

Supporting Information

Self-Assembly Process of Dodecanuclear Pt(II)-Linked Cyclic Hexagon

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General information

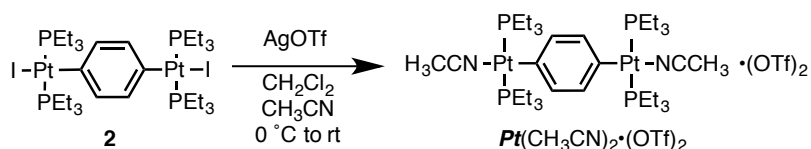
^1H NMR, ^{13}C NMR, ^{31}P NMR, and ^{19}F NMR spectra were recorded using a Bruker AV-500 (500 MHz) spectrometer. All ^1H spectra were referenced using residual solvent peaks, CD_2Cl_2 (δ 5.31) and CD_3NO_2 (δ 4.33). ^{13}C spectrum was referenced using a solvent peak, CD_3NO_2 (δ 62.81). ^{31}P NMR and ^{19}F NMR were referenced using external standards, 85% aq. H_3PO_4 solution and trichlorofluoromethane. Electrospray ionization time-of-flight (ESI-TOF) mass spectra were obtained using a Waters Xevo G2-S ToF mass spectrometer.

Materials

Unless otherwise noted, all solvents and reagents were obtained from commercial suppliers (TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., KANTO Chemical Co., Ltd., and Sigma-Aldrich Co.) and were used as received. Ditopic ligand **1** and Pt(II) dinuclear complex **2** were prepared according to the literature.^{1,2}

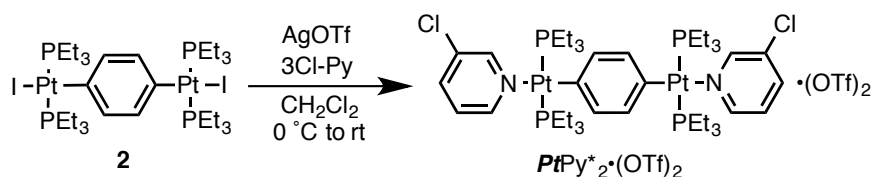
Synthesis of Pt(II) dinuclear complexes

Synthesis of $\text{Pt}(\text{CH}_3\text{CN})_2 \cdot (\text{OTf})_2$



To a stirred solution of Pt(II) dinuclear complex **2** (50.0 mg, 41.9 μmol) in CH_2Cl_2 (2 mL) and CH_3CN (0.5 mL) was added AgOTf (22.6 mg, 88.0 mmol) at 0 $^\circ\text{C}$ in the dark and under a nitrogen atmosphere. Then a light yellow suspension immediately formed. After stirring for 2 h at rt, the suspension was filtered to remove the precipitated AgI, and the filtrate was concentrated in vacuo. Then the residue was washed with water (2 mL \times 3) to remove the unreacted AgOTf and dried in vacuo with slight heating (40 $^\circ\text{C}$) to afford $\text{Pt}(\text{CH}_3\text{CN})_2 \cdot (\text{OTf})_2$ as a colorless solid (43.9 mg, 79%). ^1H NMR (500 MHz, CD_3NO_2 , 298 K): δ 6.97 (s, 4H), 2.50 (s, 6H), 1.85-1.60 (m, 24H), 1.16 (dt, $J_{\text{PH}} = 16.7$ Hz, $J_{\text{HH}} = 8.5$ Hz, 36H); ^1H NMR (500 MHz, CD_2Cl_2 , 298 K): δ 6.85 (s, 4H), 2.54 (s, 6H), 1.67-1.55 (m, 24H), 1.12 (dt, $J_{\text{PH}} = 16.8$ Hz, $J_{\text{HH}} = 8.2$ Hz, 36H); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 Hz, CD_3NO_2 , 298 K): δ 11.6 (s, $J_{\text{PPt}} = 2699$ Hz); ^{19}F NMR (470 MHz, CD_3NO_2 , 298 K): δ -82.2; ESI-TOF mass m/z 469.15 $[\text{M}-2\text{CH}_3\text{CN}-2\text{OTf}]^{2+}$. ^1H NMR spectrum of $\text{Pt}(\text{CH}_3\text{CN})_2 \cdot (\text{OTf})_2$ is shown in Figure S8.

