dark green solid. Yield: 0.24 g, 34%. $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25 °C, TMS, ppm): δ 10.94 (s, 2H), 9.39 (s, 2H), 9.05 (d, $J = 10$ Hz, 2H), 8.66 (dd, $J = 10.4, 7.6$ Hz, 4H), 7.90 (d, $J = 9.6$ Hz, 2H), 7.68 (m, 10H), 7.54 (m, 4H), 1.75 (q, $J = 7.6$ Hz, 8H), 1.46 (p, $J = 7.6$ Hz, 8H), 1.36 (m, 48H), 1.29 (m, 8H), 1.23 (m, 8H), 1.16 (m, 16H), 0.98 (t, $J = 7.6$ Hz, 8H), 0.84 (t, $J = 6.8$ Hz, 8H), 0.77 (m, 8H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3 , 25 °C, TMS, ppm): 139.1, 136.6, 133.1, 132.8, 131.6, 130.4, 129.64, 129.55, 128.8, 127.9, 127.7, 127.6, 127.5, 127.3, 126.7, 126.5, 125.0, 123.0, 122.2, 118.7, 118.7, 106.8, 106.6, 104.1, 103.3, 34.0, 33.9, 32.00, 31.95, 29.4, 29.3, 29.2, 24.7, 22.70, 22.67, 18.8, 18.7, 18.5, 18.4, 14.1, 12.1, 11.8, 10.5, 10.20. HRMS (TOF MS ESI) calc. for $\text{C}_{116}\text{H}_{150}\text{Si}_4$: 1655.0815 [M] $^-$, found: 1655.0804.



Diphenylbishexacenequinone (BH-Q): A 150 ml sealed tube reactor was charged with **6** (1.00 g, 1.38 mmol), 1,4-anthraquinone (1.14 g, 5.52 mmol), potassium iodide (1.83 g, 11.0 mmol), and N,N-dimethylacetamide (50 ml) and the tube was sealed. The mixture was then stirred at 120 °C for 2 days. The tube was allowed to cool to room temperature, unsealed, and the mixture was allowed to stir open to air for 2 hours. The mixture was then poured into 500 ml of water and filtered. The crude filtrate was taken up in 250 ml acetone, sonicated for 10 minutes, and then filtered. The filtrate was then added to 250 ml THF, sonicated for 10 minutes, and then filtered. The crude product was collected as a black solid and was used without further purification. Yield: 0.58 g, 51%.



NODIPS-BH: A flame-dried 50 ml RB flask under N₂ was charged with 20 ml anhydrous THF and NODIPS-acetylene (1.86 g, 7.36 mmol, 20 eq.). The flask was cooled to 0 °C, and then 2.5 M n-butyllithium in hexanes (2.80 ml, 6.99 mmol, 19 eq.) was added slowly and the mixture was stirred for 30 minutes. **BH-Q** (0.300 g, 0.368 mmol) was then added, and the mixture was stirred for 16 hours. The reaction was quenched with water (10 ml) and the organic layer was extracted into diethyl ether (50 ml), dried with magnesium sulfate, and the solvent removed. The crude, viscous oil was purified on a silica plug in 7:1 hexanes:ethyl acetate to give a red oil, which was carried directly to the next step. The oil was dissolved in toluene (25 ml) and added to a 100 ml RB flask along with 0.50 g tin (II) chloride hydrate, and the mixture was stirred for 1 hour. The reaction was quenched with water (50 ml) and the organic layer was extracted into diethyl ether (50 ml), dried with magnesium sulfate, and the solvent removed. The crude product was purified by column chromatography in 6:1 hexanes:DCM to give the product as a dark purple solid. Yield: 98 mg, 15%. ¹H NMR (400 MHz, CDCl₃, -15 °C, TMS, ppm): δ 10.42 (s, 2H), 9.36 (s, 2H), 9.32 (s, 2H), 8.96 (d, *J* = 10 Hz, 2H), 8.01 (m, 4H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.75 (m, 10H), 7.45 (m, 4H), 1.84 (m, 4H), 1.62 (q, *J* = 8 Hz, 4H), 1.59 (m, 8H), 1.52 (m, 40H), 1.22 (m, 48H), 1.02 (m, 4H), 0.85 (m, 16H). HRMS (TOF MS ESI⁻) calc. for C₁₂₄H₁₅₄Si₄: 1755.1128 [M]⁻, found: 1755.1125.

Optical and Electrochemical data, Emission, and EPR Spectra

Table S1: Experimental optical and electrochemical properties for NODIPS-BP and NODIPS-BH.

Compound	λ_{\max}^a (nm)	λ_{onset}^a (eV)	ϵ^a ($\text{M}^{-1}\text{cm}^{-1}$)	E_{ox1}^b (eV)	E_{ox2}^b (eV)	E_{red1}^b (eV)	E_{red2}^b (eV)
NODIPS-BP	774	1.60	38,100	0.139	0.593	-1.44	-1.62
NODIPS-BH	885	1.40	37,400	0.0370	0.418	-1.29	-1.43

^aRecorded in CHCl_3 (6×10^{-6} M). ^b Measured in DCM (3×10^{-3} M) vs. Fc/Fc^+ using 0.1 M $n\text{-Bu}_4\text{NPF}_6$ as supporting electrolyte, AgCl/Ag^+ as reference electrode, glassy carbon as working electrode, Pt wire as counter electrode, with scan rate at 100 mV/s.

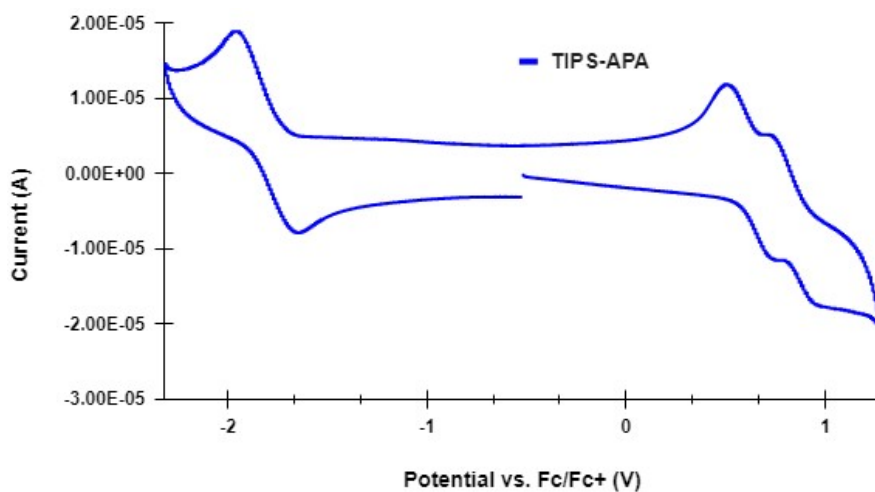


Figure S1: Normalized emission spectra of NODIPS-BP ($10 \mu\text{M}$ in CHCl_3) and NODIPS-BH ($30 \mu\text{M}$ in toluene).

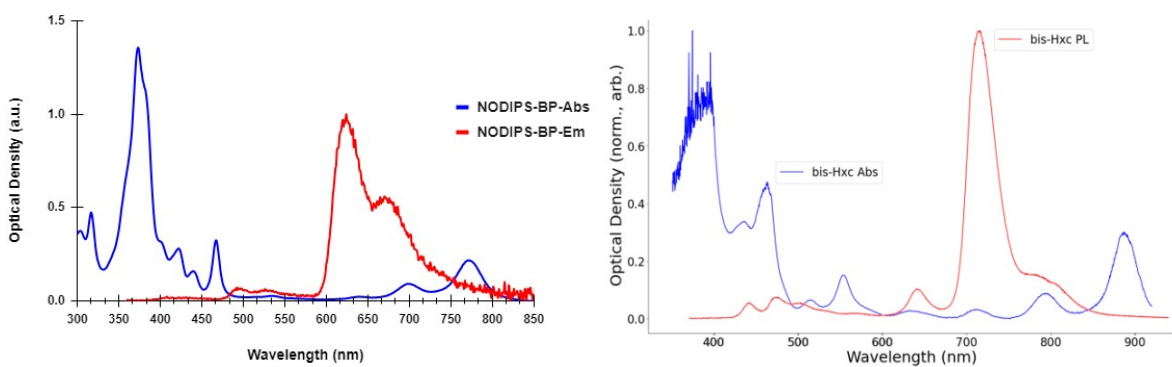


Figure S2: Normalized emission spectra of NODIPS-BP (10 μM in CHCl_3) and NODIPS-BH (30 μM in toluene).

