Supporting Information

for

Synthesis of Stable Nanographenes with OBO-Doped Zigzag Edges Based on Tandem Demethylation-Electrophilic Borylation

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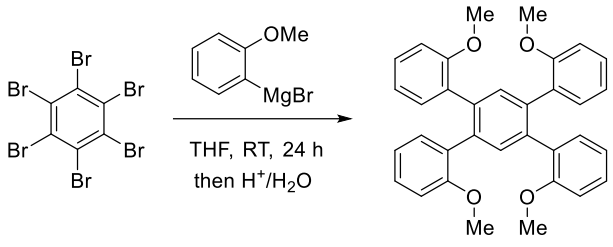
1. Experimental Section

General. All commercially available chemicals were used without further purification unless otherwise noted. Column chromatography was done with silica gel (particle size 0.063-0.200 mm) and thin layer chromatography (TLC) was performed on silica gel-coated aluminum sheets with F254 indicator. All yields given refer to isolated yields. Nuclear Magnetic Resonance (NMR) spectra were recorded on AVANCE 300 MHz, AVANCE 500 MHz, or AVANCE 700 MHz Bruker spectrometers. Chemical shifts were reported in ppm. Coupling constants (*J* values) were reported in Hertz. ^{1}H NMR chemical shifts were referenced to CD_2Cl_2 (5.320 ppm) or $C_2D_2Cl_4$ (6.000 ppm). ^{13}C NMR chemical shifts were referenced to CD_2Cl_2 (54.00 ppm), $C_2D_2Cl_4$ (73.78 ppm). The attached proton test (APT) technique of ^{13}C NMR was used to distinguish the carbon atoms with even or odd number of attached protons. The APT experiment gave methine (CH) and methyl (CH_3) signals in the upper phase and quaternary (C) and methylene (CH_2) signals in the opposite phase. ^{11}B NMR chemical shifts were referenced to the external standard boron signal of $BF_3{\cdot}Et_2O$ (0 ppm). High-resolution mass spectrometry (HRMS) was performed either on a Q-Tof Ultima 3 (micromass/Waters) by electrospray ionization (ESI) or on a SYNAPT G2 Si high resolution time-of-flight mass spectrometer (Waters Corp., Manchester, UK) by matrix-assisted laser desorption/ionization (MALDI). Melting points were measured with a Büchi B-545 apparatus.

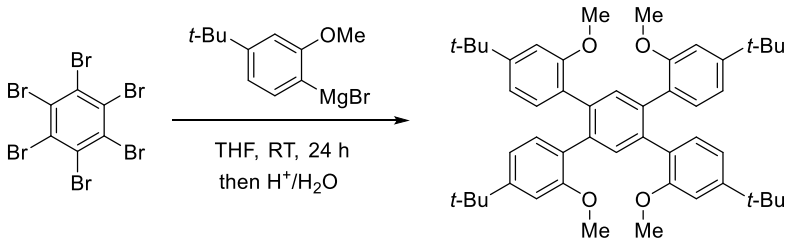
Absorption spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer. Photoluminescence spectra were recorded on a J&MTIDAS spectrofluorometer. The quantum yield was measured with 9,10-diphenylanthracene (in toluene under air, Φ_F: 0.70) as a reference.[1] Cyclic voltammetry (CV) was performed on a WaveDriver 20 Bipotentiostat/Galvanostat (Pine Instruments Company) and measurements were carried out in dichloromethane or tetrachloroethane containing 0.1 M *n*-Bu_4NPF_6 as supporting electrolyte (scan rate: 100 mV s^{-1}.). Glassy carbon electrode was used as a working electrode, a platinum wire as a counter electrode and a silver wire as a reference electrode.

Synthetic Procedures.



6a

1,2,4,5-tetra(2-methoxyphenyl)benzene (6a). To a Schlenk flask charged with hexabromobenzene (5.52 g, 10.0 mmol) was added a solution of (2-methoxyphenyl)magnesium bromide (1.0 M, 80 mL, 80 mmol) in THF under argon. The mixture was stirred at room temperature for 24 h and then quenched with ice-containing dilute hydrochloric acid. The mixture was then extracted with chloroform for three times. The combined organic layers were washed with brine and water and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography over silica gel (eluent: hexane/CH_2Cl_2 = 1 : 1) to give the product, which was further washed with hexane and a little amount of toluene (3 mL) to afford 1.61 g (32%) of compound **6a** as a white solid. M.p.: 268.1 – 269.7 °C. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K, ppm) δ 7.35 (s, 2H), 7.23 – 7.11 (m, 8H), 6.84 (t, J = 7.4 Hz, 4H), 6.74 (d, J = 8.3 Hz, 4H), 3.52 (s, 12H); ^{13}C NMR (175 MHz, CD_2Cl_2, 298 K, ppm) δ 156.9, 137.8, 133.2, 132.0, 131.2, 128.7, 120.3, 110.6, 55.4; HRMS (ESI) *m/z*: Calcd for $C_{34}H_{30}O_4Na$: 525.2042; Found: 525.2048 $[M + Na]^+$.

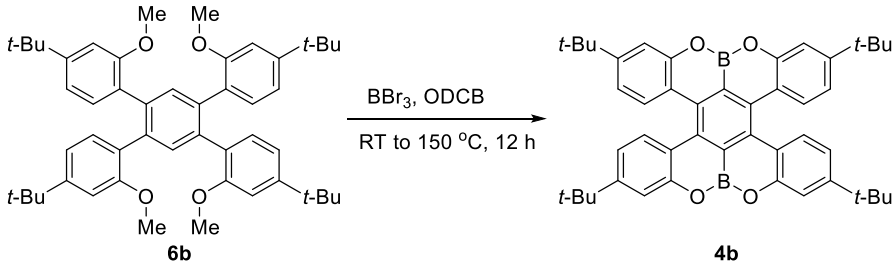


6b

1,2,4,5-tetra(4-(*tert*-butyl)-2-methoxyphenyl)benzene (6b). To a Schlenk flask charged with hexabromobenzene (1.65 g, 3.00 mmol) was added a solution of (4-(*tert*-butyl)-2-methoxyphenyl)magnesium bromide[2] (1.0 M, 24 mL, 24 mmol) in THF under argon. The mixture was stirred at room temperature for 24 h and then quenched with ice-containing dilute hydrochloric acid. The mixture was then extracted with chloroform for three times. The combined organic layers were washed with brine and water and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography over silica gel

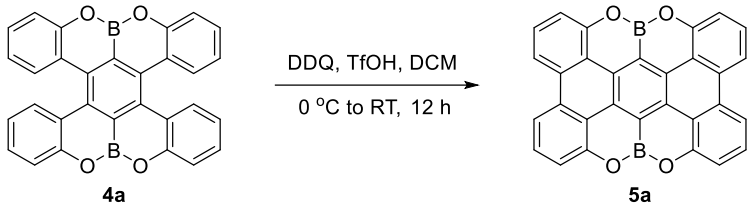
(eluent: hexane/CH_2Cl_2 = 2 : 1) to give the product, which was further washed with a little amount of hexane (3 mL) to afford 610 mg (28%) of compound **6b** as a white solid. M.p.: 276.2 – 277.5 °C. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K, ppm) δ 7.34 (s, 2H), 7.08 (d, J = 7.9 Hz, 4H), 6.87 (dd, J = 7.9, 1.7 Hz, 4H), 6.73 (d, J = 1.7 Hz, 4H), 3.45 (s, 12H), 1.29 (s, 36H); ^{13}C NMR (175 MHz, CD_2Cl_2, 298 K, ppm) δ 156.6, 152.0, 137.8, 133.2, 131.6, 128.5, 117.2, 107.9, 55.2, 35.2, 31.7; HRMS (ESI) *m/z*: Calcd for $C_{50}H_{62}O_4Na$: 749.4546; Found: 749.4576 $[M + Na]^+$.

Compound 4a. To a solution of compound **6a** (201 mg, 0.400 mmol) in anhydrous dichlorobenzene (20 mL) was added BBr_3 (1.0 M in heptane, 1.2 mL, 1.2 mmol) under argon. Then the mixture was heated to 150 °C and stirred at this temperature for 12 h. After quenching with methanol, the reaction mixture was concentrated under reduced pressure, and then the residue was purified by column chromatography over silica gel (eluent: hexane/CH_2Cl_2 = 1 : 1) to give the product, which was further recrystallized from CH_2Cl_2/MeOH to afford 170 mg (92%) of compound **4a** as a yellow solid. M.p.: >360 °C. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K, ppm) δ 8.27 (dd, J = 8.1, 1.5 Hz, 4H), 7.53 – 7.36 (m, 8H), 7.05 (ddd, J = 8.4, 6.9, 1.7 Hz, 4H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 393 K, ppm) δ 151.6, 132.7, 129.9, 128.8, 122.9, 122.0, 120.2 (The aromatic carbons *ipso* to the boron atoms were not observed due to quadrupolar relaxation); ^{11}B NMR (160 MHz, $C_2D_2Cl_4$, 393 K, ppm) δ 28.6; HRMS (MALDI) *m/z*: Calcd for $C_{30}H_{16}B_2O_4$: 462.1235; Found: 462.1191 $[M]^+$.



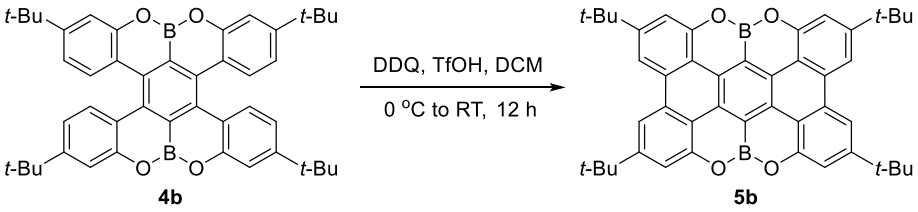
Compound 4b. To a solution of compound **6b** (218 mg, 0.300 mmol) in anhydrous dichlorobenzene (20 mL) was added BBr_3 (1.0 M in heptane, 0.9 mL, 0.9 mmol) under argon. Then the mixture was heated to 150 °C and stirred at this temperature for 12 h. After quenching with methanol, the reaction mixture was concentrated under

reduced pressure, and then the residue was purified by column chromatography over silica gel (eluent: hexane/CH_2Cl_2 = 3 : 1) to give the product, which was further recrystallized from CH_2Cl_2/MeOH to afford 185 mg (90%) of compound **4b** as a yellow solid. M.p.: 339.9 – 340.8 °C. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K, ppm) δ 8.21 (d, J = 8.5 Hz, 4H), 7.48 (d, J = 2.1 Hz, 4H), 7.10 (dd, J = 8.5, 2.1 Hz, 4H), 1.39 (s, 36H); ^{13}C NMR (175 MHz, CD_2Cl_2, 298 K, ppm) δ 154.3, 151.8, 132.6, 128.5, 121.0, 119.8, 117.3, 35.3, 31.52 (The aromatic carbons *ipso* to the boron atoms were not observed due to quadrupolar relaxation); ^{11}B NMR (160 MHz, CD_2Cl_2, 298 K, ppm) δ 29.3; HRMS (MALDI) *m/z*: Calcd for $C_{46}H_{48}B_2O_4$: 686.3739; Found: 686.3779 $[M]^+$.