Synthesis of $\text{PtPy}^*_2 \cdot (\text{OTf})_2$



To a stirred solution of Pt(II) dinuclear complex **2** (49.9 mg, 41.9 μmol) and 3-chloropyridine (Py^*) (8.4 μL , 88 mmol) in CH_2Cl_2 (2.5 mL) was added AgOTf (22.6 mg, 88.0 mmol) at 0 $^\circ\text{C}$ in the dark and under a nitrogen atmosphere. Then a light yellow suspension immediately formed. After stirring for 2 h at rt, the suspension was filtered to remove the precipitated AgI, and the filtrate was concentrated in vacuo. Then the residue was washed with water (2 mL \times 3) to remove the unreacted AgOTf and dried in vacuo with slight heating (40 $^\circ\text{C}$) to afford $\text{PtPy}^*_2 \cdot (\text{OTf})_2$ as a colorless solid (61.4 mg, 82%). ^1H NMR (500 MHz, CD_3NO_2 , 298 K): δ 8.87 (d, $J_{\text{HH}} = 2.2$ Hz, 2H), 8.80 (dd, $J_{\text{HH}} = 5.4, 1.1$ Hz, 2H), 8.09 (ddd, $J_{\text{HH}} = 8.4, 2.2, 1.1$ Hz, 2H), 7.72 (dd, $J_{\text{HH}} = 8.4, 5.4$ Hz, 2H), 7.30-7.05 (m, 4H), 1.54-1.39 (m, 24H), 1.15 (dt, $J_{\text{PH}} = 16.5$ Hz, $J_{\text{HH}} = 8.0$ Hz, 36H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 Hz, CD_3NO_2 , 298 K) δ 151.97, 151.92, 140.71, 137.80 (m, $\text{C}_\text{o}-\text{Pt}$), 136.57, 129.52, 125.83 (t, $^2J_{\text{CP}} = 9.5$ Hz, $\text{C}_\text{r}-\text{Pt}$), 122.44 (q, $^1J_{\text{CF}} = 321$ Hz, OTf), 13.60 (m, PCH_2CH_3), 7.97 (brs, PCH_2CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 Hz, CD_3NO_2 , 298 K): δ 10.7 (s, $J_{\text{PPt}} = 2712$ Hz); ^{19}F NMR (470 MHz, CD_3NO_2 , 298 K): δ -82.2; ESI-TOF mass m/z 469.15 $[\text{M}-2\text{Py}^*-2\text{OTf}]^{2+}$. ^1H and ^{13}C NMR spectra of $\text{PtPy}^*_2 \cdot (\text{OTf})_2$ are shown in Figures S9 and S10, respectively.

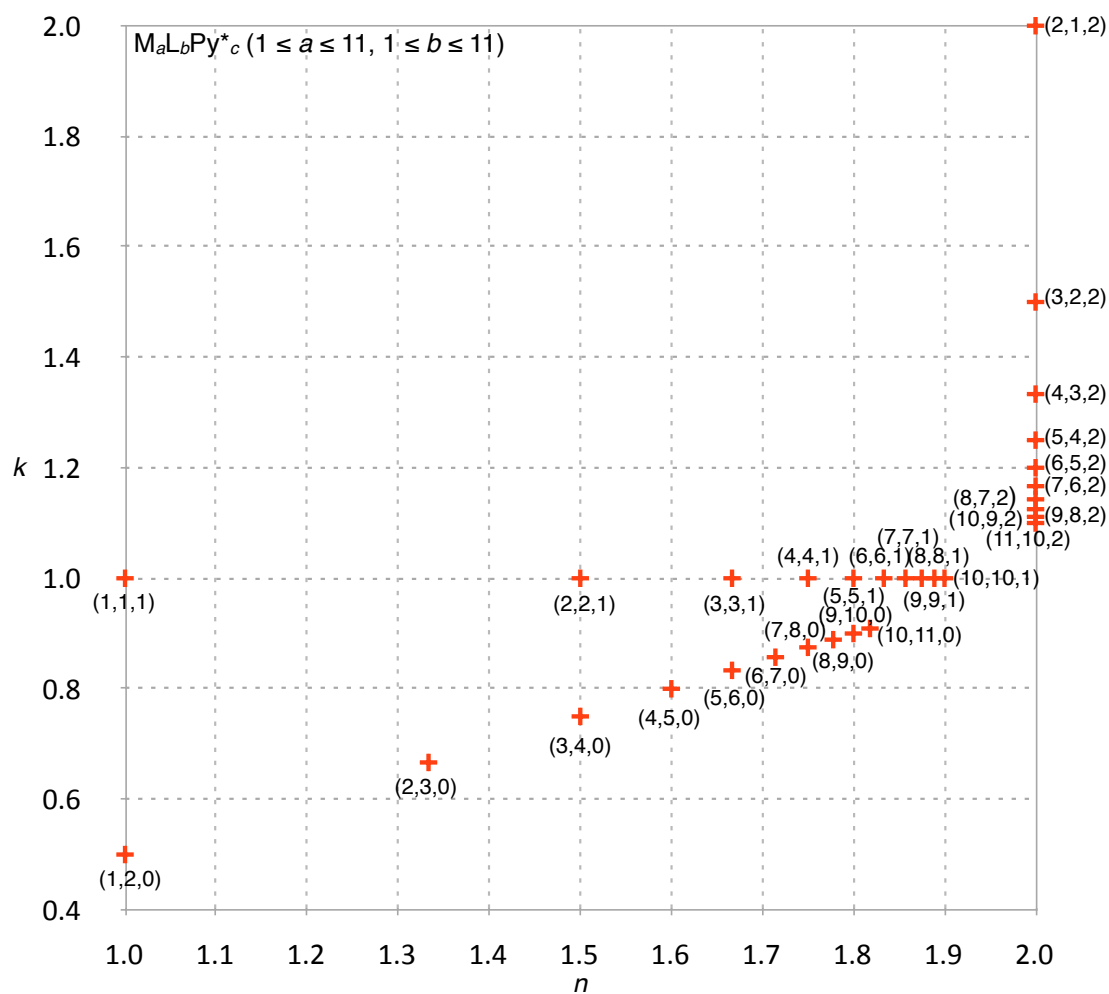


Fig. S1 An n - k map for the self-assembly of a cyclic hexagon. The (n, k) values for species from M_1L_2 to $M_{11}L_{10}Py^*_2$ (30 species) are plotted as crosshairs in red. The $M_aL_bPy^*_c$ complex is depicted as (a, b, c)

