Supporting Information for

Free Base and Metal Complexes of 5,15-Diaza-10,20-dimesitylporphyrins: Synthesis, Structures, Optical and Electrochemical Properties, and Aromaticities

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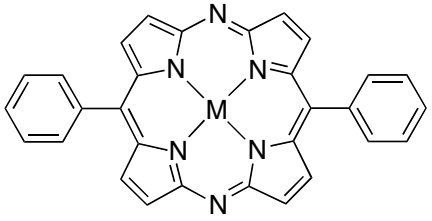
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Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; 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, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; 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, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J. Fox, D. J.; *Gaussian 09, Revision B.01*; Gaussian, Inc.: Wallingford CT, **2010**.

Table S1. Cartesian coordinates and energies of B3LYP/6-311G(d,p) & LANL2TZ(f) geometry optimized structures of M-DAP models.



$2H_2$-m (M = H_2)
2Pd-m (M = Pd)
2Pt-m (M = Pt)
2Zn-m (M = Zn)

H_2-DAP (**$2H_2$-m**): Geometry (in Å)

H	0.665770	-0.800846	-0.029680
H	-0.665770	0.800846	-0.029680
H	4.554210	-2.475068	0.071378
H	-4.554210	2.475068	0.071378
H	4.535116	2.511242	-0.101355
H	-4.535116	-2.511242	-0.101355
H	2.744637	-4.476397	0.089204
H	-2.744637	4.476397	0.089204
H	2.703620	4.502158	-0.110043
H	-2.703620	-4.502158	-0.110043
H	0.781554	5.117268	2.004890
H	-0.781554	-5.117268	2.004890
H	0.776209	-5.149776	-1.989015
H	-0.776209	5.149776	-1.989015
H	0.785265	7.589402	2.026263
H	-0.785265	-7.589402	2.026263
H	0.778015	-7.621844	-1.971313
H	-0.778015	7.621844	-1.971313
H	0.004313	8.852763	0.037305
H	-0.004313	-8.852763	0.037305
C	2.771875	-1.154379	0.001453
C	-2.771875	1.154379	0.001453
C	2.711661	1.193253	-0.022927
C	-2.711661	-1.193253	-0.022927
C	3.478396	-2.406679	0.043290
C	-3.478396	2.406679	0.043290
C	3.458319	2.447966	-0.067640
C	-3.458319	-2.447966	-0.067640
C	1.230617	2.778322	-0.014819
C	-1.230617	-2.778322	-0.014819
C	1.247667	-2.822308	0.002585
C	-1.247667	2.822308	0.002585
C	2.558686	-3.415705	0.049977
C	-2.558686	3.415705	0.049977
C	2.539703	3.437196	-0.068869
C	-2.539703	-3.437196	-0.068869
C	0.001541	-3.465272	-0.002735
C	-0.001541	3.465272	-0.002735
C	0.001541	4.961425	0.007110
C	-0.001541	-4.961425	0.007110
C	0.444377	5.666553	1.133275
C	-0.444377	-5.666553	1.133275
C	0.441253	-5.684624	-1.107493
C	-0.441253	5.684624	-1.107493
C	0.443808	7.059223	1.144269
C	-0.443808	-7.059223	1.144269
C	0.438597	-7.077536	-1.097156
C	-0.438597	7.077536	-1.097156
C	0.003074	7.768703	0.028979
C	-0.003074	-7.768703	0.028979
N	3.357286	0.027766	-0.011096
N	-3.357286	-0.027766	-0.011096
N	1.370201	1.422781	0.003878
N	-1.370201	-1.422781	0.003878
N	1.431907	-1.463652	-0.021844
N	-1.431907	1.463652	-0.021844

B3LYP/6-311G(d,p) Energy = –1484.07954895 a.u.

Pd-DAP (**2Pd-m**): Geometry (in Å)

H	0.062550	4.552076	-2.512232
H	0.062550	-4.552076	2.512232
H	-0.062550	4.552076	2.512232
H	-0.062550	-4.552076	-2.512232
H	0.073989	2.701520	-4.481918
H	0.073989	-2.701520	4.481918
H	-0.073989	2.701520	4.481918
H	-0.073989	-2.701520	-4.481918
H	2.040159	0.657114	5.101513

H	2.040159	-0.657114	-5.101513
H	-2.040159	0.657114	-5.101513
H	-2.040159	-0.657114	5.101513
H	2.042852	0.658342	7.574680
H	2.042852	-0.658342	-7.574680
H	-2.042852	0.658342	-7.574680
H	-2.042852	-0.658342	7.574680
H	0.000000	0.000000	8.821474
H	0.000000	0.000000	-8.821474
C	0.010974	2.768772	-1.169742
C	0.010974	-2.768772	1.169742
C	-0.010974	2.768772	1.169742
C	-0.010974	-2.768772	-1.169742
C	0.041167	3.476544	-2.431972
C	0.041167	-3.476544	2.431972
C	-0.041167	3.476544	2.431972
C	-0.041167	-3.476544	-2.431972
C	0.008647	1.239802	-2.775391
C	0.008647	-1.239802	2.775391
C	-0.008647	1.239802	2.775391
C	-0.008647	-1.239802	-2.775391
C	0.044911	2.543435	-3.416024
C	0.044911	-2.543435	3.416024
C	-0.044911	2.543435	3.416024
C	-0.044911	-2.543435	-3.416024
C	0.000000	0.000000	3.433481
C	0.000000	0.000000	-3.433481
C	0.000000	0.000000	4.931594
C	0.000000	0.000000	-4.931594
C	1.145631	0.373213	5.644252
C	1.145631	-0.373213	-5.644252
C	-1.145631	0.373213	-5.644252
C	-1.145631	-0.373213	5.644252
C	1.145828	0.371733	7.037284
C	1.145828	-0.371733	-7.037284
C	-1.145828	0.371733	-7.037284
C	-1.145828	-0.371733	7.037284
C	0.000000	0.000000	7.737378
C	0.000000	0.000000	-7.737378
N	0.000000	3.389263	0.000000
N	0.000000	-3.389263	0.000000
N	0.004127	1.419870	1.418000
N	0.004127	-1.419870	-1.418000
N	-0.004127	1.419870	-1.418000
N	-0.004127	-1.419870	1.418000
Pd	0.000000	0.000000	0.000000

B3LYP/6-311G(d,p) & LANL2TZ(f) Energy = –1609.72704839 a.u.

Pt-DAP (**2Pt-m**): Geometry (in Å)

H	0.047492	4.550347	-2.512445
H	0.047492	-4.550347	2.512445
H	-0.047492	4.550347	2.512445
H	-0.047492	-4.550347	-2.512445
H	0.056901	2.698300	-4.480509
H	0.056901	-2.698300	4.480509
H	-0.056901	2.698300	4.480509
H	-0.056901	-2.698300	-4.480509
H	2.062495	0.583022	5.100006
H	2.062495	-0.583022	-5.100006
H	-2.062495	0.583022	-5.100006
H	-2.062495	-0.583022	5.100006
H	2.065370	0.583986	7.573735
H	2.065370	-0.583986	-7.573735
H	-2.065370	0.583986	-7.573735
H	-2.065370	-0.583986	7.573735
H	0.000000	0.000000	8.820277
H	0.000000	0.000000	-8.820277
C	0.008607	2.770962	-1.168983
C	0.008607	-2.770962	1.168983
C	-0.008607	2.770962	1.168983
C	-0.008607	-2.770962	-1.168983
C	0.031164	3.474921	-2.431546
C	0.031164	-3.474921	2.431546
C	-0.031164	3.474921	2.431546
C	-0.031164	-3.474921	-2.431546
C	0.006368	1.238105	-2.776177
C	0.006368	-1.238105	2.776177
C	-0.006368	1.238105	2.776177
C	-0.006368	-1.238105	-2.776177
C	0.034188	2.541351	-3.414364
C	0.034188	-2.541351	3.414364
C	-0.034188	2.541351	3.414364
C	-0.034188	-2.541351	-3.414364
C	0.000000	0.000000	3.432608
C	0.000000	0.000000	-3.432608

C	0.000000	0.000000	4.931331
C	0.000000	0.000000	-4.931331
C	1.158641	0.331140	5.643120
C	1.158641	-0.331140	-5.643120
C	-1.158641	0.331140	-5.643120
C	-1.158641	-0.331140	5.643120
C	1.158686	0.329814	7.036245
C	1.158686	-0.329814	-7.036245
C	-1.158686	0.329814	-7.036245
C	-1.158686	-0.329814	7.036245
C	0.000000	0.000000	7.736180
C	0.000000	0.000000	-7.736180
N	0.000000	3.388532	0.000000
N	0.000000	-3.388532	0.000000
N	0.001777	1.416759	1.414944
N	0.001777	-1.416759	-1.414944
N	-0.001777	1.416759	-1.414944
N	-0.001777	-1.416759	1.414944
Pt	0.000000	0.000000	0.000000

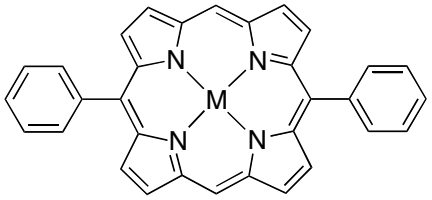
B3LYP/6-311G(d,p) & LANL2TZ(f) Energy = –1602.17823328 a.u.