4a **5a**

Compound 5a. To a solution of compound **4a** (46 mg, 0.10 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (57 mg, 0.25 mmol) in dichloromethane (60 mL) was added triflic acid (3.0 mL) under argon at 0 °C. Then the mixture was warmed to room temperature and stirred for 12 h. After quenching with triethylamine, the reaction mixture was concentrated under reduced pressure, and then the residue was dispersed in methanol. The solid was filtrated, washed with methanol, THF, and CH_2Cl_2 to afford 43 mg (94%) of compound **5a** as a pale yellow solid. M.p.: >360 °C. The insolubility of this compound prohibited NMR characterizations. HRMS (MALDI) *m/z*: Calcd for $C_{30}H_{12}B_2O_4$: 458.0922; Found: 458.0884 $[M]^+$.



4b **5b**

Compound 5b. To a solution of compound **4b** (69 mg, 0.10 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (57 mg, 0.25 mmol) in dichloromethane (60 mL) was added triflic acid (3.0 mL) under argon at 0 °C. Then the mixture was warmed to room temperature and stirred for 12 h. After quenching with triethylamine, the reaction mixture was concentrated under reduced pressure, and then the residue was dispersed in methanol. The solid was filtrated and washed with methanol. The crude product was further purified by flash chromatography over silica gel (eluent:

CH_2Cl_2) to afford 62 mg (91%) of compound **5b** as a yellow solid. M.p.: >360 °C. ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 298 K, ppm) δ 8.45 (s, 4H), 7.80 (s, 4H), 1.61 (s, 36H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 413 K, ppm) δ 153.4, 152.8, 131.1, 126.0, 118.0, 115.7, 115.1, 35.8, 31.8 (The aromatic carbons *ipso* to the boron atoms were not observed due to quadrupolar relaxation). No obvious signal was observed from ^{11}B NMR even at 413 K in $C_2D_2Cl_4$ due to the low solubility. HRMS (MALDI) *m/z*: Calcd for $C_{46}H_{44}B_2O_4$: 682.3426; Found: 682.3406 $[M]^+$.

2. Photophysical and Electrochemical Properties

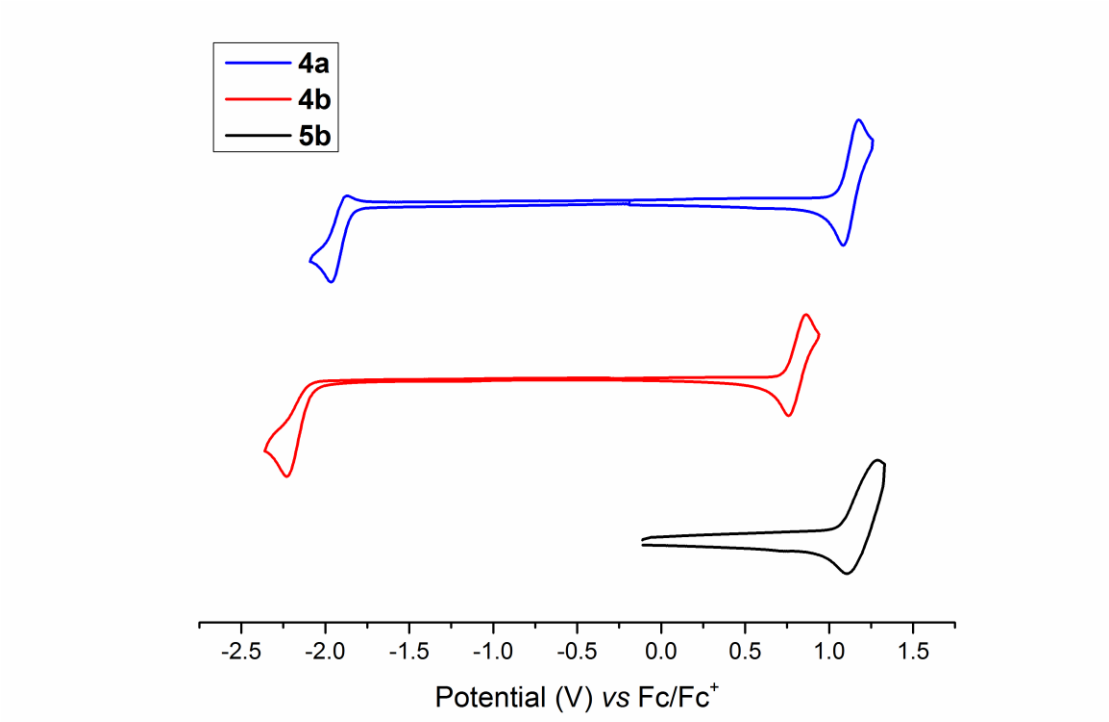


Figure S1. Cyclic voltammograms of compounds **4a**, **4b**, and **5b**. The reductive wave of compound **5b** was not detected.

Table S1. Summary of the photophysical and electrochemical properties of compounds **4a**, **4b**, and **5b**.

Compound	λ_{abs}^{max}/nm	λ_{em}^{max}/nm	Φ_F	E_g^{opt}/eV	HOMO/eV	LUMO/eV	E_g^{CV}/eV
4a	310,405	434,458	0.61	2.88	−5.86	−2.96 eV	2.90
4b	322,400,416	441,467	0.52	2.83	−5.54	−2.72 eV	2.82
5b	305,405,430	437,463,494	0.27	2.84	−5.87	−3.03 eV[a]	N.A.

[a] Calculated from the HOMO level and the optical gap.

3. Single Crystal X-Ray Analysis

The single crystal of compound **4a** suitable for X-ray analysis was obtained by slow evaporation of its solution in $CHCl_3$/EtOH. The structure was deposited at Cambridge Crystallographic Data Centre (CCDC number: 1455827).

Crystal data

formula	$C_{30}H_{16}B_2O_4$
molecular weight	462.05 g mol^{-1}

absorption	$\mu = 0.083\ mm^{-1}$
crystal size	$0.020 \times 0.040 \times 0.260$ mm^3 yellow needle
space group	P-1 (triclinic)
lattice parameters	a = 7.0696(7)Å α = 105.252(8)°
(calculate from	b = 10.6921(10)Å ß = 91.082(8)°
4366 reflections with	c = 16.9433(16)Å γ = 103.892(8)°
$2.50° < \theta < 28.46°$)	$V = 1194.9(2)Å^3$ z = 2 F(000) = 476
temperature	130K
density	$d_{xray} = 1.284\ g\ cm^{-3}$

Data collection

diffractometer	STOE IPDS 2T
radiation	Mo-K_α Graphitmonochromator
Scan – type	ω scans
Scan – width	1°
scan range	$2° \leq \theta < 28°$
	$-9 \leq h \leq 8$ $-14 \leq k \leq 14$ $-22 \leq l \leq 22$
number of reflections:	
measured	12499
unique	5892 ($R_{int} = 0.0978$)
observed	2287 ($\|F\|/\sigma(F) > 4.0$)

Data correction, structure solution and refinement

corrections	Lorentz and polarization correction.
Structure solution	Program: SIR-2004 (Direct methods)
refinement	Program: SHELXL-2014 (full matrix). 325 refined parameters, weighting scheme: $w=1/[\sigma^2(F_o^2) + (0.0812*P)^2]$ with $(Max(F_o^2,0)+2*F_c^2)/3$. H-atoms at calculated positions and refined with isotropic displacement parameters, non H- atoms refined anisotropically.
R-values	wR2 = 0.212 (R1 = 0.072 for observed reflections, 0.1905 for all reflections)
goodness of fit	S = 0.925
maximum deviation of parameters	0.001 * e.s.d
maximum peak height in diff. Fourier synthesis	$0.33, -0.30\ eÅ^{-3}$
remark	crystal contains probably one molecule $CHCl_3$ in a channel parallel to the *a*-axis. SQUEEZE was used.

4. Computational Studies

Calculations were performed using the Gaussian 09 software package.[3] The geometries were optimized at the B3LYP/6-311G(d,p) level, and energies were calculated at the same level of theory. Nucleus independent chemical shifts (NICS) were calculated using the gauge invariant atomic orbital (GIAO) approach at the GIAO-B3LYP/6-311+G(2d,p) level.[4] NICS(1) values were averaged by two positions (above and below the plane).

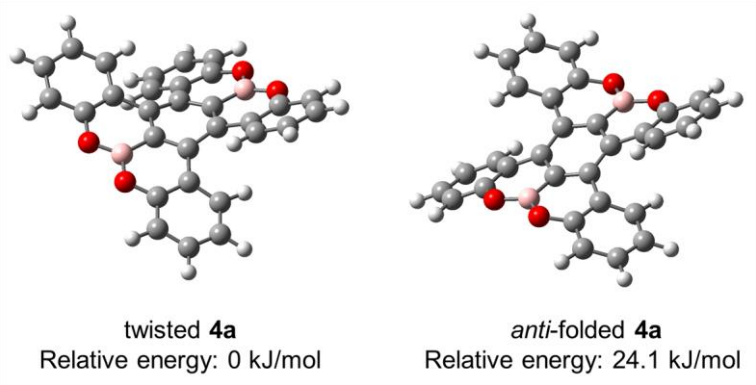


Figure S2. Twisted and *anti*-folded conformations of compound **4a** and their corresponding relative energies, showing that the twisted one is favored in energy.

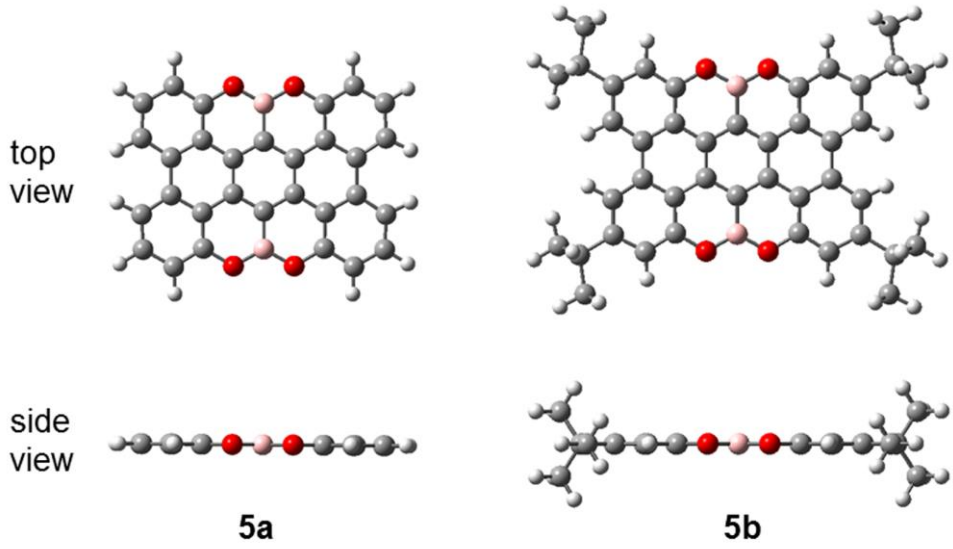


Figure S3. DFT-optimized geometries of compounds **5a** and **5b**, showing completely planar structures.

