

Supporting Information

The Effect of Solvent and Coordination Environment of Metal Source on the Self-Assembly Pathway of a Pd(II)-mediated Coordination Capsule

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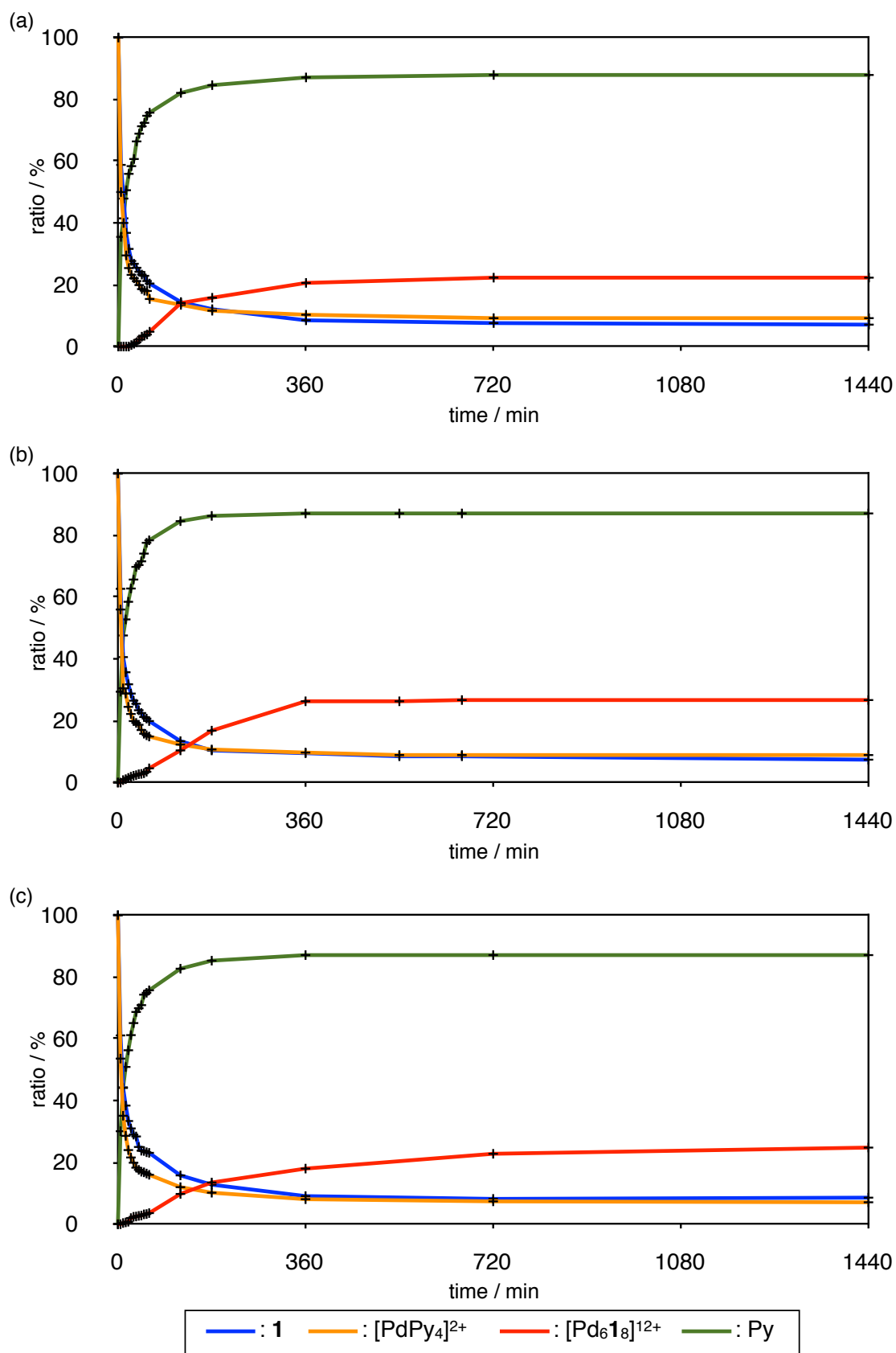


Figure S1. Existence ratios of the substrates ($\mathbf{1}$ and $[\text{PdPy}_4]^{2+}$) and the products ($[\text{Pd}_6\mathbf{1}_8]^{12+}$ and Py) for the self-assembly of the $\text{Pd}_6\mathbf{1}_8$ capsule from $\mathbf{1}$ and $[\text{PdPy}_4]^{2+}$ in $\text{CD}_3\text{NO}_2/\text{CD}_2\text{Cl}_2$ (v/v = 4/1) at 298 K. (a) run 1, (b) run 2, (c) run 3.

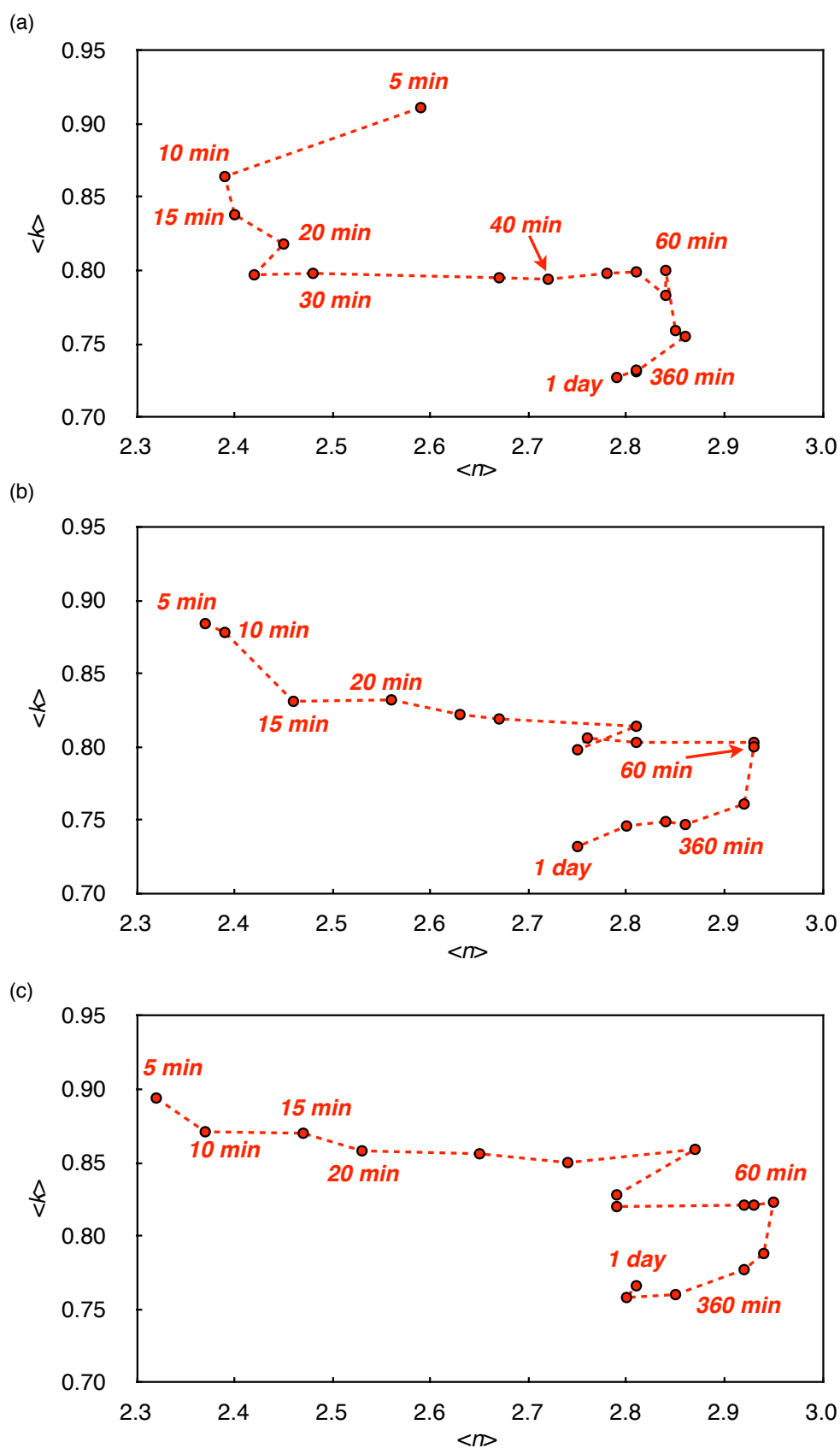


Figure S2. The $\langle n \rangle$, $\langle k \rangle$ plots for the self-assembly of the $\text{Pd}_6\mathbf{1}_8$ capsule from **1** and $[\text{PdPy}_4]^{2+}$ in $\text{CD}_3\text{NO}_2/\text{CD}_2\text{Cl}_2$ ($v/v = 4/1$) at 298 K. (a) run 1, (b) run 2, (c) run 3.

Table S1 The quantities of **1**, [PdPy₄]²⁺, Py, and [Pd₆**1**₈]¹²⁺ and the (<*n*>, <*k*>) values at each time point for the self-assembly of [Pd₆**1**₈]¹²⁺ from **1** and [PdPy₄]²⁺ in CD₃NO₂/CD₂Cl₂ (v/v = 4/1) (run 1).

Time (min)	1 (%)	[PdPy ₄] ²⁺ (%)	Py (%)	[Pd ₆ 1 ₈] ¹²⁺ (%)	<i>a</i>	<i>b</i>	<i>c</i>	< <i>n</i> >	< <i>k</i> >
0	100	100	0	0	—	—	—	—	—
5	58.8	50.0	35.5	0	0.166	0.182	0.192	2.59	0.911
10	47.9	40.0	41.5	0	0.199	0.230	0.246	2.39	0.864
15	36.8	29.5	50.6	0	0.234	0.279	0.264	2.40	0.838
20	31.6	25.4	55.9	0	0.247	0.302	0.247	2.45	0.818
25	27.7	23.2	58.4	0.5	0.253	0.317	0.244	2.42	0.797
30	26.8	22.1	60.7	0.9	0.255	0.320	0.228	2.48	0.798
35	25.5	21.2	66.4	1.4	0.257	0.323	0.164	2.67	0.795
40	24.2	19.9	68.9	2.3	0.258	0.325	0.148	2.72	0.794
45	23.3	18.6	71.3	3.2	0.259	0.325	0.133	2.78	0.798
50	22.9	18.1	72.4	3.5	0.260	0.325	0.126	2.81	0.799
55	21.2	18.0	74.7	3.9	0.259	0.331	0.098	2.84	0.783
60	20.4	15.4	75.7	4.8	0.265	0.331	0.119	2.84	0.800
120	14.4	13.5	82.1	14.1	0.240	0.316	0.058	2.85	0.759
180	12.1	11.6	84.6	15.8	0.241	0.319	0.050	2.86	0.755
360	8.5	10.3	87.1	20.6	0.229	0.313	0.035	2.81	0.731
720	7.6	9.2	87.9	22.3	0.227	0.310	0.038	2.81	0.732
1440	7.1	9.2	87.9	22.3	0.227	0.312	0.038	2.79	0.727

Table S2 The quantities of **1**, [PdPy₄]²⁺, Py, and [Pd₆**1**₈]¹²⁺ and the (<*n*>, <*k*>) values at each time point for the self-assembly of [Pd₆**1**₈]¹²⁺ from **1** and [PdPy₄]²⁺ in CD₃NO₂/CD₂Cl₂ (v/v = 4/1) (run 2).

Time (min)	1 (%)	[PdPy ₄] ²⁺ (%)	Py (%)	[Pd ₆ 1 ₈] ¹²⁺ (%)	<i>a</i>	<i>b</i>	<i>c</i>	< <i>n</i> >	< <i>k</i> >
0	100	100	0	0	—	—	—	—	—
5	62.7	56.0	29.4	0	0.146	0.165	0.193	2.37	0.884
10	40.6	30.5	47.6	0.8	0.228	0.259	0.291	2.39	0.878
15	35.7	28.8	52.8	1.1	0.232	0.279	0.243	2.46	0.831
20	31.8	24.5	58.5	1.5	0.245	0.295	0.226	2.56	0.832
25	28.8	22.2	62.8	1.9	0.252	0.306	0.200	2.63	0.822
30	26.5	19.9	65.7	2.2	0.258	0.315	0.191	2.67	0.819
35	25.5	19.3	69.8	2.4	0.259	0.319	0.143	2.81	0.814
40	23.4	18.7	70.4	2.7	0.261	0.327	0.145	2.75	0.798
45	22.5	17.0	71.6	2.8	0.266	0.330	0.152	2.76	0.806
50	21.2	15.8	74.1	3.0	0.269	0.335	0.134	2.81	0.803
55	20.7	15.3	77.6	3.5	0.269	0.335	0.093	2.93	0.803
60	19.9	14.9	78.4	4.6	0.267	0.334	0.089	2.93	0.800
120	13.4	12.3	84.6	10.4	0.256	0.337	0.041	2.92	0.761
180	10.4	10.7	86.3	16.8	0.240	0.322	0.041	2.86	0.747
360	9.5	9.7	87.1	26.3	0.212	0.284	0.043	2.84	0.749
540	8.5	8.9	87.1	26.3	0.215	0.288	0.053	2.80	0.746
660	8.5	8.9	87.1	26.7	0.213	0.286	0.053	2.80	0.746
1440	7.4	8.9	87.1	26.7	0.213	0.291	0.053	2.75	0.732

Table S3 The quantities of **1**, [PdPy₄]²⁺, Py, and [Pd₆**1**₈]¹²⁺ and the (<*n*>, <*k*>) values at each time point for the self-assembly of [Pd₆**1**₈]¹²⁺ from **1** and [PdPy₄]²⁺ in CD₃NO₂/CD₂Cl₂ (v/v = 4/1) (run 3).

Time (min)	1 (%)	[PdPy ₄] ²⁺ (%)	Py (%)	[Pd ₆ 1 ₈] ¹²⁺ (%)	<i>a</i>	<i>b</i>	<i>c</i>	< <i>n</i> >	< <i>k</i> >
0	100.0	100.0	0	0	—	—	—	—	—
5	61.1	53.6	30.1	0	0.148	0.165	0.208	2.32	0.894
10	44.1	35.1	44.3	0.4	0.206	0.236	0.262	2.37	0.871
15	38.4	28.6	50.9	0.6	0.226	0.259	0.261	2.47	0.870
20	33.4	24.0	56.3	0.8	0.240	0.280	0.252	2.53	0.858
25	31.0	21.6	61.2	2.0	0.244	0.285	0.220	2.65	0.856
30	29.0	19.9	65.1	2.4	0.248	0.291	0.192	2.74	0.850
35	28.4	18.3	68.7	2.5	0.252	0.294	0.166	2.87	0.859
40	25.0	17.6	69.9	2.7	0.254	0.307	0.160	2.79	0.828
45	23.8	17.0	70.9	2.8	0.255	0.312	0.154	2.79	0.820
50	23.7	16.8	74.3	3.2	0.255	0.311	0.114	2.92	0.821
55	23.3	16.4	74.9	3.3	0.256	0.312	0.112	2.93	0.821
60	23.1	16.0	75.7	3.6	0.256	0.311	0.105	2.95	0.823
120	15.8	12.0	82.7	9.8	0.249	0.316	0.066	2.94	0.788
180	12.8	10.2	85.3	13.5	0.243	0.313	0.058	2.92	0.777
360	9.1	8.1	87.1	18.0	0.235	0.310	0.060	2.85	0.760
720	8.2	7.4	87.1	22.8	0.222	0.293	0.069	2.80	0.758
1440	8.6	7.1	87.1	24.8	0.217	0.283	0.073	2.81	0.766

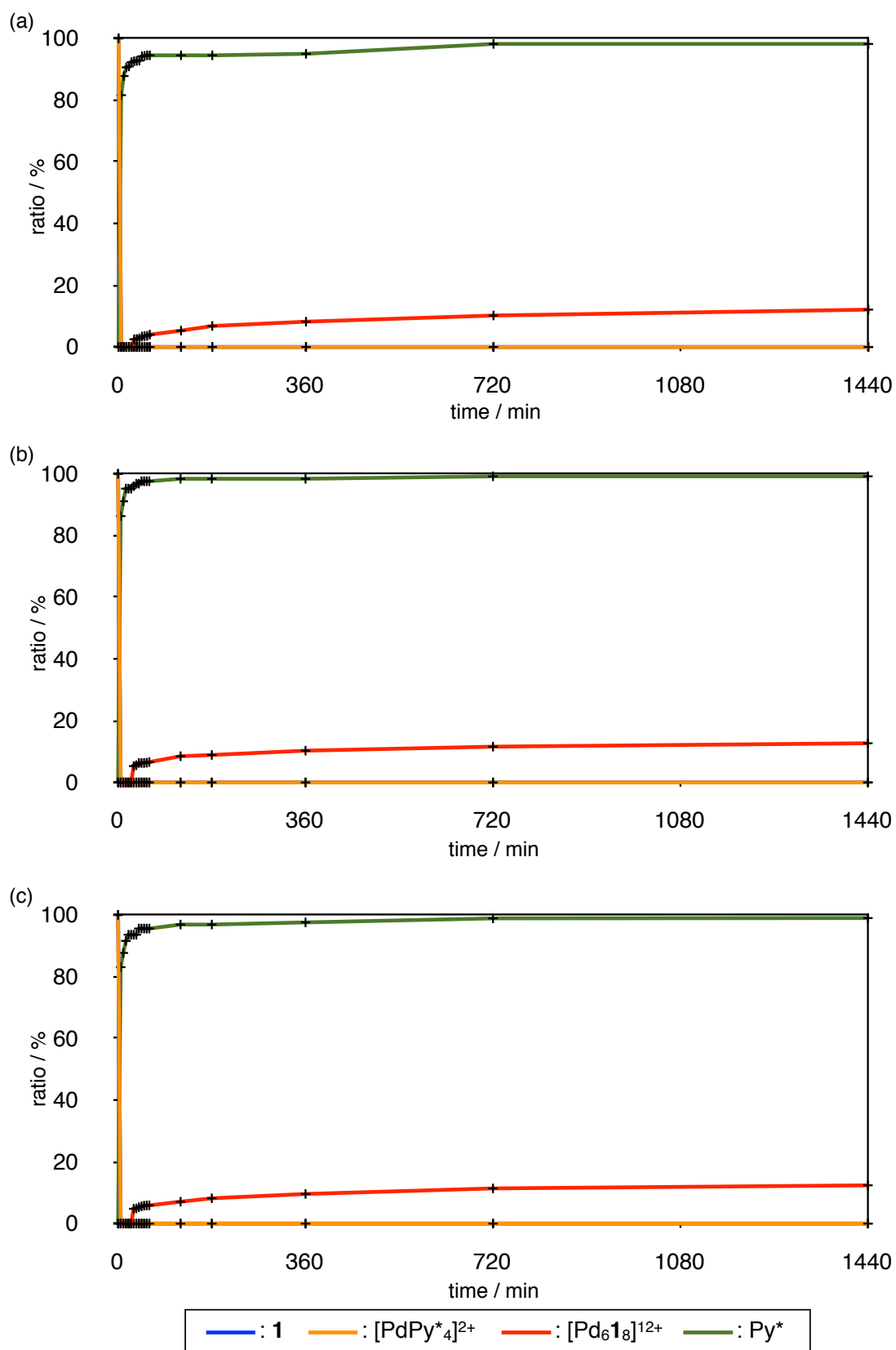


Figure S3. Existence ratios of the substrates (**1** and $[\text{PdPy}^*_4]^{2+}$) and the products ($[\text{Pd}_6\mathbf{1}_8]^{12+}$ and Py^*) for the self-assembly of the $\text{Pd}_6\mathbf{1}_8$ capsule from **1** and $[\text{PdPy}^*_4]^{2+}$ in $\text{CD}_3\text{NO}_2/\text{CD}_2\text{Cl}_2$ (v/v = 4/1) at 298 K. (a) run 1, (b) run 2, (c) run 3.

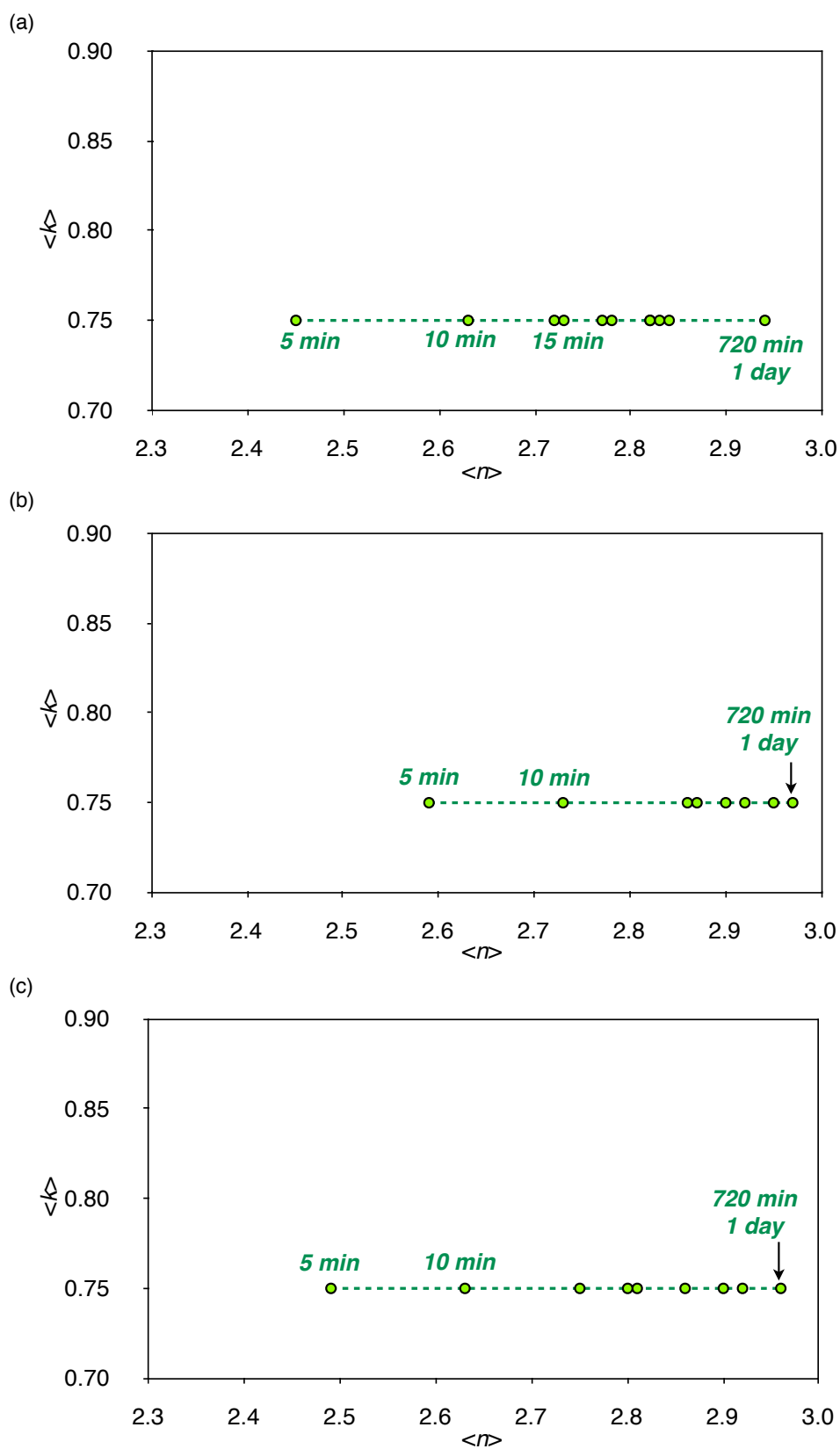


Figure S4. The ($\langle n \rangle$, $\langle k \rangle$) plots for the self-assembly of the Pd₆1₈ capsule from **1** and [PdPy*₄]²⁺ in CD₃NO₂/CD₂Cl₂ (v/v = 4/1) at 298 K. (a) run 1, (b) run 2, (c) run 3.

Table S4 The quantities of **1**, [PdPy*₄]²⁺, Py*, and [Pd₆**1**₈]¹²⁺ and the (<*n*>, <*k*>) values at each time point for the self-assembly of [Pd₆**1**₈]¹²⁺ from **1** and [PdPy*₄]²⁺ in CD₃NO₂/CD₂Cl₂ (v/v = 4/1) (run 1).

Time (min)	1 (%)	[PdPy* ₄] ²⁺ (%)	Py* (%)	[Pd ₆ 1 ₈] ¹²⁺ (%)	<i>a</i>	<i>b</i>	<i>c</i>	< <i>n</i> >	< <i>k</i> >
0	100	100	0	0	–	–	–	–	–
5	0	0	81.6	0	0.352	0.469	0.259	2.45	0.750
10	0	0	87.8	0	0.352	0.469	0.172	2.63	0.750
15	0	0	90.6	0	0.352	0.469	0.133	2.72	0.750
20	0	0	90.9	0	0.352	0.469	0.128	2.73	0.750
25	0	0	92.3	0	0.352	0.469	0.109	2.77	0.750
30	0	0	92.6	2.5	0.343	0.458	0.104	2.77	0.750
35	0	0	92.7	2.6	0.343	0.457	0.102	2.78	0.750
40	0	0	92.8	2.8	0.342	0.456	0.102	2.78	0.750
45	0	0	94.2	3.4	0.340	0.453	0.081	2.82	0.750
50	0	0	94.3	3.5	0.340	0.453	0.081	2.82	0.750
55	0	0	94.5	3.6	0.339	0.453	0.078	2.83	0.750
60	0	0	94.5	4.1	0.338	0.450	0.078	2.83	0.750
120	0	0	94.5	5.3	0.333	0.444	0.078	2.83	0.750
180	0	0	94.5	6.8	0.328	0.437	0.078	2.82	0.750
360	0	0	95.0	8.2	0.323	0.431	0.070	2.84	0.750
720	0	0	98.2	10.2	0.316	0.421	0.026	2.94	0.750
1440	0	0	98.2	12.1	0.309	0.413	0.025	2.94	0.750

Table S5 The quantities of **1**, [PdPy*₄]²⁺, Py*, and [Pd₆**1**₈]¹²⁺ and the (<*n*>, <*k*>) values at each time point for the self-assembly of [Pd₆**1**₈]¹²⁺ from **1** and [PdPy*₄]²⁺ in CD₃NO₂/CD₂Cl₂ (v/v = 4/1) (run 2).

Time (min)	1 (%)	[PdPy* ₄] ²⁺ (%)	Py* (%)	[Pd ₆ 1 ₈] ¹²⁺ (%)	<i>a</i>	<i>b</i>	<i>c</i>	< <i>n</i> >	< <i>k</i> >
0	100	100	0	0	–	–	–	–	–
5	0	0	86.3	0	0.349	0.466	0.192	2.59	0.750
10	0	0	91.1	0	0.349	0.466	0.124	2.73	0.750
15	0	0	95.2	0	0.349	0.466	0.068	2.86	0.750
20	0	0	95.2	0	0.349	0.466	0.068	2.86	0.750
25	0	0	95.2	0	0.349	0.466	0.068	2.86	0.750
30	0	0	96.0	5.3	0.331	0.441	0.056	2.87	0.750
35	0	0	96.8	5.6	0.330	0.440	0.045	2.90	0.750
40	0	0	96.8	6.3	0.327	0.436	0.045	2.90	0.750
45	0	0	97.6	6.3	0.327	0.436	0.034	2.92	0.750
50	0	0	97.6	6.3	0.328	0.437	0.034	2.92	0.750
55	0	0	97.6	6.4	0.327	0.436	0.034	2.92	0.750
60	0	0	97.6	6.6	0.326	0.435	0.034	2.92	0.750
120	0	0	98.4	8.5	0.320	0.426	0.022	2.95	0.750
180	0	0	98.4	8.9	0.318	0.425	0.022	2.95	0.750
360	0	0	98.4	10.3	0.313	0.418	0.022	2.95	0.750
720	0	0	99.2	11.6	0.309	0.412	0.011	2.97	0.750
1440	0	0	99.2	12.7	0.305	0.407	0.011	2.97	0.750

Table S6 The quantities of **1**, [PdPy*₄]²⁺, Py*, and [Pd₆**1**₈]¹²⁺ and the (<*n*>, <*k*>) values at each time point for the self-assembly of [Pd₆**1**₈]¹²⁺ from **1** and [PdPy*₄]²⁺ in CD₃NO₂/CD₂Cl₂ (v/v = 4/1) (run 3).

Time (min)	1 (%)	[PdPy* ₄] ²⁺ (%)	Py* (%)	[Pd ₆ 1 ₈] ¹²⁺ (%)	<i>a</i>	<i>b</i>	<i>c</i>	< <i>n</i> >	< <i>k</i> >
0	100	100	0	0	–	–	–	–	–
5	0	0	83.1	0	0.436	0.581	0.295	2.49	0.750
10	0	0	87.7	0	0.436	0.581	0.215	2.63	0.750
15	0	0	91.6	0	0.436	0.581	0.146	2.75	0.750
20	0	0	93.6	0	0.436	0.581	0.111	2.81	0.750
25	0	0	93.6	0	0.436	0.581	0.111	2.81	0.750
30	0	0	93.6	4.8	0.415	0.553	0.111	2.80	0.750
35	0	0	93.6	4.9	0.415	0.553	0.111	2.80	0.750
40	0	0	95.6	5.3	0.413	0.551	0.077	2.86	0.750
45	0	0	95.6	5.6	0.412	0.549	0.077	2.86	0.750
50	0	0	95.6	5.8	0.411	0.548	0.077	2.86	0.750
55	0	0	95.6	5.9	0.410	0.547	0.077	2.86	0.750
60	0	0	95.6	5.9	0.410	0.547	0.077	2.86	0.750
120	0	0	96.9	7.1	0.405	0.540	0.054	2.90	0.750
180	0	0	96.9	8.2	0.400	0.534	0.054	2.90	0.750
360	0	0	97.6	9.6	0.394	0.525	0.042	2.92	0.750
720	0	0	98.9	11.4	0.386	0.515	0.019	2.96	0.750
1440	0	0	99.0	12.4	0.382	0.509	0.018	2.96	0.750

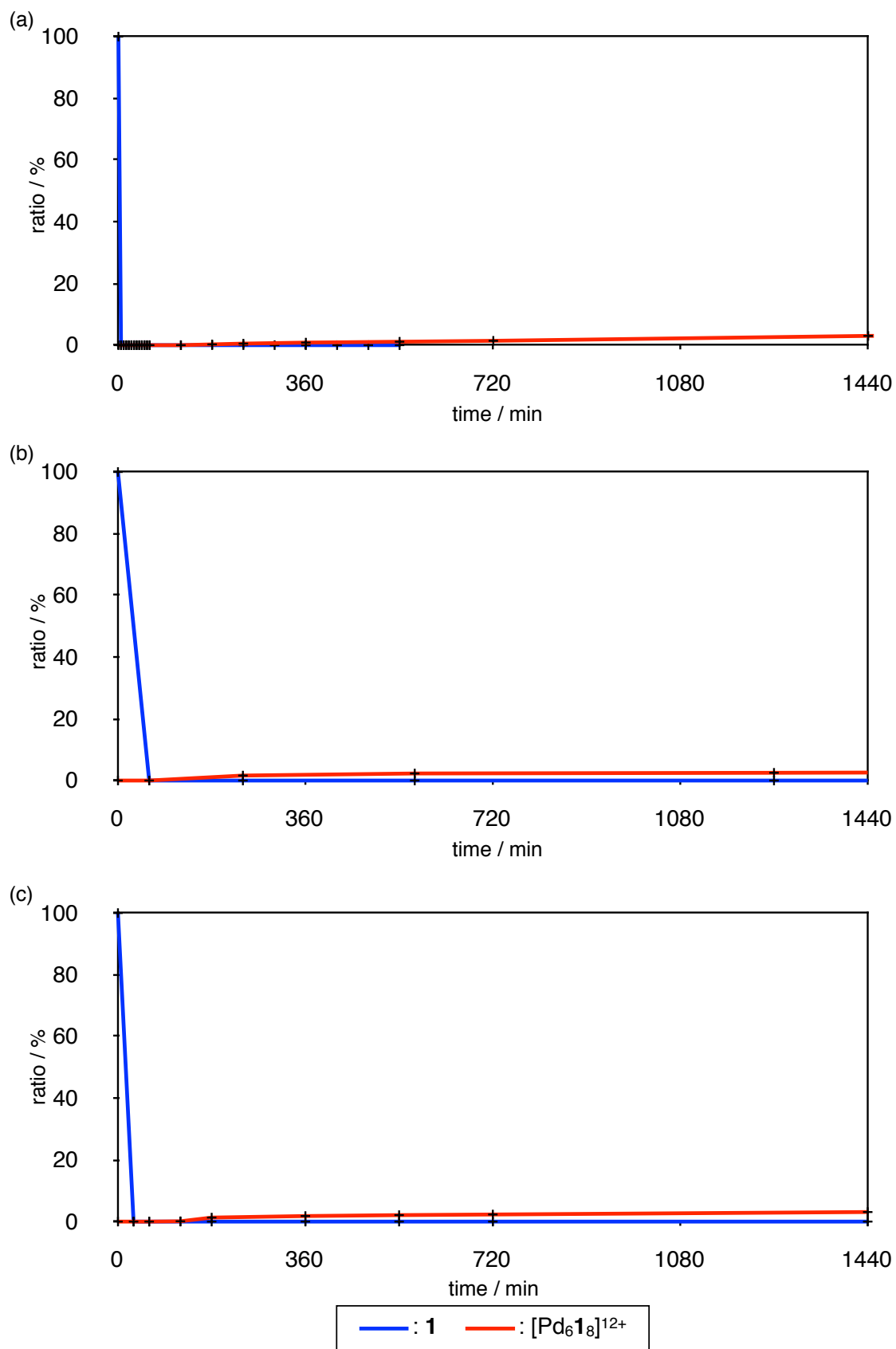


Figure S5. Existence ratios of **1** and $[\text{Pd}_6\mathbf{1}_8]^{12+}$ for the self-assembly of the $\text{Pd}_6\mathbf{1}_8$ capsule from **1** and $[\text{Pd}(\text{CH}_3\text{CN})_4]^{2+}$ in $\text{CD}_3\text{NO}_2/\text{CD}_2\text{Cl}_2$ ($v/v = 4/1$) at 298 K. (a) run 1, (b) run 2, (c) run 3.

