Self-Assembly of supramolecular triangles with neutral *trans*-$PdCl_2$ directing units

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Supporting Information

Materials, methods and instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded in CD_3CN at room temperatutre (r.t.) on a Bruker AV400 (400 MHz) spectrometer for ^1H NMR and at 100 and for ^{13}C NMR. Chemical shifts are reported in part per million (ppm) relative to residual solvent protons (1.94 ppm for CD_3CN) and the carbon resonance (118.69 ppm for CD_3CN) of the solvent.

Absorption spectra were measured in deaerated acetonitrile at room temperature (r.t.) on a Cary 500i UV-Vis-NIR Spectrophotometer. For luminescence spectra a Cary Eclipse Fluorescence spectrofluorimeter was used. Accurate mass measurements were performed on a 6210 TOF mass spectrometer from Agilent technologies, coupled to a 1100 series LC system in positive electrospray mode. Appropriate $[M\text{-}PF_6]^{n+}$ species were used for empirical formula determination, and exact masses were calculated using Analyst® QS Software from Applied Biosystems. Electrochemical measurements were carried out in argon-purged purified acetonitrile at room temperature with a BAS CV50W multipurpose potentiostat. The working electrode was a glassy carbon electrode. The counter electrode was a Pt wire, and the pseudo-reference electrode was a silver wire. The reference was set using an internal 1 mM ferrocene/ferrocinium sample at 395 mV *vs.* SCE in acetonitrile. The concentration of the compounds was about 1 mM. Tetrabutylammonium hexafluorophosphate (TBAP) was used as supporting electrolyte and its concentration was 0.10 M. Cyclic voltammograms of **1-4** were obtained at scan rate of 50 mV/s. The criteria for reversibility were the separation of 60 mV between cathodic and anodic peaks, the close to unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate.

Experimental uncertainties are as follows: absorption maxima, ±2 nm; molar absorption coefficient, 10%; redox potentials, ± 10 mV; emission maxima, ±2 nm.

tert-Butylamine, pyridine, 3-picoline and nicotinic acid were purchased from VWR and used as received. 2-Acetylpyridine and pyridine-3-carboxaldehyde were purchased from Aldrich and used as received. Fe and Ru-metal salts were used as supplied from Aldrich. $PdCl_2$ was received from Pressure Chemicals and used as received. $Pd(CH_3CN)_2Cl_2$ was synthesized using literature procedure.[1] 4-(3-Pyridyl)-2,2':6',2''-terpyridine (3-pytpy) was synthesized using a literature procedure.[2] Fe- and Ru-metallo-ligands were synthesized according to reported literature procedure.[3]

Experimental:

$(PdCl_2[\mu\text{-}(3\text{-pytpy})_2Fe])_3(PF_6)_6$ (1):

A 100 mL round-bottomed flask was charged with Fe-metallo-ligand ($[(3\text{-pytpy})_2Fe]$ $[(PF_6)_2]$) (100 mg, 0.103 mmol) and to it $Pd(CH_3CN)_2Cl_2$ (28 mg, 0.109 mmol) was added, followed by the addition of nitromethane (50 mL). The resulting purple solution was heated at reflux for 2 days in the dark, after which time the solution was cooled down to r.t. and the solution was concentrated to *ca.* 6-8 mL. Precipitation as a purple solid of the desired metallo-triangle was induced by the addition of diethyl ether (~ 20 mL). The solid was isolated by filtration and was triturated with acetone (~ 3 mL) and dried under vacuum. Yield = 101 mg (85%). ^1H NMR: (400 MHz, CD_3CN) (see Scheme 1 in main text for numbering) δ ppm 9.59 (s, 2 $H_{2'''}$), 9.20 (s, 4 $H_{3''}$), 9.01 (d, J^d = 8 Hz, 2 $H_{6'''}$), 8.77 (d, J^d = 8 Hz, 2 $H_{4'''}$), 8.61 (d, J^d = 8 Hz, 4 H_3), 7.94 (t, J^t = 8 Hz, 4 H_4), 7.88 (t, J^t = 8 Hz, 2 $H_{5'''}$), 7.19 (d, J^d = 8 Hz, 4 H_6), 7.11 (t, J^t = 8 Hz, 4 H_5). $^{13}C\{^1H\}$ NMR: (100 MHz, CD_3CN) δ ppm 162.47, 159.43, 155.79 , 154.79, 153.68, 150.43, 140.62, 136.98, 136.49, 129.19, 127.84, 126.01, 123.65. HRMS (ESI), m/z: calculated for $C_{40}H_{28}N_8PF_6Fe$: 821.14281; found: 821.14316 $[(\text{Fe-metallo-ligand})\text{-}PF_6)]^+$, calculated for $C_{40}H_{28}N_8Fe$: 338.08931; found: 338.08955 $[(\text{Fe-metallo-ligand})\text{-}2PF_6)]^{2+}$, calculated for $C_{120}H_{84}N_{24}Fe_3Pd_3Cl_6P_3F_{18}$: 998.98427; found: 998.98427, calculated for $C_{120}H_{84}N_{24}Fe_3Pd_3Cl_6P_2F_{12}$: 712.99702; found: 712.99702, calculated for $C_{120}H_{84}N_{24}Fe_3Pd_3Cl_6P_1F_6$: 541.40467; found: 541.40458. Anal. Calc. for $C_{120}H_{84}N_{24}Fe_3Pd_3Cl_6P_2F_{12}\cdot C_3H_6O$: C: 42.34; N: 9.63; H: 2.60. Found: C: 42.58; N: 9.35; H: 2.38 (presence of acetone molecule was also confirmed in the ^1H NMR spectrum of this compound).