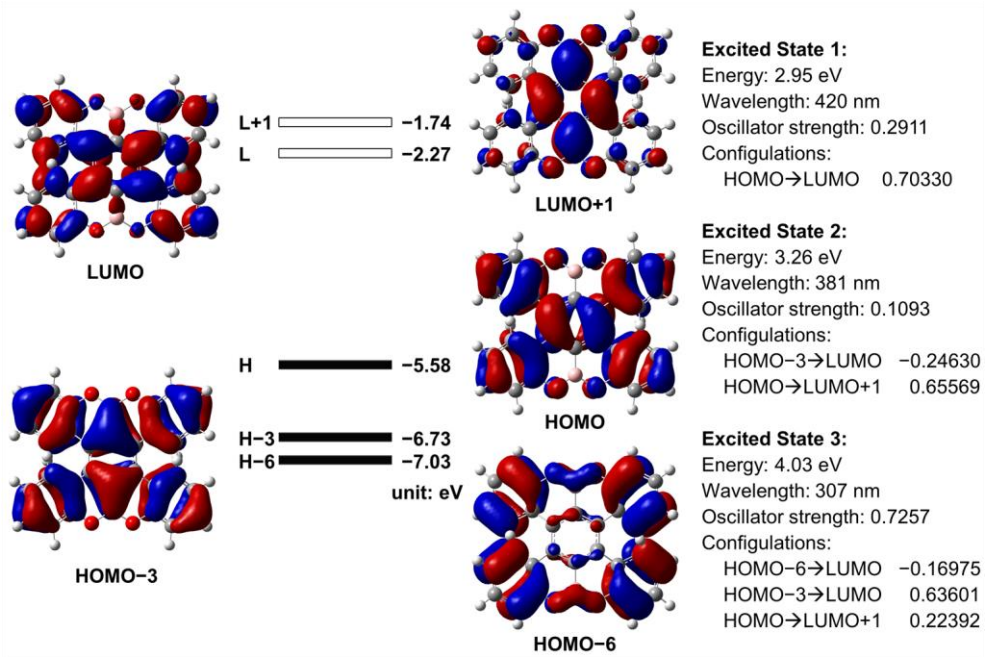


Figure S4. Molecular orbitals and their energy levels of compound **4a**, as well as some major excitations calculated by TD-DFT at the B3LYP/6-311G(d,p) level.

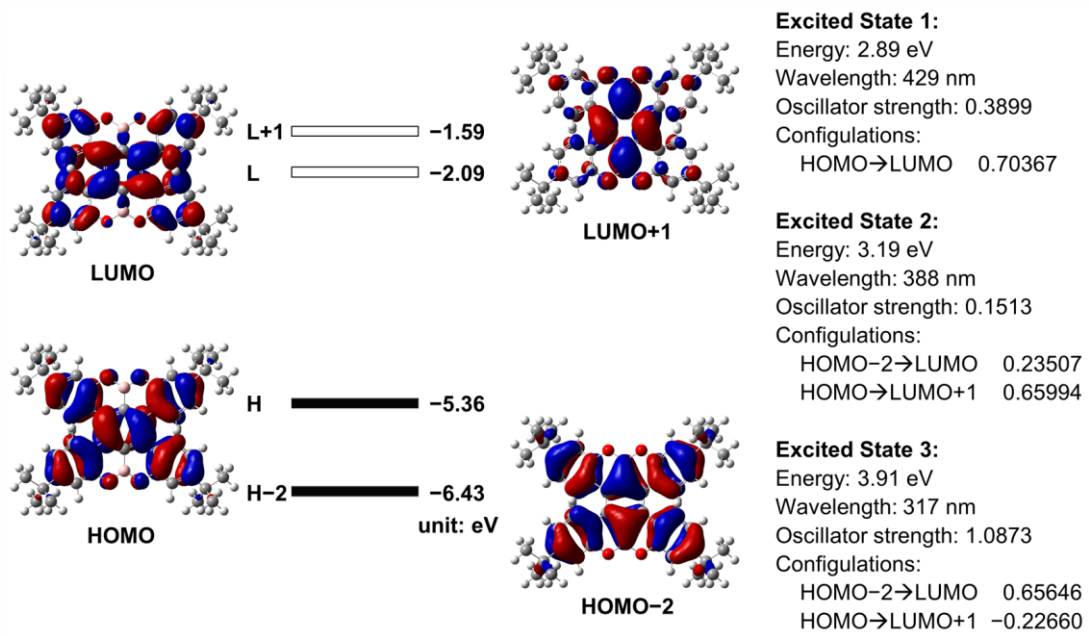


Figure S5. Molecular orbitals and their energy levels of compound **4b**, as well as some major excitations calculated by TD-DFT at the B3LYP/6-311G(d,p) level.

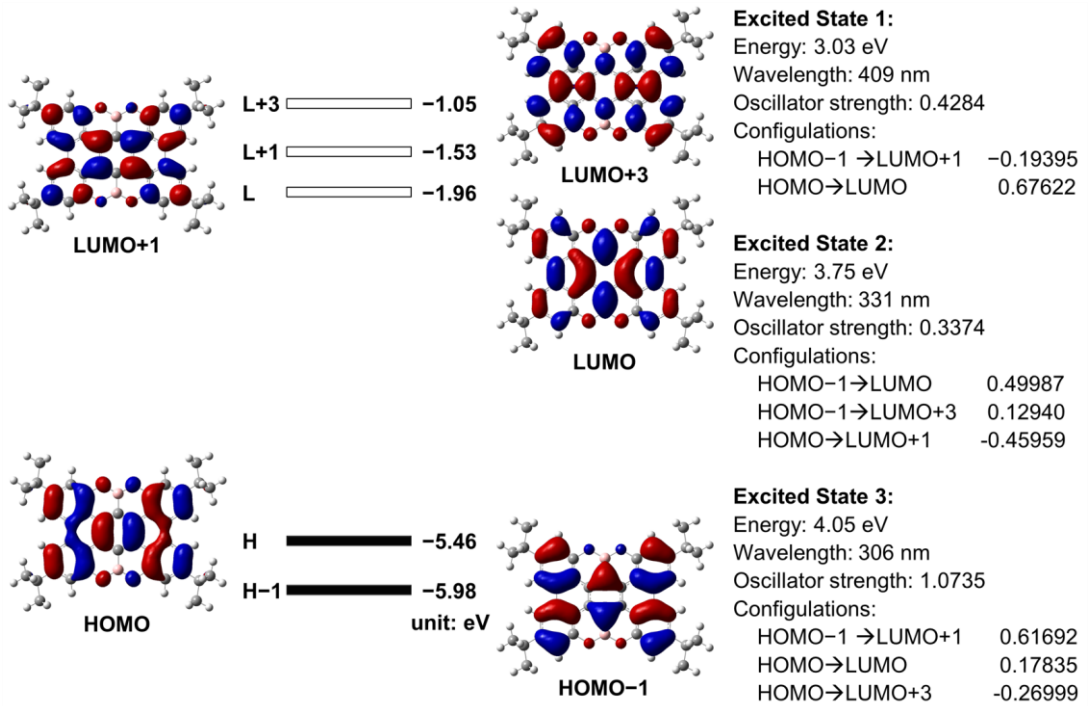


Figure S6. Molecular orbitals and their energy levels of compound **5b**, as well as some major excitations calculated by TD-DFT at the B3LYP/6-311G(d,p) level.

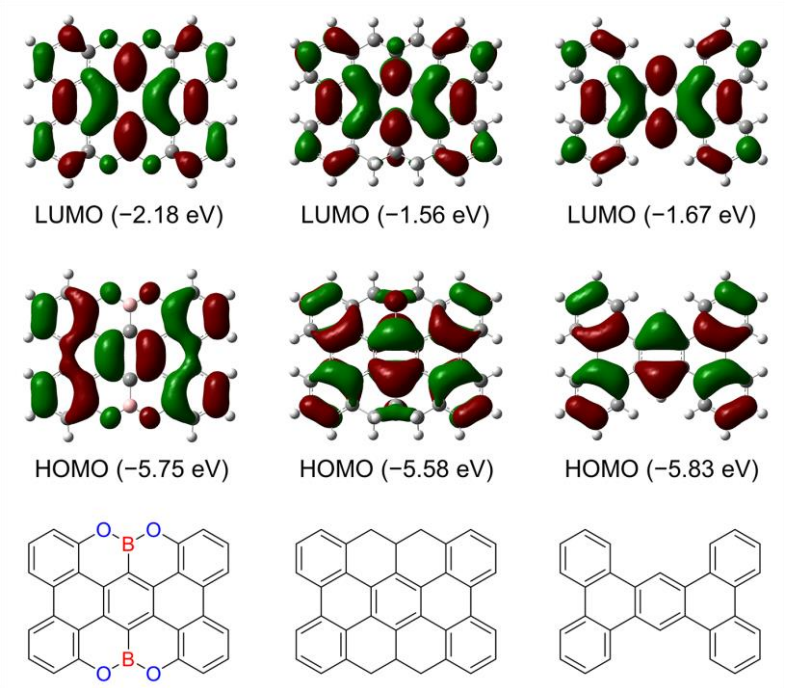


Figure S7. Frontier molecular orbitals and their energy levels of OBO-doped peritetracene **5a** and its reference compounds calculated at the B3LYP/6-311G(d,p) level. OBO-peritetracene displayed different orbital distributions from the CH_2-CH-CH_2 analogue, which showed the same pattern with tetrabenzoanthracene. These observations suggested that the CH_2-CH-CH_2 unit mainly functioned as a

structural element with little effect on the conjugation. However, the OBO unit cannot be simply viewed as a linkage, since the electronic structure was significantly changed and the large orbital distribution on boron cannot be neglected. Furtheremore, compared with tetrabenzoanthracene, OBO-doped peritetracene exhibited lower HOMO-LUMO energy gap, which is a benefit of the OBO inclusion.