Table S7 The quantities of **1** and $[\text{Pd}_6\mathbf{1}_8]^{12+}$ at each time point for the assembly of $[\text{Pd}_6\mathbf{1}_8]^{12+}$ from **1** and $[\text{Pd}(\text{CH}_3\text{CN})_4]^{2+}$ in $\text{CD}_3\text{NO}_2/\text{CD}_2\text{Cl}_2$ (v/v = 4/1) (run 1).

Time (min)	1 (%)	$[\text{Pd}_6\mathbf{1}_8]^{12+}$ (%)
0	100	0
5	0	0
10	0	0
15	0	0
20	0	0
25	0	0
30	0	0
35	0	0
40	0	0
45	0	0
50	0	0
55	0	0
60	0	0
120	0	0
180	0	0.3
360	0	0.5
720	0	0.8
1440	0	1.1

Table S8 The quantities of **1** and $[\text{Pd}_6\mathbf{1}_8]^{12+}$ at each time point for the assembly of $[\text{Pd}_6\mathbf{1}_8]^{12+}$ from **1** and $[\text{Pd}(\text{CH}_3\text{CN})_4]^{2+}$ in $\text{CD}_3\text{NO}_2/\text{CD}_2\text{Cl}_2$ (v/v = 4/1) (run 2).

Time (min)	1 (%)	$[\text{Pd}_6\mathbf{1}_8]^{12+}$ (%)
0	100	0
60	0	0
240	0	1.6
570	0	2.2
1260	0	2.5
1680	0	2.6

Table S9 The quantities of **1** and $[\text{Pd}_6\mathbf{1}_8]^{12+}$ at each time point for the assembly of $[\text{Pd}_6\mathbf{1}_8]^{12+}$ from **1** and $[\text{Pd}(\text{CH}_3\text{CN})_4]^{2+}$ in $\text{CD}_3\text{NO}_2/\text{CD}_2\text{Cl}_2$ (v/v = 4/1) (run 3).

Time (min)	1 (%)	$[\text{Pd}_6\mathbf{1}_8]^{12+}$ (%)
0	100	0
30	0	0
60	0	0
120	0	0.1
180	0	1.3
360	0	1.8
540	0	2.1
720	0	2.3
1440	0	3.1

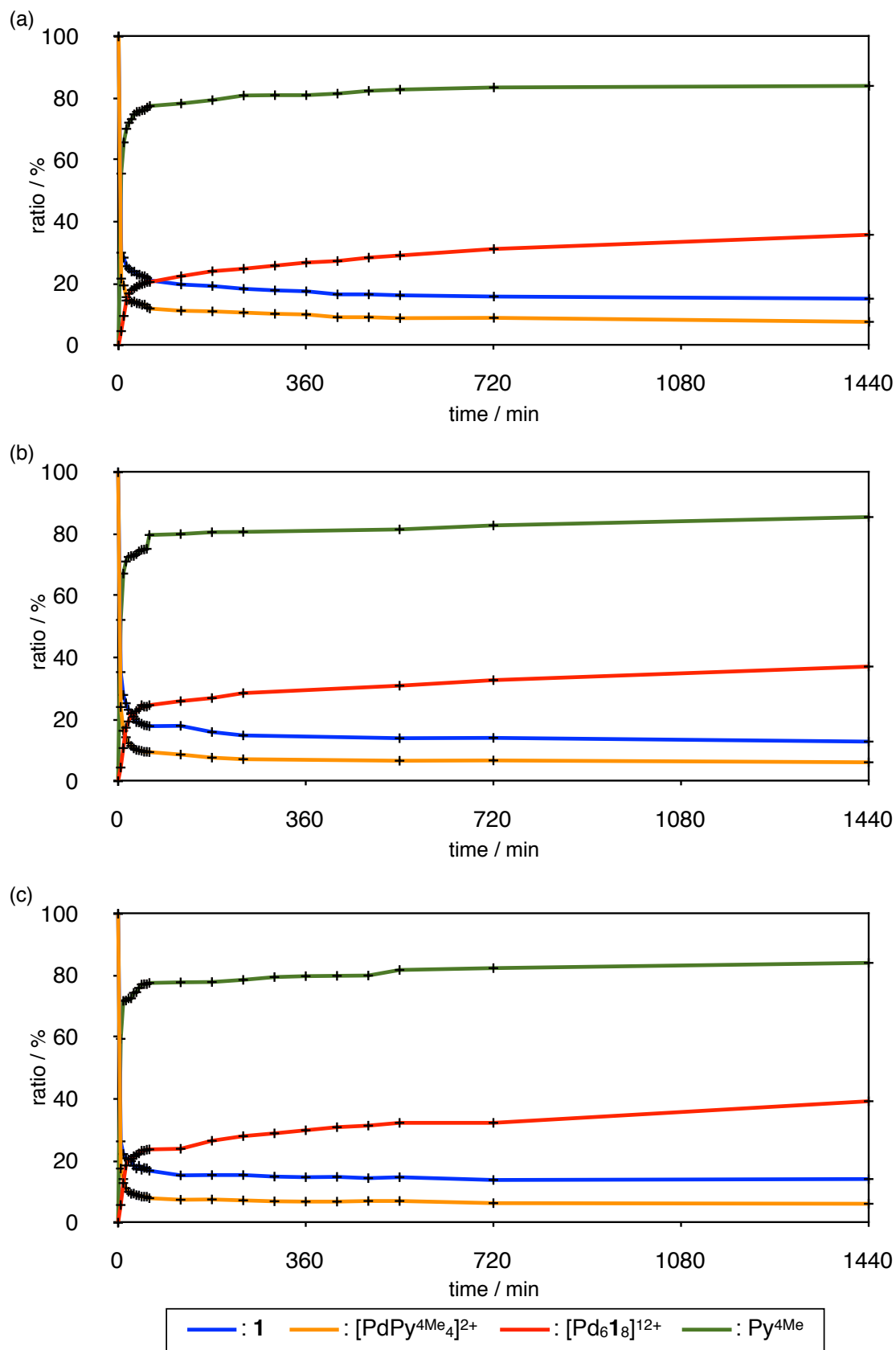


Figure S6. Existence ratios of the substrates ($\mathbf{1}$ and $[\text{Pd}(\text{Py}^{4\text{Me}})_4]^{2+}$) and the products ($[\text{Pd}_6\mathbf{1}_8]^{12+}$ and $\text{Py}^{4\text{Me}}$) for the self-assembly of the $\text{Pd}_6\mathbf{1}_8$ capsule from $\mathbf{1}$ and $[\text{Pd}(\text{Py}^{4\text{Me}})_4]^{2+}$ in $\text{CD}_3\text{NO}_2/\text{CD}_2\text{Cl}_2$ (v/v = 4/1) at 298 K. (a) run 1, (b) run 2, (c) run 3.

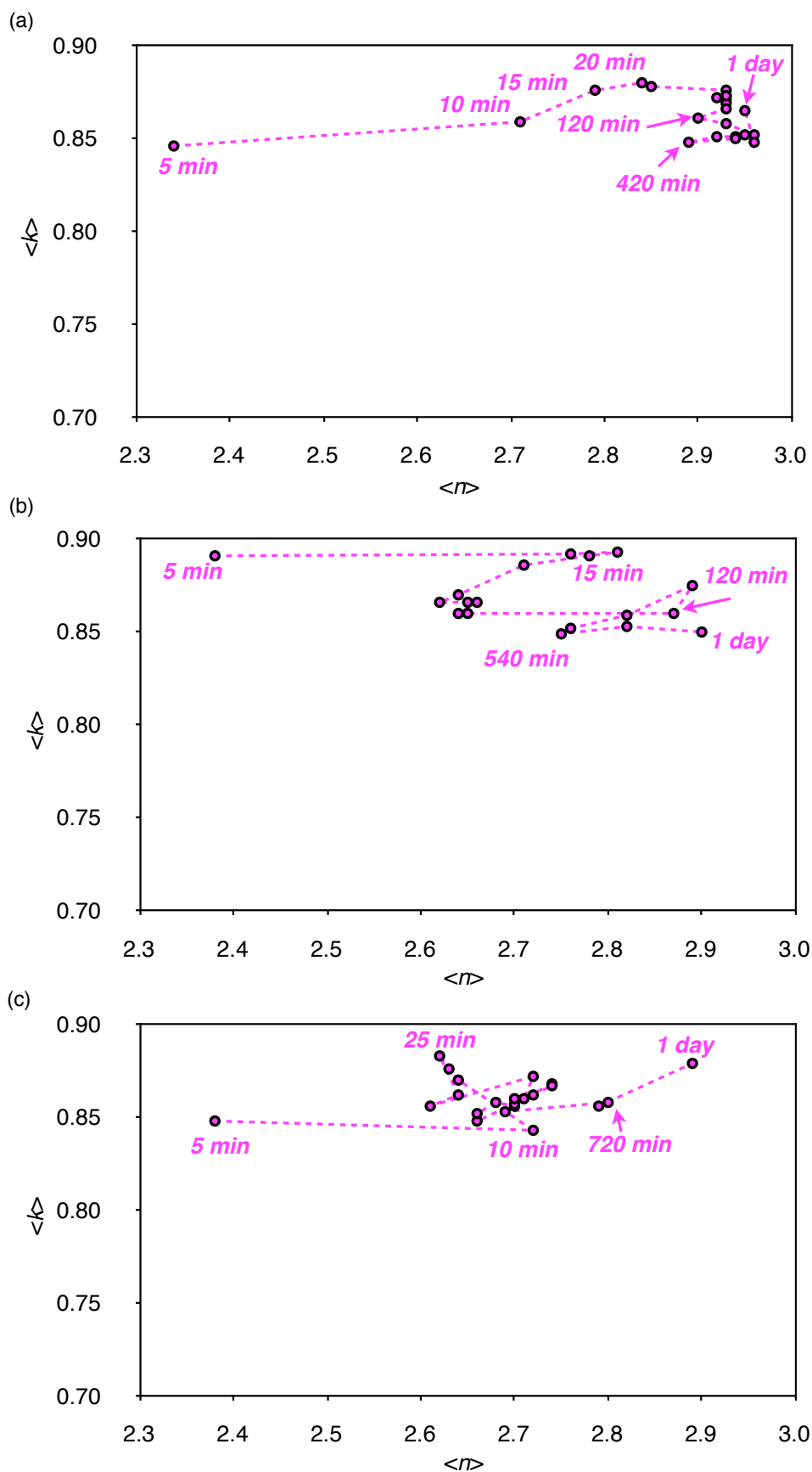


Figure S7. The $\langle n \rangle$, $\langle k \rangle$ plots for the self-assembly of the $\text{Pd}_6\mathbf{1}_8$ capsule from **1** and $[\text{Pd}(\text{Py}^{4\text{Me}})_4]^{2+}$ in $\text{CD}_3\text{NO}_2/\text{CD}_2\text{Cl}_2$ ($v/v = 4/1$) at 298 K. (a) run 1, (b) run 2, (c) run 3.

Table S10 The quantities of **1**, [Pd(Py^{4Me})₄]²⁺, Py^{4Me}, and [Pd₆**1**]¹²⁺ and the (<*n*>, <*k*>) values at each time point for the self-assembly of [Pd₆**1**]¹²⁺ from **1** and [Pd(Py^{4Me})₄]²⁺ in CD₃NO₂/CD₂Cl₂ (v/v = 4/1) (run 1).

Time (min)	1 (%)	[Pd(Py ^{4Me}) ₄] ²⁺ (%)	Py ^{4Me} (%)	[Pd ₆ 1] ¹²⁺ (%)	<i>a</i>	<i>b</i>	<i>c</i>	< <i>n</i> >	< <i>k</i> >
0	100	100	0	0	–	–	–	–	–
5	30.0	21.6	55.6	4.6	0.220	0.259	0.271	2.34	0.846
10	28.4	19.4	65.7	9.5	0.212	0.246	0.178	2.71	0.859
15	25.6	15.6	70.1	14.5	0.208	0.237	0.170	2.79	0.876
20	24.8	14.7	72.1	16.8	0.204	0.232	0.157	2.84	0.880
25	23.9	13.9	73.2	17.9	0.203	0.231	0.153	2.85	0.878
30	23.9	14.2	74.8	18.5	0.200	0.229	0.131	2.93	0.876
35	22.9	13.6	75.6	19.0	0.201	0.230	0.128	2.93	0.871
40	22.9	13.5	75.7	19.6	0.199	0.228	0.129	2.93	0.873
45	22.4	13.1	76.1	19.8	0.200	0.229	0.129	2.92	0.872
50	22.4	13.2	76.2	20.1	0.198	0.228	0.125	2.93	0.869
55	21.8	12.3	77.0	20.5	0.200	0.229	0.127	2.93	0.873
60	21.0	11.9	77.5	20.5	0.201	0.232	0.125	2.93	0.866
120	19.7	11.2	78.3	22.4	0.197	0.229	0.124	2.90	0.861
180	19.2	11.0	79.4	24.0	0.193	0.226	0.114	2.93	0.858
240	18.3	10.6	80.9	24.8	0.192	0.226	0.102	2.96	0.852
300	17.8	10.2	81.0	25.8	0.190	0.223	0.105	2.94	0.851
360	17.5	10.0	81.0	26.8	0.188	0.221	0.107	2.92	0.851
420	16.5	9.1	81.5	27.3	0.189	0.223	0.112	2.89	0.848
480	16.5	9.1	82.4	28.4	0.186	0.219	0.102	2.94	0.850
540	16.2	8.8	82.8	29.1	0.185	0.217	0.100	2.95	0.852
720	15.8	8.9	83.5	31.2	0.178	0.210	0.091	2.96	0.848
1440	15.1	7.6	84.0	35.8	0.168	0.195	0.099	2.95	0.865

Table S11 The quantities of **1**, $[\text{Pd}(\text{Py}^{4\text{Me}})_4]^{2+}$, $\text{Py}^{4\text{Me}}$, and $[\text{Pd}_6\mathbf{1}_8]^{12+}$ and the $\langle n \rangle$, $\langle k \rangle$ values at each time point for the self-assembly of $[\text{Pd}_6\mathbf{1}_8]^{12+}$ from **1** and $[\text{Pd}(\text{Py}^{4\text{Me}})_4]^{2+}$ in $\text{CD}_3\text{NO}_2/\text{CD}_2\text{Cl}_2$ (v/v = 4/1) (run 2).

Time (min)	1 (%)	$[\text{Pd}(\text{Py}^{4\text{Me}})_4]^{2+}$ (%)	$\text{Py}^{4\text{Me}}$ (%)	$[\text{Pd}_6\mathbf{1}_8]^{12+}$ (%)	<i>a</i>	<i>b</i>	<i>c</i>	$\langle n \rangle$	$\langle k \rangle$
0	100	100	0	0	–	–	–	–	–
5	35.3	24.0	52.2	4.4	0.215	0.241	0.286	2.38	0.891
10	27.9	16.3	67.2	10.7	0.219	0.245	0.197	2.76	0.892
15	25.2	14.2	71.1	17.3	0.206	0.230	0.176	2.81	0.893
20	23.1	12.3	72.6	19.3	0.205	0.230	0.181	2.78	0.891
25	21.7	11.4	72.9	22.0	0.200	0.225	0.188	2.71	0.886
30	20.1	10.6	72.9	20.9	0.205	0.236	0.198	2.64	0.870
35	19.1	10.1	73.5	22.7	0.202	0.233	0.197	2.62	0.866
40	19.0	10.0	74.4	23.3	0.200	0.231	0.188	2.65	0.866
45	18.6	9.8	74.9	24.6	0.197	0.227	0.184	2.66	0.866
50	18.1	9.5	75.0	24.1	0.199	0.232	0.186	2.64	0.860
55	18.0	9.5	75.2	24.1	0.199	0.232	0.183	2.65	0.860
60	17.8	9.4	79.7	24.6	0.198	0.230	0.131	2.87	0.860
120	17.9	8.6	80.0	25.9	0.197	0.225	0.138	2.89	0.875
180	15.9	7.6	80.6	26.9	0.196	0.229	0.142	2.82	0.859
240	14.8	7.1	80.7	28.5	0.193	0.227	0.147	2.76	0.852
540	13.9	6.6	81.5	30.9	0.188	0.221	0.143	2.75	0.849
720	14.0	6.7	82.8	32.7	0.182	0.213	0.126	2.82	0.853
1440	12.8	6.1	85.5	37.1	0.170	0.200	0.101	2.90	0.850

Table S12 The quantities of **1**, $[\text{Pd}(\text{Py}^{4\text{Me}})_4]^{2+}$, $\text{Py}^{4\text{Me}}$, and $[\text{Pd}_6\mathbf{1}_8]^{12+}$ and the $\langle n \rangle$, $\langle k \rangle$ values at each time point for the self-assembly of $[\text{Pd}_6\mathbf{1}_8]^{12+}$ from **1** and $[\text{Pd}(\text{Py}^{4\text{Me}})_4]^{2+}$ in $\text{CD}_3\text{NO}_2/\text{CD}_2\text{Cl}_2$ (v/v = 4/1) (run 3).

Time (min)	1 (%)	$[\text{Pd}(\text{Py}^{4\text{Me}})_4]^{2+}$ (%)	$\text{Py}^{4\text{Me}}$ (%)	$[\text{Pd}_6\mathbf{1}_8]^{12+}$ (%)	<i>a</i>	<i>b</i>	<i>c</i>	$\langle n \rangle$	$\langle k \rangle$
0	100	100	0	0	–	–	–	–	–
5	26.3	17.5	59.5	5.7	0.229	0.270	0.274	2.38	0.848
10	22.2	14.1	71.8	12.8	0.217	0.258	0.167	2.72	0.843
15	20.8	11.1	71.9	18.5	0.210	0.241	0.202	2.64	0.870
20	20.1	10.0	72.6	20.4	0.207	0.236	0.207	2.63	0.876
25	19.9	9.3	72.6	20.7	0.208	0.236	0.215	2.62	0.883
30	18.4	9.4	74.4	21.5	0.206	0.238	0.193	2.64	0.862
35	17.5	8.9	74.6	21.9	0.206	0.241	0.197	2.61	0.856
40	18.4	8.8	76.0	22.4	0.204	0.234	0.180	2.72	0.872
45	17.1	8.4	77.1	23.3	0.203	0.237	0.173	2.71	0.860
50	17.7	8.4	77.2	23.3	0.203	0.234	0.172	2.74	0.868
55	17.6	8.4	77.2	23.6	0.202	0.233	0.170	2.74	0.867
60	16.8	7.9	77.6	23.7	0.203	0.236	0.172	2.72	0.862
120	15.3	7.4	77.8	23.9	0.204	0.241	0.177	2.66	0.848
180	15.4	7.5	77.9	26.5	0.196	0.230	0.173	2.66	0.852
240	15.4	7.2	78.6	28.0	0.193	0.224	0.169	2.68	0.858
300	14.9	6.9	79.5	28.9	0.191	0.223	0.162	2.70	0.856
360	14.7	6.8	79.8	29.9	0.188	0.220	0.160	2.70	0.857
420	14.8	6.8	79.9	30.9	0.185	0.216	0.158	2.70	0.860
480	14.4	7.0	80.0	31.4	0.183	0.215	0.155	2.69	0.853
540	14.7	7.0	81.8	32.3	0.181	0.211	0.133	2.80	0.858
720	13.8	6.3	82.4	32.3	0.183	0.214	0.135	2.79	0.856
1440	14.1	6.1	84.1	39.3	0.162	0.185	0.116	2.89	0.879

Determination of rate of ligand exchanges

The rate of ligand exchanges was determined based on the reported method.³ A solution of PdPy₄(OTf)₂ (1.4 mg, 2.0 μmol) and Py (0.63 mg, 8.0 μmol) in a solvent (500 μL) was prepared in an NMR tube. The irradiation of the α-position proton signal for the free pyridine decreased the integral values of the proton signal for the coordinating pyridine by spin-saturation transfer process (Figure S8). The rate constant k_{obs} was determined according to the equation (1), where T_{1py} = spin relaxation time of the free pyridine, M_{py} = the net magnetization of the free pyridine, and M_{0py} = the net magnetization of the free pyridine at thermal equilibrium (Table S13).

$$k_{obs} = \frac{1}{T_{1py}} \left(\frac{M_{0py}}{M_{py}} - 1 \right) \quad (1)$$

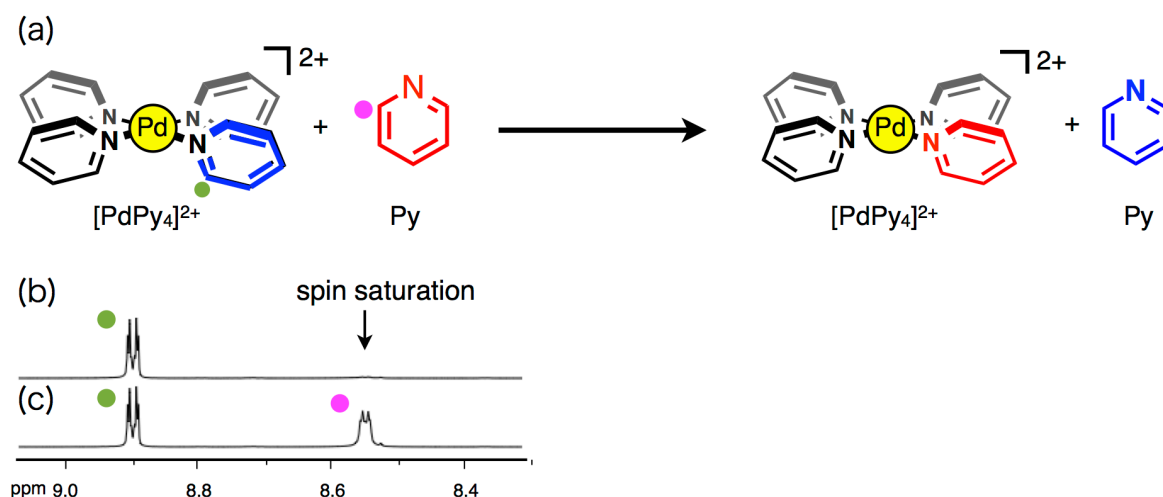


Figure S8. ¹H NMR spectra (500 MHz, CD₃NO₂, 298 K) for the magnetization transfer experiment. (a) The scheme of the exchange of the free Py and Py in the [PdPy₄]²⁺. (b) A spin saturation transfer spectrum with irradiation at the arrow position. (c) A reference ¹H NMR spectrum for the region of α-protons of pyridine.

Table S13 The values of k_{obs} (s⁻¹), T_{1py} (s), M_{0py} , and M_{py} in each solvent.

solvent	k_{obs} / s^{-1}	T_{1py} / s	M_{0py}	M_{py}
CD ₃ CN/CD ₂ Cl ₂ (v/v = 4/1)	1.9×10^{-2}	2.62	3.19	3.04
CD ₃ NO ₂ /CD ₂ Cl ₂ (v/v = 4/1)	4.6×10^{-3}	2.60	2.87	2.84
CD ₃ CN	2.0×10^{-2}	2.30	1.41	1.32
CD ₃ NO ₂	3.4×10^{-3}	2.33	2.53	2.51

^1H NMR spectra for the self-assembly of $[\text{Pd}_6\mathbf{1}_8]^{12+}$ from $[\text{PdPy}_4]^{2+}$ and **1 in $\text{CD}_3\text{CN}/\text{CD}_2\text{Cl}_2$ (v/v = 4/1)**

The monitor of the self-assembly of $[\text{Pd}_6\mathbf{1}_8]^{12+}$ from $[\text{PdPy}_4]^{2+}$ and **1** in $\text{CD}_3\text{CN}/\text{CD}_2\text{Cl}_2$ (v/v = 4/1) at 298 K has been reported previously.²

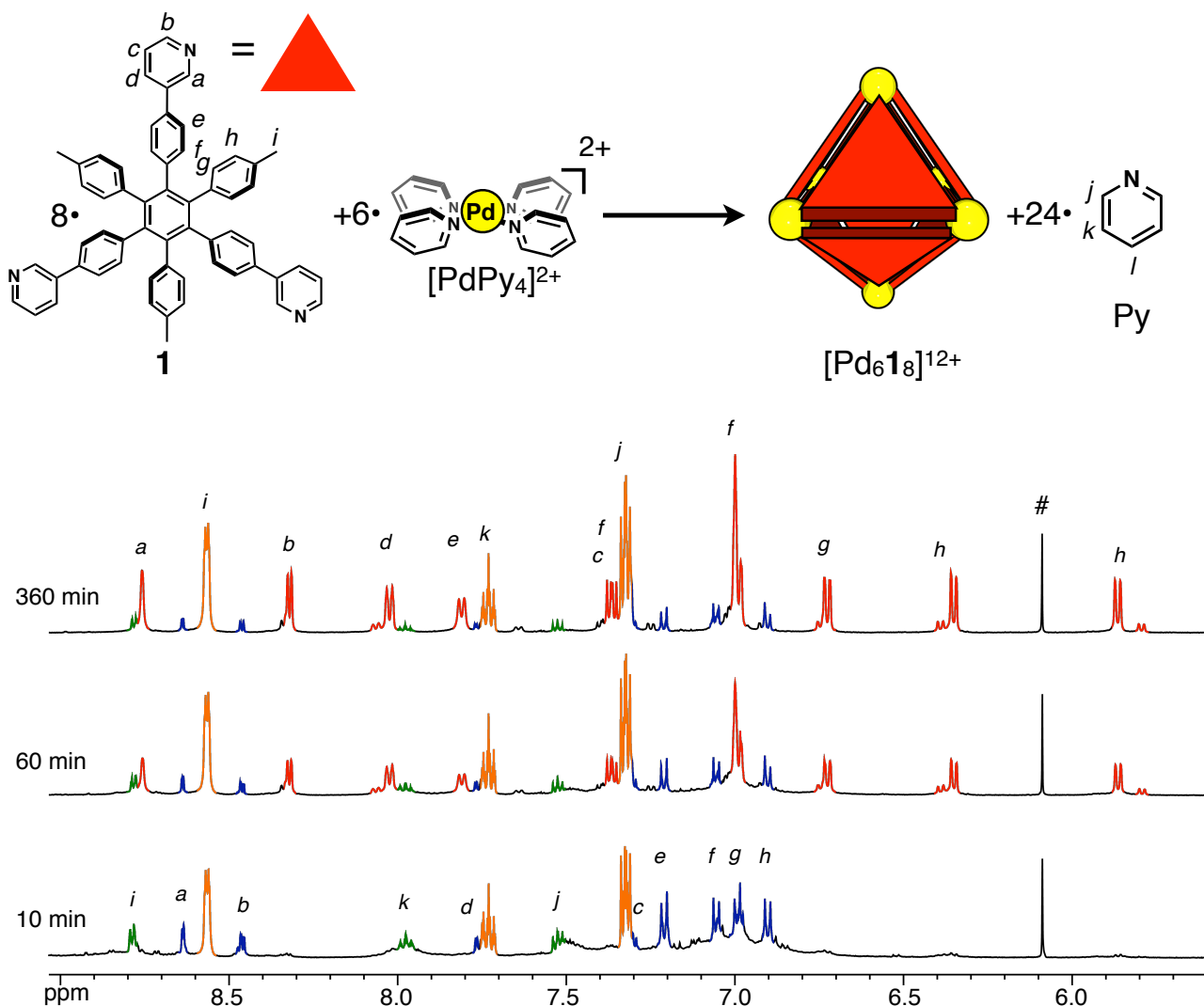
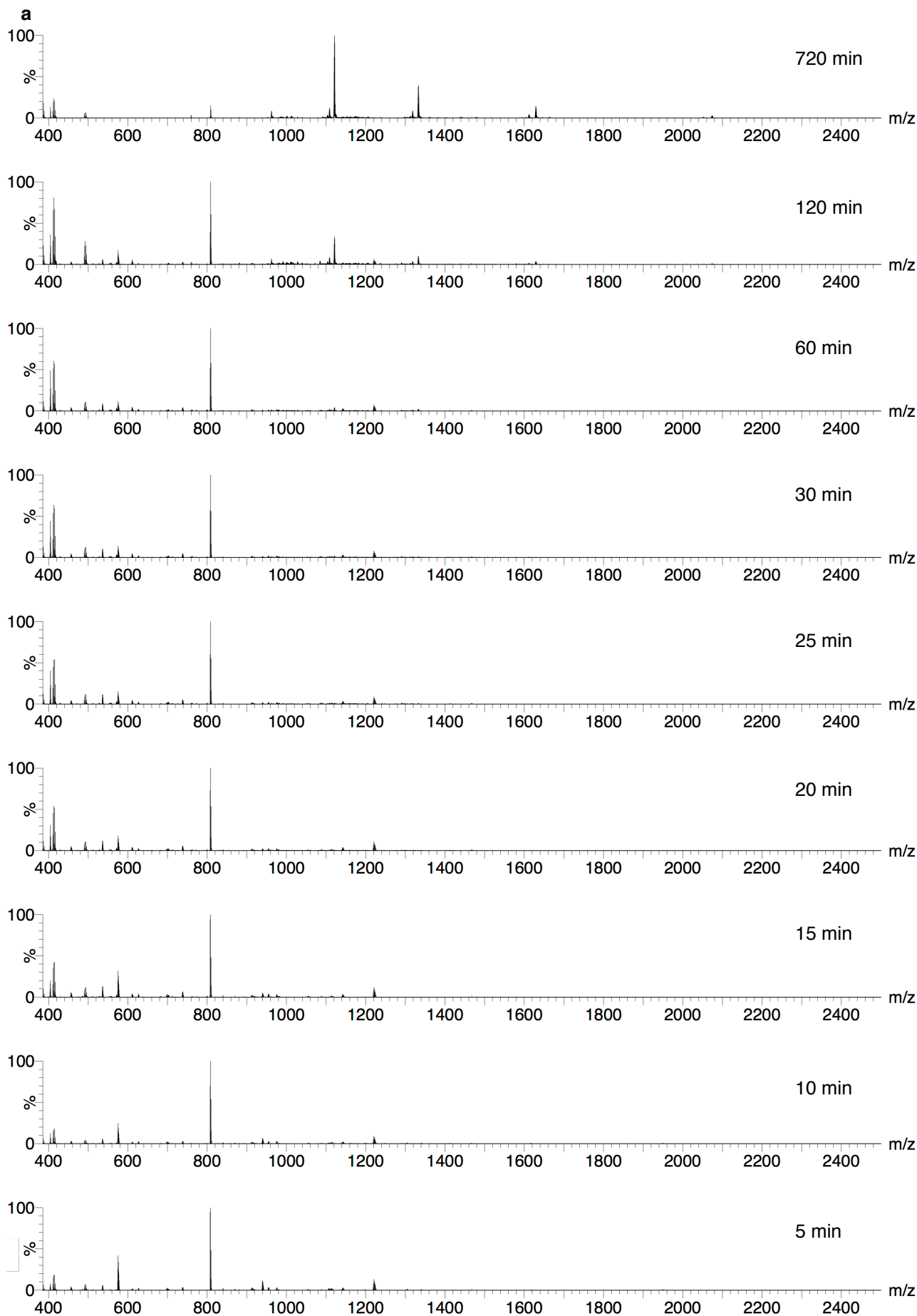
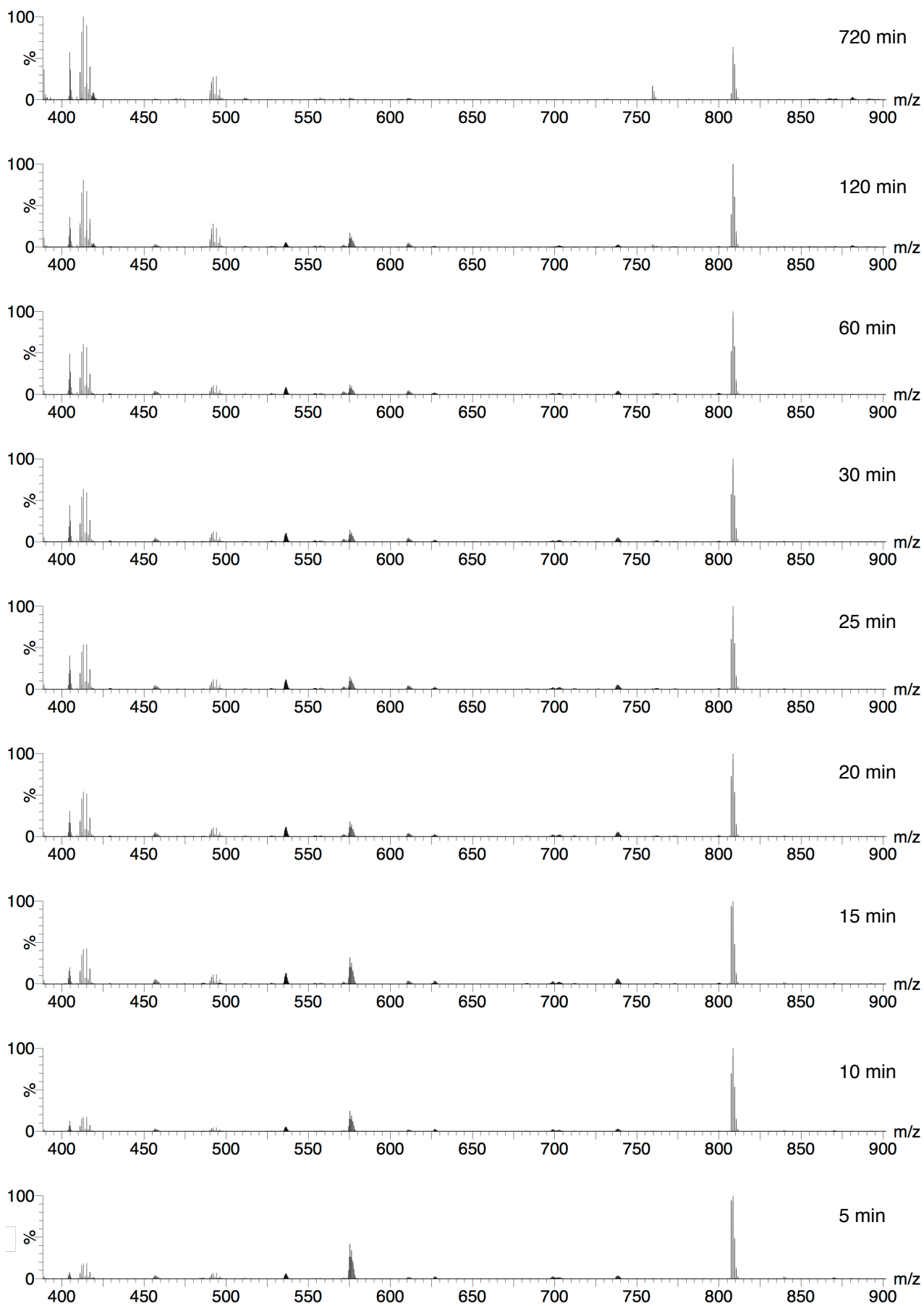
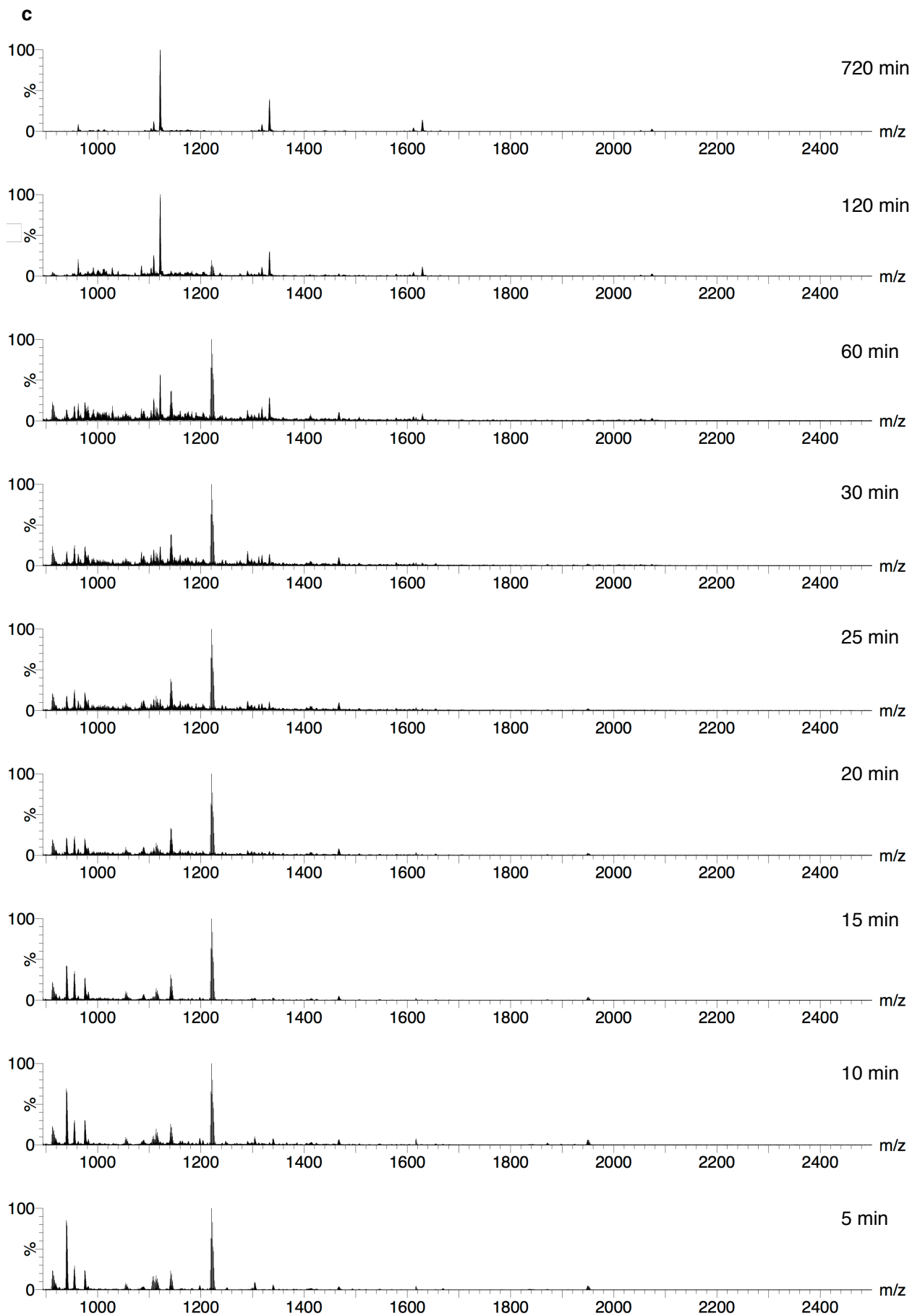


