Electronic Supplementary Information

Modulation of singlet oxygen and superoxide radical generation by peripherally functionalized porphyrin(2.1.2.1) organopalladium complexes

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1. Supporting Figures, Tables and Scheme

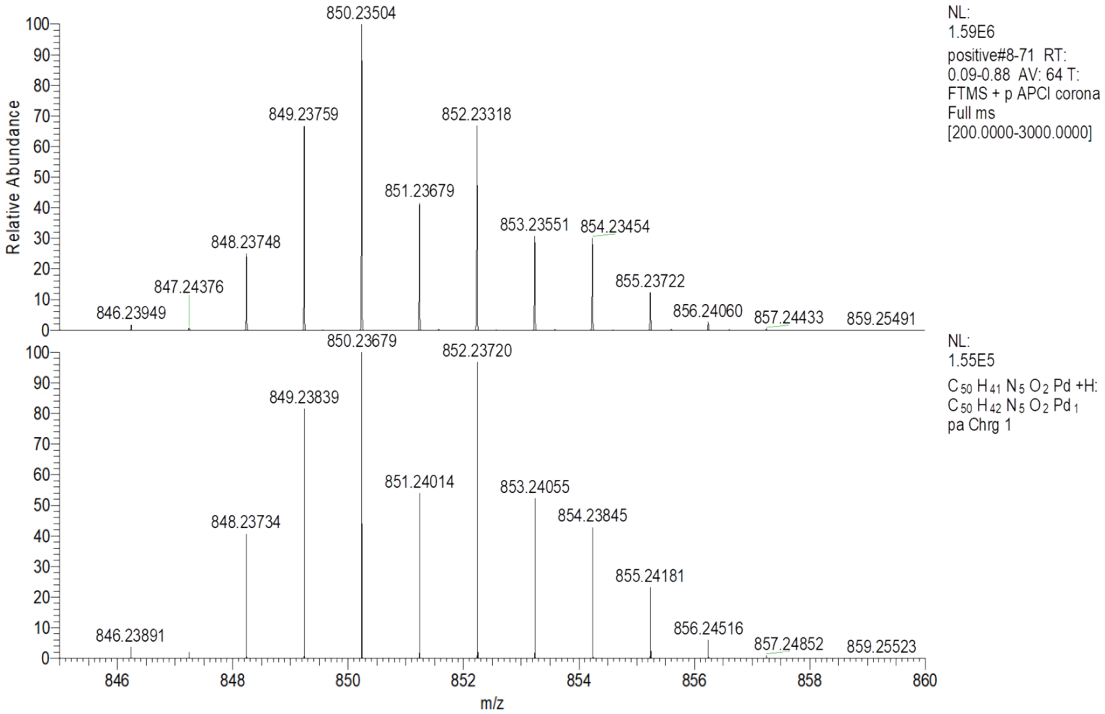


Figure S1. HR-APCI-MS spectrum of **Pd1**.

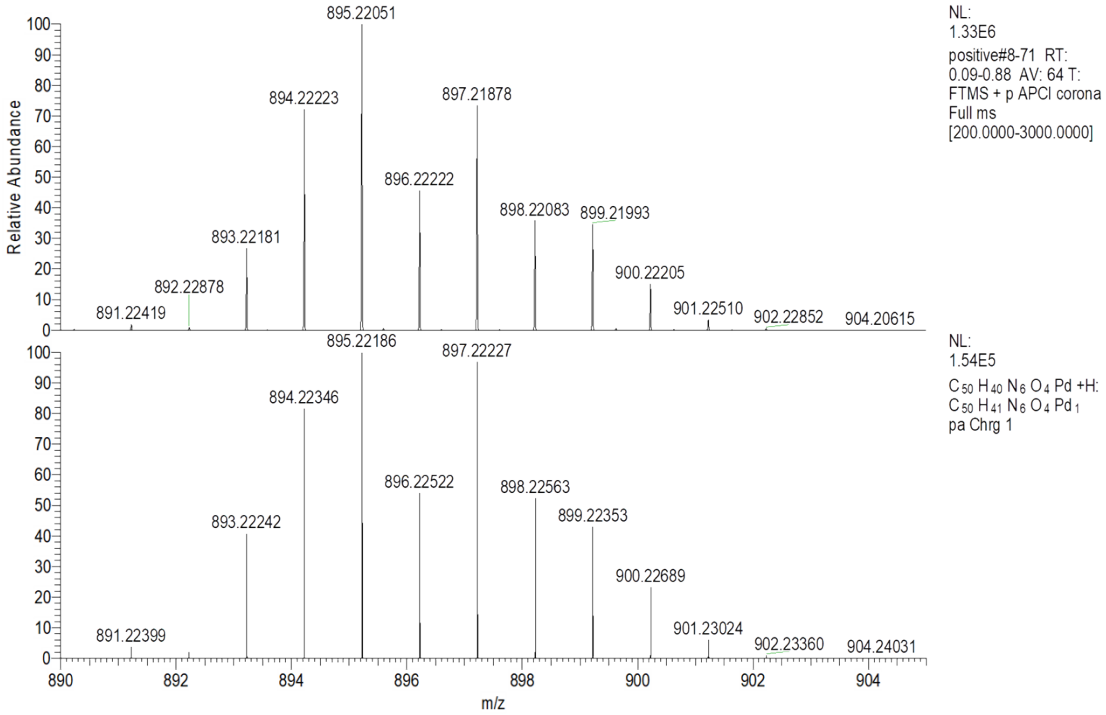


Figure S2. HR-APCI-MS spectrum of **Pd2**.

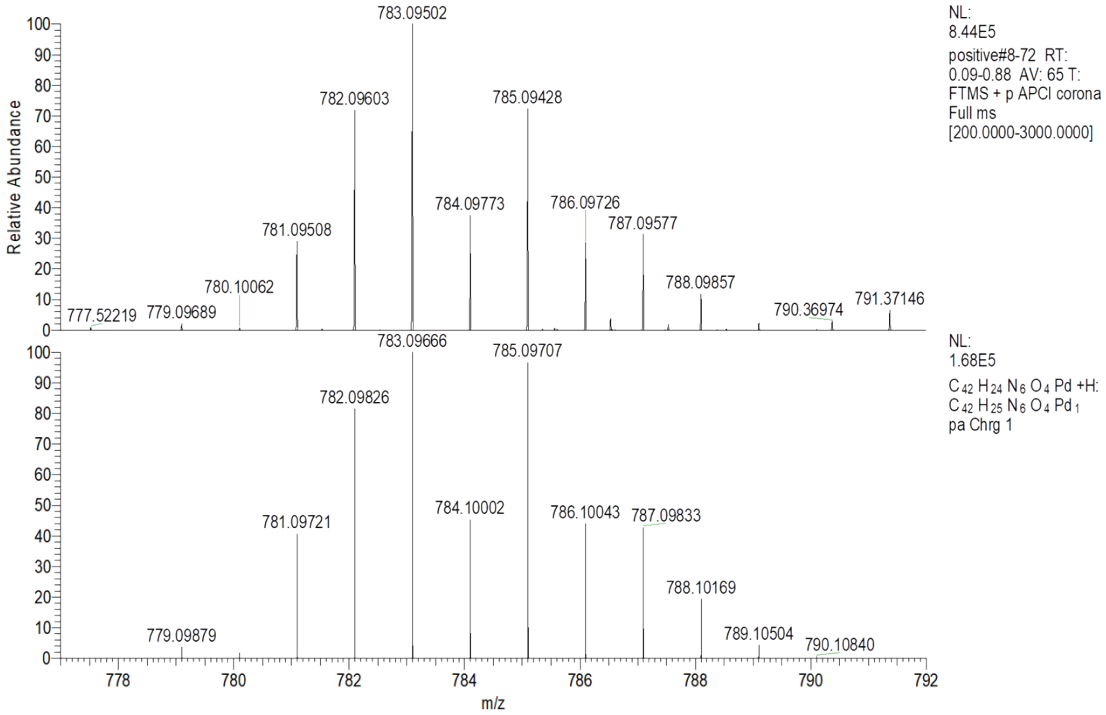


Figure S3. HR-APCI-MS spectrum of **Pd3**.

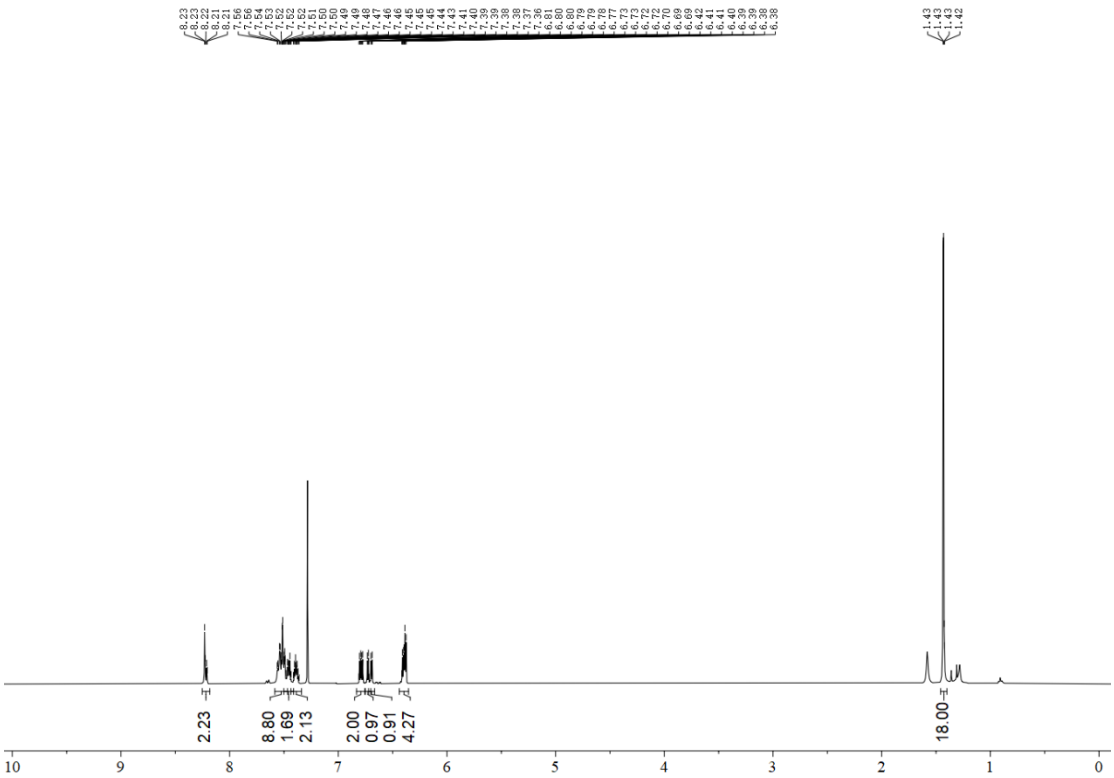


Figure S4. ^{1}H NMR spectrum of **Pd1** recorded at 298 K in $CDCl_3$.