$(PdCl_2[\mu\text{-}(3\text{-pytpy})_2Ru])_3(PF_6)_6$ (2):

A 100 mL round-bottomed flask was charged with Ru-metallo-ligand ($[(3\text{-pytpy})_2Ru]$ $[(PF_6)_2]$) (100 mg, 0.098 mmol) and to it $Pd(CH_3CN)_2Cl_2$ (27 mg, 0.103 mmol) was added, followed by the addition of nitromethane (50 mL). The resulting red solution was heated at reflux for 2 days in the dark, after which time the solution was cooled down to r.t. and the solution was concentrated to *ca.* 6-8 mL. Precipitation of the desired metallo-triangle was induced by addition of an aliquot of saturated aqueous KPF_6 solution (3 mL), followed by the addition of diethyl ether (~ 20 mL). The red solid was isolated by filteration and was triturated with acetone (~ 3 mL) and was dried under vacuum. Yield = 85 mg (72%). ^1H NMR: (400 MHz, CD_3CN) (see Scheme 1 for numbering) δ ppm 9.48 (s, 2 $H_{2'''}$), 9.02 (s, 4 $H_{3''}$), 8.96 (d, J^d = 8 Hz, 2 $H_{6'''}$), 8.66 (d, J^d = 8 Hz, 2 $H_{4'''}$), 8.63 (d, J^d = 8 Hz, 4 H_3), 7.98 (t, J^t = 8 Hz, 4 H_4), 7.82 (t, J^t = 8 Hz, 2 $H_{5'''}$), 7.43 (d, J^d = 8 Hz, 4 H_6), 7.21 (t, J^t = 8 Hz, 4 H_5). $^{13}C\{^1H\}$ NMR: (100 MHz, CD_3CN) δ ppm 158.74, 158.69, 156.74, 156.68, 154.88, 153.52, 152.92, 139.59, 139.23, 128.62, 126.95, 125.77, 123.12. HRMS (ESI), m/z: calculated for $C_{40}H_{28}N_8Ru$: 361.07402; found: 361.07234 [(Ru-metallo-ligand)-

$2PF_6)]^{2+}$, calculated for $C_{120}H_{84}N_{24}Ru_3Pd_3Cl_6P_3F_{18}$: 1042.95340; found: 1042.95428, calculated for $C_{120}H_{84}N_{24}Ru_3Pd_3Cl_6P_2F_{12}$: 745.97400; found: 745.97521, calculated for $C_{120}H_{84}N_{24}Ru_3Pd_3Cl_6P_1F_6$: 567.78637; found: 567.78785, calculated for $C_{120}H_{84}N_{24}Ru_3Pd_3Cl_6$: 448.99461; found: 448.99572. Anal. Calc. for $C_{120}H_{84}N_{24}Ru_3Pd_3Cl_6P_2F_{12}\cdot 3KPF_6$: C: 34.99; N: 8.16; H: 2.06. Found: C: 34.65; N: 7.99; H: 2.27.

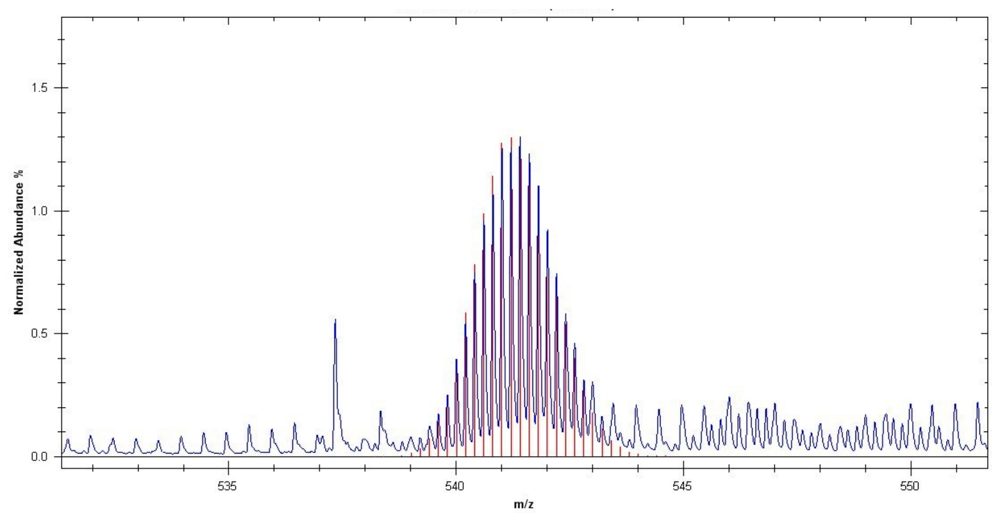

Figure S1. Overlay of observed high-res LC-TOF MS of $[C_{120}H_{84}N_{24}Fe_3Pd_3Cl_3 (PF_6)]^{5+}$ (blue, outer trace) with simulated isotope pattern (red, inner trace).

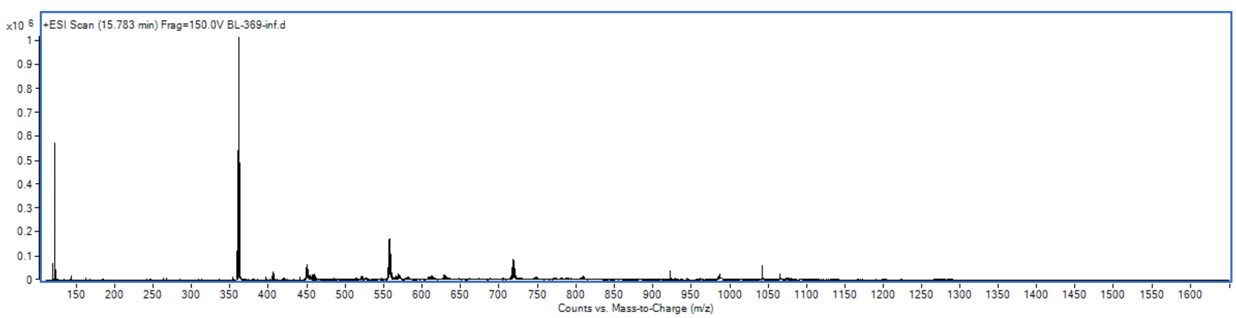

Figure S2. High-res LC-TOF MS of complex **2** or $C_{120}H_{84}N_{24}Ru_3Pd_3Cl_3 (PF_6)_6$.

