Supporting Information

for

Library of Azabenz-Annulated Core-Extended Perylene Derivatives with Diverse Substitution Patterns and Tunable Electronic and Optical Properties

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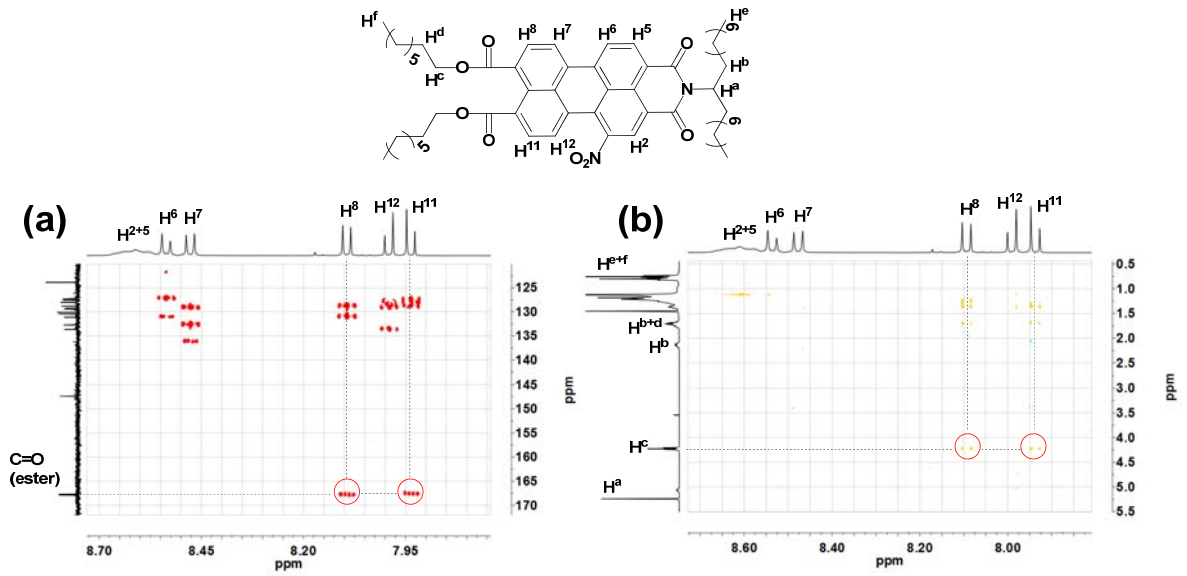


Figure S1. 2D NMR correlation spectra of 1-nitro-PMIDE **10** in CD_2Cl_2 at room temperature (400 MHz). (a) $^1H,^{13}C$-HMBC spectrum; (b) $^1H,^1H$-NOESY spectrum.

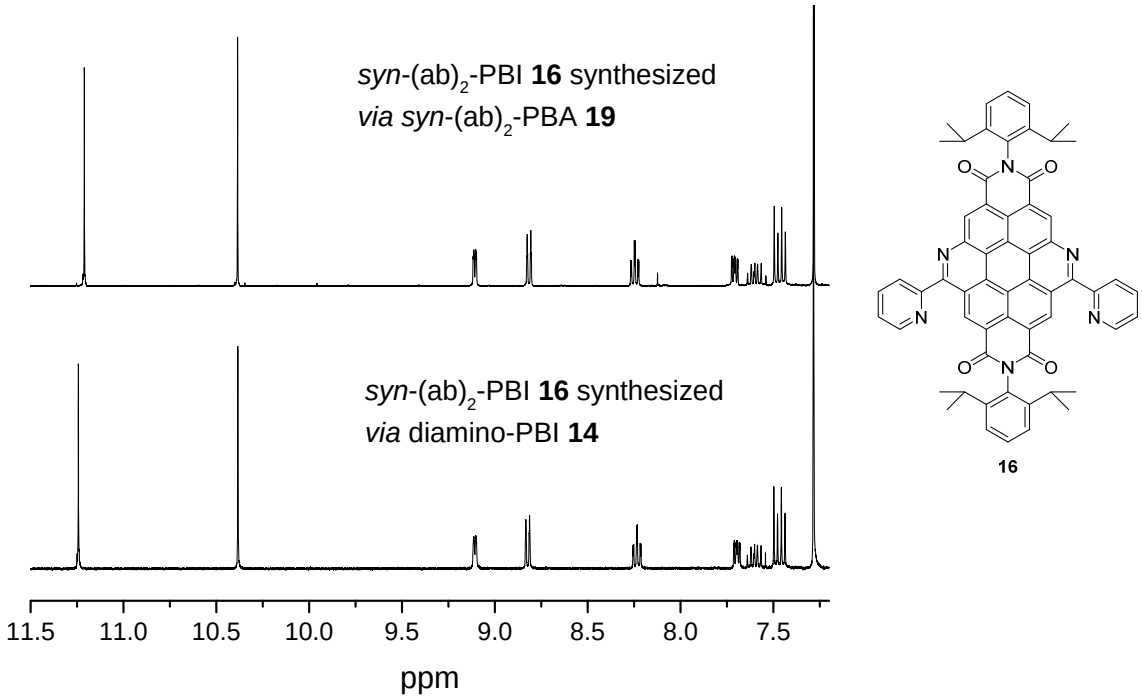


Figure S2. ^1H NMR ($CDCl_3$, 400 MHz) spectra (aromatic regions) of *syn*-(ab)$_2$-PBI **16** synthesized either by imidization of *syn*-(ab)$_2$-PBA **19** with 2,6-diisopropylaniline (top) or Pictet-Spengler reaction of diamino-PBI **14** with pyridine-2-carboxaldehyde **2a** (bottom).

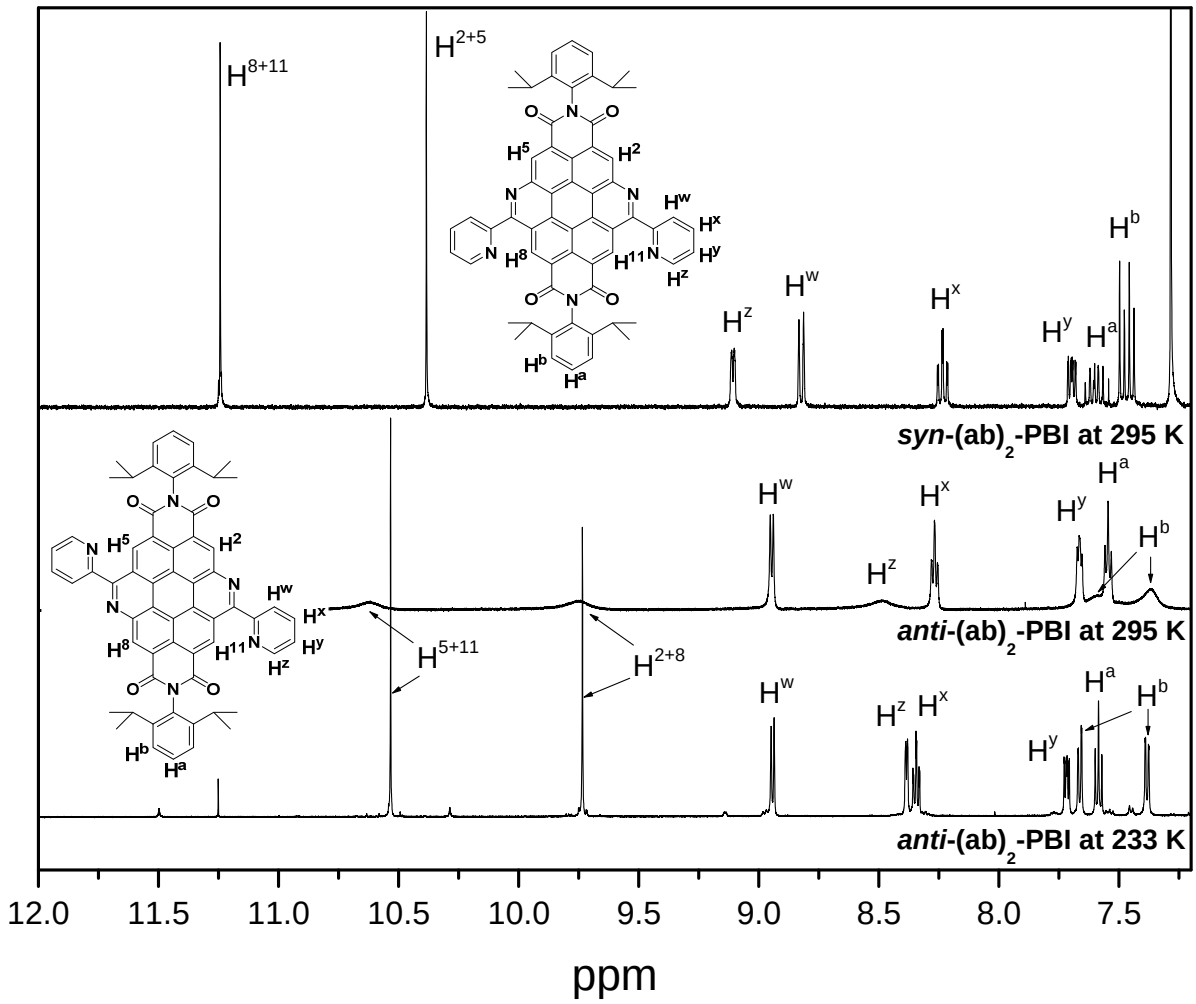


Figure S3. Comparison of the ^{1}H NMR spectra (aromatic regions) of *syn*-(ab)$_2$-PBI **16** at 295 K (top) and *anti*-(ab)$_2$-PBI **15** at 295 K (middle) and 233 K (bottom) in d$_8$-THF (400 MHz).

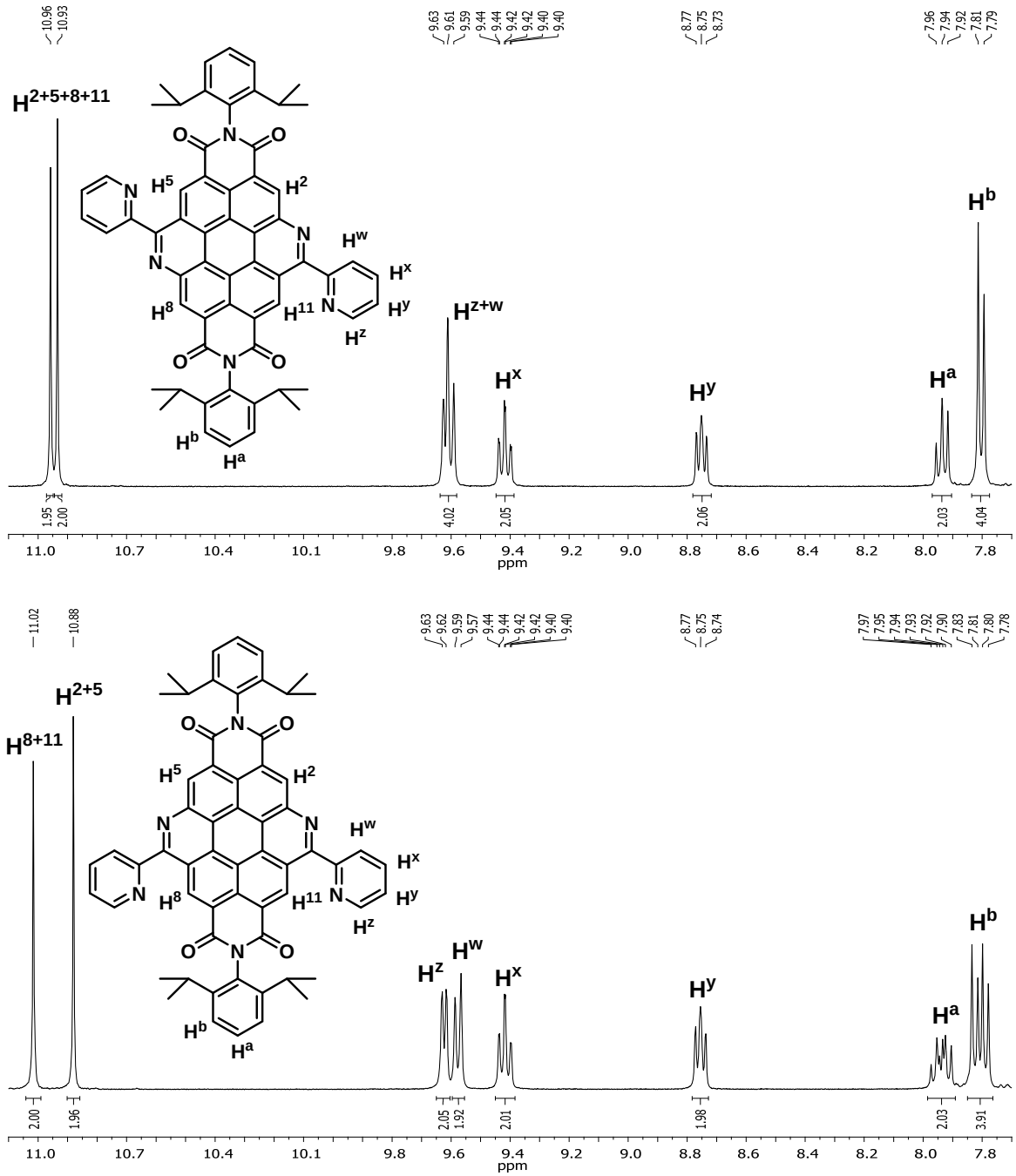


Figure S4. Comparison of the ^{1}H NMR spectra (aromatic regions) of *anti*-(ab)$_2$-PBI **15** (top) and *syn*-(ab)$_2$-PBI **16** (bottom) in d$_1$-trifluoroacetic acid (400 MHz, 295 K).

Table S1. Summary of the Optical Data of the ab-PBIs 3a-f[a]

compounds	λ_{abs} / nm (ε / 10^3 M^{-1} cm^{-1})	λ_{em} / nm	Φ_F
3a	475 (68.4)	484	0.69
3b	473 (66.2)	482	0.52
3c	477 (60.0)	488	0.62
3d	477 (56.4)	487	0.63
3e	477 (59.5)	488	0.55
3f	477 (60.4)	489	0.55

[a] Measured in dichloromethane at 298 K.

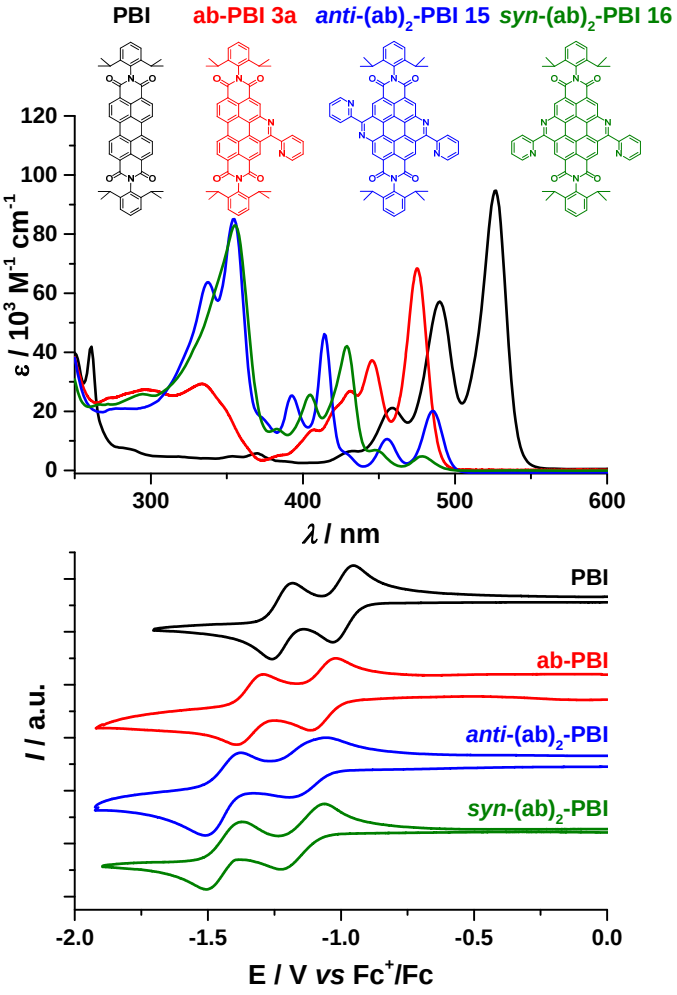


Figure S5. UV/Vis absorption spectra (top, $c = 1 \cdot 10^{-5}$ M) and cyclic voltammograms (bottom, $c = 2.5 \cdot 10^{-4}$ M, electrolyte: 0.1 M *n*-Bu_4NPF_6) of a reference PBI and newly synthesized different core-extended perylene bisimides in dichloromethane at room temperature. The electrochemical values were corrected *vs* ferrocenium/ferrocene as an internal standard.

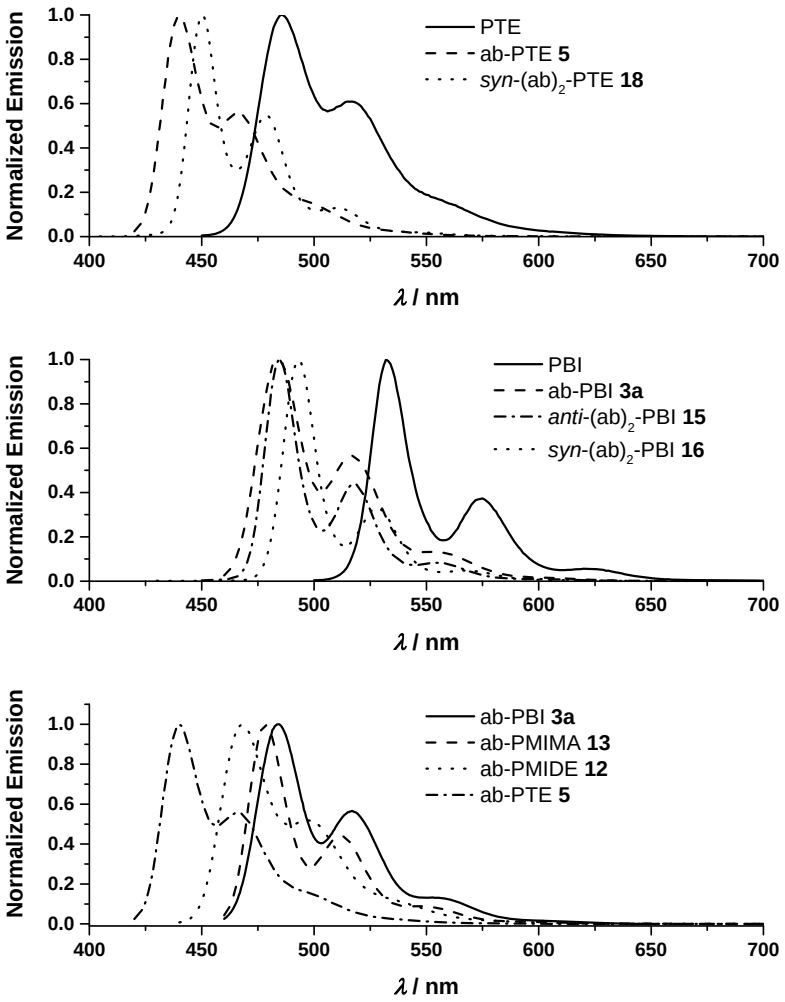


Figure S6. Normalized emission spectra of azabenz-annulated perylene derivatives measured in dichloromethane at room temperature (λ_{ex} in the lowest energetic absorption band).

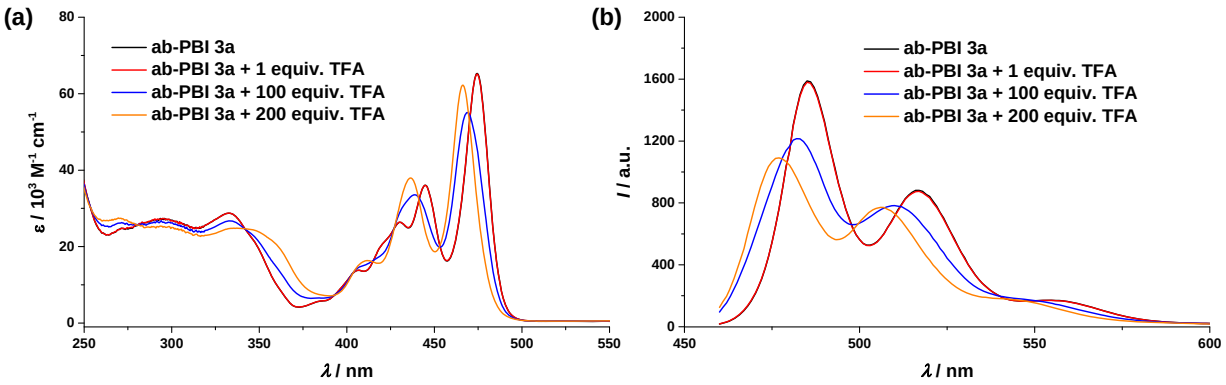


Figure S7. UV/Vis absorption (a) and emission spectra (b) of ab-PBI **3a** after addition of different equivalents of trifluoroacetic acid (TFA). Measurements were performed in dichloromethane at room temperature (c = ~1·10^{-5} M).

Table S2. Data Obtained from (TD)-DFT Calculations (B3LYP, def2-SVP) for Different Azabenz-annulated Perylene Derivatives

compounds	E^{HOMO} / eV	E^{LUMO} / eV	S_0-S_1 transition				
			λ / nm	E / eV	f^a	excitation[b]	coefficient
PTE	–5.74	–2.97	481	2.58	0.601	H→L	0.7046
ab-PTE (**5**)	–5.97	–2.80	430	2.88	0.373	H→L	0.6843
syn-(ab)$_2$-PTE (**18**)	–6.18	–2.65	426	2.91	0.029	multiple excitations[c]	
PBI	–6.22	–3.70	519	2.39	0.787	H→L	0.6945
ab-PBI (**3a**)	–6.39	–3.51	473	2.62	0.346	H→L	0.6036
anti-(ab)$_2$-PBI (**15**)	–6.40	–3.36	467	2.65	0.2086	multiple excitations[c]	
syn-(ab)$_2$-PBI (**16**)	–6.51	–3.36	453	2.74	0.028	multiple excitations[c]	
ab-PBI (**3a**)	–6.39	–3.51	473	2.62	0.346	H→L	0.6036
ab-PMIMA (**13**)	–6.55	–3.66	465	2.67	0.396	H→L	0.6856
ab-PMIDE (**12**)	–6.14	–3.16	455	2.73	0.431	H→L	0.6890
ab-PTE (**5**)	–5.97	–2.80	430	2.88	0.373	H→L	0.6843

[a] Oscillator strength. [b] H = HOMO and L = LUMO. [c] More than one specific excitation contributes to the lowest energetic transition.

2 NMR and mass spectra of ab-PBIs 3a-f

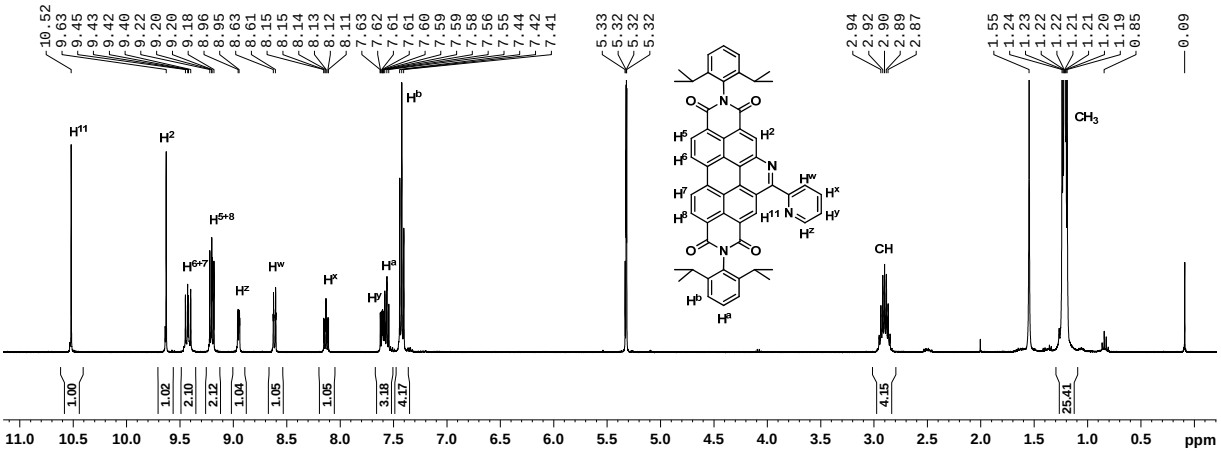


Figure S8. ^{1}H NMR spectrum of ab-PBI **3a** with tentative assignment of the protons (400 MHz, CD_2Cl_2).

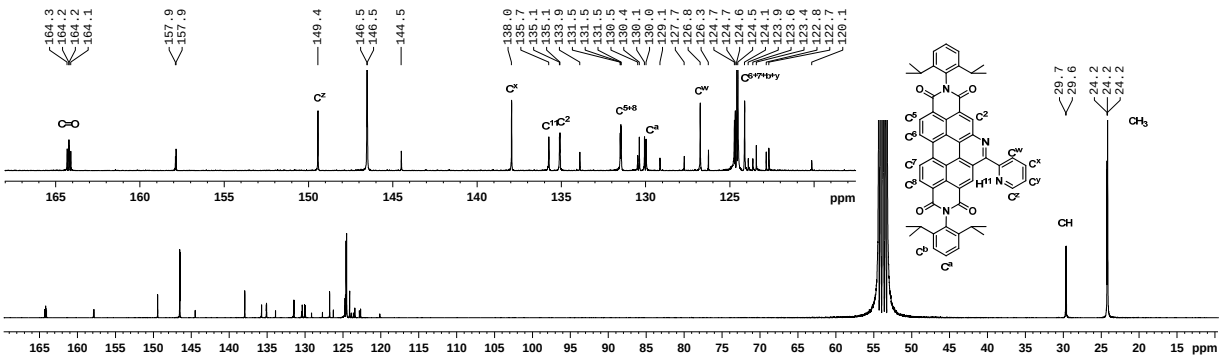


Figure S9. ^{13}C NMR spectrum of ab-PBI **3a** and expansion of the aromatic region with tentative assignment of non-quaternary carbon atoms (100 MHz, CD_2Cl_2).

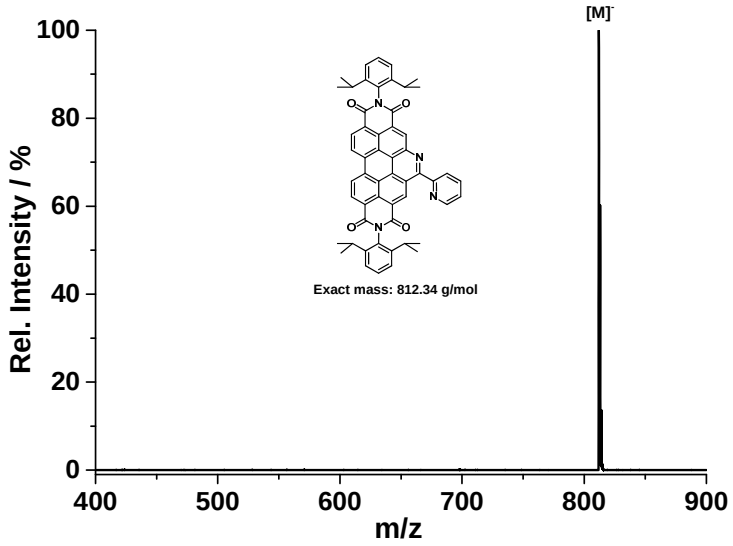


Figure S10. MALDI-TOF mass spectrum of ab-PBI **3a** with the $[M]^-$ peak at 811.95 *m/z* (matrix: DCTB in chloroform, mode: negative).