Zn-DAP (**2Zn-m**): Geometry (in Å)

H	0.074034	4.559853	-2.519530
H	0.074034	-4.559853	2.519530
H	-0.074034	4.559853	2.519530
H	-0.074034	-4.559853	-2.519530
H	0.086722	2.713668	-4.487217
H	0.086722	-2.713668	4.487217
H	-0.086722	2.713668	4.487217
H	-0.086722	-2.713668	-4.487217
H	2.012446	0.737118	5.103429
H	2.012446	-0.737118	-5.103429
H	-2.012446	0.737118	-5.103429
H	-2.012446	-0.737118	5.103429
H	2.014992	0.738916	7.575643
H	2.014992	-0.738916	-7.575643
H	-2.014992	0.738916	-7.575643
H	-2.014992	-0.738916	7.575643
H	0.000000	0.000000	8.823015
H	0.000000	0.000000	-8.823015
C	0.007564	2.771687	-1.175062
C	0.007564	-2.771687	1.175062
C	-0.007564	2.771687	1.175062
C	-0.007564	-2.771687	-1.175062
C	0.045722	3.484444	-2.436021
C	0.045722	-3.484444	2.436021
C	-0.045722	3.484444	2.436021
C	-0.045722	-3.484444	-2.436021
C	0.004133	1.248195	-2.776948
C	0.004133	-1.248195	2.776948
C	-0.004133	1.248195	2.776948
C	-0.004133	-1.248195	-2.776948
C	0.049626	2.550647	-3.422107
C	0.049626	-2.550647	3.422107
C	-0.049626	2.550647	3.422107
C	-0.049626	-2.550647	-3.422107
C	0.000000	0.000000	3.433276
C	0.000000	0.000000	-3.433276
C	0.000000	0.000000	4.930970
C	0.000000	0.000000	-4.930970
C	1.129277	0.418603	5.645506
C	1.129277	-0.418603	-5.645506
C	-1.129277	0.418603	-5.645506
C	-1.129277	-0.418603	5.645506
C	1.129841	0.417082	7.038423
C	1.129841	-0.417082	-7.038423
C	-1.129841	0.417082	-7.038423
C	-1.129841	-0.417082	7.038423
C	0.000000	0.000000	7.738909
C	0.000000	0.000000	-7.738909
N	0.000000	3.393564	0.000000
N	0.000000	-3.393564	0.000000
N	0.015344	1.423682	1.419347
N	0.015344	-1.423682	-1.419347
N	-0.015344	1.423682	-1.419347
N	-0.015344	-1.423682	1.419347
Zn	0.000000	0.000000	0.000000

B3LYP/6-311G(d,p) Energy = –3262.28427530 a.u.

Table S2. Cartesian coordinates and energies of B3LYP/6-311G(d,p) & LANL2TZ(f) geometry optimized structures of M-porphyrin models.



$4H_2$-m (M = H_2)
4Pd-m (M = Pd)
4Pt-m (M = Pt)
4Zn-m (M = Zn)

H_2-Por (**$4H_2$-m**): Geometry (in Å)

H	-1.070971	5.217801	-0.093649
H	1.070971	-5.217801	-0.093649
H	-1.088568	0.226128	-0.029315
H	1.088568	-0.226128	-0.029315
H	1.604154	4.980537	-0.089754
H	-1.604154	-4.980537	-0.089754
H	-2.922381	4.376059	2.010489
H	2.922381	-4.376059	2.010489
H	3.247740	2.999227	-0.018696
H	-3.247740	-2.999227	-0.018696
H	-4.090478	3.372683	-1.989147
H	4.090478	-3.372683	-1.989147
H	-4.580850	6.209599	2.038072
H	4.580850	-6.209599	2.038072
H	-5.098276	1.534631	0.067852
H	5.098276	-1.534631	0.067852
H	5.100032	1.147042	0.047547
H	-5.100032	-1.147042	0.047547
H	-5.753650	5.201703	-1.965967
H	5.753650	-5.201703	-1.965967
H	-6.005398	6.629954	0.048850
H	6.005398	-6.629954	0.048850
C	-0.483824	4.313993	-0.057189
C	0.483824	-4.313993	-0.057189
C	0.863853	4.193771	-0.058375
C	-0.863853	-4.193771	-0.058375
C	-1.014213	2.953388	-0.010913
C	1.014213	-2.953388	-0.010913
C	1.150058	2.765349	-0.022311
C	-1.150058	-2.765349	-0.022311
C	-2.388378	2.634895	-0.003210
C	2.388378	-2.634895	-0.003210
C	2.453051	2.261376	-0.016577
C	-2.453051	-2.261376	-0.016577
C	-2.879546	1.320430	-0.004306
C	2.879546	-1.320430	-0.004306
C	2.883780	0.938149	-0.007635
C	-2.883780	-0.938149	-0.007635
C	-3.391270	3.744537	0.009814
C	3.391270	-3.744537	0.009814
C	-3.540077	4.560259	1.138919
C	3.540077	-4.560259	1.138919
C	-4.203835	3.989392	-1.104736
C	4.203835	-3.989392	-1.104736
C	4.243974	0.489831	0.024941
C	-4.243974	0.878796	0.033261
C	-4.243974	-0.489831	0.024941
C	4.243974	-0.878796	0.033261
C	-4.476202	5.591491	1.153291
C	4.476202	-5.591491	1.153291
C	-5.138262	5.022472	-1.091294
C	5.138262	-5.022472	-1.091294
C	-5.277867	5.826215	0.038081
C	5.277867	-5.826215	0.038081
N	-0.000464	2.041275	0.002516
N	0.000464	-2.041275	0.002516
N	-2.102911	0.187883	-0.024923
N	2.102911	-0.187883	-0.024923

B3LYP/6-311G(d,p) Energy = –1451.99315446 a.u.

Pd-Por (**4Pd-m**): Geometry (in Å)

H	0.000000	4.488721	0.000000
H	0.000000	-4.488721	0.000000
H	0.040197	4.544717	-2.618584
H	0.040197	-4.544717	2.618584
H	-0.040197	4.544717	2.618584
H	-0.040197	-4.544717	-2.618584
H	0.047274	2.666059	-4.544062

H	0.047274	-2.666059	4.544062
H	-0.047274	2.666059	4.544062
H	-0.047274	-2.666059	-4.544062
H	2.089132	0.474655	5.142726
H	2.089132	-0.474655	-5.142726
H	-2.089132	0.474655	-5.142726
H	-2.089132	-0.474655	5.142726
H	2.093011	0.475338	7.617164
H	2.093011	-0.475338	-7.617164
H	-2.093011	0.475338	-7.617164
H	-2.093011	-0.475338	7.617164
H	0.000000	0.000000	8.864245
H	0.000000	0.000000	-8.864245
C	0.000000	3.405160	0.000000
C	0.000000	-3.405160	0.000000
C	0.006733	2.781229	-1.239552
C	0.006733	-2.781229	1.239552
C	-0.006733	2.781229	1.239552
C	-0.006733	-2.781229	-1.239552
C	0.025668	3.470886	-2.504129
C	0.025668	-3.470886	2.504129
C	-0.025668	3.470886	2.504129
C	-0.025668	-3.470886	-2.504129
C	0.004304	1.235612	-2.816942
C	0.004304	-1.235612	2.816942
C	-0.004304	1.235612	2.816942
C	-0.004304	-1.235612	-2.816942
C	0.000000	0.000000	3.474004
C	0.000000	0.000000	-3.474004
C	0.027889	2.522814	-3.475925
C	0.027889	-2.522814	3.475925
C	-0.027889	2.522814	3.475925
C	-0.027889	-2.522814	-3.475925
C	0.000000	0.000000	4.973316
C	0.000000	0.000000	-4.973316
C	1.173854	0.269242	5.686378
C	1.173854	-0.269242	-5.686378
C	-1.173854	0.269242	-5.686378
C	-1.173854	-0.269242	5.686378
C	1.174202	0.268489	7.079700
C	1.174202	-0.268489	-7.079700
C	-1.174202	0.268489	-7.079700
C	-1.174202	-0.268489	7.079700
C	0.000000	0.000000	7.780052
C	0.000000	0.000000	-7.780052
N	0.003416	1.428237	1.457005
N	0.003416	-1.428237	-1.457005
N	-0.003416	1.428237	-1.457005
N	-0.003416	-1.428237	1.457005
Pd	0.000000	0.000000	0.000000

B3LYP/6-311G(d,p) & LANL2TZ(f) Energy = –1577.63732188 a.u.