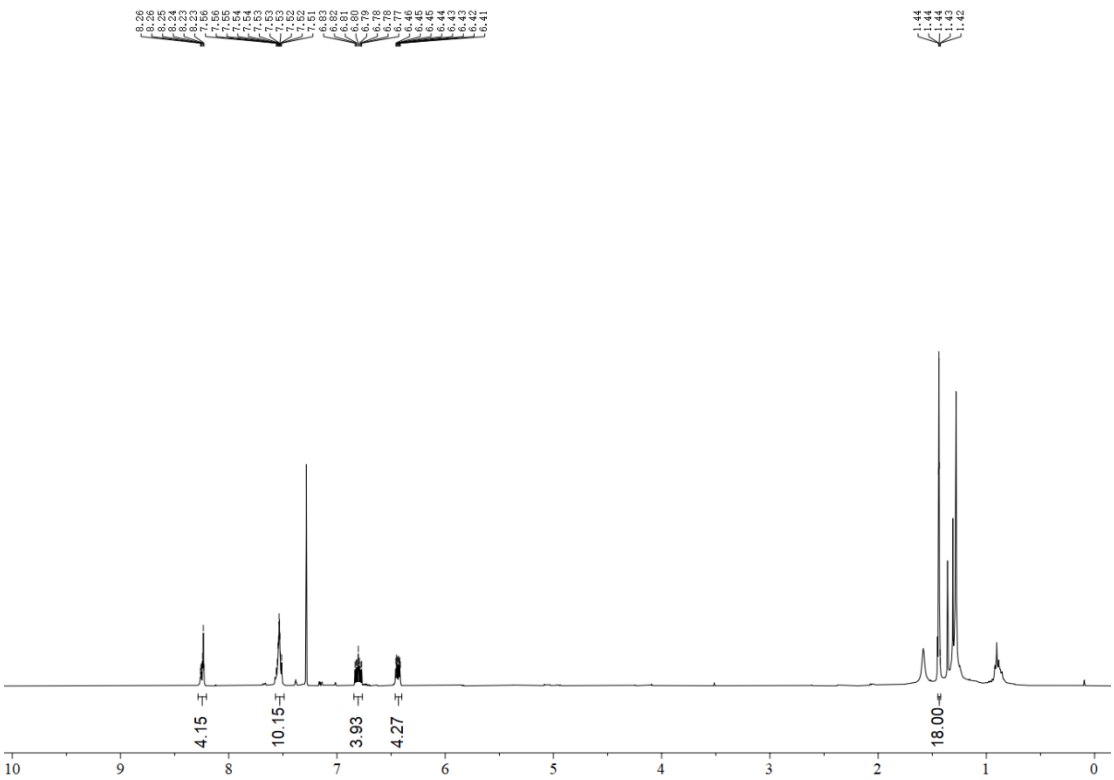


Figure S5. ^{1}H NMR spectrum of **Pd2** recorded at 298 K in $CDCl_3$.

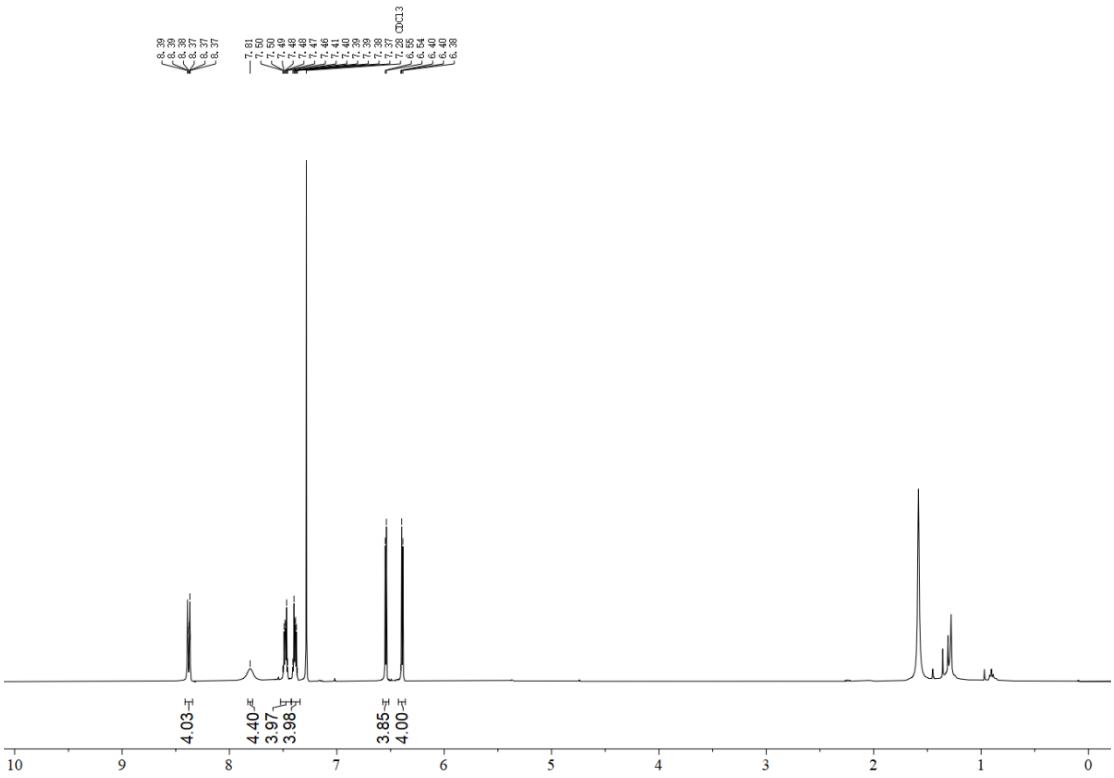


Figure S6. ^{1}H NMR spectrum of **Pd3** recorded at 298 K in $CDCl_3$.

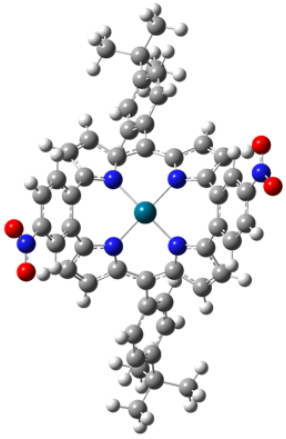
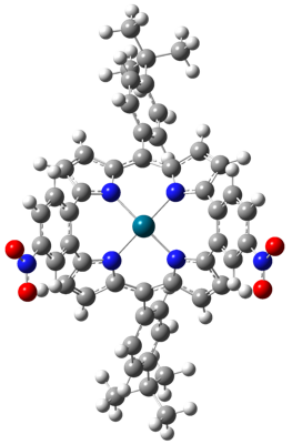
	a) *trans*-Pd2	b) *cis*-Pd2
		
Total energy (hartree)	−2686.876866	− 2686.876339
Relative energy (kcal/mol)	0	+1.38

Figure S7. Optimized structures of two isomers of **Pd2**. Total energy estimation including zero-point energy correction for two isomers of **Pd2**, calculated at the theoretical level of B3LYP/6-31G*-SDD (for Pd).