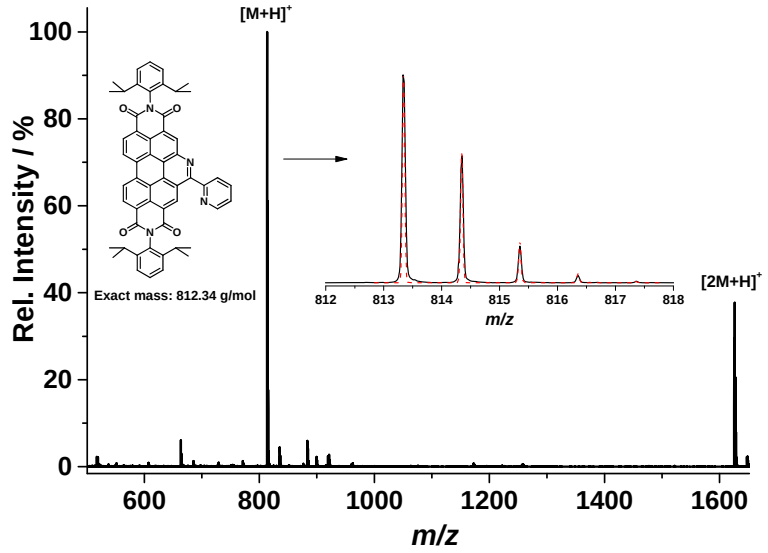


Figure S11. ESI-TOF mass spectrum of ab-PBI **3a** in acetonitrile/chloroform 1:1 in positive mode. Inset: Zoomed spectrum of the $[M+H]^+$ peak (black solid) und the simulated spectrum (red dashed) of ab-PBI **3a**.

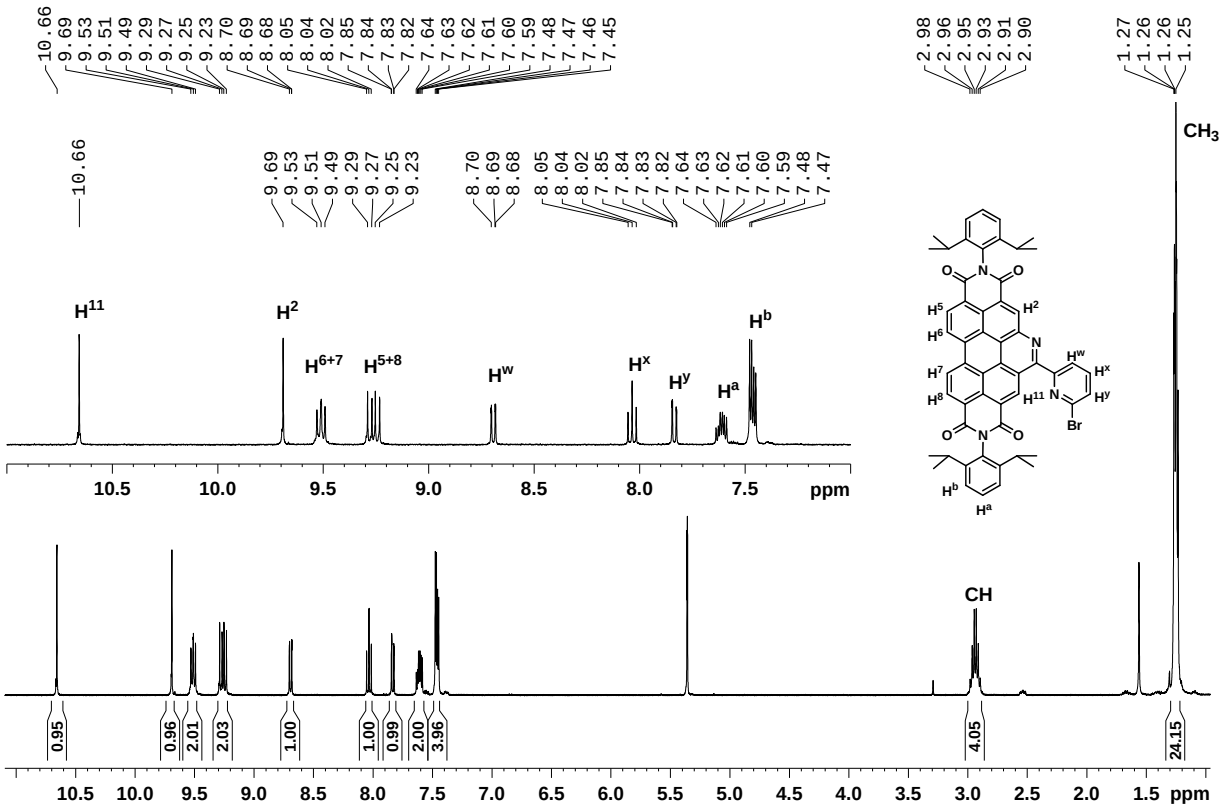


Figure S12. ^{1}H NMR spectrum of ab-PBI **3b** and expansion of the aromatic region with tentative assignment of the protons (400 MHz, CD_2Cl_2).

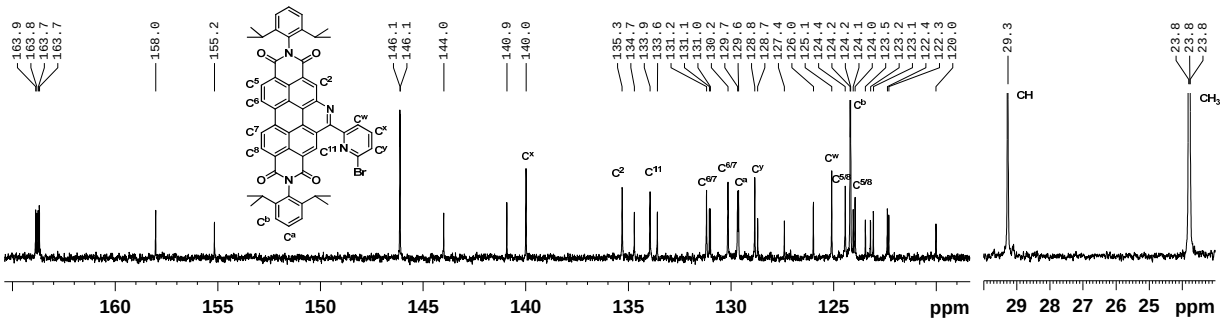


Figure S13. ^{13}C NMR spectrum of ab-PBI **3b** with tentative assignment of non-quaternary carbon atoms (100 MHz, CD_2Cl_2).

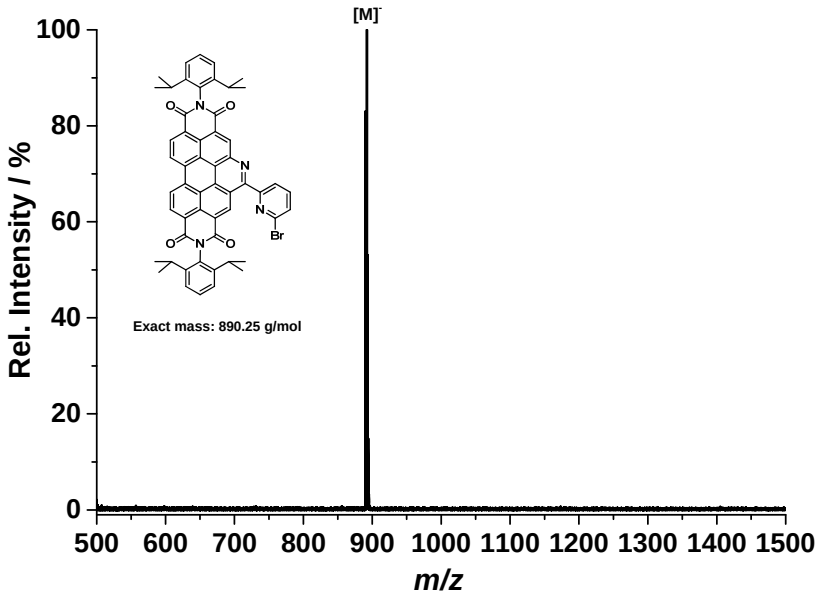


Figure S14. MALDI-TOF mass spectrum of ab-PBI **3b** with the $[M]^-$ peak at 890.19 *m/z* (matrix: DCTB in chloroform, mode: negative).

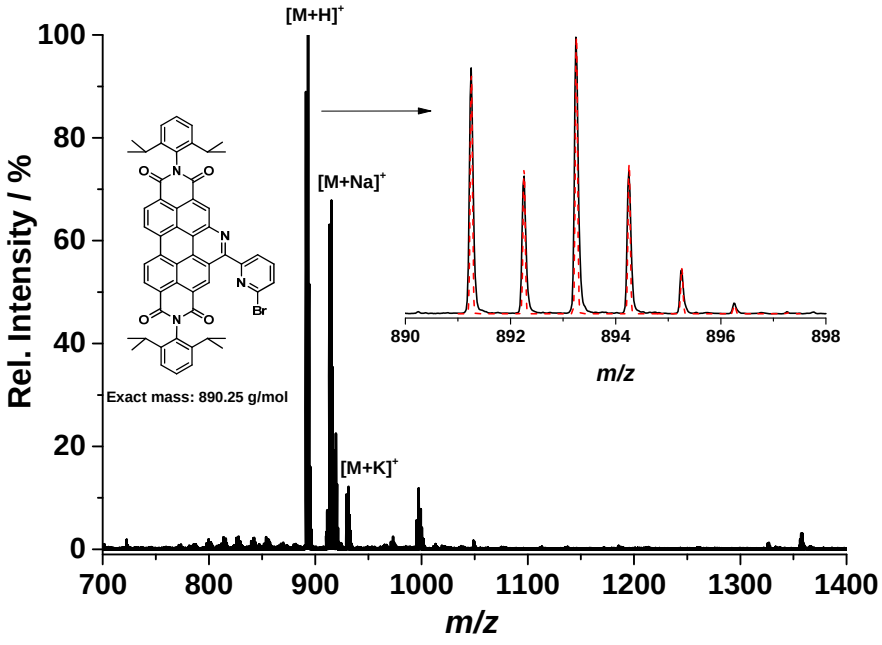


Figure S15. ESI-TOF mass spectrum of ab-PBI **3b** in acetonitrile/chloroform 1:1 in positive mode. Inset: Zoomed spectrum of the $[M+H]^+$ peak (black solid) und the simulated spectrum (red dashed) of ab-PBI **3b**.

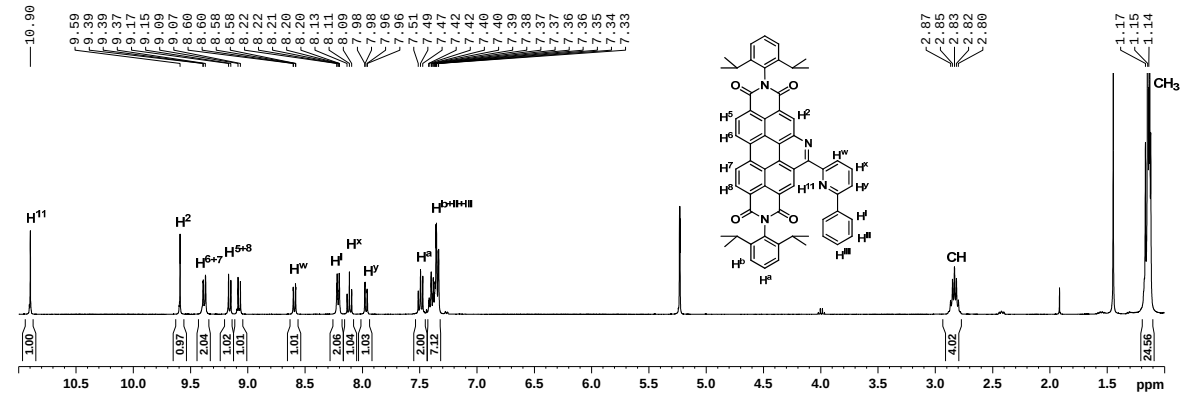


Figure S16. ^{1}H NMR spectrum of ab-PBI **3c** with tentative assignment of the protons (400 MHz, CD_2Cl_2).

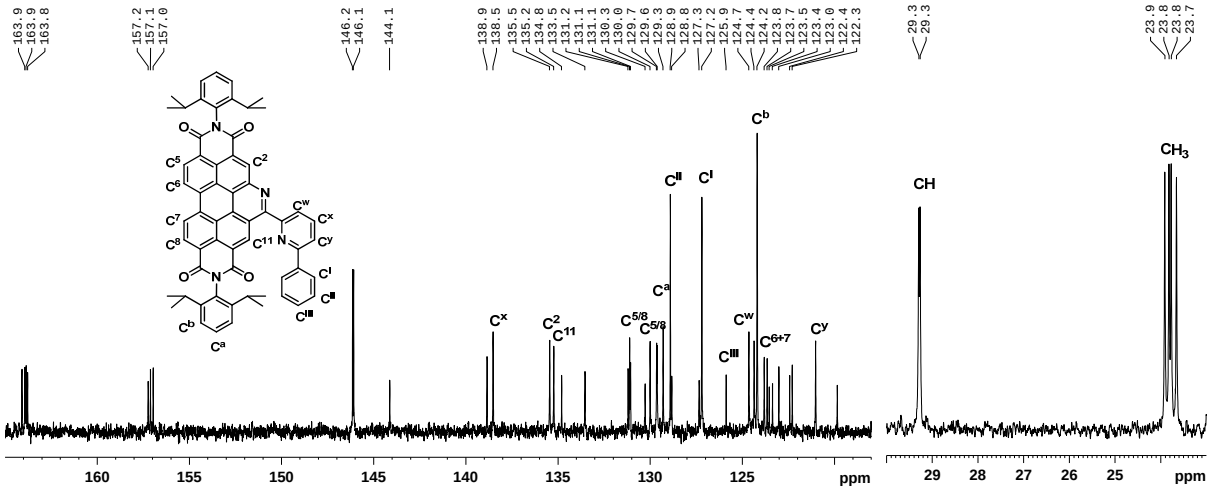


Figure S17. ^{13}C NMR spectrum (aromatic and alkyl regions) of ab-PBI **3c** with tentative assignment of non-quaternary carbon atoms (100 MHz, CD_2Cl_2).

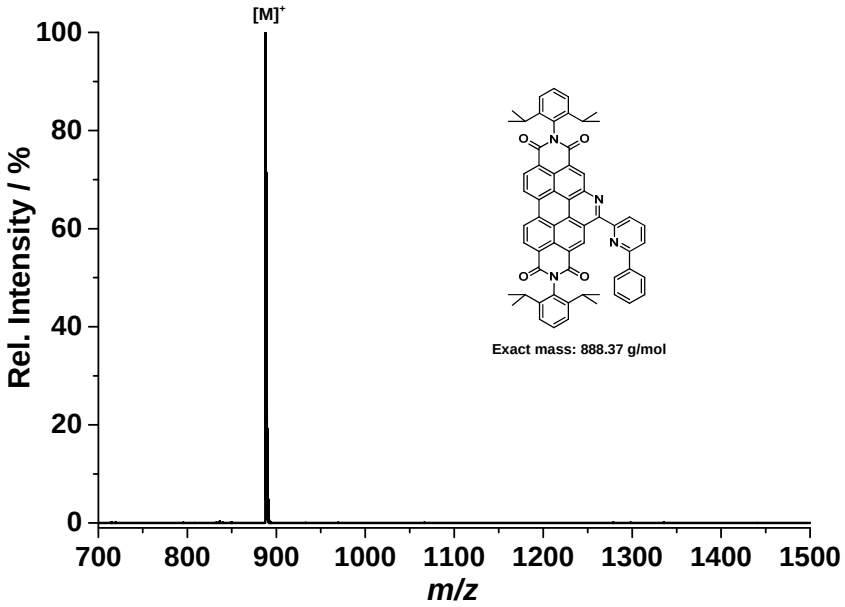


Figure S18. MALDI-TOF mass spectrum of ab-PBI **3c** with the $[M]^+$ peak at 887.96 *m/z* (matrix: DCTB in chloroform, mode: positive).

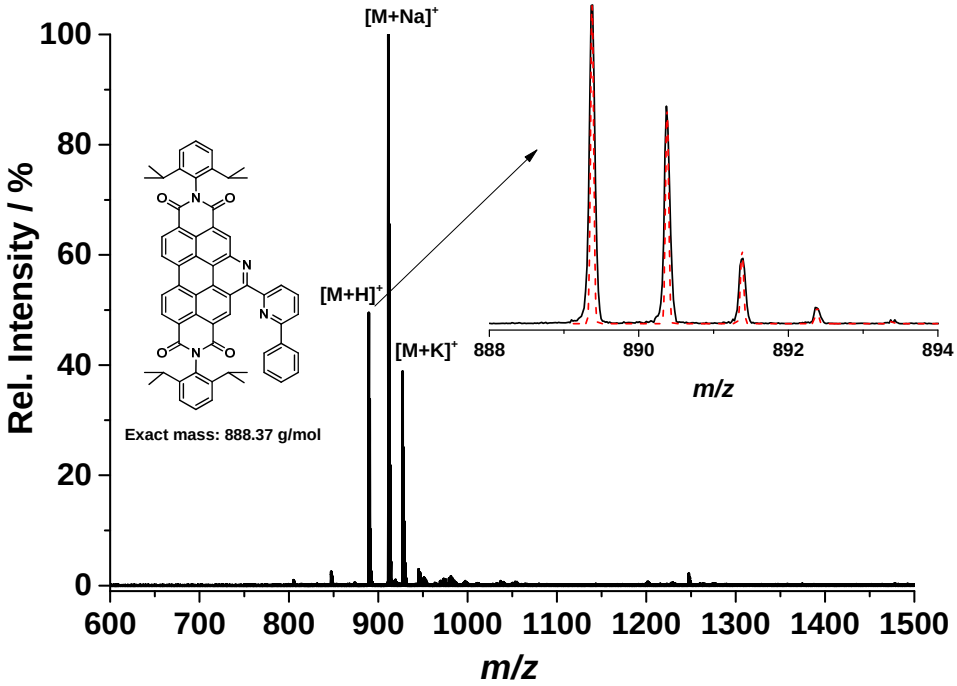


Figure S19. ESI-TOF mass spectrum of ab-PBI **3c** in acetonitrile/chloroform 1:1 in positive mode. Inset: Zoomed spectrum of the $[M+H]^+$ peak (black solid) und the simulated spectrum (red dashed) of ab-PBI **3c**.

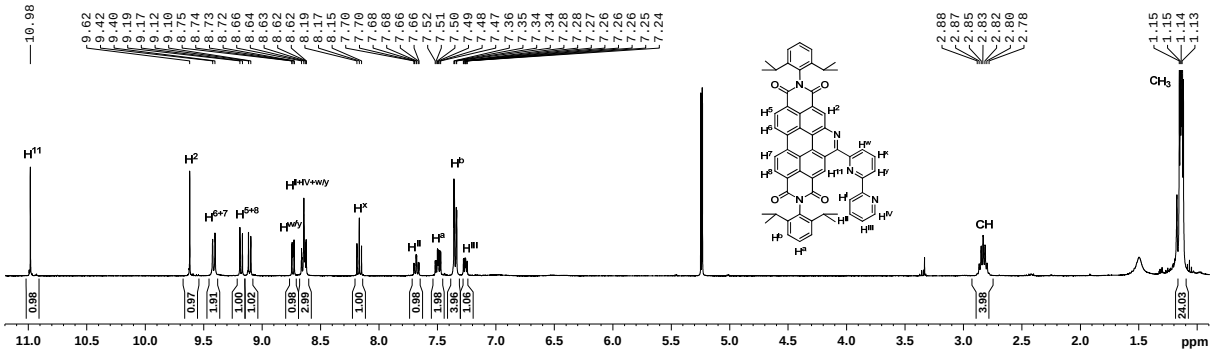


Figure S20. ^{1}H NMR spectrum of ab-PBI **3d** with tentative assignment of the protons (400 MHz, CD_2Cl_2).

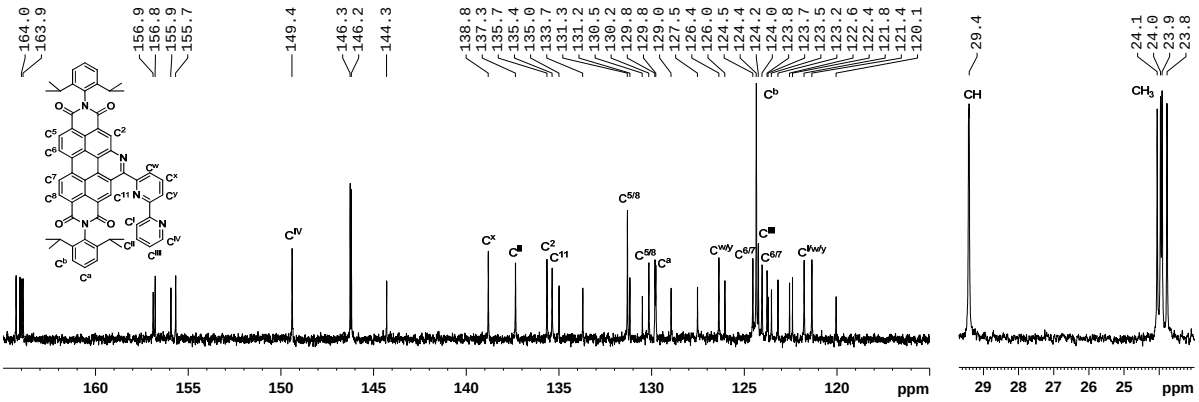


Figure S21. ^{13}C NMR spectrum (aromatic and alkyl regions) of ab-PBI **3d** with tentative assignment of non-quaternary carbon atoms (100 MHz, CD_2Cl_2).

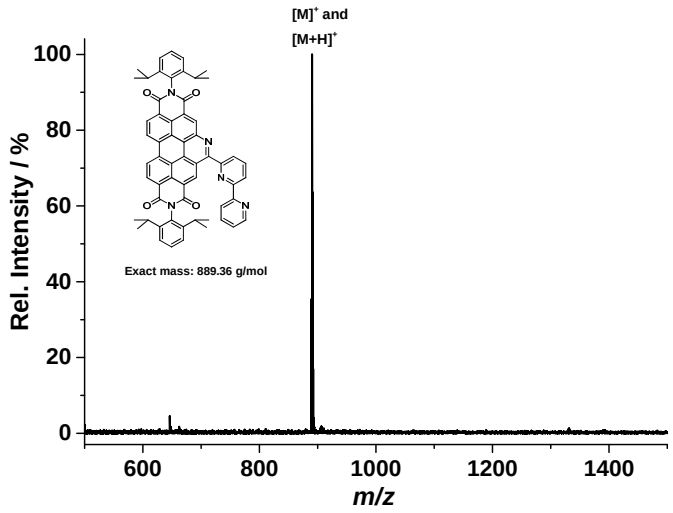


Figure S22. MALDI-TOF mass spectrum of ab-PBI **3d** with the $[M]^+$ peak at 889.29 *m/z* (matrix: DCTB in chloroform, mode: positive).

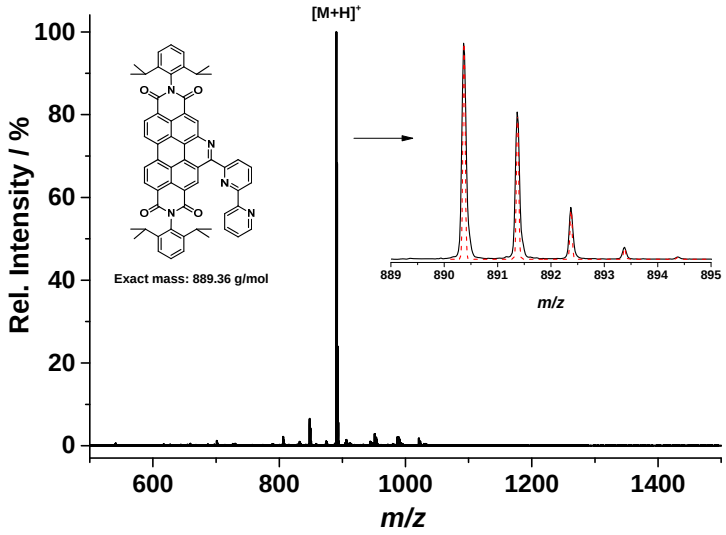


Figure S23. ESI-TOF mass spectrum of ab-PBI **3d** in acetonitrile/chloroform 1:1 in positive mode. Inset: Zoomed spectrum of the $[M+H]^+$ peak (black solid) und the simulated spectrum (red dashed) of ab-PBI **3d**.

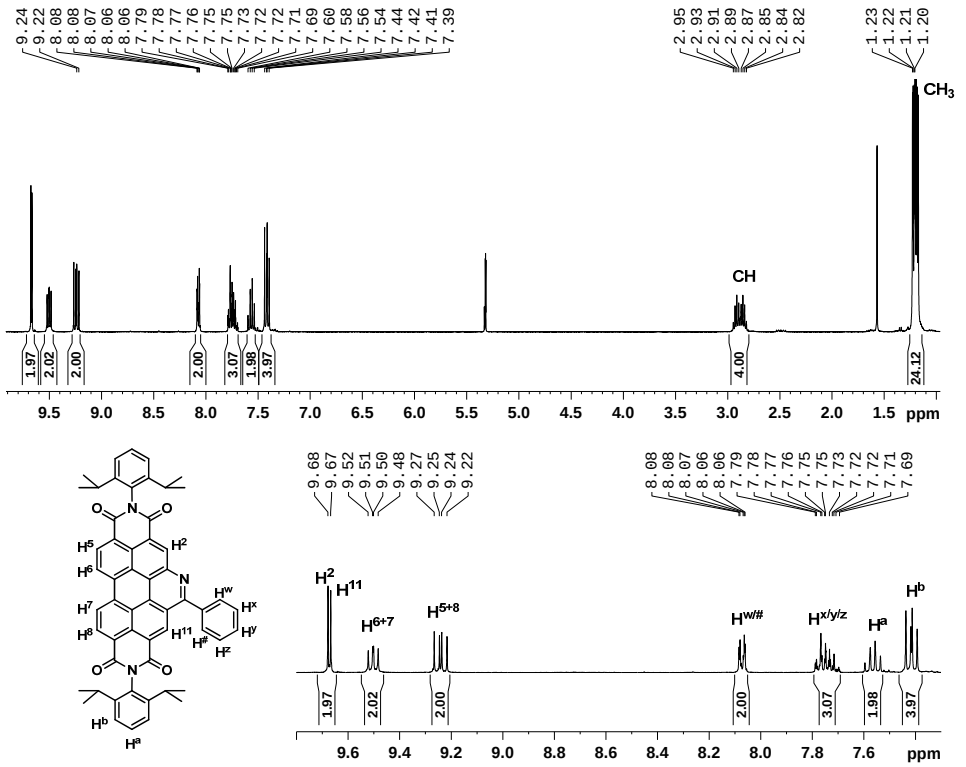


Figure S24. ^{1}H NMR spectrum of ab-PBI **3e** and expansion of the aromatic region with tentative assignment of the protons (400 MHz, CD_2Cl_2).

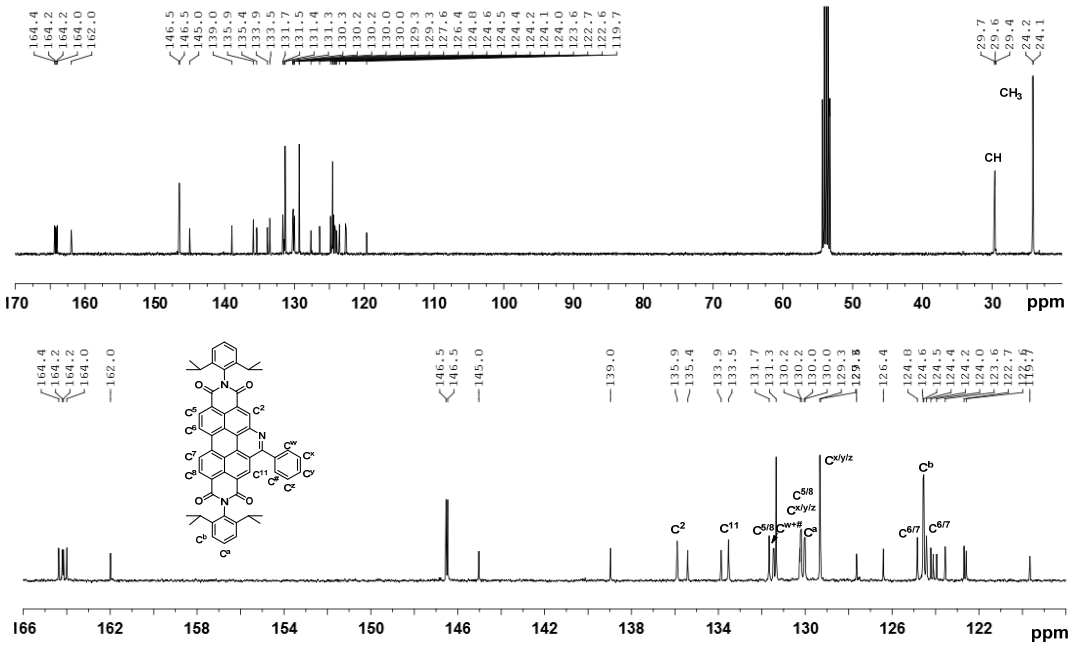


Figure S25. ^{13}C NMR spectrum of ab-PBI **3e** and expansion of the aromatic region with tentative assignment of non-quaternary carbon atoms (100 MHz, CD_2Cl_2).