Pt-Por (**4Pt-m**): Geometry (in Å)

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H	-2.617994	4.541153	0.000000
H	2.617994	-4.541153	0.000000
H	-2.617994	-4.541153	0.000000
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H	-4.540848	2.657997	0.000000
H	4.540848	-2.657997	0.000000
H	-4.540848	-2.657997	0.000000
H	5.136067	0.000000	2.142387
H	-5.136067	0.000000	2.142387
H	5.136067	0.000000	-2.142387
H	-5.136067	0.000000	-2.142387
H	7.611368	0.000000	2.146322
H	-7.611368	0.000000	2.146322
H	7.611368	0.000000	-2.146322
H	-7.611368	0.000000	-2.146322
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C	1.236775	-2.782448	0.000000
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Pt	0.000000	0.000000	0.000000

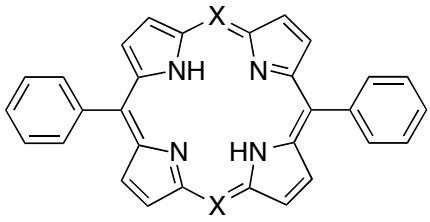
B3LYP/6-311G(d,p) & LANL2TZ(f) Energy = –1570.08770071 a.u.

Zn-Por (**4Zn-m**): Geometry (in Å)

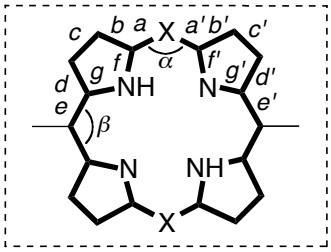
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H	-0.048047	-4.554212	-2.629090
H	0.058251	2.681447	-4.552287
H	0.058251	-2.681447	4.552287
H	-0.058251	2.681447	4.552287
H	-0.058251	-2.681447	-4.552287
H	2.052004	0.615224	5.149383
H	2.052004	-0.615224	-5.149383
H	-2.052004	0.615224	-5.149383
H	-2.052004	-0.615224	5.149383
H	2.055611	0.616973	7.622540
H	2.055611	-0.616973	-7.622540
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H	-2.055611	-0.616973	7.622540
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C	0.000000	3.406723	0.000000
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C	-0.003544	2.785993	1.247862
C	-0.003544	-2.785993	-1.247862
C	0.028197	3.480576	-2.510899
C	0.028197	-3.480576	2.510899
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C	-0.028197	-3.480576	-2.510899
C	0.000532	1.244568	-2.823152
C	0.000532	-1.244568	2.823152
C	-0.000532	1.244568	2.823152
C	-0.000532	-1.244568	-2.823152
C	0.000000	0.000000	3.478196
C	0.000000	0.000000	-3.478196
C	0.031401	2.531852	-3.484966
C	0.031401	-2.531852	3.484966
C	-0.031401	2.531852	3.484966
C	-0.031401	-2.531852	-3.484966
C	0.000000	0.000000	4.976926
C	0.000000	0.000000	-4.976926
C	1.151984	0.349206	5.692188
C	1.151984	-0.349206	-5.692188
C	-1.151984	0.349206	-5.692188
C	-1.151984	-0.349206	5.692188
C	1.152697	0.348392	7.085338
C	1.152697	-0.348392	-7.085338
C	-1.152697	0.348392	-7.085338
C	-1.152697	-0.348392	7.085338
C	0.000000	0.000000	7.786210
C	0.000000	0.000000	-7.786210
N	0.011462	1.433177	1.463498
N	0.011462	-1.433177	-1.463498
N	-0.011462	1.433177	-1.463498
N	-0.011462	-1.433177	1.463498
Zn	0.000000	0.000000	0.000000

B3LYP/6-311G(d,p) Energy = –3230.19714314 a.u.

Table S3. **Bond Lengths, Bond Angles, and HOMA Values of $2H_2$-m and $4H_2$-m**.



$2H_2$-m (X = N)
$4H_2$-m (X = CH)



	$2H_2$-m	**$4H_2$-m**
Bond lengths/distances (Å)		
a, a’	1.332, 1.319	1.397, 1.392
b, *b*’	1.461, 1.439	1.457, 1.433
c, *c*’	1.350, 1.365	1.353, 1.369
d, *d*’	1.467, 1.440	1.461, 1.435
e, *e*’	1.411, 1.402	1.411, 1.403
f,*f*’	1.361, 1.375	1.360, 1.370
g, *g*’	1.363, 1.371	1.364, 1.373
Bond angles (°)		
α	124.7	129.2
β	123.6	123.5
HOMA values		
all	0.612	0.666
18π	0.653	0.725

Average of two 18π circuits.

Table S4. Excitation energies and oscillator strengths of **2M-m** and **4M-m** (**M** = **H_2**, **Zn**) calculated by the TD-DFT method with solvent effects (PCM, CH_2Cl_2).[a]

State	Excitation energy		Oscillator	Excitation			Weight (%)
	(eV)	(nm)	strength				
2H_2-m							
1	2.25	551	0.075	HOMO	–>	LUMO	41.4
				HOMO–1	–>	LUMO	25.2
2	2.39	519	0.074	HOMO	–>	LUMO	32.9
				HOMO–1	–>	LUMO	31.7
				HOMO	–>	LUMO+1	14.1
3	3.06	405	0.511	HOMO–3	–>	LUMO	30.6
				HOMO	–>	LUMO+1	28.4
5	3.23	384	1.312	HOMO–1	–>	LUMO+1	58.3
				HOMO	–>	LUMO	18.3
6	3.32	373	0.418	HOMO–3	–>	LUMO	66.3
				HOMO	–>	LUMO+1	14.5
2Zn-m							
2	2.34	530	0.184	HOMO	–>	LUMO	78.4
				HOMO–1	–>	LUMO+1	21.2
3	2.81	442	0.006	HOMO–2	–>	LUMO	97.7
4	3.18	390	0.515	HOMO–2	–>	LUMO+1	58.1
				HOMO–1	–>	LUMO+1	28.6
5	3.22	385	0.810	HOMO	–>	LUMO+1	49.4
				HOMO–1	–>	LUMO	40.8
6	3.27	379	0.677	HOMO–2	–>	LUMO+1	37.9

				HOMO–1	–>	LUMO+1	26.1
8	3.38	367	0.488	HOMO–4	–>	LUMO	68.9
				HOMO–1	–>	LUMO+1	21.4
4H$_2$-m							
1	2.21	560	0.018	HOMO	–>	LUMO	44.2
				HOMO–1	–>	LUMO+1	22.9
2	2.35	527	0.024	HOMO	–>	LUMO+1	38.6
				HOMO–1	–>	LUMO	28.7
3	3.14	395	1.261	HOMO–1	–>	LUMO+1	48.5
				HOMO	–>	LUMO	23.3
4	3.20	387	1.499	HOMO–1	–>	LUMO	46.1
				HOMO	–>	LUMO+1	34.0
4Zn-m							
2	2.32	534	0.016	HOMO	–>	LUMO	59.6
				HOMO–1	–>	LUMO+1	38.6
3	3.18	390	1.905	HOMO–1	–>	LUMO+1	58.4
				HOMO	–>	LUMO	38.6
4	3.21	387	1.015	HOMO–1	–>	LUMO	55.5
				HOMO	–>	LUMO+1	40.8

[a] The states whose oscillator strengths are less than 0.2 are not included except for Q bands.

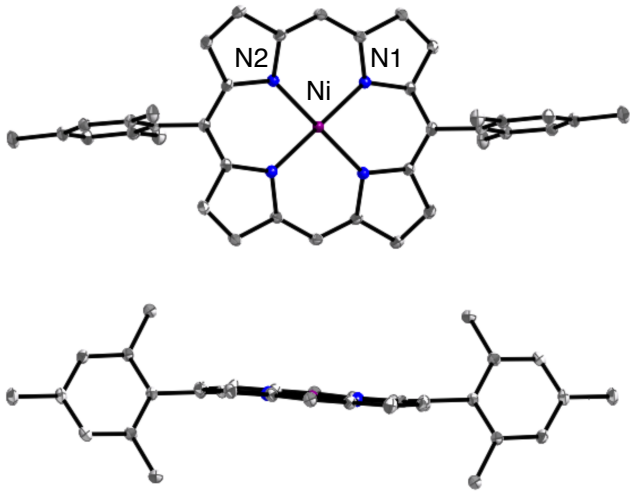


Figure S1. Crystal structure of **4Ni** (30% probability ellipsoids): Top view (top) and side view (bottom). Hydrogen atoms are omitted for clarity. Gray (C), Blue (N), Purple (Ni). Δd_{RMS} (24 atoms) = 0.047 Å.