Appendix: Cartesian coordinates for DFT calculations

Twisted **4a**

Tag	Symbol	X	Y	Z
1	C	-1.242564	-0.696592	0.143734
2	C	-1.242430	0.696821	-0.143428
3	C	0.000119	1.353589	0.000135
4	C	1.242547	0.696598	0.143700
5	C	1.242410	-0.696827	-0.143437
6	C	-0.000131	-1.353589	0.000165
7	C	-2.373718	-1.512887	0.623696
8	C	-2.373388	1.513283	-0.623551
9	C	2.373720	1.512912	0.623562
10	C	2.373391	-1.513308	-0.623461
11	C	2.274947	2.923597	0.646219
12	C	3.317895	3.722602	1.114057
13	C	4.464827	3.138397	1.627347
14	C	4.559990	1.745888	1.692961
15	C	3.531543	0.957067	1.204670
16	C	-3.531318	0.957565	-1.204572
17	C	-4.559564	1.746503	-1.693099
18	C	-4.464099	3.139004	-1.627796
19	C	-3.317066	3.723073	-1.114578
20	C	-2.274317	2.923945	-0.646505
21	C	-2.274931	-2.923571	0.646464
22	C	-3.317889	-3.722554	1.114315
23	C	-4.464838	-3.138329	1.627550
24	C	-4.560011	-1.745820	1.693072
25	C	-3.531581	-0.957020	1.204708
26	C	3.531262	-0.957608	-1.204609
27	C	4.559528	-1.746563	-1.693069
28	C	4.464135	-3.139063	-1.627562
29	C	3.317132	-3.723119	-1.114260
30	C	2.274347	-2.923973	-0.646307
31	O	-1.144415	-3.585480	0.245007
32	O	1.143745	-3.585703	-0.244797
33	O	-1.143710	3.585683	-0.245037
34	O	1.144423	3.585486	0.244745
35	B	-0.000249	-2.875753	0.000197
36	B	0.000265	2.875743	0.000013
37	H	3.187369	4.797315	1.084888
38	H	5.269741	3.762381	1.997940
39	H	5.432971	1.277709	2.132052
40	H	3.613772	-0.118190	1.279210
41	H	-3.613774	-0.117690	-1.278890
42	H	-5.432619	1.278419	-2.132141
43	H	-5.268865	3.763082	-1.998551
44	H	-3.186327	4.797767	-1.085621
45	H	-3.187363	-4.797269	1.085204
46	H	-5.269756	-3.762296	1.998161
47	H	-5.433000	-1.277621	2.132124
48	H	-3.613831	0.118240	1.279179
49	H	3.613662	0.117644	-1.279060
50	H	5.432555	-1.278497	-2.132188
51	H	5.268922	-3.763151	-1.998252
52	H	3.186427	-4.797813	-1.085176

Anti-folded **4a**

Tag	Symbol	X	Y	Z
1	C	1.253459	-0.709560	-0.001580
2	C	1.253477	0.709637	0.001630
3	C	0.000036	1.358947	0.077214
4	C	-1.253450	0.709629	0.001644
5	C	-1.253433	-0.709527	-0.001614
6	C	0.000024	-1.358850	-0.077210
7	C	2.422301	-1.608983	0.156405

8	C	-2.422311	-1.608965	0.156345
9	C	2.335296	-2.956614	-0.257642
10	C	3.416042	-3.830284	-0.145506
11	C	4.588265	-3.408344	0.462218
12	C	4.666947	-2.114650	0.982327
13	C	3.601835	-1.240428	0.831844
14	C	-3.601847	-1.240401	0.831759
15	C	-4.667008	-2.114587	0.982136
16	C	-4.588363	-3.408249	0.461949
17	C	-3.416119	-3.830208	-0.145728
18	C	-2.335346	-2.956568	-0.257778
19	C	2.422396	1.608977	-0.156349
20	C	-2.422359	1.608993	-0.156281
21	C	-2.335355	2.956709	0.257499
22	C	-3.416216	3.830269	0.145542
23	C	-4.588601	3.408122	-0.461710
24	C	-4.667319	2.114331	-0.981583
25	C	-3.602081	1.240238	-0.831295
26	C	3.602120	1.240184	-0.831337
27	C	4.667336	2.114291	-0.981727
28	C	4.588597	3.408131	-0.461990
29	C	3.416222	3.830302	0.145270
30	C	2.335390	2.956725	0.257335
31	B	0.000008	-2.828533	-0.496628
32	B	0.000033	2.828741	0.496163
33	O	1.170058	-3.495688	-0.740412
34	O	-1.170070	-3.495701	-0.740456
35	O	1.170087	3.496023	0.739683
36	O	-1.170029	3.496011	0.739775
37	H	3.292101	-4.842925	-0.508888
38	H	5.422859	-4.092723	0.560715
39	H	5.555977	-1.789971	1.509829
40	H	3.676462	-0.247926	1.252235
41	H	-3.676430	-0.247936	1.252254
42	H	-5.556028	-1.789901	1.509648
43	H	-5.422998	-4.092594	0.560335
44	H	-3.292193	-4.842833	-0.509160
45	H	-3.292228	4.842978	0.508718
46	H	-5.423302	4.092397	-0.560022
47	H	-5.556469	1.789481	-1.508777
48	H	-3.676732	0.247697	-1.251581
49	H	3.676814	0.247593	-1.251497
50	H	5.556494	1.789398	-1.508879
51	H	5.423271	4.092424	-0.560408
52	H	3.292226	4.843038	0.508366

Compound **4b**

Tag	Symbol	X	Y	Z
1	C	1.242873	0.697292	0.140931
2	C	1.243030	-0.697088	-0.141637
3	C	0.000134	-1.354374	-0.000377
4	C	-1.242876	-0.697307	0.140935
5	C	-1.243035	0.697072	-0.141630
6	C	-0.000138	1.354358	-0.000376
7	C	2.374256	1.516381	0.612496
8	C	2.374623	-1.515945	-0.613076
9	C	-2.374258	-1.516397	0.612499
10	C	-2.374629	1.515930	-0.613060
11	C	-2.277659	-2.926567	0.636561
12	C	-3.318153	-3.726453	1.097038
13	C	-4.491328	-3.177792	1.615274
14	C	-4.565385	-1.777815	1.671986
15	C	-3.538365	-0.980202	1.190156
16	C	3.538909	-0.979555	-1.190198
17	C	4.566232	-1.776985	-1.671673
18	C	4.492360	-3.176979	-1.615092
19	C	3.318987	-3.725842	-1.097527
20	C	2.278169	-2.926131	-0.637467
21	C	2.277655	2.926551	0.636561
22	C	3.318146	3.726436	1.097046
23	C	4.491321	3.177776	1.615282
24	C	4.565379	1.777799	1.671992
25	C	3.538361	0.980185	1.190159
26	C	-3.538925	0.979539	-1.190158
27	C	-4.566253	1.776966	-1.671625
28	C	-4.492379	3.176965	-1.615067
29	C	-3.319005	3.725824	-1.097498
30	C	-2.278179	2.926115	-0.637452
31	O	1.144132	3.588906	0.239506
32	O	-1.144548	3.588693	-0.241098
33	O	1.144547	-3.588708	-0.241087
34	O	-1.144134	-3.588922	0.239511
35	B	-0.000189	2.877194	-0.000615
36	B	0.000185	-2.877210	-0.000613
37	H	-3.160852	-4.797093	1.056321
38	H	-5.430522	-1.291982	2.102157
39	H	-3.635748	0.093543	1.270955
40	H	3.636213	0.094207	-1.270827

41	H	5.431491	-1.290998	-2.101431
42	H	3.161772	-4.796502	-1.056995
43	H	3.160845	4.797077	1.056330
44	H	5.430515	1.291966	2.102163
45	H	3.635744	-0.093558	1.270957
46	H	-3.636232	-0.094225	-1.270772
47	H	-5.431518	1.290967	-2.101348
48	H	-3.161789	4.796486	-1.056970
49	C	-5.614508	-4.101549	2.114251
50	C	-5.079503	-4.993627	3.258706
51	H	-5.872218	-5.651744	3.627435
52	H	-4.249736	-5.623231	2.929838
53	H	-4.725815	-4.384864	4.095151
54	C	-6.095444	-4.996665	0.948602
55	H	-5.288023	-5.617935	0.554889
56	H	-6.895565	-5.662407	1.286485
57	H	-6.482881	-4.390195	0.125422
58	C	-6.824852	-3.312103	2.645641
59	H	-6.558514	-2.683864	3.499861
60	H	-7.264182	-2.673681	1.874371
61	H	-7.599102	-4.008605	2.977962
62	C	-5.615940	4.100520	-2.113533
63	C	-6.826458	3.310914	-2.644302
64	H	-6.560408	2.682461	-3.498459
65	H	-7.265505	2.672693	-1.872712
66	H	-7.600831	4.007320	-2.976533
67	C	-6.096416	4.995599	-0.947640
68	H	-5.288800	5.616757	-0.554161
69	H	-6.896580	5.661425	-1.285249
70	H	-6.483647	4.389077	-0.124406
71	C	-5.081600	4.992669	-3.258217
72	H	-4.251718	5.622322	-2.929727
73	H	-4.728286	4.383998	-4.094893
74	H	-5.874533	5.650765	-3.626518
75	C	5.614494	4.101534	2.114274
76	C	5.079513	4.993497	3.258831
77	H	5.872224	5.651606	3.627582
78	H	4.249711	5.623104	2.930053
79	H	4.725880	4.384650	4.095238
80	C	6.095338	4.996764	0.948676
81	H	5.287872	5.618028	0.555046
82	H	6.895442	5.662517	1.286576
83	H	6.482768	4.390378	0.125431
84	C	6.824897	3.312091	2.645537
85	H	6.558613	2.683722	3.499678
86	H	7.264253	2.673800	1.874174
87	H	7.599110	4.008597	2.977936
88	C	5.615954	-4.100496	-2.113536
89	C	5.081656	-4.992888	-3.258048
90	H	5.874695	-5.650832	-3.626385
91	H	4.251960	-5.622700	-2.929400
92	H	4.728096	-4.384385	-4.094746
93	C	6.826270	-3.310756	-2.644542
94	H	6.560008	-2.682451	-3.498743
95	H	7.265300	-2.672361	-1.873084
96	H	7.600722	-4.007076	-2.976770
97	C	6.096693	-4.995308	-0.947533
98	H	5.289226	-5.616579	-0.553925
99	H	6.896980	-5.661019	-1.285084
100	H	6.483834	-4.388591	-0.124403

Compound **5b**

Tag	Symbol	X	Y	Z
1	C	1.216273	0.700370	-0.000013
2	C	1.216274	-0.700369	-0.000001
3	C	0.000003	-1.381363	0.000007
4	C	-1.216269	-0.700372	0.000006
5	C	-1.216270	0.700368	-0.000002
6	C	0.000000	1.381362	-0.000011
7	C	2.441761	1.433941	-0.000017
8	C	-2.441759	1.433937	0.000008
9	C	2.441763	-1.433939	-0.000010
10	C	-2.441757	-1.433943	0.000003
11	C	-2.403620	-2.846449	-0.000001
12	C	-3.583759	-3.573300	-0.000004
13	C	-4.824781	-2.918377	-0.000013
14	C	-4.851332	-1.518245	-0.000010
15	C	-3.684238	-0.743187	-0.000005
16	C	3.684244	-0.743182	-0.000013
17	C	4.851337	-1.518238	-0.000020
18	C	4.824795	-2.918371	-0.000043
19	C	3.583771	-3.573294	-0.000017
20	C	2.403628	-2.846445	-0.000008
21	C	2.403623	2.846448	-0.000019
22	C	3.583761	3.573299	-0.000013
23	C	4.824782	2.918375	-0.000005
24	C	4.851336	1.518243	0.000001
25	C	3.684242	0.743185	-0.000007