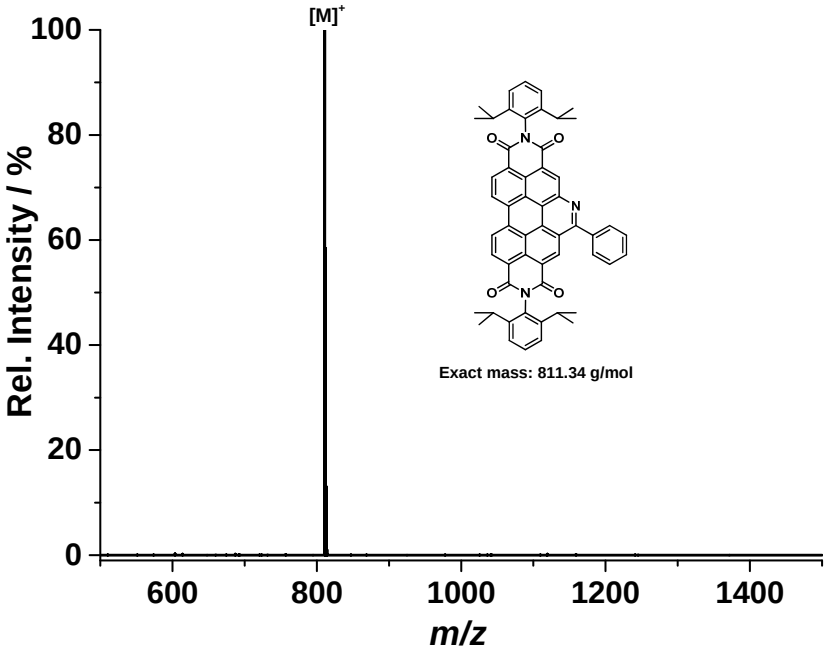


Figure S26. MALDI-TOF mass spectrum of ab-PBI **3e** with the $[M]^+$ peak at 810.95 *m/z* (matrix: DCTB in chloroform, mode: positive).

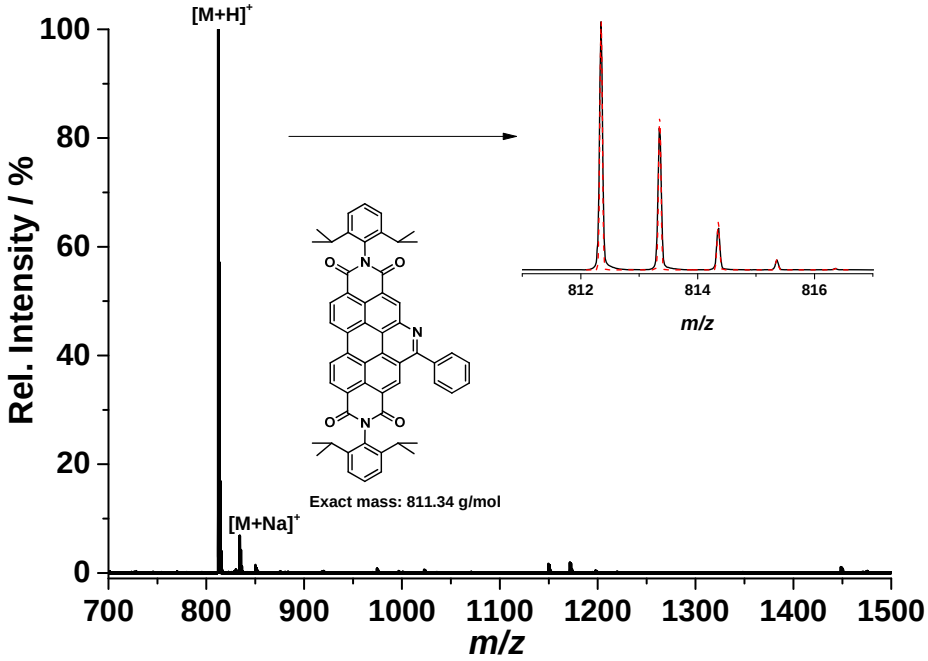


Figure S27. ESI-TOF mass spectrum of ab-PBI **3e** in acetonitrile/chloroform 1:1 in positive mode. Inset: Zoomed spectrum of the $[M+H]^+$ peak (black solid) und the simulated spectrum (red dashed) of ab-PBI **3e**.

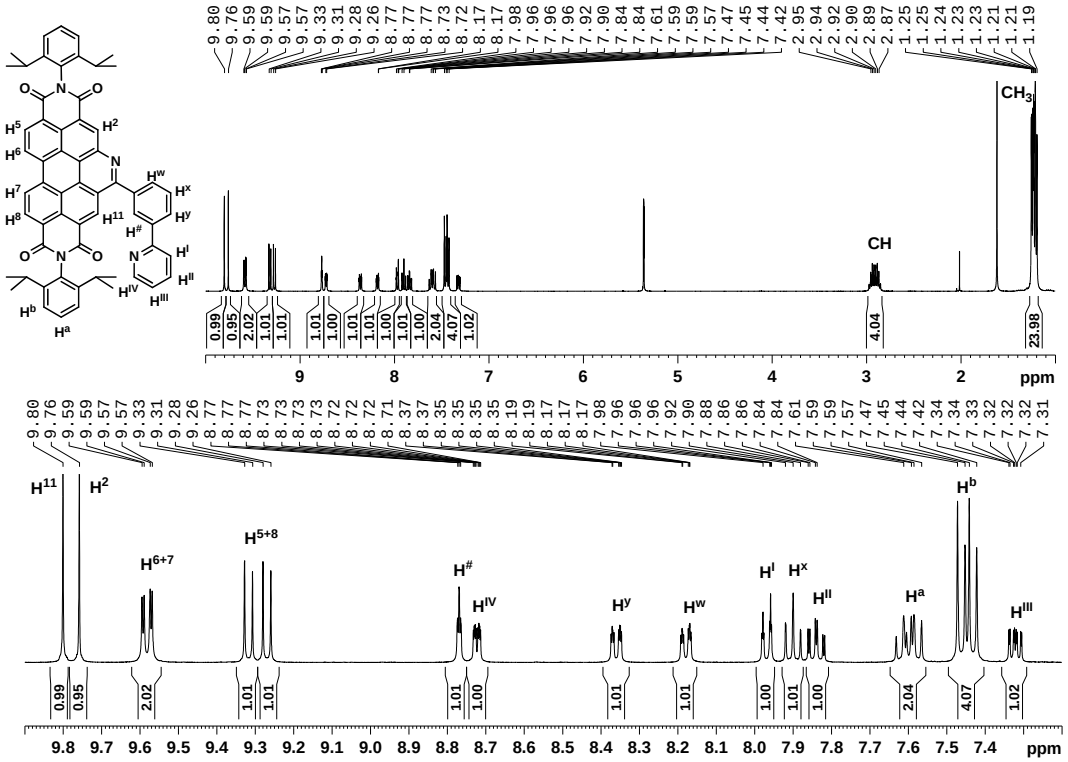


Figure S28. ^{1}H NMR spectrum of ab-PBI **3f** and expansion of the aromatic region with tentative assignment of the protons (400 MHz, CD_2Cl_2).

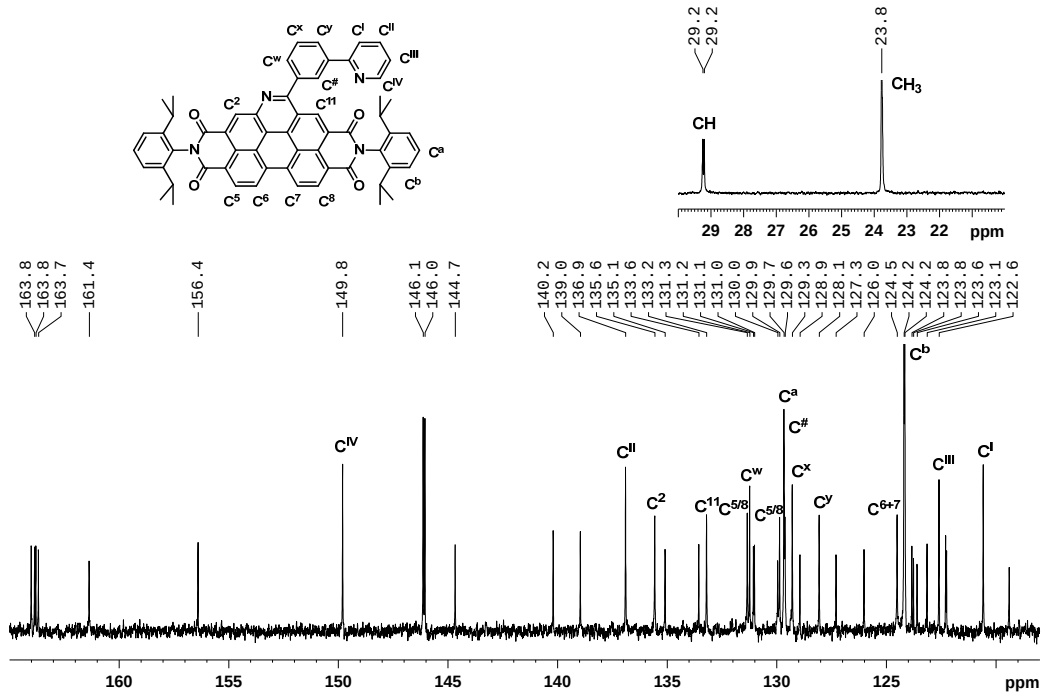


Figure S29. ^{13}C NMR spectrum (aromatic and alkyl regions) of ab-PBI **3f** with tentative assignment of non-quaternary carbon atoms (100 MHz, CD_2Cl_2).

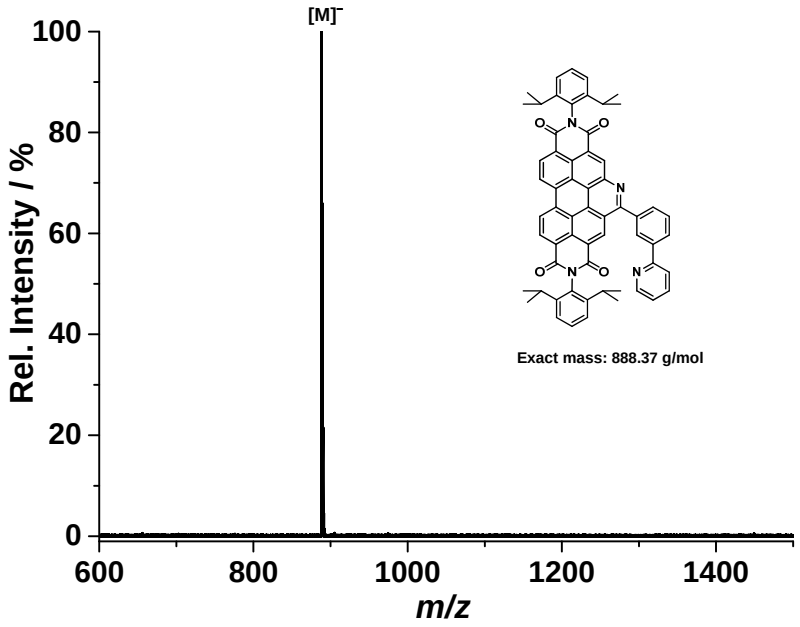


Figure S30. MALDI-TOF mass spectrum of ab-PBI **3f** with the $[M]^-$ peak at 888.31 *m/z* (matrix: DCTB in chloroform, mode: negative).

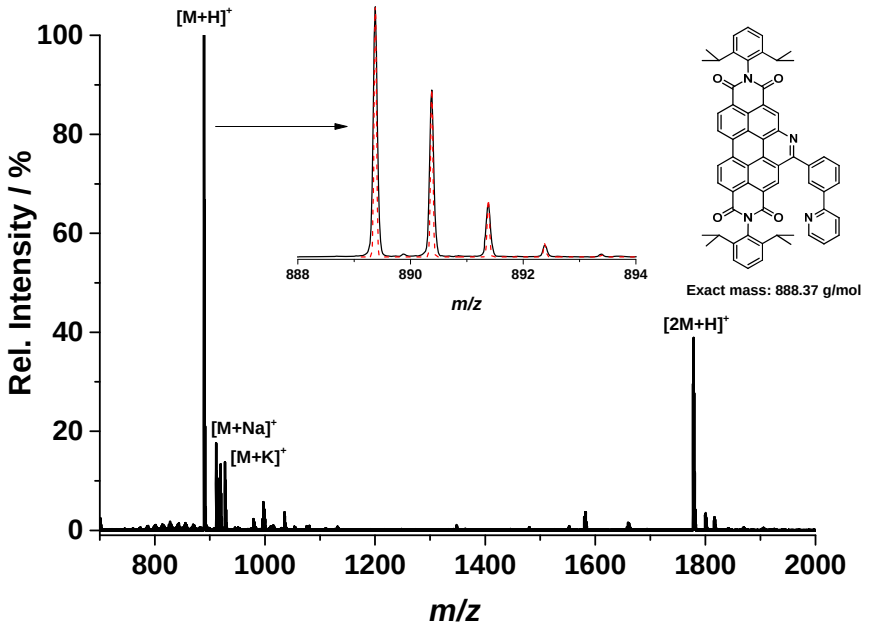


Figure S31. ESI-TOF mass spectrum of ab-PBI **3f** in acetonitrile/chloroform 1:1 in positive mode. Inset: Zoomed spectrum of the $[M+H]^+$ peak (black solid) und the simulated spectrum (red dashed) of ab-PBI **3f**.

3 NMR and mass spectra of ab-PTE 5, ab-PBA 6 and ab-PBI^{OEG} 8

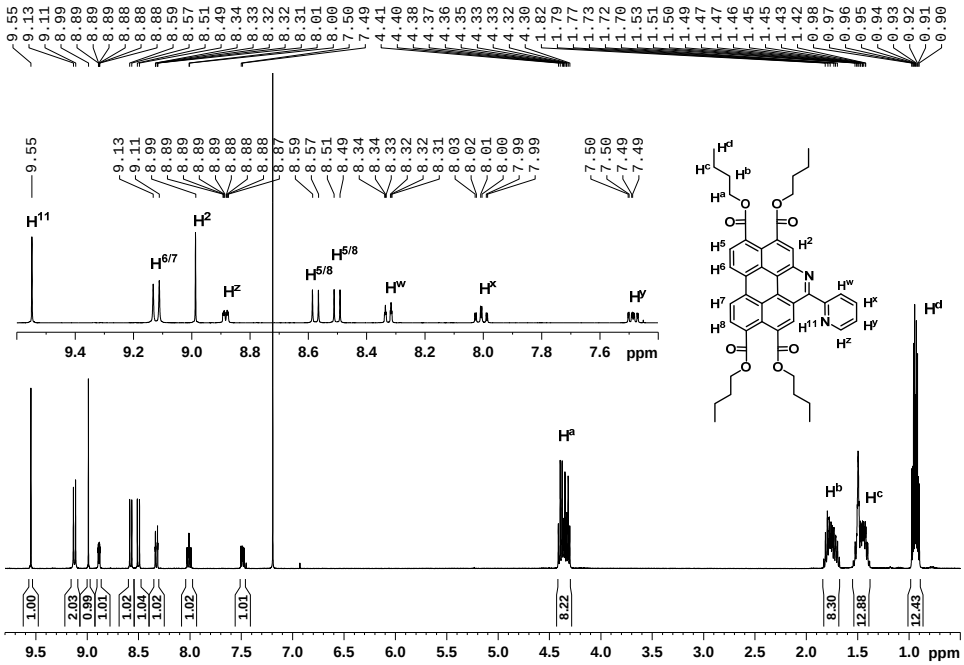


Figure S32. ^{1}H NMR spectrum of ab-PTE **5** and expansion of the aromatic region with tentative assignment of the protons (400 MHz, CD_2Cl_2).

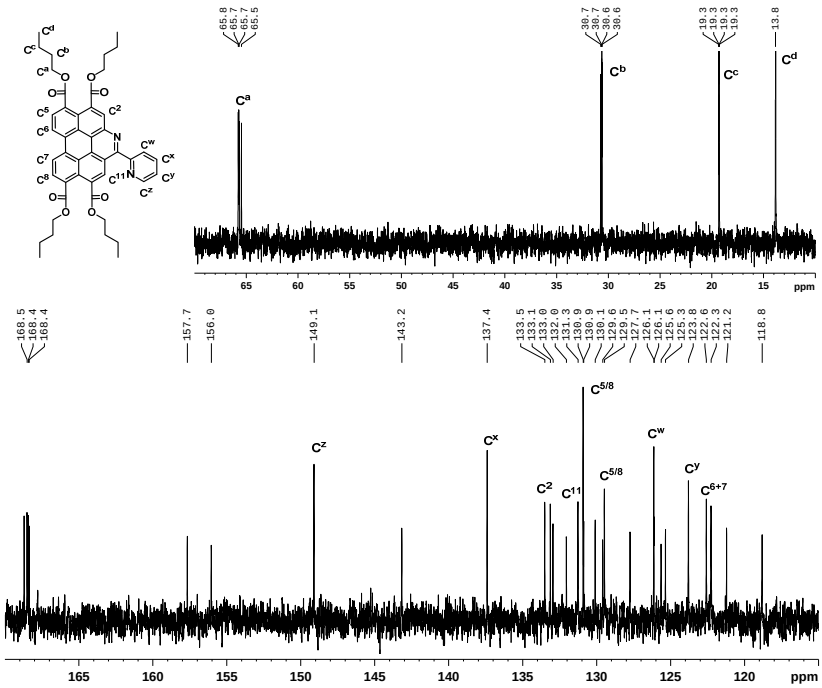


Figure S33. ^{13}C NMR spectrum (aromatic and alkyl regions) of ab-PTE **5** with tentative assignment of non-quaternary carbon atoms (100 MHz, CD_2Cl_2).

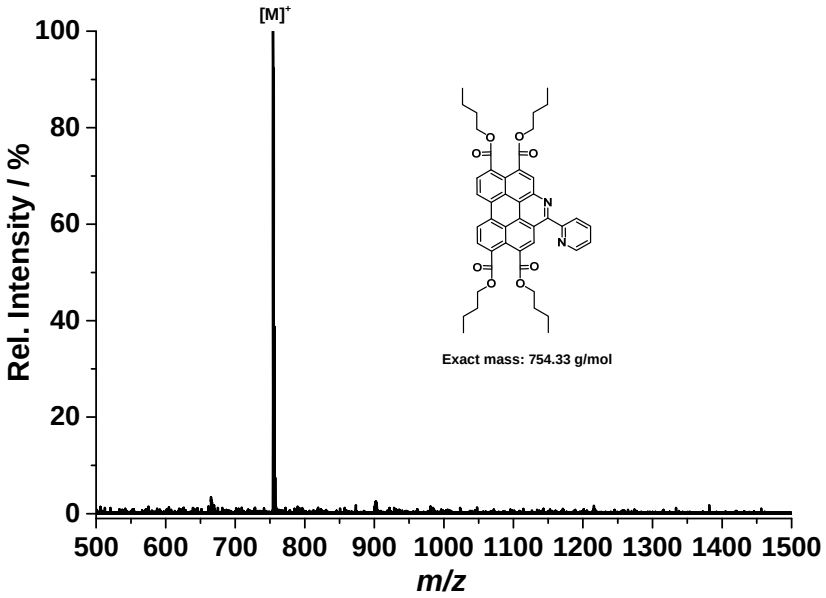


Figure S34. MALDI-TOF mass spectrum of ab-PTE **5** with the $[M]^+$ peak at 754.34 *m/z* (matrix: DCTB in chloroform, mode: positive).

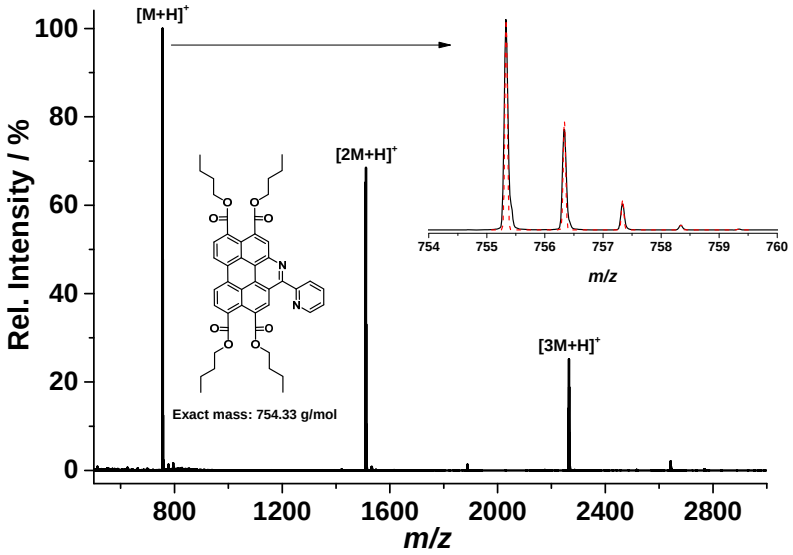


Figure S35. ESI-TOF mass spectrum of ab-PTE **5** in acetonitrile/chloroform 1:1 in positive mode. Inset: Zoomed spectrum of the $[M+H]^+$ peak (black solid) und the simulated spectrum (red dashed) of ab-PTE **5**.

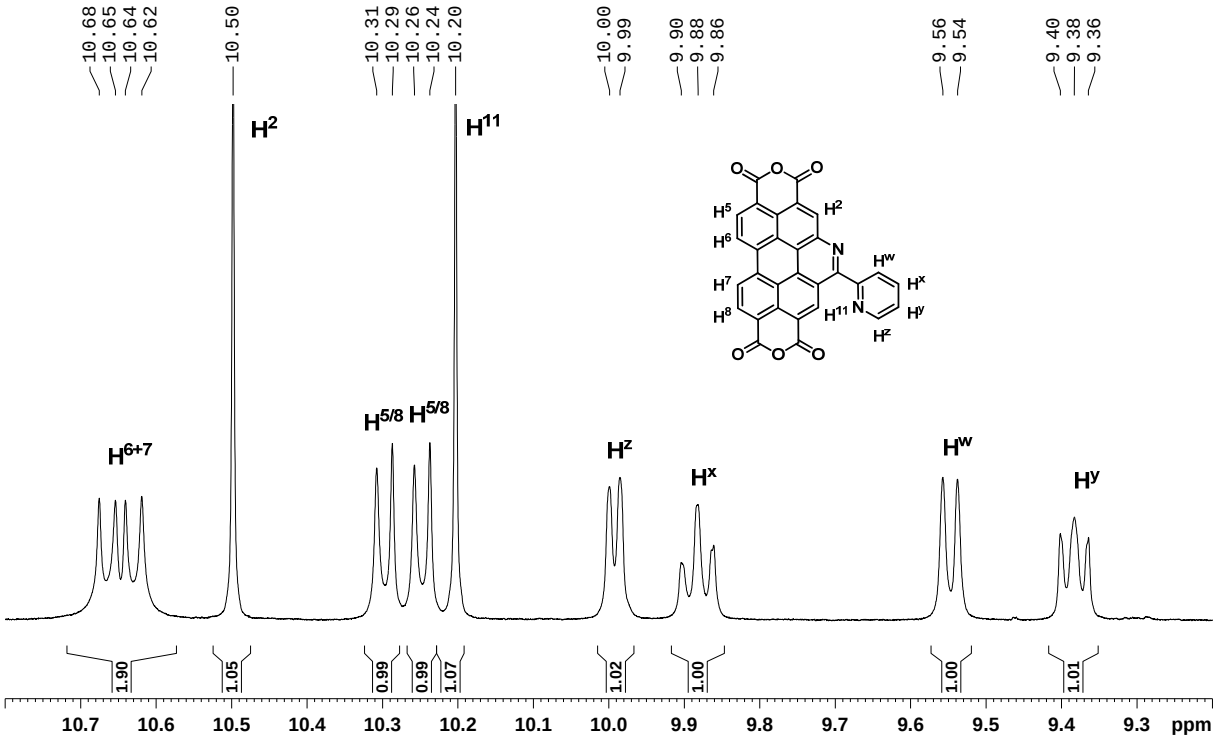


Figure S36. ^{1}H NMR spectrum (aromatic region) of ab-PBA **6** with tentative assignment of the protons (400 MHz, D_2SO_4).

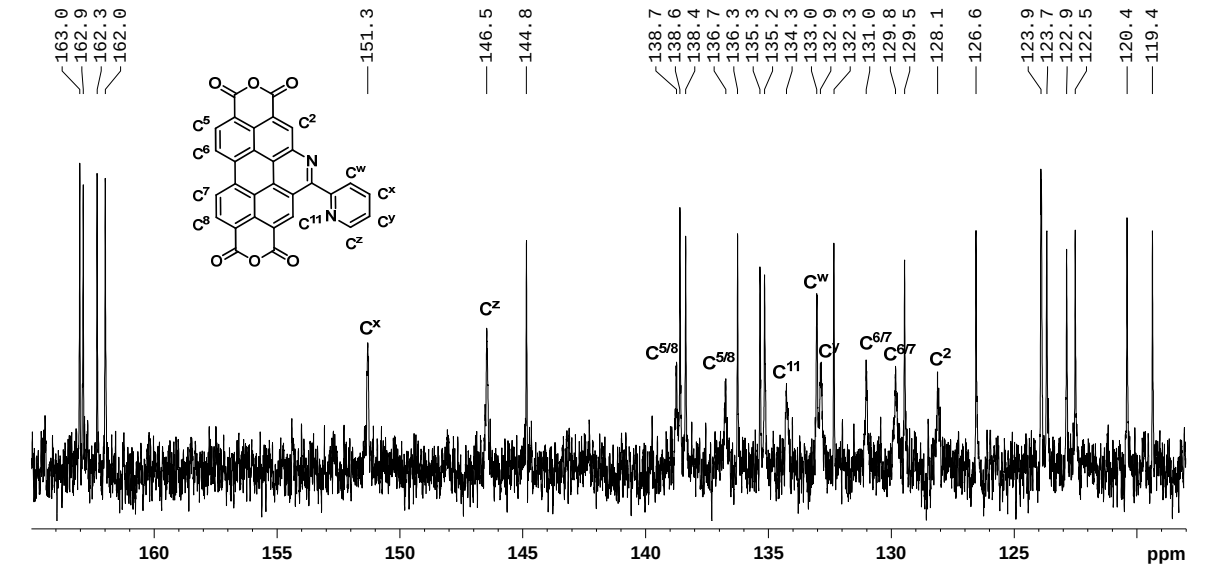


Figure S37. ^{13}C NMR spectrum (aromatic region) of ab-PBA **6** with tentative assignment of non-quaternary carbon atoms (100 MHz, D_2SO_4).