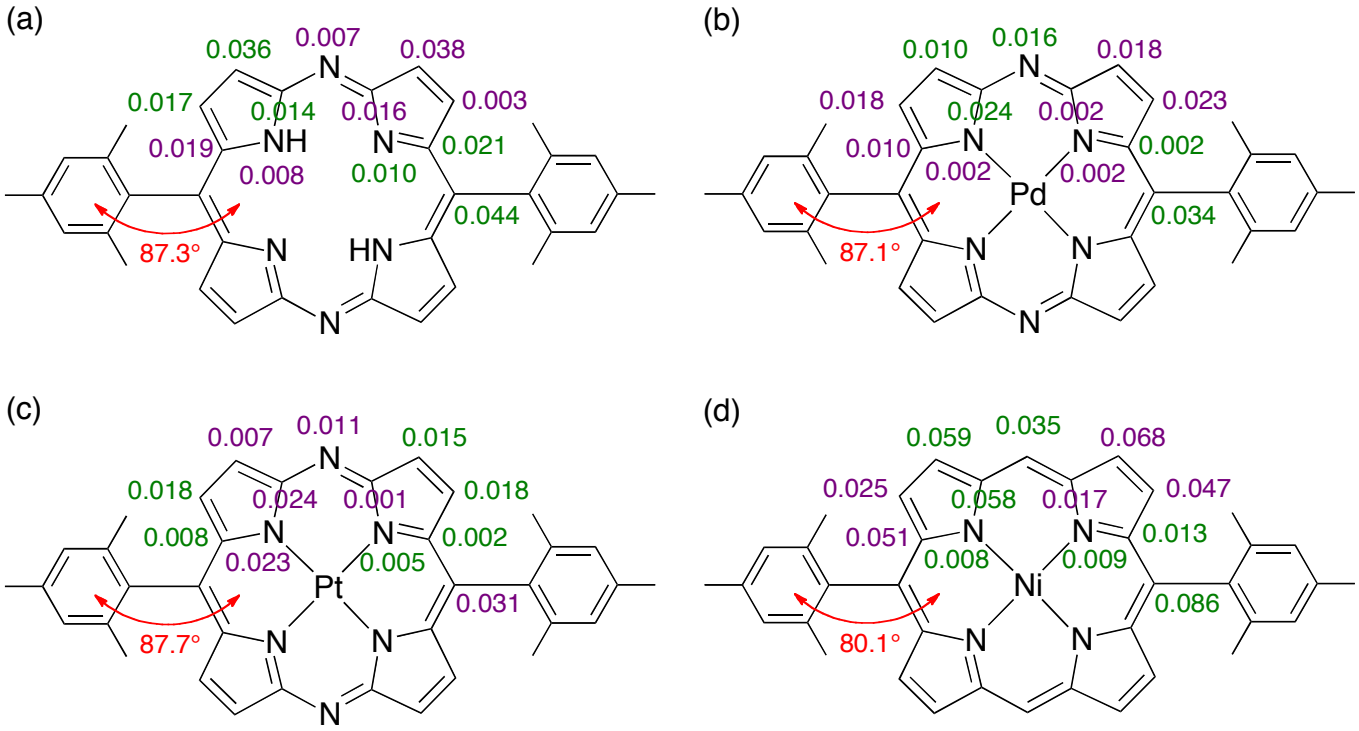


Figure S2. Deviations (green, plus; purple, minus) from the mean 24-atom DAP π-planes and dihedral angles (red) between the peripheral benzene rings and the mean 24-atom DAP π-planes: (a) **2H$_2$**, (b) **2Pd**, (c) **2Pt**, (d) **4Ni**.

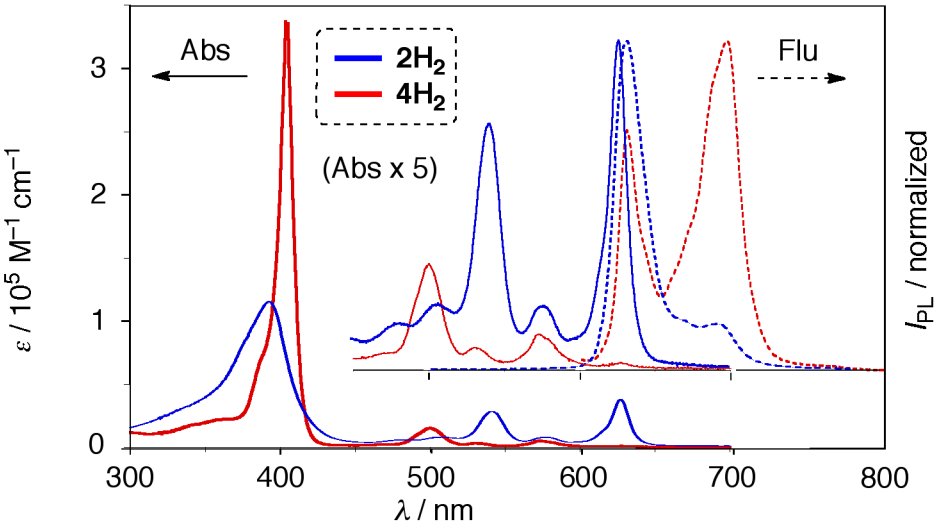


Figure S3. UV-Vis absorption (solid line) and fluorescence (dotted line) spectra of **$2H_2$** (blue) and **$4H_2$** (red) in CH_2Cl_2.

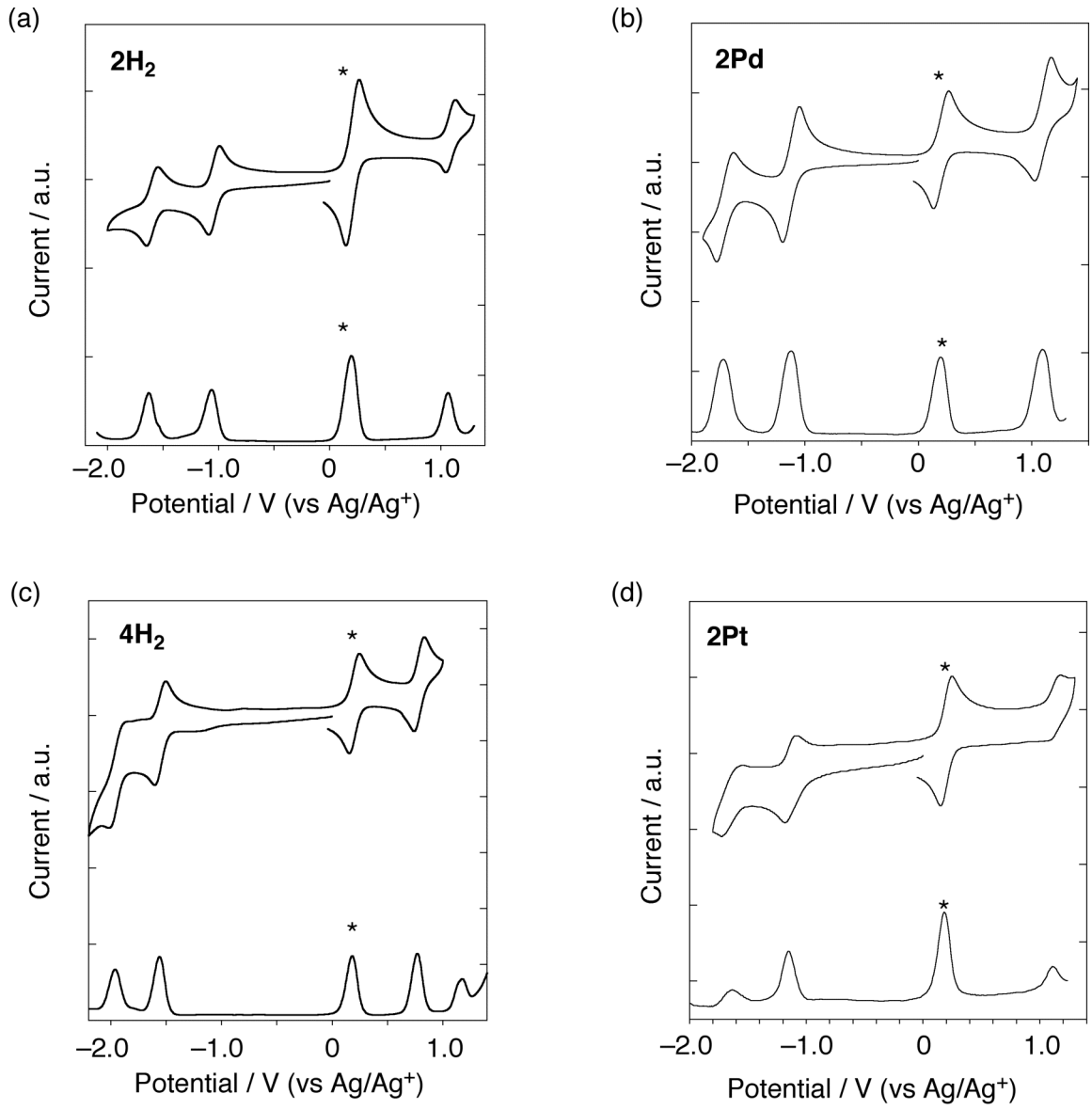


Figure S4. Cyclic voltammograms (upper) and differential pulse voltammograms (lower) of (a) **$2H_2$**, (b) **2Pd**, (c) **$4H_2$**, and (d) **2Pt**. Measured in CH_2Cl_2 with 0.1 M $n$$Bu_4N^+PF_6^-$ as an electrolyte; Ag/Ag^+ [$AgNO_3$ (MeCN)] as a reference electrode; Scan rate 60 mV s^{-1}. Asterisk (*) indicates Fc/Fc^+.