Figure S9. ^1H NMR spectra (500 MHz, $\text{CD}_3\text{CN}/\text{CD}_2\text{Cl}_2$ (v/v = 4/1), 298 K) for the self-assembly of $[\text{Pd}_6\mathbf{1}_8]^{12+}$ from $[\text{PdPy}_4]^{2+}$ and **1** in $\text{CD}_3\text{CN}/\text{CD}_2\text{Cl}_2$ (v/v = 4/1) at 298 K. The signals coloured in red, green, blue, and orange indicate $[\text{Pd}_6\mathbf{1}_8]^{12+}$, $[\text{PdPy}_4]^{2+}$, **1**, and Py, respectively. The hash indicates one of the proton signals for 1,3,5-trimethoxybenzene, which was used as the internal standard.

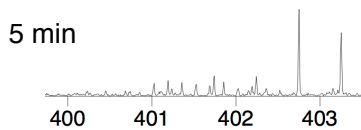
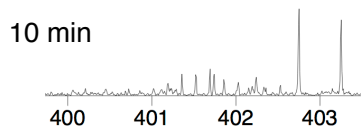
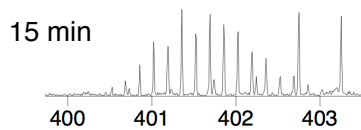
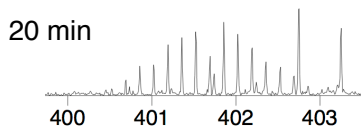
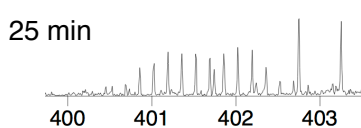
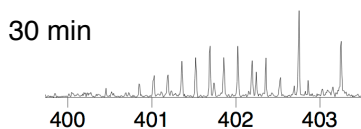
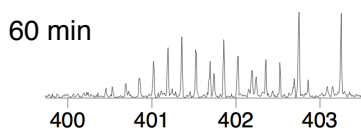
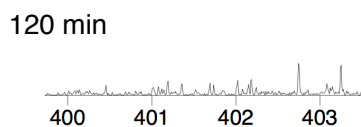
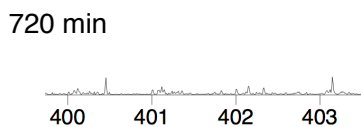
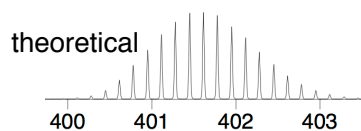


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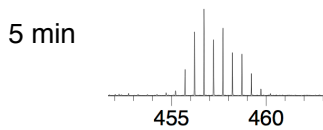
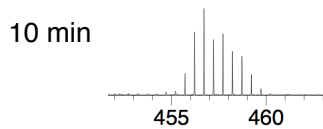
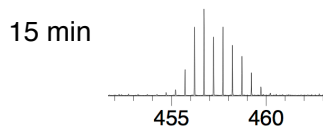
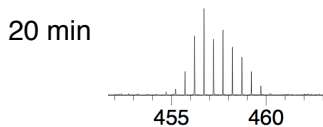
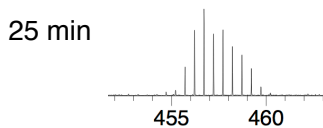
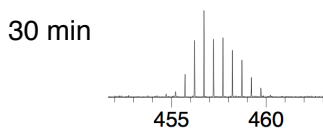
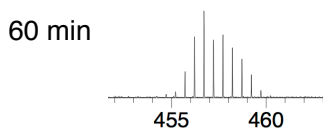
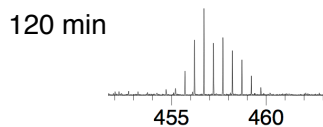
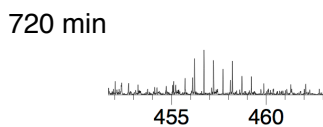
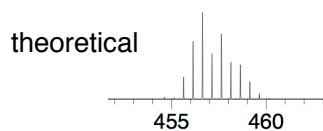




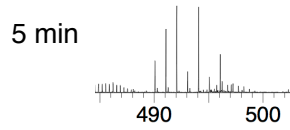
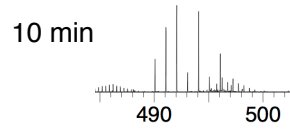
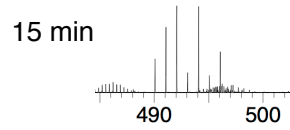
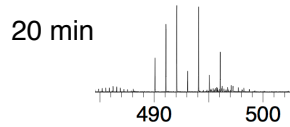
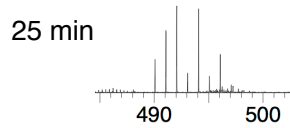
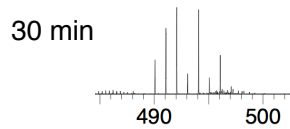
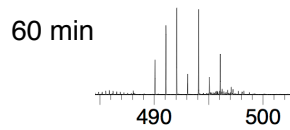
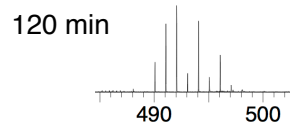
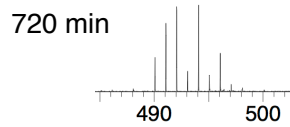
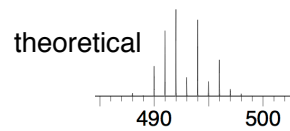
d $[\text{Pd}_3\text{1}_2\text{Py}_6]^{6+}$



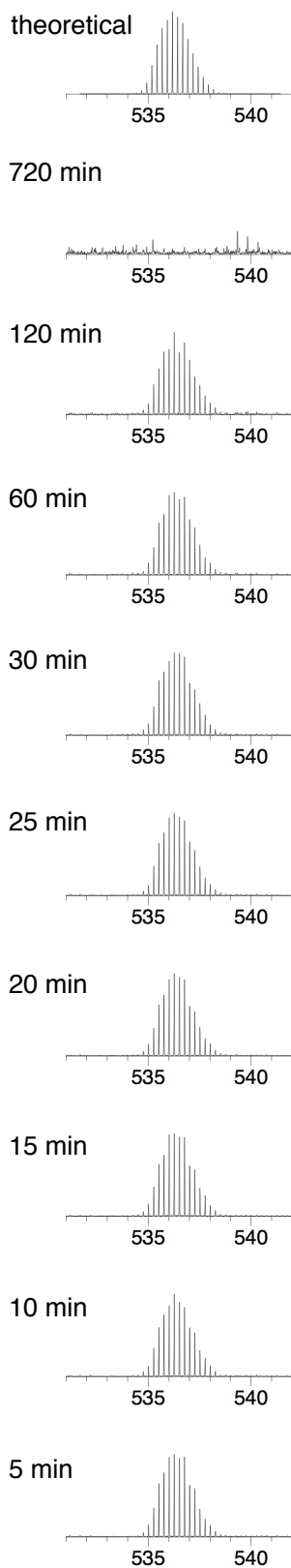
e $[\text{Pd1}]^{2+}$



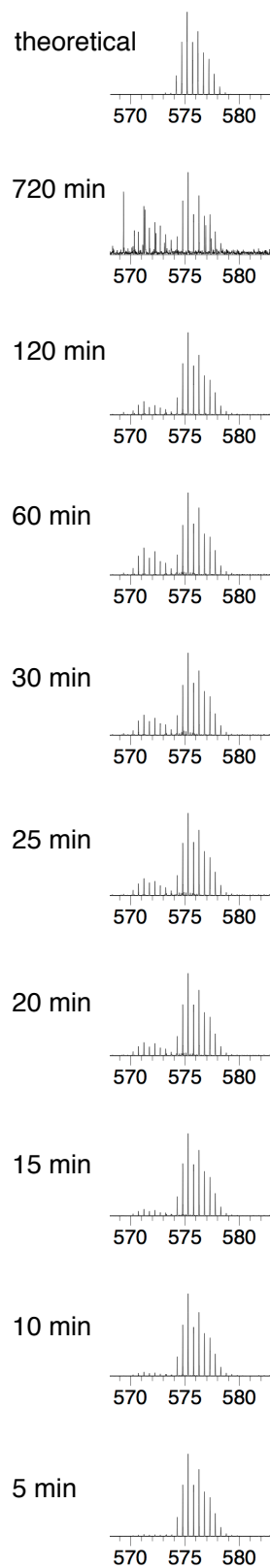
f $[\text{PdPy}_3(\text{OTf})]^+$



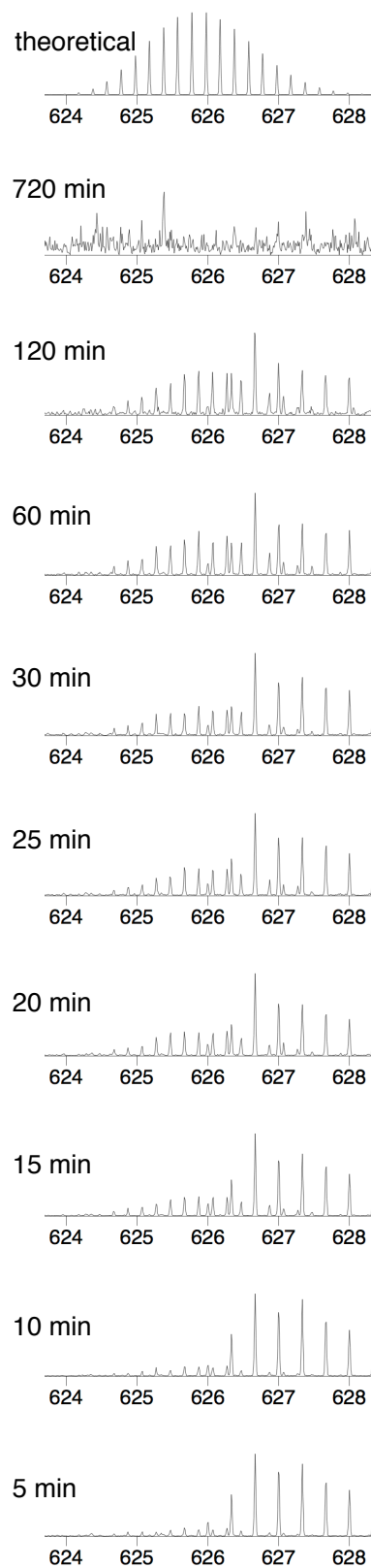
g $[\text{Pd}_2\text{1}_2\text{Py}_4]^{4+}$



h $[\text{Pd1Py}_3]^{2+}$

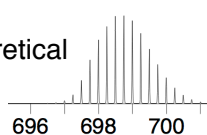


i $[\text{Pd}_3\text{1}_3\text{Py}_3(\text{OTf})]^{5+}$

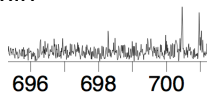


j $[\text{Pd}_2\text{1}_3\text{Py}_2]^{4+}$

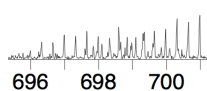
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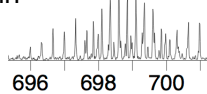
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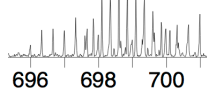
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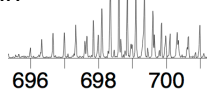
60 min



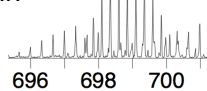
30 min



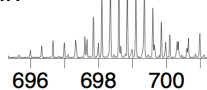
25 min



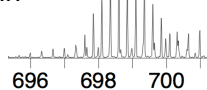
20 min



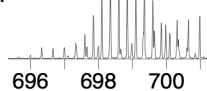
15 min



10 min

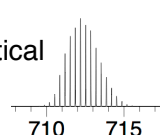


5 min

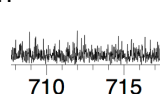


k $[\text{Pd}_2\text{1}_2\text{Py}_2(\text{OTf})]^{3+}$

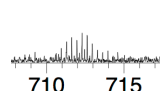
theoretical



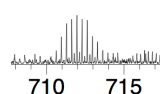
720 min



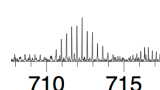
120 min



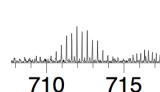
60 min



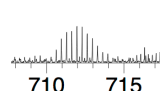
30 min



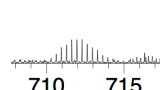
25 min



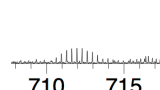
20 min



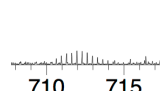
15 min



10 min

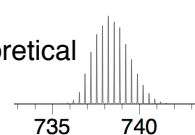


5 min

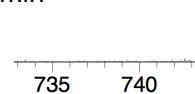


l $[\text{Pd}_2\text{1}_2\text{Py}_3(\text{OTf})]^{3+}$

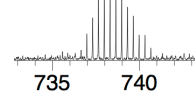
theoretical



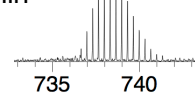
720 min



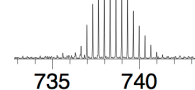
120 min



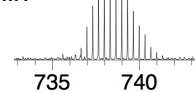
60 min



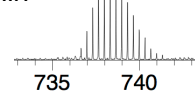
30 min



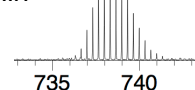
25 min



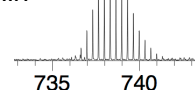
20 min



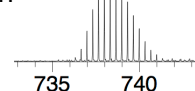
15 min



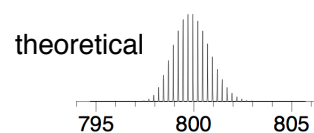
10 min



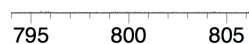
5 min



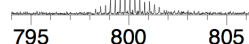
m $[\text{Pd}_3\text{1}_3\text{Py}_2(\text{OTf})_2]^{4+}$



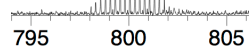
720 min



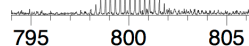
120 min



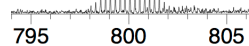
60 min



30 min



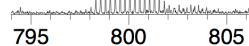
25 min



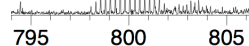
20 min



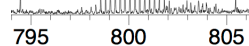
15 min



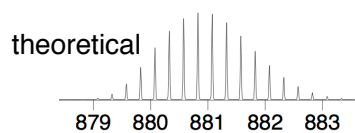
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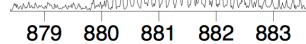
5 min



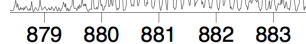
n $[\text{Pd}_2\text{1}_4\text{Py}]^{4+}$



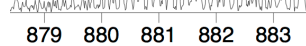
720 min



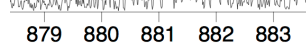
120 min



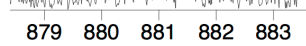
60 min



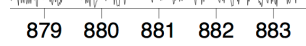
30 min



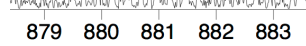
25 min



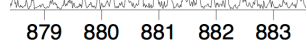
20 min



15 min



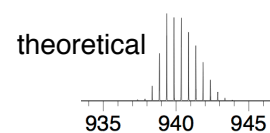
10 min



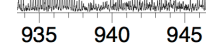
5 min



o $[\text{Pd}\text{1}_2\text{Py}_2]^{2+}$



720 min



120 min



60 min



30 min



25 min



20 min



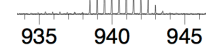
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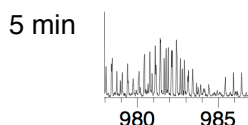
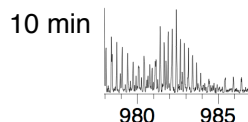
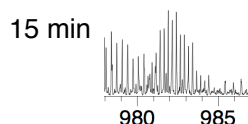
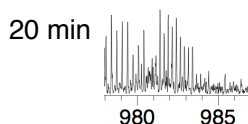
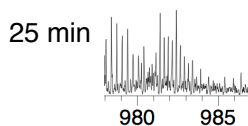
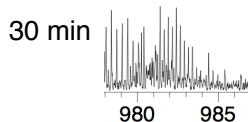
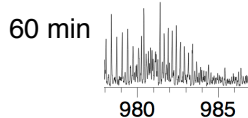
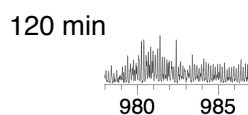
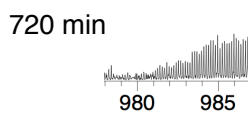
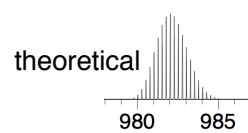
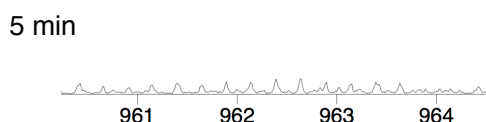
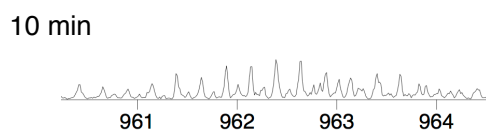
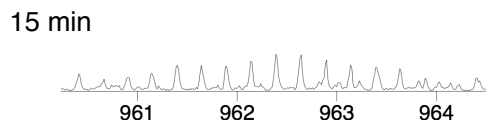
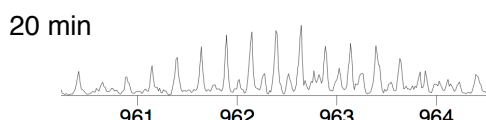
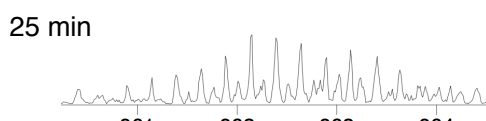
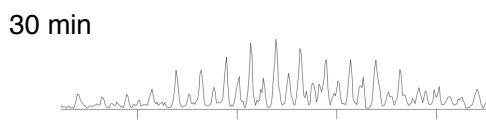
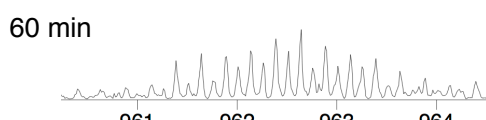
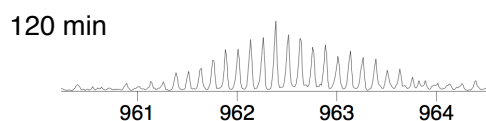
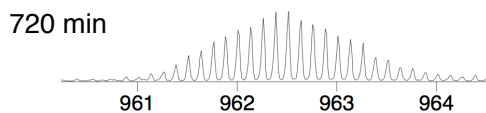
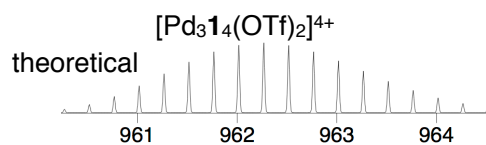
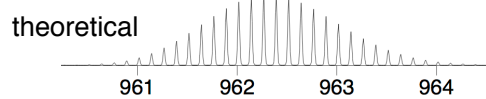
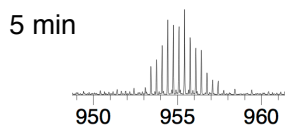
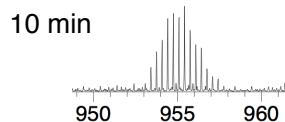
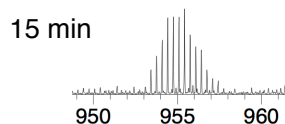
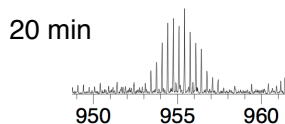
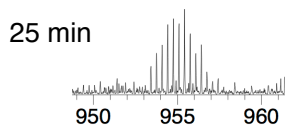
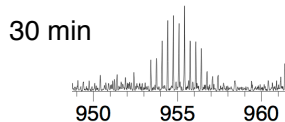
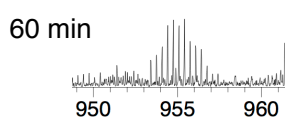
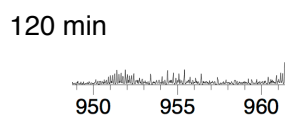
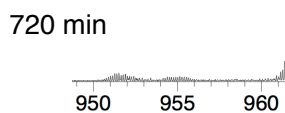
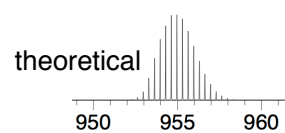
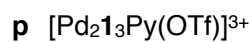


10 min

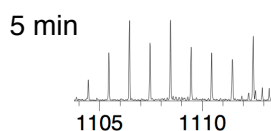
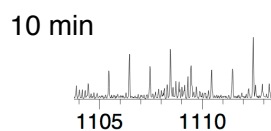
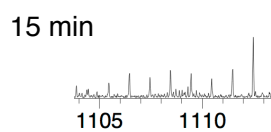
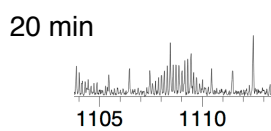
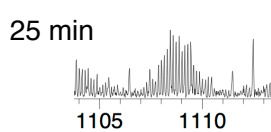
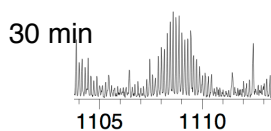
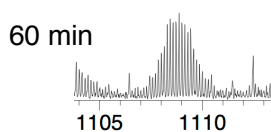
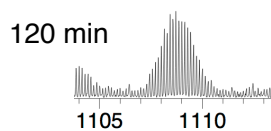
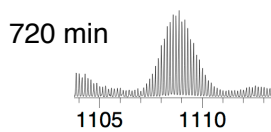
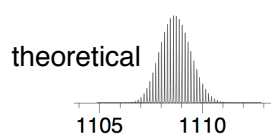


5 min

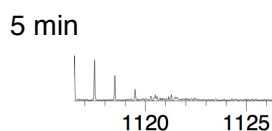
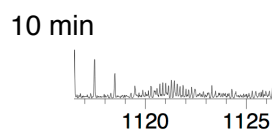
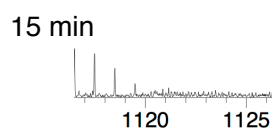
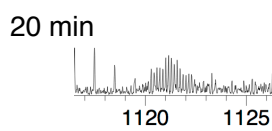
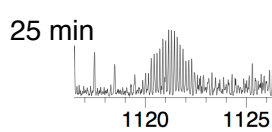
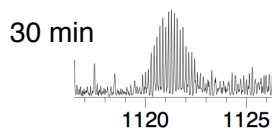
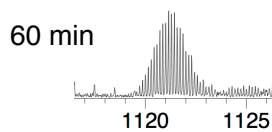
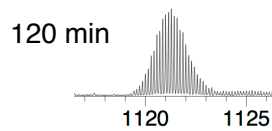
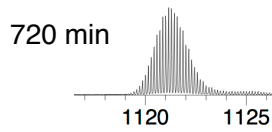
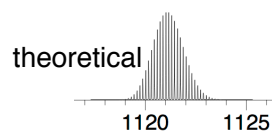




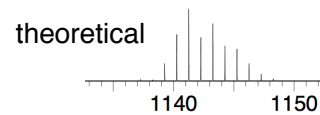
s $[\text{Pd}_6\text{1}_8(\text{OTf})_4(\text{NO}_3)]^{7+}$



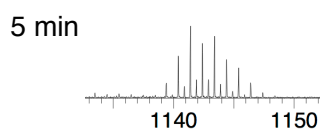
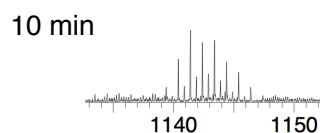
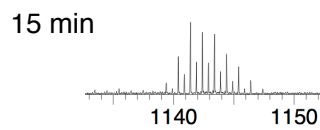
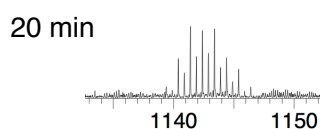
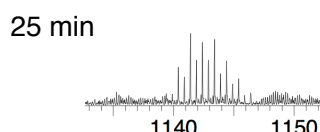
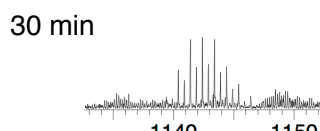
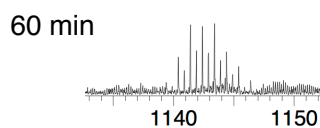
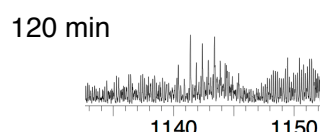
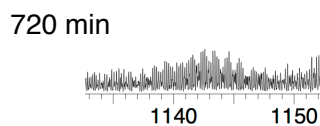
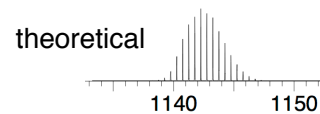
t $[\text{Pd}_6\text{1}_8(\text{OTf})_5]^{7+}$



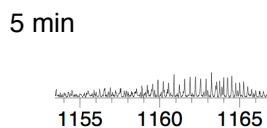
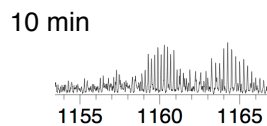
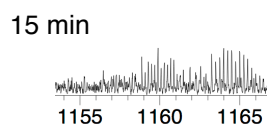
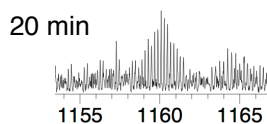
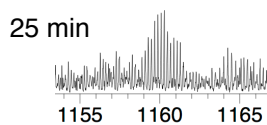
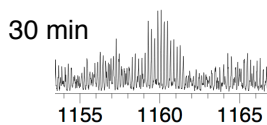
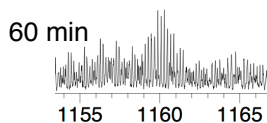
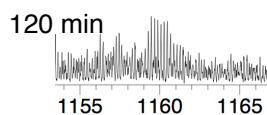
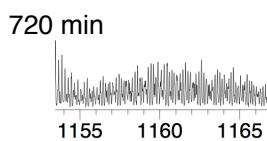
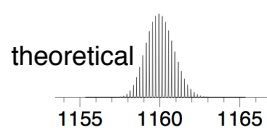
u $[\text{Pd1Py}(\text{OTf})]^+$



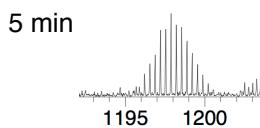
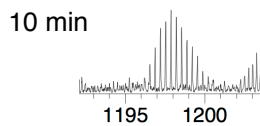
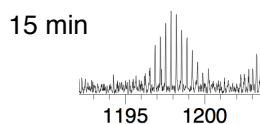
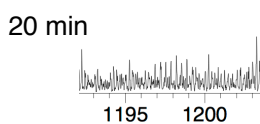
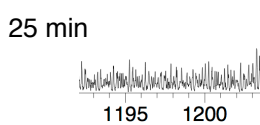
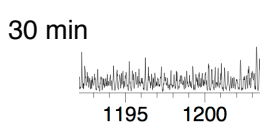
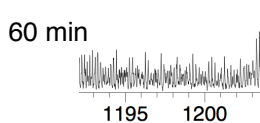
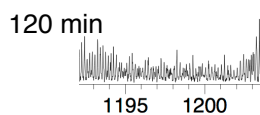
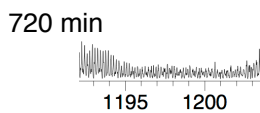
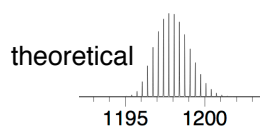
$[\text{Pd}_2\text{1}_2\text{Py}_2(\text{OTf})_2]^{2+}$



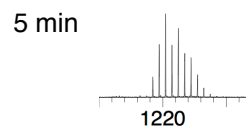
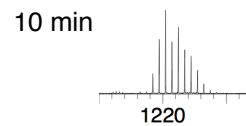
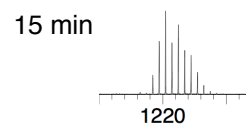
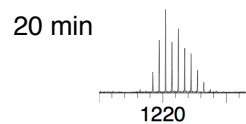
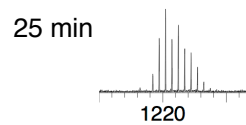
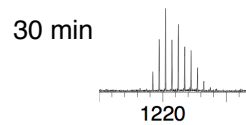
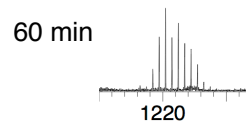
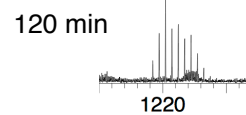
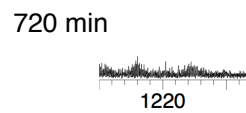
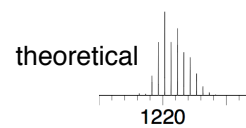
v [Pd₄1₆Py(OTf)₃]⁵⁺