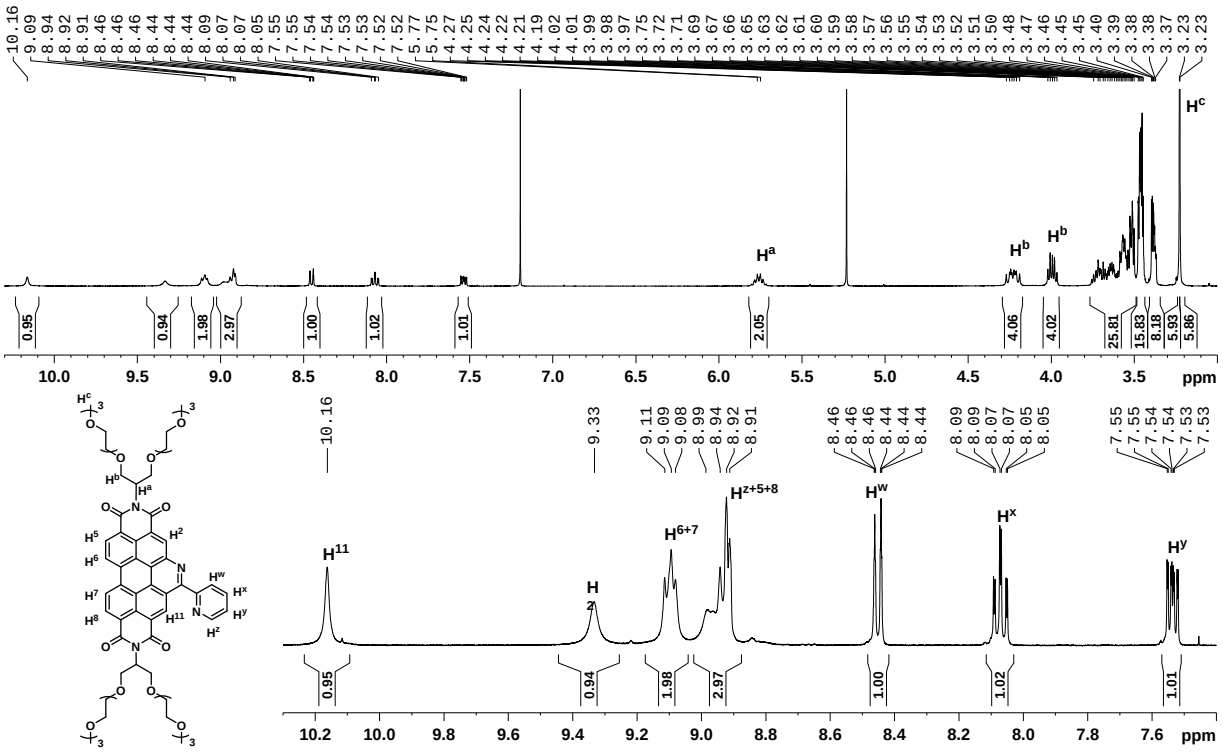


Figure S38. ^{1}H NMR spectrum of ab-PBI^{OEG} **8** and expansion of the aromatic region with tentative assignment of the protons (400 MHz, $CDCl_3$).

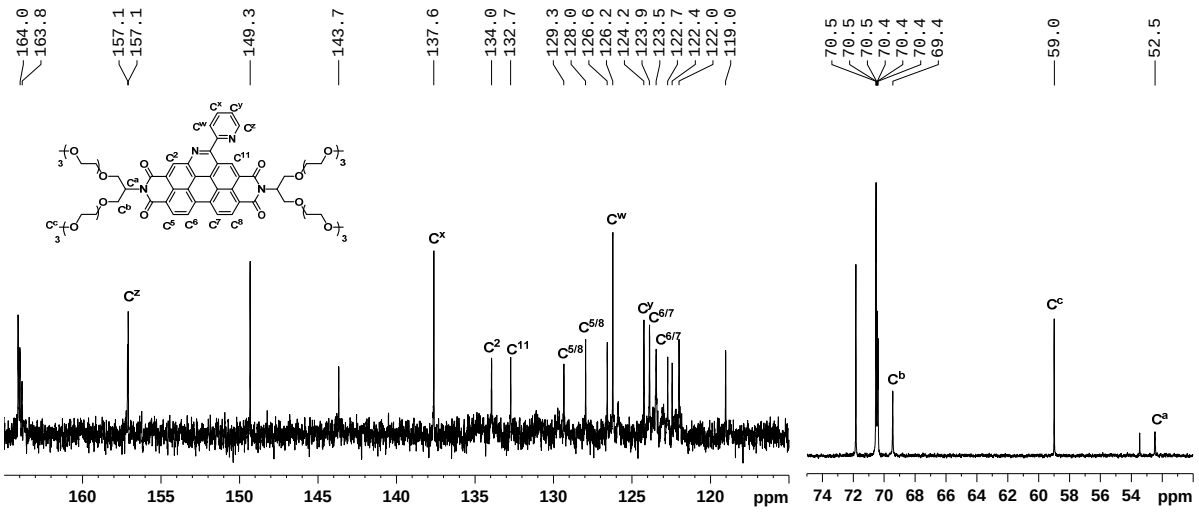


Figure S39. ^{13}C NMR spectrum (aromatic and alkyl regions) of ab-PBI^{OEG} **8** with tentative assignment of non-quaternary carbon atoms (100 MHz, $CDCl_3$).

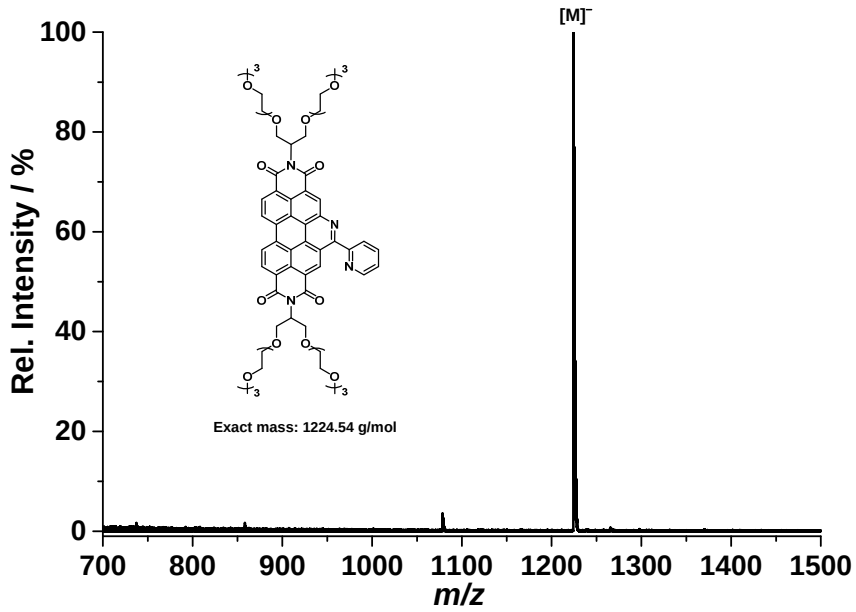


Figure S40. MALDI-TOF mass spectrum of ab-PBI^{OEG} **8** with the $[M]^-$ peak at 1224.48 *m/z* (matrix: DCTB in chloroform, mode: negative).

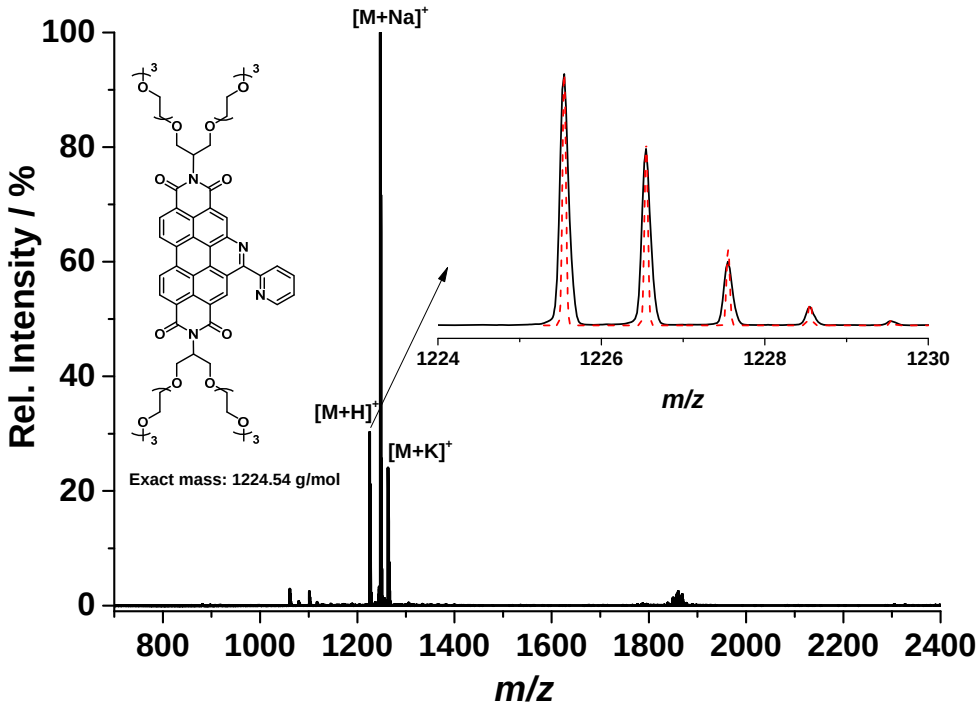


Figure S41. ESI-TOF mass spectrum of ab-PBI^{OEG} **8** in acetonitrile/chloroform 1:1 in positive mode. Inset: Zoomed spectrum of the $[M+H]^+$ peak (black solid) und the simulated spectrum (red dashed) of ab-PBI^{OEG} **8**.

4 NMR and mass spectra of 1-nitro-PMIDE 10, 1-amino-PMIDE 11, ab-PMIDE 12 and ab-PMIMA 13

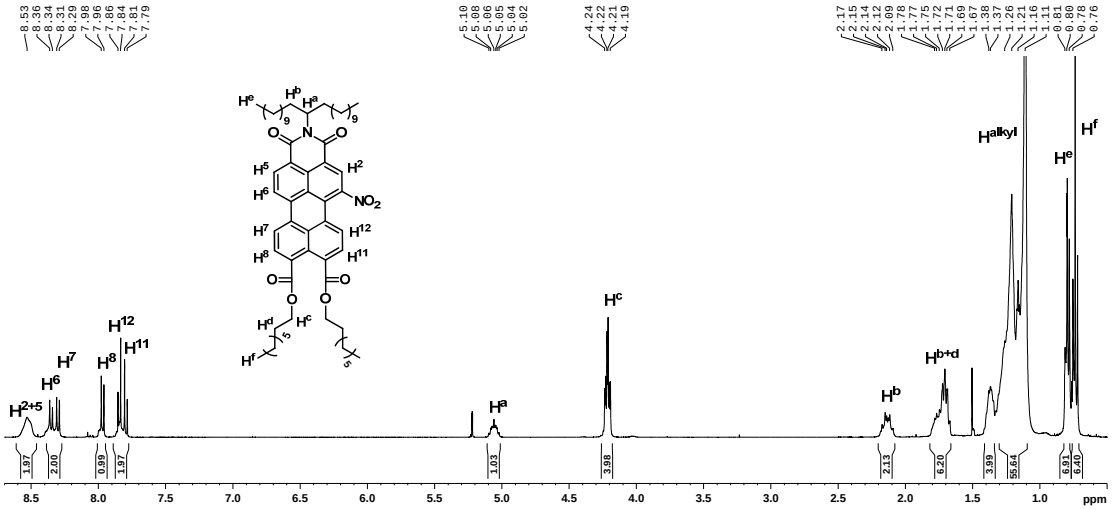


Figure S42. ^{1}H NMR spectrum of 1-nitro-PMIDE **10** with assignment of the protons (400 MHz, CD_2Cl_2).

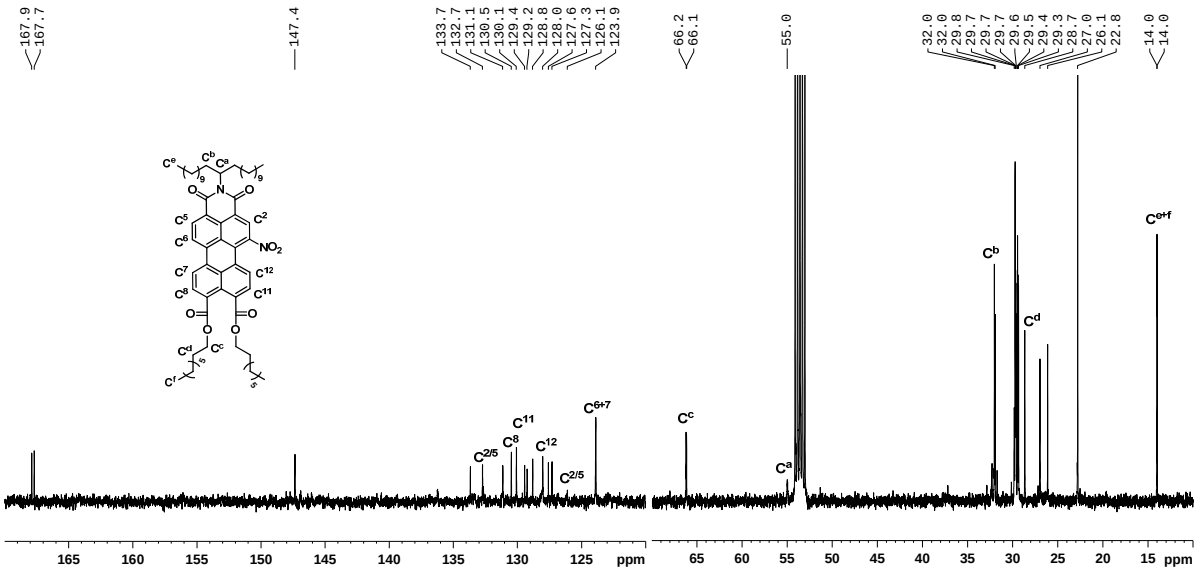


Figure S43. ^{13}C NMR spectrum of 1-nitro-PMIDE **10** with assignment of non-quaternary carbon atoms (100 MHz, CD_2Cl_2).

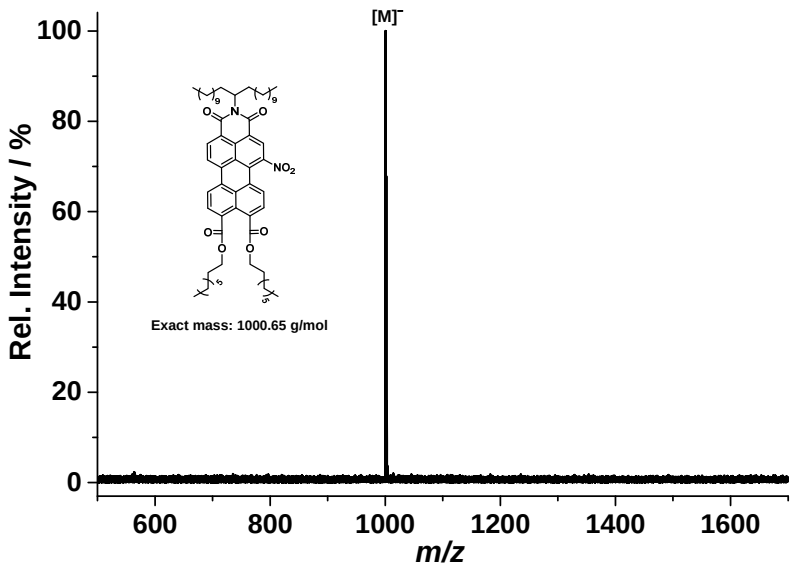


Figure S44. MALDI-TOF mass spectrum of 1-nitro-PMIDE **10** with the $[M]^-$ peak at 1000.64 *m/z* (matrix: DCTB in chloroform, mode: negative).

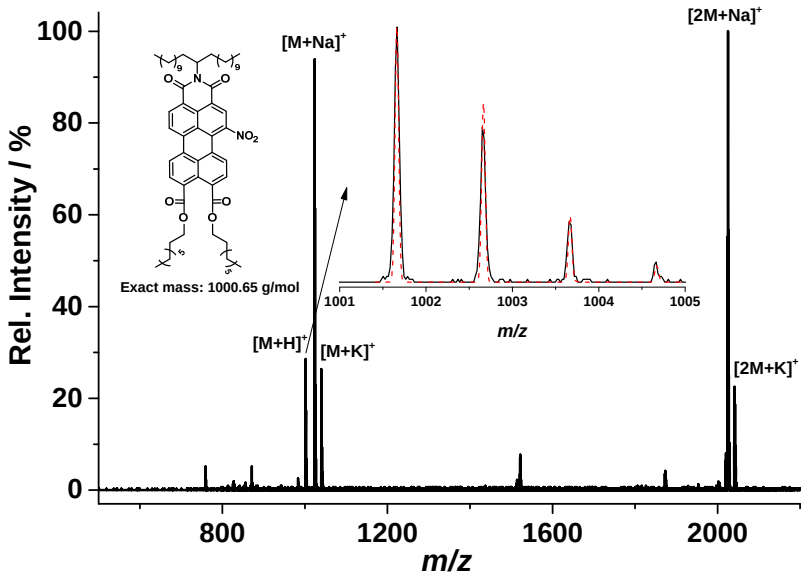


Figure S45. ESI-TOF mass spectrum of 1-nitro-PMIDE **10** in acetonitrile/chloroform 1:1 in positive mode. Inset: Zoomed spectrum of the $[M+H]^+$ peak (black solid) und the simulated spectrum (red dashed) of 1-nitro-PMIDE **10**.

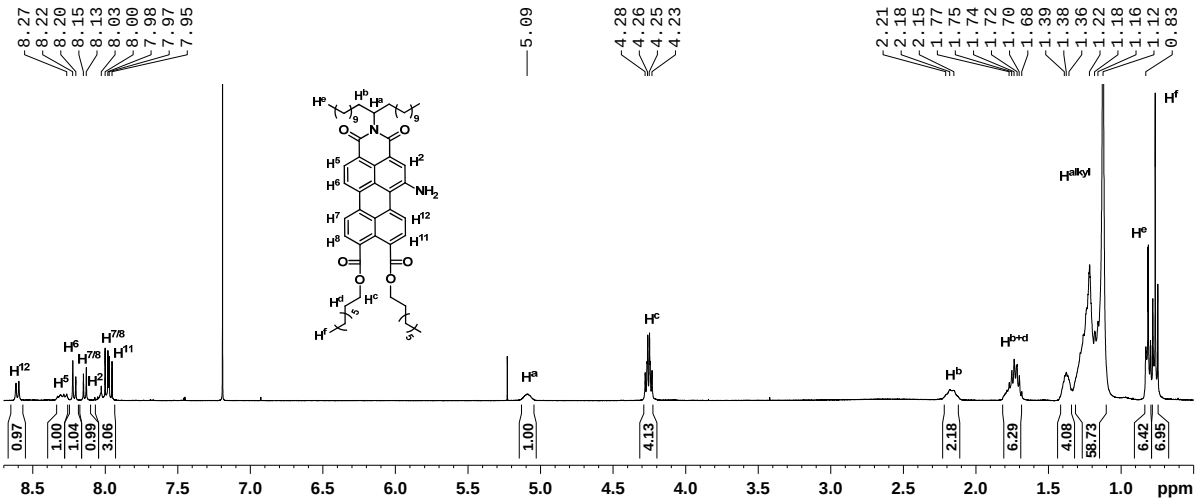


Figure S46. ^{1}H NMR spectrum of 1-amino-PMIDE **11** with tentative assignment of the protons (400 MHz, $CDCl_3$).

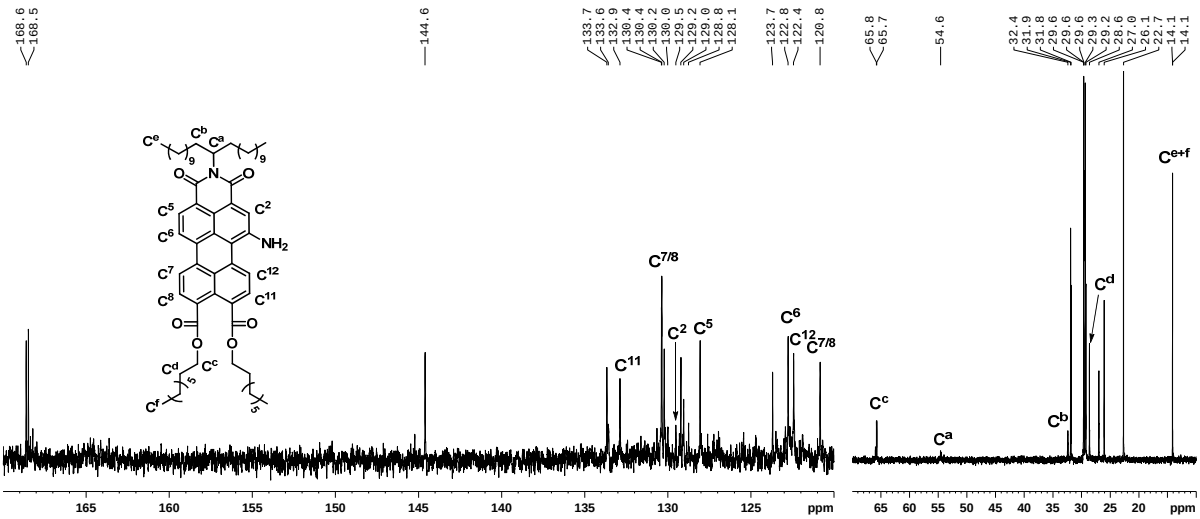


Figure S47. ^{13}C NMR spectrum (aromatic and alkyl regions) of 1-amino-PMIDE **11** with tentative assignment of non-quaternary carbon atoms (100 MHz, $CDCl_3$).

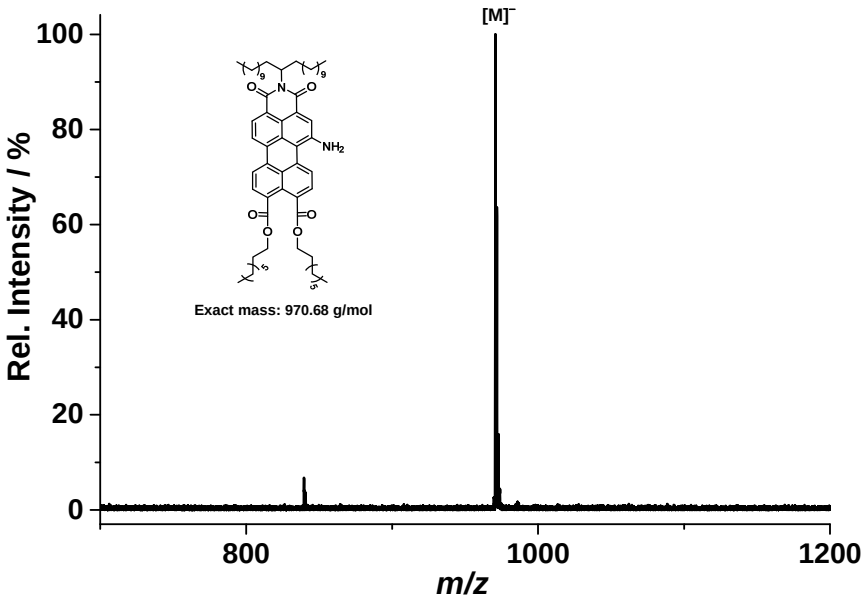


Figure S48. MALDI-TOF mass spectrum of 1-amino-PMIDE **11** with the $[M]^-$ peak at 970.68 *m/z* (matrix: DCTB in chloroform, mode: negative).

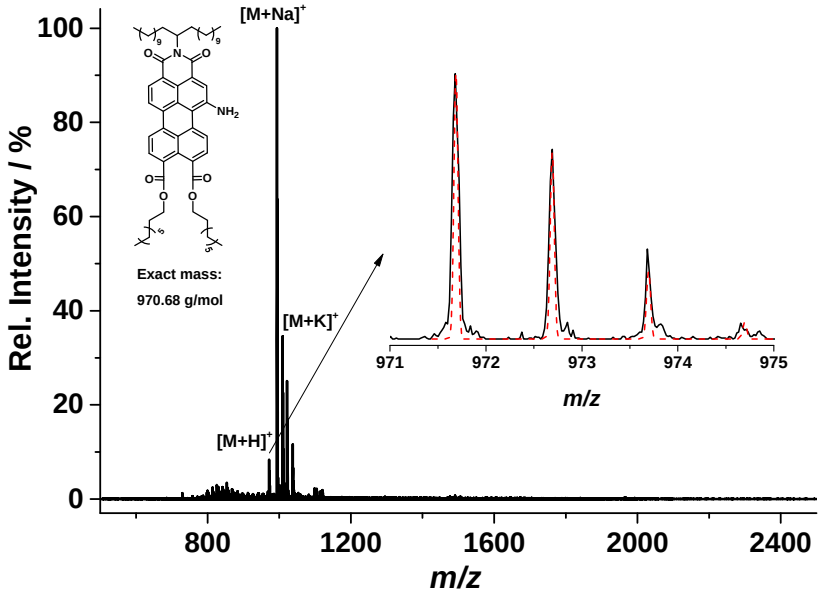


Figure S49. ESI-TOF mass spectrum of 1-amino-PMIDE **11** in acetonitrile/chloroform 1:1 in positive mode. Inset: Zoomed spectrum of the $[M+H]^+$ peak (black solid) und the simulated spectrum (red dashed) of 1-amino-PMIDE **11**.

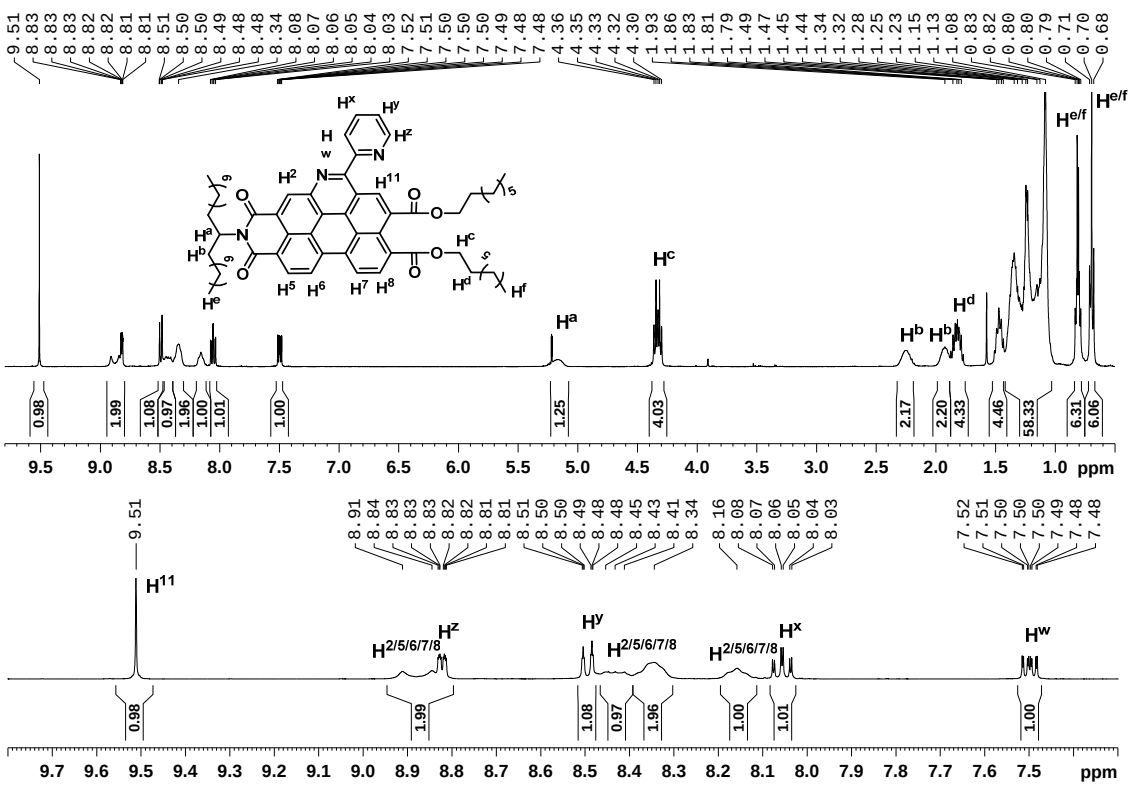


Figure S50. ^{1}H NMR spectrum of ab-PMIDE **12** and expansion of the aromatic region with tentative assignment of the protons (400 MHz, CD_2Cl_2).