Procedure for the investigation of the self-assembly of a cyclic hexagon

As an internal standard solution, [2.2]paracyclophane (4.21 mg) was dissolved in CHCl_3 (8.00 mL). The internal standard solution (40 μL) was introduced to two NMR tubes (tube A and B) and concentrated in vacuo. Then the mixture of $\text{PtPy}^*_2\cdot(\text{OTf})_2$ (10.0 mg, 6.83 μmol) and 25 μL of a 1,2,4,5-tetramethylbenzene solution in CD_3NO_2 (1.00 mg in 100 μL CD_3NO_2) was diluted with CD_3NO_2 (225 μL) (solution A). Then 50 μL of solution A was added to tube A and diluted with CD_3NO_2 (400 μL). At this stage, the exact concentration of $\text{PtPy}^*_2\cdot(\text{OTf})_2$ in this solution was unambiguously determined through the comparison with the quantity of [2.2]paracyclophane, 1,2,4,5-tetramethylbenzene, and $\text{PtPy}^*_2\cdot(\text{OTf})_2$ by ^1H NMR. Based on this concentration, the exact concentration of solution A was exactly determined. In parallel, ditopic ligand **1** (3.83 mg, 13.7 μmol) was dissolved in CHCl_3 (500 μL) (solution B). Then 50 μL of solution B was added to tube B, concentrated in vacuo, and dissolved in CD_3NO_2 (450 μL). At this stage, the exact amount of ditopic ligand **1** in tube B was unambiguously quantified by ^1H NMR using [2.2]paracyclophane as the internal standard. Then to the solution in tube B was added exactly 1 eq. of $\text{PtPy}^*_2\cdot(\text{OTf})_2$ to ditopic ligand **1** in solution A at 273 K, and the self-assembly of the cyclic hexagon was monitored at 298 K by ^1H NMR every 2 hours. The quantities of **1**, $[\text{PtPy}^*_2]^{2+}$, $[\text{Pt}_6\mathbf{1}_6]^{12+}$, and Py^* were quantified by the integral of each ^1H signal against the signal of the internal standard ([2.2]paracyclophane).

For the monitor of the self-assembly process, ^1H NMR spectrum was measured with 30 s delay time and scanned 32 times. It took 20 min to obtain one ^1H NMR spectrum. Because the detection of the species that converts to another species during the measurement is expected to be difficult, we estimate that the lifetime of the unobservable intermediates should be less than 20 min.

For the investigation of the self-assembly of a cyclic hexagon from **1** and $\text{Pt}(\text{CH}_3\text{CN})_2\cdot(\text{OTf})_2$, the same procedure was adopted in a different interval and the quantities of **1** and $[\text{Pt}_6\mathbf{1}_6]^{12+}$ were quantified.

Determination of the average composition of the fragment species, $[Pt_a1_bPy^*_c]^{2a+}$, in each time point

The amounts of **1**, $[PtPy^*_2]^{2+}$, $[Pt_61_6]^{12+}$, and Py^* at each time point during the self-assembly process were quantified by 1H NMR measurements using [2.2]paracyclophane as an internal standard.

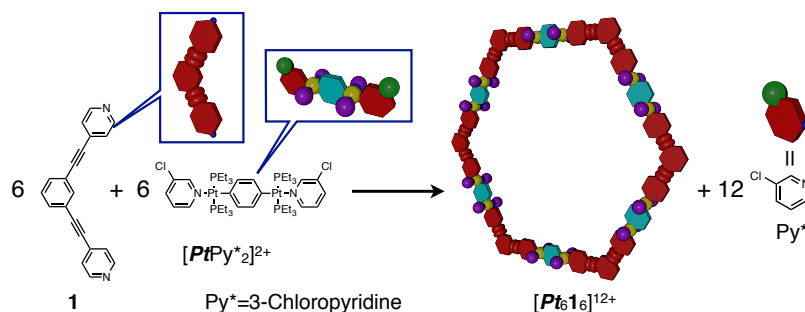


Table S1. The quantities of each component of the above scheme

Time	1	$[PtPy^*_2]^{2+}$	$[Pt_61_6]^{12+}$	Py^*
0	l_0	m_0	0	0
t	l_t	m_t	n_t	o_t

At time t , the average composition of the intermediates, $(Pt_a1_bPy^*_c)_{ave}$, is expressed by equations (3) – (5).

$$a = m_0 - m_t - 6 \cdot n_t \quad \dots\dots (3)$$

$$b = l_0 - l_t - 6 \cdot n_t \quad \dots\dots (4)$$

$$c = 2 \cdot m_0 - 2 \cdot m_t - o_t \quad \dots\dots (5)$$

where l_0 and m_0 are the quantities for **1** and $[PtPy^*_2]^{2+}$, respectively at time = 0 and l_t , m_t , n_t , and o_t are the quantities for **1**, $[PtPy^*_2]^{2+}$, $[Pt_61_6]^{12+}$, and Py^* , respectively at time = t (Table S1).

Then the $\langle n \rangle$, $\langle k \rangle$ values for $(Pt_a1_bPy^*_c)_{ave}$ at each time point were determined by equations (1) and (2) in the main text. The data obtained for the self-assembly of $[Pt_61_6]^{12+}$ are listed in Table S2.