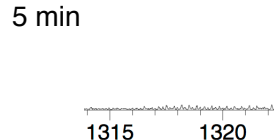
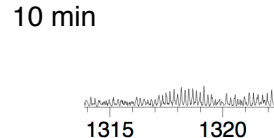
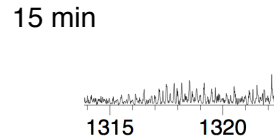
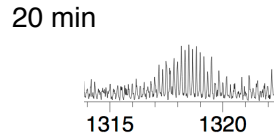
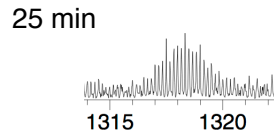
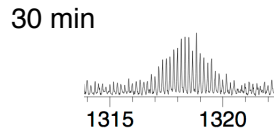
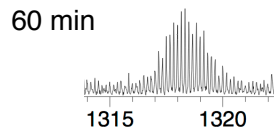
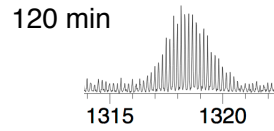
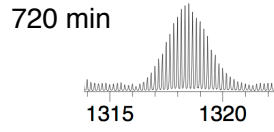
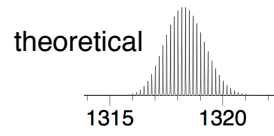
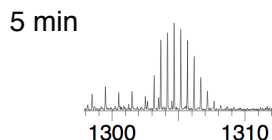
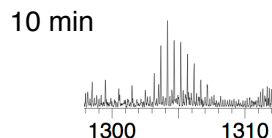
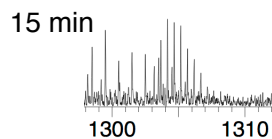
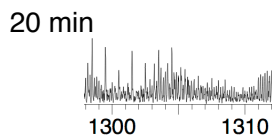
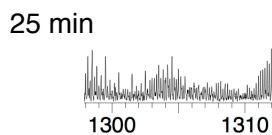
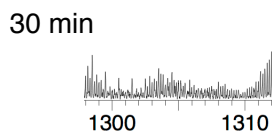
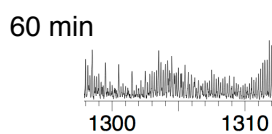
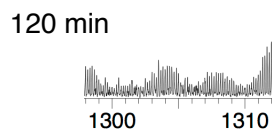
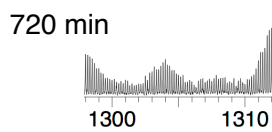
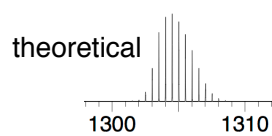
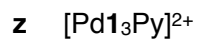
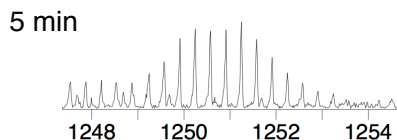
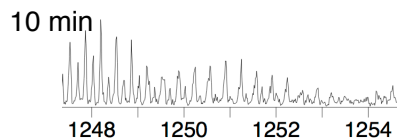
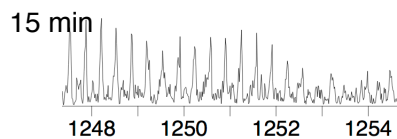
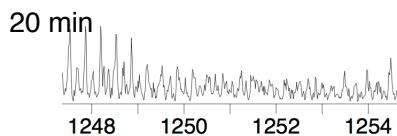
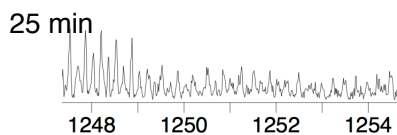
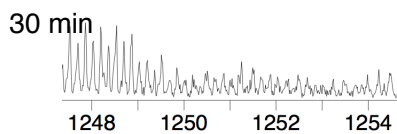
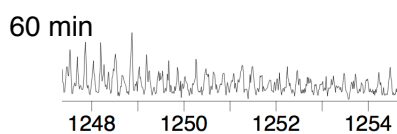
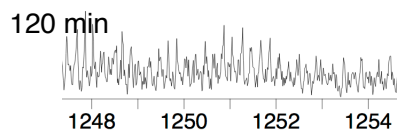
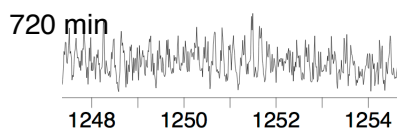
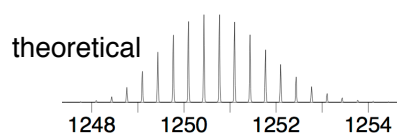
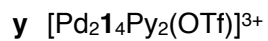


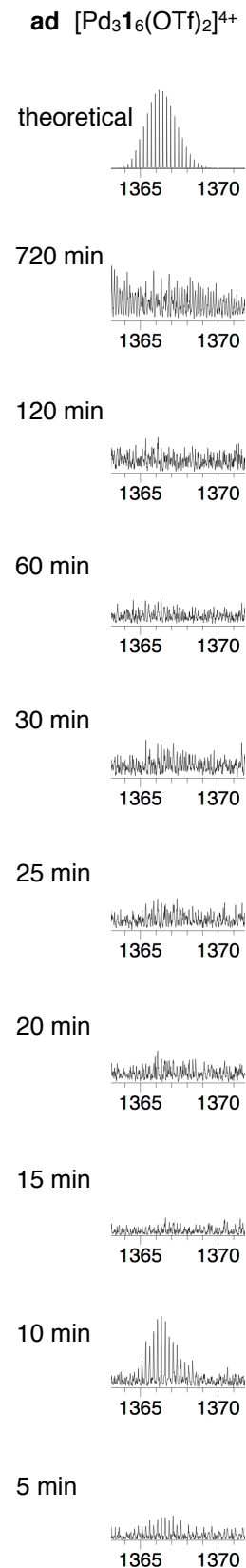
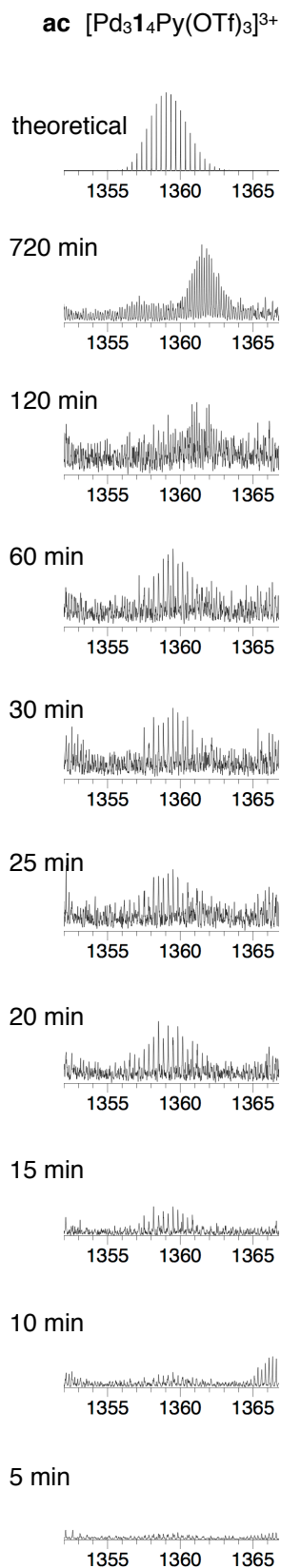
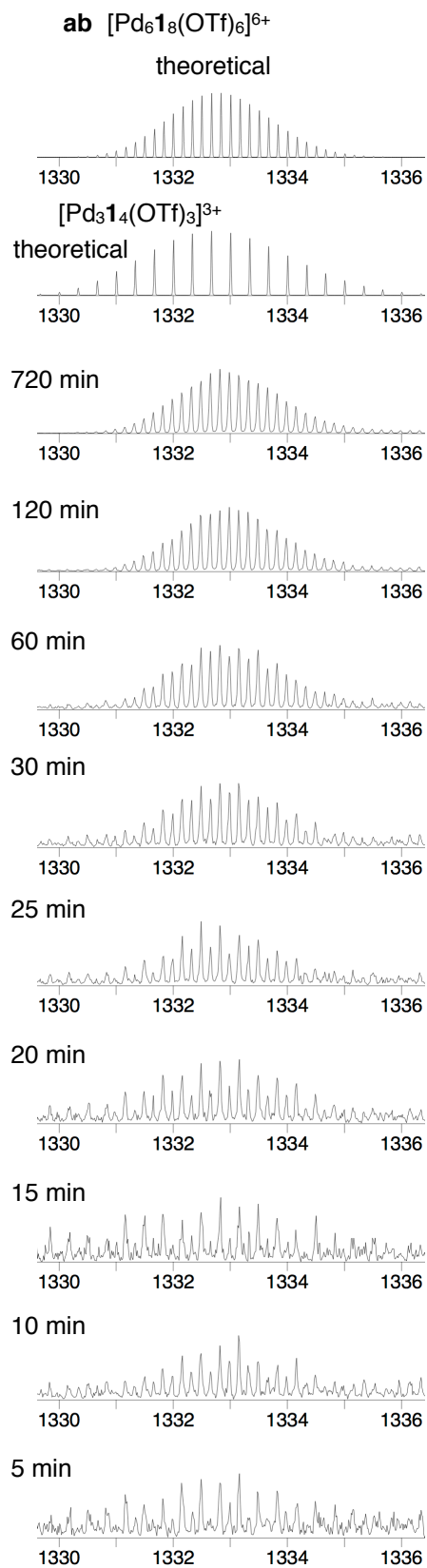
w [Pd₂1₄(OTf)₃]³⁺



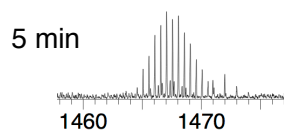
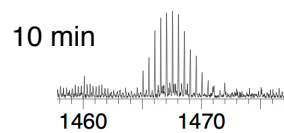
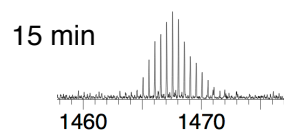
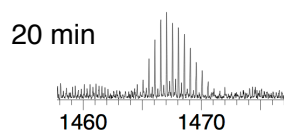
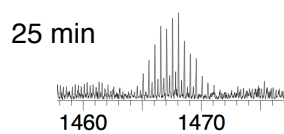
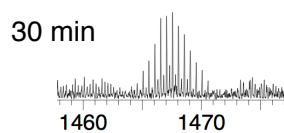
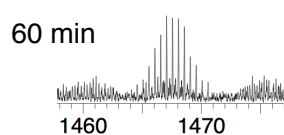
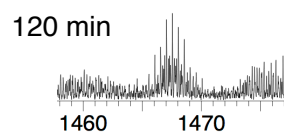
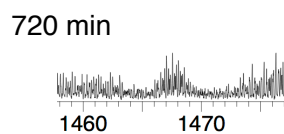
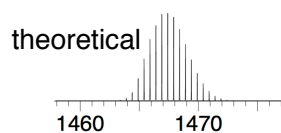
x [Pd1Py₂(OTf)]⁺



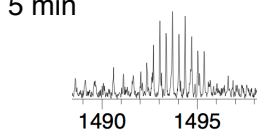
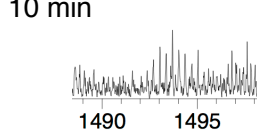
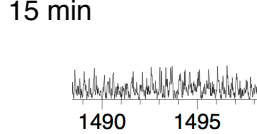
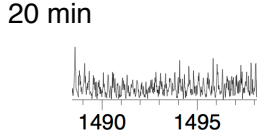
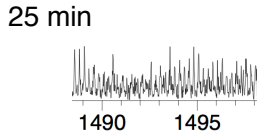
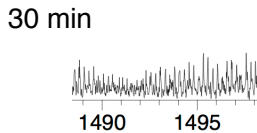
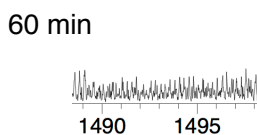
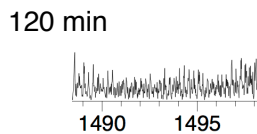
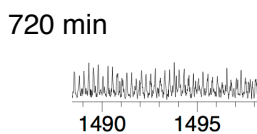
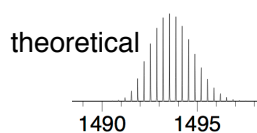




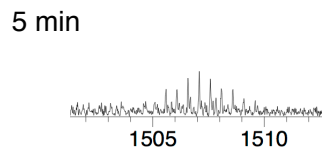
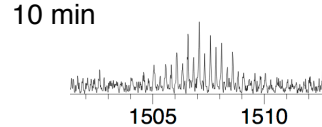
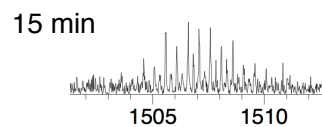
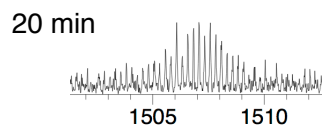
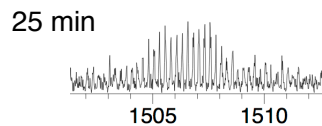
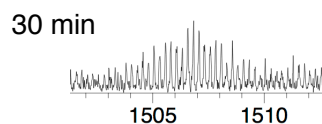
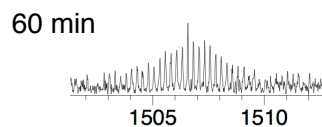
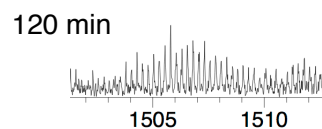
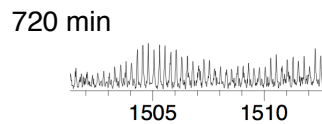
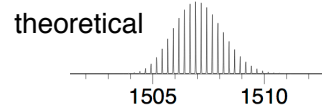
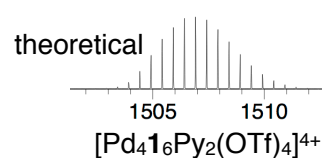
ae $[\text{Pd}_2\text{1}_3(\text{OTf})_2]^{2+}$



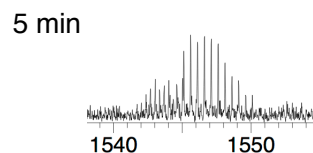
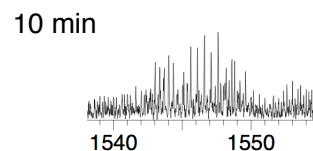
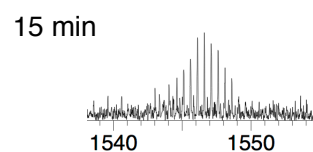
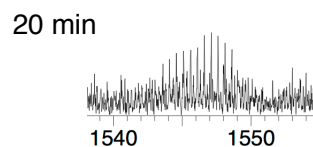
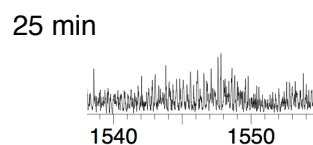
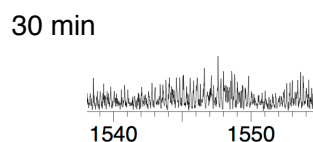
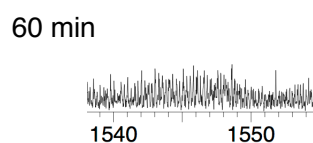
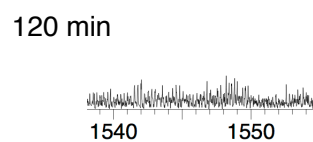
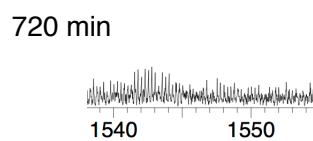
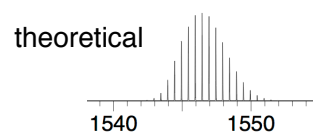
af $[\text{Pd}_2\text{1}_5\text{Py}(\text{OTf})]^{3+}$



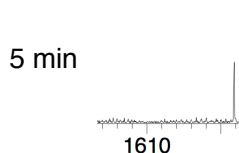
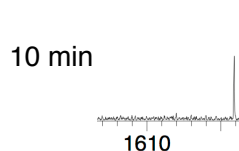
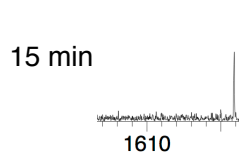
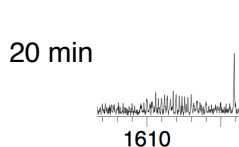
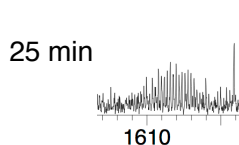
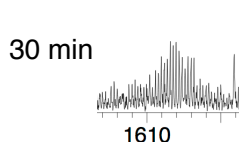
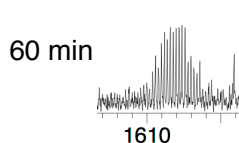
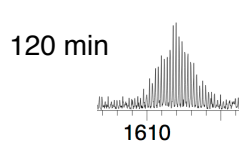
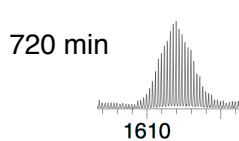
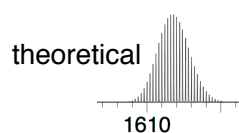
ag $[\text{Pd}_2\text{1}_3\text{Py}(\text{OTf})_2]^{2+}$



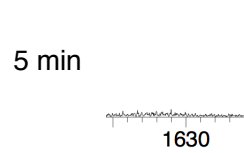
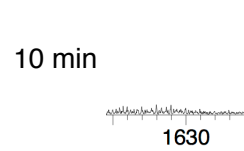
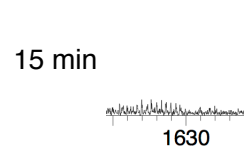
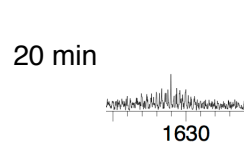
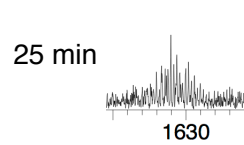
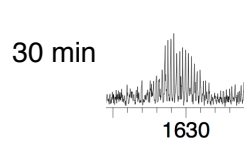
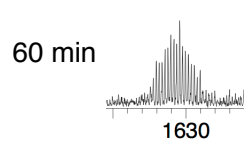
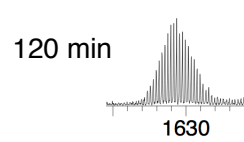
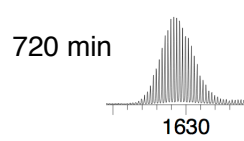
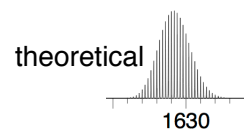
ah $[\text{Pd}_2\text{1}_3\text{Py}_2(\text{OTf})_2]^{2+}$



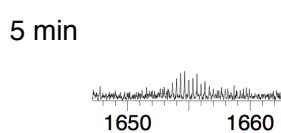
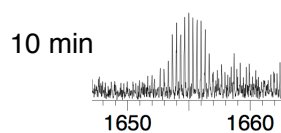
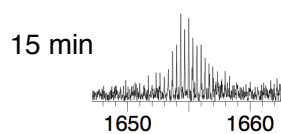
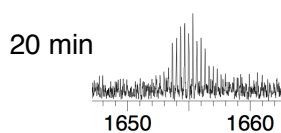
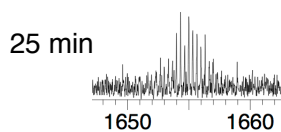
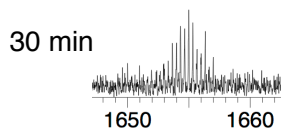
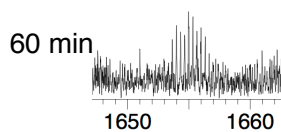
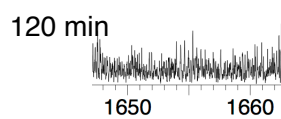
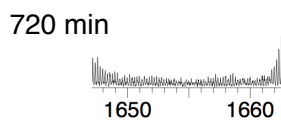
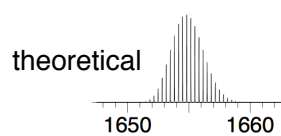
ai $[\text{Pd}_6\text{1}_8(\text{OTf})_6(\text{NO}_3)]^{5+}$



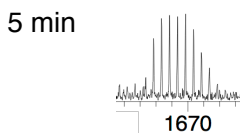
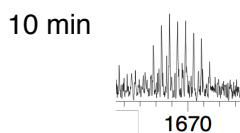
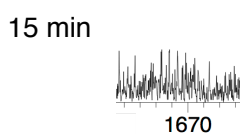
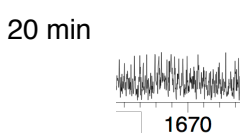
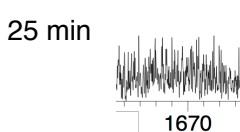
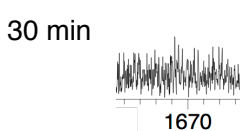
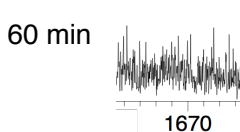
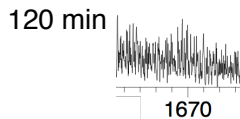
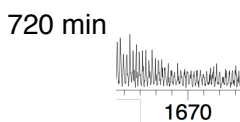
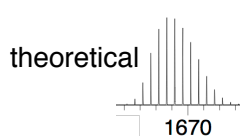
aj $[\text{Pd}_6\text{1}_8(\text{OTf})_7]^{5+}$



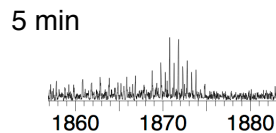
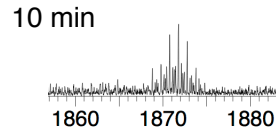
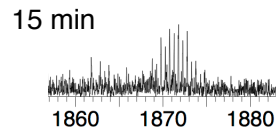
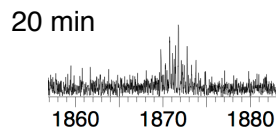
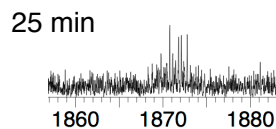
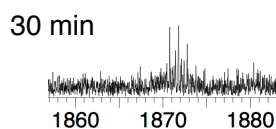
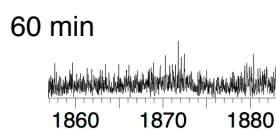
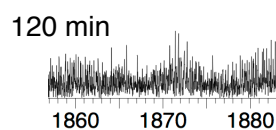
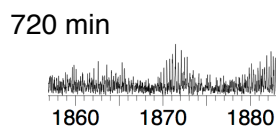
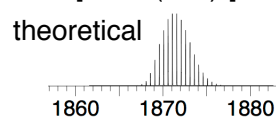
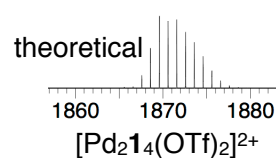
ak $[\text{Pd}_3\text{1}_5\text{Py}_2(\text{OTf})_3]^{3+}$



al $[\text{Pd1}_4]^{2+}$



am $[\text{Pd1}_2(\text{OTf})]^+$



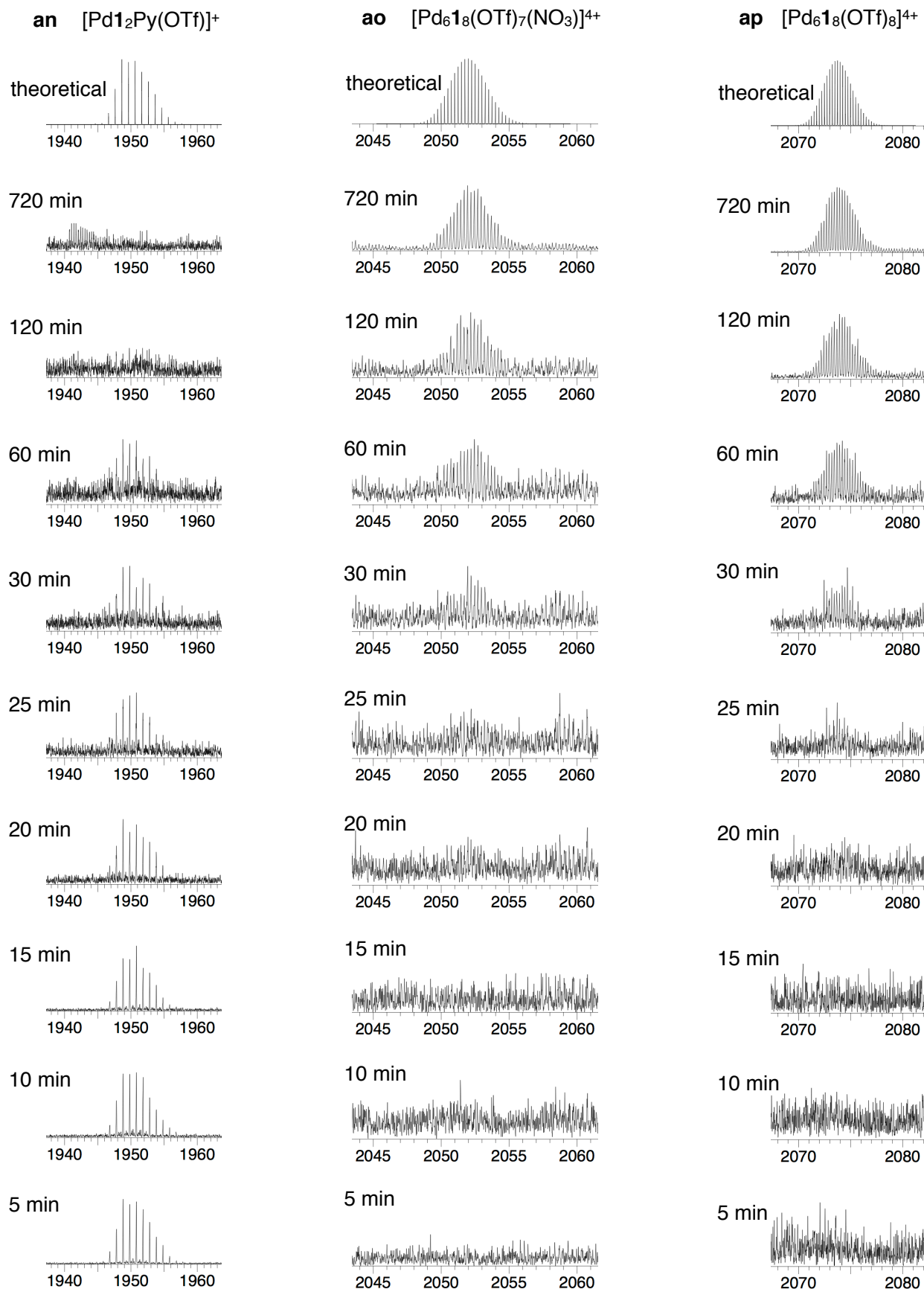


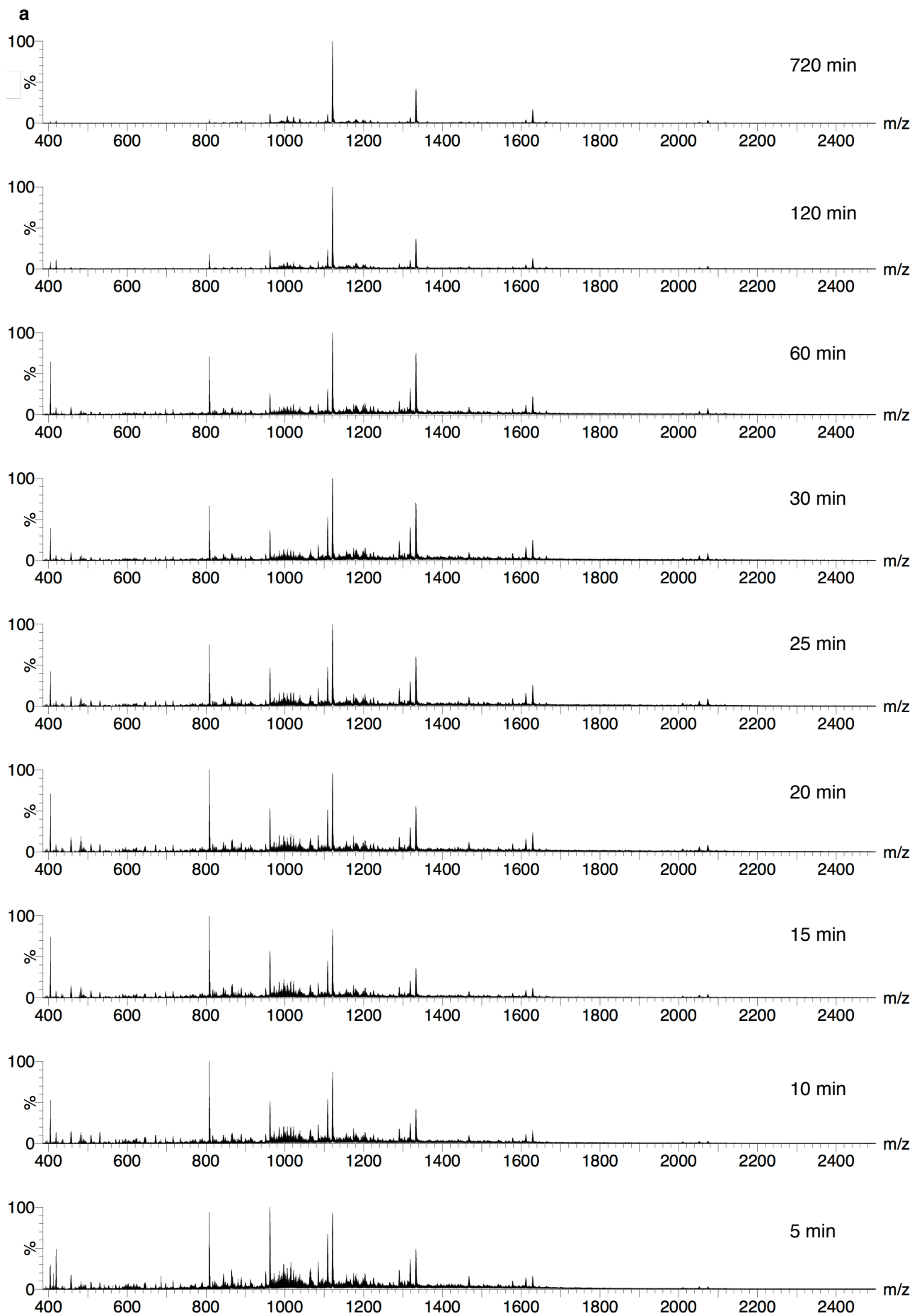
Figure S10. (a)–(c) ESI-TOF mass spectra ($m/z = 390\text{--}2480$) for the self-assembly of $[\text{Pd}_6\mathbf{1}_8]^{12+}$ from $[\text{PdPy}_4]^{2+}$ and $\mathbf{1}$ in $\text{CD}_3\text{NO}_2/\text{CD}_2\text{Cl}_2$ (v/v = 4/1) at 298 K. (d)–(ap) Time variation of the signal for (d) $[\text{Pd}_3\mathbf{1}_2\text{Py}_6]^{6+}$, (e) $[\text{Pd}\mathbf{1}]^{2+}$, (f) $[\text{PdPy}_3(\text{OTf})]^+$, (g) $[\text{Pd}_2\mathbf{1}_2\text{Py}_4]^{4+}$, (h) $[\text{Pd}\mathbf{1Py}_3]^{2+}$, (i) $[\text{Pd}_3\mathbf{1}_3\text{Py}_3(\text{OTf})]^{5+}$, (j) $[\text{Pd}_2\mathbf{1}_3\text{Py}_2]^{4+}$, (k) $[\text{Pd}_2\mathbf{1}_2\text{Py}_2(\text{OTf})]^{3+}$, (l)

[Pd₂1₂Py₃(OTf)]³⁺, (m) [Pd₃1₃Py₂(OTf)₂]⁴⁺, (n) [Pd₂1₄Py]⁴⁺, (o) [Pd₁2Py₂]²⁺, (p) [Pd₂1₃Py(OTf)]³⁺, (q) [Pd₃1₄(OTf)₂]⁴⁺ and [Pd₆1₈(OTf)₄]⁸⁺, (r) [Pd₃1₄Py(OTf)₂]⁴⁺, (s) [Pd₆1₈(OTf)₄(NO₃)₇]⁷⁺, (t) [Pd₆1₈(OTf)₅]⁷⁺, (u) [Pd₁Py(OTf)]⁺ and [Pd₂1₂Py₂(OTf)₂]²⁺, (v) [Pd₄1₆Py(OTf)₃]⁵⁺, (w) [Pd₂1₄(OTf)]³⁺, (x) [Pd₁Py₂(OTf)]⁺, (y) [Pd₂1₄Py₂]³⁺, (z) [Pd₁3Py]²⁺, (aa) [Pd₆1₈(OTf)₅(NO₃)₆]⁶⁺, (ab) [Pd₃1₄(OTf)₃]³⁺ and [Pd₆1₈(OTf)₆]⁶⁺, (ac) [Pd₃1₄Py(OTf)₃]³⁺, (ad) [Pd₃1₆(OTf)₂]⁴⁺, (ae) [Pd₂1₃(OTf)₂]²⁺, (af) [Pd₂1₅Py(OTf)]³⁺, (ag) [Pd₄1₆Py₂(OTf)₄]⁴⁺ and [Pd₂1₃Py(OTf)₂]²⁺, (ah) [Pd₂1₃Py₂(OTf)₂]²⁺, (ai) [Pd₆1₈(OTf)₆(NO₃)₅]⁵⁺, (aj) [Pd₆1₈(OTf)₇]⁵⁺, (ak) [Pd₃1₅Py₂(OTf)₃]³⁺, (al) [Pd₁4]²⁺, (am) [Pd₂1₄(OTf)₂]²⁺ and [Pd₁2(OTf)]⁺, (an) [Pd₁2Py(OTf)]⁺, (ao) [Pd₆1₈(OTf)₇(NO₃)₄]⁴⁺, and (ap) [Pd₆1₈(OTf)₈]⁴⁺.

Table S14. Time variation of the species detected by ESI-TOF mass spectrometry for the self-assembly of the capsule from **1** and PdPy₄·(OTf)₂ in CD₃NO₂/CD₂Cl₂ (v/v = 4/1) at 298 K.