26	C	-3.684239	0.743181	0.000006
27	C	-4.851333	1.518236	0.000009
28	C	-4.824791	2.918368	0.000039
29	C	-3.583767	3.573292	0.000019
30	C	-2.403625	2.846443	0.000008
31	B	-0.000001	2.885780	-0.000018
32	O	1.210026	3.552483	-0.000027
33	O	-1.210031	3.552480	-0.000014
34	O	1.210034	-3.552482	0.000012
35	B	0.000005	-2.885782	0.000008
36	O	-1.210023	-3.552484	0.000013
37	H	-3.507926	-4.651189	0.000009
38	H	-5.811502	-1.020307	-0.000008
39	H	5.811505	-1.020297	-0.000014
40	H	3.507933	-4.651181	0.000013
41	H	3.507933	4.651189	-0.000019
42	H	5.811508	1.020308	0.000013
43	H	-5.811501	1.020295	-0.000002
44	H	-3.507931	4.651179	-0.000013
45	C	6.153256	-3.701270	-0.000009
46	C	-6.153230	-3.701287	-0.000002
47	C	-6.153253	3.701266	0.000011
48	C	6.153222	3.701294	0.000014
49	C	-6.967469	-3.334031	-1.262434
50	H	-7.913339	-3.884130	-1.275569
51	H	-7.201659	-2.267899	-1.300722
52	H	-6.414050	-3.587275	-2.170628
53	C	-6.967455	-3.334031	1.262445
54	H	-7.201663	-2.267902	1.300714
55	H	-7.913319	-3.884142	1.275596
56	H	-6.414017	-3.587257	2.170628
57	C	-5.934947	-5.225390	0.000008
58	H	-5.388598	-5.558935	-0.886200
59	H	-5.388524	-5.558919	0.886178
60	H	-6.903329	-5.732439	0.000054
61	C	-6.967567	3.333889	1.262354
62	H	-7.913465	3.883942	1.275456
63	H	-7.201707	2.267742	1.300563
64	H	-6.414224	3.587102	2.170605
65	C	-5.935025	5.225379	0.000128
66	H	-5.388889	5.558900	0.886474
67	H	-5.388421	5.558978	-0.885904
68	H	-6.903427	5.732391	-0.000103
69	C	-6.967399	3.334093	-1.262510
70	H	-6.413877	3.587327	-2.170639
71	H	-7.201656	2.267977	-1.300835
72	H	-7.913234	3.884252	-1.275710
73	C	5.934906	5.225390	0.000141
74	H	5.388424	5.558971	-0.885972
75	H	5.388597	5.558855	0.886404
76	H	6.903277	5.732460	0.000080
77	C	6.967424	3.334150	-1.262479
78	H	7.913285	3.884266	-1.275605
79	H	7.201632	2.268026	-1.300852
80	H	6.413969	3.587456	-2.170632
81	C	6.967489	3.333950	1.262409
82	H	7.201700	2.267818	1.300593
83	H	7.913352	3.884062	1.275571
84	H	6.414082	3.587106	2.170631
85	C	6.967494	-3.334053	-1.262448
86	H	7.201665	-2.267918	-1.300787
87	H	7.913376	-3.884134	-1.275551
88	H	6.414085	-3.587350	-2.170634
89	C	6.967484	-3.333945	1.262413
90	H	7.913332	-3.884081	1.275603
91	H	7.201716	-2.267819	1.300610
92	H	6.414034	-3.587096	2.170611
93	C	5.935024	-5.225383	0.000070
94	H	5.388554	-5.558885	0.886221
95	H	5.388752	-5.558998	-0.886158
96	H	6.903423	-5.732399	0.000212

NICS calculation of OBO-peritetracene **5a**

Tag	Symbol	X	Y	Z
1	C	-1.218562	-0.701406	0.000096
2	C	-1.218622	0.701330	0.000219
3	C	-0.000058	1.380683	0.000285
4	C	1.218550	0.701394	0.000173
5	C	1.218598	-0.701340	0.000022
6	C	0.000046	-1.380671	0.000060
7	C	-2.444794	-1.438533	-0.000035
8	C	2.444851	-1.438448	-0.000058
9	C	-2.444889	1.438430	0.000141
10	C	2.444777	1.438546	0.000076
11	C	2.399792	2.856453	-0.000093
12	C	3.578794	3.582934	-0.000374
13	C	4.798342	2.899891	-0.000593
14	C	4.858359	1.511998	-0.000463

15	C	3.684320	0.740824	-0.000055
16	C	-3.684400	0.740628	0.000109
17	C	-4.858485	1.511715	0.000161
18	C	-4.798559	2.899617	0.000193
19	C	-3.579071	3.582738	0.000139
20	C	-2.399981	2.856366	0.000106
21	C	-2.399805	-2.856428	-0.000187
22	C	-3.578791	-3.582932	-0.000274
23	C	-4.798339	-2.899904	-0.000338
24	C	-4.858376	-1.512005	-0.000260
25	C	-3.684350	-0.740821	-0.000062
26	C	3.684357	-0.740626	0.000084
27	C	4.858459	-1.511688	0.000447
28	C	4.798559	-2.899590	0.000495
29	C	3.579088	-3.582735	0.000223
30	C	2.399997	-2.856386	-0.000020
31	B	0.000280	-2.886095	-0.000081
32	O	-1.205805	-3.555532	-0.000133
33	O	1.206200	-3.555798	-0.000119
34	O	-1.206116	3.555665	0.000149
35	B	-0.000173	2.886152	0.000181
36	O	1.205795	3.555596	-0.000018
37	H	3.534421	4.664773	-0.000523
38	H	5.719899	3.470602	-0.000906
39	H	5.828710	1.033409	-0.000831
40	H	-5.828805	1.033065	0.000247
41	H	-5.720156	3.470265	0.000268
42	H	-3.534782	4.664583	0.000131
43	H	-3.534396	-4.664770	-0.000341
44	H	-5.719891	-3.470622	-0.000458
45	H	-5.828736	-1.033436	-0.000361
46	H	5.828770	-1.033022	0.000822
47	H	5.720169	-3.470216	0.000806
48	H	3.534818	-4.664579	0.000310
49	Bq	0.000000	0.000000	0.000000
50	Bq	0.000000	0.000000	1.000000
51	Bq	0.000000	0.000000	-1.000000
52	Bq	-2.449333	-0.000167	0.000000
53	Bq	-2.449333	-0.000167	1.000000
54	Bq	-2.449333	-0.000167	-1.000000
55	Bq	-1.211667	-2.136500	0.000000
56	Bq	-1.211667	-2.136500	1.000000
57	Bq	-1.211667	-2.136500	-1.000000
58	Bq	-3.627333	-2.171833	0.000000
59	Bq	-3.627333	-2.171833	1.000000
60	Bq	-3.627333	-2.171833	-1.000000

NICS calculation of peritetracene

Tag	Symbol	X	Y	Z
1	C	4.868444	2.892292	0.000410
2	C	4.884537	1.484157	0.000412
3	C	3.714371	0.735533	0.000092
4	C	2.459598	1.429681	0.000000
5	C	2.445712	2.871362	0.000029
6	C	3.681933	3.576445	0.000177
7	C	1.234272	0.721048	-0.000025
8	C	-0.000001	1.421642	-0.000031
9	C	0.000000	2.865023	-0.000058
10	C	1.226091	3.548144	-0.000032
11	C	-1.234274	0.721048	-0.000014
12	C	-2.459600	1.429682	-0.000039
13	C	-2.445711	2.871363	-0.000093
14	C	-1.226090	3.548145	-0.000087
15	C	3.714372	-0.735533	-0.000105
16	C	4.884536	-1.484157	-0.000437
17	C	4.868443	-2.892292	-0.000447
18	C	3.681933	-3.576445	-0.000203
19	C	2.445711	-2.871362	-0.000027
20	C	2.459598	-1.429681	0.000000
21	C	1.226091	-3.548144	0.000077
22	C	0.000000	-2.865024	0.000114
23	C	-0.000002	-1.421642	0.000055
24	C	1.234272	-0.721048	0.000029
25	C	-1.226090	-3.548145	0.000154
26	C	-2.445712	-2.871363	0.000117
27	C	-2.459601	-1.429682	0.000037
28	C	-1.234274	-0.721048	0.000024
29	C	-3.681930	-3.576450	0.000144
30	C	-4.868441	-2.892299	0.000190
31	C	-4.884536	-1.484165	0.000175
32	C	-3.714373	-0.735533	0.000045
33	C	-3.714374	0.735534	-0.000058
34	C	-4.884536	1.484166	-0.000205
35	C	-4.868440	2.892300	-0.000239
36	C	-3.681929	3.576450	-0.000166
37	H	5.809354	3.431011	0.000600
38	H	5.846495	0.989270	0.000718
39	H	3.664351	4.660721	0.000161

40	H	1.223520	4.633218	-0.000025
41	H	-1.223518	4.633219	-0.000106
42	H	5.846495	-0.989271	-0.000744
43	H	5.809354	-3.431011	-0.000656
44	H	3.664350	-4.660722	-0.000200
45	H	1.223520	-4.633218	0.000080
46	H	-1.223519	-4.633219	0.000228
47	H	-3.664346	-4.660726	0.000153
48	H	-5.809350	-3.431022	0.000217
49	H	-5.846495	-0.989285	0.000317
50	H	-5.846495	0.989286	-0.000311
51	H	-5.809349	3.431023	-0.000329
52	H	-3.664345	4.660727	-0.000197
53	Bq	3.675833	2.164833	0.000000
54	Bq	3.675833	2.164833	1.000000
55	Bq	3.675833	2.164833	-1.000000
56	Bq	1.227667	2.142833	0.000000
57	Bq	1.227667	2.142833	1.000000
58	Bq	1.227667	2.142833	-1.000000
59	Bq	2.469333	0.000000	0.000000
60	Bq	2.469333	0.000000	1.000000
61	Bq	2.469333	0.000000	-1.000000
62	Bq	0.000000	0.000000	0.000000
63	Bq	0.000000	0.000000	1.000000
64	Bq	0.000000	0.000000	-1.000000

Reference:

(1) Galanin M. D.; Kut'enkov A. A.; Smorchkov V. N.; Timofeev Y. P.; Chizhikov Z. A. *Opt. Spektrosk*. **1982**, *53*, 683.

(2) Martínez-Peragón, A.; Miguel, D.; Orte, A.; Mota, A. J.; Ruedas-Rama, M. J.; Justicia, J.; Alvarez-Pez, J. M.; Cuerva, J. M.; Crovetto, L. *Org. Biomol. Chem.* **2014**, *12*, 6432.

(3) Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.;Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2013.