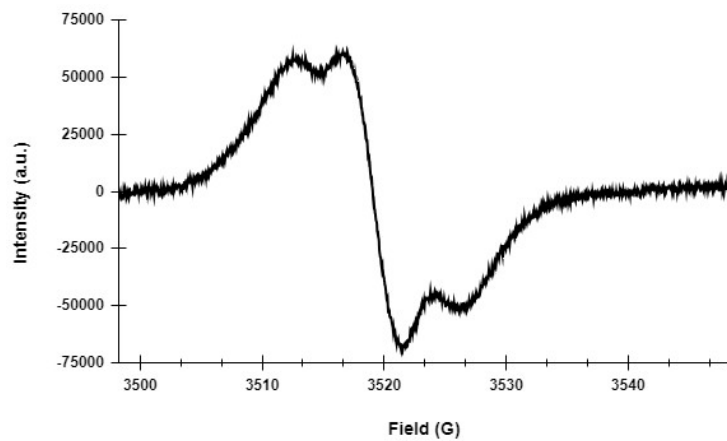


Figure S3: EPR spectrum of **NODIPS-BH** powder at r.t. ($g = 2.0048$)

Stability Experiments

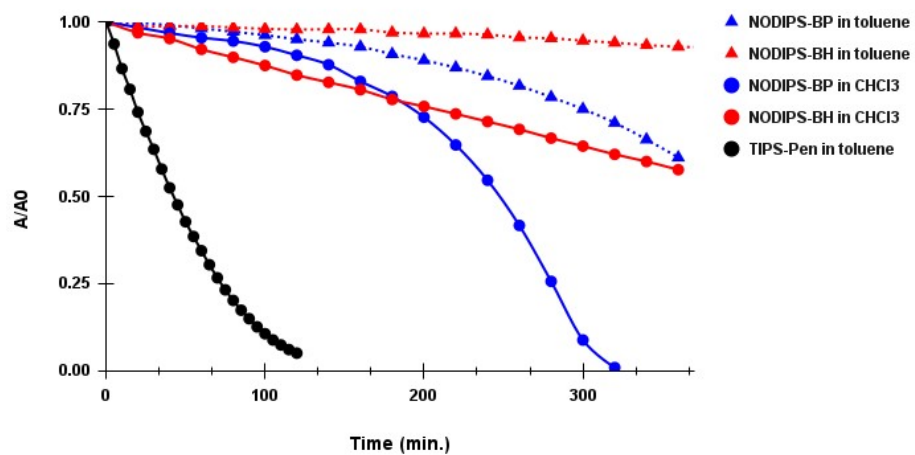


Figure S4: Solution stability experiments, where onset absorbance normalized at $t=0$ is monitored over time under exposure to 150-watt white light source.

Variable-temperature NMR

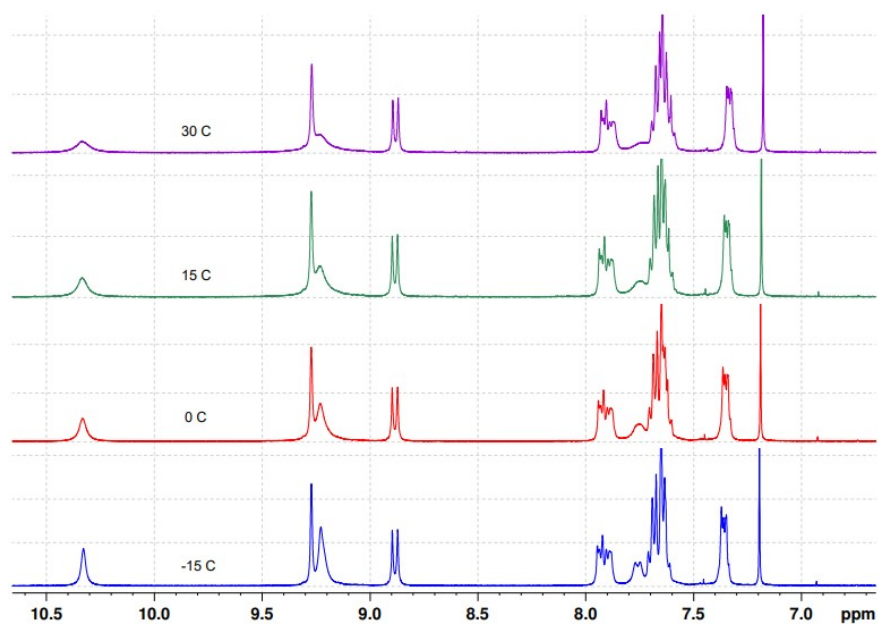
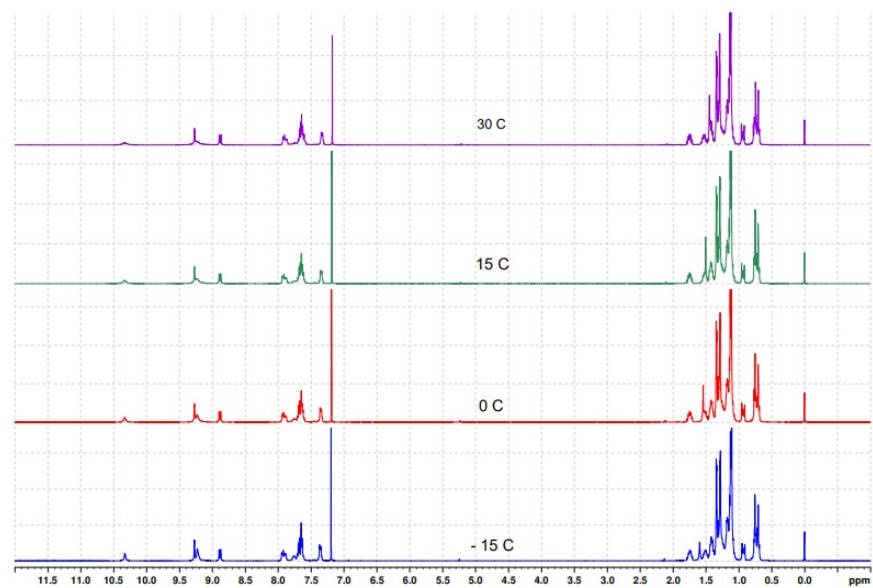


Figure S5: Variable temperature ^1H NMR spectrum of **NODIPS-BH**.