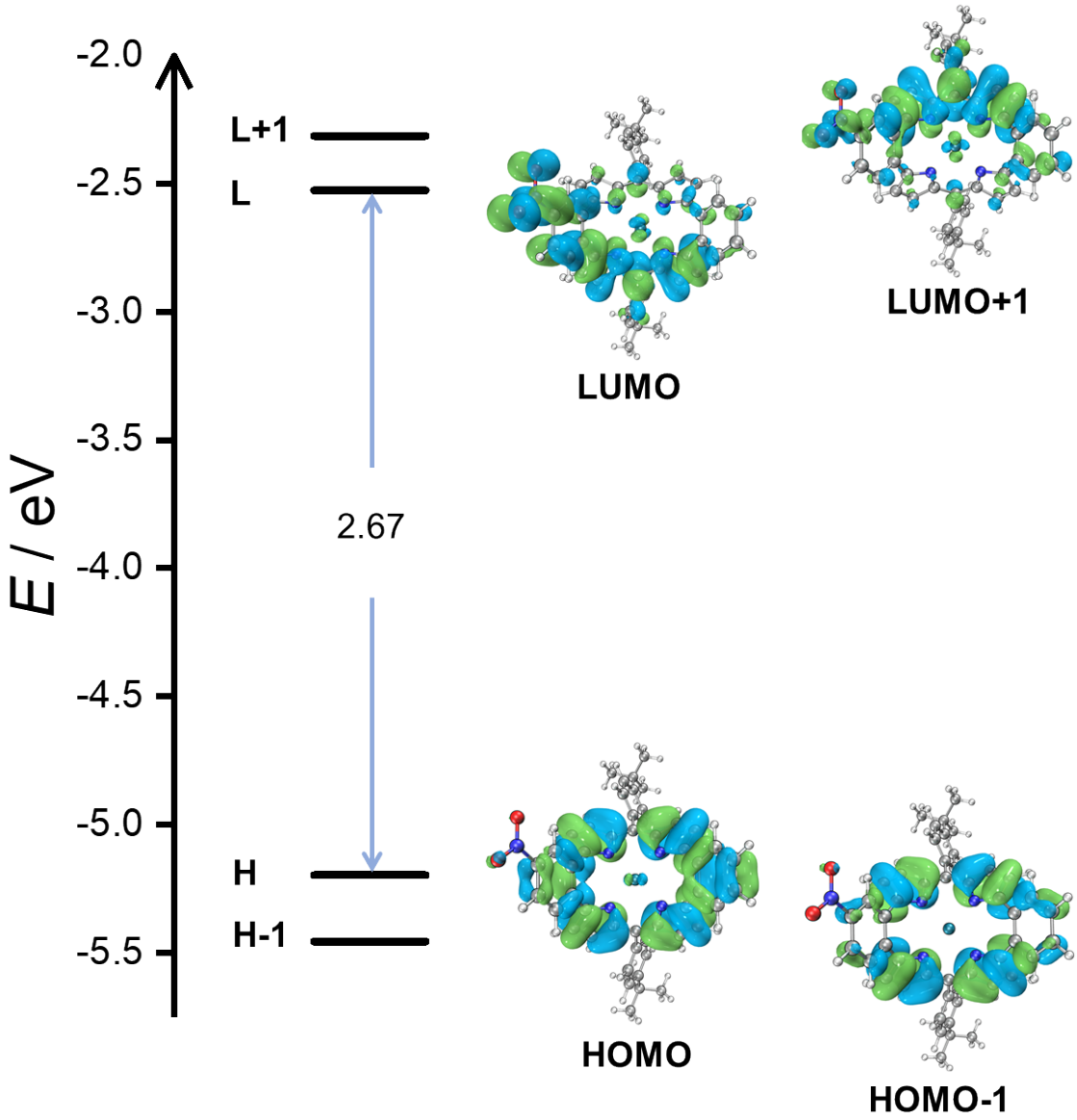


Figure S8. The molecular orbitals (isovalue = 0.02) and HOMO-LUMO gap of **Pd1**, calculated at the theoretical level of B3LYP/6-31G*-SDD (for Pd).

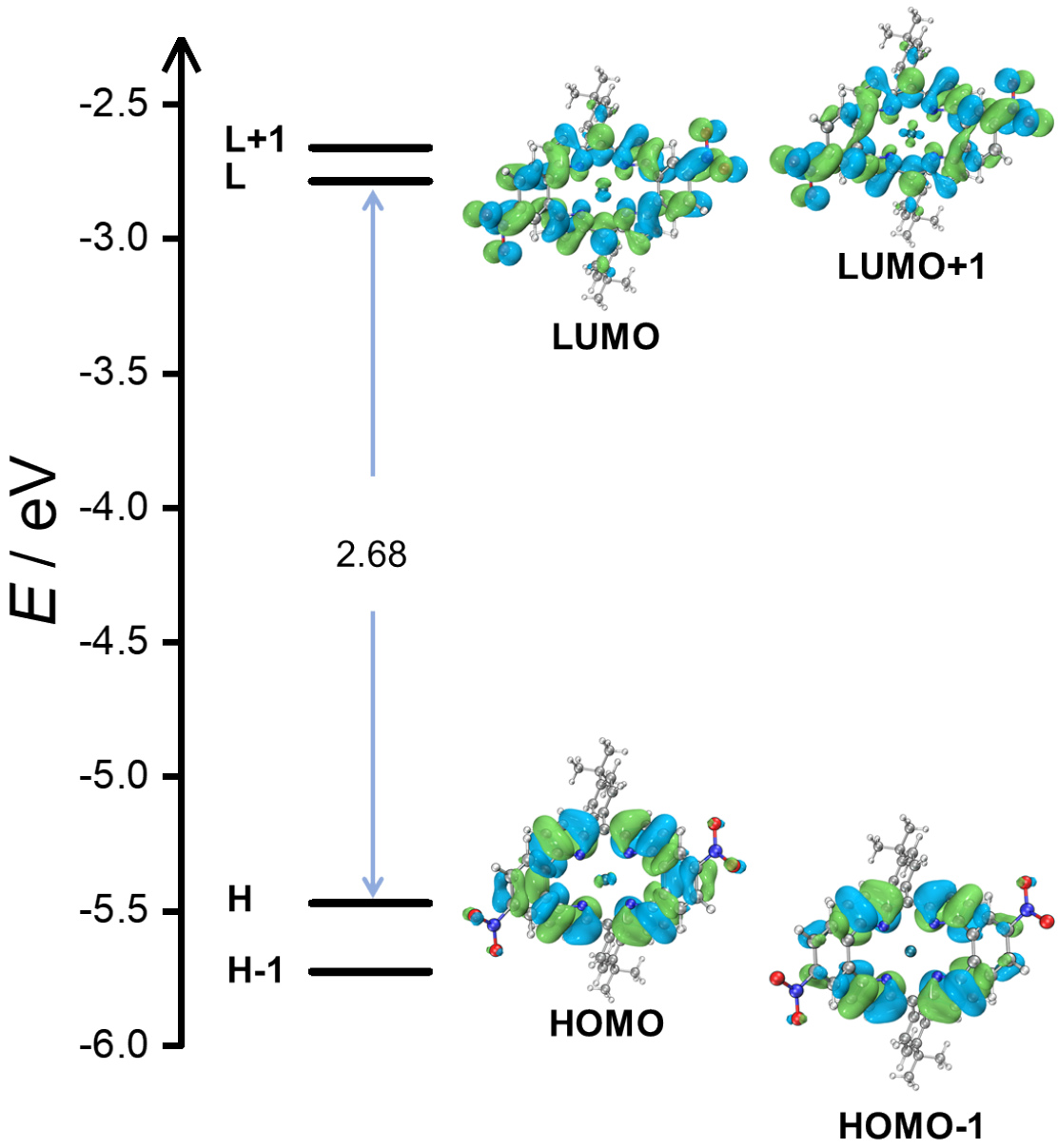


Figure S9. The molecular orbitals (isovalue = 0.02) and HOMO-LUMO gap of **Pd2**, calculated at the theoretical level of B3LYP/6-31G*-SDD (for Pd).

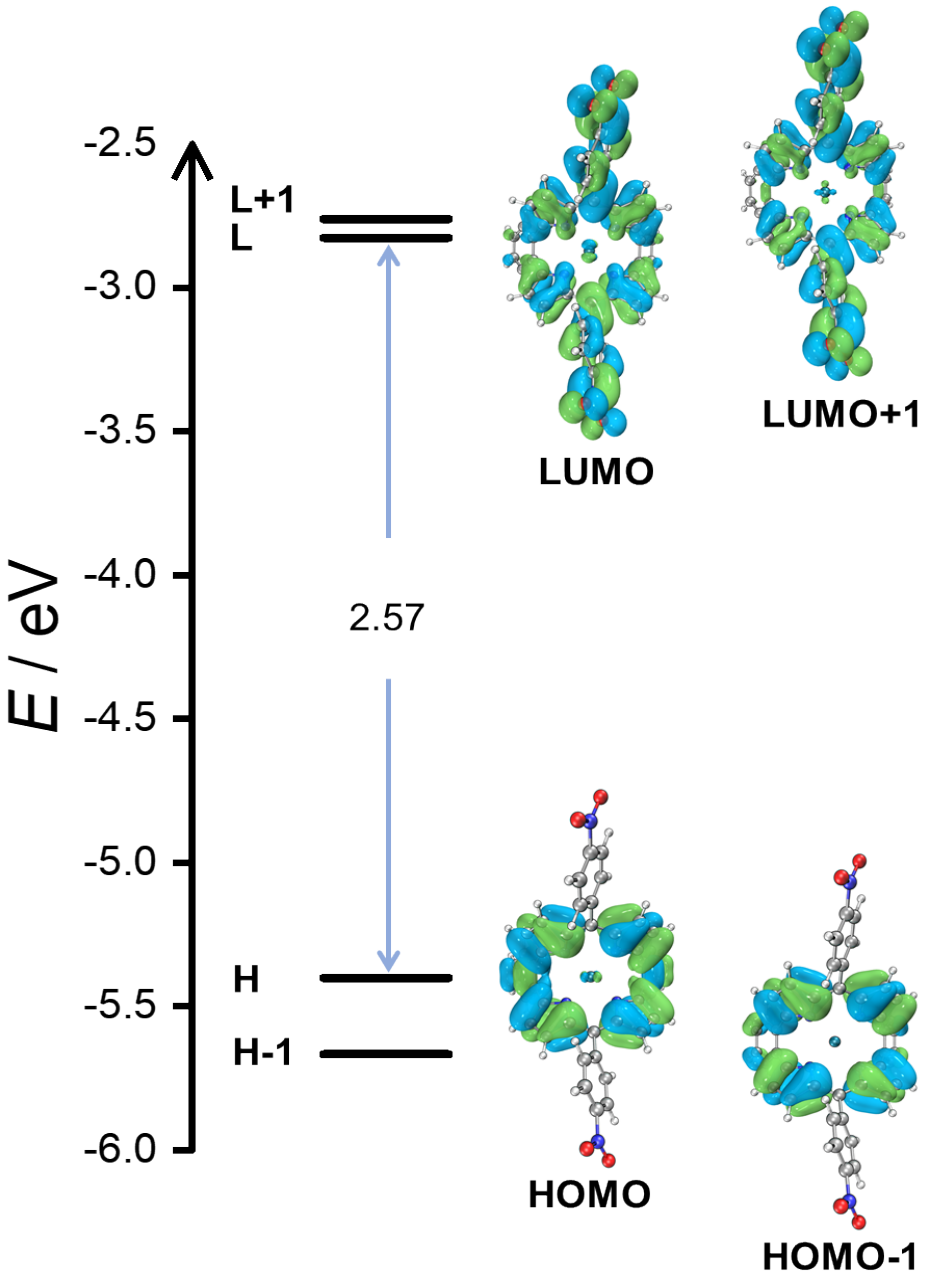


Figure S10. The molecular orbitals (isovalue = 0.02) and HOMO-LUMO gap of **Pd3**, calculated at the theoretical level of B3LYP/6-31G*-SDD (for Pd).