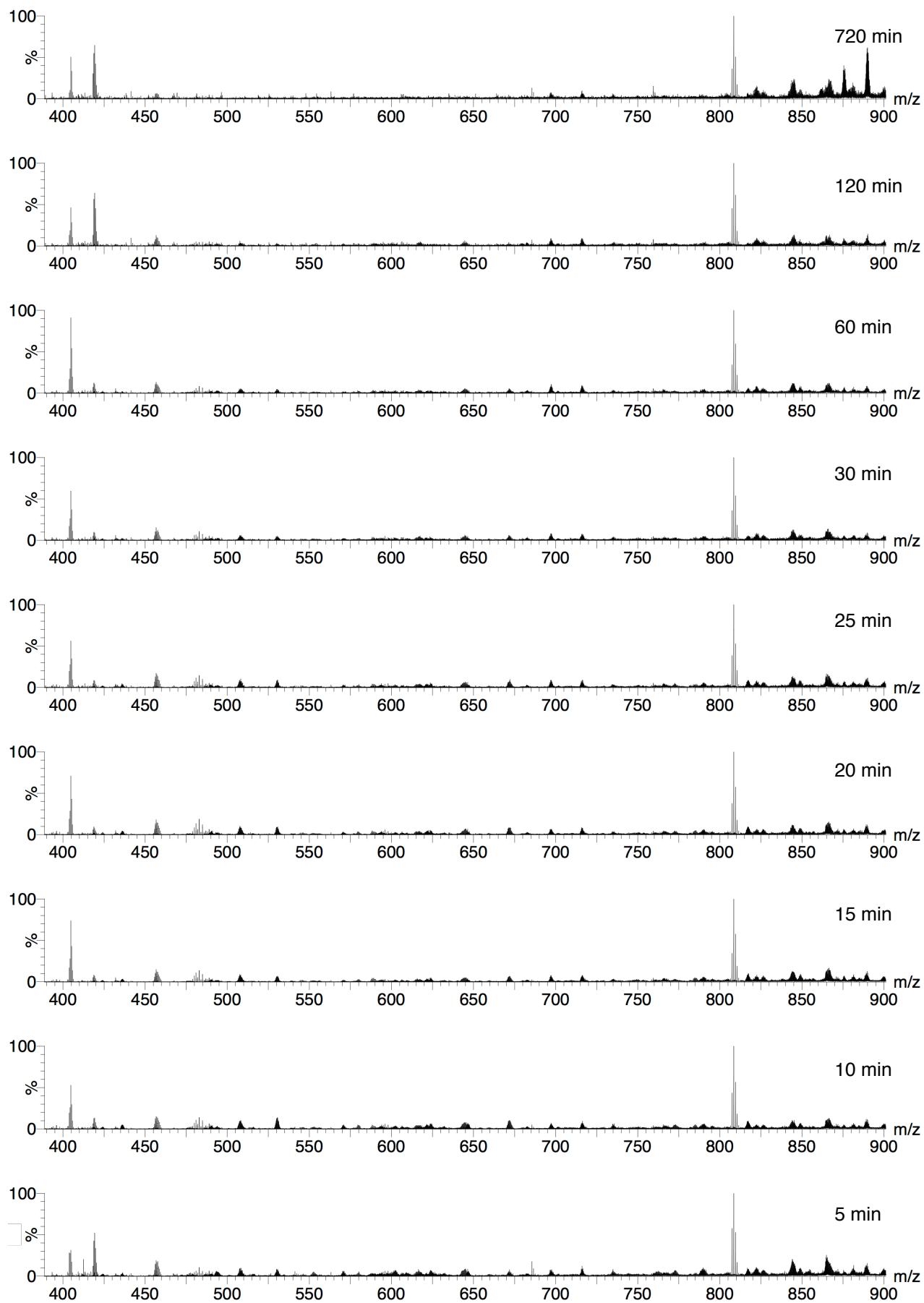
5 min	10 min	15 min	20 min	25 min	30 min	60 min	120 min	720 min
(1, 0, 3)	(1, 0, 3)	(1, 0, 3)	(1, 0, 3)	(1, 0, 3)	(1, 0, 3)	(1, 0, 3)	(1, 0, 3)	(1, 0, 3)
(1, 1, 0)	(1, 1, 0)	(1, 1, 0)	(1, 1, 0)	(1, 1, 0)	(1, 1, 0)	(1, 1, 0)	(1, 1, 0)	(1, 1, 0) ↓
(1, 1, 1)	(1, 1, 1)	(1, 1, 1)	(1, 1, 1)	(1, 1, 1)	(1, 1, 1)	(1, 1, 1)	(1, 1, 1) ↓	
(1, 1, 2)	(1, 1, 2)	(1, 1, 2)	(1, 1, 2)	(1, 1, 2)	(1, 1, 2)	(1, 1, 2)	(1, 1, 2)	
(1, 1, 3)	(1, 1, 3)	(1, 1, 3)	(1, 1, 3)	(1, 1, 3)	(1, 1, 3)	(1, 1, 3)	(1, 1, 3)	(1, 1, 3) ↓
(1, 2, 0)	(1, 2, 0)	(1, 2, 0)	(1, 2, 0)	(1, 2, 0)	(1, 2, 0)			
(1, 2, 1)	(1, 2, 1)	(1, 2, 1)	(1, 2, 1)	(1, 2, 1)	(1, 2, 1)	(1, 2, 1) ↓		
(1, 2, 2)	(1, 2, 2)	(1, 2, 2)	(1, 2, 2)	(1, 2, 2)	(1, 2, 2)	(1, 2, 2)	(1, 2, 2) ↓	
(1, 3, 1)	(1, 3, 1)	(1, 3, 1)						
(1, 4, 0)	(1, 4, 0)	(1, 4, 0) ↓						
(2, 2, 2)	(2, 2, 2)	(2, 2, 2)	(2, 2, 2)	(2, 2, 2)	(2, 2, 2)	(2, 2, 2)	(2, 2, 2) ↓	
(2, 2, 3)	(2, 2, 3)	(2, 2, 3)	(2, 2, 3)	(2, 2, 3)	(2, 2, 3)	(2, 2, 3)	(2, 2, 3)	
(2, 2, 4)	(2, 2, 4)	(2, 2, 4)	(2, 2, 4)	(2, 2, 4)	(2, 2, 4)	(2, 2, 4)	(2, 2, 4) ↓	
(2, 3, 0)	(2, 3, 0)	(2, 3, 0)	(2, 3, 0)	(2, 3, 0)	(2, 3, 0)	(2, 3, 0)	(2, 3, 0)	(2, 3, 0)
(2, 3, 1)	(2, 3, 1)	(2, 3, 1)	(2, 3, 1)	(2, 3, 1)	(2, 3, 1)	(2, 3, 1)		
(2, 3, 2)	(2, 3, 2)	(2, 3, 2)	(2, 3, 2)	(2, 3, 2)	(2, 3, 2)	(2, 3, 2)		
(2, 4, 0)	(2, 4, 0)	(2, 4, 0)						
(2, 4, 1)	(2, 4, 1)	(2, 4, 1)						
(2, 4, 2)	(2, 4, 2)	(2, 4, 2) ↓						
(2, 5, 1)	(2, 5, 1) ↓							
		(3, 2, 6)	(3, 2, 6)	(3, 2, 6)	(3, 2, 6)	(3, 2, 6)		
(3, 3, 2)	(3, 3, 2)	(3, 3, 2)	(3, 3, 2)	(3, 3, 2)	(3, 3, 2)	(3, 3, 2)	(3, 3, 2)	
(3, 3, 3)	(3, 3, 3)	(3, 3, 3)	(3, 3, 3)	(3, 3, 3)	(3, 3, 3)	(3, 3, 3)	(3, 3, 3)	
(3, 4, 0)	(3, 4, 0)	(3, 4, 0)	(3, 4, 0)	(3, 4, 0)	(3, 4, 0)	(3, 4, 0)		
(3, 4, 1)	(3, 4, 1)	(3, 4, 1)	(3, 4, 1)	(3, 4, 1)	(3, 4, 1)	(3, 4, 1)		
(3, 5, 2)	(3, 5, 2)	(3, 5, 2)	(3, 5, 2)	(3, 5, 2)	(3, 5, 2)	(3, 5, 2)		
(3, 6, 0)	(3, 6, 0)							
	(3, 6, 1)							
	(4, 6, 1)	(4, 6, 1)	(4, 6, 1)	(4, 6, 1)	(4, 6, 1)	(4, 6, 1)	(4, 6, 1)	
		(4, 6, 2)	(4, 6, 2)	(4, 6, 2)	(4, 6, 2)	(4, 6, 2)	(4, 6, 2)	
			(6, 8, 0)	(6, 8, 0)	(6, 8, 0)	(6, 8, 0)	(6, 8, 0)	(6, 8, 0)

(a, b, c) indicates species Pd_a1_bPy_c. Up and down arrows, ↑ and ↓, indicate increase and decrease of the signal intensity, respectively.

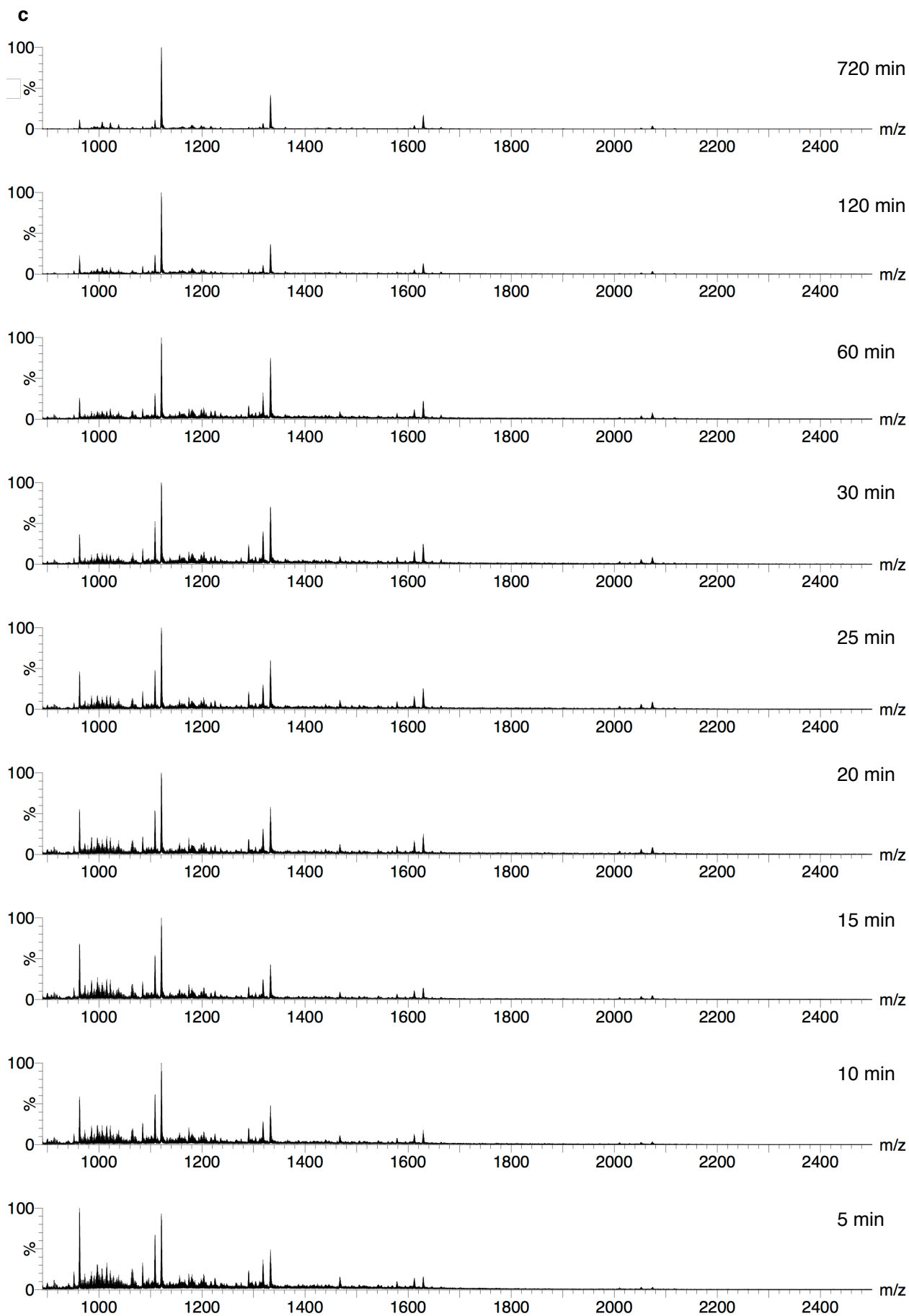


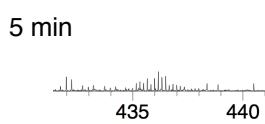
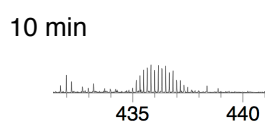
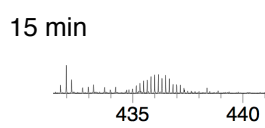
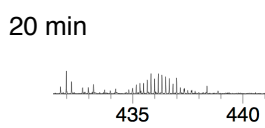
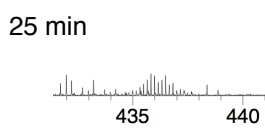
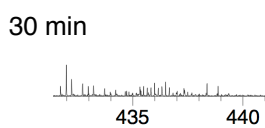
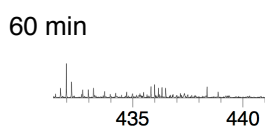
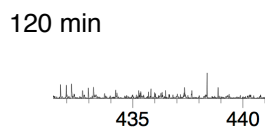
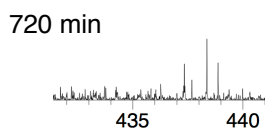
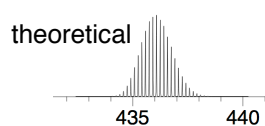
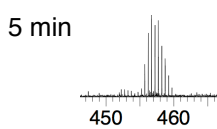
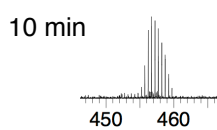
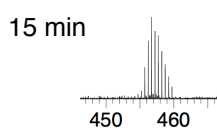
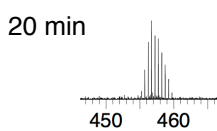
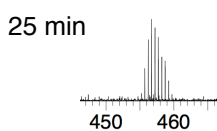
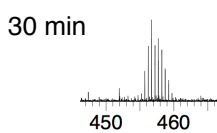
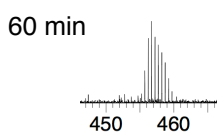
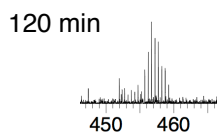
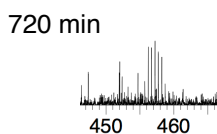
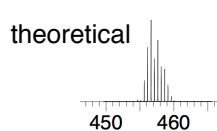
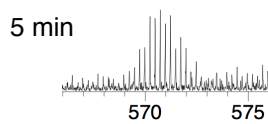
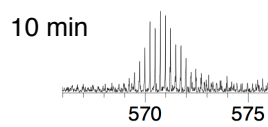
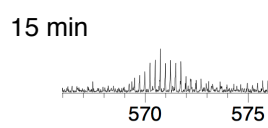
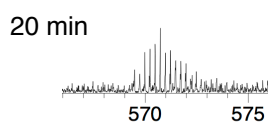
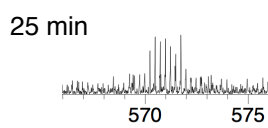
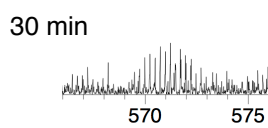
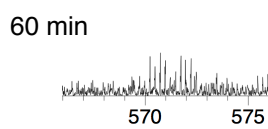
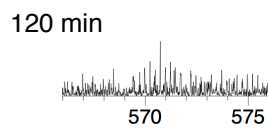
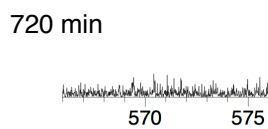
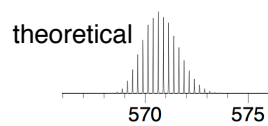
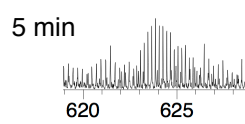
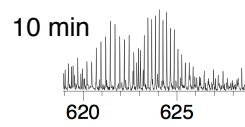
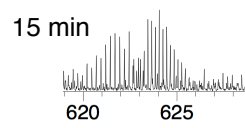
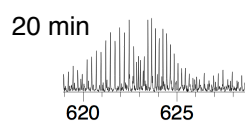
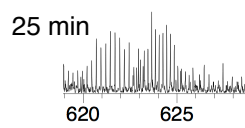
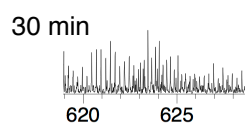
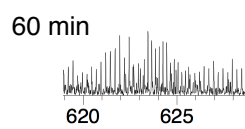
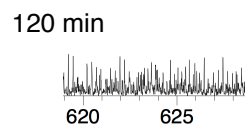
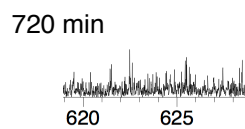
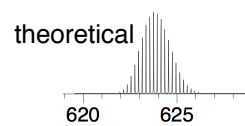
S38

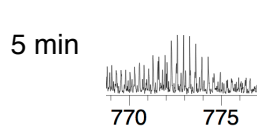
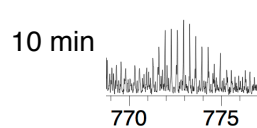
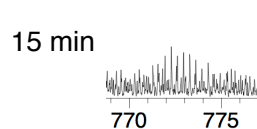
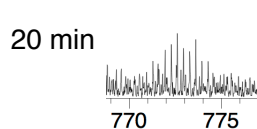
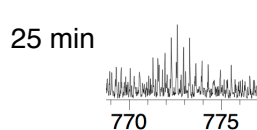
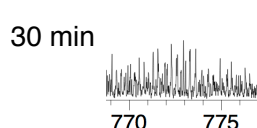
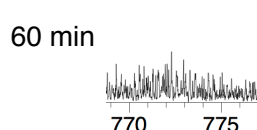
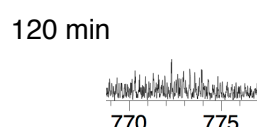
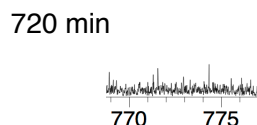
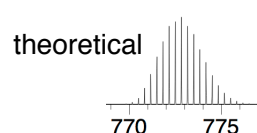
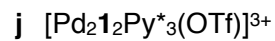
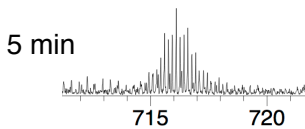
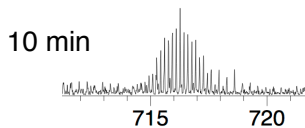
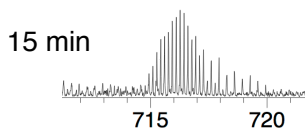
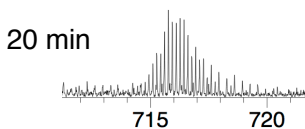
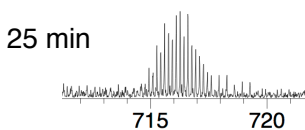
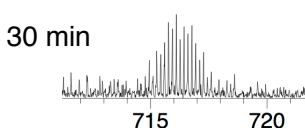
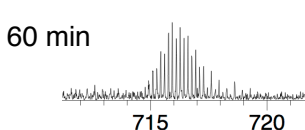
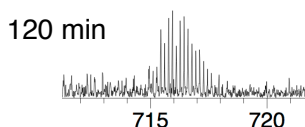
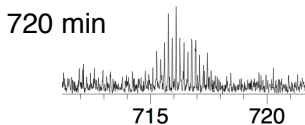
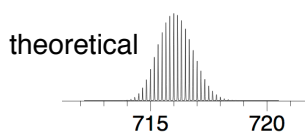
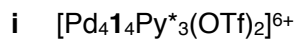
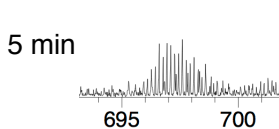
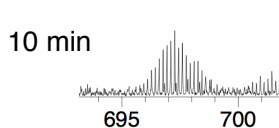
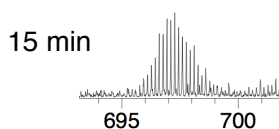
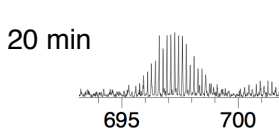
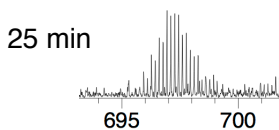
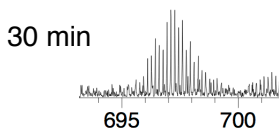
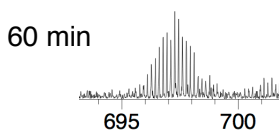
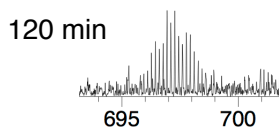
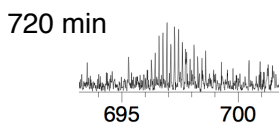
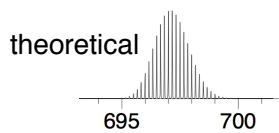
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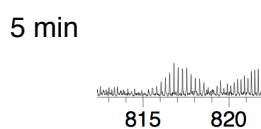
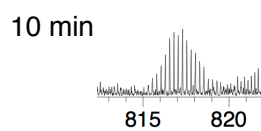
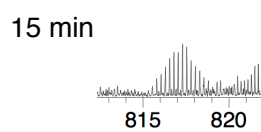
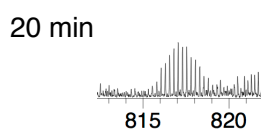
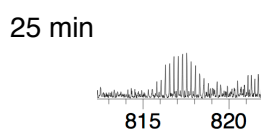
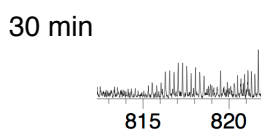
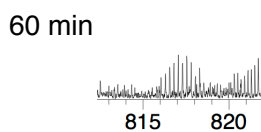
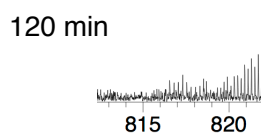
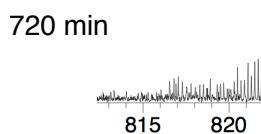
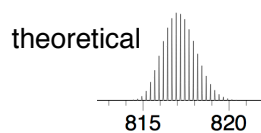
S39



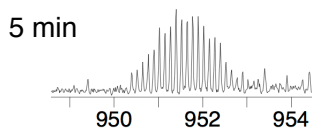
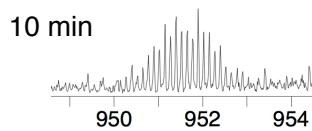
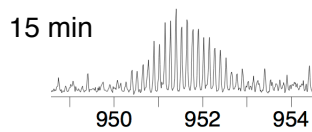
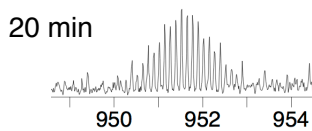
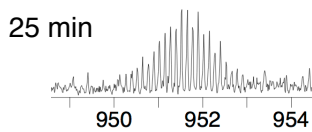
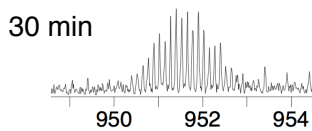
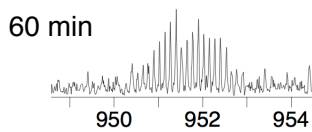
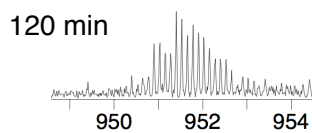
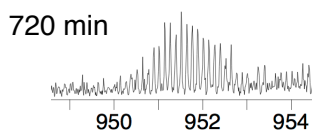
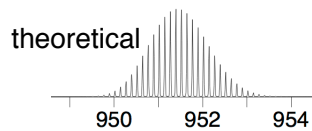
d $[\text{Pd}_3\text{1}_2\text{Py}^*_6]^{6+}$ **e** $[\text{Pd1}]^{2+}$ **f** $[\text{Pd}_2\text{1}_2\text{Py}^*_4]^{4+}$ **g** $[\text{Pd}_3\text{1}_3\text{Py}^*_2(\text{OTf})]^{5+}$ 



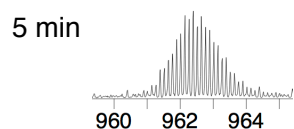
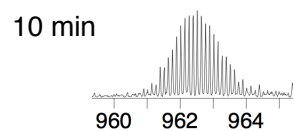
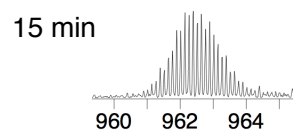
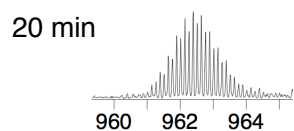
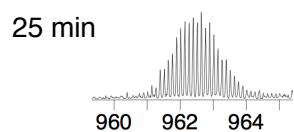
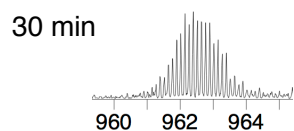
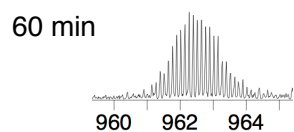
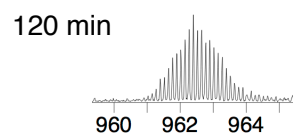
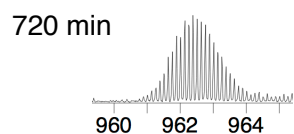
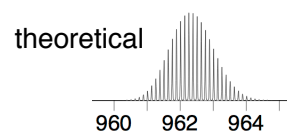
k $[\text{Pd}_3\text{1}_3\text{Py}^*_2(\text{OTf})_2]^{4+}$

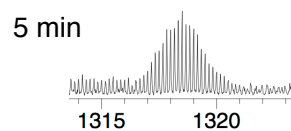
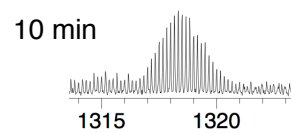
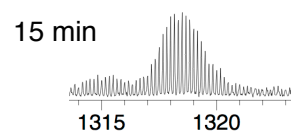
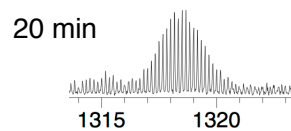
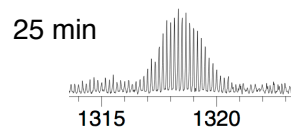
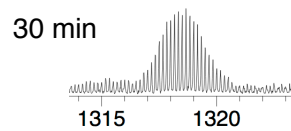
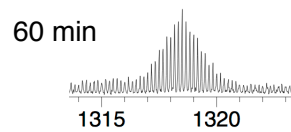
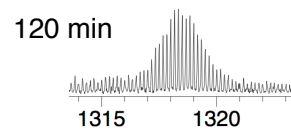
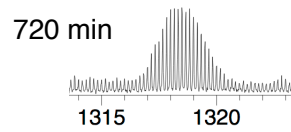
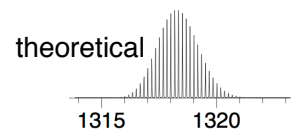
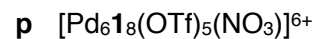
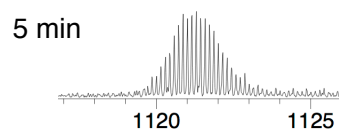
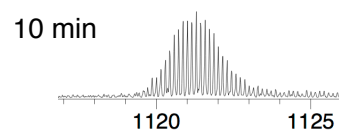
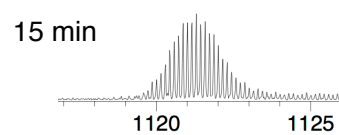
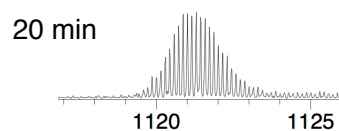
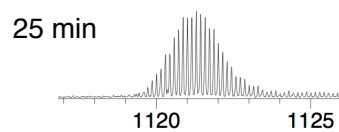
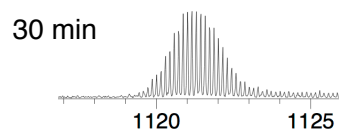
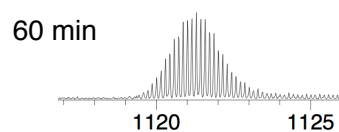
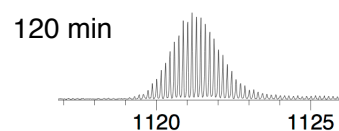
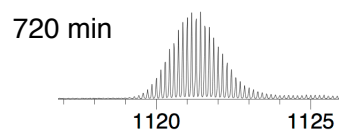
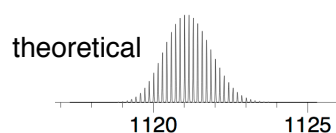
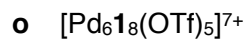
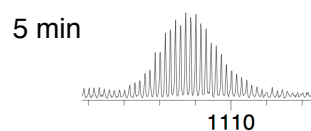
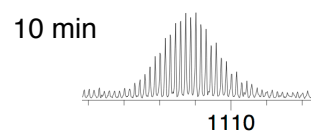
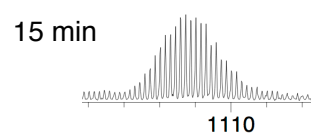
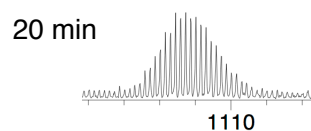
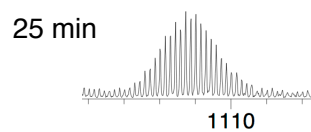
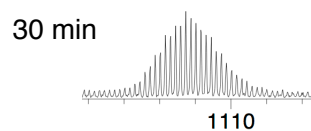
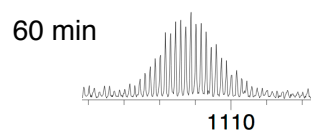
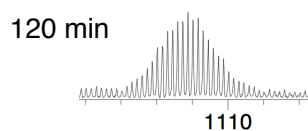
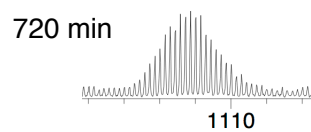
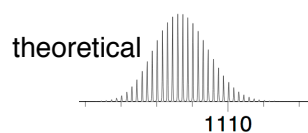


l $[\text{Pd}_6\text{1}_8(\text{OTf})_3(\text{NO}_3)]^{8+}$



m $[\text{Pd}_6\text{1}_8(\text{OTf})_4]^{8+}$





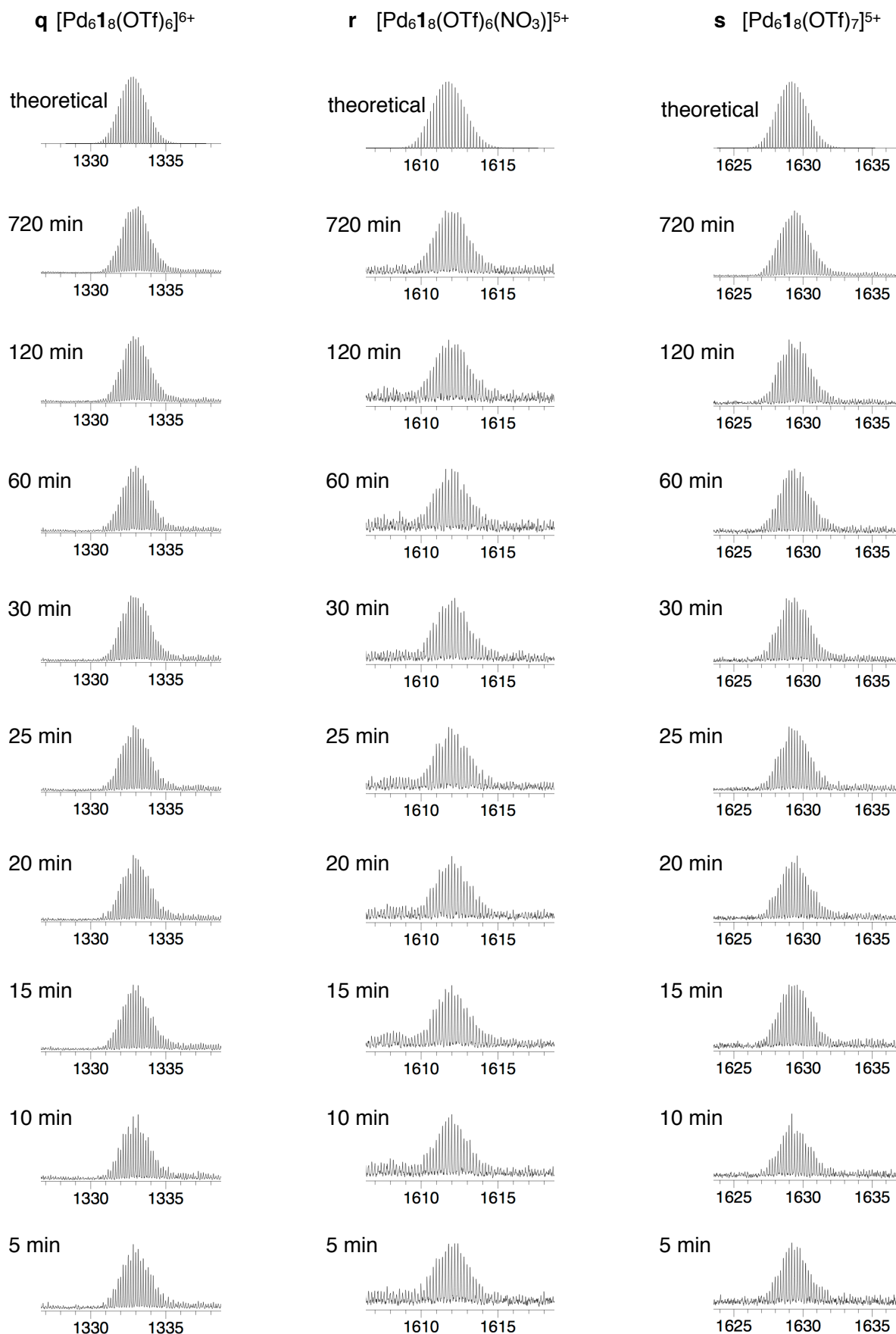


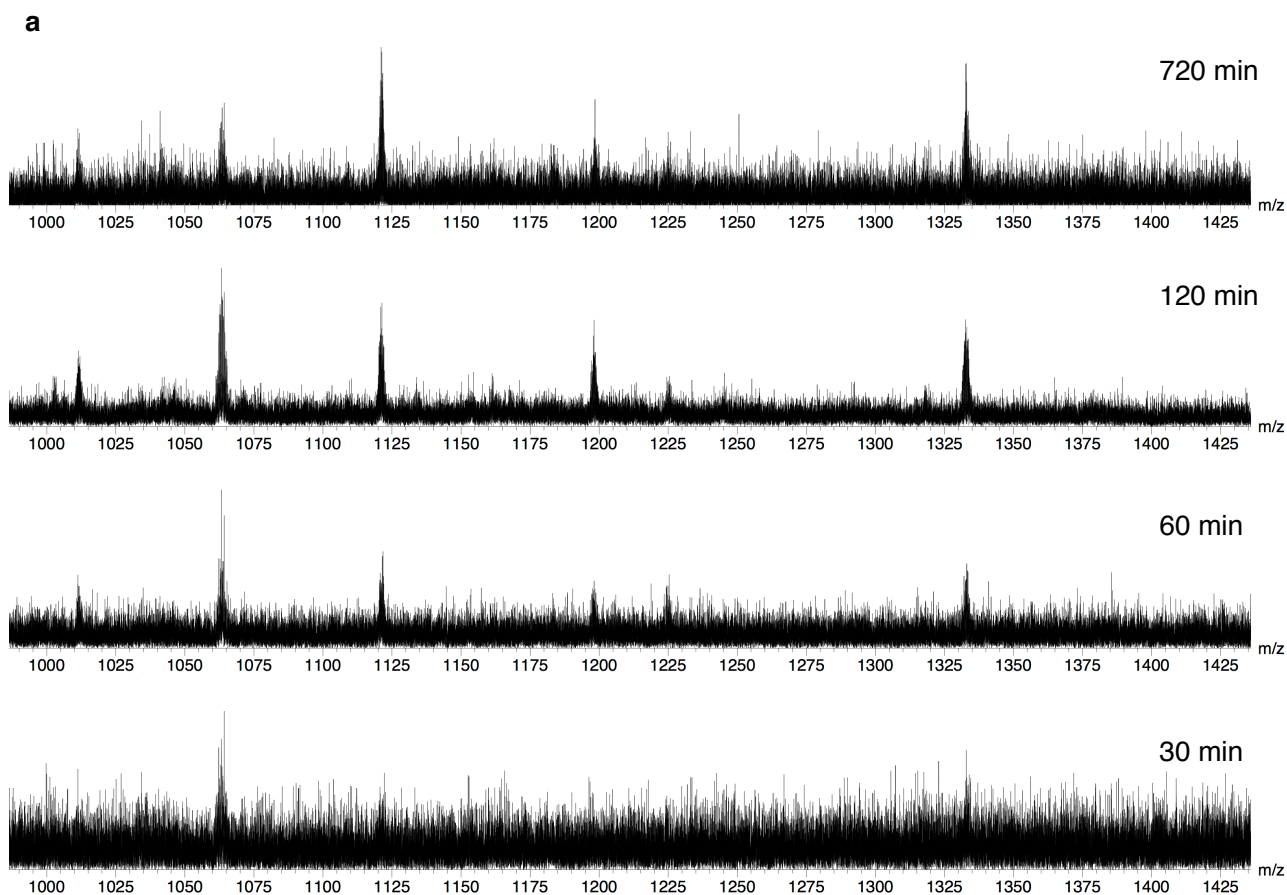
Figure S11. (a)–(c) ESI-TOF mass spectra ($m/z = 390\text{--}2480$) for the self-assembly of $[\text{Pd}_6\mathbf{1}_8]^{12+}$ from $[\text{PdPy}^*_4]^{2+}$ and **1** in $\text{CD}_3\text{NO}_2/\text{CD}_2\text{Cl}_2$ ($v/v = 4/1$) at 298 K. (d)–(s) Time variation of the signal for (d) $[\text{Pd}_3\mathbf{1}_2\text{Py}^*_6]^{6+}$, (e) $[\text{Pd}\mathbf{1}]^{2+}$ (f) $[\text{Pd}_2\mathbf{1}_2\text{Py}^*_4]^{4+}$,