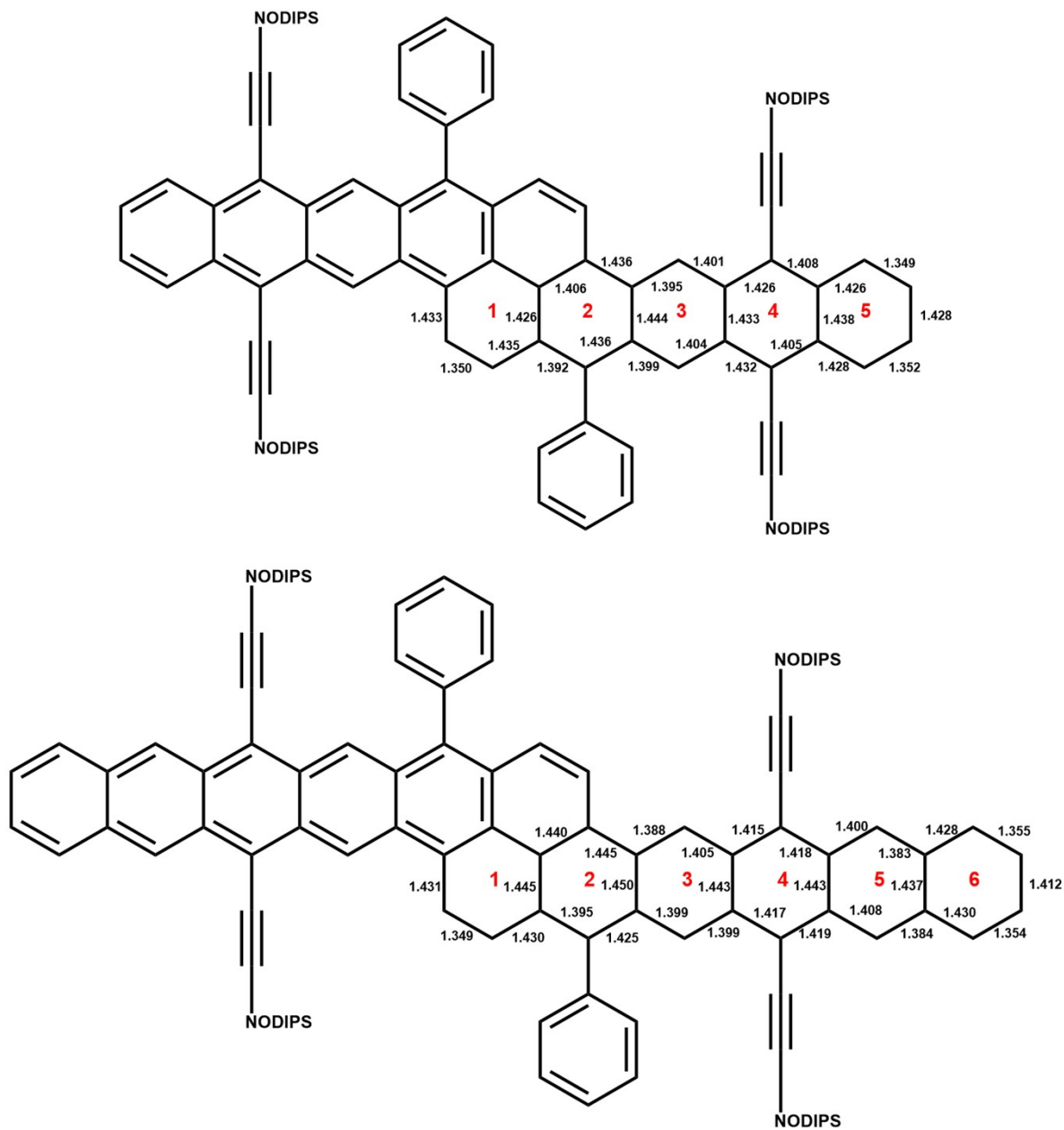


Figure S6: Experimental bond lengths for NODIPS-BP (top) and NODIPS-BH obtained from XRD of single crystals.

Computational Details

All density functional theory calculations were carried out using Gaussian 16 Rev A.03.⁴

For optoelectronic properties, a bespoke ω B97XD range separated functional was employed.⁵ Initial geometry optimization was performed using ω B97XD/6-31G* with CHCl₃ polarizable continuum (PCM) and with range-separation parameter ω set to a ball-park value of 0.1 Bohr⁻¹. Upon obtaining a minimum energy structure, the optimal ω value was determined to best fit Koopmans' theorem (IP and ϵ HOMO are equal magnitude but opposite sign) in the gas phase. This value of ω was then used in single point and time-dependent calculations to determine optoelectronic properties. Different ω values were obtained for each distinct chemical species.

For reactions energies, the hybrid M06-2X functional was used in place of a range separated functional due to its reliable employment for thermochemistry. For each endoperoxide, the two C-O bond lengths were varied by 0.1Å and geometry optimization was performed for each step, resulting in a potential energy surface for the formation / breaking of the endoperoxide bonds in a similar manner to previous work.⁶ The minimum energy structures of this PES were further relaxed without any bond length constraints, while extra structures were generated around the maximum transition state using 0.01Å increments. Reaction energies were calculated by comparing energies of the minima, and the activation energies calculated comparing energies of starting materials and the maximum of the PES.

Diradical character was calculated using unrestricted Hartree-Fock and examining partial occupation of frontier orbitals using Yamaguchi's formula.⁷

Comment [KT]: Reference:

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, V. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16, Revision A.03*, Gaussian, Inc., Wallingford CT, 2016

Comment [KT]:

dx.doi.org/10.1039/c8tc06000b

Comment [KT]:

dx.doi.org/10.1039/D2TC02922G

Comment [KT]:

[dx.doi.org/10.1016/0009-2614\(75\)80169-2](https://dx.doi.org/10.1016/0009-2614(75)80169-2)