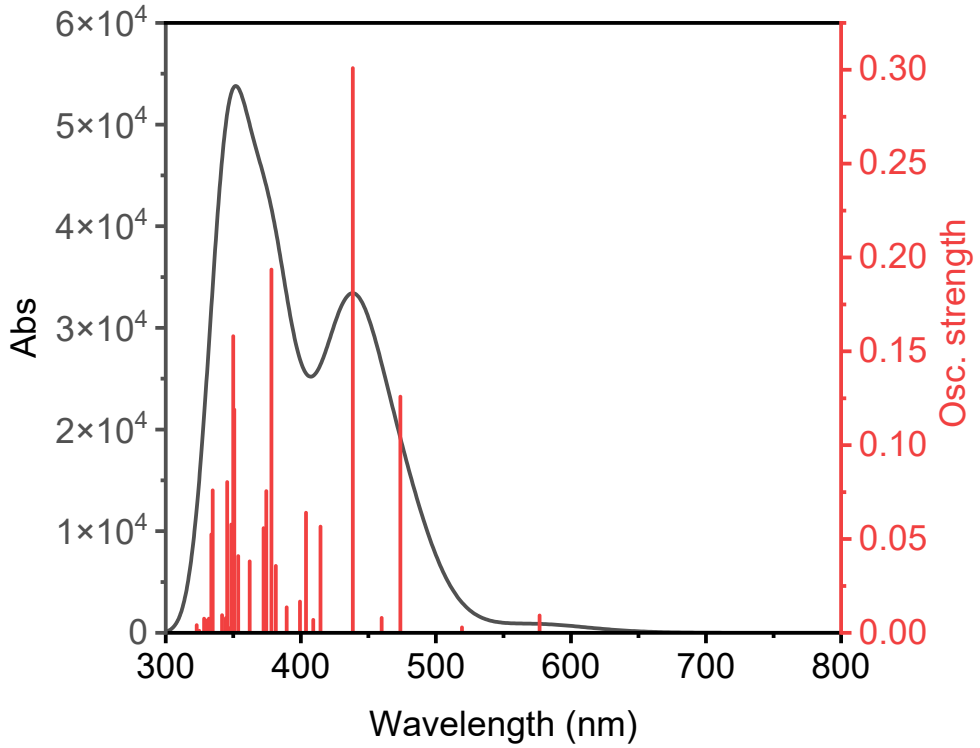


Figure S11. The simulated electronic absorption spectrum of **Pd1** with oscillators, calculated at the theoretical level of B3LYP/6-31G**-SDD (for Pd).

Table S1. TD-DFT (B3LYP/6-31G**-SDD(for Pd)) calculated energies, oscillator strength, and major molecular orbital contribution of **Pd1**.

No.	Energy (cm-1)	Wavelength (nm)	f	Major contribs
1	17336.89	576.8048	0.0093	HOMO->LUMO (96%)
2	19254.87	519.349	0.0029	H-1->LUMO (39%), HOMO->L+1 (56%)
3	21112.37	473.656	0.1259	H-1->LUMO (33%), H-1->L+1 (35%), HOMO->L+1 (13%), HOMO->L+2 (16%)
4	21745.51	459.865	0.008	H-1->L+1 (22%), HOMO->L+2 (69%)
5	22807.75	438.4475	0.3009	H-1->LUMO (16%), H-1->L+1 (31%), H-1->L+2 (20%), HOMO->L+1 (18%)
6	24123.24	414.5381	0.0566	H-3->LUMO (45%), H-1->L+2 (35%)
7	24435.37	409.2428	0.0069	H-3->LUMO (20%), H-2->LUMO (65%)
8	24760.41	403.8705	0.064	H-3->LUMO (16%), H-3->L+1 (16%), H-2->LUMO (26%), H-1->L+2 (22%)
9	25040.29	399.3564	0.0167	H-5->LUMO (12%), H-4->LUMO (62%)
10	25675.05	389.4832	0.0136	H-2->L+1 (87%)
11	26213.02	381.4898	0.0357	H-3->L+1 (11%), HOMO->L+3 (82%)
12	26440.47	378.2081	0.1936	H-4->L+1 (13%), H-3->L+1 (45%), HOMO->L+3 (12%)
13	26702.6	374.4954	0.0755	H-5->L+1 (14%), H-4->L+1 (55%), H-3->L+1 (11%)
14	26853.42	372.392	0.0558	H-8->LUMO (12%), H-5->LUMO (53%), H-4->LUMO (18%)
15	27609.97	362.188	0.0381	H-6->LUMO (84%)
16	28280.22	353.6041	0.0409	H-5->L+1 (21%), H-1->L+3 (62%)
17	28512.51	350.7233	0.1189	H-8->LUMO (23%), H-5->L+1 (25%), H-2->L+2 (18%), H-1->L+3 (11%)
18	28577.84	349.9215	0.1581	H-8->LUMO (36%), H-5->LUMO (10%), H-1->L+3 (18%)
19	28696.4	348.4758	0.0577	H-2->L+2 (56%)
20	28731.08	348.0551	0.0027	H-5->L+3 (12%), H-4->L+3 (39%)
21	28940.79	345.5331	0.0804	H-7->LUMO (57%)
22	29031.12	344.4579	0.0079	H-6->L+1 (20%), H-3->L+2 (40%)
23	29266.63	341.686	0.0094	H-6->L+1 (59%), H-3->L+2 (22%)
24	29868.32	334.8029	0.0759	H-8->L+1 (23%), H-7->L+1 (39%)
25	29962.69	333.7484	0.0524	H-2->L+3 (64%)
26	30128.03	331.9168	0.0076	H-15->LUMO (15%), H-15->L+2 (15%), H-3->L+3 (39%)
27	30236.92	330.7215	0.0067	H-15->LUMO (28%), H-15->L+2 (29%), H-3->L+3 (20%)
28	30446.62	328.4436	0.0076	H-4->L+2 (72%)
29	30782.96	324.8551	0.0011	H-8->L+3 (18%), H-5->L+2 (20%), H-5->L+3 (11%), H-4->L+3 (24%)
30	30963.62	322.9596	0.0041	H-8->L+1 (48%), H-7->L+1 (31%)

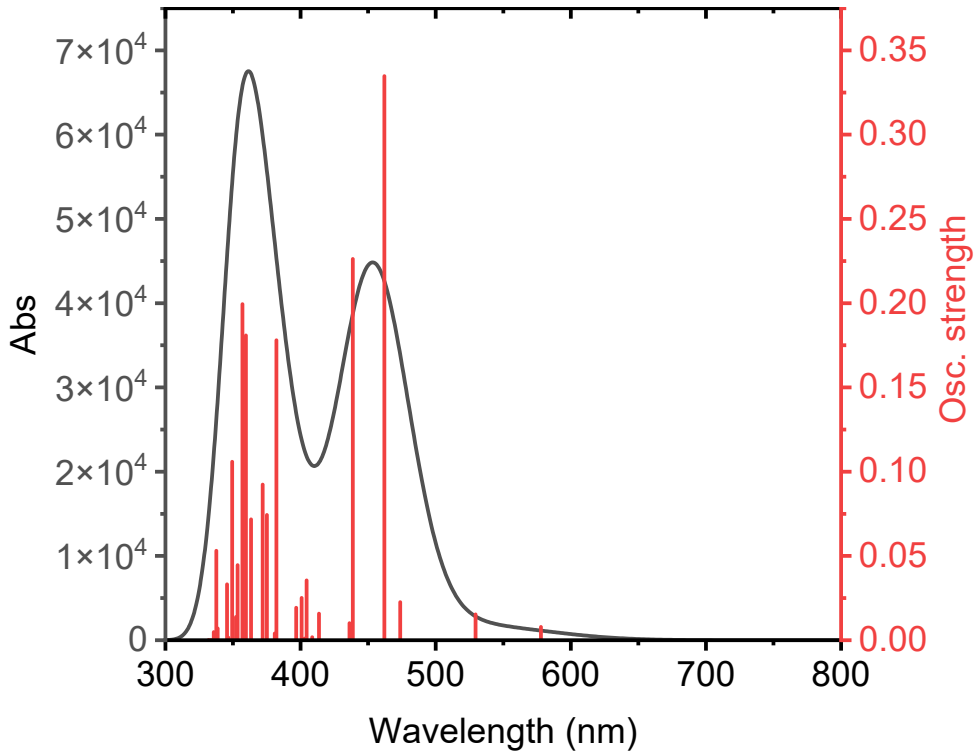


Figure S12. The simulated electronic absorption spectrum of **Pd2** with oscillators, calculated at the theoretical level of B3LYP/6-31G**-SDD (for Pd).

Table S2. TD-DFT (B3LYP/6-31G**-SDD(for Pd)) calculated energies, oscillator strength, and major molecular orbital contribution of **Pd2**.