(4) (a) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. R. *Chem. Rev.* **2005,** *105*, 3842. (b) Schleyer, P. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

5. NMR Spectra

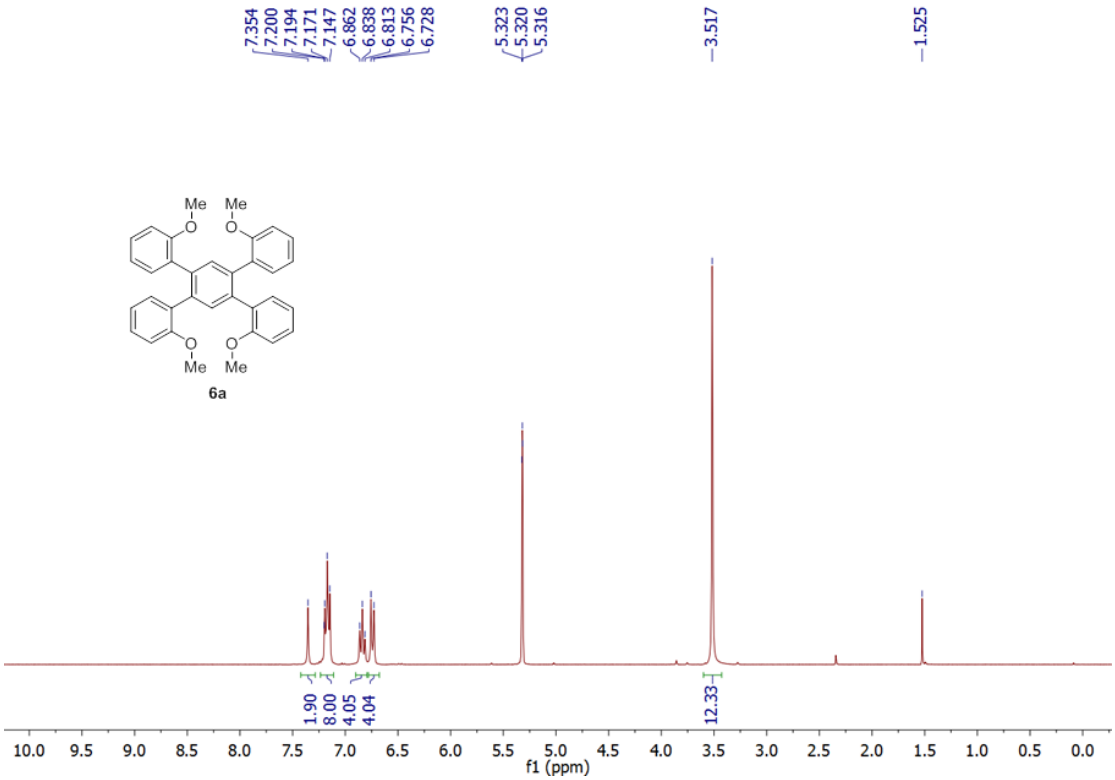


Figure S8. ^{1}H NMR spectrum of compound **6a** (300 MHz, CD_2Cl_2, 298 K).

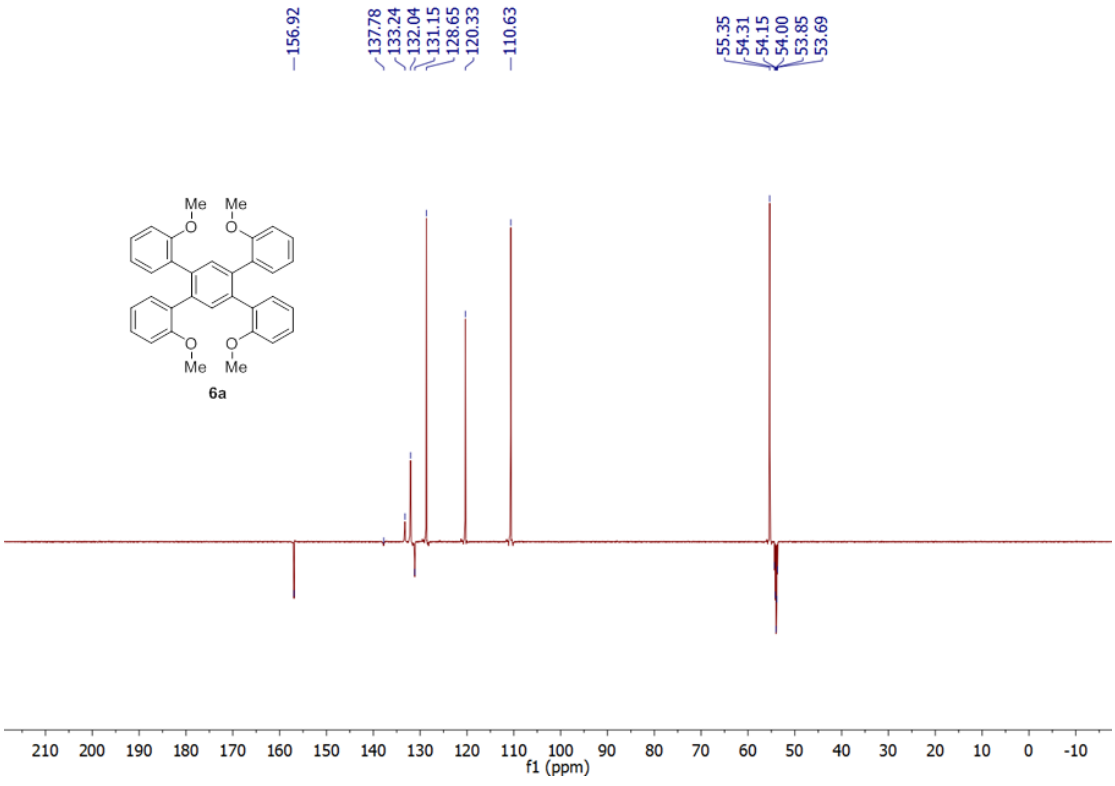


Figure S9. ^{13}C NMR (ATP) spectrum of compound **6a** (175 MHz, CD_2Cl_2, 298 K).

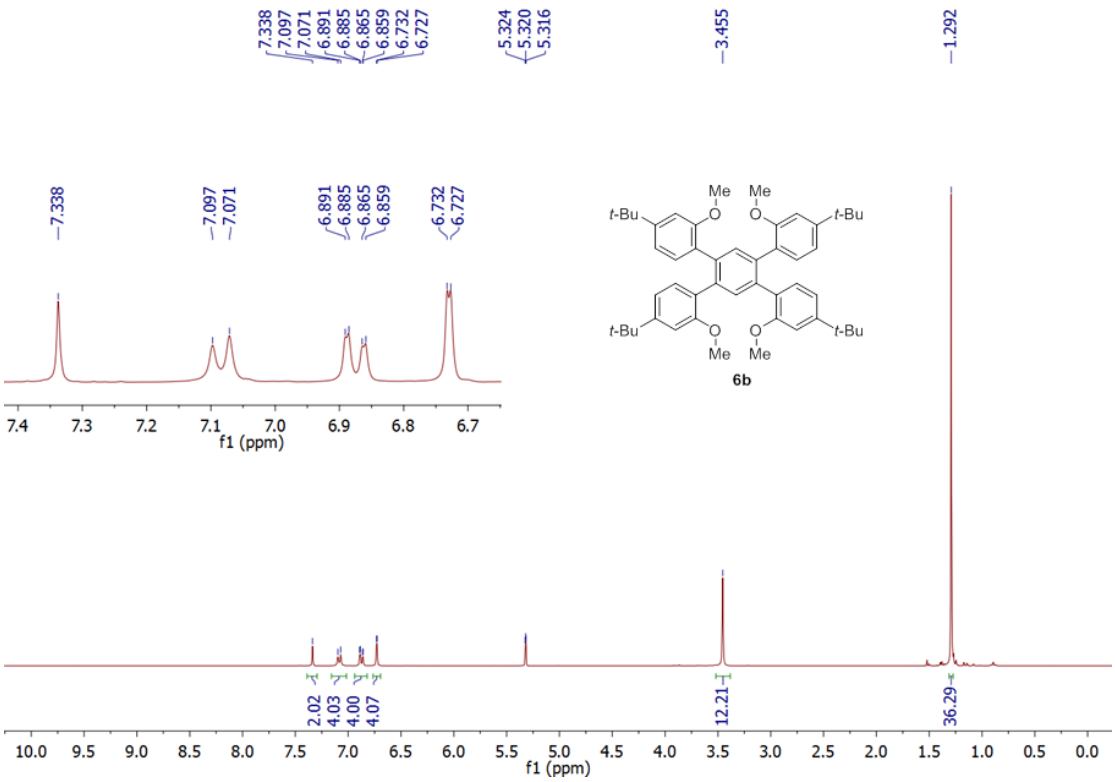


Figure S10. ^{1}H NMR spectrum of compound **6b** (300 MHz, CD_2Cl_2, 298 K).

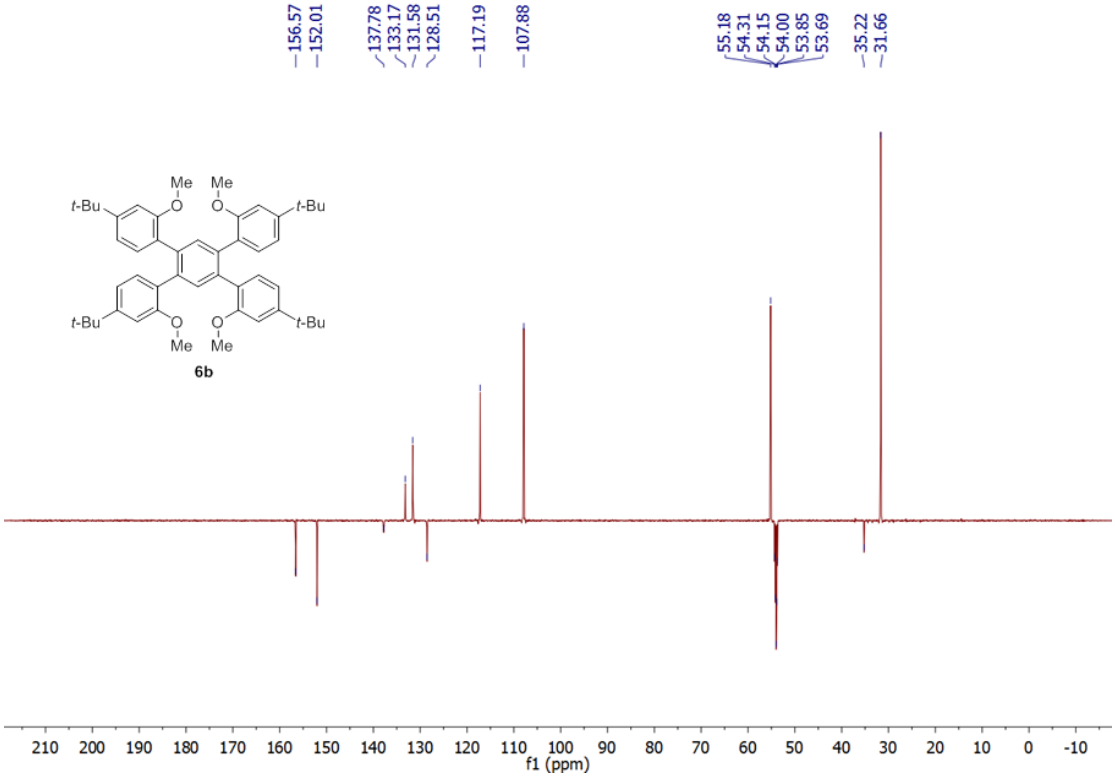


Figure S11. ^{13}C NMR (ATP) spectrum of compound **6b** (175 MHz, CD_2Cl_2, 298 K).