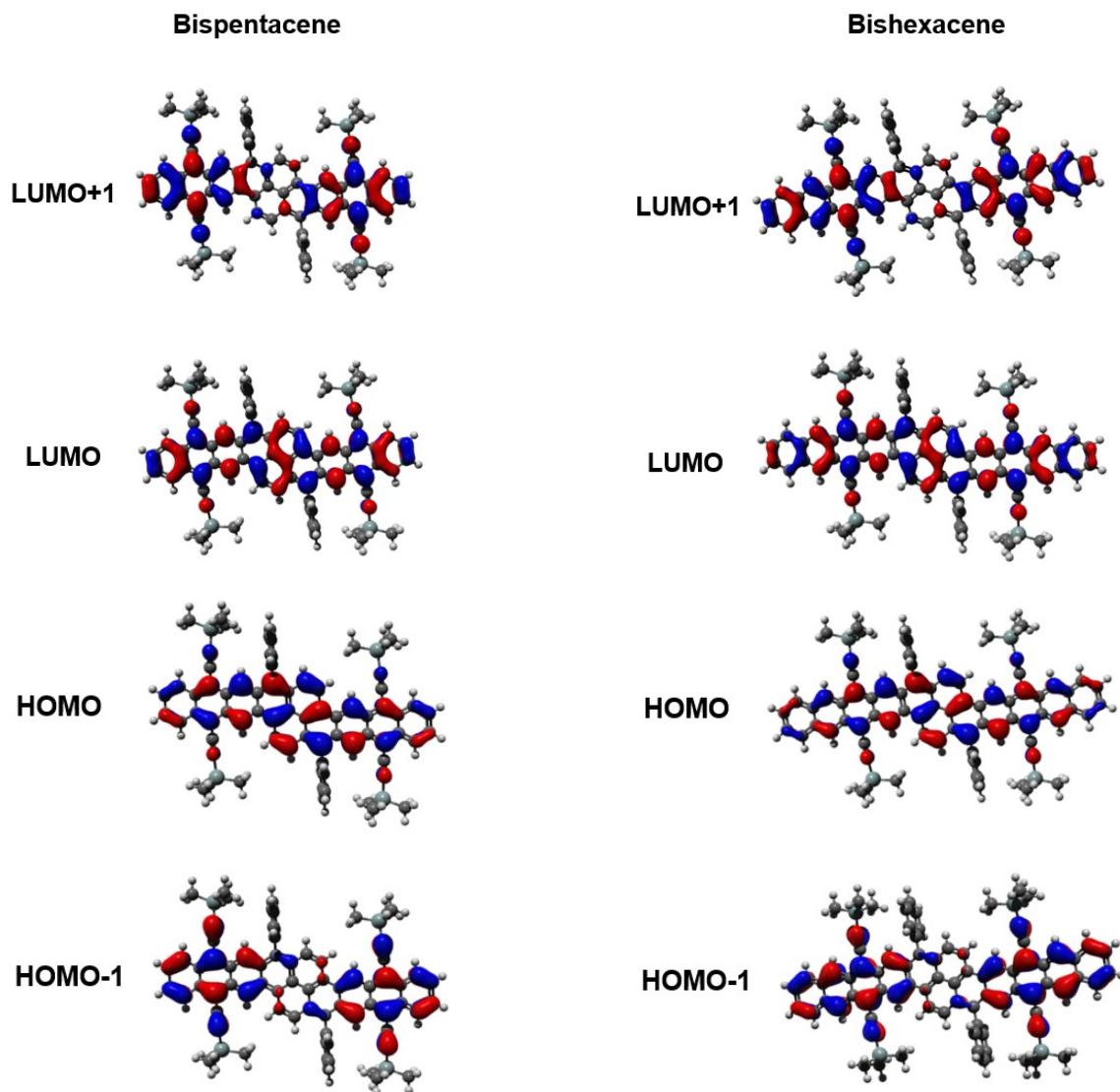


Figure S7: Frontier molecular orbitals for **BP** and **BH**.

Table S2: Energy level calculations for bispentacene (**BP**) and bisHexacene (**BH**).

	BP (eV)	BH (eV)
HOMO	-5.53	-5.33
HOMO-1	-6.17	-5.84
HOMO-2	-6.76	-6.48
HOMO-3	-7.46	-7.30

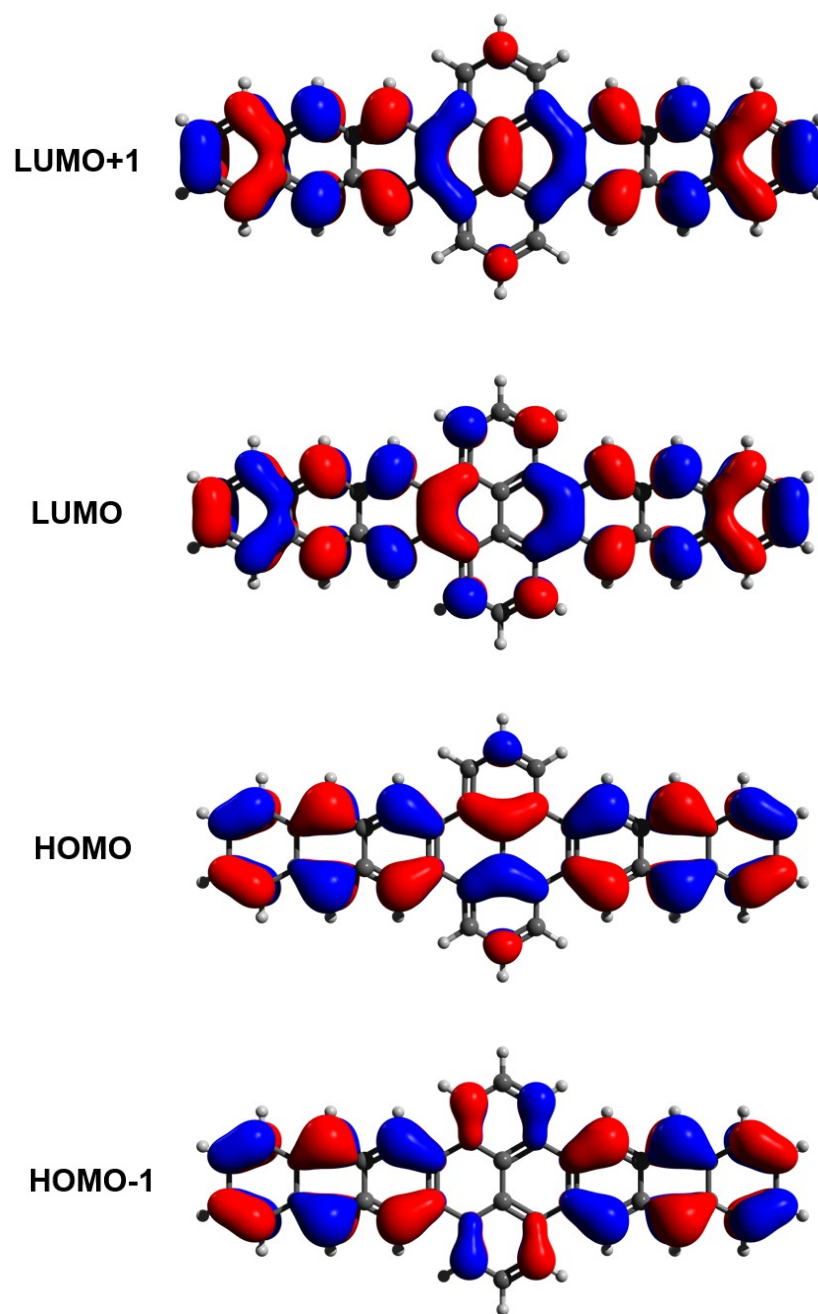


Figure S8: Frontier molecular orbitals for **APA**.

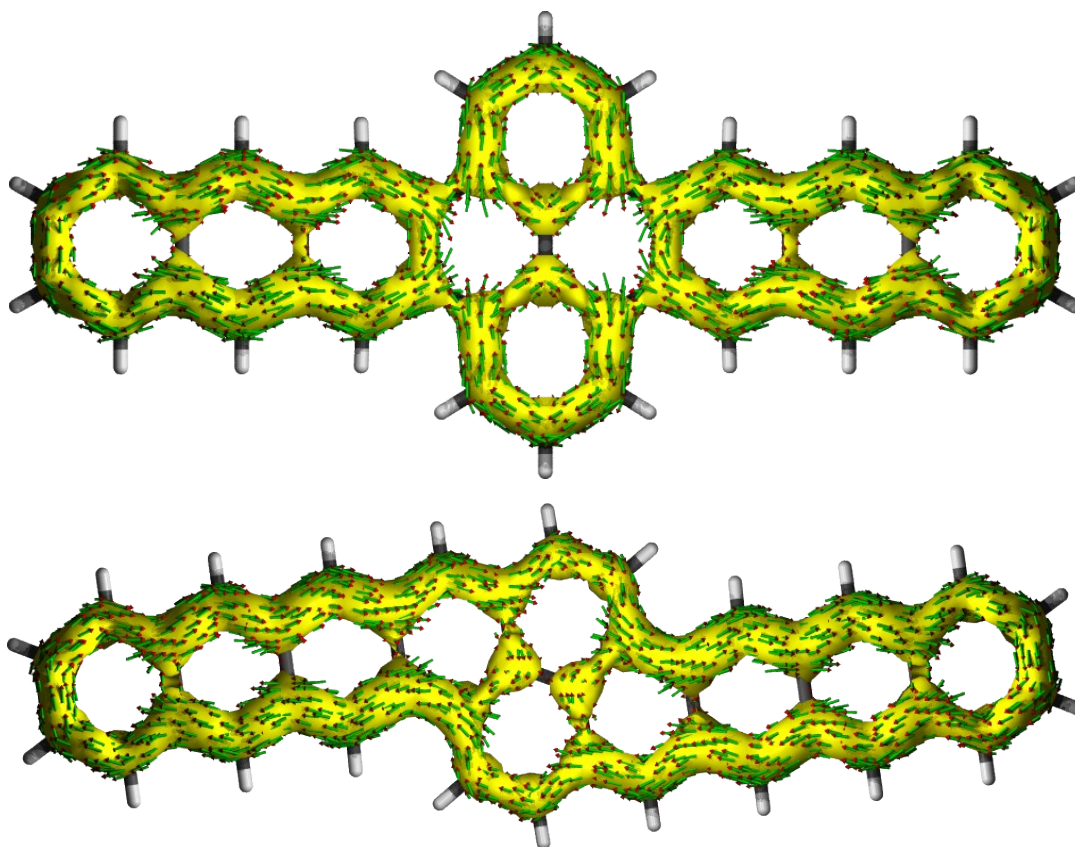
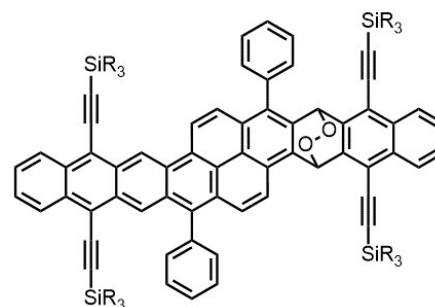