No.	Energy (cm-1)	Wavelength (nm)	*f*	Major contribs
1	17303.82	577.9071	0.0079	HOMO->LUMO (99%)
2	18885.47	529.5076	0.0153	H-1->LUMO (35%), HOMO->L+1 (64%)
3	21106.72	473.7827	0.0226	H-1->L+1 (97%)
4	21645.5	461.9898	0.3347	H-1->LUMO (37%), HOMO->L+1 (24%), HOMO->L+2 (35%)
5	22794.03	438.7113	0.2262	H-1->LUMO (19%), H-1->L+3 (10%), HOMO->L+2 (54%)
6	22923.89	436.2261	0.0101	H-1->L+2 (12%), HOMO->L+3 (85%)
7	24173.24	413.6805	0.0158	H-3->LUMO (70%), H-1->L+2 (22%)
8	24475.7	408.5685	0.0018	H-2->LUMO (96%)
9	24722.51	404.4897	0.0355	H-3->LUMO (24%), H-1->L+2 (62%), HOMO->L+3 (11%)
10	24817.68	402.9386	0.001	H-5->LUMO (29%), H-3->L+1 (14%), H-2->L+1 (14%), H-1->L+3 (29%)
11	24953.99	400.7376	0.0251	H-5->LUMO (25%), H-4->LUMO (11%), H-3->L+1 (19%), H-1->L+3 (30%)
12	25203.21	396.7748	0.0193	H-2->L+1 (73%)
13	26170.27	382.113	0.178	H-3->L+1 (43%), H-1->L+3 (19%), HOMO->L+4 (25%)
14	26257.38	380.8453	0.004	H-5->L+1 (55%), H-4->L+1 (26%)
15	26657.43	375.1299	0.0743	H-8->LUMO (12%), H-5->LUMO (31%), H-4->LUMO (42%)
16	26888.91	371.9005	0.0924	H-3->L+1 (11%), HOMO->L+4 (59%)
17	27519.64	363.3769	0.0717	H-7->LUMO (87%)
18	27809.19	359.5934	0.1809	H-6->LUMO (27%), H-5->L+1 (22%), H-4->L+1 (40%)
19	28011.64	356.9945	0.1994	H-8->LUMO (63%), H-6->L+1 (17%), H-4->LUMO (14%)
20	28294.74	353.4226	0.0446	H-8->L+1 (19%), H-6->LUMO (53%), H-5->L+1 (12%)
21	28398.78	352.1278	0.0138	H-7->L+1 (49%), H-5->L+4 (12%)
22	28620.58	349.3989	0.1059	H-2->L+2 (56%), H-2->L+4 (18%)
23	28652.04	349.0153	0.0002	H-7->L+1 (37%), H-5->L+4 (19%), H-4->L+4 (11%)
24	28852.87	346.586	0.0015	H-1->L+4 (86%)
25	28935.95	345.5909	0.0332	H-3->L+2 (53%), H-3->L+4 (23%)
26	29525.54	338.6898	0.007	H-8->LUMO (11%), H-6->L+1 (75%)
27	29611.84	337.7028	0.0531	H-8->L+1 (53%), H-6->LUMO (10%), H-4->L+1 (19%)
28	29785.25	335.7367	0.0048	H-2->L+3 (80%)
29	29991.73	333.4253	0	H-15->L+2 (10%), H-3->L+3 (33%)
30	30122.39	331.979	0.0002	H-16->L+1 (16%), H-16->L+2 (19%), H-15->LUMO (21%), H-15->L+3 (27%)

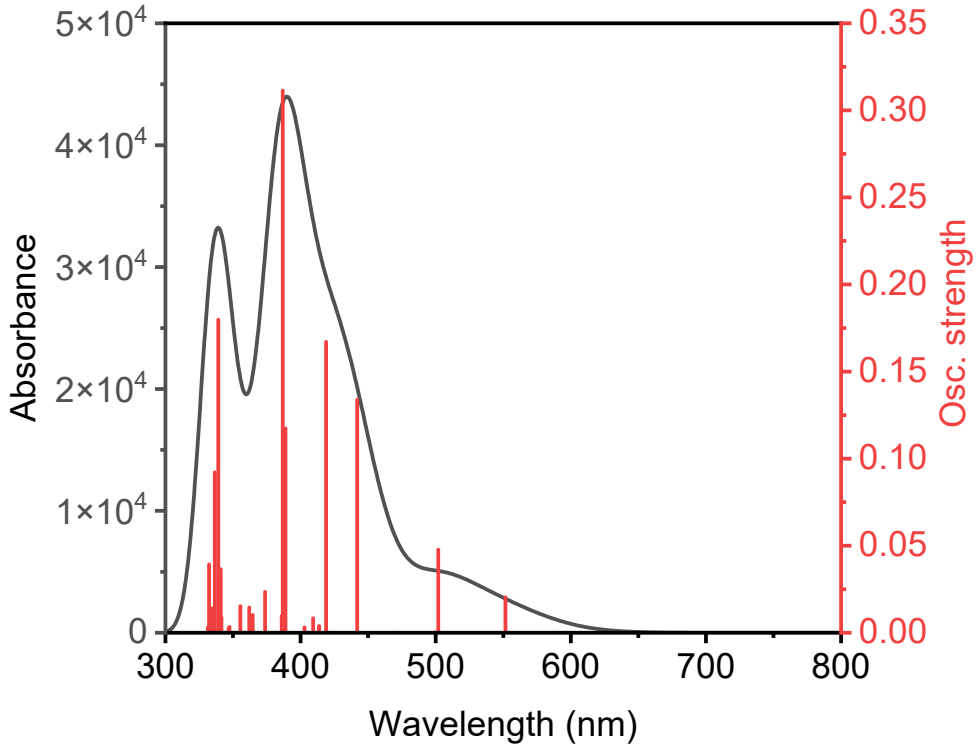


Figure S13. The simulated electronic absorption spectrum of **Pd3** with oscillators, calculated at the theoretical level of B3LYP/6-31G**-SDD (for Pd).

Table S3. TD-DFT (B3LYP/6-31G**-SDD(for Pd)) calculated energies, oscillator strength, and major molecular orbital contribution of **Pd3**.

No.	Energy (cm-1)	Wavelength (nm)	*f*	Major contribs
1	16986.04	588.7189	0	HOMO->LUMO (96%)
2	18129.73	551.5802	0.0204	H-1->LUMO (17%), HOMO->L+1 (79%)
3	19922.7	501.94	0.0477	H-1->LUMO (54%), HOMO->L+1 (13%), HOMO->L+3 (31%)
4	20020.29	499.4932	0.0003	H-1->L+1 (74%), HOMO->L+2 (24%)
5	21174.47	472.2668	0	H-1->L+1 (24%), HOMO->L+2 (70%)
6	22629.5	441.9011	0.1338	H-1->LUMO (19%), H-1->L+2 (20%), HOMO->L+3 (55%)
7	23630.43	423.1831	0.0001	H-3->LUMO (14%), H-1->L+3 (78%)
8	23875.62	418.8372	0.1671	H-3->L+1 (28%), H-1->L+2 (52%)
9	24170.02	413.7358	0.0039	H-3->LUMO (32%), H-2->LUMO (49%)
10	24170.82	413.7219	0.0034	H-3->LUMO (37%), H-2->LUMO (42%)
11	24436.18	409.2293	0.0083	H-4->LUMO (30%), H-2->L+1 (54%)
12	24822.52	402.86	0.0031	H-5->LUMO (12%), H-4->LUMO (45%), H-2->L+1 (31%)
13	25721.02	388.7871	0.1174	H-4->L+1 (52%), H-3->L+1 (18%)
14	25848.46	386.8703	0.3114	H-4->L+1 (24%), H-3->L+1 (36%), H-1->L+2 (13%)
15	25906.53	386.0031	0.0096	HOMO->L+4 (97%)
16	26759.06	373.7053	0.0235	H-5->LUMO (71%), H-4->LUMO (13%)
17	27428.5	364.5843	0.0102	H-6->LUMO (91%)
18	27627.72	361.9554	0.0145	H-5->L+1 (68%), H-4->L+1 (10%)
19	28056	356.4301	0.0003	H-6->L+1 (90%)
20	28136.65	355.4083	0.0153	H-1->L+4 (89%)
21	28539.93	350.3863	0	H-5->L+4 (19%), H-4->L+4 (51%), H-3->L+2 (15%)
22	28785.12	347.4017	0.0034	H-2->L+3 (83%)
23	28847.23	346.6538	0.0025	H-2->L+2 (86%)
24	29287.6	341.4414	0.0086	H-4->L+4 (11%), H-3->L+2 (64%)
25	29336	340.8781	0.0365	H-3->L+3 (86%)
26	29490.05	339.0974	0.1798	H-7->LUMO (71%)
27	29718.3	336.493	0.0922	H-2->L+4 (79%)
28	29864.29	334.8481	0.0141	H-3->L+4 (72%)
29	30096.58	332.2637	0.0393	H-18->L+1 (23%), H-18->L+3 (13%), H-17->LUMO (18%), H-17->L+2 (16%), H-7->L+1 (15%)
30	30178.85	331.3579	0.0031	H-18->LUMO (24%), H-18->L+2 (20%), H-17->L+1 (28%), H-17->L+3 (15%)

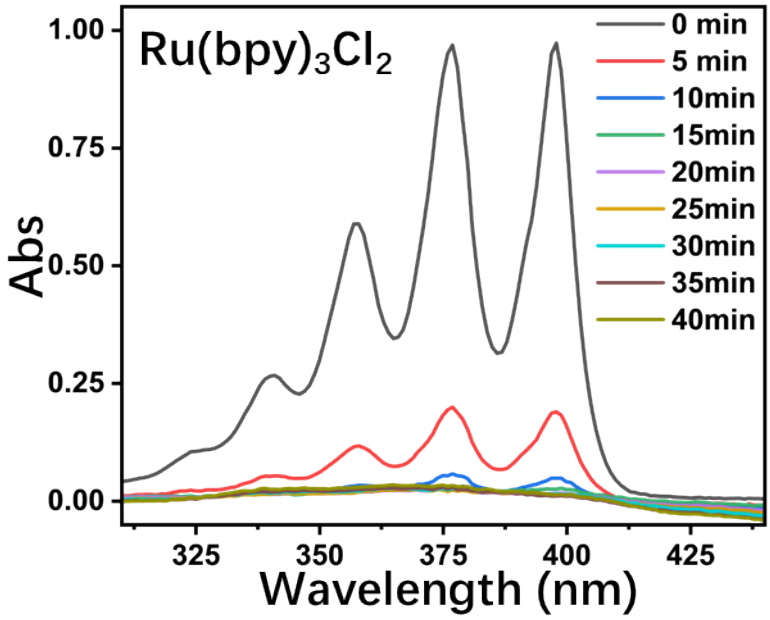


Figure S14. UV-vis absorption spectral changes of ABDA in MeCN during singlet oxygen generation photosensitized by $Ru(bpy)_3Cl_2$ upon blue photoirradiation.