Table S2. The quantities of **1**, [**PrPy*₂**]²⁺, [**Pr₆1₆**]¹²⁺, Py*, and [**Pr1₂**]²⁺ and the values of *a*, *b*, and *c* and the (*<n>*, *<k>*) values at each time point for the self-assembly of [**Pr₆1₆**]¹²⁺

Time (min)	1	[PrPy*₂] ²⁺	[Pr₆1₆] ¹²⁺	Py*	[Pr1₂] ²⁺	<i>a</i>	<i>b</i>	<i>c</i>	<i><n></i>	<i><k></i>
0	1.717	1.635	0.000	0.000	0.000	0.000	0.000	0.000	–	–
120	1.588	1.366	0.000	0.279	0.278	0.129	0.269	-0.021	1.040	0.480
240	1.510	1.210	0.007	0.481	0.466	0.163	0.381	-0.068	1.033	0.427
360	1.407	1.023	0.010	0.627	0.570	0.248	0.550	-0.008	0.916	0.451
480	1.348	0.913	0.014	0.806	0.678	0.284	0.638	-0.070	1.000	0.445
800	1.220	0.727	0.018	1.007	0.798	0.389	0.801	-0.014	0.990	0.486
900	1.135	0.597	0.023	1.133	0.857	0.444	0.900	0.030	0.953	0.493
1200	1.068	0.509	0.030	1.288	0.935	0.466	0.943	0.010	0.977	0.494
1440	1.031	0.445	0.037	1.416	0.978	0.461	0.965	-0.045	1.001	0.478
2340	0.880	0.288	0.055	1.674	1.017	0.505	1.016	0.000	0.995	0.497
2460	0.850	0.255	0.058	1.712	1.010	0.517	1.030	0.022	0.983	0.502
2880	0.825	0.226	0.063	1.742	0.988	0.511	1.028	0.041	0.953	0.497
3570	0.784	0.196	0.073	1.842	0.966	0.498	1.004	0.024	0.969	0.496
4320	0.725	0.165	0.086	1.981	0.962	0.474	0.953	0.002	0.994	0.498
5040	0.703	0.144	0.091	1.979	0.928	0.470	0.947	0.048	0.941	0.496
5400	0.680	0.136	0.094	2.030	0.911	0.474	0.937	0.042	0.967	0.506
7860	0.657	0.127	0.110	2.151	0.864	0.401	0.850	-0.032	0.981	0.472
8610	0.637	0.128	0.112	2.166	0.830	0.405	0.832	-0.006	0.981	0.487
9390	0.620	0.117	0.115	2.142	0.815	0.406	0.828	0.051	0.920	0.491
10020	0.603	0.115	0.117	2.218	0.820	0.410	0.816	0.010	0.993	0.502
11460	0.590	0.115	0.123	2.214	0.800	0.389	0.783	0.040	0.944	0.497
12990	0.571	0.113	0.122	2.225	0.759	0.411	0.787	0.067	0.960	0.522
14130	0.599	0.119	0.127	2.246	0.766	0.355	0.754	-0.011	0.957	0.471
18000	0.603	0.128	0.133	2.294	0.760	0.317	0.711	-0.068	0.987	0.446
19440	0.601	0.126	0.132	2.301	0.754	0.323	0.716	-0.069	0.999	0.451
19650	0.595	0.127	0.130	2.250	0.767	0.340	0.726	-0.007	0.945	0.468
20940	0.635	0.150	0.128	2.250	0.785	0.317	0.720	-0.087	0.945	0.440