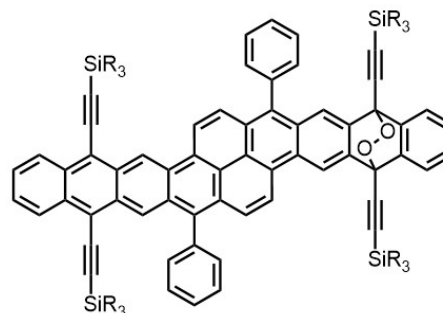
Figure S9: ACID plots for Vertical (top) and oblique (bottom) pyrene derivatives with 10 consecutively fused rings.

Bisacene-endoperoxide Electronic Calculations

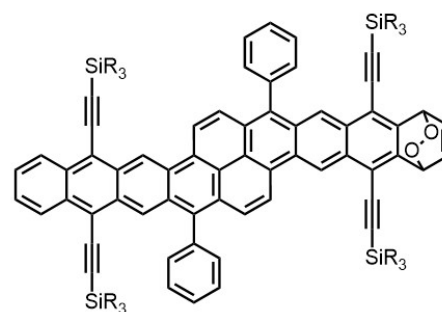
S_1 (eV)	S_1 (nm)	f_{S_1}	T_1 (eV)	T_1 (nm)
2.08	597	0.37	1.20	1031
2.82	440	0.33	1.94	638
2.97	417	0.18	2.48	500
3.27	379	0.03	2.79	445
3.43	361	0.34	2.88	430
3.52	352	0.27	3.11	399
3.63	342	2.20	3.24	383
3.78	328	0.10	3.38	366
3.83	324	0.22	3.40	364
3.87	320	0.02	3.47	357



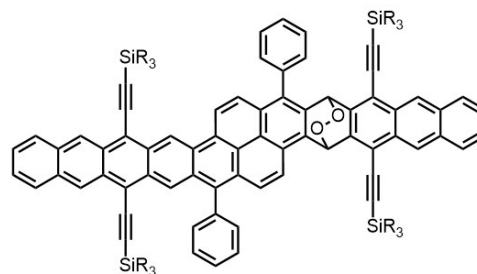
S_1 (eV)	S_1 (nm)	f_{S_1}	T_1 (eV)	T_1 (nm)
1.89	656	0.38	1.06	1168
2.50	496	0.00	1.69	734
2.61	475	0.25	2.20	563
2.79	445	0.09	2.21	562
3.14	395	0.01	2.50	496
3.42	362	0.00	2.57	483
3.51	354	2.24	2.77	447
3.57	347	0.28	2.90	428
3.65	340	0.45	3.07	404
3.65	340	0.32	3.34	372



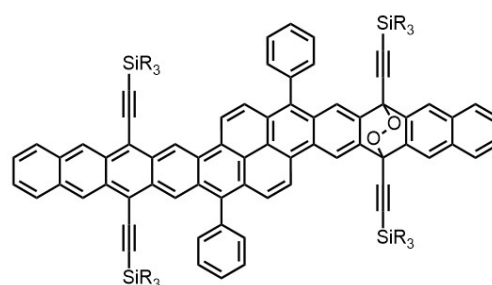
S_1 (eV)	S_1 (nm)	f_{S_1}	T_1 (eV)	T_1 (nm)
1.76	705	0.40	0.97	1283
2.34	530	0.09	1.47	843
2.60	477	0.04	2.05	605
2.95	421	0.22	2.53	490
2.99	414	0.17	2.67	464
3.25	382	0.13	2.87	431
3.44	360	2.61	2.89	429
3.50	354	0.05	3.17	392
3.59	345	0.99	3.22	385
3.64	340	0.25	3.29	377



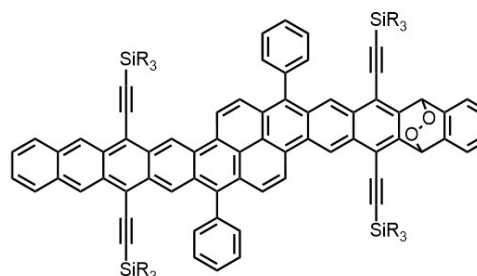
S_1 (eV)	S_1 (nm)	f_{S_1}	T_1 (eV)	T_1 (nm)
1.71	724	0.27	0.85	1461
2.50	495	0.28	1.74	711
2.75	450	0.11	1.98	627
2.92	425	0.28	2.39	520
3.04	408	0.13	2.65	468
3.18	390	0.31	2.79	444
3.26	380	0.11	2.92	425
3.34	371	0.06	2.97	417
3.44	360	2.35	3.01	412
3.58	347	0.03	3.15	394



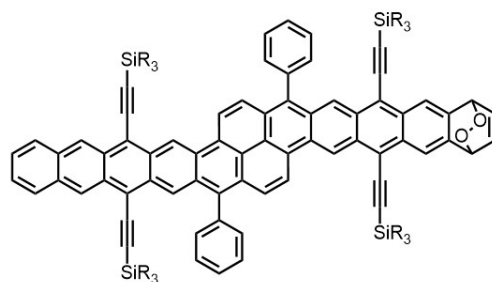
S_1 (eV)	S_1 (nm)	f_{S_1}	T_1 (eV)	T_1 (nm)
1.58	784	0.28	0.75	1650
2.30	539	0.19	1.50	829
2.59	479	0.12	2.26	549
3.00	413	0.12	2.50	495
3.14	394	0.10	2.66	466
3.35	370	1.04	2.81	440
3.42	363	1.83	2.95	420
3.50	354	0.71	3.13	397
3.60	344	0.34	3.23	384
3.68	337	0.32	3.27	379



S_1 (eV)	S_1 (nm)	f_{S_1}	T_1 (eV)	T_1 (nm)
1.49	834	0.30	0.69	1794
2.09	593	0.15	1.28	969
2.32	534	0.03	1.90	652
2.75	450	0.15	2.29	542
2.89	429	0.03	2.37	524
3.02	410	0.32	2.63	471
3.20	388	0.25	2.79	445
3.25	381	1.77	2.81	441
3.36	369	0.20	3.02	411
3.45	359	2.35	3.08	403



S_1 (eV)	S_1 (nm)	f_{S_1}	T_1 (eV)	T_1 (nm)
1.40	889	0.32	0.64	1939
1.83	679	0.05	1.03	1209
2.13	582	0.02	1.52	818
2.40	518	0.24	2.07	600
2.63	472	0.01	2.24	555
2.93	423	0.38	2.49	498
3.00	414	0.26	2.57	483
3.02	410	0.59	2.69	461
3.21	386	0.12	2.84	436
3.23	384	0.10	2.95	421