(g) $[\text{Pd}_3\mathbf{1}_3\text{Py}^*_2(\text{OTf})]^{5+}$, (h) $[\text{Pd}_4\mathbf{1}_4\text{Py}^*_2(\text{OTf})_2]^{6+}$, (i) $[\text{Pd}_4\mathbf{1}_4\text{Py}^*_3(\text{OTf})_2]^{6+}$, (j) $[\text{Pd}_2\mathbf{1}_2\text{Py}^*_3(\text{OTf})]^{3+}$, (k) $[\text{Pd}_3\mathbf{1}_3\text{Py}^*_2(\text{OTf})_2]^{4+}$, (l) $[\text{Pd}_6\mathbf{1}_8(\text{OTf})_3(\text{NO}_3)]^{8+}$, (m) $[\text{Pd}_6\mathbf{1}_8(\text{OTf})_4]^{8+}$, (n) $[\text{Pd}_6\mathbf{1}_8(\text{OTf})_4(\text{NO}_3)]^{7+}$, (o) $[\text{Pd}_6\mathbf{1}_8(\text{OTf})_5]^{7+}$, (p) $[\text{Pd}_6\mathbf{1}_8(\text{OTf})_5(\text{NO}_3)]^{6+}$, (q) $[\text{Pd}_6\mathbf{1}_8(\text{OTf})_6]^{6+}$, (r) $[\text{Pd}_6\mathbf{1}_8(\text{OTf})_6(\text{NO}_3)]^{5+}$, and (s) $[\text{Pd}_6\mathbf{1}_8(\text{OTf})_7]^{5+}$.

Table S15. Time variation of the species detected by ESI-TOF mass spectrometry for the self-assembly of the capsule from **1** and $\text{PdPy}^*_4(\text{OTf})_2$ in $\text{CD}_3\text{NO}_2/\text{CD}_2\text{Cl}_2$ (v/v = 4/1) at 298 K.

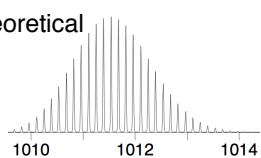
5 min	10 min	15 min	20 min	25 min	30 min	60 min	120 min	720 min
(1, 1, 0)	(1, 1, 0)	(1, 1, 0)	(1, 1, 0)	(1, 1, 0)	(1, 1, 0)	(1, 1, 0)	(1, 1, 0)	(1, 1, 0)
(2, 2, 3)	(2, 2, 3)	(2, 2, 3)	(2, 2, 3)	(2, 2, 3)				
(2, 2, 4)	(2, 2, 4)	(2, 2, 4)	(2, 2, 4)	(2, 2, 4)	(2, 2, 4)	(2, 2, 4)	(2, 2, 4) ↓	
(3, 2, 6)	(3, 2, 6)	(3, 2, 6)	(3, 2, 6)	(3, 2, 6)				
(3, 3, 2)	(3, 3, 2)	(3, 3, 2)	(3, 3, 2)	(3, 3, 2)	(3, 3, 2)	(3, 3, 2)		
(4, 4, 2)	(4, 4, 2)	(4, 4, 2)	(4, 4, 2)	(4, 4, 2)	(4, 4, 2)	(4, 4, 2)	(4, 4, 2)	(4, 4, 2)
(4, 4, 3)	(4, 4, 3)	(4, 4, 3)	(4, 4, 3)	(4, 4, 3)	(4, 4, 3)	(4, 4, 3)	(4, 4, 3)	(4, 4, 3)
(6, 8, 0)	(6, 8, 0)	(6, 8, 0)	(6, 8, 0)	(6, 8, 0)	(6, 8, 0)	(6, 8, 0)	(6, 8, 0)	(6, 8, 0)

(a, b, c) indicates species $\text{Pd}_a\mathbf{1}_b\text{Py}^*_c$. Up and down arrows, ↑ and ↓, indicate increase and decrease of the signal intensity, respectively.

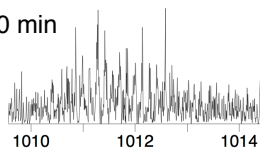


b $[\text{Pd}_6\text{1}_7(\text{CH}_3\text{CN})(\text{OTf})_5]^{7+}$

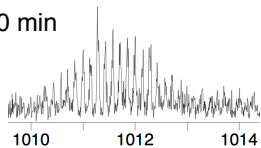
theoretical



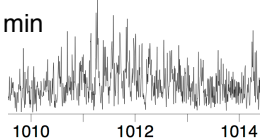
720 min



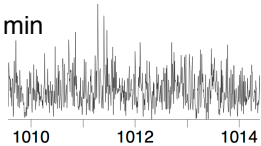
120 min



60 min

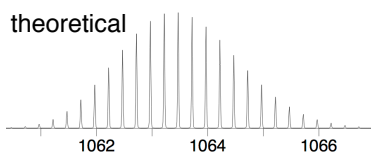


30 min

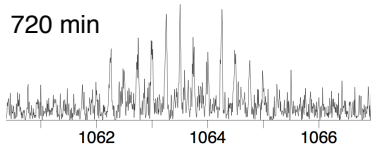


c $[\text{Pd}_4\text{1}_4(\text{OTf})_4]^{4+}$

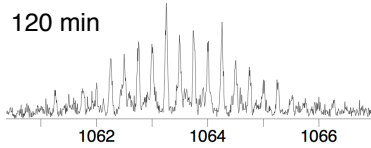
theoretical



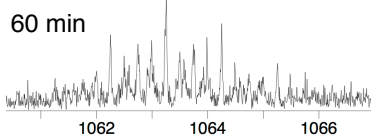
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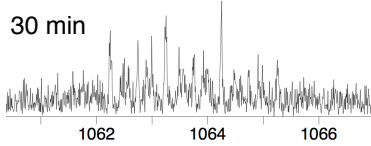
120 min



60 min

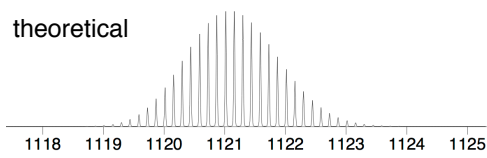


30 min

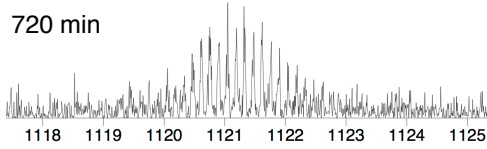


d $[\text{Pd}_6\text{1}_8(\text{OTf})_5]^{7+}$

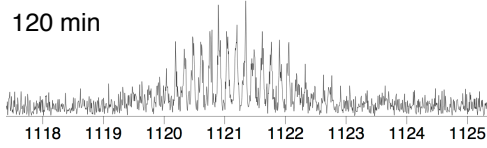
theoretical



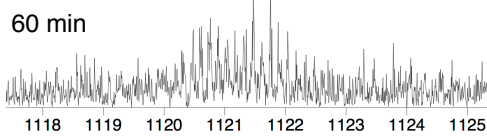
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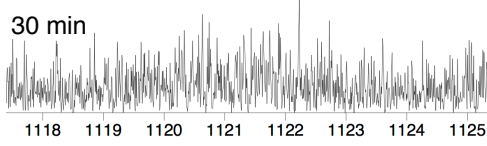
120 min



60 min



30 min



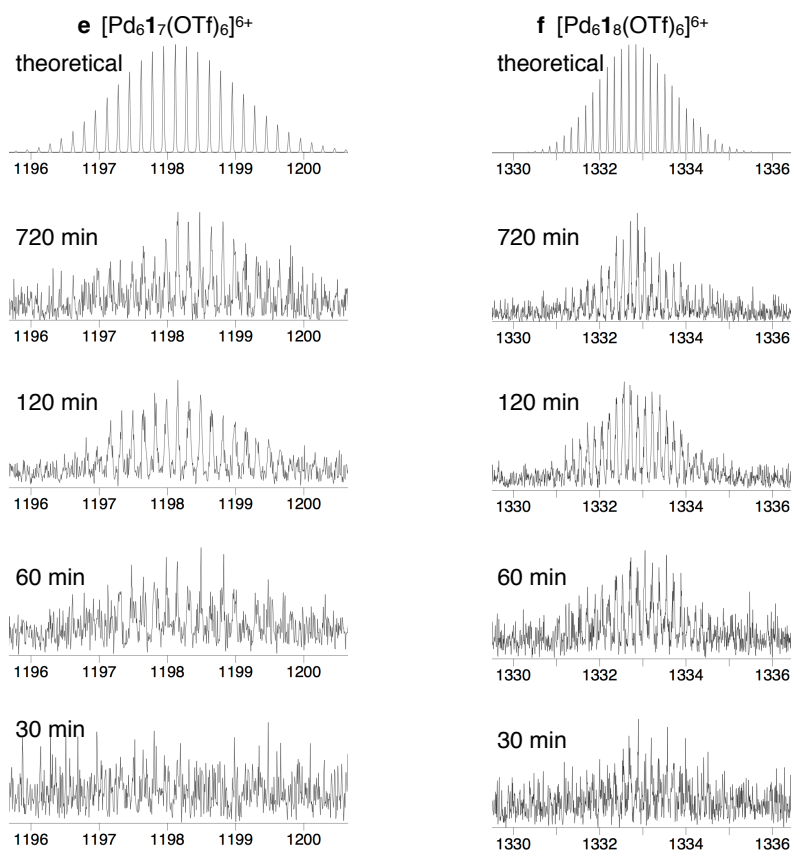
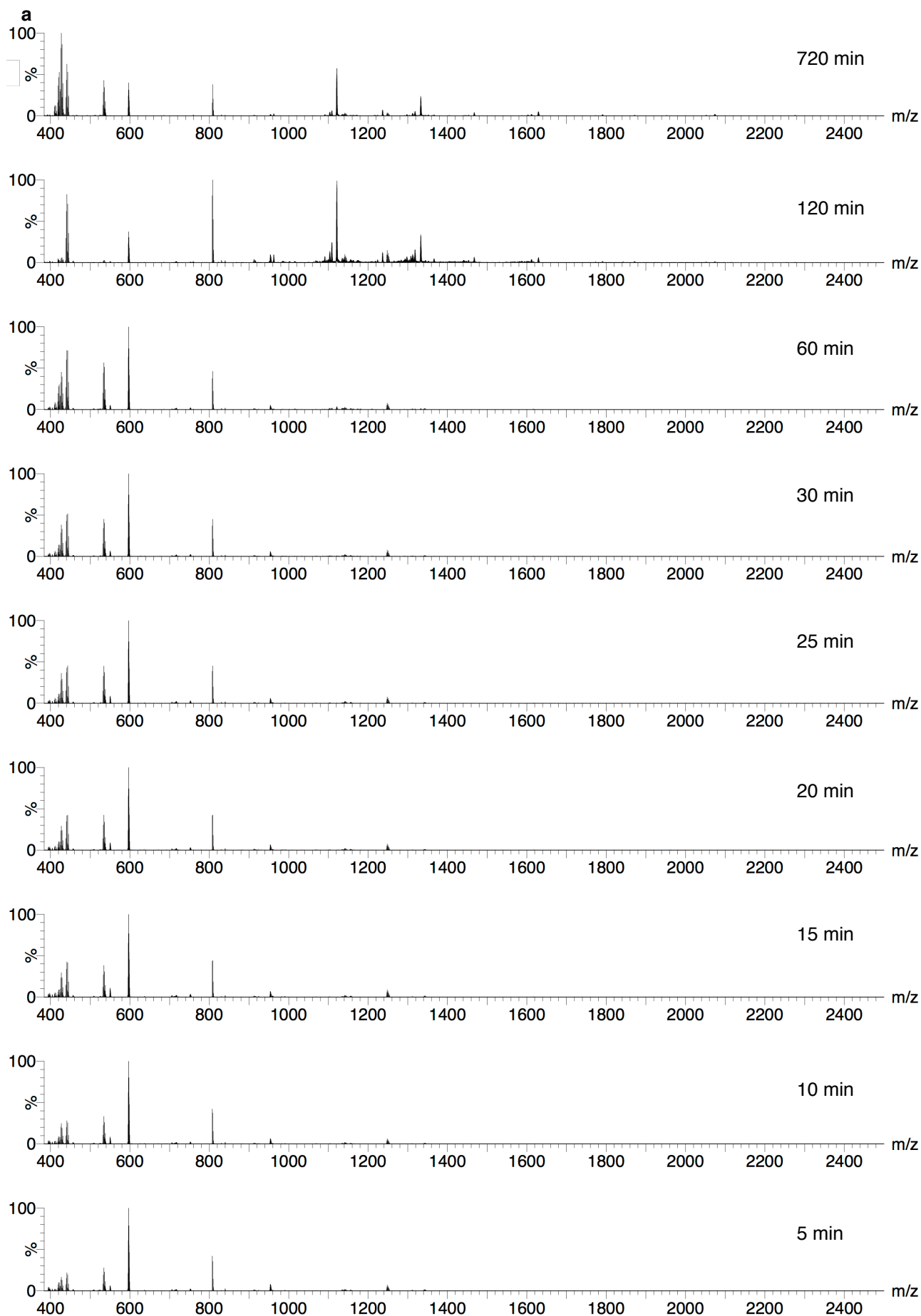


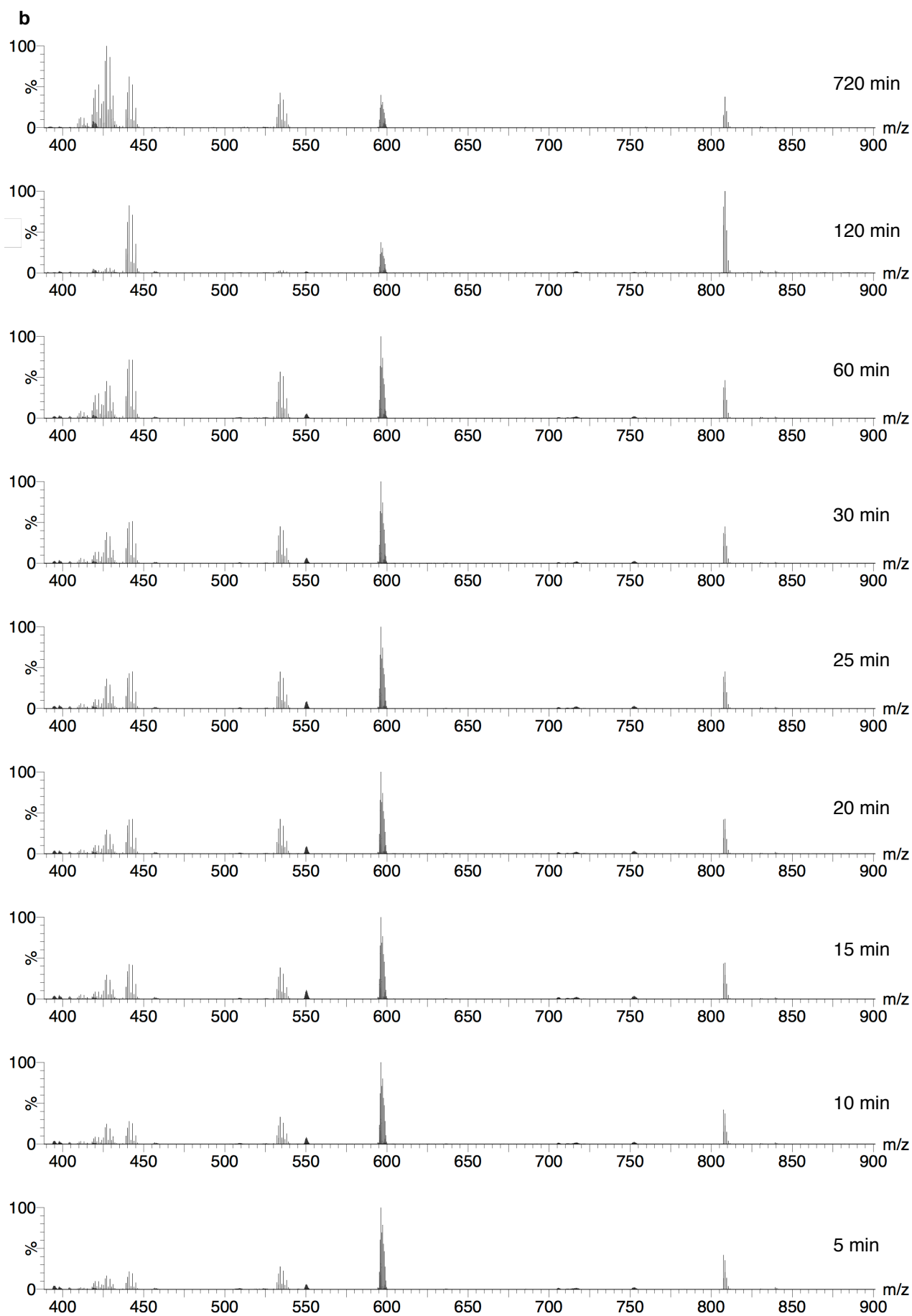
Figure S12. (a) ESI-TOF mass spectra ($m/z = 985\text{--}1435$) for the self-assembly of $[\text{Pd}_6\mathbf{1}_8]^{12+}$ from $[\text{Pd}(\text{CH}_3\text{CN})_4]^{2+}$ and **1** in $\text{CD}_3\text{NO}_2/\text{CD}_2\text{Cl}_2$ ($v/v = 4/1$) at 298 K. (b)–(f) Time variation of the signal for (b) $[\text{Pd}_6\mathbf{1}_7(\text{CH}_3\text{CN})(\text{OTf})_5]^{7+}$, (c) $[\text{Pd}_4\mathbf{1}_4(\text{OTf})_4]^{4+}$, (d) $[\text{Pd}_6\mathbf{1}_8(\text{OTf})_5]^{7+}$, (e) $[\text{Pd}_6\mathbf{1}_7(\text{OTf})_6]^{6+}$, and (f) $[\text{Pd}_6\mathbf{1}_8(\text{OTf})_6]^{6+}$.

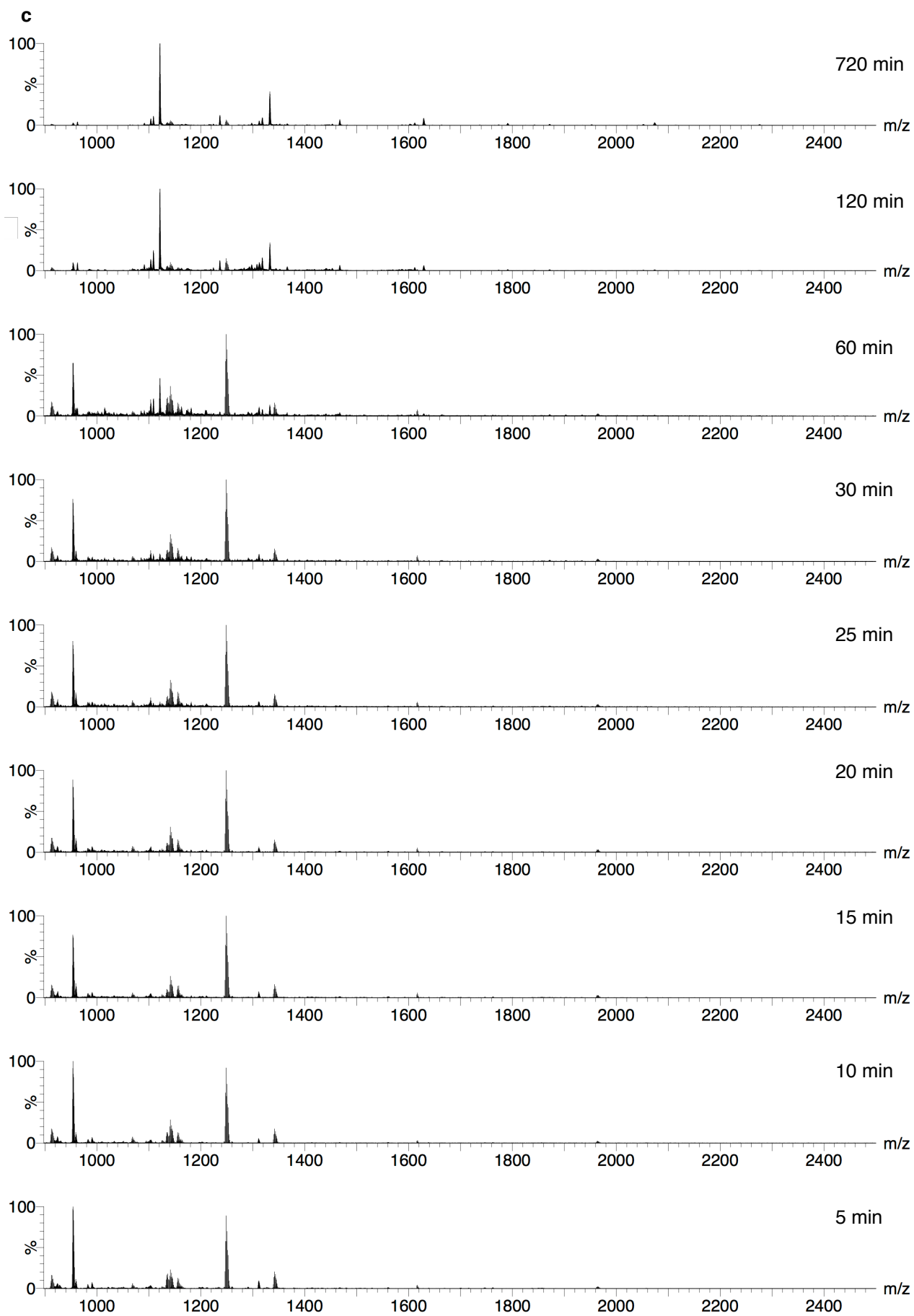
Table S16. Time variation of the species detected by ESI-TOF mass spectrometry for the self-assembly of the capsule from **1** and $\text{Pd}(\text{CH}_3\text{CN})_4(\text{OTf})_2$ in $\text{CD}_3\text{NO}_2/\text{CD}_2\text{Cl}_2$ ($v/v = 4/1$) at 298 K.

30 min	60 min	120 min	720 min
(4, 4, 0)	(4, 4, 0) ↑	(4, 4, 0) ↑	(4, 4, 0) ↓
	(6, 7, 0)	(6, 7, 0) ↑	(6, 7, 0)
	(6, 7, 1)	(6, 7, 1) ↑	(6, 7, 1) ↓
(6, 8, 0)	(6, 8, 0) ↑	(6, 8, 0) ↑	(6, 8, 0) ↑

(a, b, c) indicates species $\text{Pd}_a\mathbf{1}_b \cdot (\text{CH}_3\text{CN})_c$. Up and down arrows, ↑ and ↓, indicate increase and decrease of the signal intensity, respectively.

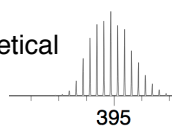




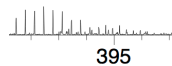


d $[\text{Pd}_2\text{1Py}^4\text{Me}_6]^{4+}$

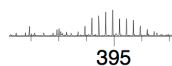
theoretical



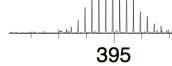
720 min



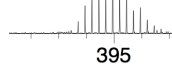
120 min



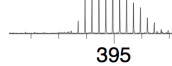
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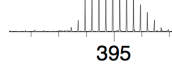
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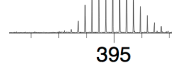
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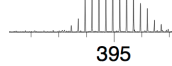
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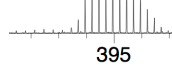
15 min



10 min

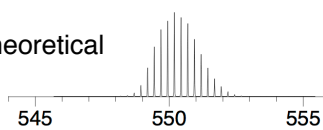


5 min

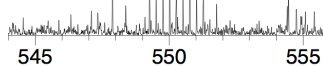


e $[\text{Pd}_2\text{1}_2\text{Py}^4\text{Me}_4]^{4+}$

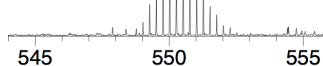
theoretical



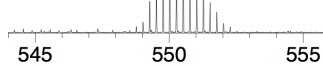
720 min



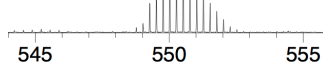
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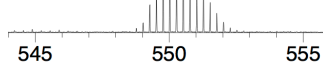
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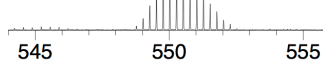
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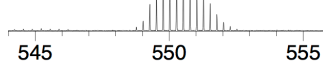
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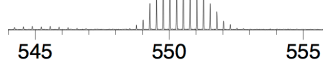
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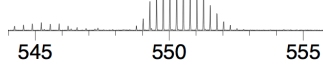
15 min



10 min

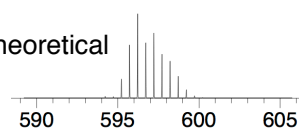


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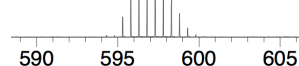


f $[\text{Pd1Py}^4\text{Me}_3]^{2+}$

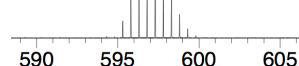
theoretical



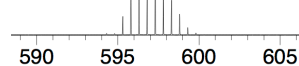
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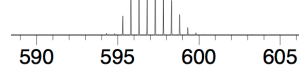
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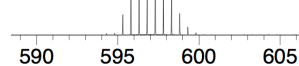
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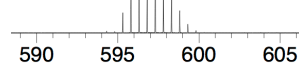
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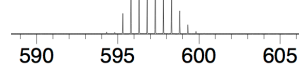
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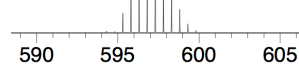
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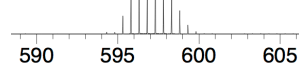
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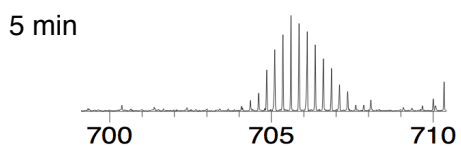
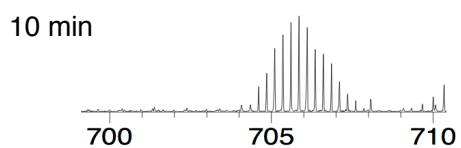
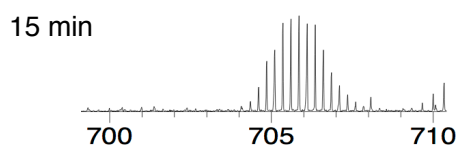
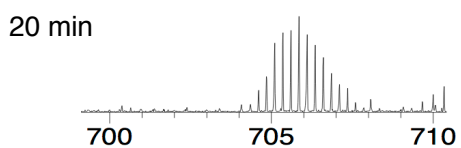
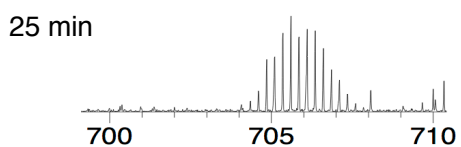
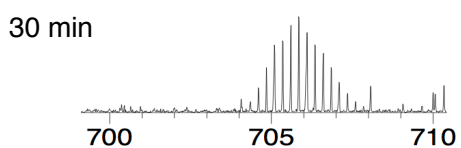
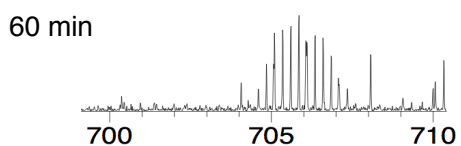
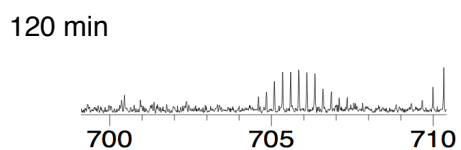
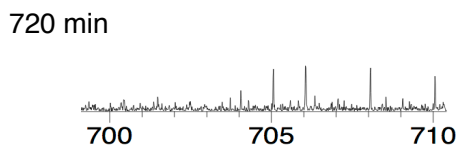
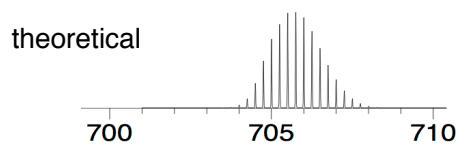
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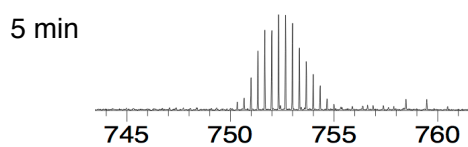
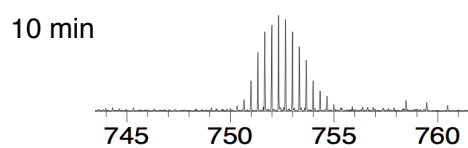
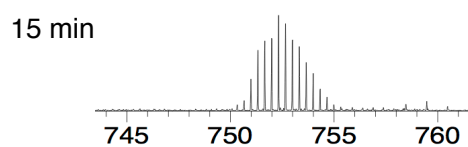
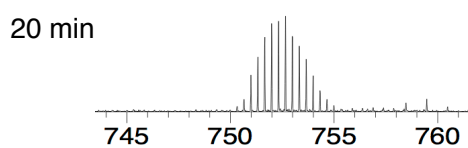
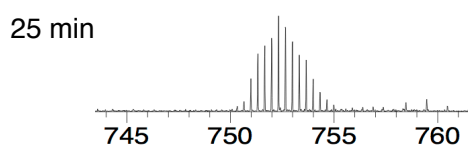
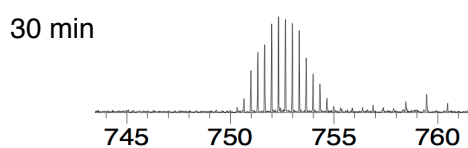
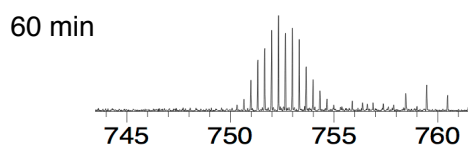
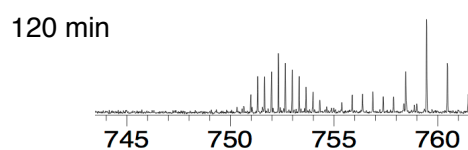
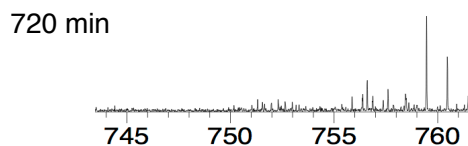
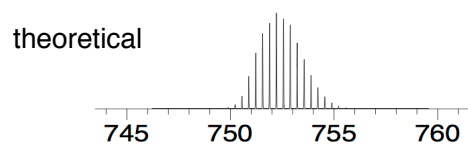
5 min



g $[\text{Pd}_2\text{1}_3\text{Py}^4\text{Me}_2]^{4+}$

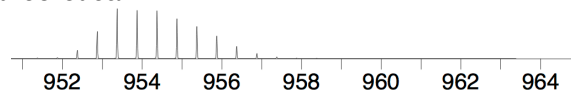


h $[\text{Pd}_2\text{1}_2\text{Py}^4\text{Me}_3(\text{OTf})]^{3+}$

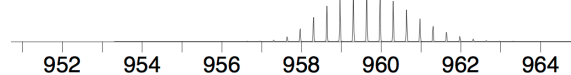


i $[\text{Pd}_2\text{1}_2\text{Py}^{4\text{Me}}_2]^{2+}$

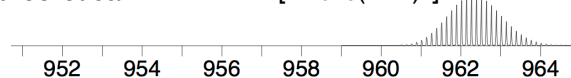
theoretical



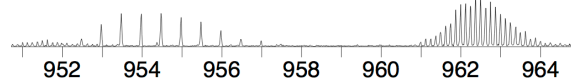
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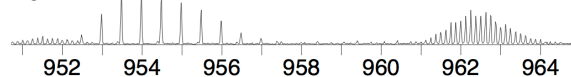
theoretical