ESI-TOF mass study for the self-assembly of $[Pt_6\mathbf{1}_6]^{12+}$

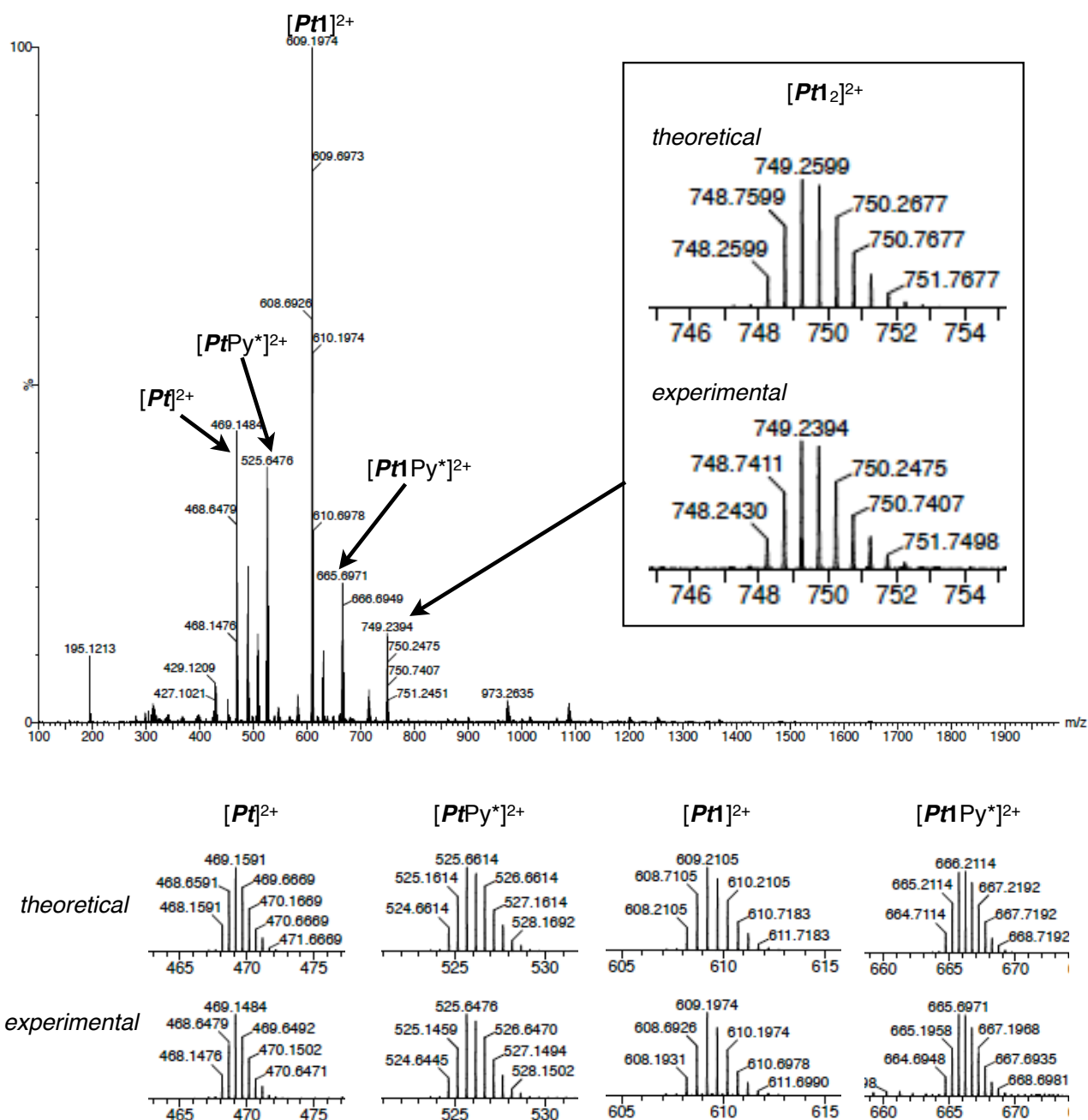


Fig. S2 ESI-TOF mass spectrum of the equilibrated sample of the self-assembly of $[Pt_6\mathbf{1}_6]^{12+}$ from **1** and $[PtPy^*_2]^{2+}$.

¹H DOSY study for the self-assembly of [Pt₆1₆]¹²⁺

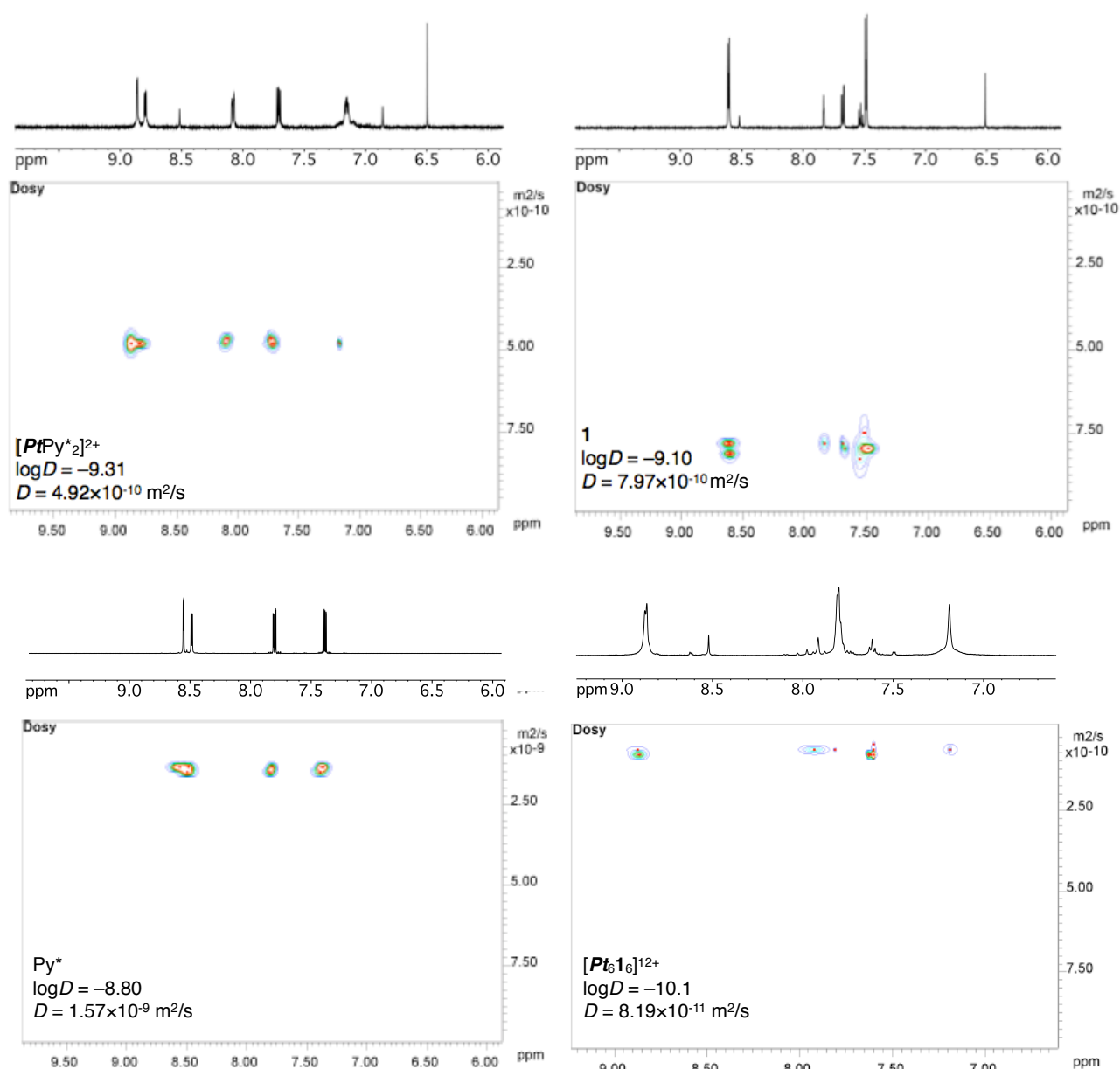


Fig. S3 ¹H DOSY spectra (500 MHz, CD₃NO₂, 298 K) of [PtPy*]₂²⁺, **1**, Py*, and [Pt₆1₆]¹²⁺. [Pt₆1₆]¹²⁺ was selectively obtained by mixing Pt(CH₃CN)₂·(OTf)₂ and **1** in a 1:1 ratio in CD₂Cl₂ and then the solvent was replaced to CD₃NO₂.