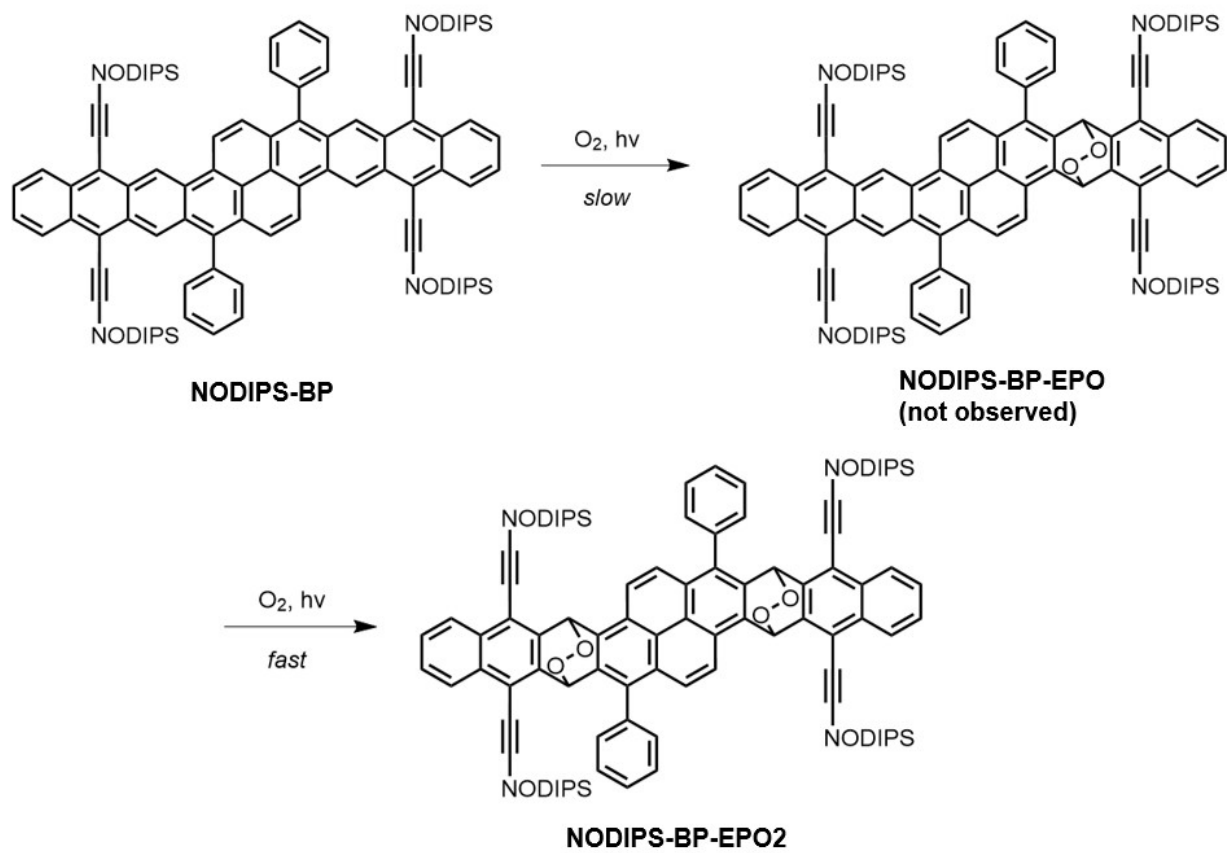
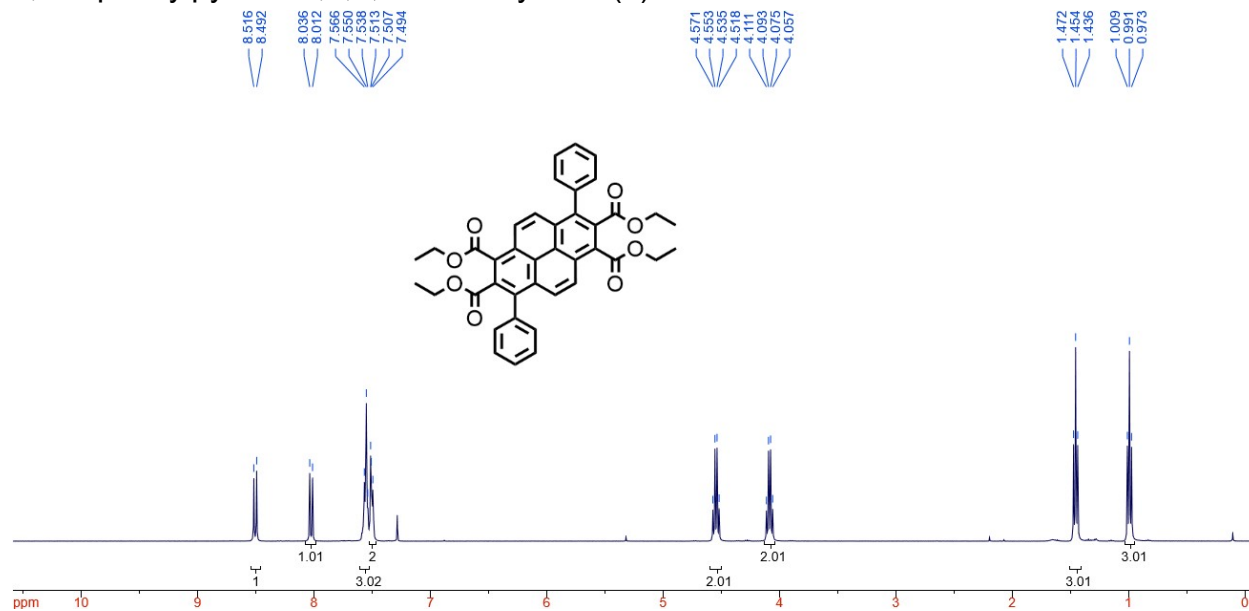


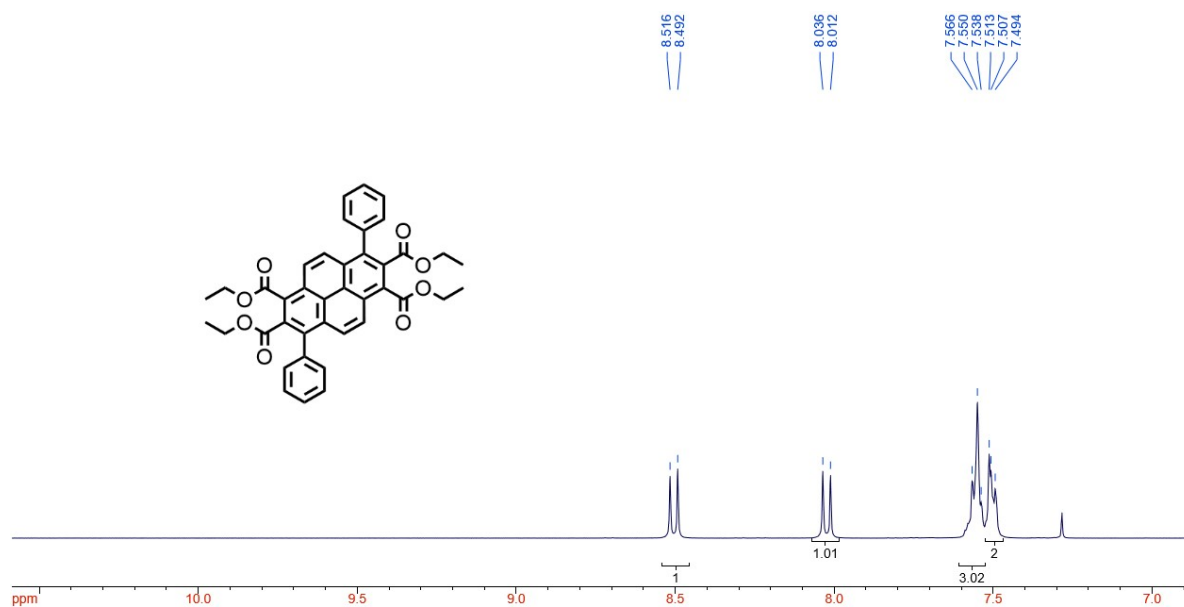
Figure S10: Proposed decomposition pathway for **NODIPS-BP**.