720 min



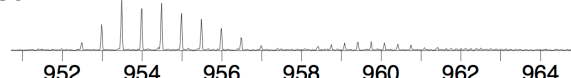
120 min



60 min



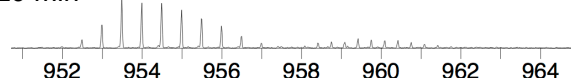
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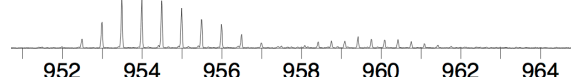
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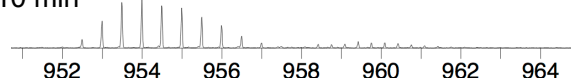
20 min



15 min



10 min

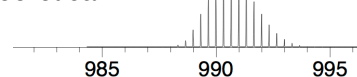


5 min

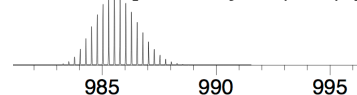


j $[\text{Pd}_2\text{1}_3\text{Py}^{4\text{Me}}_2(\text{OTf})]^{3+}$

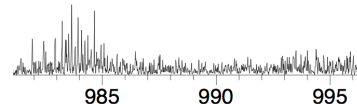
theoretical



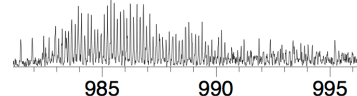
theoretical $[\text{Pd}_3\text{1}_4\text{Py}^{4\text{Me}}(\text{OTf})_2]^{4+}$



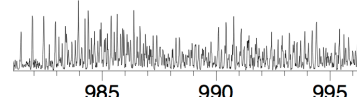
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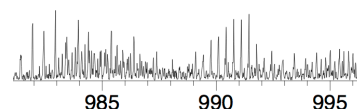
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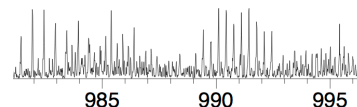
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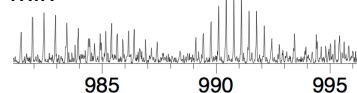
30 min



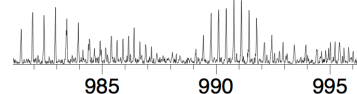
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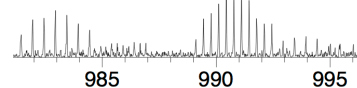
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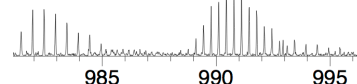
15 min



10 min

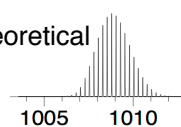


5 min

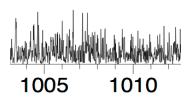


k $[\text{Pd}_3\text{1}_4\text{Py}^4\text{Me}_2(\text{OTf})_2]^{4+}$

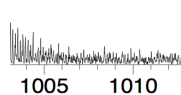
theoretical



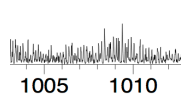
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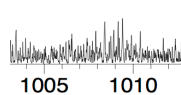
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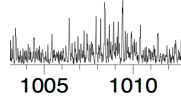
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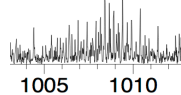
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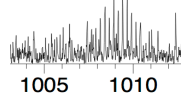
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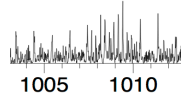
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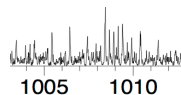
15 min



10 min

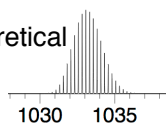


5 min

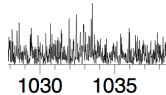


l $[\text{Pd}_3\text{1}_4\text{Py}^4\text{Me}_3(\text{OTf})_2]^{4+}$

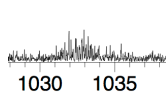
theoretical



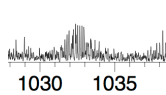
720 min



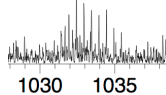
120 min



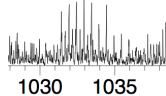
60 min



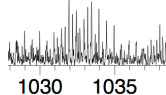
30 min



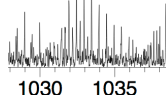
25 min



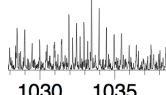
20 min



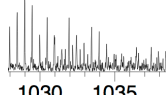
15 min



10 min

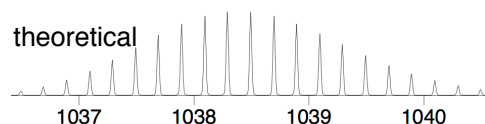


5 min

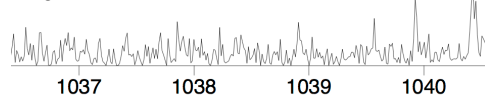


m $[\text{Pd}_4\text{1}_5\text{Py}^4\text{Me}_3(\text{OTf})_3]^{5+}$

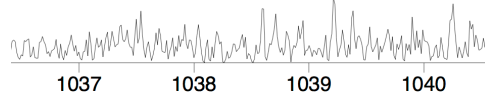
theoretical



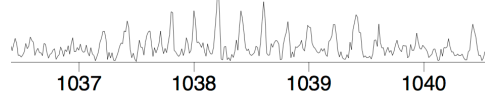
720 min



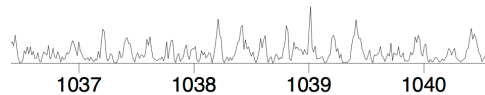
120 min



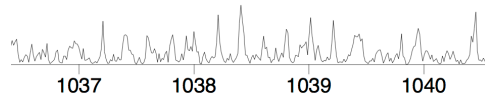
60 min



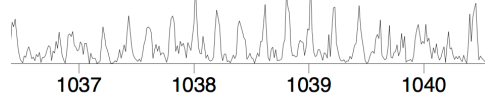
30 min



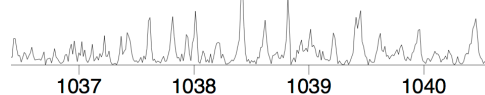
25 min



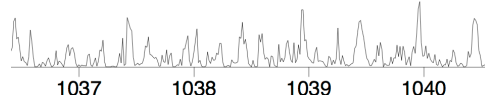
20 min



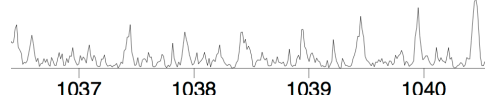
15 min



10 min

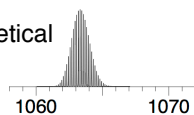


5 min

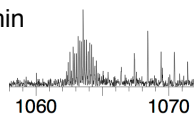


n $[\text{Pd}_6\text{1}_9(\text{OTf})_4]^{8+}$

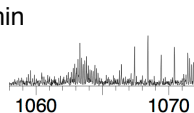
theoretical



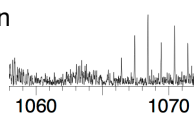
720 min



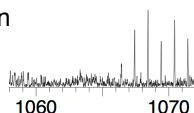
120 min



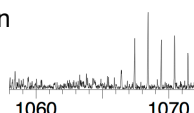
60 min



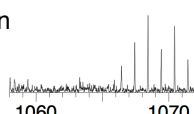
30 min



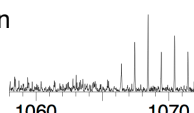
25 min



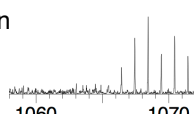
20 min



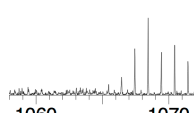
15 min



10 min

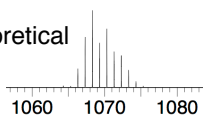


5 min

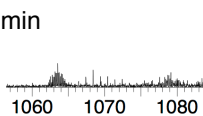


o $[\text{Pd1Py}^4\text{Me}(\text{NO}_3)]^+$

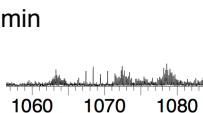
theoretical



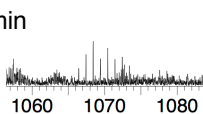
720 min



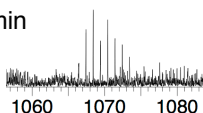
120 min



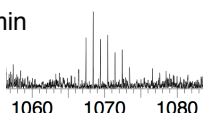
60 min



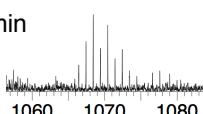
30 min



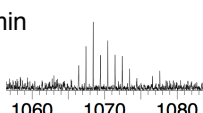
25 min



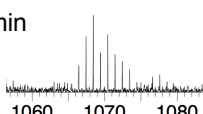
20 min



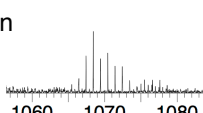
15 min



10 min

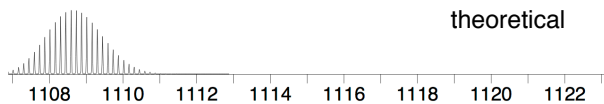


5 min



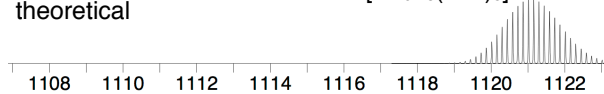
p $[\text{Pd}_6\text{1}_8(\text{OTf})_4(\text{NO}_3)]^{7+}$

theoretical

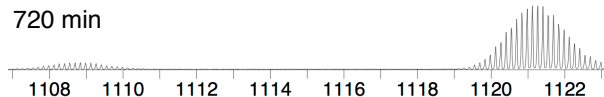


theoretical

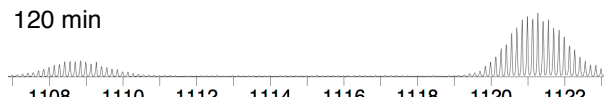
$[\text{Pd}_6\text{1}_8(\text{OTf})_5]^{7+}$



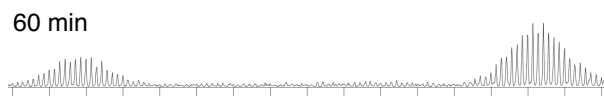
720 min



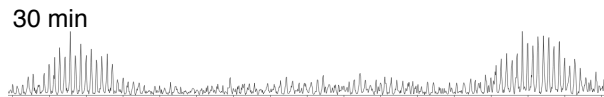
120 min



60 min



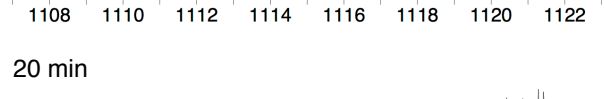
30 min



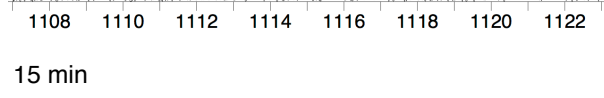
25 min



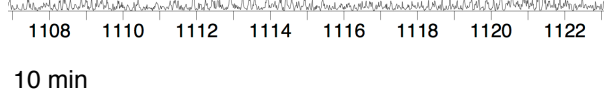
20 min



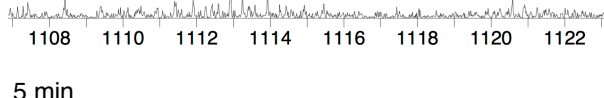
15 min



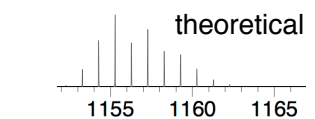
10 min



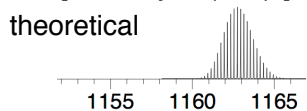
5 min



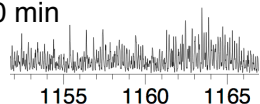
q $[\text{Pd}_1\text{Py}^4\text{Me}(\text{OTf})]^+$



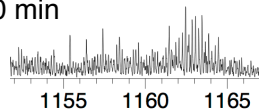
$[\text{Pd}_4\text{1}_6\text{Py}^4\text{Me}(\text{OTf})_3]^{5+}$



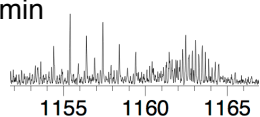
720 min



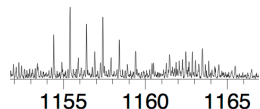
120 min



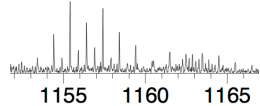
60 min



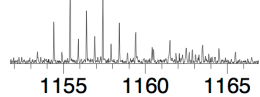
30 min



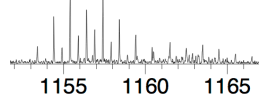
25 min



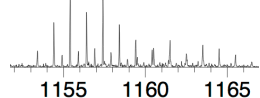
20 min



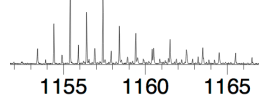
15 min



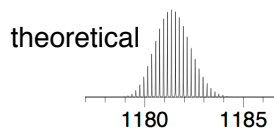
10 min



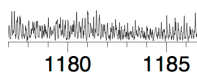
5 min



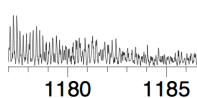
r $[\text{Pd}_4\text{1}_6\text{Py}^4\text{Me}_2(\text{OTf})_3]^{5+}$



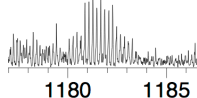
720 min



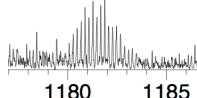
120 min



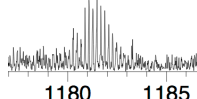
60 min



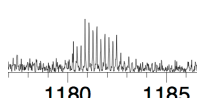
30 min



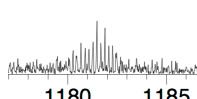
25 min



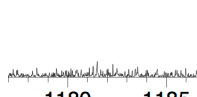
20 min



15 min



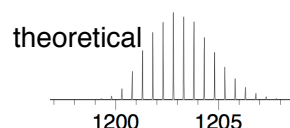
10 min



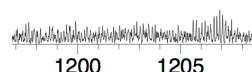
5 min



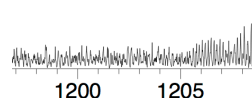
s $[\text{Pd}_2\text{1}_2\text{Py}^4\text{Me}_3(\text{OTf})_2]^{2+}$



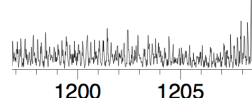
720 min



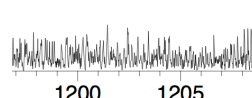
120 min



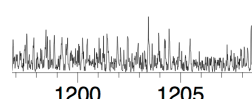
60 min



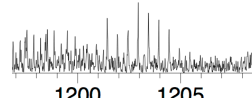
30 min



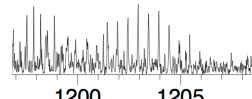
25 min



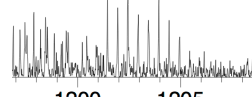
20 min



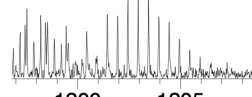
15 min



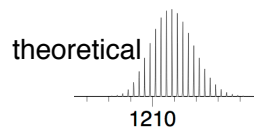
10 min



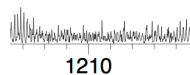
5 min



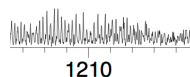
t $[\text{Pd}_3\text{1}_5\text{Py}^4\text{Me}_2(\text{OTf})_2]^{4+}$



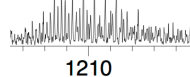
720 min



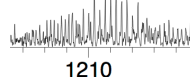
120 min



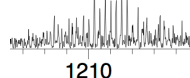
60 min



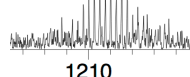
30 min



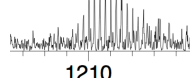
25 min



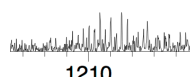
20 min



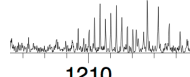
15 min



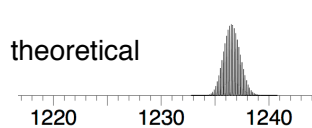
10 min



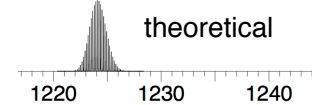
5 min



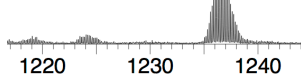
u $[\text{Pd}_6\text{1}_9(\text{OTf})_5]^{7+}$



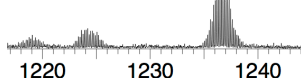
$[\text{Pd}_6\text{1}_9(\text{OTf})_4(\text{NO}_3)]^{7+}$



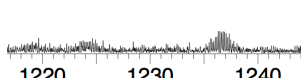
720 min



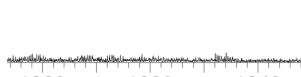
120 min



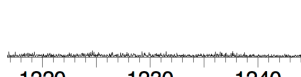
60 min



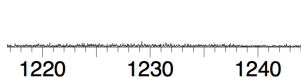
30 min



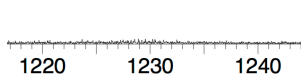
25 min



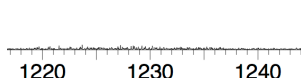
20 min



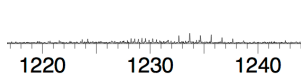
15 min



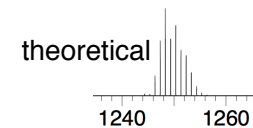
10 min



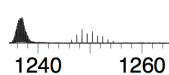
5 min



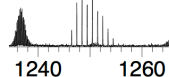
v $[\text{Pd1Py}^4\text{Me}_2(\text{OTf})]^{+}$



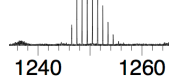
720 min



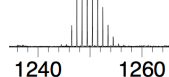
120 min



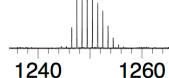
60 min



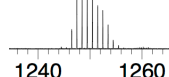
30 min



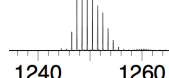
25 min



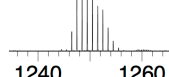
20 min



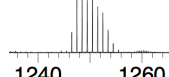
15 min



10 min

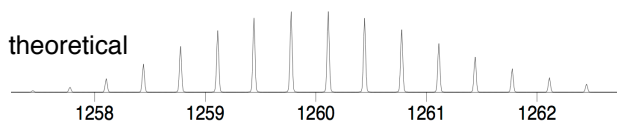


5 min

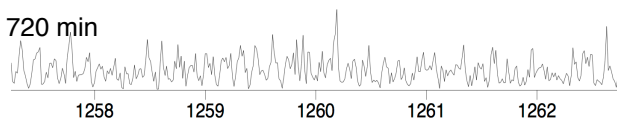


w $[\text{Pd}_2\text{1}_4\text{Py}^4\text{Me}_2(\text{OTf})]^{3+}$

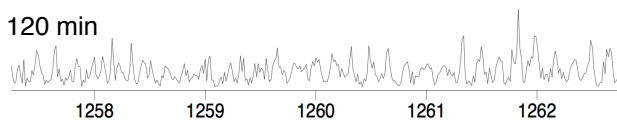
theoretical



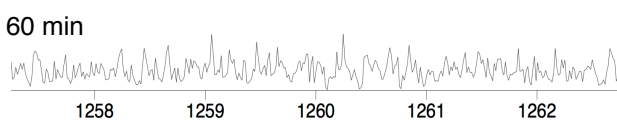
720 min



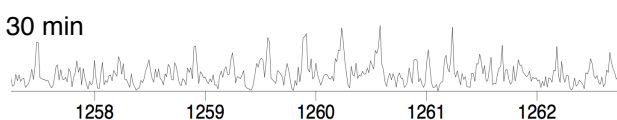
120 min



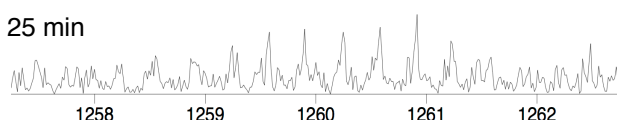
60 min



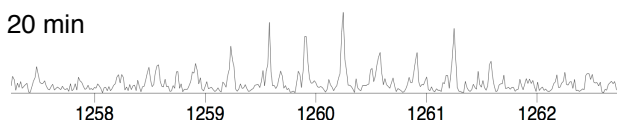
30 min



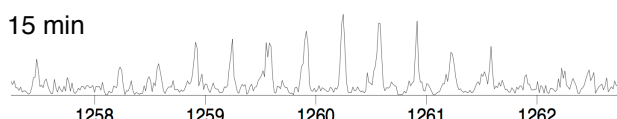
25 min



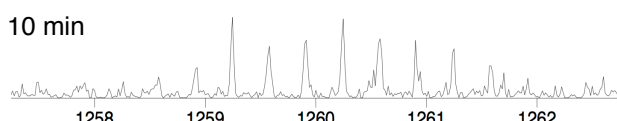
20 min



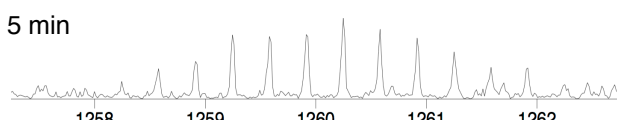
15 min



10 min

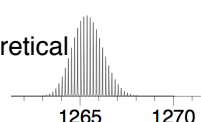


5 min

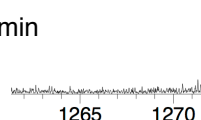


x $[\text{Pd}_5\text{1}_8(\text{OTf})_4]^{6+}$

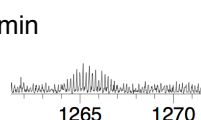
theoretical



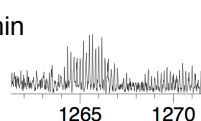
720 min



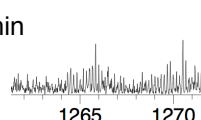
120 min



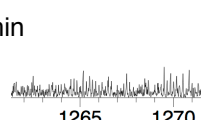
60 min



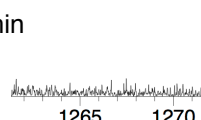
30 min



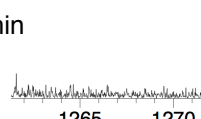
25 min



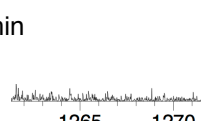
20 min



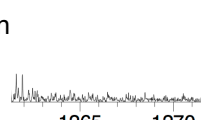
15 min



10 min

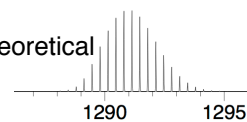


5 min

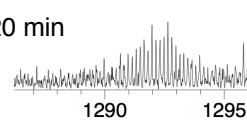


y $[\text{Pd}_2\text{1}_4\text{Py}^4\text{Me}_3(\text{OTf})]^{3+}$

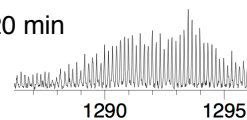
theoretical



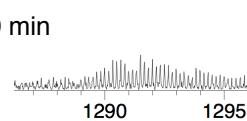
720 min



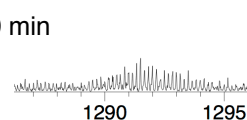
120 min



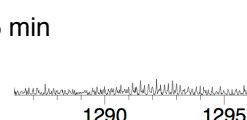
60 min



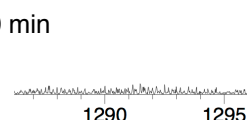
30 min



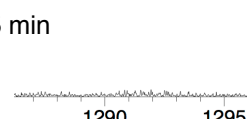
25 min



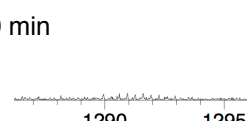
20 min



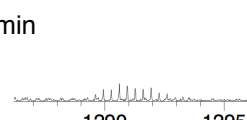
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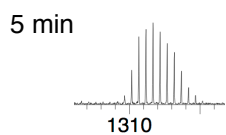
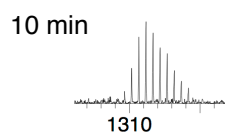
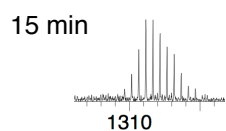
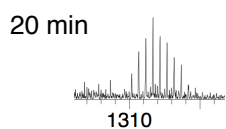
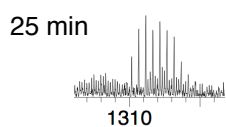
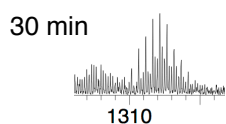
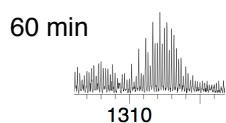
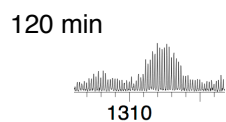
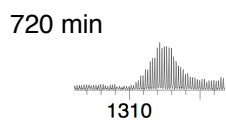
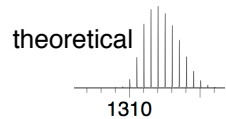
10 min



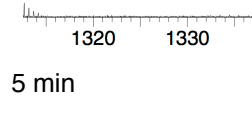
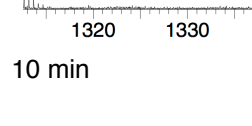
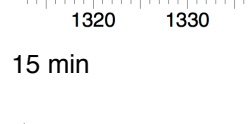
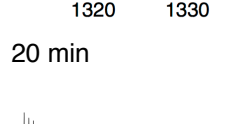
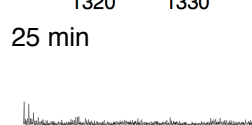
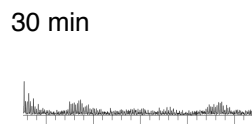
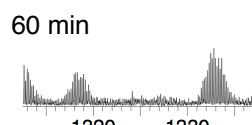
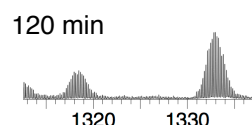
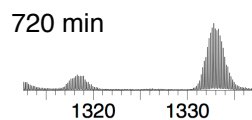
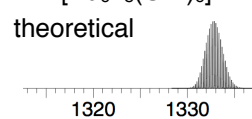
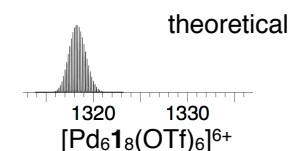
5 min



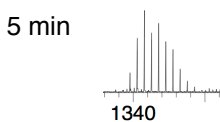
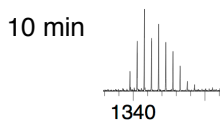
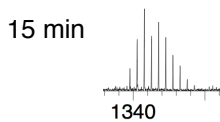
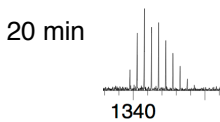
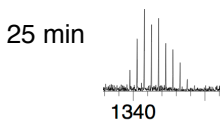
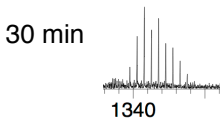
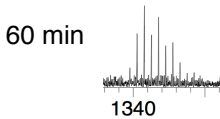
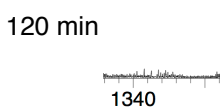
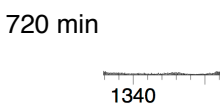
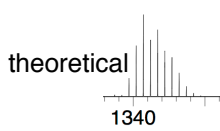
z $[\text{Pd}_6\text{Py}_4\text{Me}_3]^{2+}$



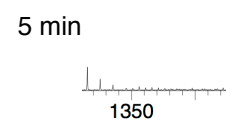
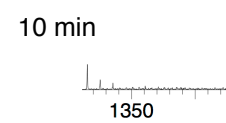
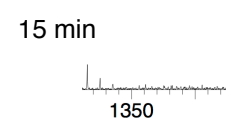
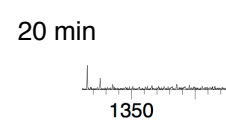
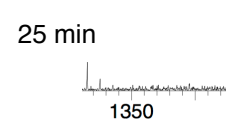
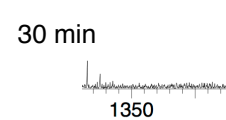
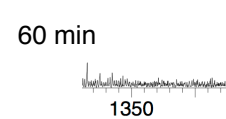
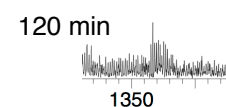
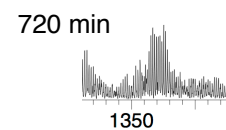
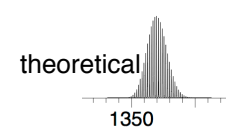
aa $[\text{Pd}_6\text{1}_8(\text{OTf})_5(\text{NO}_3)]^{6+}$



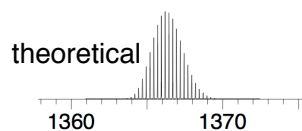
ab $[\text{Pd}_6\text{Py}_4\text{Me}_3(\text{OTf})]^{+}$



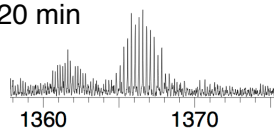
ac $[\text{Pd}_6\text{1}_{10}(\text{OTf})_5]^{7+}$



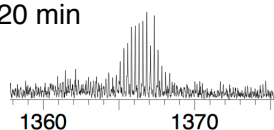
ad $[\text{Pd}_3\text{1}_6(\text{OTf})_2]^{4+}$



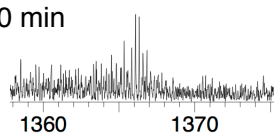
720 min



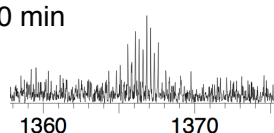
120 min



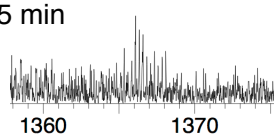
60 min



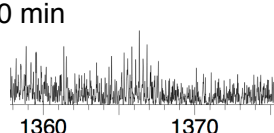
30 min



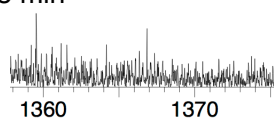
25 min



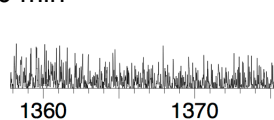
20 min



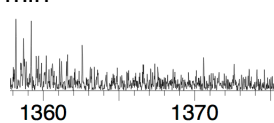
15 min



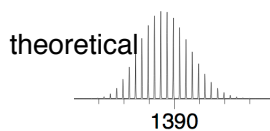
10 min



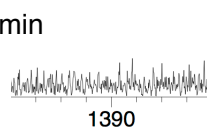
5 min



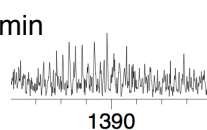
ae $[\text{Pd}_3\text{1}_6\text{Py}^{\text{4Me}}(\text{OTf})_2]^{4+}$