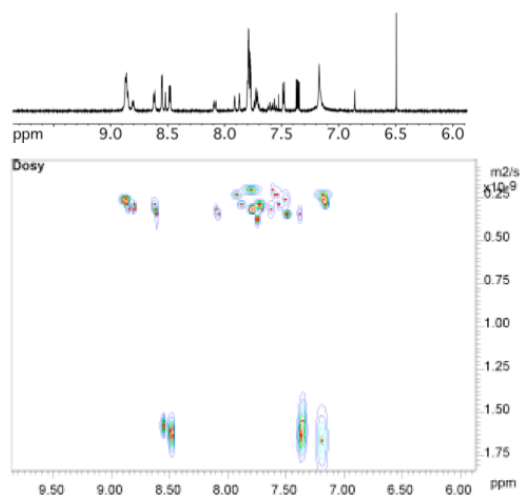


Fig. S4 ¹H DOSY spectrum (500 MHz, CD₃NO₂, 298 K) of the equilibrated sample of the self-assembly of [Pt₆L₆]¹²⁺ from **1** and [PtPy*₂]²⁺.

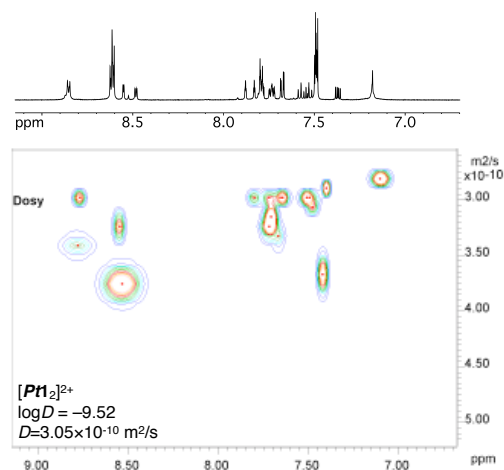


Fig. S5 ¹H DOSY spectrum (500 MHz, CD₃NO₂, 298 K) of the mixture of **1** and [PtL₂]²⁺. This mixture was obtained by mixing [PtPy*₂]²⁺ and **1** in a 1:4 ratio.

^1H NMR study for the self-assembly of $[\text{Pt}_6\text{1}_6]^{12+}$ from **1 and $[\text{Pt}(\text{CH}_3\text{CN})_2]^{2+}$**

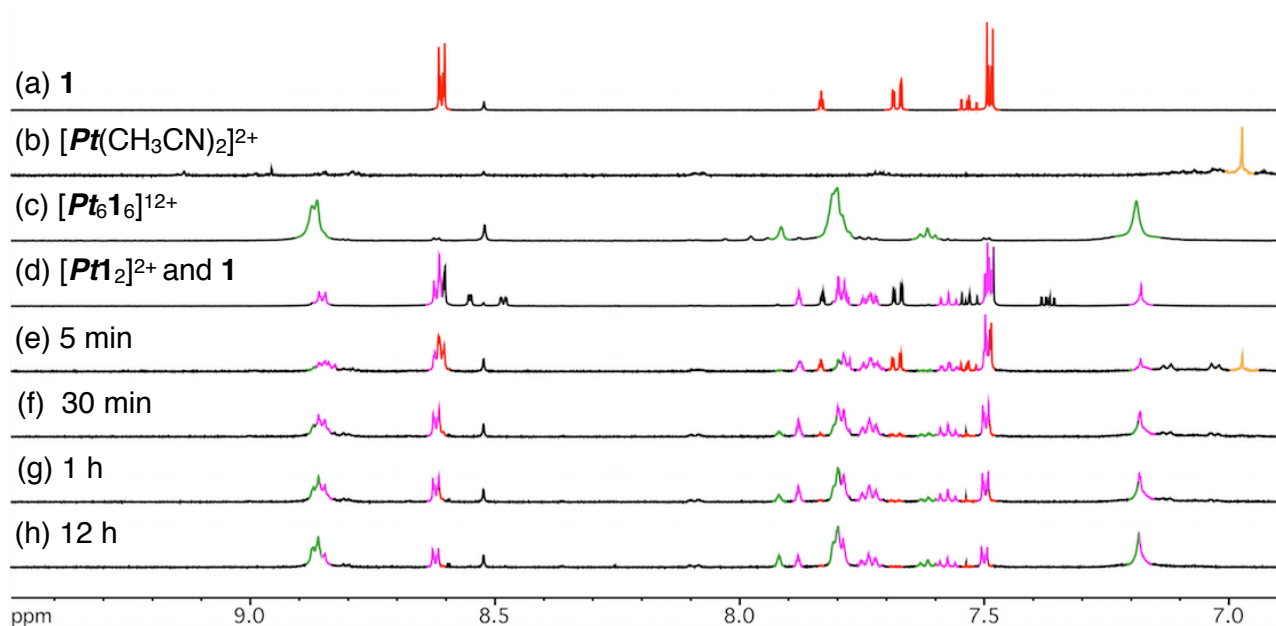


Fig. S6 ^1H NMR spectra of each component for the cyclic hexagon and the reaction mixture (500 MHz, CD_3NO_2 , 298 K). (a) **1**, (b) $[\text{Pt}(\text{CH}_3\text{CN})_2]^{2+}$, (c) $[\text{Pt}_6\text{1}_6]^{12+}$, (d) a mixture of $[\text{Pt1}_2]^{2+}$ and **1**, and the reaction mixture monitored at (e) 5 min, (f) 30 min, (g) 1 h, and (h) 12 h. Signals colored in red, yellow, green, and purple indicate **1**, $[\text{Pt}(\text{CH}_3\text{CN})_2]^{2+}$, $[\text{Pt}_6\text{1}_6]^{12+}$, and $[\text{Pt1}_2]^{2+}$, respectively.