NMR Spectra

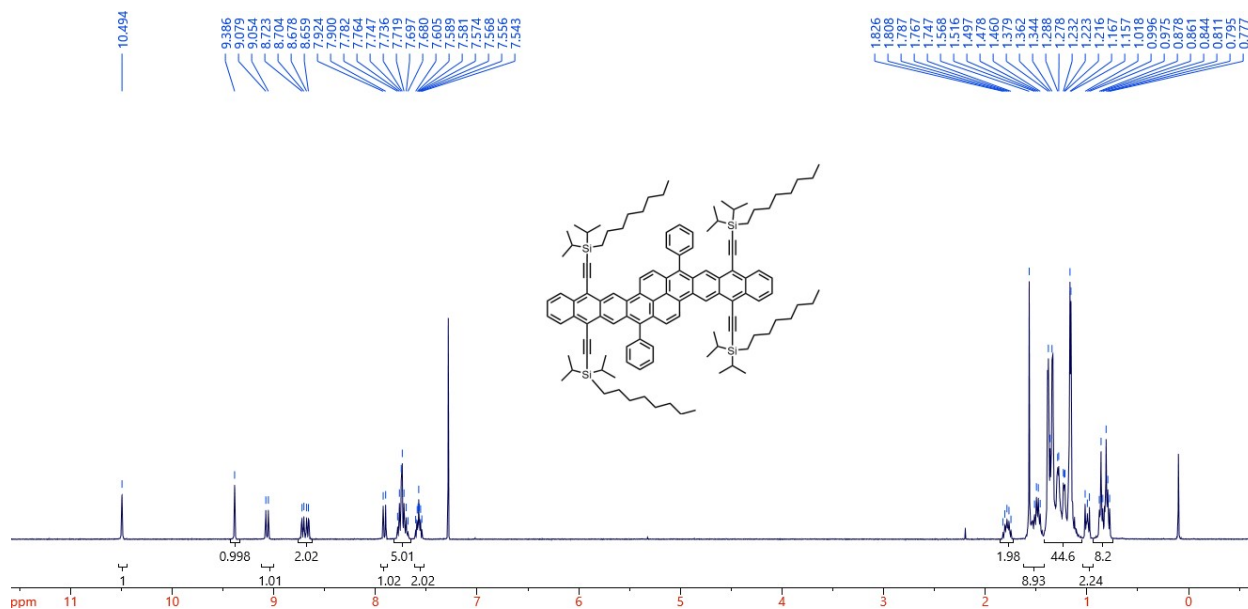
1,6-Diphenylpyrene-2,3,7,8-tetraethylate (2) ¹H NMR



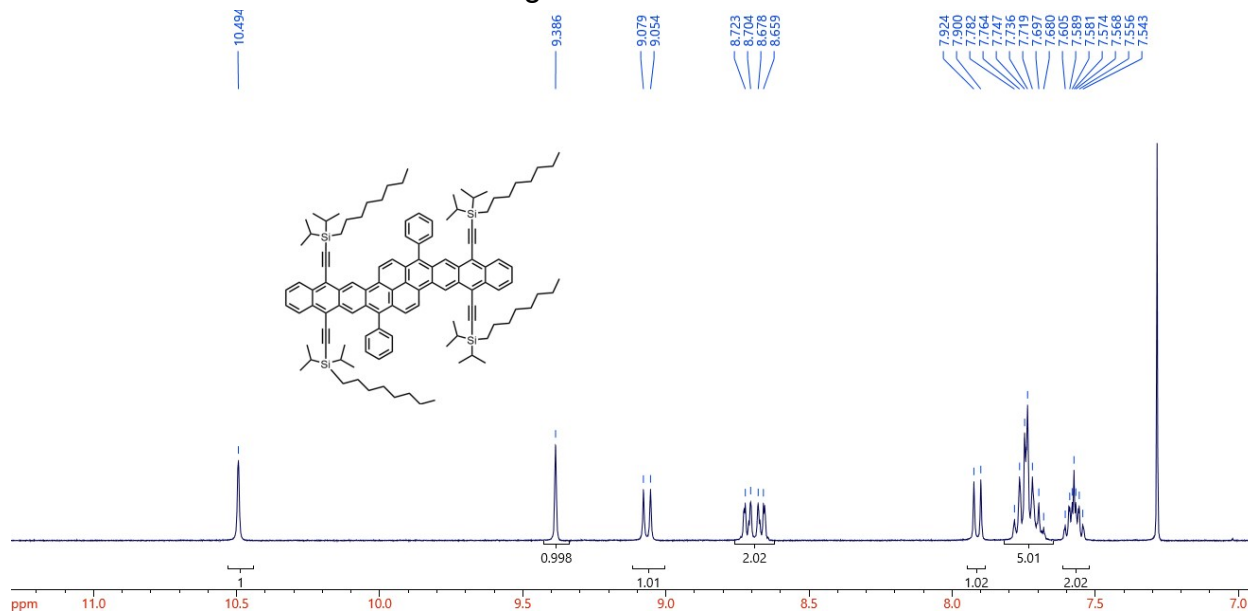
1,6-Diphenylpyrene-2,3,7,8-tetraethylate (2) ¹H NMR – Aromatic Region