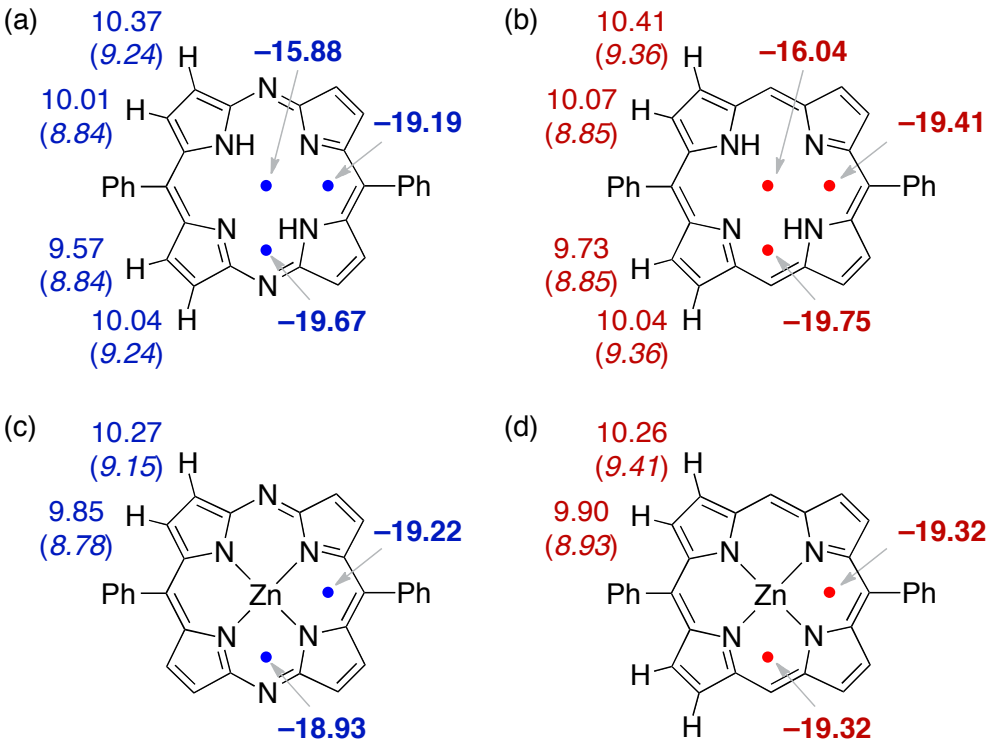
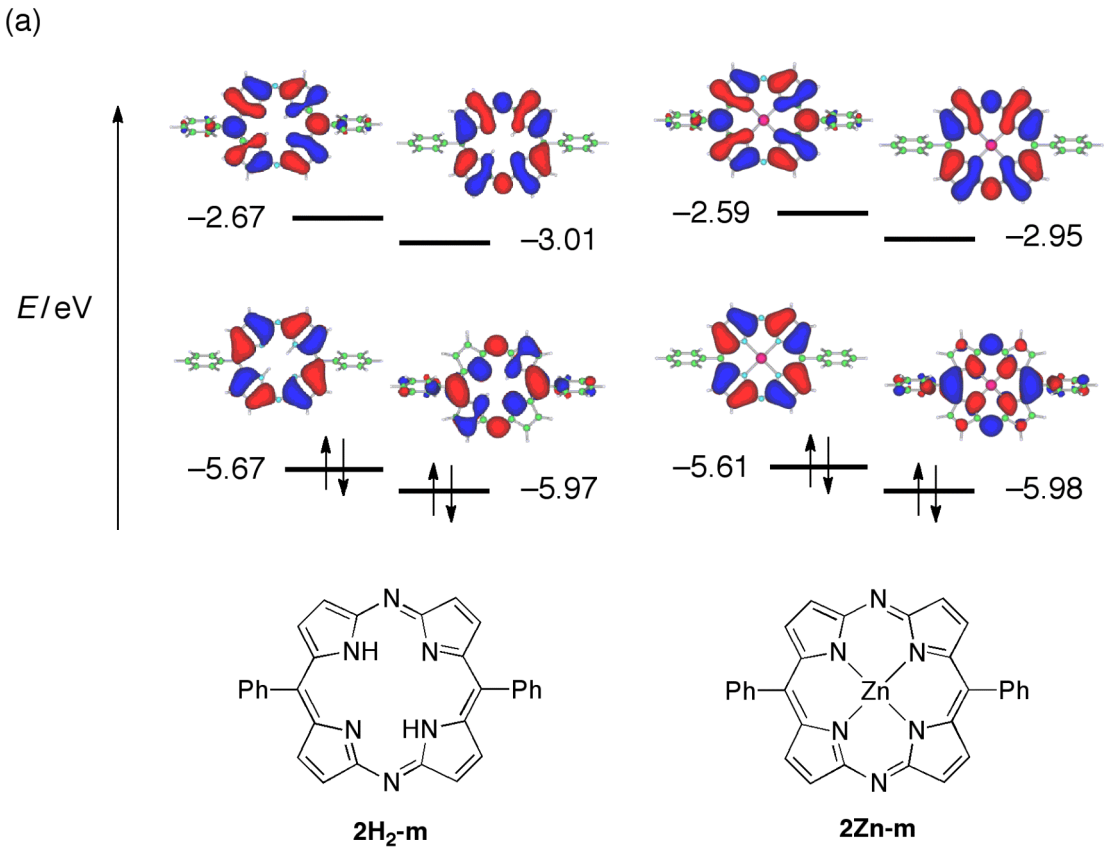


Figure S5. NICS values (bold, in ppm) and chemical shifts at the β protons (plane, in ppm, vs. tetramethylsilane) of (a) **2H$_2$-m**, (b) **4H$_2$-m**, (c) **2Zn-m**, and (d) **4Zn-m** calculated by the RHF/6-31+G(d). The experimentally observed ^{1}H NMR chemical shifts (italic, in ppm vs. tetramethylsilane) of (a) **2H$_2$**, (b) **4H$_2$**, (c) **2Zn**, and (d) **4Zn** are also listed in parentheses.