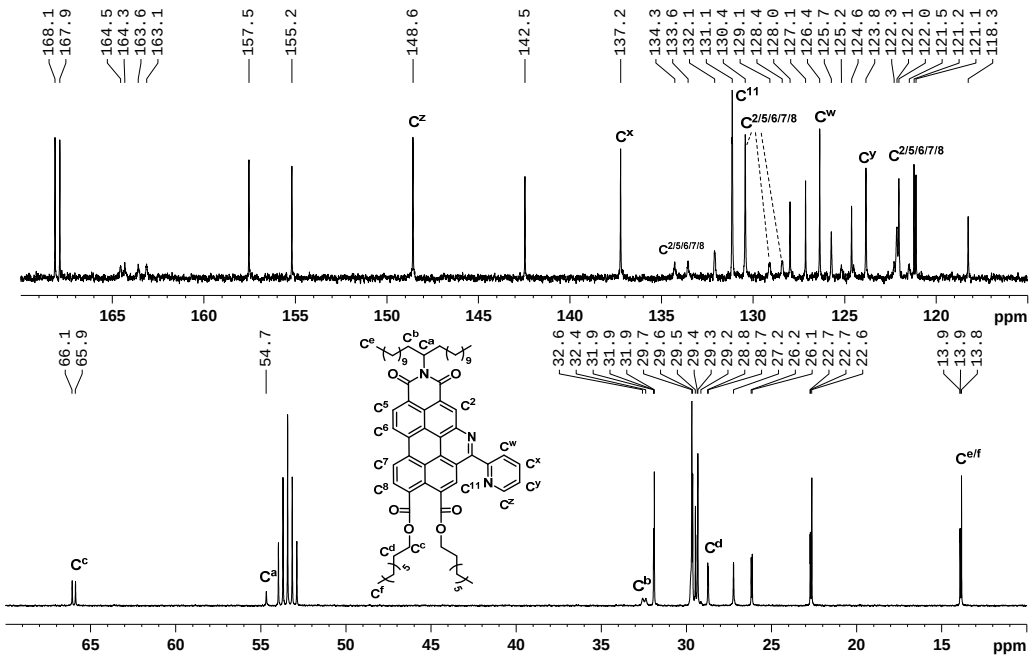


Figure S51. ^{13}C NMR spectrum (aromatic and alkyl regions) of ab-PMIDE **12** with tentative assignment of non-quaternary carbon atoms (100 MHz, CD_2Cl_2).

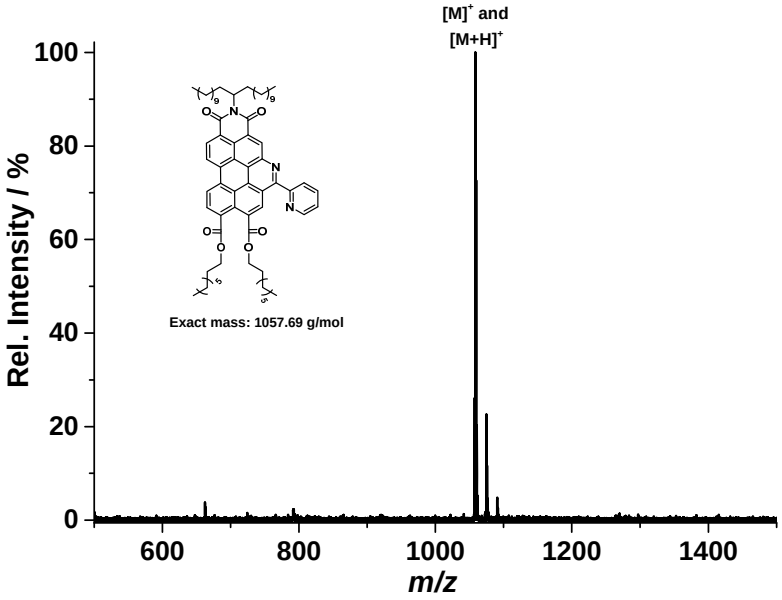


Figure S52. MALDI-TOF mass spectrum of ab-PMIDE **12** with the $[M]^+$ peak at 1057.67 *m/z* (matrix: DCTB in chloroform, mode: positive).

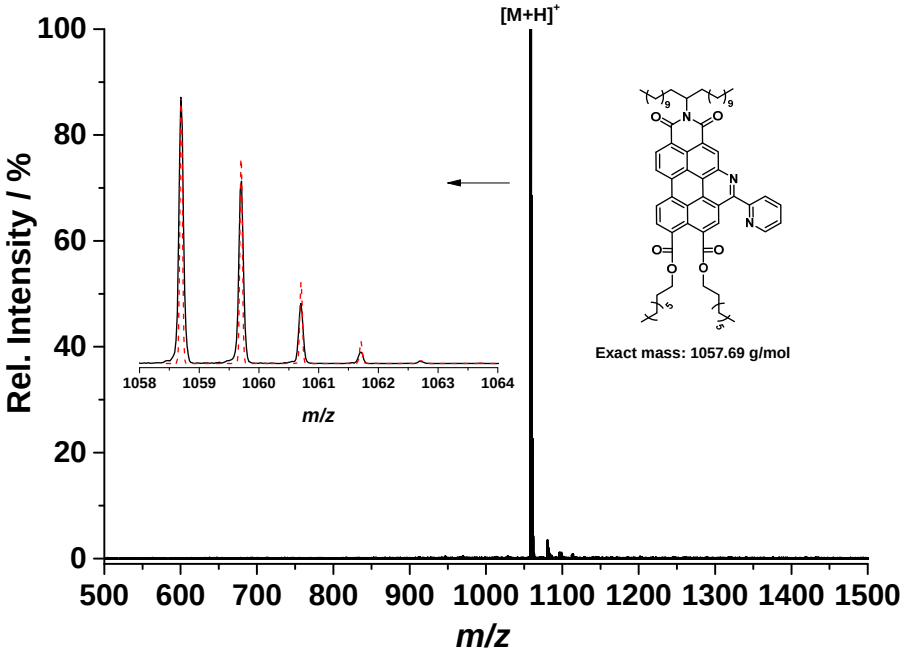


Figure S53. ESI-TOF mass spectrum of ab-PMIDE **12** in acetonitrile/chloroform 1:1 in positive mode. Inset: Zoomed spectrum of the $[M+H]^+$ peak (black solid) und the simulated spectrum (red dashed) of ab-PMIDE **12**.

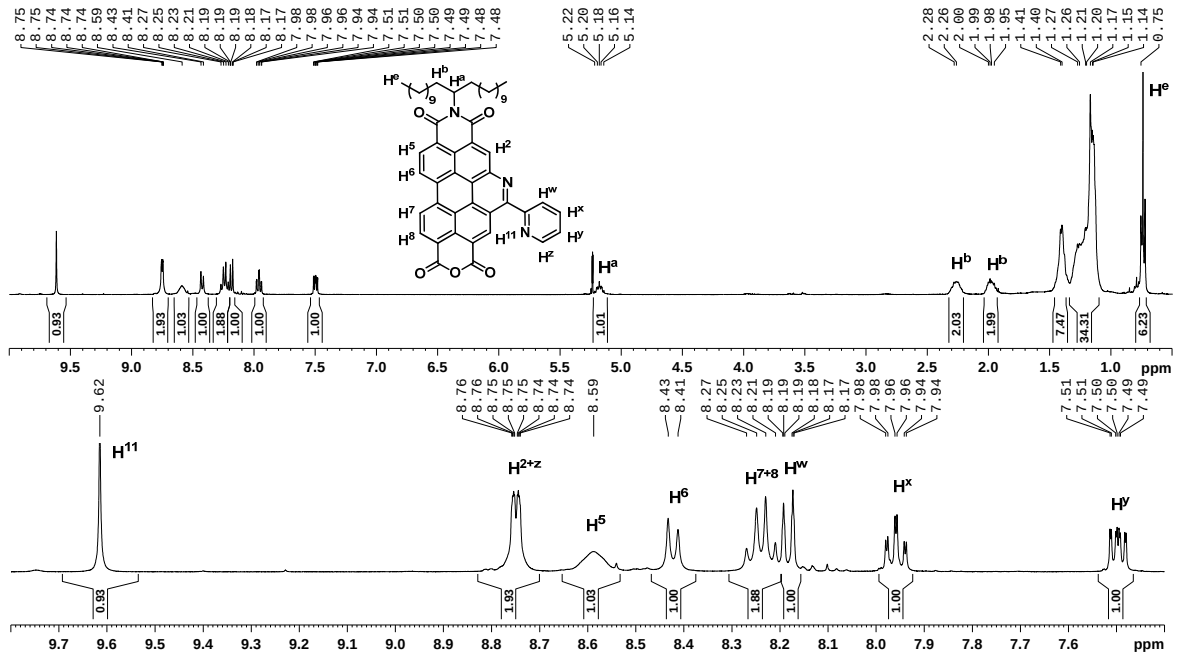


Figure S54. ^{1}H NMR spectrum of ab-PMIMA **13** and expansion of the aromatic region with tentative assignment of the protons (400 MHz, CD_2Cl_2).

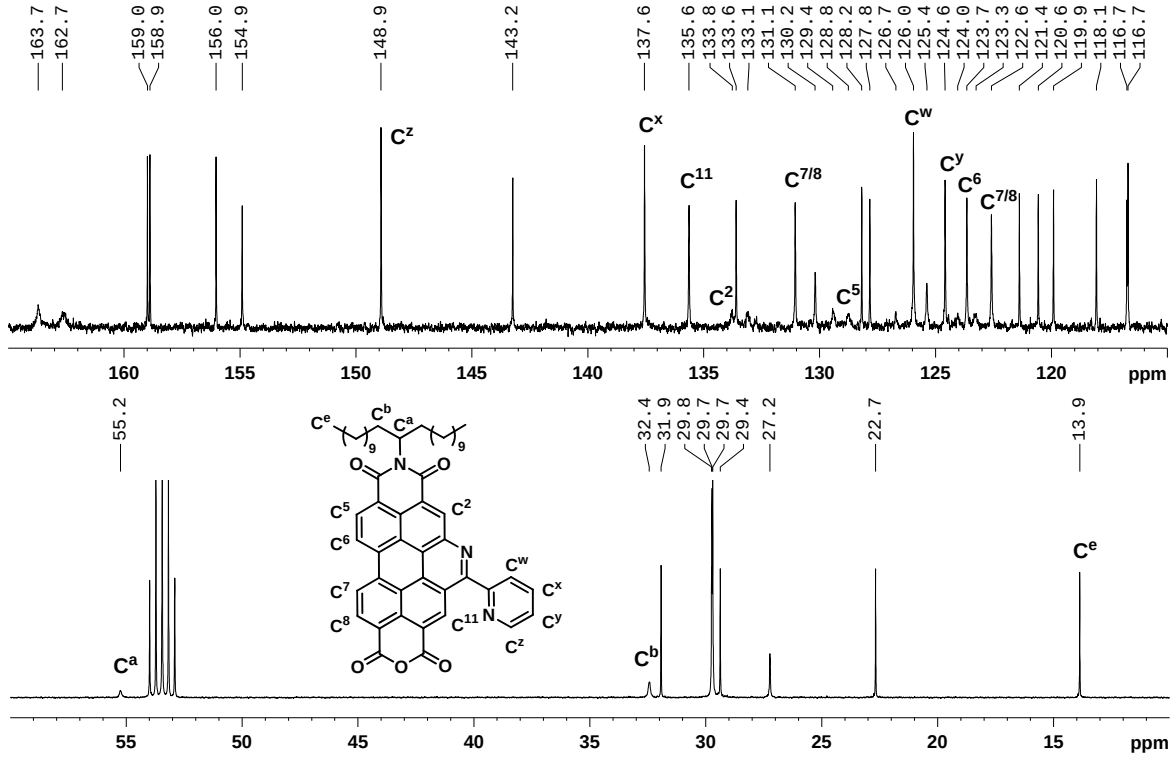


Figure S55. ^{13}C NMR spectrum (aromatic and alkyl regions) of ab-PMIMA **13** with tentative assignment of non-quaternary carbon atoms (100 MHz, CD_2Cl_2).

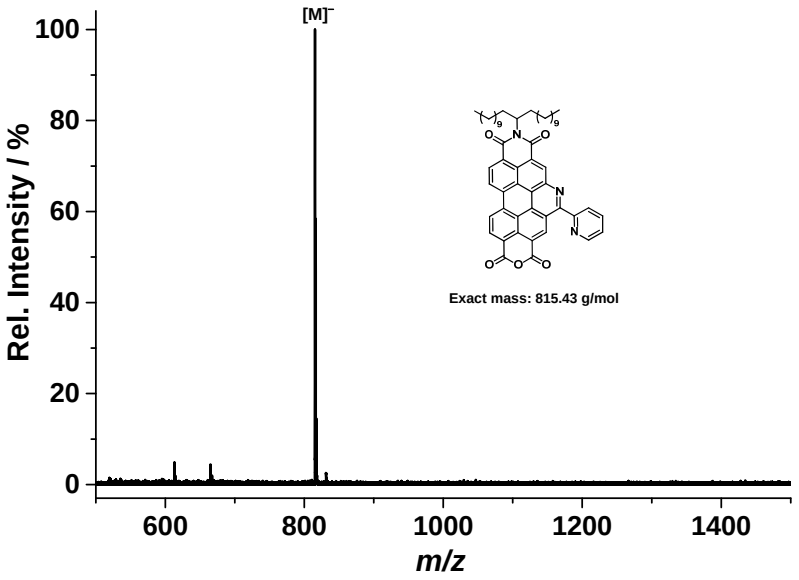


Figure S56. MALDI-TOF mass spectrum of ab-PMIMA **13** with the $[M]^-$ peak at 815.38 *m/z* (matrix: DCTB in chloroform, mode: negative).

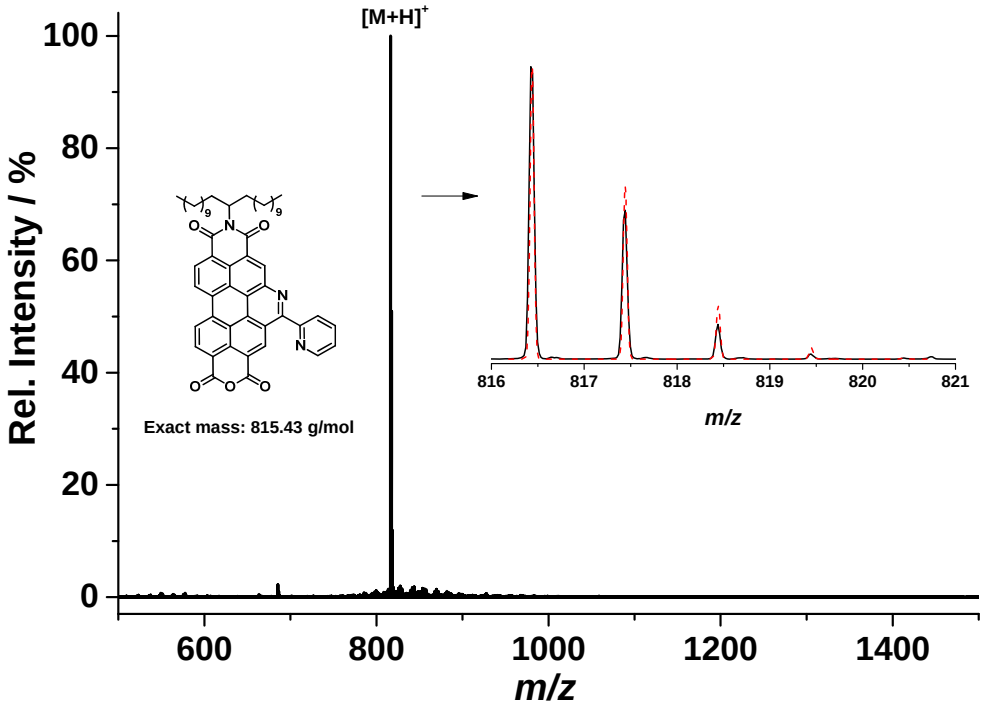


Figure S57. ESI-TOF mass spectrum of ab-PMIMA **13** in acetonitrile/chloroform 1:1 in positive mode. Inset: Zoomed spectrum of the $[M+H]^+$ peak (black solid) und the simulated spectrum (red dashed) of ab-PMIMA **13**.

5 NMR and mass spectra of *anti*-(ab)$_2$-PBI 15, *syn*-(ab)$_2$-PBI 16, *syn*-(ab)$_2$-PTE 18 and *syn*-(ab)$_2$-PBA 19

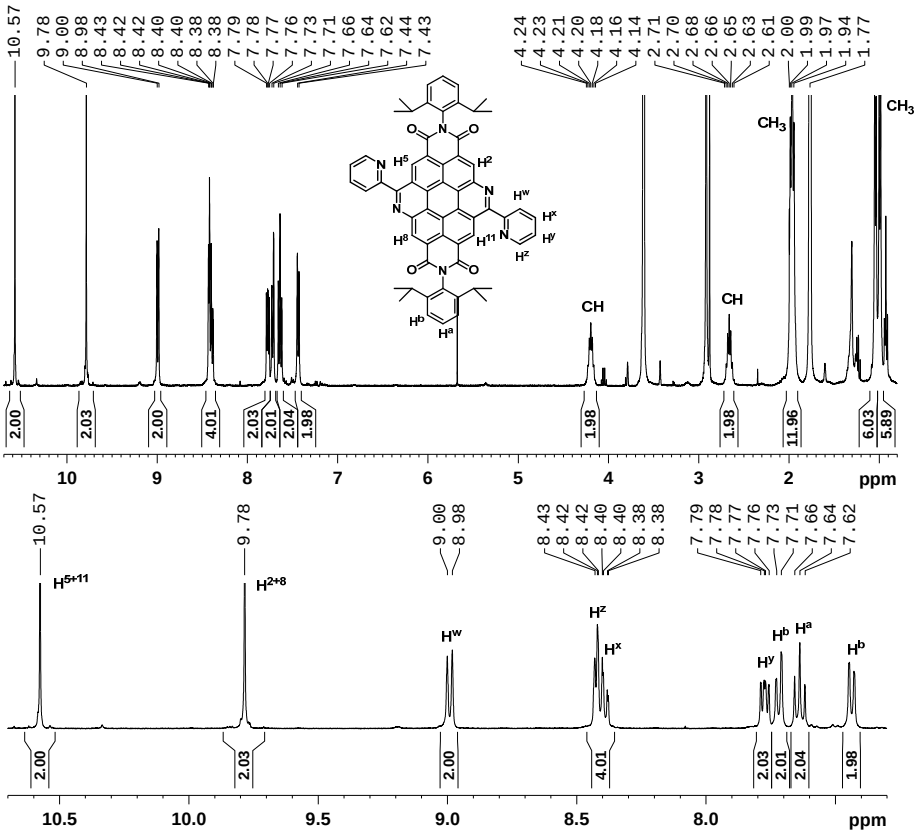


Figure S58. ^{1}H NMR spectrum of *anti*-(ab)$_2$-PBI **15** and expansion of the aromatic region with tentative assignment of the protons (400 MHz, d$_8$-THF, 233 K).

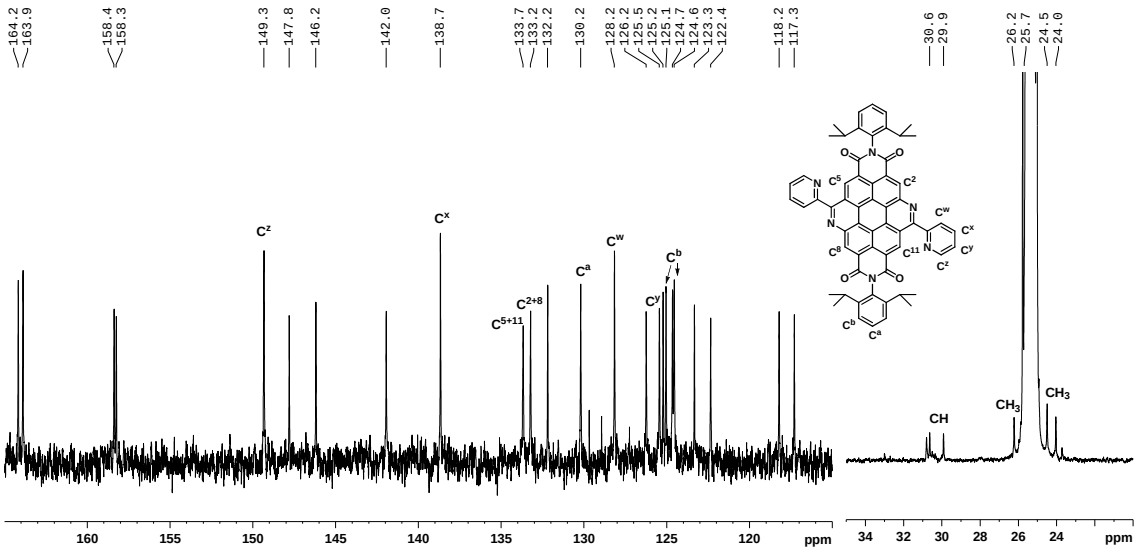


Figure S59. ^{13}C NMR spectrum (aromatic and alkyl regions) of *anti*-(ab)$_2$-PBI **15** with tentative assignment of non-quaternary carbon atoms (100 MHz, d_8-THF, 233 K).

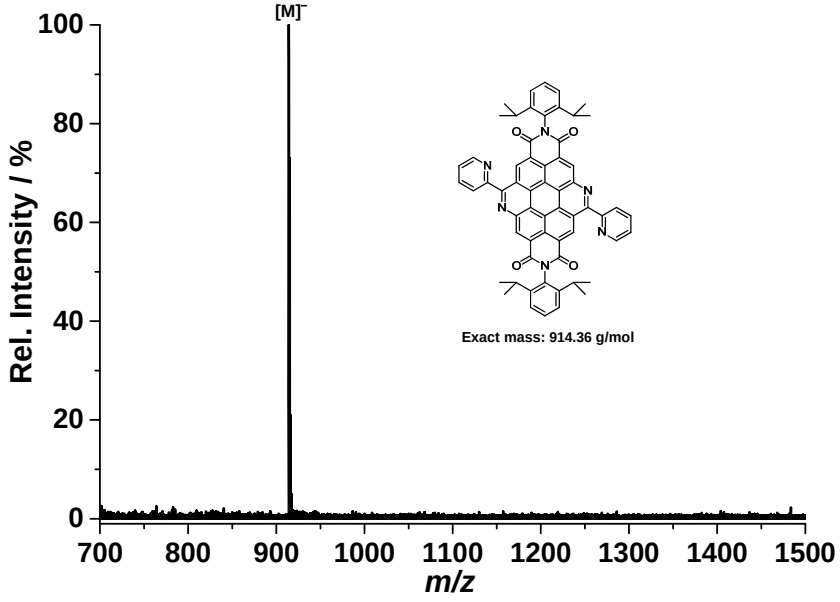


Figure S60. MALDI-TOF mass spectrum of *anti*-(ab)$_2$-PBI **15** with the $[M]^-$ peak at 914.31 *m/z* (matrix: DCTB in chloroform, mode: negative).

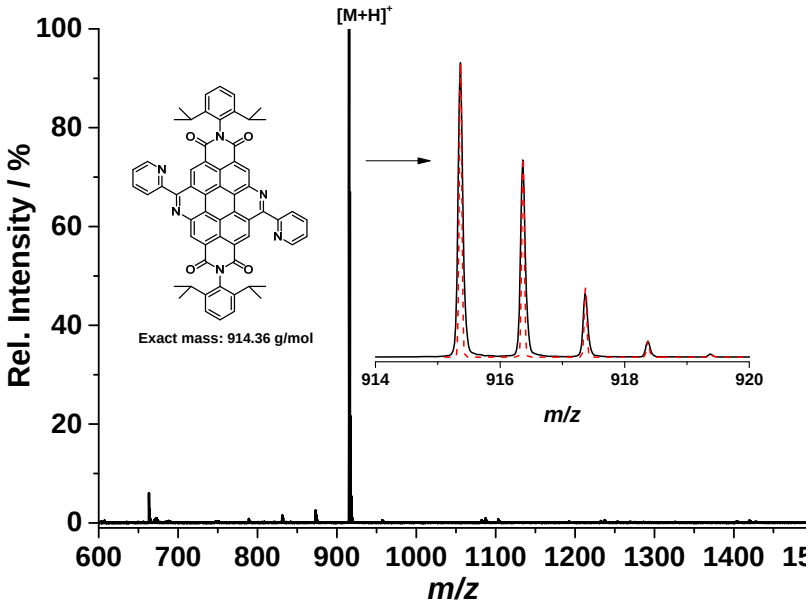


Figure S61. ESI-TOF mass spectrum of *anti*-(ab)$_2$-PBI **15** in acetonitrile/chloroform 1:1 in positive mode. Inset: Zoomed spectrum of the $[M+H]^+$ peak (black solid) und the simulated spectrum (red dashed) of *anti*-(ab)$_2$-PBI **15**.

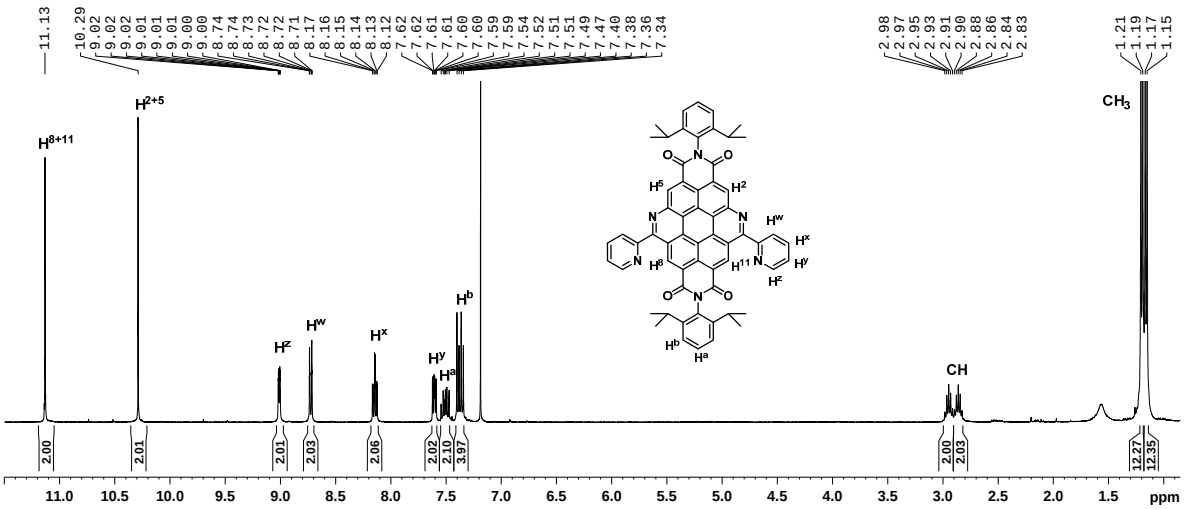


Figure S62. ^{1}H NMR spectrum of *syn*-(ab)$_2$-PBI **16** with tentative assignment of the protons (400 MHz, $CDCl_3$).

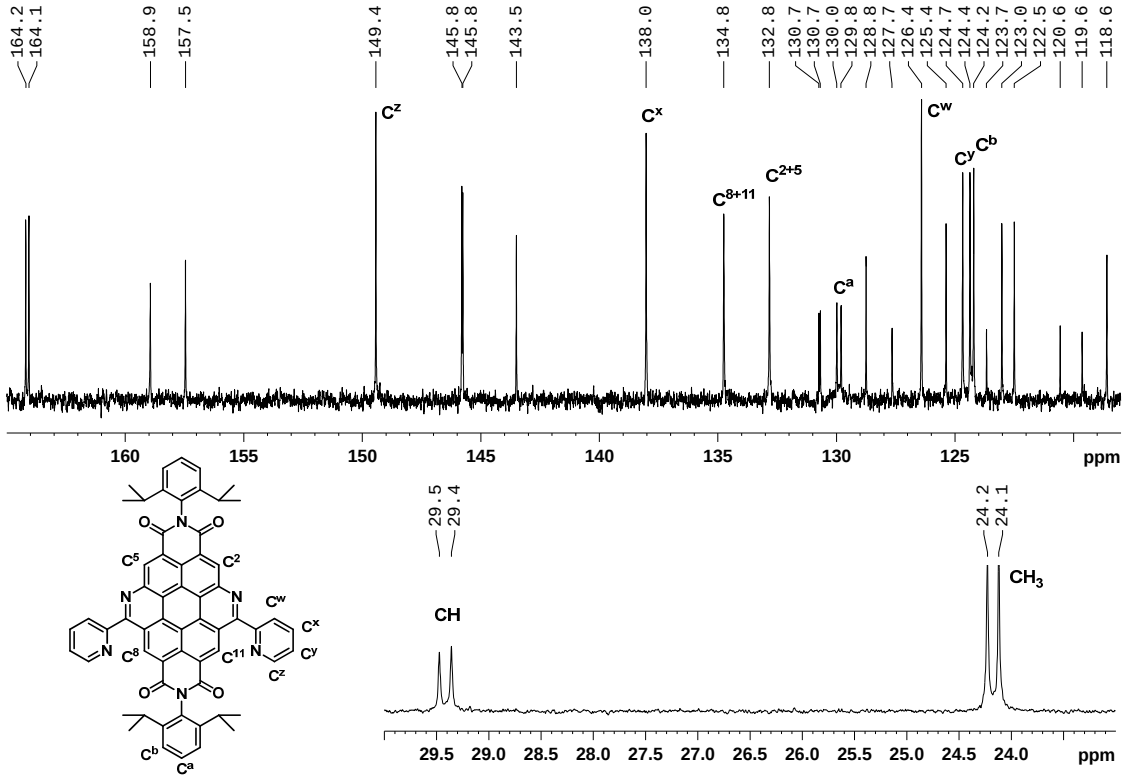


Figure S63. ^{13}C NMR spectrum (aromatic and alkyl regions) of *syn*-(ab)$_2$-PBI **16** with tentative assignment of non-quaternary carbon atoms (100 MHz, $CDCl_3$).