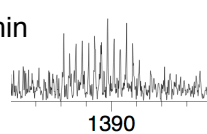
720 min



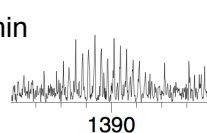
120 min



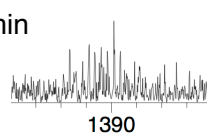
60 min



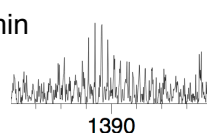
30 min



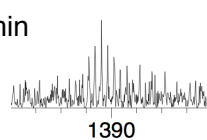
25 min



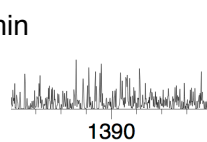
20 min



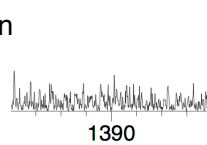
15 min



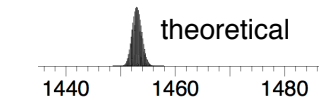
10 min



5 min

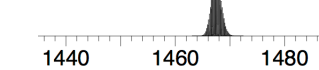


af $[\text{Pd}_6\text{1}_9(\text{OTf})_5(\text{NO}_3)]^{6+}$



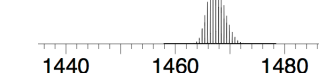
$[\text{Pd}_6\text{1}_9(\text{OTf})_6]^{6+}$

theoretical

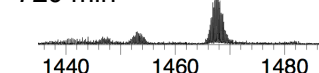


$[\text{Pd}_2\text{1}_3(\text{OTf})_2]^{2+}$

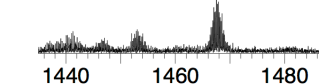
theoretical



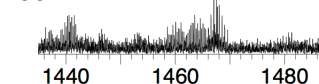
720 min



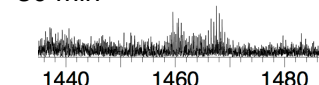
120 min



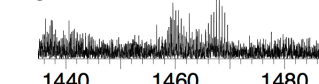
60 min



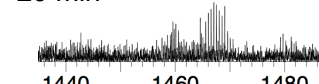
30 min



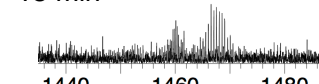
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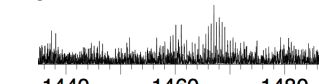
20 min



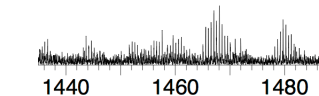
15 min



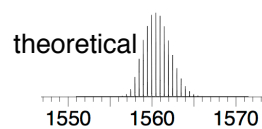
10 min



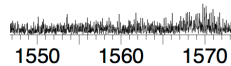
5 min



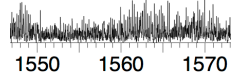
ag $[\text{Pd}_2\text{1}_3\text{Py}^4\text{Me}_2(\text{OTf})_2]^{2+}$



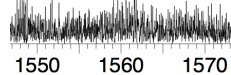
720 min



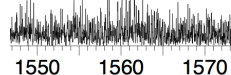
120 min



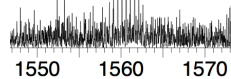
60 min



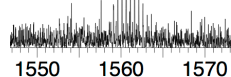
30 min



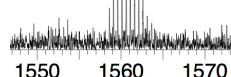
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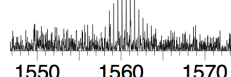
20 min



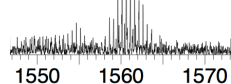
15 min



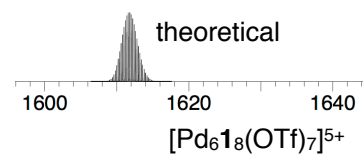
10 min



5 min

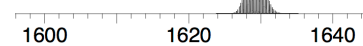


ah $[\text{Pd}_6\text{1}_8(\text{OTf})_6(\text{NO}_3)]^{5+}$

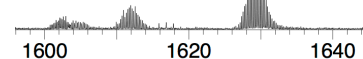


ah $[\text{Pd}_6\text{1}_8(\text{OTf})_7]^{5+}$

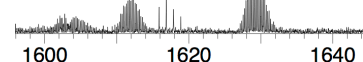
theoretical



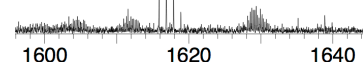
720 min



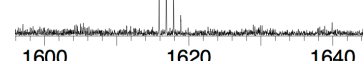
120 min



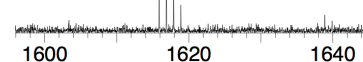
60 min



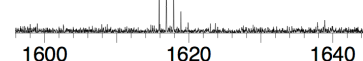
30 min



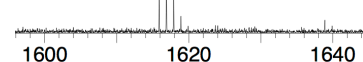
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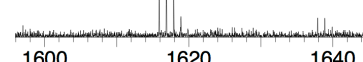
20 min



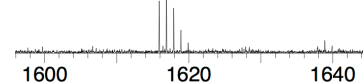
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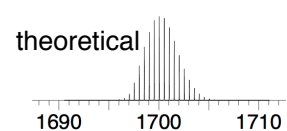
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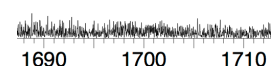
5 min



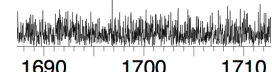
ai $[\text{Pd}_2\text{1}_3\text{Py}^4\text{Me}_5(\text{OTf})_2]^{2+}$



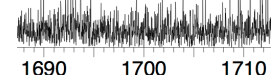
720 min



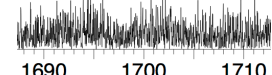
120 min



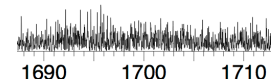
60 min



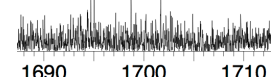
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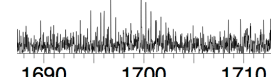
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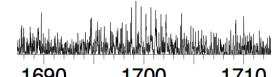
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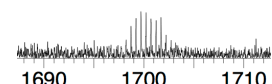
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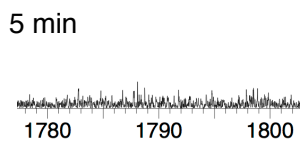
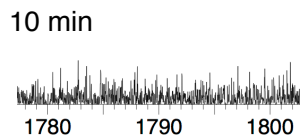
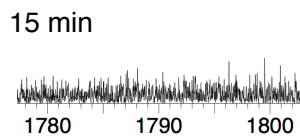
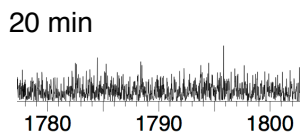
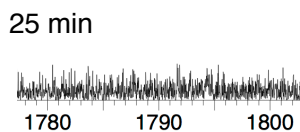
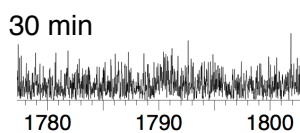
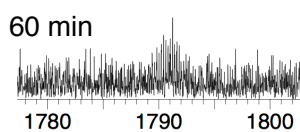
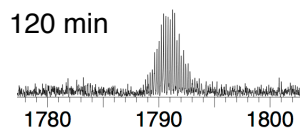
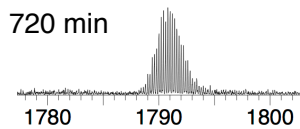
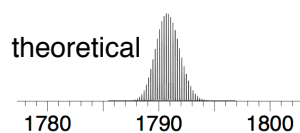
10 min



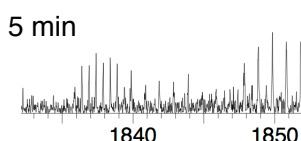
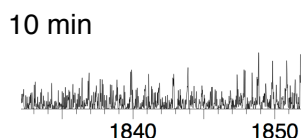
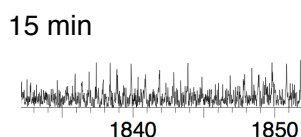
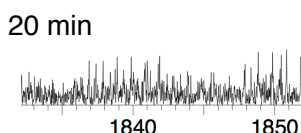
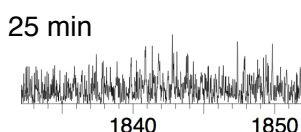
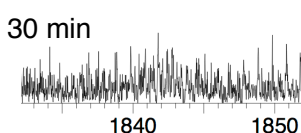
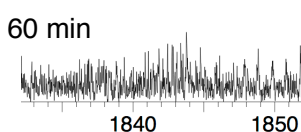
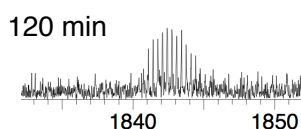
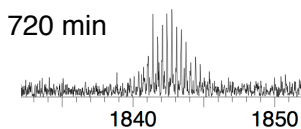
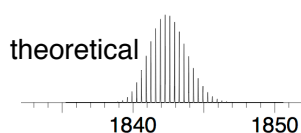
5 min



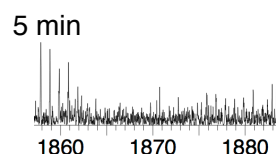
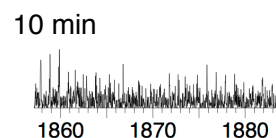
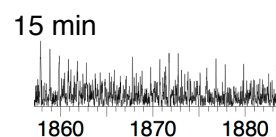
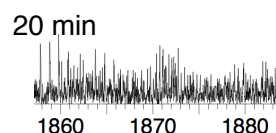
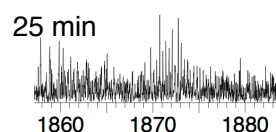
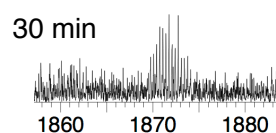
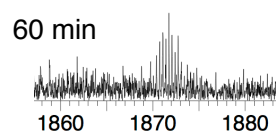
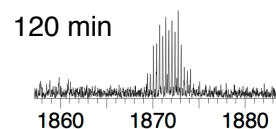
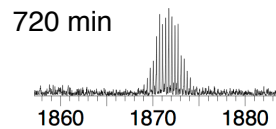
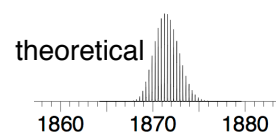
aj $[\text{Pd}_6\text{1}_9(\text{OTf})_7]^{5+}$



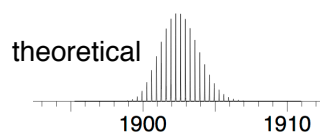
ak $[\text{Pd}_3\text{1}_6(\text{OTf})_2(\text{NO}_3)]^{3+}$



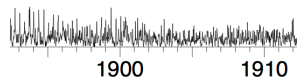
al $[\text{Pd}_3\text{1}_6(\text{OTf})_3]^{3+}$



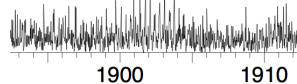
am $[\text{Pd}_3\text{1}_6\text{Py}^4\text{Me}(\text{OTf})_3]^{3+}$



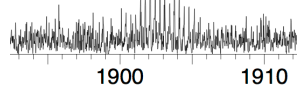
720 min



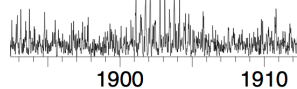
120 min



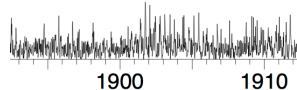
60 min



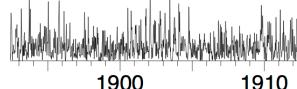
30 min



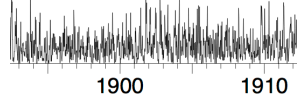
25 min



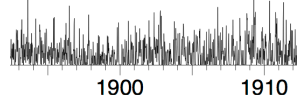
20 min



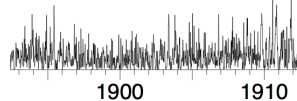
15 min



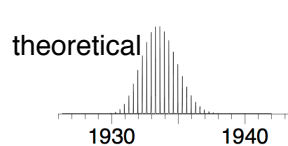
10 min



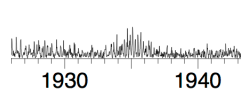
5 min



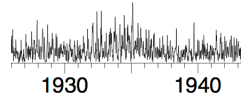
an $[\text{Pd}_3\text{1}_6\text{Py}^4\text{Me}_2(\text{OTf})_3]^{3+}$



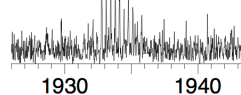
720 min



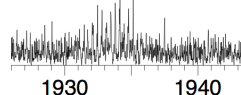
120 min



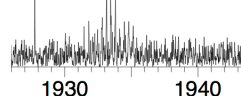
60 min



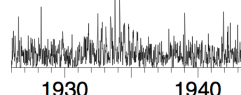
30 min



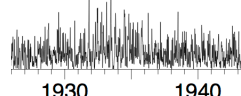
25 min



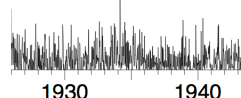
20 min



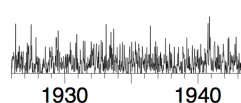
15 min



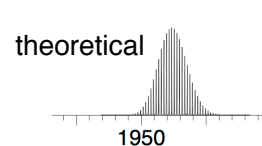
10 min



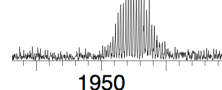
5 min



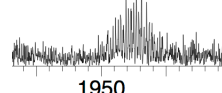
ao $[\text{Pd}_6\text{1}_{10}(\text{OTf})_7]^{5+}$



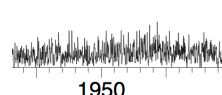
720 min



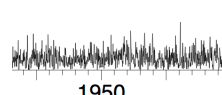
120 min



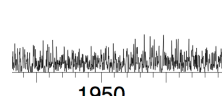
60 min



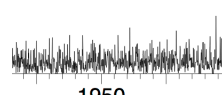
30 min



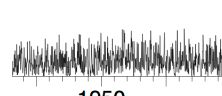
25 min



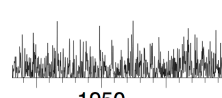
20 min



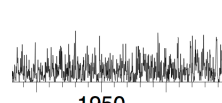
15 min



10 min



5 min



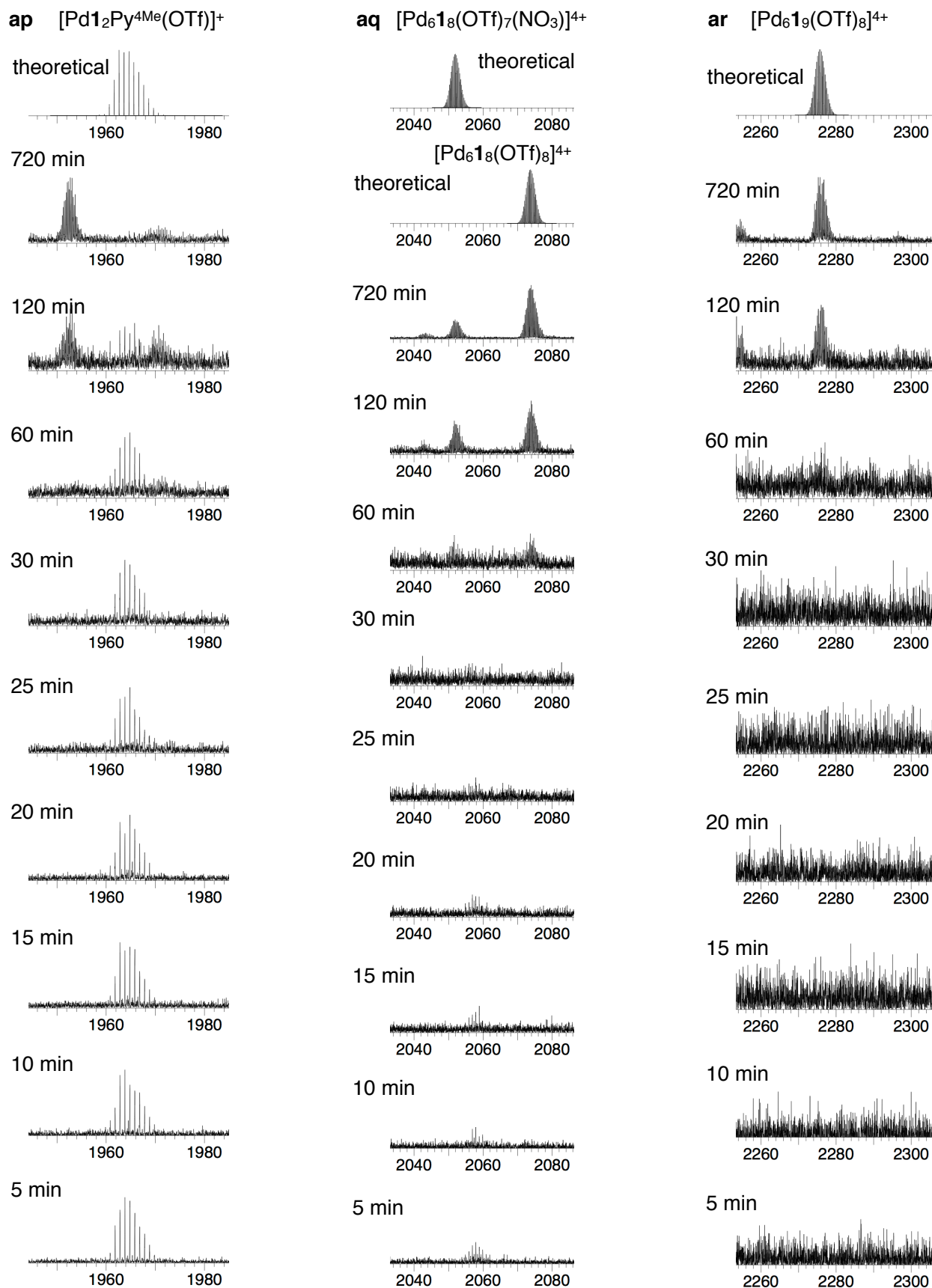


Figure S13. (a)–(c) ESI-TOF mass spectra ($m/z = 390\text{--}2480$) for the self-assembly of $[\text{Pd}_6\mathbf{1}_8]^{12+}$ from $[\text{Pd}(\text{Py}^{4\text{Me}})_4]^{2+}$ and $\mathbf{1}$ in $\text{CD}_3\text{NO}_2/\text{CD}_2\text{Cl}_2$ ($v/v = 4/1$) at 298 K. (d)–(ar) Time variation of the signal for (d) $[\text{Pd}_2\mathbf{1Py}^{4\text{Me}}_6]^{4+}$, (e) $[\text{Pd}_2\mathbf{1}_2\text{Py}^{4\text{Me}}_4]^{4+}$, (f) $[\text{Pd}\mathbf{1Py}^{4\text{Me}}_3]^{2+}$, (g) $[\text{Pd}_2\mathbf{1}_3\text{Py}^{4\text{Me}}_2]^{4+}$, (h) $[\text{Pd}_2\mathbf{1}_2\text{Py}^{4\text{Me}}_3(\text{OTf})]^{3+}$, (i) $[\text{Pd}\mathbf{1}_2\text{Py}^{4\text{Me}}_2]^{2+}$, $[\text{Pd}_2\mathbf{1}_3\text{Py}^{4\text{Me}}(\text{OTf})]^{3+}$, and $[\text{Pd}_6\mathbf{1}_8(\text{OTf})_4]^{8+}$, (j) $[\text{Pd}_2\mathbf{1}_3\text{Py}^{4\text{Me}}_2(\text{OTf})]^{3+}$ and $[\text{Pd}_3\mathbf{1}_4\text{Py}^{4\text{Me}}(\text{OTf})_2]^{4+}$, (k) $[\text{Pd}_3\mathbf{1}_4\text{Py}^{4\text{Me}}_2(\text{OTf})_2]^{4+}$, (l)

[Pd₃1₄Py^{4Me}₃(OTf)₂]⁴⁺, (m) [Pd₄1₅Py^{4Me}₃(OTf)₃]⁵⁺, (n) [Pd₆1₉(OTf)₄]⁸⁺, (o) [Pd1Py^{4Me}(NO₃)]⁺, (p) [Pd₆1₈(OTf)₄(NO₃)]⁷⁺ and [Pd₆1₈(OTf)₅]⁷⁺, (q) [Pd1Py^{4Me}(OTf)]⁺ and [Pd₄1₆Py^{4Me}(OTf)₃]⁵⁺, (r) [Pd₄1₆Py^{4Me}₂(OTf)₃]⁵⁺, (s) [Pd₂1₂Py^{4Me}₃(OTf)₂]²⁺, (t) [Pd₃1₅Py^{4Me}₂(OTf)₂]⁴⁺, (u) [Pd₆1₉(OTf)₄(NO₃)]⁷⁺ and [Pd₆1₉(OTf)₅]⁷⁺, (v) [Pd1Py^{4Me}₂(OTf)]⁺, (w) [Pd₂1₄Py^{4Me}₂(OTf)]³⁺, (x) [Pd₃1₈(OTf)₄]⁶⁺, (y) [Pd₂1₄Py^{4Me}₃(OTf)]³⁺, (z) [Pd1₃Py^{4Me}]²⁺, (aa) [Pd₆1₈(OTf)₅(NO₃)]⁶⁺ and [Pd₆1₈(OTf)₆]⁶⁺, (ab) [Pd1Py^{4Me}₃(OTf)]⁺, (ac) [Pd₆1₁₀(OTf)₅]⁷⁺, (ad) [Pd₃1₆(OTf)₂]⁴⁺, (ae) [Pd₃1₆Py^{4Me}(OTf)₂]⁴⁺, (af) [Pd₆1₉(OTf)₅(NO₃)]⁶⁺, [Pd₆1₉(OTf)₆]⁶⁺, and [Pd₂1₃(OTf)₂]²⁺, (ag) [Pd₂1₃Py^{4Me}₂(OTf)₂]²⁺, (ah) [Pd₆1₈(OTf)₆(NO₃)]⁵⁺ and [Pd₆1₈(OTf)₇]⁵⁺, (ai) [Pd₂1₃Py^{4Me}₅(OTf)₂]²⁺, (aj) [Pd₆1₉(OTf)₇]⁵⁺, (ak) [Pd₃1₆(OTf)₂(NO₃)]³⁺, (al) [Pd₃1₆(OTf)₃]³⁺, (am) [Pd₃1₆Py^{4Me}(OTf)₃]³⁺, (an) [Pd₃1₆Py^{4Me}₂(OTf)₃]³⁺, (ao) [Pd₆1₁₀(OTf)₇]⁵⁺, (ap) [Pd1₂Py^{4Me}(OTf)]⁺, (aq) [Pd₆1₈(OTf)₇(NO₃)]⁴⁺ and [Pd₆1₈(OTf)₈]⁴⁺, and (ar) [Pd₆1₉(OTf)₈]⁴⁺.

Table S17. Time variation of the species detected by ESI-TOF mass spectrometry for the self-assembly of the capsule from **1** and Pd(Py^{4Me})₄·(OTf)₂ in CD₃NO₂/CD₂Cl₂ (v/v = 4/1) at 298 K.

5 min	10 min	15 min	20 min	25 min	30 min	60 min	120 min	720 min
(1, 1, 1)	(1, 1, 1)	(1, 1, 1)	(1, 1, 1)	(1, 1, 1)	(1, 1, 1)	(1, 1, 1) ↓		
(1, 1, 2)	(1, 1, 2)	(1, 1, 2)	(1, 1, 2)	(1, 1, 2)	(1, 1, 2)	(1, 1, 2)	(1, 1, 2) ↓	
(1, 1, 3)	(1, 1, 3)	(1, 1, 3)	(1, 1, 3)	(1, 1, 3)	(1, 1, 3)	(1, 1, 3)	(1, 1, 3) ↓	
(1, 2, 1)	(1, 2, 1)	(1, 2, 1)	(1, 2, 1)	(1, 2, 1)	(1, 2, 1)	(1, 2, 1)	(1, 2, 1) ↓	
(1, 2, 2)	(1, 2, 2)	(1, 2, 2)	(1, 2, 2)	(1, 2, 2)	(1, 2, 2)	(1, 2, 2)	(1, 2, 2)	(1, 2, 2) ↓
(1, 3, 1)	(1, 3, 1)	(1, 3, 1)	(1, 3, 1)	(1, 3, 1)	(1, 3, 1)	(1, 3, 1) ↓		
(2, 1, 6)	(2, 1, 6)	(2, 1, 6)	(2, 1, 6)	(2, 1, 6)	(2, 1, 6)	(2, 1, 6)	(2, 1, 6)	
(2, 2, 3)	(2, 2, 3) ↓	(2, 2, 3) ↓	(2, 2, 3) ↓					
(2, 2, 4)	(2, 2, 4)	(2, 2, 4)	(2, 2, 4)	(2, 2, 4)	(2, 2, 4)	(2, 2, 4)	(2, 2, 4)	(2, 2, 4)
(2, 3, 0)	(2, 3, 0)	(2, 3, 0)	(2, 3, 0)	(2, 3, 0)	(2, 3, 0)	(2, 3, 0)		
(2, 3, 1)	(2, 3, 1)	(2, 3, 1)	(2, 3, 1)	(2, 3, 1)	(2, 3, 1)	(2, 3, 1) ↓		
(2, 3, 2)	(2, 3, 2)	(2, 3, 2)	(2, 3, 2)	(2, 3, 2)	(2, 3, 2) ↓	(2, 3, 2) ↓		
(2, 3, 5)	(2, 3, 5) ↓							
(2, 4, 2)	(2, 4, 2) ↓	(2, 4, 2) ↓	(2, 4, 2) ↓					
(2, 4, 3)	(2, 4, 3) ↓							
	(3, 4, 1)	(3, 4, 1)	(3, 4, 1)					
	(3, 4, 2)	(3, 4, 2)	(3, 4, 2)					
	(3, 4, 3)	(3, 4, 3)	(3, 4, 3)	(3, 4, 3)				
		(3, 5, 2)	(3, 5, 2)	(3, 5, 2)	(3, 5, 2)			
				(3, 6, 0)	(3, 6, 0)	(3, 6, 0)	(3, 6, 0) ↑	(3, 6, 0)
					(3, 6, 1)	(3, 6, 1)	(3, 6, 1) ↓	
					(3, 6, 2)	(3, 6, 2)		
		(4, 5, 3)	(4, 5, 3)	(4, 5, 3)				
				(4, 6, 1) ↑	(4, 6, 1) ↑	(4, 6, 1)	(4, 6, 1)	
		(4, 6, 2)	(4, 6, 2) ↑	(4, 6, 2)	(4, 6, 2)	(4, 6, 2)		
						(5, 8, 0)	(5, 8, 0)	
					(6, 8, 0)	(6, 8, 0) ↑	(6, 8, 0) ↑	(6, 8, 0)
						(6, 9, 0)	(6, 9, 0) ↑	(6, 9, 0)
							(6, 10, 0)	(6, 10, 0)

(a, b, c) indicates species Pd_a1_b(Py^{4Me})_c. Up and down arrows, ↑ and ↓, indicate increase and decrease of the signal intensity, respectively.

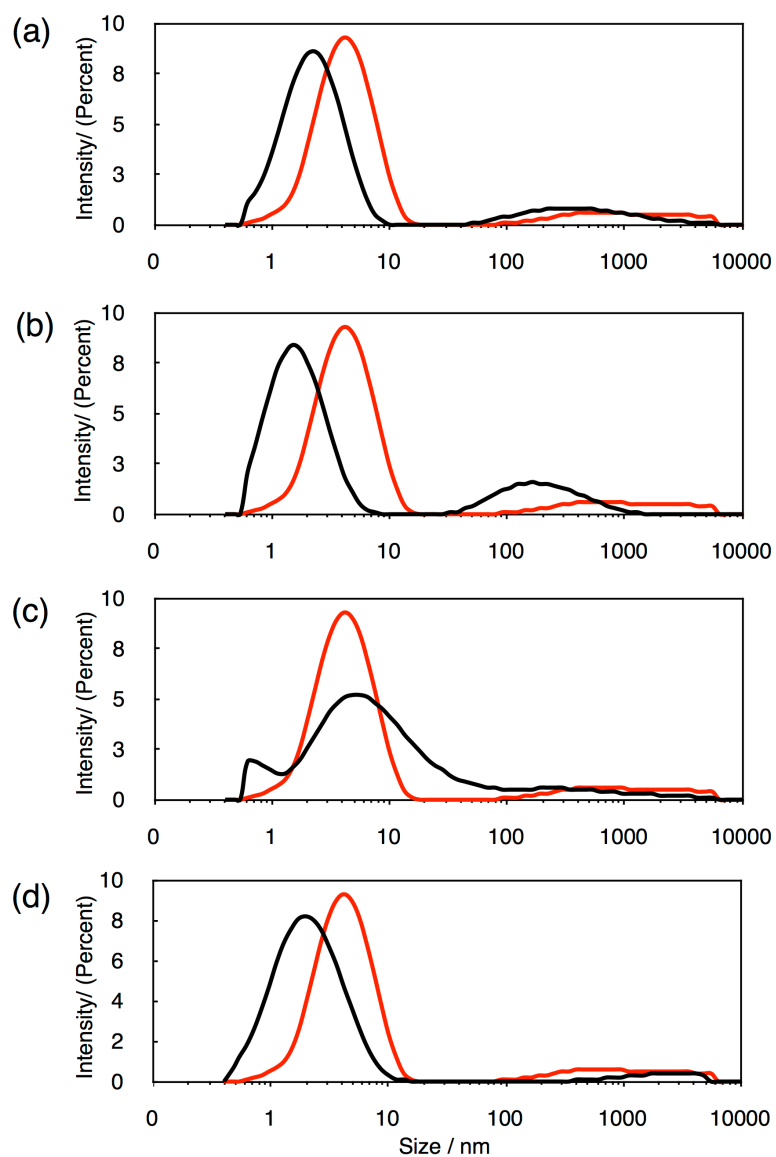


Figure S14. DLS data for the reaction mixtures obtained after convergence. All the reactions were performed in $\text{CD}_3\text{NO}_2/\text{CD}_2\text{Cl}_2$ ($v/v = 4/1$) at 298 K and then were diluted with an equal volume of CH_3NO_2 before measurements. (a) **1** and $\text{PdPy}_4 \cdot (\text{OTf})_2$. (b) **1** and $\text{PdPy}^*_4 \cdot (\text{OTf})_2$. (c) **1** and $\text{Pd}(\text{CH}_3\text{CN})_4 \cdot (\text{OTf})_2$. (d) **1** and $\text{Pd}(\text{Py}^{4\text{Mc}})_4 \cdot (\text{OTf})_2$. Red lines indicate the DLS profile for the Pd_6I_8 capsule.

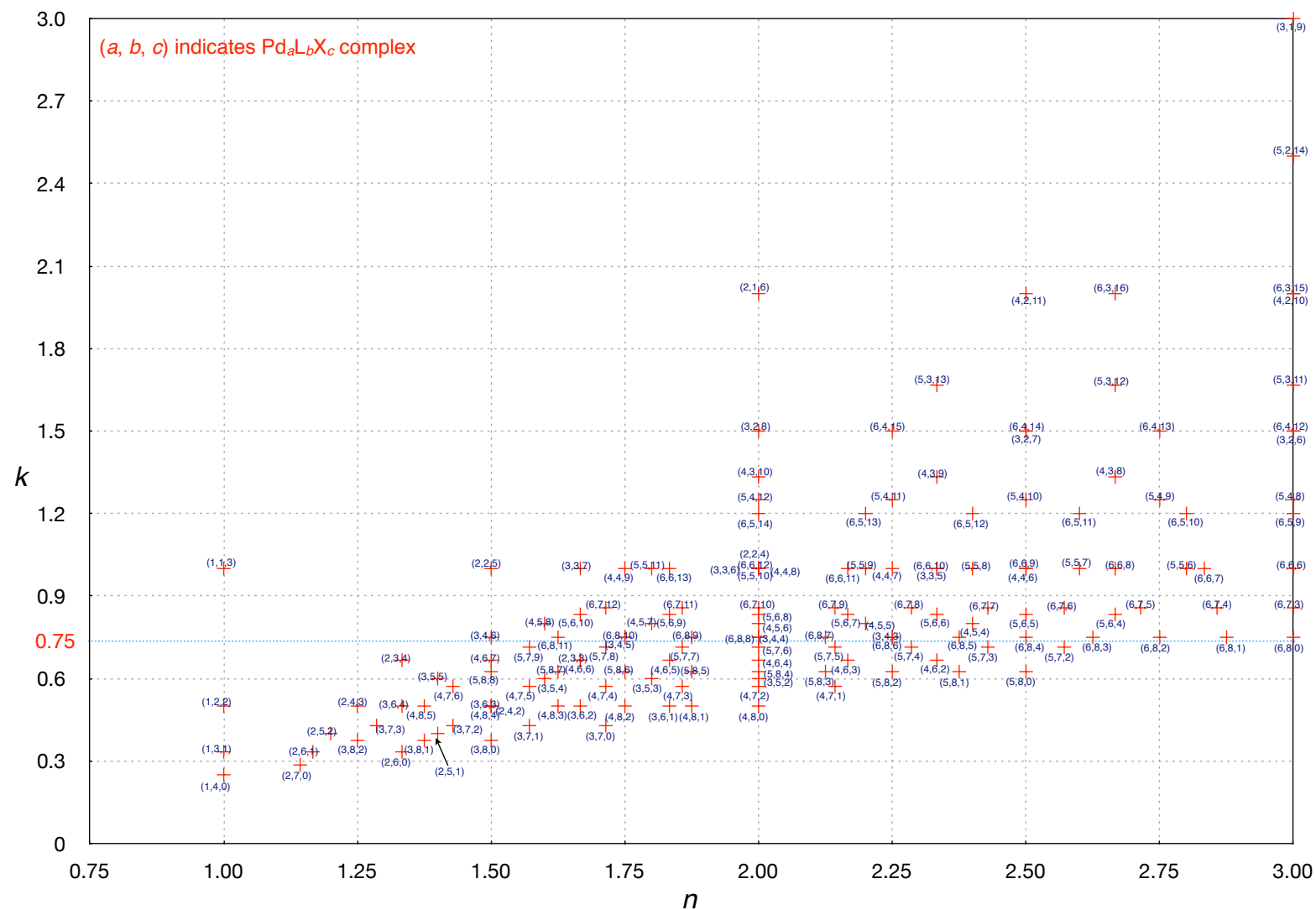


Figure S15 (n, k) map for the assembly of octahedron-shaped M_6L_8 capsules. The (n, k) values for species from $Pd_1L_1X_3$ to Pd_6L_8 (155 species) are plotted as crosshairs in red. The $Pd_aL_bX_c$ complex is depicted as (a, b, c) .

References

- (1) Sato, S.; Ishido, Y.; Fujita, M. Remarkable Stabilization of $M_{12}L_{24}$ Spherical Frameworks through the Cooperation of 48 Pd(II)–Pyridine Interactions. *J. Am. Chem. Soc.* **2009**, *131*, 6064–6065.