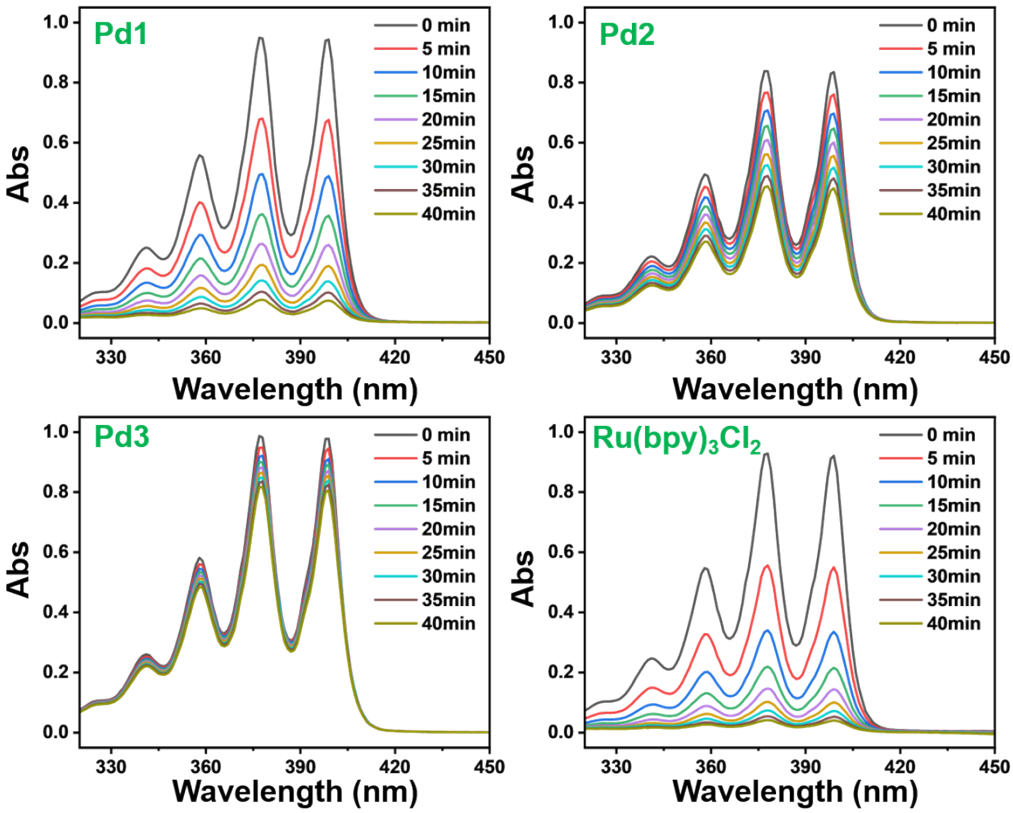


Figure S15. UV-vis absorption spectral changes of ABDA in MeCN for $^1O_2$ generation by **Pd1**, **Pd2**, **Pd3**, and $Ru(bpy)_3Cl_2$ upon blue photoirradiation. The complex : ABDA ratio is 1: 30.

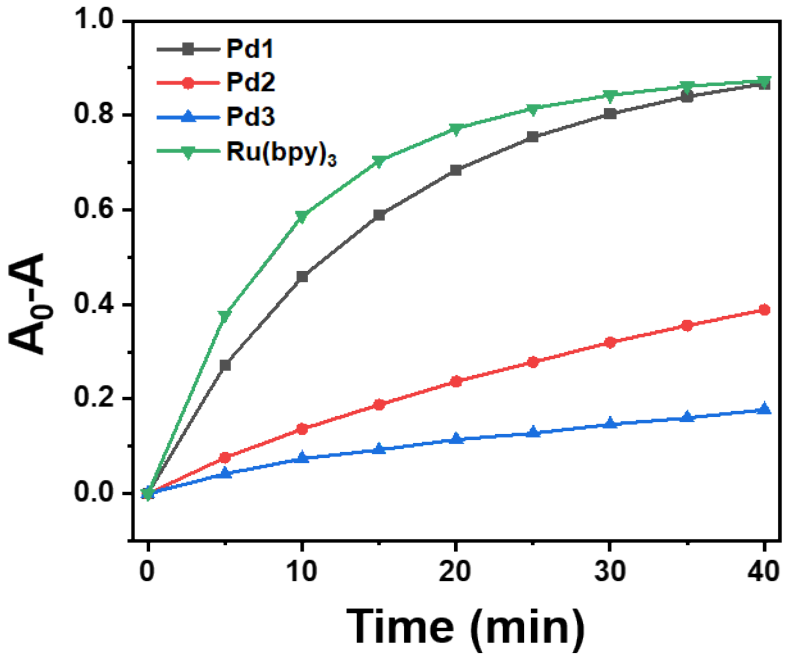


Figure S16. Kenetic curves of **Pd1**, **Pd2**, **Pd3**, and $Ru(bpy)_3Cl_2$ for the absorbance change of ABDA at 398 nm.

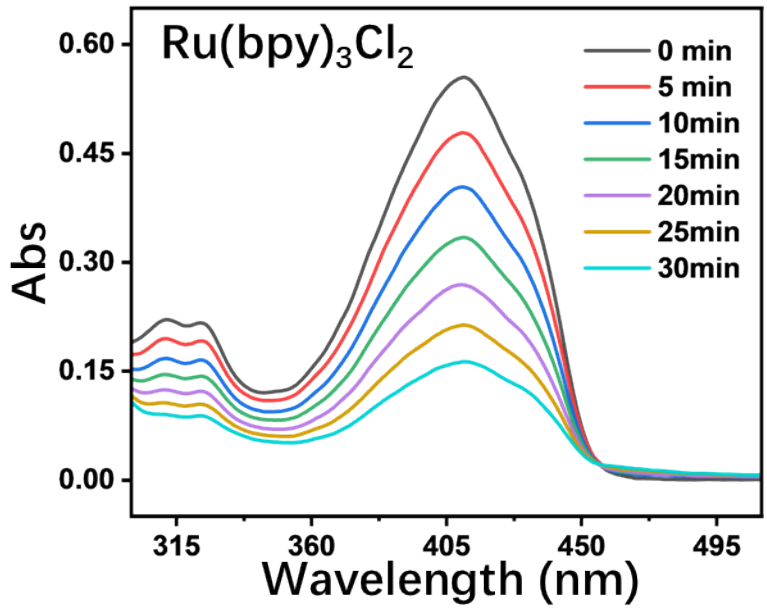


Figure S17. UV-vis absorption spectral changes of DPBF in MeCN during singlet oxygen generation photosensitized by $Ru(bpy)_3Cl_2$ upon red photoirradiation.

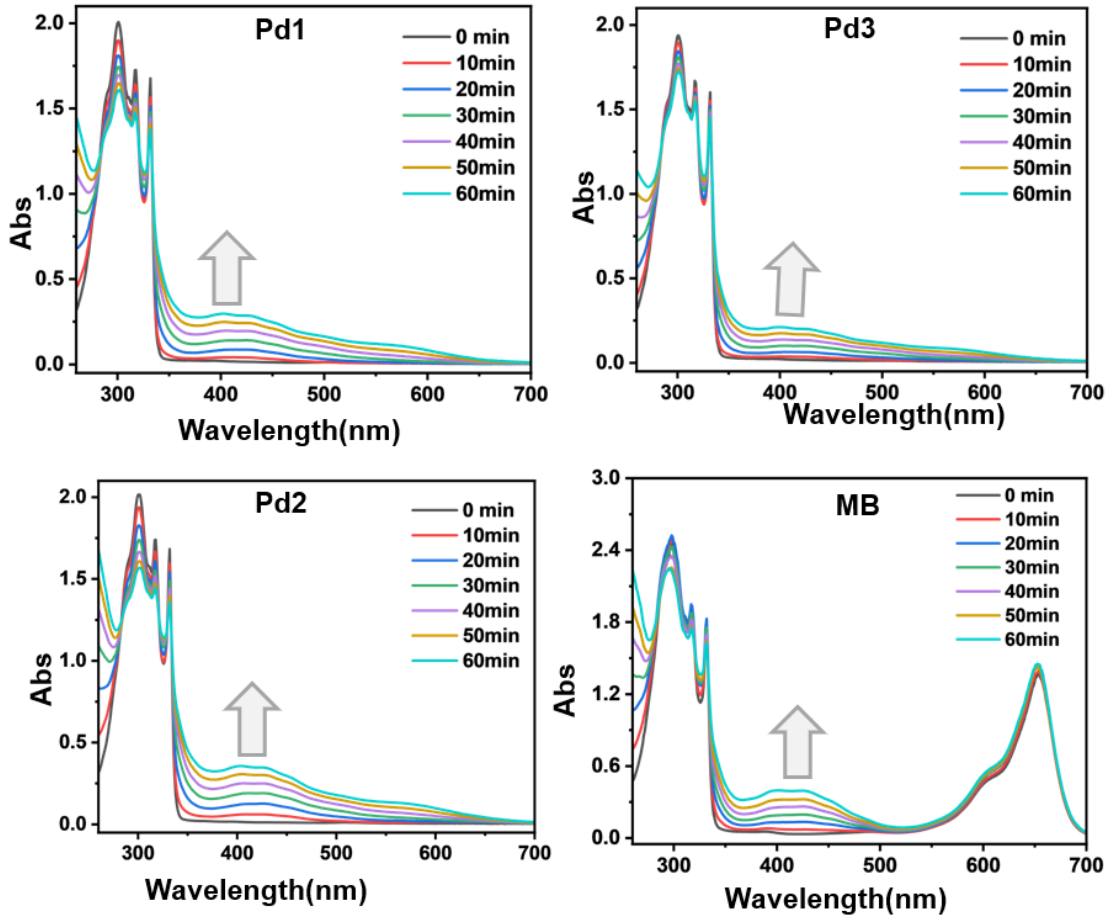
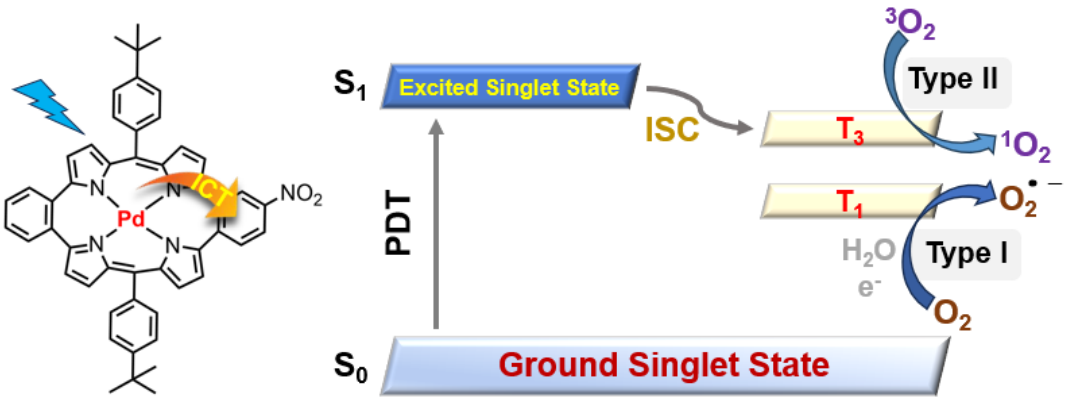


Figure S18. UV-vis absorption spectral changes of DHN in MeCN during singlet oxygen generation photosensitized by **Pd1**, **Pd2**, and **Pd3** upon photoirradiation.