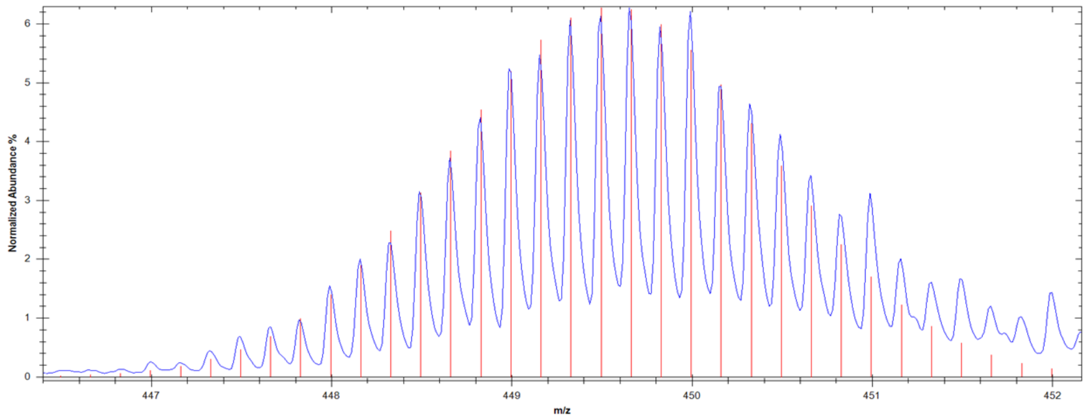

Figure S3. Overlay of observed high-res LC-TOF MS of (**2**)$^{6+}$ or $[C_{120}H_{84}N_{24}Ru_3Pd_3Cl_3]^{6+}$ (blue, outer trace) with simulated isotope pattern (red, inner trace).

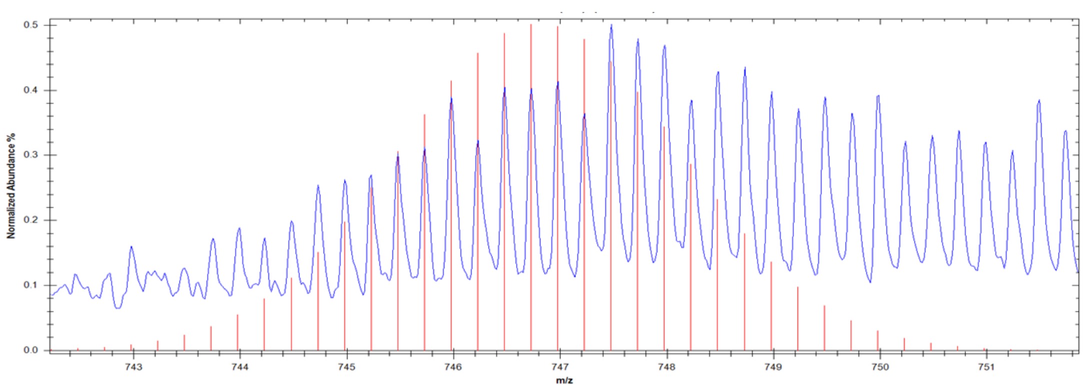

Figure S4. Overlay of observed high-res LC-TOF MS of (**2**)$^{4+}$ or $[C_{120}H_{84}N_{24}Ru_3Pd_3Cl_3(PF_6)_2]^{4+}$ (blue, outer trace) with simulated isotope pattern (red, inner trace).

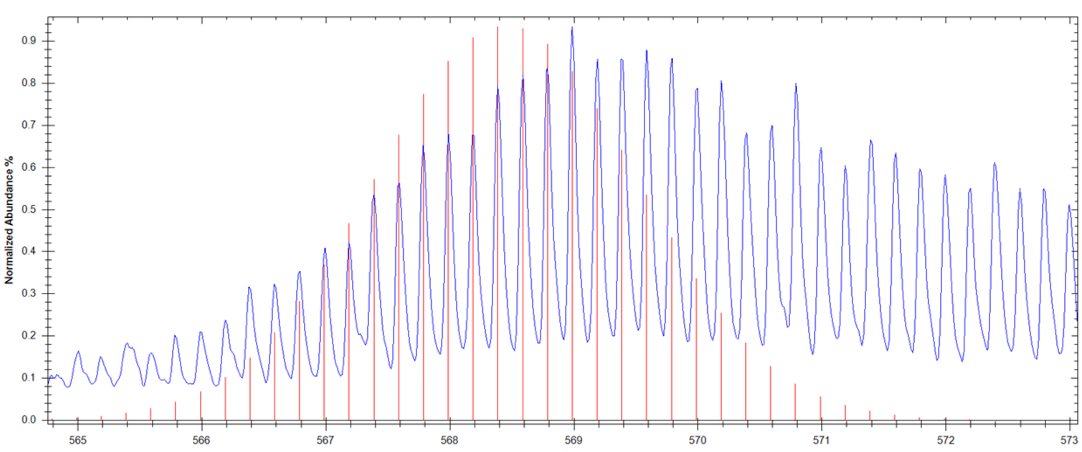

Figure S5. Overlay of observed high-res LC-TOF MS of (**2**)$^{5+}$ or $[C_{120}H_{84}N_{24}Ru_3Pd_3Cl_3(PF_6)]^{5+}$ (blue, outer trace) with simulated isotope pattern (red, inner trace).

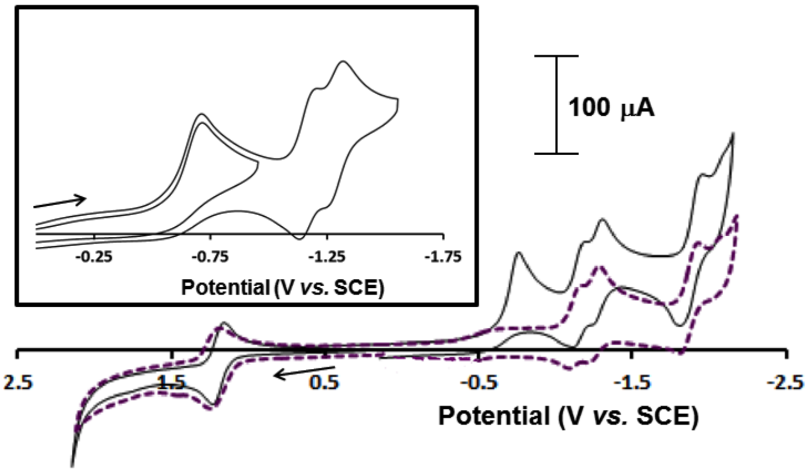

Figure S6: Cyclic voltammograms of complex **1** (bold line) and Fe-metallo-ligand (dashed line). Inset shows the irreversible and quasi-reversible natures of individual reduction peaks of complex **1**.