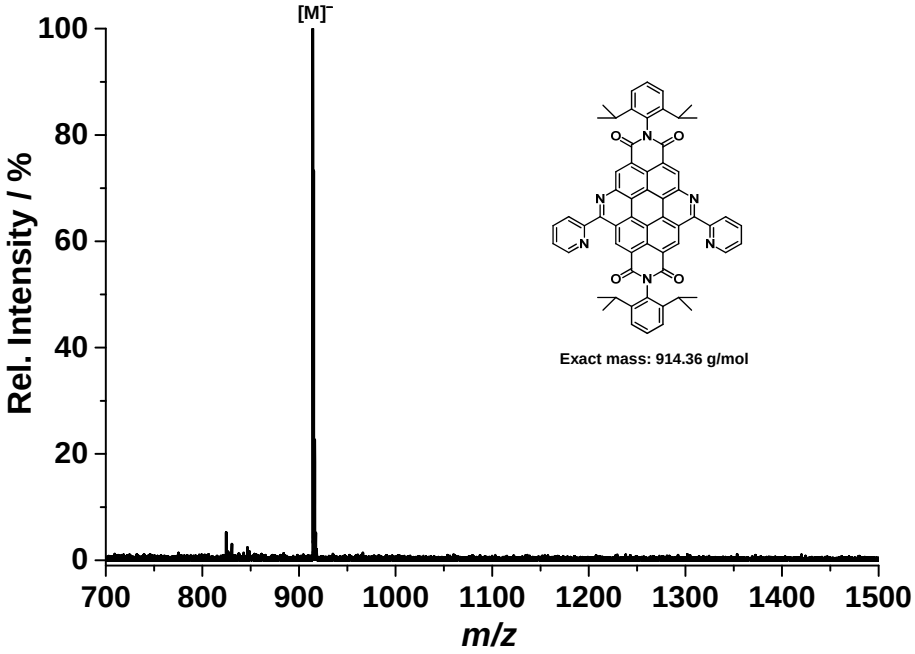


Figure S64. MALDI-TOF mass spectrum of *syn*-(ab)$_2$-PBI **16** with the $[M]^-$ peak at 914.32 *m/z* (matrix: DCTB in chloroform, mode: negative).

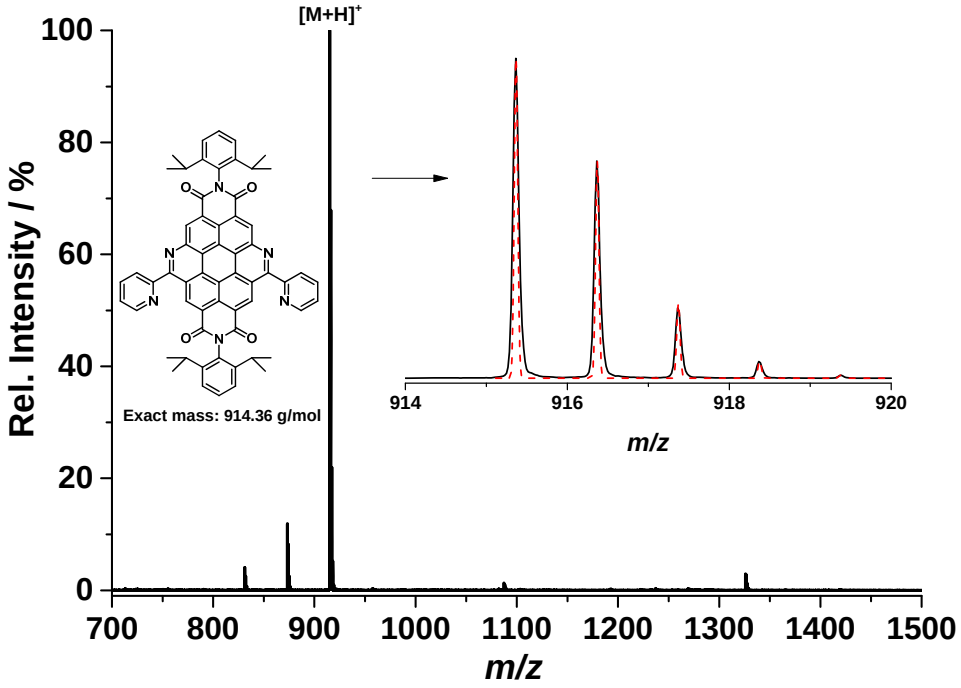


Figure S65. ESI-TOF mass spectrum of *syn*-(ab)$_2$-PBI **16** in acetonitrile/chloroform 1:1 in positive mode. Inset: Zoomed spectrum of the $[M+H]^+$ peak (black solid) und the simulated spectrum (red dashed) of *syn*-(ab)$_2$-PBI **16**.

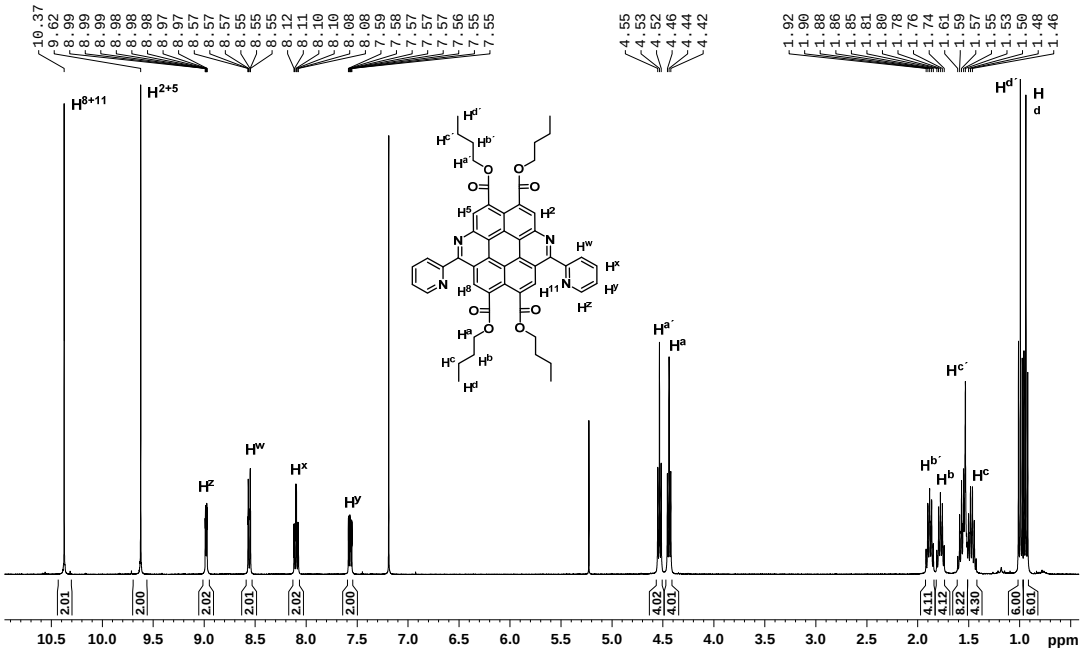


Figure S66. ^{1}H NMR spectrum of *syn*-(ab)$_2$-PTE **18** with tentative assignment of the protons (400 MHz, $CDCl_3$).

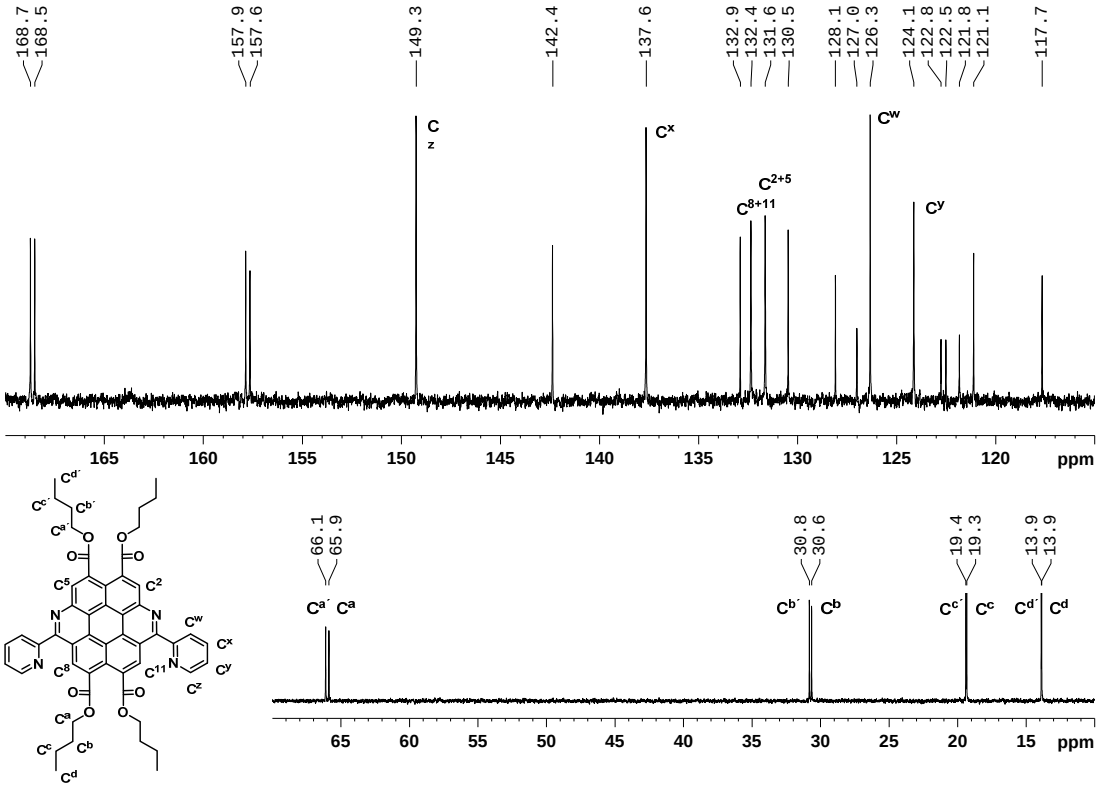


Figure S67. ^{13}C NMR spectrum (aromatic and alkyl regions) of *syn*-(ab)$_2$-PTE **18** with tentative assignment of non-quaternary carbon atoms (100 MHz, $CDCl_3$).

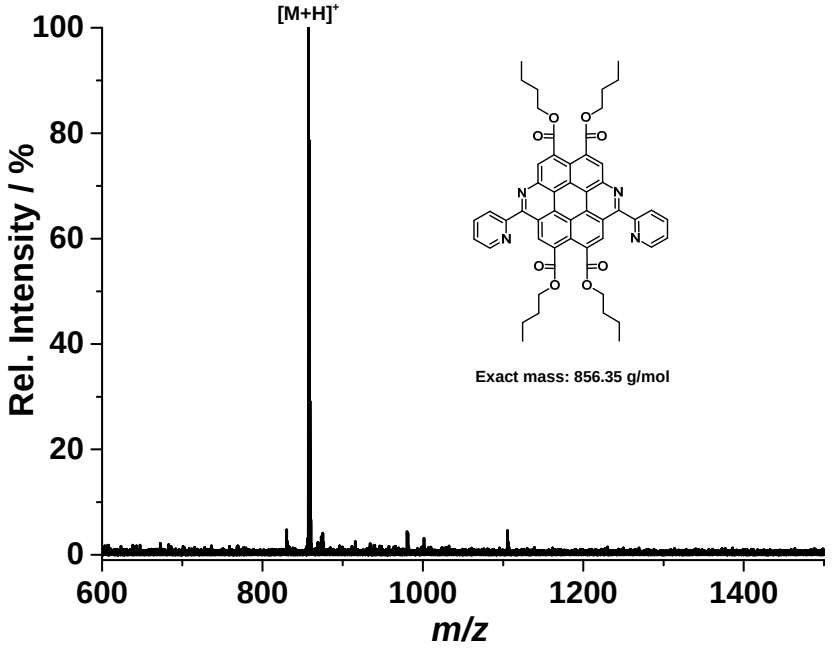


Figure S68. MALDI-TOF mass spectrum of *syn*-(ab)$_2$-PTE **18** with the $[M+H]^+$ peak at 857.25 *m/z* (matrix: DCTB in chloroform, mode: positive).

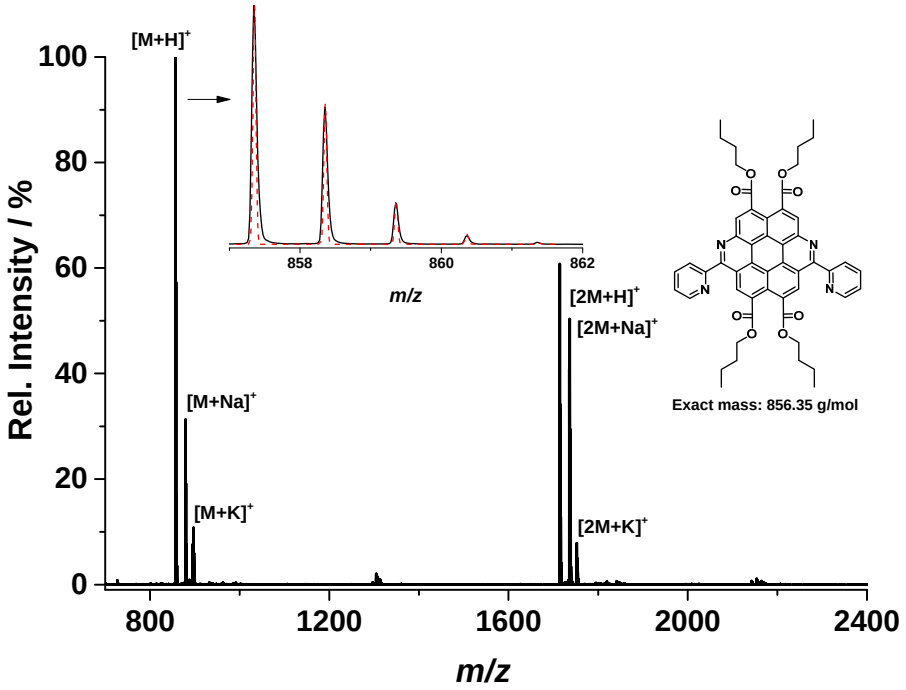


Figure S69. ESI-TOF mass spectrum of *syn*-(ab)$_2$-PTE **18** in acetonitrile/chloroform 1:1 in positive mode. Inset: Zoomed spectrum of the $[M+H]^+$ peak (black solid) und the simulated spectrum (red dashed) of *syn*-(ab)$_2$-PTE **18**.

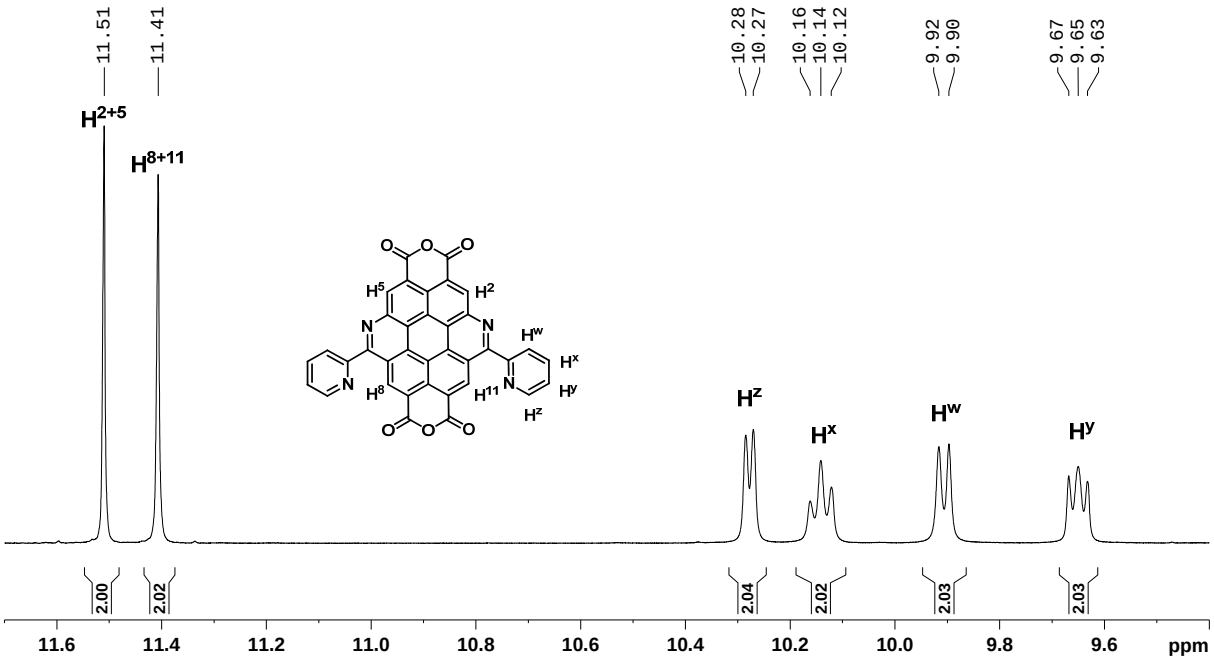


Figure S70. ^{1}H NMR spectrum (aromatic region) of *syn*-(ab)$_2$-PBA **19** with tentative assignment of the protons (400 MHz, D_2SO_4).

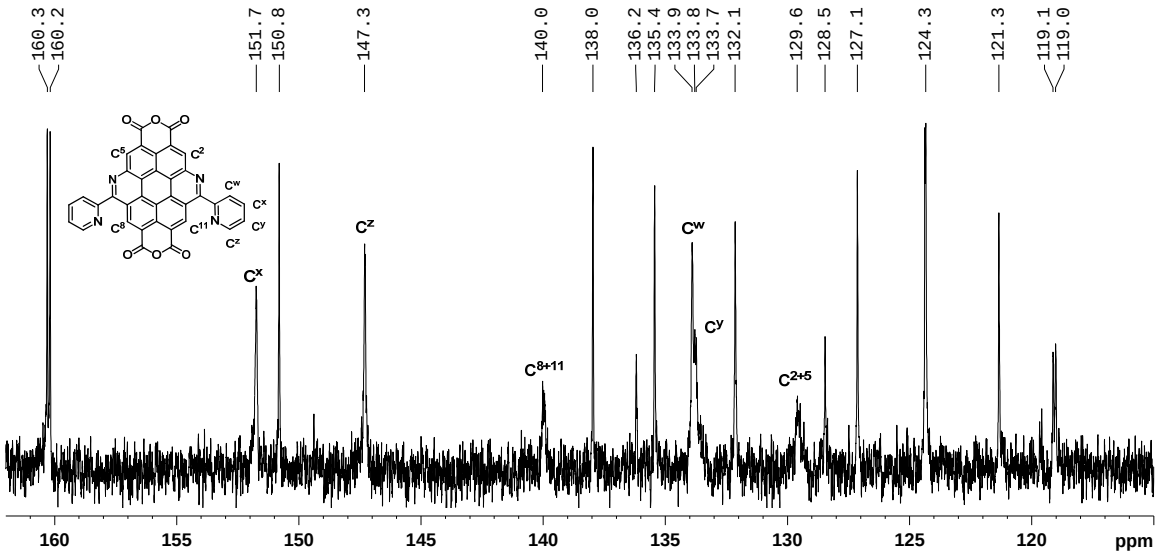


Figure S71. ^{13}C NMR spectrum (aromatic region) of *syn*-(ab)$_2$-PBA **19** with tentative assignment of non-quaternary carbon atoms (100 MHz, D_2SO_4).

6 Crystal structure of *anti*-(ab)$_2$-PBI 15

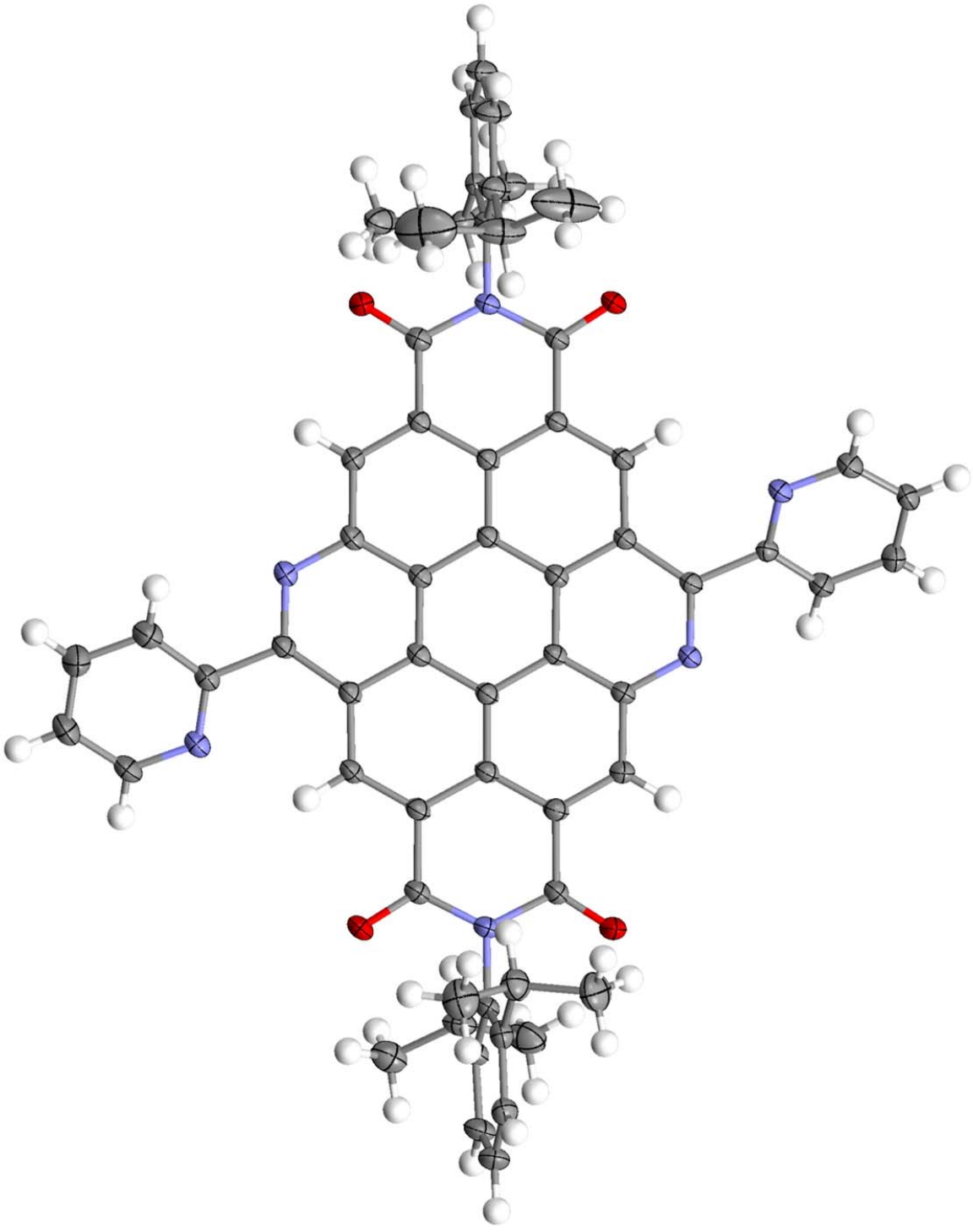


Figure S72. Top view of the molecular structure of *anti*-(ab)$_2$-PBI **15** in the solid state (ellipsoids set at 50% probability level; THF solvent molecules are omitted for clarity).

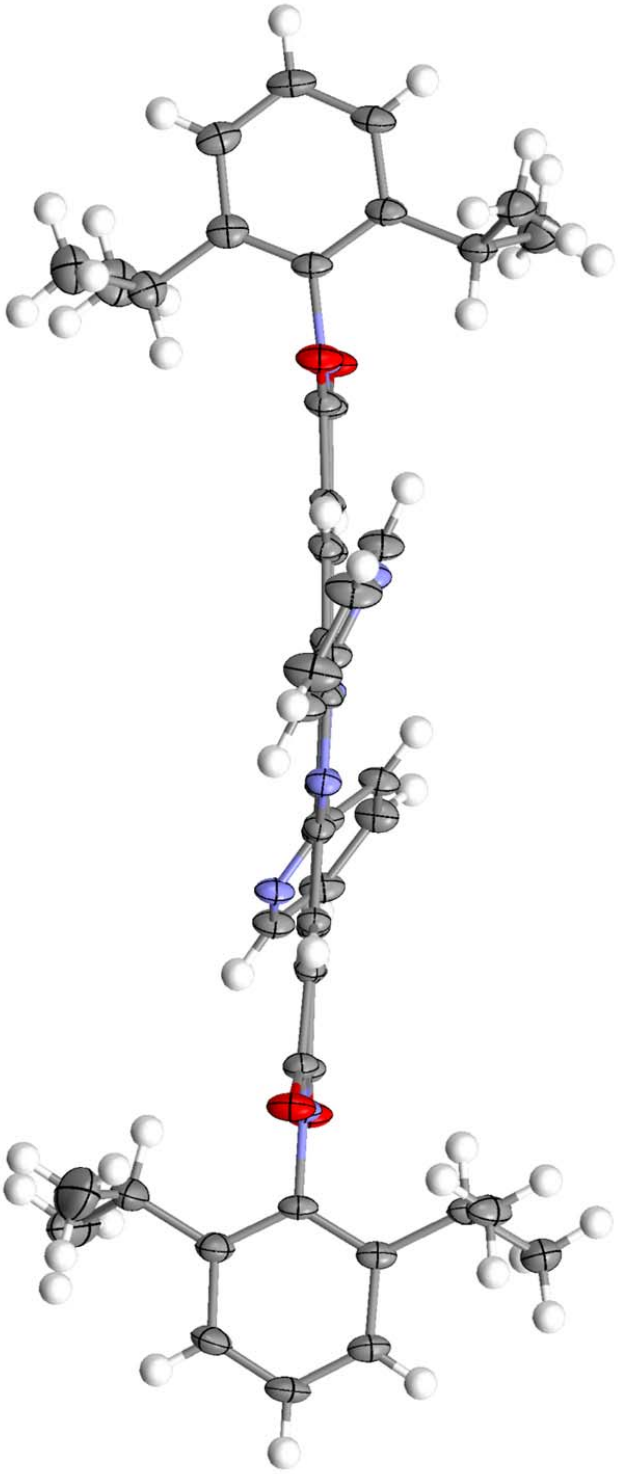


Figure S73. Side view of the molecular structure of *anti*-(ab)$_2$-PBI **15** in the solid state (ellipsoids set at 50% probability level; THF solvent molecules are omitted for clarity).

7 DFT calculations

For all calculated optimized structures no negative frequencies were found proofing that the found geometry is a true energetic minimum.