Table S4. Comparison of **Pd1**, **Pd2**, and **Pd3** with representative PDT photosensitizers.

Photosensitizer	Absorption λ_{max} (nm)	Singlet Oxygen Quantum Yield ($\Phi\Delta$)	Potential Toxicity	Ref.
Pd1	501	0.29 (Blue light, ABDA)	Currently unavailable	This work
Pd2	507	0.23 (Blue light, ABDA)	Currently unavailable	This work
Pd3	503	0.04 (Blue light, ABDA)	Currently unavailable	This work
Rose Bengal	550	0.75 (in H_2O)	high phototoxicity	1
Temoporfin (m-THPC)	650	0.43-0.62 (in MeOH)	high phototoxicity	2
Methylene Blue	660	0.50-0.52 (in D_2O)	clinical applications, favorable local safety	3
Chlorin e6	405	0.65(in H_2O)	transient photosensitivity	4

Scheme S1. The possible mechanistic scheme of superoxide by Pd complexes in this work.



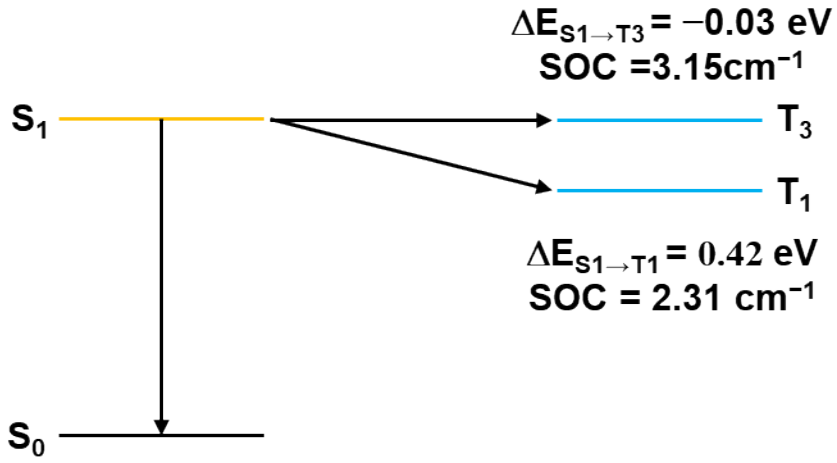


Figure S19. ΔE_{st} and SOC of $S_1 \rightarrow T_1$ and $S_1 \rightarrow T_3$ of **Pd1**, calculated at the theoretical level of B3LYP/DKH-def2-TZVP-SARC-DKH-TZVP (for Pd).

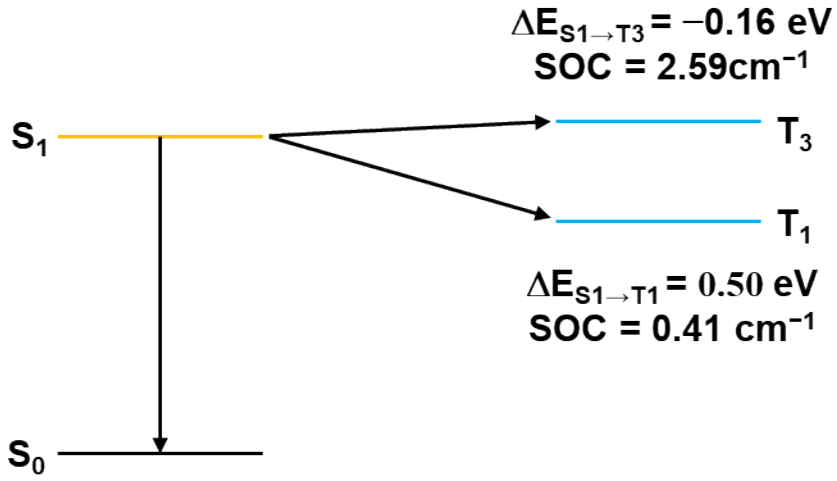


Figure S20. ΔE_{st} and SOC of $S_1 \rightarrow T_1$ and $S_1 \rightarrow T_3$ of **Pd3**, calculated at the theoretical level of B3LYP/DKH-def2-TZVP-SARC-DKH-TZVP (for Pd).

2. Cartesian Coordinates

Table S5. Cartesian coordinates of the DFT optimized geometry for **Pd1**.

Energy = –2482.373024 hartree

Tag	Symbol	X	Y	Z
1	C	-1.65021	0.332153	3.154796
2	C	1.379909	-0.02666	3.217868
3	N	1.340806	0.032474	1.874561
4	C	2.268122	-0.88438	1.377471
5	C	2.870824	-1.55573	2.486481
6	C	2.333746	-1.00416	3.631447
7	C	-2.82146	-0.39741	3.522971
8	C	-3.42581	-0.80968	2.354065
9	C	-2.63997	-0.29638	1.274539
10	N	-1.54474	0.379715	1.815482
11	C	-0.7622	1.020285	4.100435
12	C	0.638982	0.855591	4.128436
13	N	-1.38145	1.487936	-0.75496
14	C	-2.47306	0.658217	-1.0181
15	C	-3.02734	1.031563	-2.27927
16	C	-2.31858	2.133209	-2.72143
17	C	2.666365	1.51253	-2.63238
18	C	3.080298	0.279012	-2.16441
19	C	2.41722	0.061157	-0.9194
20	N	1.550312	1.13329	-0.69146
21	C	1.709187	2.006315	-1.70297
22	C	-1.29689	2.378637	-1.76192
23	C	1.056037	3.320366	-1.78865
24	C	-0.34508	3.494117	-1.82063
25	C	2.721042	-0.91516	0.047957
26	C	-3.03554	-0.21925	-0.06977
27	C	3.686154	-1.99152	-0.30114
28	C	-4.21283	-1.03815	-0.46498
29	C	5.001858	-1.7092	-0.69744
30	C	5.886155	-2.73919	-0.99758
31	C	5.501858	-4.08843	-0.92245
32	C	4.188756	-4.35916	-0.51894
33	C	3.298119	-3.33244	-0.20462
34	C	-4.14875	-2.43675	-0.37556
35	C	-5.24085	-3.22003	-0.73176
36	C	-6.44534	-2.64838	-1.17407
37	C	-6.50465	-1.25096	-1.24151
38	C	-5.41026	-0.45755	-0.89644
39	C	-0.87321	4.784003	-2.01286
40	C	-0.05158	5.893408	-2.1566

41	C	1.327246	5.697941	-2.12129
42	C	1.885403	4.437334	-1.94856
43	C	1.378351	1.499213	5.135726
44	C	0.76142	2.303282	6.088714
45	C	-0.62474	2.465524	6.061277
46	C	-1.37251	1.821357	5.08089
47	C	-7.62525	-3.55204	-1.55341
48	C	6.511846	-5.1895	-1.26904
49	C	5.90943	-6.59772	-1.13458
50	C	7.722965	-5.08791	-0.31584
51	C	6.987476	-5.00343	-2.72657
52	C	-8.854	-2.74773	-2.00877
53	C	-8.02988	-4.40324	-0.32984
54	C	-7.20045	-4.48357	-2.70983
55	Pd	0.008942	0.914564	0.627614
56	N	2.21705	6.853858	-2.27938
57	O	1.694649	7.958795	-2.42992
58	O	3.430973	6.650765	-2.25529
59	H	3.642771	-2.30759	2.412323
60	H	2.565702	-1.24595	4.659659
61	H	-3.14371	-0.57757	4.539419
62	H	-4.34759	-1.36182	2.243381
63	H	-3.8652	0.552527	-2.76284
64	H	-2.46912	2.700889	-3.6296
65	H	2.976996	2.020539	-3.53522
66	H	3.795015	-0.38957	-2.62009
67	H	5.333674	-0.67713	-0.74705
68	H	6.900042	-2.48303	-1.28969
69	H	3.841465	-5.38276	-0.44242
70	H	2.286728	-3.56983	0.111181
71	H	-3.23096	-2.9042	-0.03191
72	H	-5.14995	-4.29971	-0.66142
73	H	-7.41582	-0.75871	-1.56036
74	H	-5.49236	0.623709	-0.94139
75	H	-1.95119	4.90391	-2.04117
76	H	-0.45142	6.889765	-2.2935
77	H	2.962068	4.327028	-1.93885
78	H	2.455553	1.365076	5.151771
79	H	1.359084	2.799931	6.847369
80	H	-1.1209	3.090019	6.798337
81	H	-2.45143	1.93943	5.054029
82	H	5.578769	-6.80181	-0.11018
83	H	5.056008	-6.73994	-1.80673
84	H	6.665021	-7.34691	-1.39438

85	H	7.409923	-5.21716	0.72611
86	H	8.458371	-5.86613	-0.55172
87	H	8.223778	-4.11806	-0.39772
88	H	6.144424	-5.0724	-3.42282
89	H	7.467196	-4.03096	-2.87596
90	H	7.714761	-5.78015	-2.99089
91	H	-9.22179	-2.08521	-1.21745
92	H	-8.63592	-2.13948	-2.89355
93	H	-9.6663	-3.43433	-2.27031
94	H	-8.33672	-3.76351	0.504978
95	H	-8.86999	-5.05986	-0.58503
96	H	-7.20512	-5.03416	0.016424
97	H	-6.90867	-3.90186	-3.59113
98	H	-6.35234	-5.11646	-2.43013
99	H	-8.03103	-5.14103	-2.9926

Table S6. Cartesian coordinates of the DFT optimized geometry for **Pd2**.