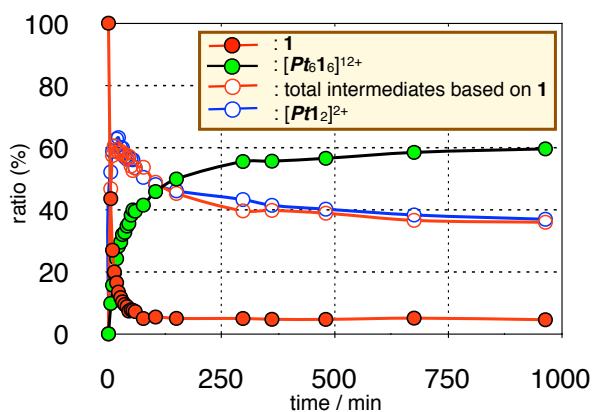


Fig. S7 Time variation of each species in the reaction mixture of the self-assembly of the cyclic hexagon and the abundance ratio of total intermediates based on **1**.

¹H and ¹³C NMR spectra of Pt(II) dinuclear complexes

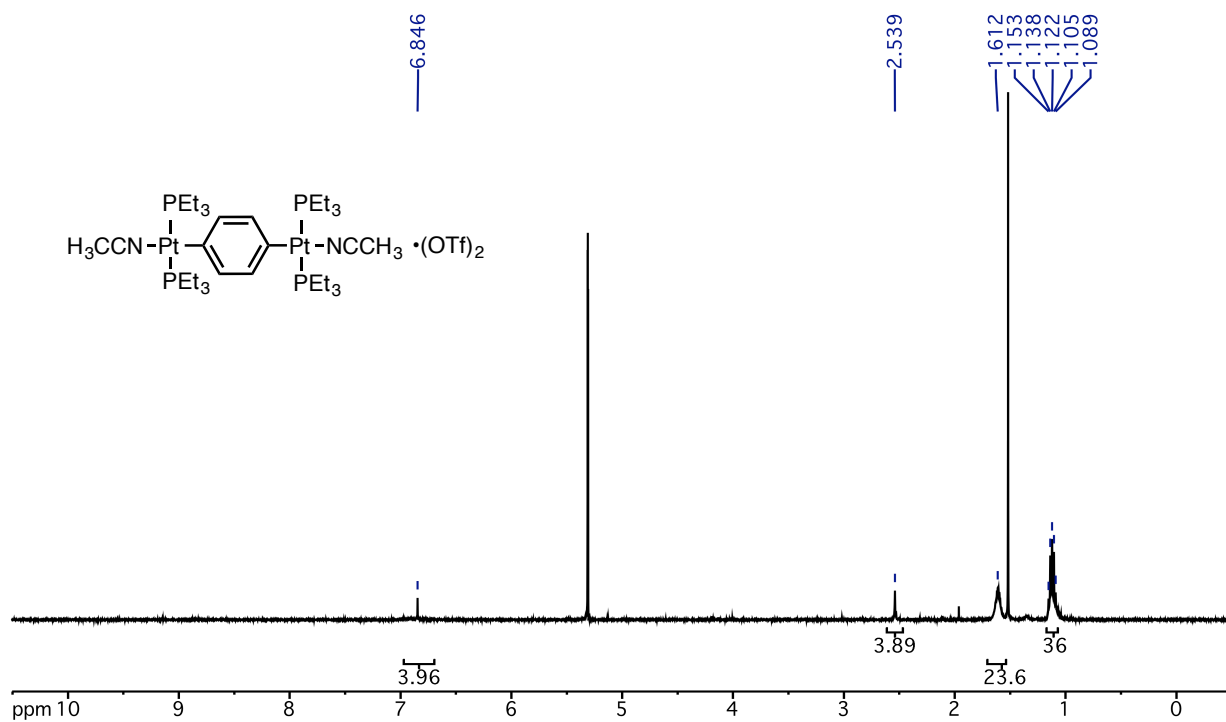


Fig. S8 ¹H NMR spectrum (500 MHz, CD₂Cl₂, 298 K) of **Pt**(CH₃CN)₂·(OTf)₂.