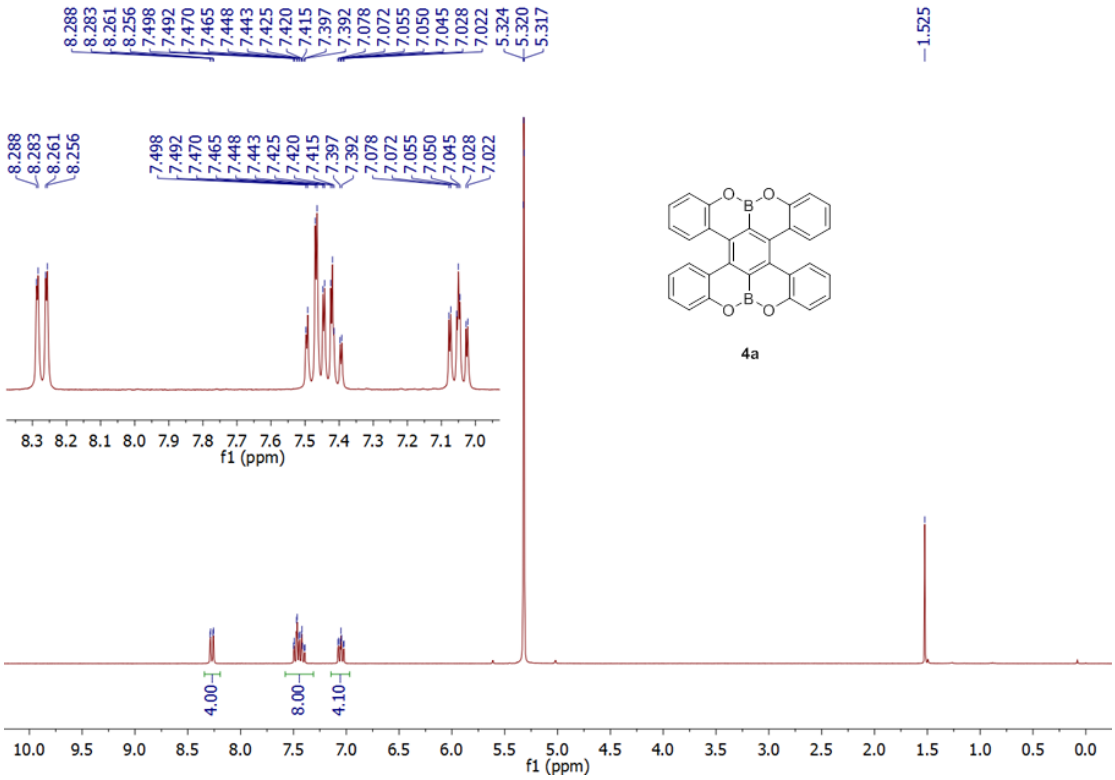


Figure S12. ^{1}H NMR spectrum of compound **4a** (300 MHz, CD_2Cl_2, 298 K).

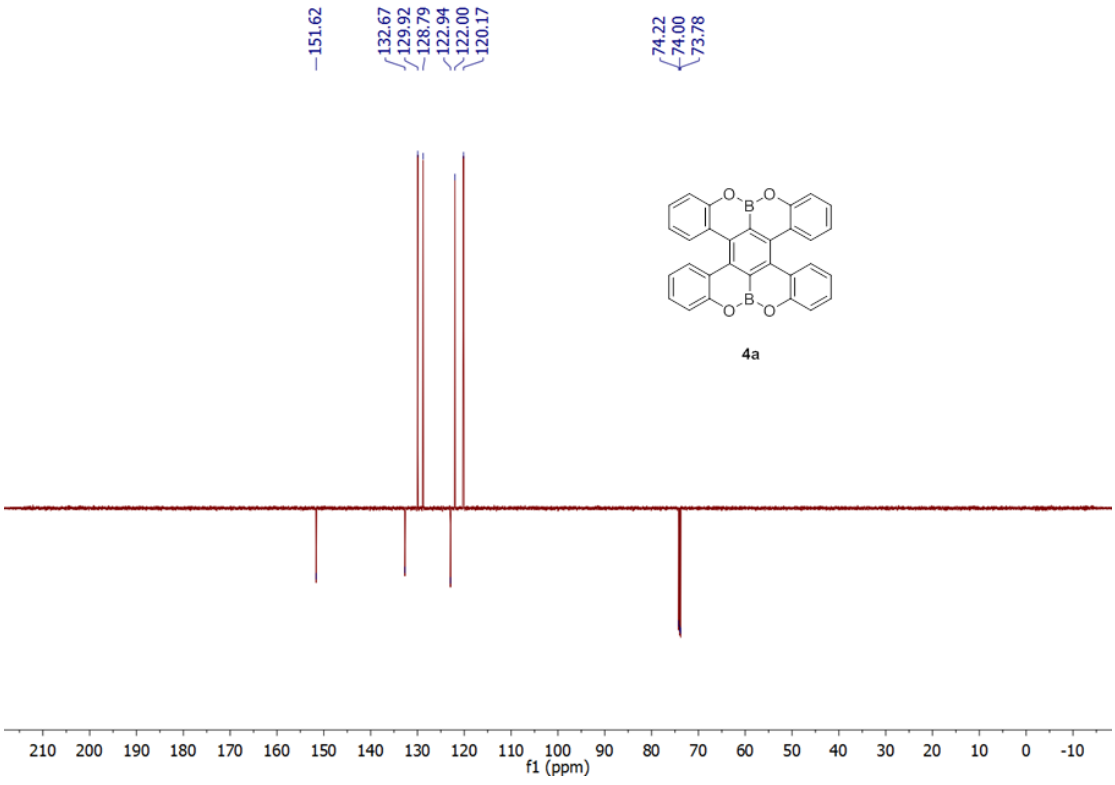


Figure S13. ^{13}C NMR (ATP) spectrum of compound **4a** (125 MHz, $C_2D_2Cl_4$, 393 K).

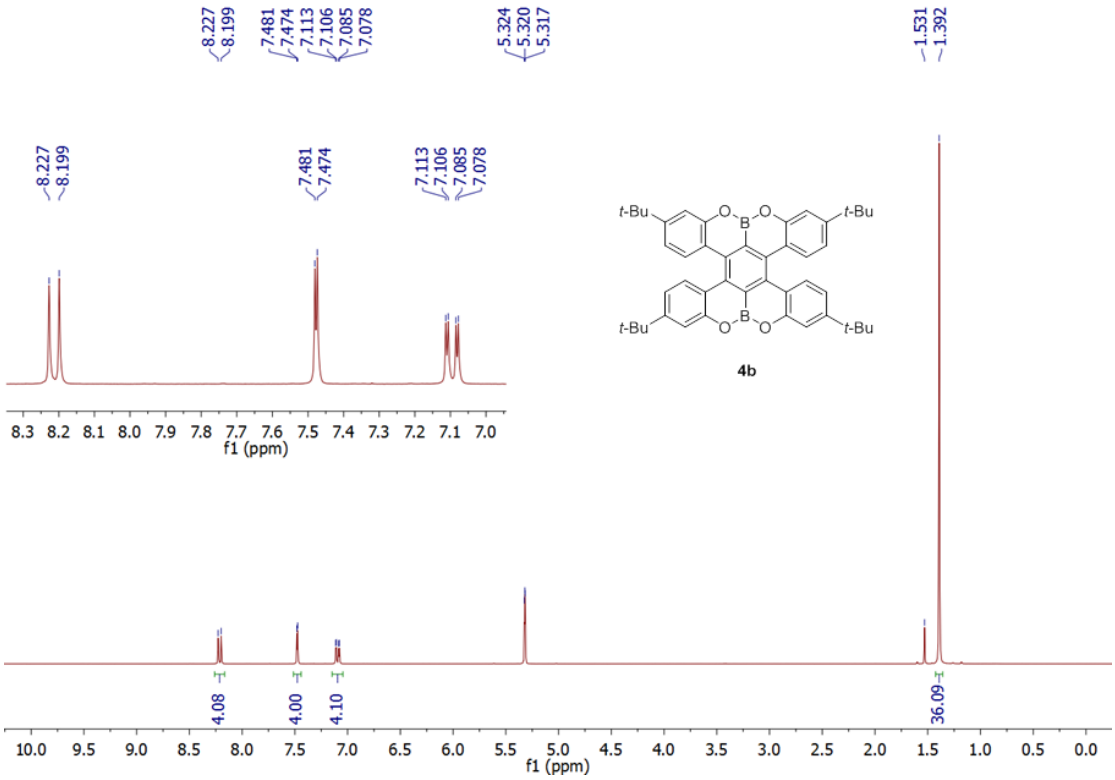


Figure S14. ^{1}H NMR spectrum of compound **4b** (300 MHz, CD_2Cl_2, 298 K).

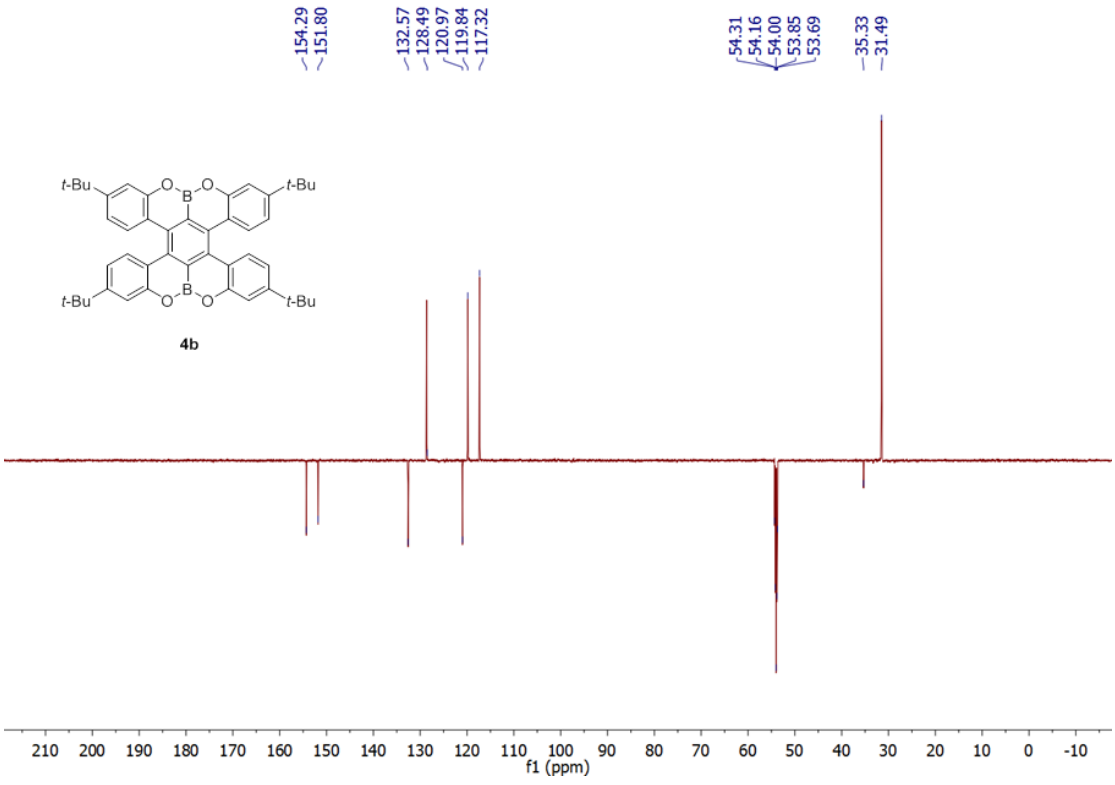


Figure S15. ^{13}C NMR (ATP) spectrum of compound **4b** (175 MHz, CD_2Cl_2, 298 K).