DFT Calculations:

All calculations were performed with the Gaussian09[4] employing the DFT method, the Becke three-parameter hybrid functional,[5] and Lee-Yang-Parr's gradient-corrected correlation functional (B3LYP).[6] Singlet ground state geometry optimizations for $\mathbf{1}^{6+}$ and $\mathbf{2}^{6+}$ in acetonitrile were carried out at the (R)B3LYP level in the gas phase, using their respective crystallographic structures as starting points. All elements except Fe, Ru and Pd were assigned the 6−31G(d,f) basis set.[7] The double-ζ quality LANL2DZ ECP basis set[8] with an effective core potential and one additional f-type polarization was employed for the Fe, Ru and Pd atoms. Vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima and there are only positive eigenvalues. Gaussview 5.0,[9] Mercury 3.1,[10] ORTEP3[11] and POV-Ray v3.62[12] were employed to draw the geometry optimized structures.

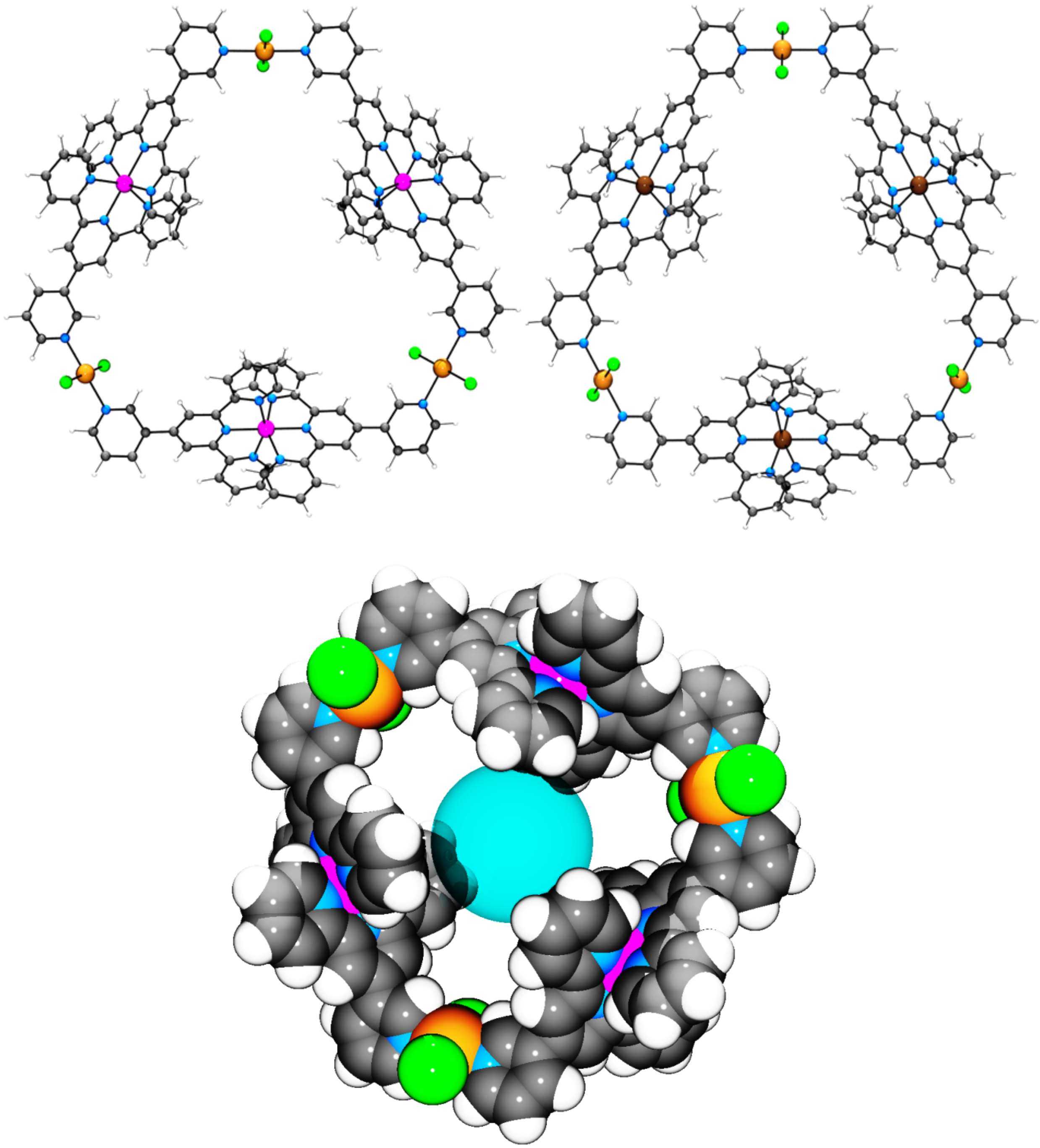

Figure S7: DFT optimized structures of [**1**]$^{6+}$ (top-left) and [**2**]$^{6+}$ (top-right). The bottom figure shows a tight-fit of a hollow-sphere of 4 Å radii in the DFT optimized structure of [**1**]$^{6+}$.