Table S3. Cartesian Coordinates and Total Energy of Ground State Structure of PTE

Center Number	Atomic Number	Atomic type	Coordinates (Å)		
			X	Y	Z
1	6	0	1.346.590	2.505.020	0.115265
2	6	0	0.678847	1.287.506	0.007613
3	6	0	3.510.971	1.414.568	0.285363
4	6	0	1.456.072	0.081057	-0.028571
5	6	0	2.735.592	2.562.415	0.275412
6	6	0	2.898.241	0.144707	0.021844
7	6	0	0.791885	-1.188.976	-0.113950
8	1	0	3.229.186	3.521.599	0.442244
9	6	0	1.570.019	-2.343.264	-0.160021
10	6	0	2.966.249	-2.278.154	-0.225952
11	1	0	3.552.069	-3.190.464	-0.352109
12	6	0	3.636.957	-1.066.313	-0.194105
13	6	0	4.931.413	1.621.846	0.719059
14	6	0	5.092.347	-1.147.523	-0.540409
15	8	0	5.575.156	2.620.436	0.495505
16	8	0	5.800.903	-2.095.372	-0.287488
17	6	0	-1.570.543	2.379.904	-0.087870
18	6	0	-0.794522	1.223.729	-0.066826
19	6	0	-3.642.223	1.113.131	-0.063076
20	6	0	-1.459.535	-0.046986	-0.122696
21	6	0	-2.969.652	2.324.281	-0.075633
22	6	0	-2.899.973	-0.109380	-0.166136
23	6	0	-0.682902	-1.253.517	-0.148865
24	1	0	-3.545.332	3.249.515	-0.030674
25	6	0	-1.353.990	-2.470.932	-0.219656

26	6	0	-2.749.773	-2.532.934	-0.323204
27	1	0	-3.228.305	-3.506.072	-0.454693
28	6	0	-3.528.168	-1.386.989	-0.328113
29	6	0	-5.109.667	1.132.764	0.223058
30	6	0	-4.961.613	-1.544.220	-0.776709
31	8	0	-5.672.016	0.329855	0.938737
32	8	0	-5.372.265	-0.975724	-1.757.491
33	1	0	0.793826	3.443.008	0.130412
34	1	0	-1.102.126	3.362.891	-0.080298
35	1	0	-0.801791	-3.409.273	-0.236722
36	1	0	1.104.598	-3.326.978	-0.199117
37	8	0	5.493.121	-0.092817	-1.275.917
38	8	0	5.371.370	0.619318	1.501.939
39	8	0	-5.727.710	2.180.405	-0.331631
40	8	0	-5.726.742	-2.451.051	-0.146907
41	6	0	-7.145.079	2.297.934	-0.098935
42	1	0	-7.322.693	2.378.536	0.985842
43	1	0	-7.629.478	1.370.718	-0.442536
44	6	0	-5.536.035	-2.795.695	1.236.484
45	1	0	-4.882.445	-2.055.002	1.717.889
46	1	0	-5.044.772	-3.782.673	1.284.982
47	6	0	6.698.464	0.741390	2.045.523
48	1	0	6.742.717	1.652.500	2.664.202
49	1	0	7.411.564	0.882143	1.217.378
50	6	0	6.850.014	-0.073894	-1.760.673
51	1	0	7.110.187	0.993157	-1.810.745
52	1	0	7.499.387	-0.572599	-1.026.645
53	6	0	-7.642.731	3.513.314	-0.851824
54	1	0	-8.728.131	3.625.103	-0.704118
55	1	0	-7.449.363	3.412.675	-1.930.625
56	1	0	-7.150.722	4.431.717	-0.495493

57	6	0	-6.895.099	-2.827.102	1.909.123
58	1	0	-7.567.803	-3.536.967	1.403.746
59	1	0	-7.350.778	-1.826.695	1.880.849
60	1	0	-6.788.459	-3.137.007	2.961.137
61	6	0	6.957.397	-0.740012	-3.121.726
62	1	0	6.274.032	-0.269075	-3.845.065
63	1	0	6.718.049	-1.811.663	-3.052.779
64	1	0	7.985.774	-0.642927	-3.505.199
65	6	0	6.991.691	-0.512420	2.843.007
66	1	0	6.933.459	-1.404.600	2.201.614
67	1	0	6.271.964	-0.630110	3.667.760
68	1	0	8.003.399	-0.453369	3.273.989

Total energy of PTE: –2175.95138846 a.u. Number of imaginary frequencies: 0.

Table S4. Cartesian Coordinates and Total Energy of Ground State Structure of ab-PTE 5

Center Number	Atomic Number	Atomic type	Coordinates (Å)		
			X	Y	Z
1	6	0	-0.778456	-3.539.137	0.177612
2	6	0	-0.219129	-2.260.142	0.061661
3	6	0	-3.030.378	-2.627.374	0.312018
4	6	0	-1.106.995	-1.137.489	0.011913
5	6	0	-2.152.284	-3.711.164	0.320337
6	6	0	-2.529.479	-1.320.668	0.055344
7	6	0	-0.557657	0.188702	-0.059713
8	1	0	-2.568.959	-4.707.916	0.476626
9	6	0	-1.403.984	1.331.386	-0.075507
10	6	0	-2.811.363	1.107.483	-0.176665
11	1	0	-3.475.071	1.959.076	-0.297124
12	6	0	-3.356.026	-0.152082	-0.175103
13	6	0	-4.441.203	-2.956.855	0.699492
14	6	0	-4.799.108	-0.203225	-0.583186
15	8	0	-4.986.123	-4.009.452	0.461392

16	8	0	-5.609.842	0.664623	-0.356439
17	6	0	2.140.346	-3.125.616	0.008104
18	6	0	1.235.738	-2.056.639	-0.002089
19	6	0	4.048.370	-1.614.316	-0.012074
20	6	0	1.763.197	-0.730988	-0.080250
21	6	0	3.515.797	-2.904.599	0.010939
22	6	0	3.177.957	-0.496418	-0.130152
23	6	0	0.852994	0.374188	-0.102372
24	1	0	4.199.217	-3.752.608	0.066901
25	6	0	1.340.800	1.699.436	-0.174180
26	6	0	2.749.371	1.908.934	-0.301420
27	1	0	3.083.625	2.937.587	-0.447391
28	6	0	3.640.725	0.867753	-0.312885
29	6	0	5.514.221	-1.458.855	0.244245
30	6	0	5.039.459	1.178.766	-0.796173
31	8	0	5.990.994	-0.579016	0.930454
32	8	0	5.485.375	0.638054	-1.777.249
33	1	0	-0.142068	-4.422.810	0.202661
34	1	0	1.784.023	-4.154.503	0.040122
35	8	0	-5.060.855	-1.287.103	-1.340.970
36	8	0	-4.994.055	-1.990.654	1.453.865
37	8	0	6.239.121	-2.439.710	-0.301926
38	8	0	5.714.896	2.172.360	-0.199766
39	6	0	7.665.542	-2.383.426	-0.101822
40	1	0	7.873.925	-2.397.776	0.980237
41	1	0	8.030.470	-1.421.124	-0.493464
42	6	0	5.513.844	2.529.691	1.179.564
43	1	0	4.957.364	1.733.606	1.693.238
44	1	0	4.915.343	3.455.814	1.215.440
45	6	0	-6.328.752	-2.216.280	1.944.218
46	1	0	-6.326.679	-3.130.060	2.560.408

47	1	0	-6.994.733	-2.408.538	1.087.707
48	6	0	-6.386.401	-1.433.645	-1.885.859
49	1	0	-6.537.689	-2.520.429	-1.955.602
50	1	0	-7.113.043	-1.010.350	-1.177.244
51	6	0	8.284.839	-3.563.150	-0.820237
52	1	0	9.378.713	-3.543.009	-0.696195
53	1	0	8.058.561	-3.529.980	-1.896.810
54	1	0	7.910.275	-4.516.555	-0.416209
55	6	0	6.874.666	2.729.406	1.818.668
56	1	0	7.452.232	3.498.308	1.282.912
57	1	0	7.439.657	1.786.083	1.800.371
58	1	0	6.755.936	3.049.900	2.866.167
59	6	0	-6.500.966	-0.764470	-3.244.886
60	1	0	-5.743.012	-1.155.558	-3.941.032
61	1	0	-6.373.284	0.324733	-3.156.554
62	1	0	-7.496.793	-0.958858	-3.674.570
63	6	0	-6.748.782	-0.990436	2.728.275
64	1	0	-6.733.567	-0.095712	2.088.087
65	1	0	-6.073.048	-0.819653	3.580.398
66	1	0	-7.769.190	-1.128.237	3.118.894
67	7	0	0.528673	2.776.682	-0.155075
68	6	0	-0.784016	2.635.144	-0.084747
69	6	0	-3.456.386	5.084.658	0.538598
70	6	0	-0.902390	5.119.599	-0.421659
71	6	0	-2.905.074	6.313.421	0.166418
72	6	0	-1.597.715	6.322.162	-0.327202
73	6	0	-1.541.689	3.928.771	-0.022034
74	1	0	-3.486.526	7.233.255	0.260730
75	1	0	-1.124.120	7.258.009	-0.635343
76	1	0	0.121822	5.074.123	-0.788791
77	7	0	-2.796.982	3.929.759	0.447619

78	1	0	-4.479.112	5.030.105	0.929568

Total energy of ab-PTE **5**: −1836.81856905 a.u. Number of imaginary frequencies: 0.

Table S5. Cartesian Coordinates and Total Energy of Ground State Structure of *syn*-(ab)$_2$-PTE 18

Center Number	Atomic Number	Atomic type	Coordinates (Å)		
			X	Y	Z
1	6	0	0.738366	2.609.167	0.063180
2	6	0	0.220705	1.283.198	0.008851
3	6	0	2.999.724	1.660.541	0.249785
4	6	0	1.099.363	0.150271	-0.008819
5	6	0	2.146.295	2.746.011	0.214746
6	6	0	2.511.159	0.326301	0.026768
7	6	0	0.529687	-1.164.192	-0.068039
8	1	0	2.562.274	3.743.029	0.332714
9	6	0	1.360.083	-2.320.144	-0.082887
10	6	0	2.764.073	-2.108.055	-0.162483
11	1	0	3.422.987	-2.967.693	-0.249337
12	6	0	3.324.445	-0.845693	-0.166564
13	6	0	4.406.641	1.988.333	0.661749
14	6	0	4.781.661	-0.815009	-0.525135
15	8	0	4.984.184	3.014.459	0.393513
16	8	0	5.577.205	-1.682.304	-0.248978
17	6	0	-2.019.295	2.235.084	-0.044484
18	6	0	-1.188.861	1.091.055	-0.041128
19	6	0	-4.000.333	0.791990	-0.050326
20	6	0	-1.765.377	-0.210909	-0.096010
21	6	0	-3.430.152	2.049.726	-0.044444
22	6	0	-3.178.054	-0.388272	-0.143199
23	6	0	-0.883062	-1.329.188	-0.109437
24	1	0	-4.059.341	2.938.229	0.006165
25	6	0	-1.403.167	-2.642.296	-0.172652

26	6	0	-2.812.880	-2.807.016	-0.278872
27	1	0	-3.187.451	-3.825.177	-0.399046
28	6	0	-3.678.721	-1.731.277	-0.293452
29	6	0	-5.472.766	0.695387	0.210388
30	6	0	-5.099.036	-2.012.654	-0.731306
31	8	0	-5.969.685	-0.138461	0.938011
32	8	0	-5.549.809	-1.495.349	-1.722.605
33	8	0	5.074.858	0.249979	-1.296.390
34	8	0	4.914.523	1.043.407	1.475.748
35	8	0	-6.168.670	1.666.765	-0.383493
36	8	0	-5.794.150	-2.954.048	-0.076563
37	6	0	-7.596.119	1.662.829	-0.180384
38	1	0	-7.801.812	1.754.219	0.898471
39	1	0	-7.987.793	0.687368	-0.508293
40	6	0	-5.564.789	-3.261.824	1.310.421
41	1	0	-4.964.709	-2.466.526	1.774.087
42	1	0	-4.999.165	-4.207.251	1.368.027
43	6	0	6.235.320	1.266.283	2.002.364
44	1	0	6.227.177	2.199.910	2.588.097
45	1	0	6.932.188	1.420.715	1.162.967
46	6	0	6.420.305	0.384434	-1.794.636
47	1	0	6.579.612	1.469.669	-1.869.184
48	1	0	7.118.202	-0.035943	-1.056.113
49	6	0	-8.183.366	2.809.851	-0.974552
50	1	0	-9.277.044	2.829.163	-0.848536
51	1	0	-7.960.761	2.699.039	-2.046.665
52	1	0	-7.780.214	3.776.514	-0.634862
53	6	0	-6.912.108	-3.383.510	1.996.145
54	1	0	-7.533.009	-4.151.559	1.509.968
55	1	0	-7.442.566	-2.421.121	1.954.088
56	1	0	-6.773.563	-3.664.911	3.052.388

57	6	0	6.578.411	-0.299298	-3.141.869
58	1	0	5.848.243	0.089344	-3.868.374
59	1	0	6.440.740	-1.386.849	-3.047.569
60	1	0	7.590.104	-0.115254	-3.537.655
61	6	0	6.611.509	0.061846	2.840.126
62	1	0	6.606.851	-0.853570	2.229.603
63	1	0	5.904.700	-0.072477	3.673.415
64	1	0	7.619.623	0.199743	3.261.493
65	7	0	-0.603643	-3.735.685	-0.158188
66	6	0	0.709197	-3.618.784	-0.098894
67	6	0	3.363.536	-6.125.358	0.386875
68	6	0	0.749996	-6.111.254	-0.395820
69	6	0	2.759.671	-7.345.492	0.073037
70	6	0	1.421.640	-7.328.838	-0.329655
71	6	0	1.441.696	-4.929.903	-0.059017
72	1	0	3.324.613	-8.277.787	0.141730
73	1	0	0.905848	-8.256.901	-0.589841
74	1	0	-0.294872	-6.045.589	-0.694721
75	7	0	2.726.077	-4.956.571	0.322775
76	1	0	4.411.775	-6.089.513	0.705702
77	6	0	1.771.742	6.818.751	-0.053120
78	6	0	-0.864561	6.133.973	0.084526
79	6	0	0.824606	7.843.848	0.001803
80	6	0	-0.523574	7.483.381	0.073214
81	6	0	0.160344	5.166.680	0.024630
82	1	0	1.137.736	8.890.182	-0.011049
83	1	0	-1.303.657	8.247.852	0.119081
84	1	0	-1.899.796	5.801.807	0.135115
85	7	0	1.449.499	5.525.898	-0.042674
86	1	0	2.841.499	7.051.450	-0.109071
87	7	0	-1.514.382	3.491.100	-0.021648

88	6	0	-0.213776	3.708.546	0.022143

Total energy of *syn*-$(ab)_2$-PTE **18**: –2515.07836100 a.u. Number of imaginary frequencies: 0.

Table S6. Cartesian Coordinates and Total Energy of Ground State Structure of PBI

Center Number	Atomic Number	Atomic type	Coordinates (Å)		
			X	Y	Z
1	6	0	-1.579.377	1.806.379	-1.538.666
2	6	0	-0.785776	0.927302	-0.794456
3	6	0	-3.599.167	1.093.912	-0.411427
4	6	0	-1.419.137	0.093837	0.184240
5	6	0	-2.965.598	1.891.058	-1.353.058
6	6	0	-2.836.186	0.187327	0.368093
7	6	0	-0.671112	-0.831138	0.983584
8	1	0	-3.570.422	2.582.038	-1.942.986
9	6	0	-1.356.534	-1.612.813	1.919.184
10	6	0	-2.743.349	-1.514.571	2.093.176
11	1	0	-3.262.578	-2.132.210	2.828.181
12	6	0	-3.486.692	-0.626159	1.330.508
13	6	0	-5.072.555	1.205.084	-0.238454
14	6	0	-4.957.362	-0.544976	1.538.053
15	8	0	-5.749.211	1.972.285	-0.896113
16	8	0	-5.538.533	-1.230.636	2.357.009
17	7	0	-5.657.986	0.372238	0.732848
18	6	0	1.356.534	1.612.813	-1.919.184
19	6	0	0.671112	0.831138	-0.983584
20	6	0	3.486.692	0.626159	-1.330.508
21	6	0	1.419.137	-0.093837	-0.184240
22	6	0	2.743.349	1.514.571	-2.093.176
23	6	0	2.836.186	-0.187327	-0.368093
24	6	0	0.785776	-0.927302	0.794456
25	1	0	3.262.578	2.132.210	-2.828.181
26	6	0	1.579.377	-1.806.379	1.538.666

27	6	0	2.965.598	-1.891.058	1.353.058
28	1	0	3.570.422	-2.582.038	1.942.986
29	6	0	3.599.167	-1.093.912	0.411427
30	6	0	4.957.362	0.544976	-1.538.053
31	6	0	5.072.555	-1.205.084	0.238454
32	8	0	5.538.533	1.230.636	-2.357.009
33	8	0	5.749.211	-1.972.285	0.896113
34	7	0	5.657.986	-0.372238	-0.732848
35	1	0	-1.124.708	2.451.872	-2.289.512
36	1	0	0.813822	2.324.721	-2.540.367
37	1	0	9.420.666	-2.171.605	-2.716.762
38	6	0	8.995.393	-1.461.210	-2.003.776
39	6	0	7.931.941	0.380588	-0.158997
40	6	0	9.845.156	-0.639007	-1.266.270
41	6	0	7.604.097	-1.391.564	-1.846.647
42	6	0	7.094.853	-0.463234	-0.916600
43	6	0	9.315.875	0.272076	-0.354196
44	1	0	10.927.444	-0.708393	-1.403.556
45	1	0	9.990.997	0.912544	0.218409
46	6	0	7.386.088	1.386.746	0.848279
47	1	0	6.288.495	1.316.565	0.832501
48	6	0	6.702.612	-2.305.586	-2.669.419
49	1	0	5.660.098	-2.080.677	-2.399.956
50	6	0	6.941.494	-3.787.405	-2.329.737
51	1	0	6.803.871	-3.970.433	-1.253.029
52	1	0	7.962.101	-4.105.554	-2.598.865
53	1	0	6.237.000	-4.430.147	-2.882.978
54	6	0	6.842.254	-2.029.695	-4.176.882
55	1	0	7.856.557	-2.263.320	-4.539.703
56	1	0	6.637.713	-0.972046	-4.403.645
57	1	0	6.134.095	-2.649.448	-4.751.231

58	6	0	7.745.964	2.830.897	0.457636
59	1	0	8.835.312	2.997.656	0.479921
60	1	0	7.286.773	3.547.371	1.158.528
61	1	0	7.388.985	3.063.393	-0.557390
62	6	0	7.833.835	1.048.395	2.281.455
63	1	0	7.374.843	1.742.354	3.004.864
64	1	0	8.927.536	1.128.023	2.393.651
65	1	0	7.540.706	0.022583	2.552.922
66	6	0	-7.931.941	-0.380588	0.158997
67	6	0	-8.995.393	1.461.210	2.003.776
68	6	0	-7.094.853	0.463234	0.916600
69	6	0	-9.315.875	-0.272076	0.354196
70	6	0	-9.845.156	0.639007	1.266.270
71	6	0	-7.604.097	1.391.564	1.846.647
72	1	0	-9.990.997	-0.912544	-0.218409
73	1	0	-10.927.444	0.708393	1.403.556
74	1	0	-9.420.666	2.171.605	2.716.762
75	6	0	-7.386.088	-1.386.746	-0.848279
76	1	0	-6.288.495	-1.316.565	-0.832501
77	6	0	-6.702.612	2.305.586	2.669.419
78	1	0	-5.660.098	2.080.677	2.399.956
79	6	0	-7.833.835	-1.048.395	-2.281.455
80	1	0	-7.540.706	-0.022583	-2.552.922
81	1	0	-8.927.536	-1.128.023	-2.393.651
82	1	0	-7.374.843	-1.742.354	-3.004.864
83	6	0	-6.941.494	3.787.405	2.329.737
84	1	0	-7.962.101	4.105.554	2.598.865
85	1	0	-6.803.871	3.970.433	1.253.029
86	1	0	-6.237.000	4.430.147	2.882.978
87	6	0	-6.842.254	2.029.695	4.176.882
88	1	0	-7.856.557	2.263.320	4.539.703

89	1	0	-6.134.095	2.649.448	4.751.231
90	1	0	-6.637.713	0.972046	4.403.645
91	6	0	-7.745.964	-2.830.897	-0.457636
92	1	0	-8.835.312	-2.997.656	-0.479921
93	1	0	-7.388.985	-3.063.393	0.557390
94	1	0	-7.286.773	-3.547.371	-1.158.528
95	1	0	1.124.708	-2.451.872	2.289.512
96	1	0	-0.813822	-2.324.721	2.540.367

Total energy of PBI: –2263.34987733 a.u. Number of imaginary frequencies: 0.

Table S7. Cartesian Coordinates and Total Energy of Ground State Structure of ab-PBI 3a

Center	Atomic	Atomic	Coordinates (Å)		
Number	Number	type	X	Y	Z
1	6	0	-1.751.957	-3.169.517	0.166377
2	6	0	-0.947516	-2.017.115	0.110845
3	6	0	-3.786.077	-1.847.167	0.095599
4	6	0	-1.597.826	-0.748589	0.049263
5	6	0	-3.144.633	-3.086.875	0.160542
6	6	0	-3.019.627	-0.668543	0.038423
7	6	0	-0.841990	0.460603	-0.003820
8	1	0	-3.761.121	-3.986.387	0.205819
9	6	0	-1.489.414	1.718.773	-0.070513
10	6	0	-2.919.762	1.767.082	-0.085007
11	1	0	-3.418.565	2.735.609	-0.136624
12	6	0	-3.662.013	0.612226	-0.031269
13	6	0	-5.272.722	-1.792.388	0.090091
14	6	0	-5.151.476	0.703648	-0.046576
15	8	0	-5.961.272	-2.792.531	0.143684
16	8	0	-5.739.168	1.764.697	-0.109847
17	7	0	-5.857.680	-0.512862	0.018250
18	6	0	1.249.262	-3.256.024	0.159073
19	6	0	0.519721	-2.054.825	0.109347

20	6	0	3.363.042	-2.070.245	0.094333
21	6	0	1.249.974	-0.825703	0.052964
22	6	0	2.643.983	-3.265.281	0.152117
23	6	0	2.672.429	-0.844141	0.044563
24	6	0	0.577331	0.438094	0.002634
25	1	0	3.200.822	-4.203.257	0.190984
26	6	0	1.301.308	1.665.134	-0.045170
27	6	0	2.730.711	1.597.071	-0.059256
28	1	0	3.306.594	2.518.566	-0.086377
29	6	0	3.390.691	0.390791	-0.018547
30	6	0	4.849.611	-2.110.160	0.086955
31	6	0	4.882.151	0.389610	-0.040343
32	8	0	5.472.779	-3.153.149	0.135306
33	8	0	5.539.030	1.409.215	-0.103519
34	7	0	5.512.241	-0.870661	0.018364
35	1	0	-1.292.234	-4.156.803	0.215539
36	1	0	0.725472	-4.210.888	0.203744
37	7	0	-0.794210	2.876.051	-0.115420
38	6	0	0.528003	2.892.502	-0.094501
39	6	0	1.120.129	4.274.560	-0.134816
40	6	0	2.179.001	6.818.161	-0.163190
41	6	0	0.288692	5.363.261	-0.467539
42	6	0	0.830004	6.646.130	-0.482842
43	6	0	2.926.443	5.681.149	0.154263
44	1	0	-0.758751	5.179.214	-0.700034
45	1	0	0.203848	7.503.977	-0.741381
46	1	0	2.644.700	7.806.086	-0.160424
47	1	0	3.988.775	5.766.870	0.409975
48	7	0	2.413.757	4.451.294	0.166947
49	1	0	9.619.726	-0.751158	2.126.062
50	6	0	9.055.991	-0.821832	1.192.659

51	6	0	7.632.319	-1.002.646	-1.228.971
52	6	0	9.741.633	-0.931696	-0.015564
53	6	0	7.654.784	-0.799510	1.230.961
54	6	0	6.963.291	-0.891186	0.006379
55	6	0	9.033.995	-1.021.180	-1.212.763
56	1	0	10.834.646	-0.947625	-0.024268
57	1	0	9.580.835	-1.107.698	-2.154.815
58	6	0	6.890.049	-1.102.581	-2.557.496
59	1	0	5.811.465	-1.067.987	-2.344.316
60	6	0	6.936.927	-0.677367	2.570.884
61	1	0	5.854.512	-0.685283	2.375.342
62	6	0	7.254.970	0.660441	3.262.146
63	1	0	7.005.685	1.509.634	2.607.708
64	1	0	8.322.849	0.736555	3.524.756
65	1	0	6.675.886	0.760981	4.194.866
66	6	0	7.233.922	-1.881.222	3.482.370
67	1	0	8.301.424	-1.931.411	3.752.453
68	1	0	6.967.266	-2.826.771	2.985.519
69	1	0	6.657.922	-1.808.968	4.419.645
70	6	0	7.163.367	-2.445.351	-3.258.028
71	1	0	8.224.335	-2.547.061	-3.539.171
72	1	0	6.566.370	-2.528.530	-4.181.153
73	1	0	6.904.831	-3.290.516	-2.601.893
74	6	0	7.202.290	0.097007	-3.469.484
75	1	0	6.609.799	0.042870	-4.397.675
76	1	0	8.266.325	0.121595	-3.756.315
77	1	0	6.966.980	1.046.624	-2.964.725
78	6	0	-7.989.127	-0.306383	1.235.804
79	6	0	-9.384.452	-0.441123	-1.205.507
80	6	0	-7.307.548	-0.442420	0.009775
81	6	0	-9.388.974	-0.239738	1.199.907

82	6	0	-10.082.533	-0.306571	-0.006963
83	6	0	-7.984.447	-0.511319	-1.224.408
84	1	0	-9.945.623	-0.133271	2.134.036
85	1	0	-11.174.366	-0.253434	-0.013436
86	1	0	-9.937.283	-0.493254	-2.146.618
87	6	0	-7.262.439	-0.229308	2.574.539
88	1	0	-6.182.887	-0.304688	2.376.990
89	6	0	-7.252.824	-0.659033	-2.554.187
90	1	0	-6.173.283	-0.682582	-2.344.273
91	6	0	-7.631.559	-1.412.818	3.486.262
92	1	0	-7.428.234	-2.372.711	2.986.982
93	1	0	-8.698.654	-1.395.074	3.761.848
94	1	0	-7.047.576	-1.378.787	4.420.754
95	6	0	-7.602.192	-1.988.898	-3.245.890
96	1	0	-8.668.494	-2.033.253	-3.521.730
97	1	0	-7.387.857	-2.843.724	-2.586.331
98	1	0	-7.014.897	-2.109.738	-4.171.057
99	6	0	-7.501.121	0.549867	-3.473.600
100	1	0	-8.562.674	0.630572	-3.759.178
101	1	0	-6.914.214	0.456940	-4.402.197
102	1	0	-7.213.478	1.488.968	-2.976.311
103	6	0	-7.495.411	1.125.531	3.266.343
104	1	0	-8.555.823	1.267.989	3.531.398
105	1	0	-7.195.901	1.957.744	2.611.147
106	1	0	-6.909.166	1.190.143	4.197.751

Total energy of ab-PBI **3a**: –2602.47845566 a.u. Number of imaginary frequencies: 0.