Energy = –2686.876866 hartree

Tag	Symbol	X	Y	Z
1	C	1.66022	1.025786	2.577467
2	C	-1.37677	1.156535	2.746274
3	N	-1.36108	0.646366	1.499245
4	C	-2.40649	-0.26974	1.404237
5	C	-3.06145	-0.33884	2.671434
6	C	-2.43502	0.57133	3.499571
7	C	2.668978	0.27187	3.243535
8	C	3.178208	-0.62133	2.321143
9	C	2.519684	-0.36058	1.079873
10	N	1.561027	0.634548	1.295118
11	C	0.918347	2.148034	3.170993
12	C	-0.49146	2.214326	3.241623
13	N	1.36084	0.646248	-1.49911
14	C	2.406397	-0.26978	-1.40409
15	C	3.061675	-0.33843	-2.67115
16	C	2.435298	0.571832	-3.49921
17	C	-2.66884	0.272268	-3.24357
18	C	-3.17841	-0.6207	-2.32114
19	C	-2.52025	-0.35978	-1.07973
20	N	-1.56145	0.6353	-1.29488
21	C	-1.66024	1.026264	-2.57735
22	C	1.376843	1.156784	-2.74599
23	C	-0.91821	2.148445	-3.17082
24	C	0.4916	2.214617	-3.24137
25	C	-2.89461	-0.80932	0.19685
26	C	2.894302	-0.80969	-0.19679
27	C	-3.96745	-1.83118	0.312309
28	C	3.967212	-1.83148	-0.31238
29	C	-5.24914	-1.62539	-0.21028
30	C	-6.24117	-2.59596	-0.06975
31	C	-5.99261	-3.80605	0.58968
32	C	-4.70471	-3.9984	1.117162
33	C	-3.71341	-3.03196	0.993003
34	C	3.713233	-3.03217	-0.99326
35	C	4.704581	-3.99854	-1.11756
36	C	5.992475	-3.8062	-0.59006
37	C	6.240968	-2.59619	0.069557
38	C	5.248895	-1.62569	0.210226
39	C	1.093661	3.298622	-3.90825
40	C	0.339437	4.308106	-4.48894
41	C	-1.04852	4.218143	-4.41155

42	C	-1.67932	3.158491	-3.77231
43	C	-1.0934	3.298352	3.908554
44	C	-0.33906	4.307773	4.489216
45	C	1.04887	4.217693	4.411739
46	C	1.679577	3.158014	3.772453
47	C	7.056092	-4.89845	-0.75684
48	C	-7.05618	-4.89837	0.756325
49	C	6.560987	-6.19639	-0.08154
50	C	8.400257	-4.50659	-0.1214
51	C	7.288634	-5.1578	-2.26157
52	C	-7.28863	-5.15798	2.261024
53	C	-8.40039	-4.50643	0.121029
54	C	-6.56107	-6.19617	0.080775
55	N	-1.86948	5.267098	-5.02726
56	O	-1.28301	6.193667	-5.5867
57	O	-3.093	5.155871	-4.95039
58	N	1.869952	5.266581	5.027408
59	O	1.283558	6.193159	5.586912
60	O	3.093458	5.1552	4.950488
61	H	-3.91997	-0.95486	2.894821
62	H	-2.66896	0.805789	4.529016
63	H	2.950252	0.390087	4.281064
64	H	3.953136	-1.35639	2.477483
65	H	3.920278	-0.95434	-2.89452
66	H	2.669399	0.806506	-4.52857
67	H	-2.94983	0.390306	-4.2812
68	H	-3.9534	-1.35568	-2.47758
69	H	-5.47813	-0.68869	-0.70815
70	H	-7.22292	-2.38991	-0.47935
71	H	-4.46773	-4.92073	1.638606
72	H	-2.72793	-3.20411	1.414993
73	H	2.727769	-3.2043	-1.41529
74	H	4.467653	-4.9208	-1.63914
75	H	7.222706	-2.39016	0.47921
76	H	5.477825	-0.68906	0.708254
77	H	2.176607	3.340862	-3.9562
78	H	0.798025	5.149275	-4.99246
79	H	-2.76066	3.122727	-3.74168
80	H	-2.17634	3.340655	3.956592
81	H	-0.79755	5.148968	4.992792
82	H	2.760908	3.122185	3.741753
83	H	6.389073	-6.03733	0.988688
84	H	5.624354	-6.55172	-0.52268
85	H	7.307662	-6.99117	-0.19421

86	H	8.818753	-3.60385	-0.57995
87	H	8.304932	-4.33323	0.956197
88	H	9.123754	-5.31637	-0.26401
89	H	7.641562	-4.24994	-2.76309
90	H	8.043661	-5.94062	-2.39932
91	H	6.372553	-5.48438	-2.76385
92	H	-7.64157	-4.25022	2.762721
93	H	-8.04362	-5.94085	2.398689
94	H	-6.37251	-5.4846	2.763201
95	H	-8.81888	-3.60377	0.579737
96	H	-8.30514	-4.33291	-0.95655
97	H	-9.12387	-5.31625	0.263566
98	H	-6.38922	-6.03692	-0.98943
99	H	-5.62441	-6.55156	0.521812
100	H	-7.30772	-6.99099	0.193345
101	Pd	-0.00011	0.810557	0.000079

Table S7. Cartesian coordinates of the DFT optimized geometry for **Pd3**.

Energy = –2372.318496 hartree

Tag	Symbol	X	Y	Z
1	C	1.512262	-1.69654	-2.53879
2	C	-1.51234	-1.69659	-2.53894
3	N	-1.4749	-1.13274	-1.31899
4	C	-2.4636	-0.14459	-1.27747
5	C	-3.08044	-0.07432	-2.56555
6	C	-2.5128	-1.06778	-3.3375
7	C	2.513479	-1.06848	-3.33704
8	C	3.080716	-0.07453	-2.56553
9	C	2.463019	-0.14382	-1.27777
10	N	1.473971	-1.1316	-1.31942
11	C	0.704599	-2.84985	-2.95924
12	C	-0.70465	-2.84991	-2.95947
13	N	1.453984	-0.79836	1.467028
14	C	2.469084	0.120111	1.199489
15	C	3.164519	0.388421	2.419711
16	C	2.590825	-0.40546	3.391361
17	C	-2.59101	-0.40525	3.391794
18	C	-3.16445	0.388727	2.420024
19	C	-2.46924	0.119989	1.19979
20	N	-1.4544	-0.79898	1.46746
21	C	-1.52567	-1.12409	2.771023
22	C	1.525144	-1.12382	2.770479
23	C	-0.70567	-2.14407	3.436944
24	C	0.705352	-2.14399	3.436482
25	C	-2.89495	0.470547	-0.09205
26	C	2.894602	0.471046	-0.09233
27	C	-3.98001	1.487994	-0.17672
28	C	3.979894	1.488234	-0.17684
29	C	-3.73236	2.796909	0.26565
30	C	-4.72816	3.766419	0.20785
31	C	-5.98018	3.408118	-0.28606
32	C	-6.26225	2.114515	-0.71858
33	C	-5.25488	1.156987	-0.66152
34	C	5.254717	1.157031	-0.66157
35	C	6.262279	2.114401	-0.71846
36	C	5.98039	3.407982	-0.28582
37	C	4.728415	3.766476	0.20807
38	C	3.732442	2.797139	0.265701
39	C	1.385367	-3.1207	4.184033
40	C	0.698293	-4.0919	4.905212
41	C	-0.69757	-4.09188	4.905748

42	C	-1.38516	-3.12072	4.185016
43	C	-1.38658	-3.96561	-3.47155
44	C	-0.69772	-5.0732	-3.95729
45	C	0.698124	-5.0732	-3.95699
46	C	1.386777	-3.96559	-3.471
47	N	7.040253	4.425003	-0.34556
48	O	8.134948	4.081458	-0.78986
49	O	6.766873	5.556691	0.051936
50	N	-7.03984	4.425293	-0.34597
51	O	-6.76636	5.556876	0.051698
52	O	-8.13464	4.081792	-0.78999
53	H	-3.86574	0.609669	-2.85143
54	H	-2.74431	-1.32997	-4.36071
55	H	2.745731	-1.33142	-4.3599
56	H	3.866401	0.609049	-2.85135
57	H	4.013848	1.048119	2.523587
58	H	2.867071	-0.48634	4.433669
59	H	-2.86724	-0.48569	4.434144
60	H	-4.01352	1.048736	2.523977
61	H	-2.75001	3.048963	0.650779
62	H	-4.55398	4.78327	0.535691
63	H	-7.25405	1.877458	-1.08188
64	H	-5.45581	0.139648	-0.97859
65	H	5.455511	0.139691	-0.97871
66	H	7.254054	1.877199	-1.08172
67	H	4.554428	4.783321	0.536027
68	H	2.750125	3.049286	0.650841
69	H	2.470972	-3.11101	4.181689
70	H	1.24919	-4.84305	5.463408
71	H	-1.24806	-4.84299	5.464401
72	H	-2.47077	-3.11106	4.183429
73	H	-2.47229	-3.95289	-3.47616
74	H	-1.24755	-5.92953	-4.33637
75	H	1.248123	-5.92953	-4.33582
76	H	2.472486	-3.95288	-3.4752
77	Pd	-0.00018	-1.13639	0.093096

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