Table S1. Optimized Atomic coordinates obtained from DFT for $\mathbf{1}^{6+}$ in ground state (b3lyp/LanL2DZ(f)[Fe,Pd]6-31G**[C,H,N]).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.209163	9.329988	-1.863891
2	6	0	-5.591434	9.638321	-3.179791
3	7	0	-4.261790	8.545972	-1.517841
4	6	0	-3.304381	10.281773	-2.873119
5	6	0	-4.514486	10.438454	-3.541119
6	6	0	-5.420880	8.704083	-2.163924
7	6	0	-1.628298	6.669131	1.594991
8	6	0	-2.667233	4.708319	3.203894
9	6	0	-0.814903	6.087272	2.562168
10	7	0	-2.920247	6.287269	1.422009
11	6	0	-3.419976	5.331961	2.214144
12	6	0	-1.342309	5.090262	3.378009
13	26	0	-3.863549	7.271729	-0.034820
14	7	0	-4.720748	8.503302	1.284227
15	6	0	-6.192585	10.047846	3.070579
16	6	0	-4.176576	9.573460	1.871383
17	6	0	-6.000492	8.170669	1.592331
18	6	0	-6.764675	8.930262	2.471240
19	6	0	-4.874558	10.370982	2.771891
20	7	0	-5.553285	6.437350	0.092314
21	6	0	-7.996635	5.188600	0.314608
22	6	0	-6.478935	6.955823	0.913667
23	6	0	-5.790480	5.333645	-0.632828
24	6	0	-7.015383	4.682463	-0.546774
25	6	0	-7.718561	6.342869	1.056912
26	7	0	-3.569944	5.785030	-1.331148
27	6	0	-3.474254	3.628754	-3.088402
28	6	0	-2.470932	5.540358	-2.054827
29	6	0	-4.640449	4.961441	-1.471609
30	6	0	-4.621094	3.874485	-2.338910
31	6	0	-2.382091	4.475989	-2.945941
32	6	0	-9.305087	4.515978	0.435446
33	6	0	-11.693756	3.171253	0.571560
34	6	0	-10.492598	5.236401	0.585509
35	6	0	-9.390972	3.126716	0.363542
36	7	0	-10.556605	2.480763	0.423365
37	6	0	-11.695714	4.554123	0.658866
38	7	0	7.418715	7.872866	0.030055
39	6	0	9.793466	6.450683	0.177392
40	6	0	8.593802	8.525015	0.103855
41	6	0	7.400298	6.528242	0.027943
42	6	0	8.570094	5.772969	0.113860
43	6	0	9.801339	7.842087	0.170246
44	6	0	8.507068	4.295601	0.111417
45	7	0	8.431922	1.548330	0.124668
46	6	0	9.293345	3.562808	-0.785014
47	6	0	7.673096	3.616585	1.005694
48	6	0	7.653434	2.225721	0.982485
49	6	0	9.233096	2.173618	-0.752283
50	6	0	6.841758	1.331353	1.822203
51	6	0	5.435838	-0.528466	3.270527
52	7	0	7.026899	0.011594	1.558682
53	6	0	5.953875	1.766866	2.801090
54	6	0	5.239463	0.821950	3.536979
55	6	0	6.337850	-0.890878	2.273564
56	6	0	9.987781	1.227590	-1.589443
57	6	0	11.344073	-0.722604	-2.959623
58	6	0	10.913989	1.602109	-2.557865
59	7	0	9.722539	-0.076753	-1.318715
60	6	0	10.398385	-1.022667	-1.983761
61	6	0	11.599711	0.611189	-3.256632
62	26	0	8.354749	-0.340285	0.110319
63	7	0	9.781746	-0.742887	1.441386

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
64	6	0	11.708313	-1.616954	3.246993
65	6	0	10.556909	0.132066	2.088143
66	6	0	9.961845	-2.068976	1.669491
67	6	0	10.914911	-2.535673	2.567790
68	6	0	11.530336	-0.260958	3.000046
69	7	0	6.909207	-0.553792	-1.252904
70	6	0	4.928745	-1.178526	-3.105466
71	6	0	6.570011	-1.846829	-1.491387
72	6	0	6.272559	0.410426	-1.923998
73	6	0	5.278068	0.143410	-2.858542
74	6	0	5.584924	-2.189450	-2.410991
75	7	0	8.249142	-2.226573	0.087838
76	6	0	8.104710	-4.972935	0.049553
77	6	0	9.075428	-2.933743	0.874587
78	6	0	7.347958	-2.820686	-0.709342
79	6	0	7.245997	-4.207401	-0.748131
80	6	0	9.033306	-4.323562	0.872666
81	6	0	8.050210	-6.448907	0.006993
82	6	0	7.846681	-9.195854	-0.121940
83	6	0	9.214595	-7.226903	-0.046900
84	6	0	6.819034	-7.108107	0.001513
85	7	0	6.727733	-8.448504	-0.056789
86	6	0	9.107937	-8.613630	-0.119176
87	7	0	3.105381	-10.314768	-0.032013
88	6	0	0.671602	-11.631340	-0.073633
89	6	0	3.067064	-11.658010	-0.091398
90	6	0	1.961286	-9.613217	0.001239
91	6	0	0.709529	-10.232437	-0.018257
92	6	0	1.862361	-12.347693	-0.112625
93	6	0	-0.526136	-9.423007	-0.006190
94	7	0	-2.854676	-7.955171	-0.034453
95	6	0	-1.652445	-9.862568	0.701284
96	6	0	-0.598503	-8.220038	-0.719302
97	6	0	-1.786950	-7.497822	-0.706264
98	6	0	-2.814811	-9.101254	0.662481
99	6	0	-2.051560	-6.203865	-1.355232
100	6	0	-2.744481	-3.759713	-2.384313
101	7	0	-3.309855	-5.734488	-1.151920
102	6	0	-1.108399	-5.484582	-2.081782
103	6	0	-1.460965	-4.244088	-2.605919
104	6	0	-3.637157	-4.536712	-1.652569
105	7	0	-10.720510	-1.563298	-0.074136
106	6	0	-10.865200	-4.297822	-0.500101
107	6	0	-9.594917	-2.303300	-0.091176
108	6	0	-11.918568	-2.154807	-0.254675
109	6	0	-12.023031	-3.521373	-0.485414
110	6	0	-9.621804	-3.686331	-0.286542
111	6	0	-8.371278	-4.471608	-0.237062
112	7	0	-6.064947	-5.965539	-0.127522
113	6	0	-7.420702	-4.233999	0.762517
114	6	0	-8.126512	-5.467249	-1.189293
115	6	0	-6.950885	-6.204512	-1.106684
116	6	0	-6.269167	-5.013734	0.795720
117	6	0	-5.181104	-4.956702	1.784951
118	6	0	-3.070107	-5.074696	3.529788
119	6	0	-5.163676	-4.102260	2.882392
120	7	0	-4.183810	-5.850235	1.556444
121	6	0	-3.157532	-5.902062	2.414279
122	6	0	-4.089992	-4.160004	3.766935
123	6	0	-6.499608	-7.268318	-2.016828
124	6	0	-5.441760	-9.250535	-3.588534
125	7	0	-5.272782	-7.766602	-1.714026
126	6	0	-7.239920	-7.744156	-3.093531