Table S8. Cartesian Coordinates and Total Energy of Ground State Structure of *anti*-(ab)$_2$-PBI 15

Center Number	Atomic Number	Atomic type	Coordinates (Å)		
			X	Y	Z
1	6	0	1.624.832	-2.339.979	0.021703

2	6	0	0.820916	-1.163.111	-0.003413
3	6	0	3.615.170	-0.901894	-0.006122
4	6	0	1.410.365	0.133856	-0.027116
5	6	0	3.040.735	-2.163.395	0.022445
6	6	0	2.814.904	0.270376	-0.030290
7	6	0	0.591840	1.297.739	-0.043612
8	1	0	3.683.595	-3.039.595	0.046593
9	6	0	1.173.869	2.589.390	-0.058547
10	6	0	2.595.323	2.700.958	-0.057245
11	1	0	3.055.445	3.689.874	-0.066182
12	6	0	3.394.529	1.571.736	-0.045939
13	6	0	5.101.722	-0.780660	-0.001898
14	6	0	4.878.246	1.718.254	-0.044351
15	8	0	5.836.946	-1.744.864	0.067197
16	8	0	5.424.650	2.801.904	-0.010394
17	7	0	5.630.052	0.525343	-0.091360
18	6	0	-1.176.901	-2.552.913	0.022697
19	6	0	-0.594869	-1.261.438	-0.002298
20	6	0	-3.397.651	-1.535.341	0.002595
21	6	0	-1.413.397	-0.097662	-0.023059
22	6	0	-2.598.342	-2.664.398	0.026589
23	6	0	-2.817.936	-0.234136	-0.021460
24	6	0	-0.823956	1.199.385	-0.042120
25	1	0	-3.058.336	-3.653.208	0.048373
26	6	0	-1.627.901	2.376.389	-0.056857
27	6	0	-3.043.812	2.200.039	-0.048261
28	1	0	-3.686.878	3.076.310	-0.057894
29	6	0	-3.618.182	0.938326	-0.033180
30	6	0	-4.881.818	-1.682.184	0.008286
31	6	0	-5.104.121	0.816922	-0.023823
32	8	0	-5.426.721	-2.766.386	0.072786

33	8	0	-5.840.259	1.780.681	0.018222
34	7	0	-5.632.928	-0.494021	-0.074378
35	7	0	0.404114	3.706.440	-0.073541
36	6	0	-0.915020	3.651.393	-0.075136
37	6	0	-1.584.132	4.999.008	-0.096135
38	6	0	-2.798.930	7.473.109	-0.144283
39	6	0	-0.785507	6.160.541	-0.063021
40	6	0	-1.404.616	7.407.327	-0.087044
41	6	0	-3.509.350	6.270.440	-0.173537
42	1	0	0.297107	6.056.666	-0.020631
43	1	0	-0.803415	8.319.869	-0.061487
44	1	0	-3.326.379	8.429.269	-0.165397
45	7	0	-2.920.934	5.075.440	-0.150102
46	1	0	-9.657.462	-0.731960	2.163.214
47	6	0	-9.131.608	-0.729002	1.205.515
48	6	0	-7.792.862	-0.717077	-1.281.503
49	6	0	-9.858.343	-0.826569	0.022590
50	6	0	-7.734.315	-0.621181	1.186.932
51	6	0	-7.081.752	-0.617744	-0.064736
52	6	0	-9.191.055	-0.819486	-1.199.813
53	1	0	-10.948.220	-0.905011	0.051229
54	1	0	-9.765.277	-0.894749	-2.127.306
55	1	0	9.636.168	1.011.304	2.139.499
56	6	0	9.116.307	0.920541	1.182.939
57	6	0	7.793.241	0.688319	-1.301.580
58	6	0	9.847.082	0.951317	-0.001097
59	6	0	7.722.088	0.778066	1.166.759
60	6	0	7.077.674	0.661971	-0.083748
61	6	0	9.187.453	0.837525	-1.222.301
62	1	0	10.933.619	1.067.609	0.025773
63	1	0	9.764.367	0.864656	-2.150.741

64	6	0	-6.980.880	-0.508333	2.509.088
65	1	0	-5.905.829	-0.450895	2.286.438
66	6	0	-7.187.718	-0.779623	-2.689.297
67	1	0	-8.034.015	-0.539852	-3.354.796
68	6	0	-7.348.843	0.785356	3.257.648
69	1	0	-8.409.915	0.791969	3.556.266
70	1	0	-7.168.460	1.668.272	2.625.839
71	1	0	-6.745.443	0.885907	4.174.852
72	6	0	-7.183.249	-1.757.952	3.384.519
73	1	0	-8.236.622	-1.876.635	3.686.513
74	1	0	-6.581.441	-1.685.553	4.305.421
75	1	0	-6.881.182	-2.669.199	2.845.849
76	6	0	-6.096.883	0.250843	-3.025.941
77	1	0	-5.114.411	-0.026141	-2.616.515
78	1	0	-6.353.324	1.253.455	-2.654.007
79	1	0	-5.977.730	0.312387	-4.119.768
80	6	0	-6.748.475	-2.210.910	-3.055.902
81	1	0	-7.580.794	-2.921.896	-2.938.228
82	1	0	-5.927.465	-2.566.460	-2.416.892
83	1	0	-6.411.531	-2.250.268	-4.105.167
84	6	0	6.963.294	0.749063	2.490.573
85	1	0	5.892.518	0.636063	2.268.551
86	6	0	7.206.676	0.517834	-2.708.177
87	1	0	7.997.712	0.899979	-3.375.121
88	6	0	7.367.455	-0.466939	3.343.228
89	1	0	8.425.071	-0.414419	3.649.278
90	1	0	7.222.652	-1.403.648	2.783.675
91	1	0	6.758.900	-0.514789	4.261.308
92	6	0	7.118.945	2.071.823	3.261.669
93	1	0	6.797.024	2.925.345	2.645.843
94	1	0	8.165.050	2.245.787	3.562.318

95	1	0	6.509.042	2.058.002	4.180.027
96	6	0	5.952.906	1.341.932	-3.046.139
97	1	0	6.030.930	2.374.734	-2.676.558
98	1	0	5.033.887	0.898690	-2.635.589
99	1	0	5.824.487	1.379.026	-4.140.047
100	6	0	7.022.923	-0.968589	-3.072.758
101	1	0	6.272.728	-1.460.503	-2.437.171
102	1	0	7.965.091	-1.524.946	-2.950.510
103	1	0	6.702.750	-1.067.210	-4.123.384
104	6	0	3.506.804	-6.234.525	0.119146
105	6	0	0.781041	-6.123.864	0.079178
106	6	0	2.795.270	-7.436.864	0.127219
107	6	0	1.399.970	-7.370.678	0.106318
108	6	0	1.580.791	-4.962.641	0.073092
109	1	0	3.322.611	-8.393.064	0.149152
110	1	0	0.797824	-8.282.943	0.111336
111	1	0	-0.302249	-6.019.709	0.063038
112	7	0	2.918.504	-5.039.542	0.092783
113	1	0	4.602.741	-6.235.799	0.134739
114	1	0	-4.604.507	6.271.503	-0.217854
115	7	0	-0.407195	-3.669.849	0.044613
116	6	0	0.911943	-3.614.952	0.045598

Total energy of *anti*-$(ab)_2$-PBI **15**: –2941.59006821 a.u. Number of imaginary frequencies: 0.

Table S9. Cartesian Coordinates and Total Energy of Ground State Structure of *syn*-$(ab)_2$-PBI 16

Center Number	Atomic Number	Atomic type	Coordinates (Å)		
			X	Y	Z
1	6	0	1.652.434	-2.475.239	-0.042517
2	6	0	0.966778	-1.236.451	-0.058457
3	6	0	3.782.135	-1.273.574	-0.029244
4	6	0	1.686.279	-0.013473	-0.057938

5	6	0	3.078.591	-2.466.619	-0.025876
6	6	0	3.098.626	-0.024735	-0.045055
7	6	0	0.986316	1.220.812	-0.059875
8	1	0	3.619.311	-3.413.737	-0.010927
9	6	0	1.691.676	2.448.476	-0.046276
10	6	0	3.117.534	2.417.180	-0.031343
11	1	0	3.673.130	3.355.730	-0.018634
12	6	0	3.802.115	1.213.023	-0.033317
13	6	0	5.273.053	-1.296.667	-0.008359
14	6	0	5.293.727	1.212.781	-0.013805
15	8	0	5.907.591	-2.329.399	0.053311
16	8	0	5.943.604	2.237.563	0.041578
17	7	0	5.926.487	-0.045783	-0.070220
18	6	0	-1.156.551	-2.478.371	-0.058492
19	6	0	-0.452311	-1.238.804	-0.061049
20	6	0	-3.258.691	-1.214.663	-0.025942
21	6	0	-1.147.261	0.009146	-0.057361
22	6	0	-2.581.480	-2.423.012	-0.034773
23	6	0	-2.557.135	0.020348	-0.041597
24	6	0	-0.432556	1.245.874	-0.061564
25	1	0	-3.150.905	-3.348.998	-0.037293
26	6	0	-1.116.954	2.496.582	-0.058725
27	6	0	-2.542.578	2.463.784	-0.033790
28	1	0	-3.097.376	3.398.551	-0.035606
29	6	0	-3.238.786	1.266.377	-0.024355
30	6	0	-4.749.293	-1.217.069	0.008125
31	6	0	-4.728.665	1.292.112	0.010039
32	8	0	-5.399.870	-2.241.234	0.071401
33	8	0	-5.363.931	2.324.420	0.075792
34	7	0	-5.383.218	0.041261	-0.043452
35	7	0	1.032.344	3.634.549	-0.048522

36	6	0	-0.286410	3.697.998	-0.063207
37	6	0	-0.830659	5.100.083	-0.077796
38	6	0	-1.809.908	7.674.414	-0.144824
39	6	0	0.047492	6.177.388	0.157735
40	6	0	-0.453547	7.476.095	0.124818
41	6	0	-2.604.987	6.546.896	-0.365812
42	1	0	1.097.902	5.971.008	0.355519
43	1	0	0.209225	8.325.896	0.307507
44	1	0	-2.245.252	8.675.408	-0.182182
45	7	0	-2.130.711	5.302.156	-0.332273
46	1	0	-9.364.316	0.163970	2.279.662
47	6	0	-8.860.342	0.131014	1.310.803
48	6	0	-7.578.888	0.048161	-1.204.748
49	6	0	-9.617.613	0.122602	0.143102
50	6	0	-7.459.928	0.102142	1.262.596
51	6	0	-6.836.242	0.059415	-0.003035
52	6	0	-8.978.389	0.082756	-1.093.525
53	1	0	-10.709.117	0.150427	0.194906
54	1	0	-9.576.413	0.078490	-2.008.955
55	1	0	9.933.634	-0.162454	2.208.118
56	6	0	9.418.728	-0.131929	1.244.959
57	6	0	8.108.937	-0.055675	-1.256.431
58	6	0	10.162.643	-0.126255	0.068711
59	6	0	8.017.846	-0.103435	1.212.599
60	6	0	7.380.332	-0.063931	-0.046145
61	6	0	9.509.581	-0.089725	-1.160.771
62	1	0	11.254.639	-0.153708	0.108209
63	1	0	10.097.308	-0.087685	-2.082.816
64	6	0	-6.671.610	0.116282	2.569.363
65	1	0	-5.600.612	0.089366	2.322.655
66	6	0	-7.012.604	-0.051873	-2.626.420

67	1	0	-7.843.883	0.283711	-3.269.010
68	6	0	-6.912.408	1.414.617	3.359.843
69	1	0	-7.962.209	1.502.912	3.684.091
70	1	0	-6.671.352	2.296.716	2.747.351
71	1	0	-6.283.257	1.438.877	4.264.934
72	6	0	-6.961.982	-1.136.599	3.414.749
73	1	0	-8.015.431	-1.172.950	3.737.100
74	1	0	-6.337.079	-1.144.164	4.323.065
75	1	0	-6.751.345	-2.053.363	2.843.081
76	6	0	-5.829.496	0.867310	-2.973.579
77	1	0	-5.728.934	0.934683	-4.068.959
78	1	0	-4.871.839	0.484133	-2.591.913
79	1	0	-5.973.149	1.884.424	-2.580.991
80	6	0	-6.729.363	-1.514.261	-3.023.524
81	1	0	-7.626.944	-2.139.097	-2.896.652
82	1	0	-5.934.793	-1.961.960	-2.409.486
83	1	0	-6.421.349	-1.569.930	-4.080.912
84	6	0	7.244.427	-0.114671	2.528.330
85	1	0	6.170.522	-0.088334	2.294.177
86	6	0	7.526.898	0.040652	-2.672.052
87	1	0	8.351.462	-0.295528	-3.322.831
88	6	0	7.494.629	-1.411.216	3.318.856
89	1	0	8.548.252	-1.498.725	3.630.510
90	1	0	7.246.493	-2.294.978	2.711.588
91	1	0	6.876.483	-1.433.241	4.231.504
92	6	0	7.544.665	1.139.937	3.367.707
93	1	0	7.328.137	2.055.766	2.796.732
94	1	0	8.601.656	1.176.525	3.678.057
95	1	0	6.930.073	1.149.496	4.282.961
96	6	0	7.237.925	1.501.681	-3.069.877
97	1	0	8.135.395	2.128.374	-2.952.238

98	1	0	6.447.837	1.949.536	-2.450.164
99	1	0	6.920.474	1.554.475	-4.124.578
100	6	0	6.341.312	-0.880682	-3.004.674
101	1	0	5.387.194	-0.498436	-2.613.152
102	1	0	6.491.334	-1.897.165	-2.612.781
103	1	0	6.228.629	-0.949716	-4.098.728
104	7	0	0.974231	-3.650.655	-0.044515
105	6	0	-0.345342	-3.692.870	-0.061304
106	6	0	-2.708.240	-6.504.067	-0.371969
107	6	0	-0.053150	-6.176.848	0.166417
108	6	0	-1.932.890	-7.643.959	-0.144384
109	6	0	-0.575068	-7.467.285	0.132872
110	6	0	-0.912267	-5.085.874	-0.076094
111	1	0	-2.384.266	-8.637.793	-0.182596
112	1	0	0.072683	-8.327.434	0.320913
113	1	0	0.999354	-5.987.195	0.369791
114	7	0	-2.213.976	-5.267.122	-0.337780
115	1	0	-3.778.327	-6.593.569	-0.591534
116	1	0	-3.674.753	6.653.418	-0.579270

Total energy of *syn*-(ab)$_2$-PBI **16**: –2941.59011061 a.u. Number of imaginary frequencies: 0.

Table S10. Cartesian Coordinates and Total Energy of Ground State Structure of ab-PMIMA 13

Center Number	Atomic Number	Atomic type	Coordinates (Å)		
			X	Y	Z
1	6	0	-1.912.344	-3.178.454	0.008797
2	6	0	-0.873813	-2.229.874	0.005823
3	6	0	-3.605.224	-1.439.382	0.006344
4	6	0	-1.229.130	-0.848633	0.003956
5	6	0	-3.253.222	-2.791.634	0.009364
6	6	0	-2.598.232	-0.459722	0.003376
7	6	0	-0.229030	0.168312	0.001849

8	1	0	-4.052.449	-3.534.723	0.011726
9	6	0	-0.588035	1.538.465	-0.002633
10	6	0	-1.974.348	1.897.174	-0.004216
11	1	0	-2.250.284	2.952.180	-0.007082
12	6	0	-2.949.167	0.928973	-0.000831
13	6	0	-5.045.212	-1.056.396	0.006214
14	6	0	-4.384.824	1.340.094	-0.001613
15	8	0	-5.921.677	-1.902.289	0.009031
16	8	0	-4.704.613	2.513.749	-0.005687
17	7	0	-5.349.780	0.312957	0.002613
18	6	0	0.999008	-3.919.536	0.002115
19	6	0	0.549610	-2.586.391	0.002948
20	6	0	3.318.709	-3.220.705	-0.006554
21	6	0	1.529.790	-1.543.549	0.000020
22	6	0	2.357.691	-4.233.644	-0.002447
23	6	0	2.913.008	-1.872.058	-0.005215
24	6	0	1.151.179	-0.161439	0.001747
25	1	0	2.693.169	-5.272.419	-0.003281
26	6	0	2.125.059	0.880561	0.001914
27	6	0	3.505.375	0.501939	-0.005938
28	1	0	4.263.480	1.281.562	0.000071
29	6	0	3.882.940	-0.821071	-0.010399
30	6	0	4.759.245	-3.565.224	-0.012443
31	6	0	5.329.027	-1.160.307	-0.019674
32	8	0	5.196.868	-4.681.858	-0.012623
33	8	0	6.226.094	-0.366755	-0.027253
34	1	0	-1.681.703	-4.243.977	0.010498
35	1	0	0.278744	-4.737.510	0.004718
36	7	0	0.342251	2.516.938	-0.003575
37	6	0	1.637.556	2.248.913	0.002403
38	6	0	2.511.911	3.474.458	0.004346

39	6	0	4.096.080	5.731.197	0.024474
40	6	0	1.908.392	4.742.579	-0.119754
41	6	0	2.713.684	5.878.526	-0.110381
42	6	0	4.606.865	4.435.992	0.142279
43	1	0	0.826408	4.807.098	-0.217994
44	1	0	2.264.904	6.870.475	-0.207230
45	1	0	4.765.238	6.594.236	0.037808
46	1	0	5.684.846	4.269.925	0.249543
47	7	0	3.839.935	3.346.740	0.132005
48	6	0	-6.783.757	0.736411	0.002631
49	1	0	-6.717.102	1.830.244	-0.000171
50	6	0	-7.507.509	0.306670	-1.277.539
51	1	0	-6.963.024	0.651392	-2.170.757
52	1	0	-8.507.230	0.768577	-1.298.272
53	1	0	-7.626.892	-0.783461	-1.333.754
54	6	0	-7.505.628	0.313041	1.285.986
55	1	0	-6.959.583	0.661783	2.176.687
56	1	0	-7.625.393	-0.776753	1.347.624
57	1	0	-8.505.109	0.775493	1.306.103
58	8	0	5.647.230	-2.508.134	-0.019120

Total energy of ab-PMIMA **13**: −1806.98237267 a.u. Number of imaginary frequencies: 0.

Table S11. Cartesian Coordinates and Total Energy of Ground State Structure of ab-PMIDE 12

Center Number	Atomic Number	Atomic type	Coordinates (Å)		
			X	Y	Z
1	6	0	2.326.805	-3.222.193	-0.001748
2	6	0	1.444.153	-2.126.192	0.005777
3	6	0	4.266.928	-1.763.024	-0.007889
4	6	0	2.007.811	-0.818466	0.002503
5	6	0	3.710.693	-3.044.995	-0.010542
6	6	0	3.420.291	-0.641882	-0.000058

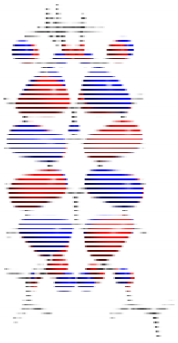
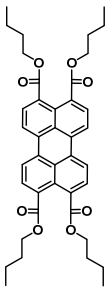
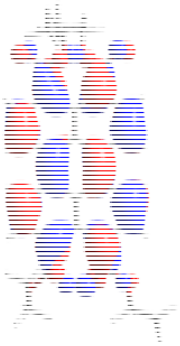
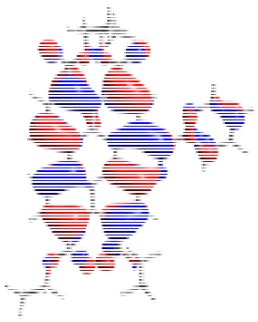
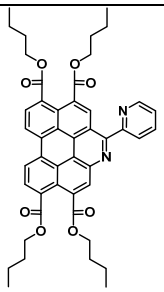
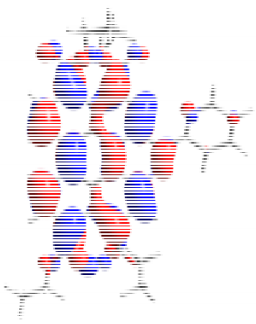
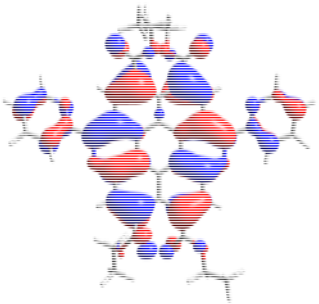
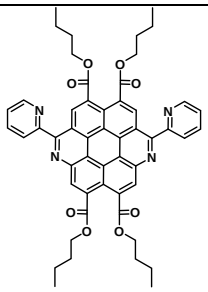
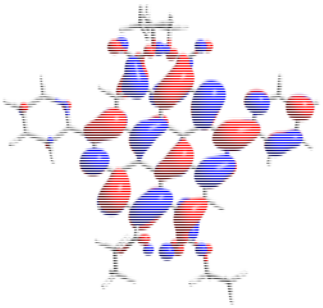
7	6	0	1.168.157	0.333613	-0.000106
8	1	0	4.386.576	-3.901.864	-0.018740
9	6	0	1.733.320	1.634.192	0.013442
10	6	0	3.157.241	1.779.474	0.014561
11	1	0	3.586.484	2.781.915	0.023274
12	6	0	3.977.349	0.677265	0.004271
13	6	0	5.746.624	-1.603.192	-0.015616
14	6	0	5.456.421	0.867424	-0.000333
15	8	0	6.488.084	-2.570.590	-0.025808
16	8	0	5.952.814	1.978.791	0.003923
17	7	0	6.254.805	-0.294877	-0.011293
18	6	0	-0.641608	-3.515.944	0.078067
19	6	0	-0.018186	-2.263.430	0.017322
20	6	0	-2.848.877	-2.496.373	0.173906
21	6	0	-0.849530	-1.094.230	-0.027689
22	6	0	-2.026.292	-3.623.005	0.183148
23	6	0	-2.277.685	-1.211.541	-0.045048
24	6	0	-0.247122	0.211771	-0.029458
25	1	0	-2.496.639	-4.599.270	0.314411
26	6	0	-1.037.976	1.392.141	-0.046764
27	6	0	-2.446.456	1.232.546	-0.230539
28	1	0	-3.065.327	2.114.455	-0.370190
29	6	0	-3.040.121	-0.004107	-0.292034
30	6	0	-4.275.402	-2.752.712	0.560581
31	6	0	-4.444.808	0.012077	-0.827018
32	8	0	-4.855.011	-3.798.169	0.378106
33	8	0	-5.232.523	0.914435	-0.667469
34	1	0	1.937.751	-4.240.375	-0.003700
35	1	0	-0.046721	-4.428.703	0.095937
36	7	0	0.966143	2.745.374	0.034510
37	6	0	-0.353524	2.665.725	0.023905

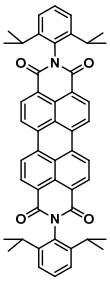
38	6	0	-1.050.508	3.993.805	0.089938
39	6	0	-2.309.782	6.435.629	0.276149
40	6	0	-0.315216	5.168.301	-0.168516
41	6	0	-0.957747	6.399.873	-0.075260
42	6	0	-2.956.791	5.220.381	0.514323
43	1	0	0.739068	5.087.584	-0.428463
44	1	0	-0.408354	7.323.757	-0.274129
45	1	0	-2.852.776	7.379.283	0.363956
46	1	0	-4.017.113	5.200.219	0.791907
47	7	0	-2.347.535	4.038.284	0.424592
48	8	0	-4.668.456	-1.037.501	-1.643.547
49	8	0	-4.794.370	-1.728.001	1.257.944
50	6	0	-5.849.316	-1.017.553	-2.471.084
51	1	0	-5.562.773	-1.594.583	-3.362.231
52	1	0	-6.051.411	0.023049	-2.765.437
53	6	0	-7.059.758	-1.633.866	-1.792.352
54	1	0	-7.391.885	-1.016.954	-0.944767
55	1	0	-6.837.040	-2.650.904	-1.435.600
56	1	0	-7.891.290	-1.694.453	-2.513.017
57	6	0	-6.097.507	-1.907.602	1.845.353
58	1	0	-6.050.490	-2.762.507	2.539.653
59	1	0	-6.814.229	-2.172.715	1.054.179
60	6	0	-6.470.510	-0.616837	2.544.480
61	1	0	-6.491.150	0.220766	1.831.005
62	1	0	-5.746.713	-0.375877	3.338.110
63	1	0	-7.466.774	-0.714785	3.003.335
64	6	0	7.734.926	-0.092382	-0.019520
65	1	0	7.833.090	0.999065	-0.013129
66	6	0	8.395.429	-0.629944	1.254.197
67	1	0	7.913.916	-0.211292	2.152.007
68	1	0	9.453.136	-0.322387	1.269.470

69	1	0	8.350.978	-1.725.854	1.306.728
70	6	0	8.378.260	-0.613537	-1.308.785
71	1	0	7.885.324	-0.182750	-2.194.600
72	1	0	8.332.090	-1.708.641	-1.375.176
73	1	0	9.435.956	-0.306620	-1.334.032

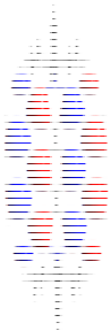
Total energy of ab-PMIDE **12**: –2040.48017596 a.u. Number of imaginary frequencies: 0.

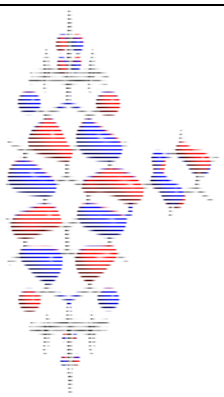
Table S12. Calculated frontier molecular orbitals of azabenz-annulated perylene derivatives at the B3LYP/def2-SVP level of theory.[a]

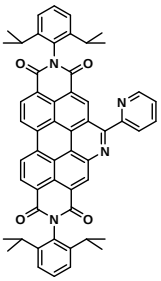
HOMO	Molecular structure	LUMO
	 PTE	
	 ab-PTE **5**	
	 *syn*-(ab)$_2$-PTE **18**	



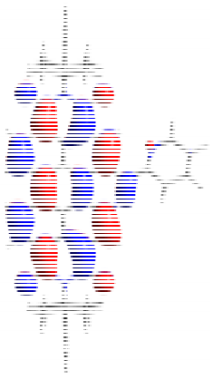
PBI

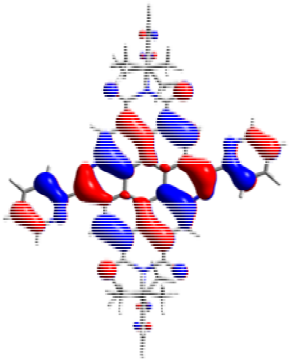


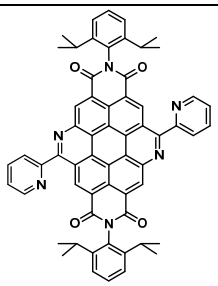




ab-PBI u**3a**

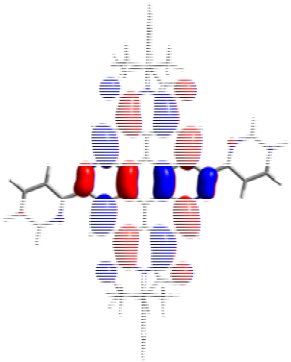


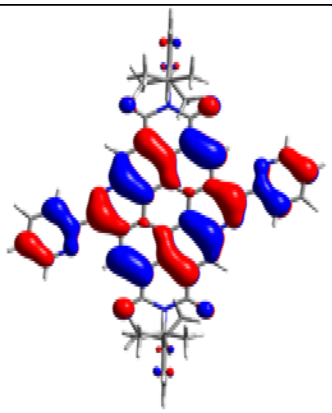


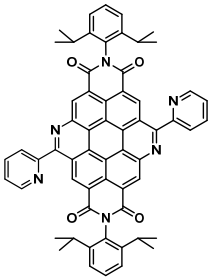


anti-(ab)$_2$-PBI

15

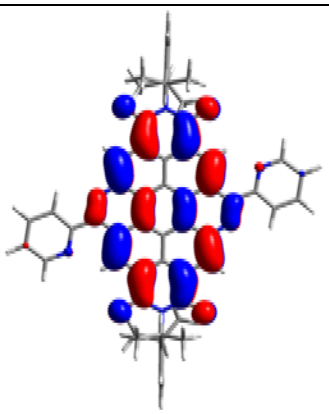


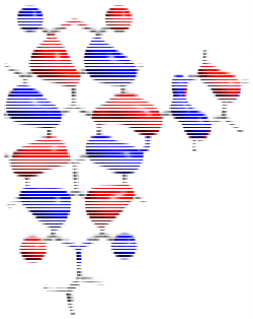
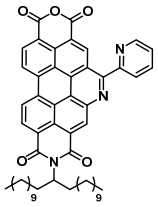
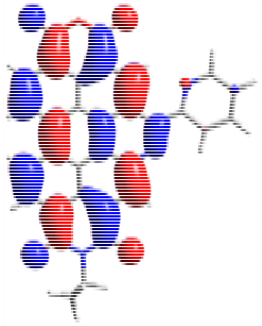
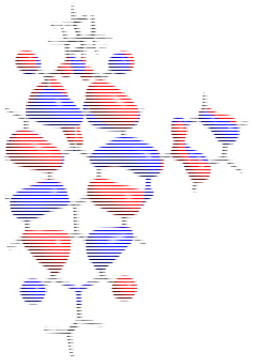
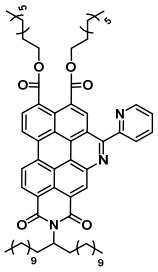
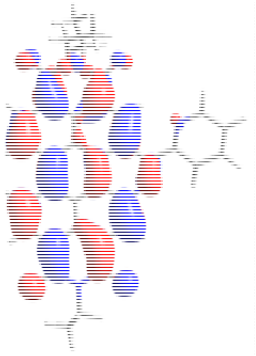




syn-(ab)$_2$-PBI

16



	 ab-PMIMA **13**	
	 ab-PMIDE **12**	

[a] Long alkyl chains were replaced by ethyl groups to simplify and thus accelerate the calculations.