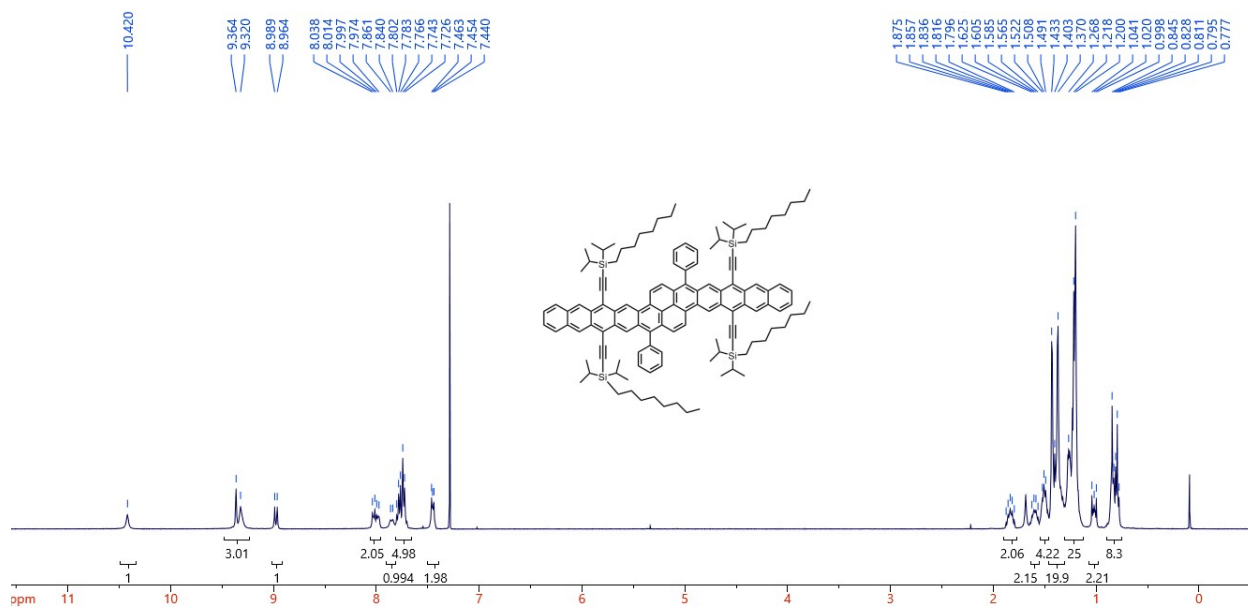
NODIPS-BP ¹H NMR



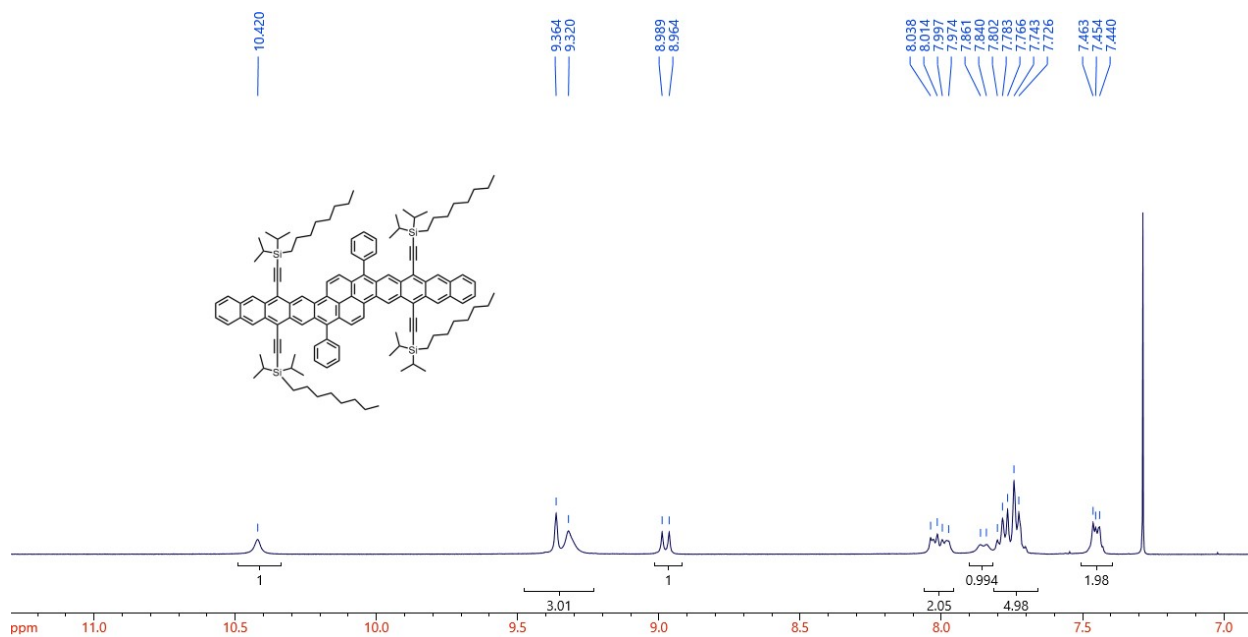
NODIPS-BP ¹H NMR – Aromatic Region



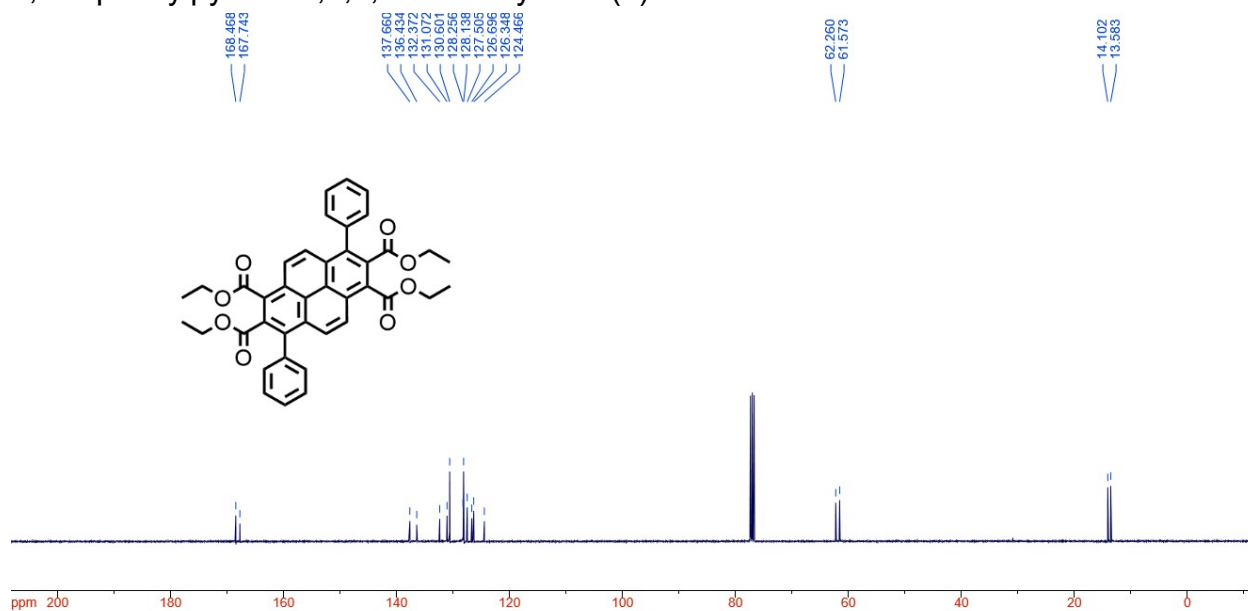
NODIPS-BH ¹H NMR



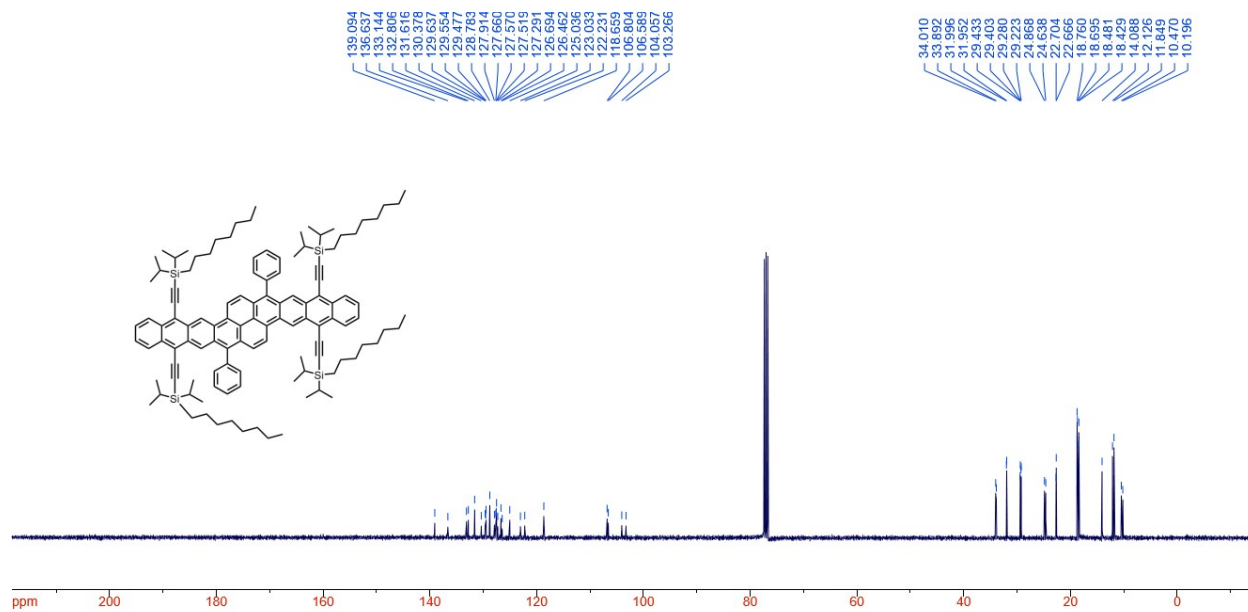
NODIPS-BH ¹H NMR – Aromatic Region



1,6-Diphenylpyrene-2,3,7,8-tetraethylate ¹³C NMR



NODIPS-BP ¹³C NMR



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