127	6	0	-6.701954	-8.749717	-3.893063
128	6	0	-4.763309	-8.735117	-2.487929
129	26	0	-4.461592	-6.963943	-0.077961
130	7	0	-5.073222	-8.491559	1.049148
131	6	0	-5.606652	-10.710097	2.640901
132	6	0	-4.100889	-9.402302	1.311388
133	6	0	-6.294253	-8.691148	1.555089
134	6	0	-6.603217	-9.784186	2.357567
135	6	0	-4.336846	-10.518815	2.105938
136	7	0	3.944551	10.004452	-0.217943
137	6	0	1.629065	11.463182	-0.599286
138	6	0	2.754893	9.392501	-0.183339
139	6	0	4.011148	11.327784	-0.427861
140	6	0	2.868373	12.086803	-0.629832
141	6	0	1.557555	10.086702	-0.361957
142	6	0	0.264309	9.376617	-0.302271
143	7	0	-2.172798	8.103976	-0.165889
144	6	0	0.049018	8.353309	0.628946
145	6	0	-0.777558	9.740834	-1.164019
146	6	0	-1.996217	9.080347	-1.069246
147	6	0	-1.193908	7.730949	0.672862
148	46	0	-10.622408	0.453935	0.186635
149	46	0	4.907192	-9.362578	-0.033750
150	46	0	5.669763	8.927664	-0.076154
151	17	0	4.255634	-8.119103	-1.933481
152	17	0	5.526566	-10.546959	1.909740
153	17	0	-9.281170	0.626318	-1.752179
154	17	0	-11.930883	0.248947	2.137822
155	17	0	4.992596	7.637643	-1.935321
156	17	0	6.365735	10.309477	1.706961
157	1	0	8.544725	9.606803	0.117562
158	1	0	10.728617	8.400232	0.225449
159	1	0	10.722514	5.894513	0.258355
160	1	0	9.925689	4.076687	-1.499421
161	1	0	6.428241	6.059194	-0.074671
162	1	0	7.076660	4.170990	1.720982
163	1	0	11.103704	2.649695	-2.760678
164	1	0	12.326184	0.881479	-4.015565
165	1	0	11.861652	-1.526610	-3.470002
166	1	0	5.000668	11.767966	-0.419041
167	1	0	2.956707	13.153442	-0.799214
168	1	0	2.774036	8.318615	-0.037423
169	1	0	0.723288	12.045304	-0.737523
170	1	0	-0.627112	10.515744	-1.906166
171	1	0	0.835419	8.060655	1.314230
172	1	0	-0.724925	4.622924	4.137727
173	1	0	0.214186	6.406297	2.679248
174	1	0	-3.121557	3.939871	3.818571
175	1	0	-4.456230	5.058862	2.048400
176	1	0	-2.449507	10.894664	-3.133976
177	1	0	-4.611243	11.177006	-4.329766
178	1	0	-6.553632	9.726742	-3.670817
179	1	0	-6.238177	8.061859	-1.855714
180	1	0	-3.150001	9.801331	1.607063
181	1	0	-4.385566	11.228662	3.219086
182	1	0	-6.770606	10.654046	3.759860
183	1	0	-1.636083	6.217269	-1.911403
184	1	0	-1.469070	4.323922	-3.509906
185	1	0	-3.438906	2.787617	-3.772476
186	1	0	-5.487199	3.229553	-2.431397
187	1	0	-7.214639	3.803529	-1.148345
188	1	0	-8.445429	6.727957	1.762317
189	1	0	-7.791353	8.656466	2.684381
190	1	0	-10.477798	6.321258	0.619987
191	1	0	-8.508689	2.506314	0.261235
192	1	0	-12.635101	5.082010	0.772887
193	1	0	10.169050	-2.051148	-1.728359
194	1	0	12.129197	0.490094	3.502089
195	1	0	12.454937	-1.958985	3.955717
196	1	0	11.040095	-3.599353	2.733171
197	1	0	10.390066	1.180509	1.867902
198	1	0	5.819468	2.825912	2.987744
199	1	0	4.543379	1.140666	4.305560
200	1	0	4.904597	-1.298125	3.818494
201	1	0	6.515579	-1.934337	2.038227
202	1	0	6.569092	1.429998	-1.704909
203	1	0	4.794668	0.964137	-3.375710
204	1	0	4.157806	-1.423757	-3.828131
205	1	0	5.332784	-3.229022	-2.584622
206	1	0	-0.740613	-3.667623	-3.176460
207	1	0	-3.062911	-2.798763	-2.771509
208	1	0	-4.650048	-4.195347	-1.470234
209	1	0	-8.661786	-1.765469	0.035969
210	1	0	-12.605502	2.590011	0.632009
211	1	0	-12.789741	-1.513241	-0.195933
212	1	0	-12.999831	-3.965455	-0.637364
213	1	0	-10.927028	-5.370503	-0.656607
214	1	0	-8.837564	-5.644264	-1.987825
215	1	0	-7.591541	-3.465401	1.507061
216	1	0	-5.978988	-3.408749	3.052119
217	1	0	-4.056717	-3.502196	4.628886
218	1	0	-2.215843	-5.156070	4.191993
219	1	0	-8.223179	-7.340388	-3.305074
220	1	0	-7.262708	-9.133706	-4.738567
221	1	0	-4.983256	-10.032108	-4.183199
222	1	0	-3.783582	-9.110034	-2.213266
223	1	0	-7.048076	-7.952410	1.306327
224	1	0	-7.608788	-9.896862	2.745967
225	1	0	-5.811741	-11.573111	3.265310
226	1	0	-3.544399	-11.231517	2.302351
227	1	0	-1.613366	-10.780384	1.275732
228	1	0	-0.279166	-12.154218	-0.103376
229	1	0	1.865568	-13.429905	-0.167637
230	1	0	4.021946	-12.168814	-0.116509
231	1	0	2.063483	-8.535202	0.046748
232	1	0	5.883090	-6.564025	0.061210
233	1	0	6.531354	-4.693013	-1.402508
234	1	0	9.689390	-4.899095	1.515093
235	1	0	10.191066	-6.752052	-0.047837
236	1	0	9.988263	-9.243295	-0.173926
237	1	0	7.710634	-10.269800	-0.162620
238	1	0	0.254163	-7.867558	-1.287781
239	1	0	-0.110776	-5.880865	-2.230469
240	1	0	-2.380849	-6.627221	2.197524