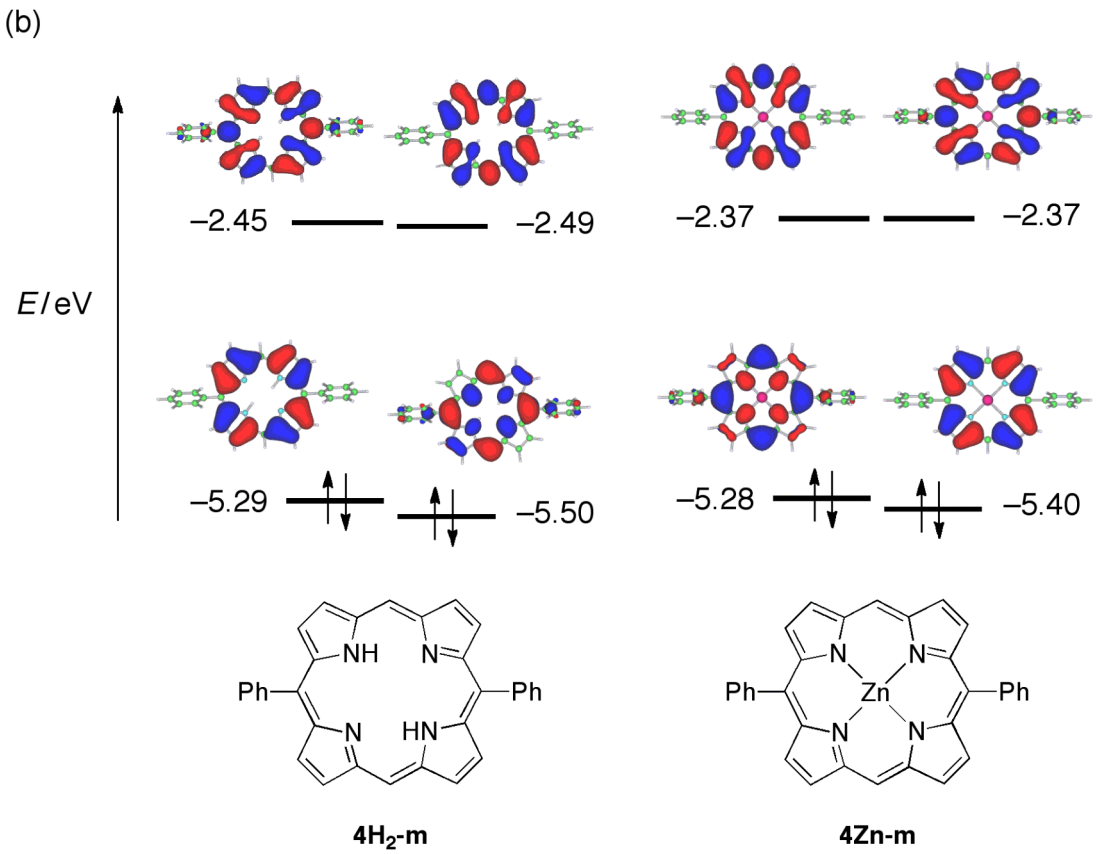
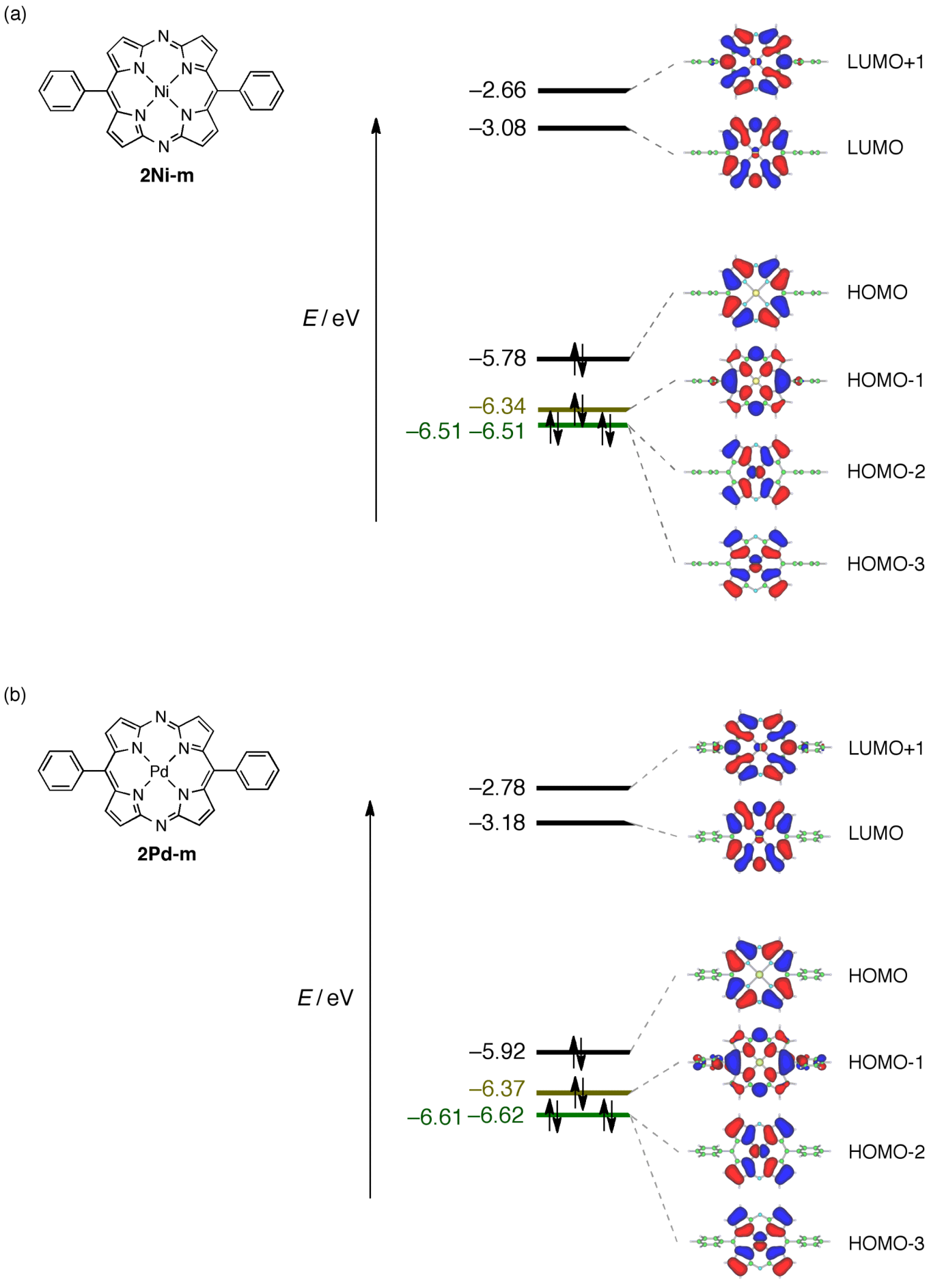


Figure S6. Selected molecular orbitals and their energies (in eV) calculated by the DFT method: (a) **$2H_2$-m** and **2Zn-m** and (b) **$4H_2$-m** and **4Zn-m**.


(a)
2Ni-m
E / eV
–2.66
–3.08
–5.78
–6.34
–6.51
–6.51
LUMO+1
LUMO
HOMO
HOMO-1
HOMO-2
HOMO-3
(b)
2Pd-m
E / eV
–2.78
–3.18
–5.92
–6.37
–6.61
–6.62
LUMO+1
LUMO
HOMO
HOMO-1
HOMO-2
HOMO-3