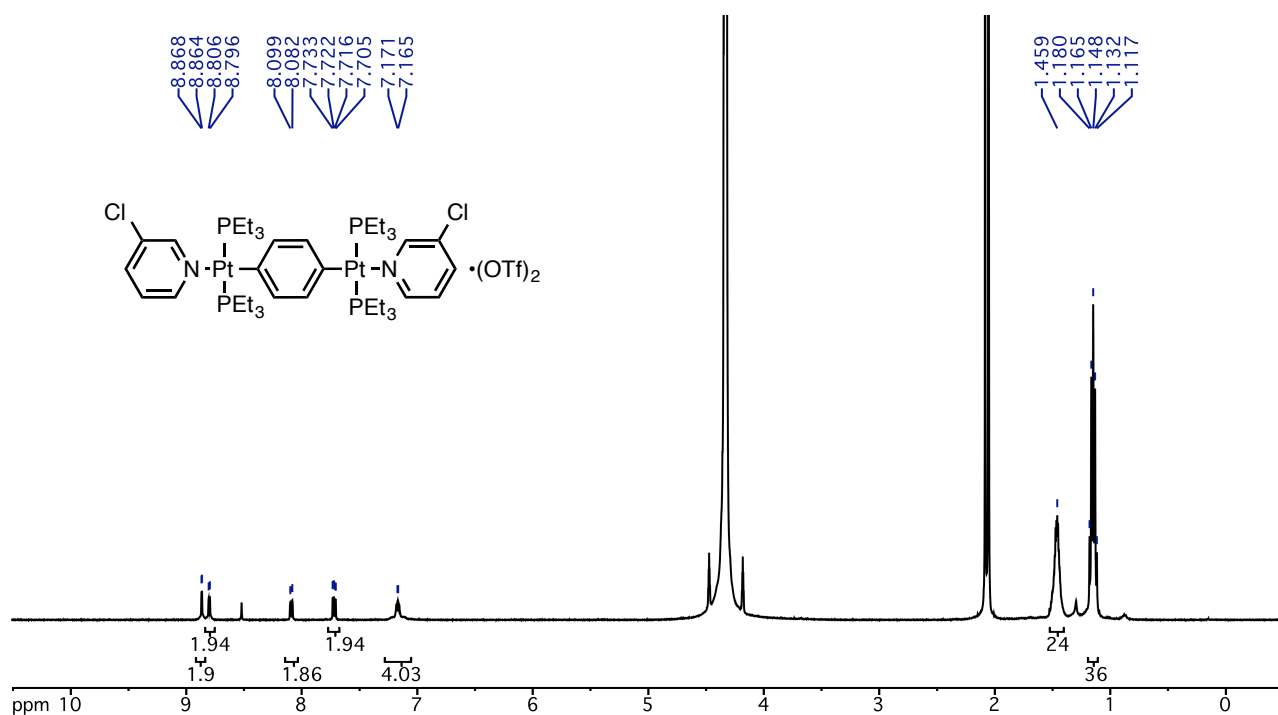


Fig. S9 ¹H NMR spectrum (500 MHz, CD₃NO₂, 298 K) of **PtPy***₂·(OTf)₂.

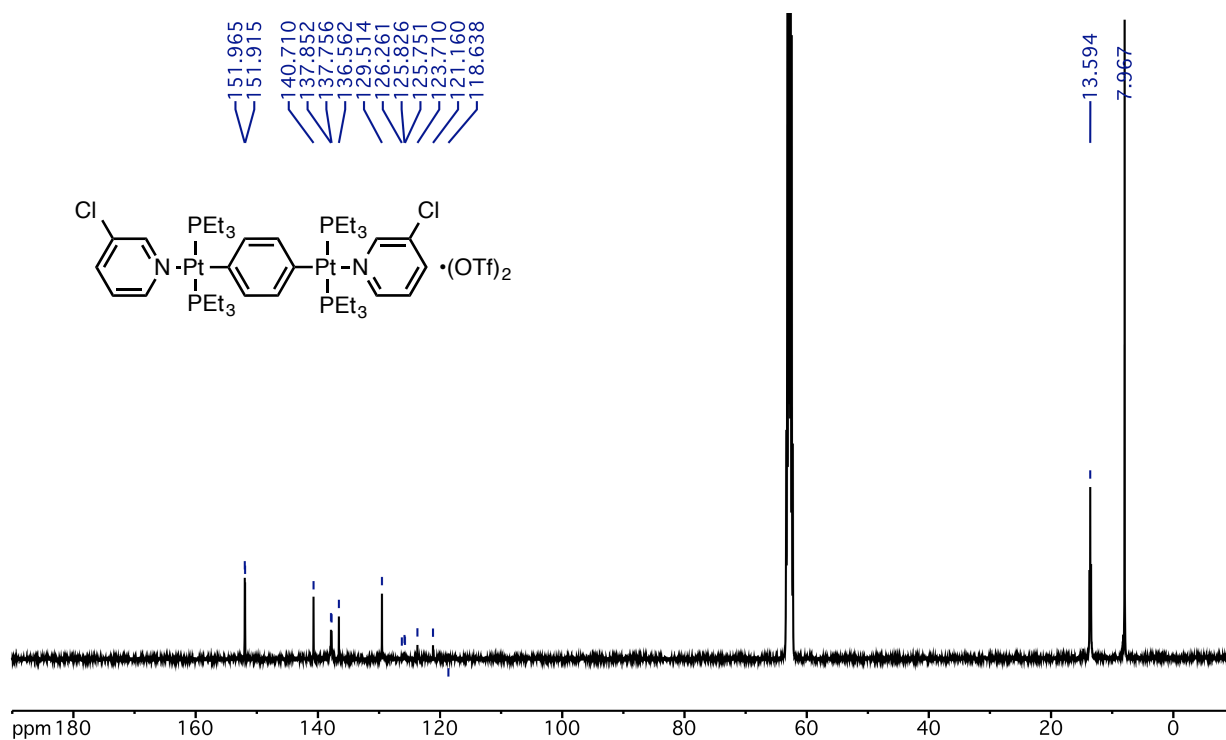


Fig. S10 ^{13}C NMR spectrum (126 MHz, CD_3NO_2 , 298 K) of $\text{PtPy}^*_2 \cdot (\text{OTf})_2$.

References

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- [2] Gardinier, J. R.; Clérac, R.; Gabbai, F. P. *J. Chem. Soc., Dalton Trans.* **2001**, 3453.