Table S2. Optimized Atomic coordinates obtained from DFT for $\mathbf{2}^{6+}$ in ground state (b3lyp/LanL2DZ(f)[Ru,Pd]6-31G**[C,H,N]).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	10.010146	-1.879097	-1.564128
2	6	0	11.557415	-0.028426	-2.879958
3	7	0	9.843276	-0.552110	-1.297471
4	6	0	10.949099	-2.311523	-2.494839
5	6	0	11.732072	-1.377588	-3.161702
6	6	0	10.602391	0.340946	-1.942208
7	6	0	6.605432	-1.929657	1.659514
8	6	0	5.163909	-0.126585	3.141162
9	6	0	5.637325	-2.391931	2.542757
10	7	0	6.849658	-0.596855	1.517511
11	6	0	6.142634	0.271882	2.243141
12	6	0	4.907423	-1.482333	3.293049
13	44	0	8.358206	-0.164195	0.127324
14	7	0	9.766704	0.123159	1.651557
15	6	0	11.567459	0.819319	3.649700
16	6	0	10.432744	-0.817623	2.328474
17	6	0	9.983550	1.434413	1.953275
18	6	0	10.878811	1.802632	2.951309
19	6	0	11.342003	-0.514039	3.332526
20	7	0	8.416526	1.827697	0.234609
21	6	0	8.451485	4.571222	0.429534
22	6	0	9.217243	2.404460	1.151376
23	6	0	7.639619	2.548252	-0.598096
24	6	0	7.638826	3.936732	-0.518820
25	6	0	9.252005	3.787937	1.269532
26	7	0	6.983727	0.368945	-1.362064
27	6	0	5.304171	1.379405	-3.334683
28	6	0	6.293083	-0.454502	-2.160592
29	6	0	6.848138	1.716929	-1.523487
30	6	0	6.015182	2.241692	-2.507633
31	6	0	5.442369	0.008172	-3.156540
32	6	0	8.464079	6.041633	0.555314
33	6	0	8.372344	8.765363	0.796959
34	6	0	9.623852	6.741421	0.885198
35	6	0	7.299762	6.777061	0.353041
36	7	0	7.265252	8.097471	0.471775
37	6	0	9.574320	8.114646	1.006819
38	7	0	3.365035	-10.350635	-0.249625
39	6	0	0.977927	-11.710586	-0.414867
40	6	0	3.356969	-11.677988	-0.353964
41	6	0	2.219008	-9.683296	-0.219671
42	6	0	0.985685	-10.323683	-0.288219
43	6	0	2.176959	-12.390896	-0.448790
44	6	0	-0.266233	-9.544099	-0.236113
45	7	0	-2.616337	-8.122512	-0.123519
46	6	0	-1.344762	-9.890053	-1.057936
47	6	0	-0.399446	-8.461814	0.641518
48	6	0	-1.596595	-7.755829	0.675477
49	6	0	-2.523423	-9.158465	-0.979785
50	6	0	-1.918926	-6.611208	1.546084
51	6	0	-2.717633	-4.514796	3.137488
52	7	0	-3.187233	-6.122631	1.427017
53	6	0	-1.016740	-6.055023	2.448176
54	6	0	-1.418263	-4.994568	3.253226
55	6	0	-3.568520	-5.104430	2.210656
56	6	0	-3.751572	-9.383267	-1.762547
57	6	0	-6.125273	-9.661331	-3.119920
58	6	0	-3.891863	-10.410649	-2.689678
59	7	0	-4.771691	-8.512561	-1.517032
60	6	0	-5.924029	-8.657205	-2.181980
61	6	0	-5.091197	-10.553037	-3.377911
62	44	0	-4.326133	-7.096065	-0.038826
63	7	0	-5.405631	-8.184090	1.391045
64	6	0	-7.092860	-9.444127	3.204605
65	6	0	-5.013476	-9.289224	2.035120
66	6	0	-6.649301	-7.681485	1.634256
67	6	0	-7.507818	-8.296704	2.539050
68	6	0	-5.824442	-9.949813	2.948131
69	7	0	-3.950131	-5.586107	-1.440645
70	6	0	-3.733172	-3.452147	-3.208541
71	6	0	-4.981511	-4.705237	-1.583411
72	6	0	-2.838097	-5.406948	-2.162213
73	6	0	-2.688467	-4.355814	-3.056932
74	6	0	-4.891301	-3.630669	-2.461879
75	7	0	-6.031205	-6.060569	0.036046
76	6	0	-8.379005	-4.637509	0.137008
77	6	0	-7.005390	-6.472944	0.870079
78	6	0	-6.165250	-4.973461	-0.747639
79	6	0	-7.344402	-4.236703	-0.716652
80	6	0	-8.201679	-5.769574	0.940589
81	6	0	-9.651695	-3.889215	0.181638
82	6	0	-11.947645	-2.417297	0.244852
83	6	0	-10.881142	-4.541445	0.178375
84	6	0	-9.652234	-2.499432	0.219271
85	7	0	-10.771829	-1.796598	0.256078
86	6	0	-12.038822	-3.795139	0.202940
87	7	0	-10.674552	2.269565	0.530585
88	6	0	-10.659697	5.035722	0.695142
89	6	0	-11.813725	2.935675	0.801984
90	6	0	-9.530282	2.950029	0.339885
91	6	0	-9.471933	4.344096	0.419570
92	6	0	-11.840040	4.322383	0.884522
93	6	0	-8.189448	5.050130	0.224868
94	7	0	-5.802691	6.373516	-0.112757
95	6	0	-7.871289	6.155514	1.022325
96	6	0	-7.275365	4.626879	-0.747009
97	6	0	-6.073578	5.310469	-0.895171
98	6	0	-6.659821	6.809491	0.830871
99	6	0	-4.994171	4.997287	-1.848610
100	6	0	-2.884623	4.569688	-3.557637
101	7	0	-3.886686	5.787958	-1.759561
102	6	0	-5.073044	3.975761	-2.789690
103	6	0	-4.007590	3.757970	-3.654586
104	6	0	-2.864909	5.572230	-2.597098
105	7	0	3.835022	10.167640	-0.266238
106	6	0	1.508727	11.609274	-0.655719
107	6	0	2.651391	9.537788	-0.287227
108	6	0	3.892587	11.499707	-0.439448
109	6	0	2.742715	12.250017	-0.646867
110	6	0	1.447023	10.221534	-0.469858
111	6	0	0.163870	9.490492	-0.460564
112	7	0	-2.244271	8.159225	-0.410131
113	6	0	-0.020673	8.382776	0.376722
114	6	0	-0.896284	9.906613	-1.274671
115	6	0	-2.102980	9.219499	-1.228794
116	6	0	-1.244871	7.724293	0.380161
117	6	0	-1.617361	6.564326	1.209886
118	6	0	-2.490124	4.411995	2.684364
119	6	0	-0.730521	5.915554	2.064463
120	7	0	-2.910381	6.146095	1.088179
121	6	0	-3.325389	5.096369	1.810210
122	6	0	-1.170143	4.828017	2.812220