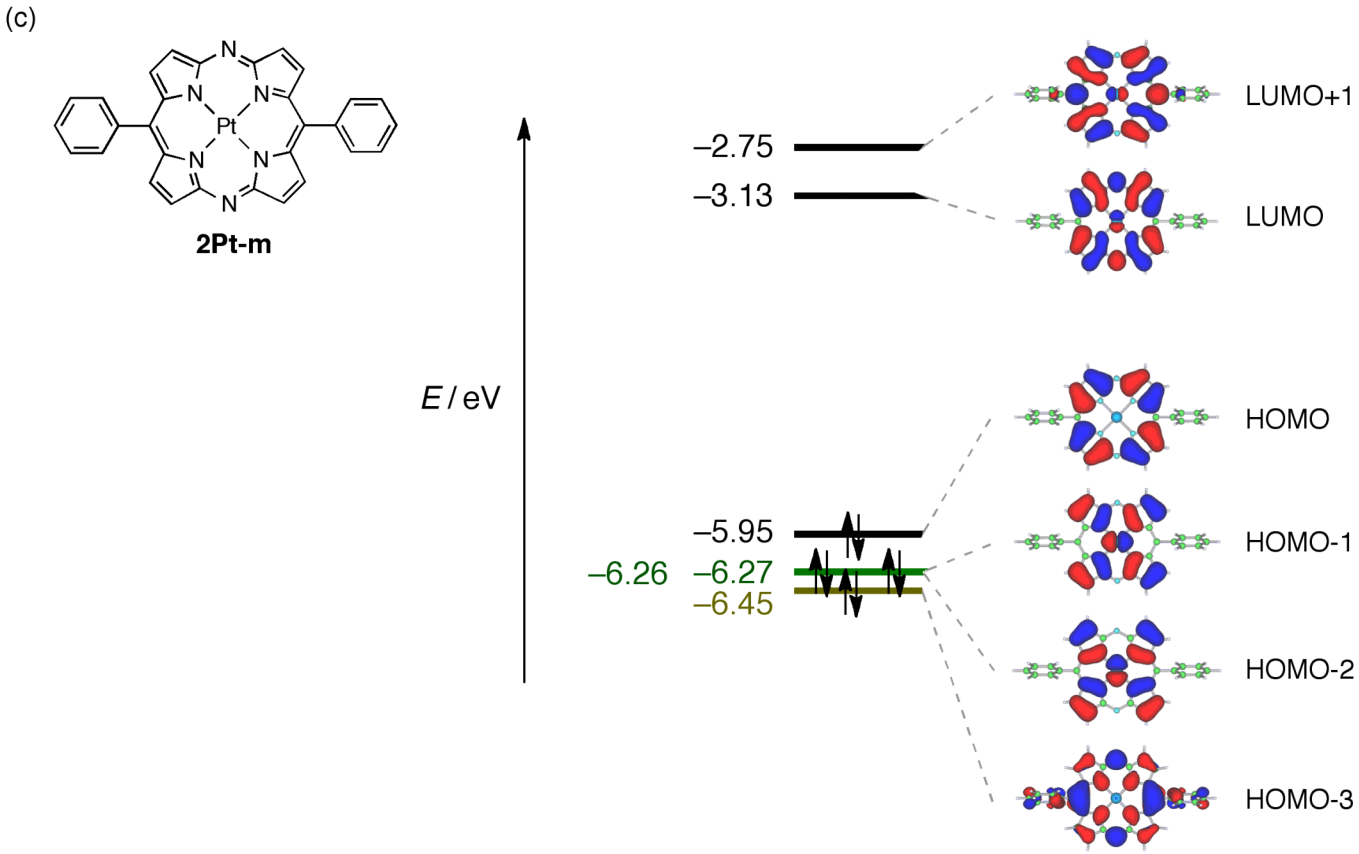
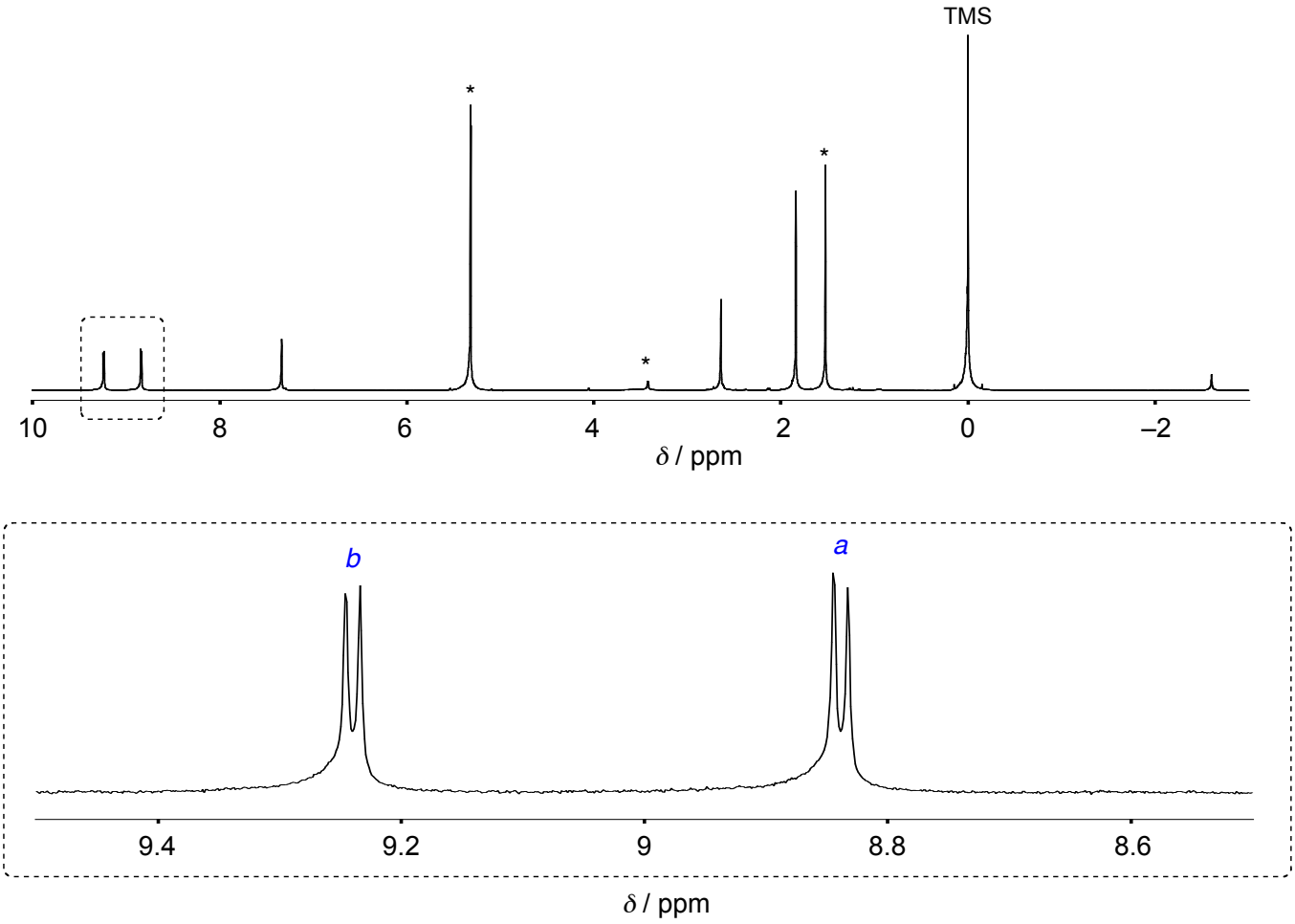
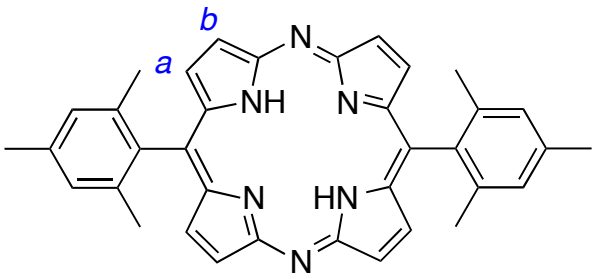


Figure S7. Molecular orbitals (from HOMO–3 to LUMO+1) and their energies (in eV) calculated by the DFT method: (a) **2Ni-m**, (b) **2Pd-m**, and (c) **2Pt-m**.

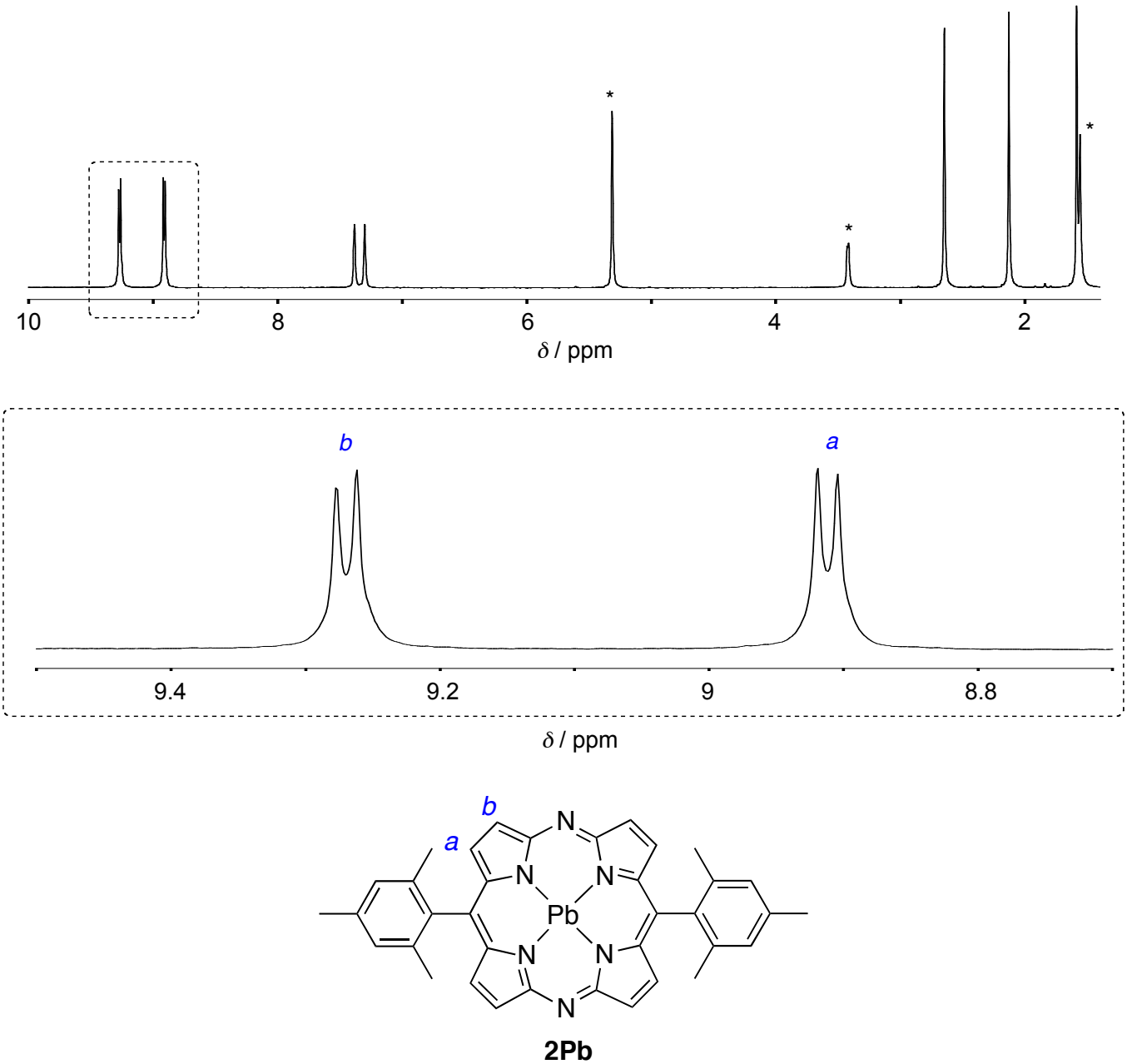
^{1}H NMR Data (Figures S8–S11)