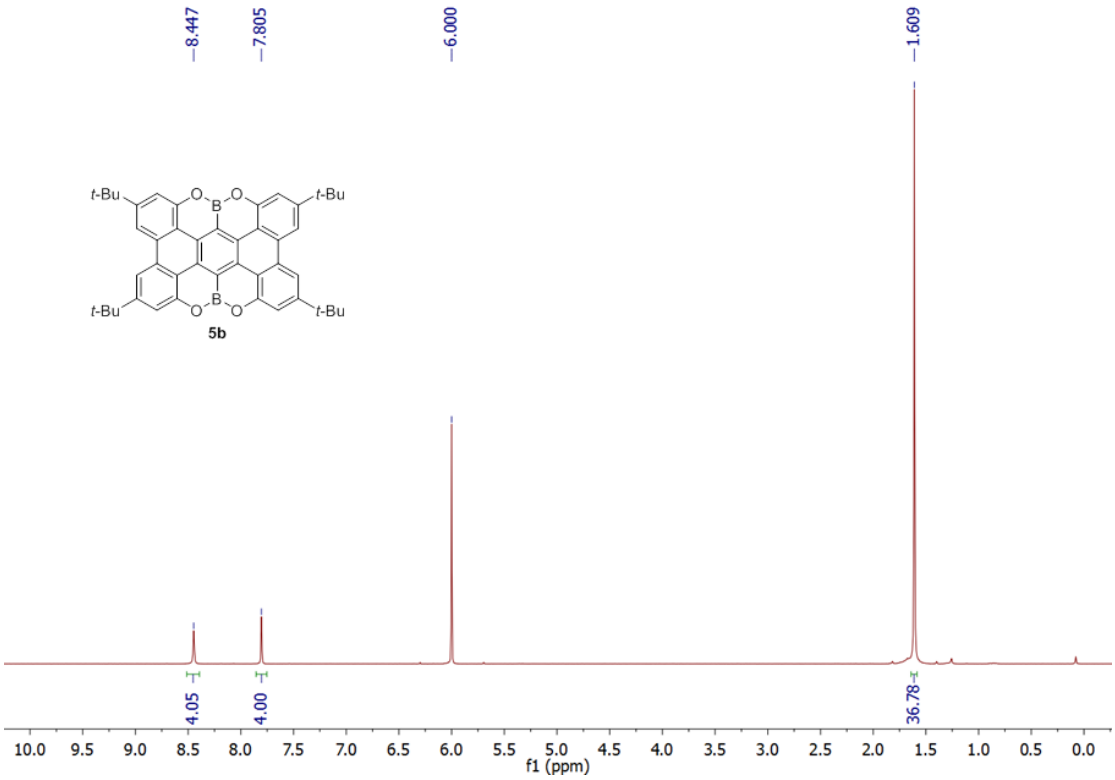


Figure S16. ^{1}H NMR spectrum of compound **5b** (300 MHz, $C_2D_2Cl_4$, 298 K).

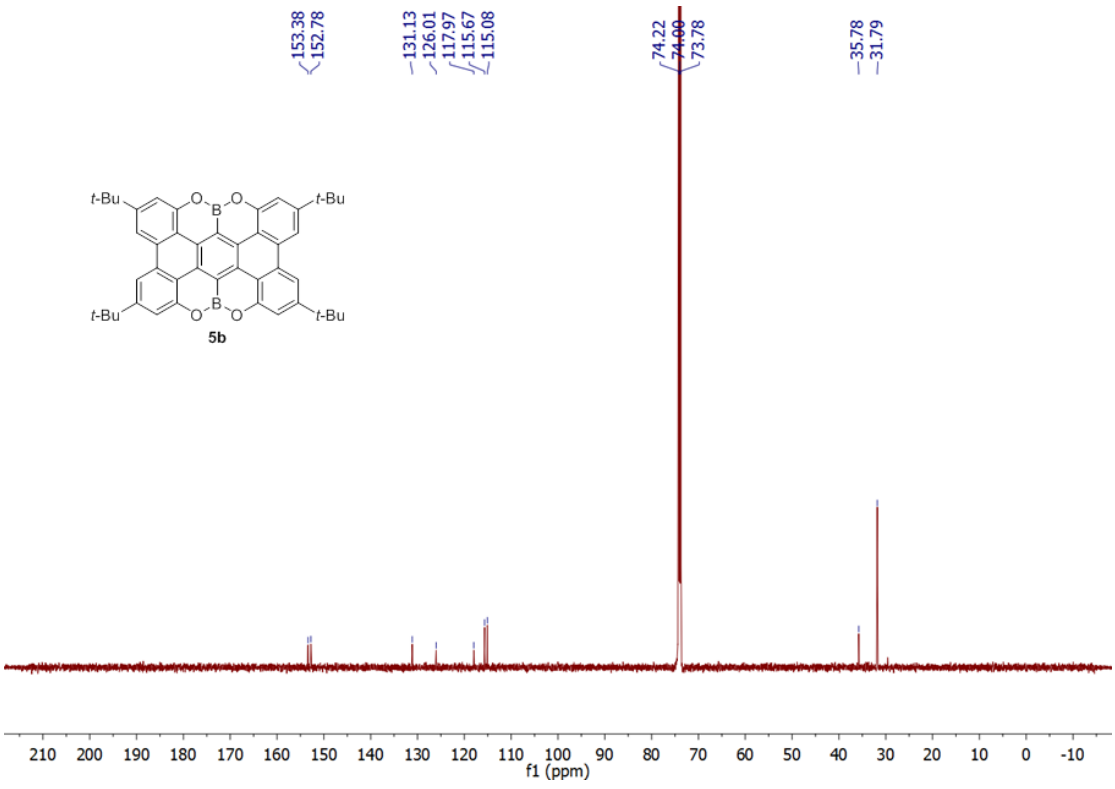


Figure S17. ^{13}C NMR spectrum of compound **5b** (125 MHz, $C_2D_2Cl_4$, 413 K).

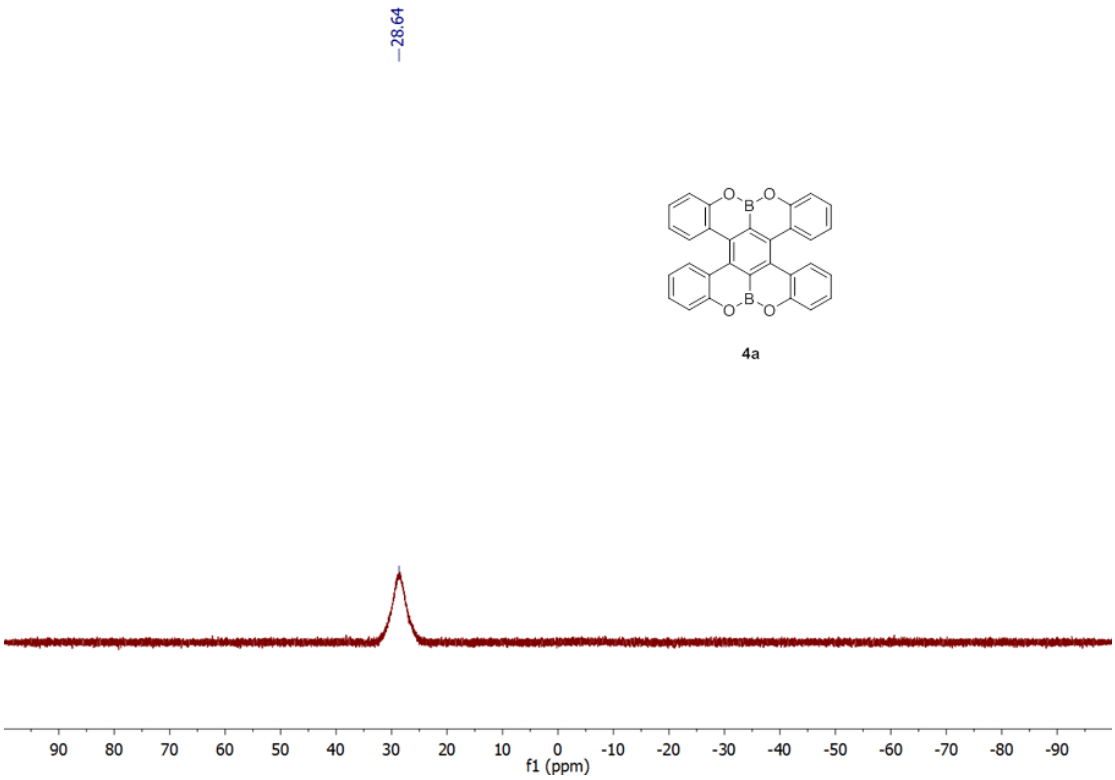


Figure S18. ^{11}B NMR spectrum of compound **4a** (160 MHz, $C_2D_2Cl_4$, 393 K).

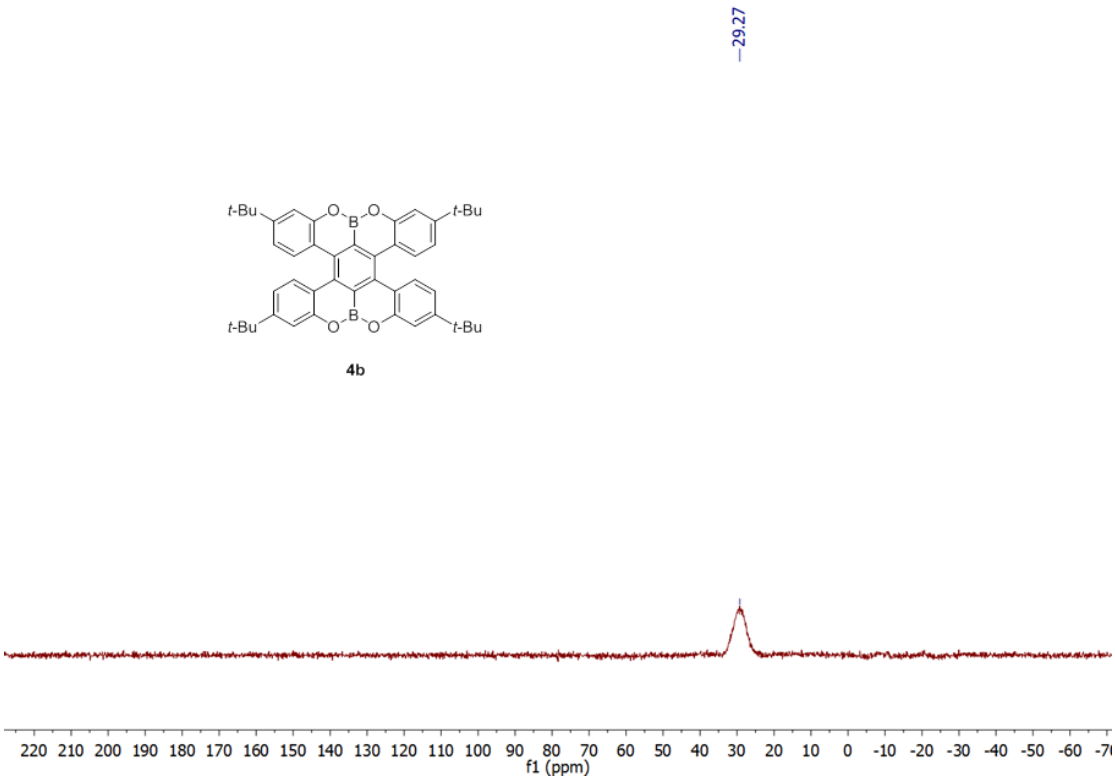


Figure S19. ^{11}B NMR spectrum of compound **4b** (160 MHz, CD_2Cl_2, 298 K).