123	6	0	-3.323403	9.534857	-1.991949
124	6	0	-5.692726	9.997501	-3.299957
125	7	0	-4.408315	8.759249	-1.709797
126	6	0	-3.392384	10.549661	-2.939853
127	6	0	-4.589600	10.785253	-3.603043
128	6	0	-5.558151	8.994918	-2.349534
129	44	0	-4.027145	7.269210	-0.285665
130	7	0	-4.908412	8.397959	1.245963
131	6	0	-6.346066	9.715191	3.227900
132	6	0	-6.158658	7.972010	1.585762
133	6	0	-4.388590	9.455296	1.879658
134	6	0	-5.072179	10.142202	2.874544
135	6	0	-6.893320	8.617954	2.575038
136	7	0	6.957051	-8.409055	-0.153847
137	6	0	9.411846	-7.128086	-0.131346
138	6	0	7.016379	-7.069062	-0.123782
139	6	0	8.093365	-9.127839	-0.169418
140	6	0	9.338944	-8.515293	-0.166827
141	6	0	8.229642	-6.379408	-0.103198
142	6	0	8.245164	-4.902872	-0.062143
143	7	0	8.297365	-2.157450	0.033450
144	6	0	7.382290	-4.207204	0.791271
145	6	0	9.134120	-4.182370	-0.868748
146	6	0	9.141783	-2.793583	-0.800899
147	6	0	7.427550	-2.818442	0.820282
148	46	0	5.540293	9.120488	0.102147
149	46	0	-10.705368	0.232560	0.393657
150	46	0	5.150234	-9.363667	-0.191209
151	17	0	-9.623456	0.333564	-1.702988
152	17	0	-11.753109	0.096550	2.503322
153	17	0	5.333563	8.060834	-1.997455
154	17	0	5.704248	10.174583	2.207009
155	17	0	4.443918	-7.972223	-1.962313
156	17	0	5.833256	-10.737769	1.600589
157	1	0	4.323522	-12.165434	-0.352016
158	1	0	2.208692	-13.470485	-0.535788
159	1	0	0.039329	-12.253596	-0.463469
160	1	0	-1.248758	-10.706702	-1.763737
161	1	0	2.297763	-8.603980	-0.172212
162	1	0	0.413978	-8.198429	1.306965
163	1	0	-3.074215	-11.097951	-2.871560
164	1	0	-5.212657	-11.350890	-4.102642
165	1	0	-7.078729	-9.733965	-3.630212
166	1	0	7.983505	-10.205046	-0.175377
167	1	0	10.234421	-9.125331	-0.181468
168	1	0	6.066843	-6.546560	-0.147654
169	1	0	10.376487	-6.630263	-0.107439
170	1	0	9.796004	-4.706661	-1.548004
171	1	0	6.704811	-4.751606	1.438692
172	1	0	4.149189	-1.830741	3.985861
173	1	0	5.454094	-3.454688	2.645367
174	1	0	4.619470	0.621249	3.705875
175	1	0	6.374882	1.320135	2.094505
176	1	0	11.068904	-3.368850	-2.698745
177	1	0	12.467441	-1.702755	-3.889674
178	1	0	12.146188	0.735892	-3.373773
179	1	0	10.432029	1.382504	-1.693676
180	1	0	10.223545	-1.844908	2.051815
181	1	0	11.856835	-1.315888	3.848933
182	1	0	12.269911	1.094486	4.428951
183	1	0	6.433942	-1.515820	-1.989654
184	1	0	4.906991	-0.702078	-3.775940
185	1	0	4.654040	1.776883	-4.106590
186	1	0	5.923478	3.314133	-2.631487
187	1	0	7.035201	4.524699	-1.199563
188	1	0	9.869752	4.258408	2.025226
189	1	0	11.039530	2.848852	3.182394
190	1	0	10.564628	6.217300	1.020092
191	1	0	6.359162	6.300002	0.106901
192	1	0	10.458548	8.688673	1.257174
193	1	0	-6.703857	-7.940292	-1.950310
194	1	0	-5.458356	-10.842604	3.441716
195	1	0	-7.754178	-9.933948	3.911146
196	1	0	-8.494038	-7.887071	2.722181
197	1	0	-4.015212	-9.646427	1.808469
198	1	0	-0.008784	-6.445536	2.523270
199	1	0	-0.724333	-4.554012	3.960918
200	1	0	-3.076670	-3.694144	3.747684
201	1	0	-4.586740	-4.755070	2.081874
202	1	0	-2.047794	-6.134141	-2.012521
203	1	0	-1.766630	-4.258144	-3.618573
204	1	0	-3.651316	-2.618037	-3.897013
205	1	0	-5.717707	-2.937204	-2.563008
206	1	0	-4.058434	2.965677	-4.393587
207	1	0	-2.030754	4.438478	-4.212122
208	1	0	-2.008039	6.227283	-2.485511
209	1	0	2.684070	8.459225	-0.182146
210	1	0	8.274620	9.839003	0.897282
211	1	0	4.876069	11.952690	-0.405252
212	1	0	2.819533	13.322360	-0.782647
213	1	0	0.599262	12.188659	-0.779041
214	1	0	-0.770896	10.747750	-1.945760
215	1	0	0.770641	8.068365	1.046332
216	1	0	0.296207	6.252323	2.144325
217	1	0	-0.488196	4.315382	3.482085
218	1	0	-2.877862	3.570156	3.246335
219	1	0	-2.518073	11.149934	-3.161875
220	1	0	-4.656080	11.573372	-4.345235
221	1	0	-6.648543	10.146568	-3.788821
222	1	0	-6.391944	8.353790	-2.087089
223	1	0	-3.391774	9.752881	1.575855
224	1	0	-4.605445	10.994536	3.354484
225	1	0	-6.910422	10.228021	3.999190
226	1	0	-7.886524	8.270699	2.833302
227	1	0	-8.554232	6.477516	1.799269
228	1	0	-10.664362	6.120497	0.742957
229	1	0	-12.775938	4.828542	1.090701
230	1	0	-12.700055	2.333459	0.959860
231	1	0	-8.648104	2.354393	0.135031
232	1	0	-8.730467	-1.929766	0.227637
233	1	0	-7.475322	-3.374976	-1.360891
234	1	0	-8.987219	-6.080013	1.619634
235	1	0	-10.927570	-5.625111	0.136341
236	1	0	-13.013376	-4.268299	0.185951
237	1	0	-12.825951	-1.785339	0.278469
238	1	0	-7.512950	3.784204	-1.385505
239	1	0	-5.960113	3.356543	-2.851335
240	1	0	-4.360261	4.800792	1.677819

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