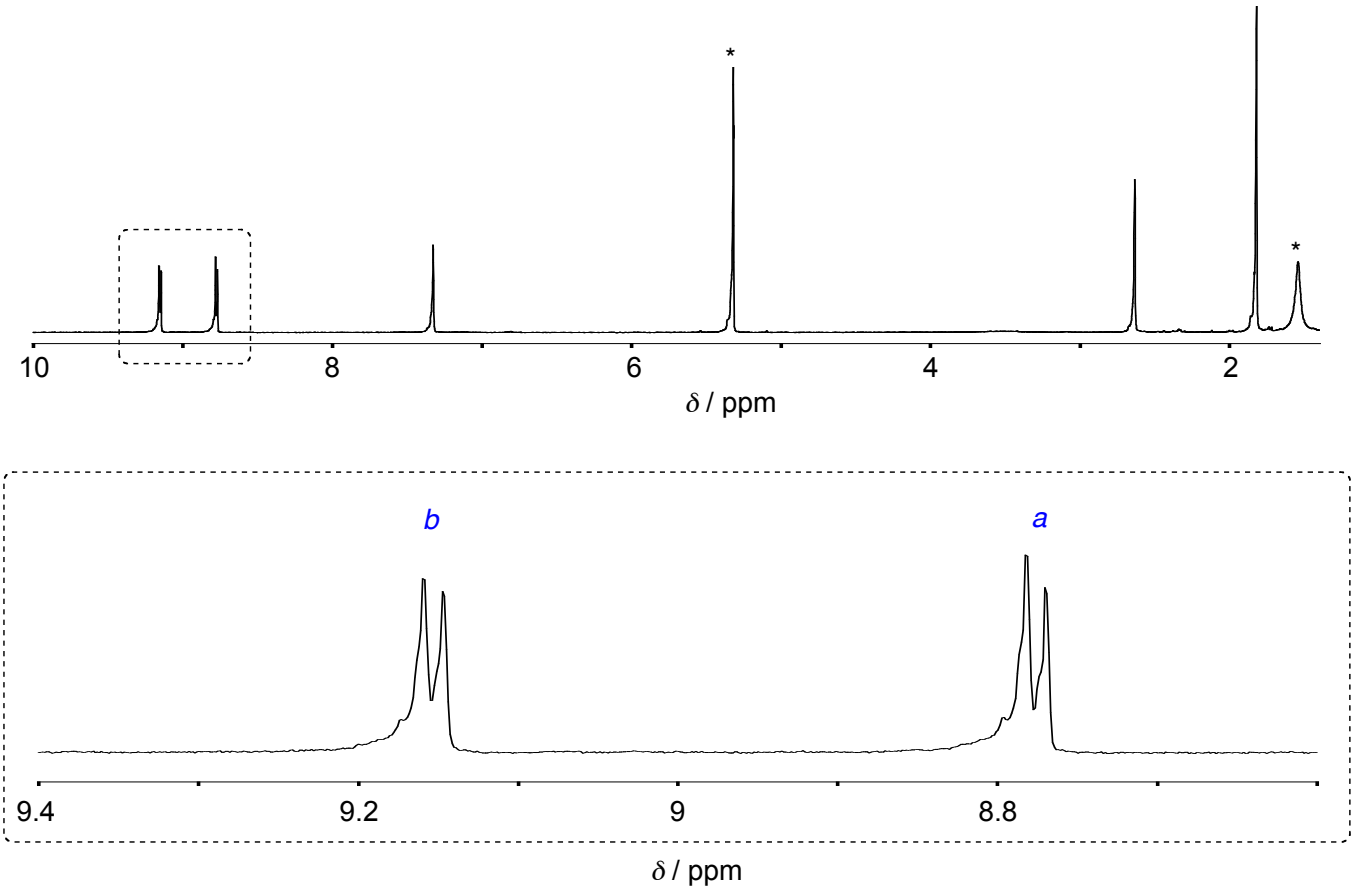
2H$_2$

Figure S8. ^{1}H NMR spectrum of **2H$_2$** in CD_2Cl_2. Asterisks indicate residual solvents and $CDHCl_2$.



2Pb

Figure S9. ^{1}H NMR spectrum of **2Pb** in CD_2Cl_2. Asterisks indicate residual solvents and $CDHCl_2$.



2Pd

Figure S10. ^{1}H NMR spectrum of **2Pd** in CD_2Cl_2. Asterisks indicate residual solvents and $CDHCl_2$.

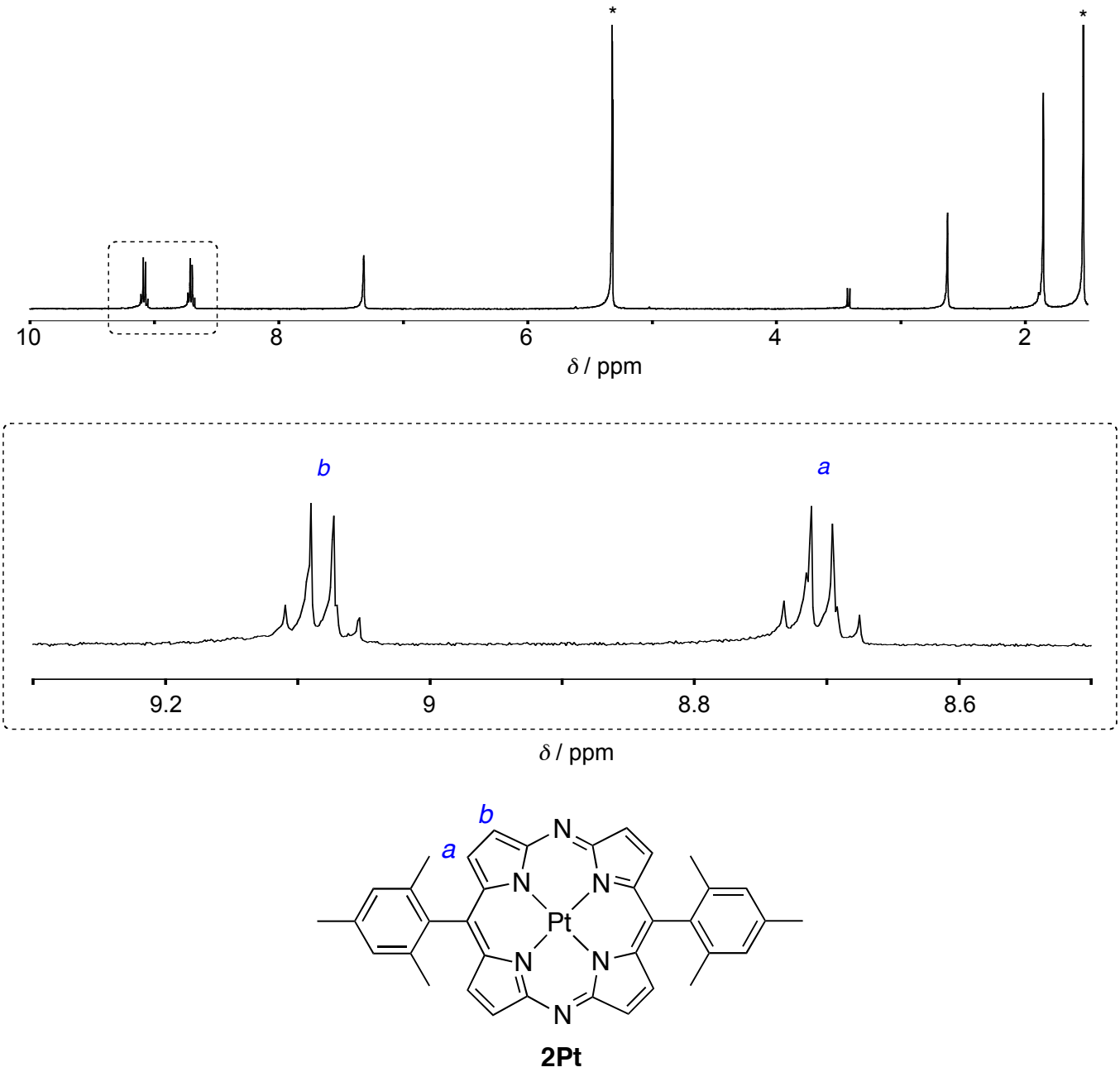


Figure S11. ^{1}H NMR spectrum of **2Pt** in CD_2Cl_2. Asterisks indicate residual solvents and $CDHCl_2$.