

Electronic Supporting Information
for
Electron-rich linear triplatinum complexes stabilized by spinning
tetraphosphine, tris(diphenylphosphinomethyl)phosphine

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Table S1. Crystallographic and experimental data of **3**·2CH₂Cl₂ and **4**·2CH₂Cl₂.

Table S2. Selected bond lengths and angles of **3** and **4**.

Figure S1. ESI–TOF mass spectra of **3** in CH₃OH.

Figure S2. ESI–TOF mass spectra of **4** in CH₃OH.

Figure S3. ³¹P{¹H} NMR spectra of **4** at (a) 60 °C, (b) 20 °C, and (c) –30 °C in CD₃CN and the assignments.

Figure S4. Variable temperature UV–vis absorption spectra of **3** in CD₃CN.

Figure S5. (a) Representative MO diagrams from the DFT calculations on [Pt₃(μ–tdpmp)₂(^tBuNC)₂]²⁺ (**4**) by B3LYP methods with lanl2dz and PCM (CH₂Cl₂), and (b) the results of TD–DFT calculations.

Figure S6. (a) Representative MO diagrams from the DFT calculations on [Pt₃(μ–dpmp)₂(^tBuNC)₂]²⁺ (**2**) by B3LYP methods with lanl2dz and PCM (CH₂Cl₂), and (b) the results of TD–DFT calculations.

Table S1. Crystallographic and experimental data of **3**·2CH₂Cl₂ and **4**·2CH₂Cl₂.

Compound	3 ·2CH ₂ Cl ₂	4 ·2CH ₂ Cl ₂
formula	C ₉₈ H ₉₄ Cl ₄ N ₂ F ₁₂ P ₁₀ Pt ₃	C ₉₀ H ₉₄ Cl ₄ N ₂ F ₁₂ P ₁₀ Pt ₃
formula wt	2564.63	2468.55
cryst. syst	triclinic	monoclinic
space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	13.328(4)	11.5968(9)
<i>b</i> , Å	14.042(5)	21.9132(13)
<i>c</i> , Å	15.350(5)	18.8936(15)
α , deg	107.847(2)	
β , deg	114.560(5)	97.800(4)
γ , deg	94.641(3)	
<i>V</i> , Å ³	2414.0(14)	4756.9(6)
<i>Z</i>	1	2
temp, °C	−120	−120
<i>D</i> _{calcd} , g cm ^{−3}	1.764	1.723
μ , mm ^{−1} (Mo K α)	4.666	4.732
2 θ range, deg	6–55	6–55
<i>R</i> _{int}	0.048	0.044
no. of reflns collected	19548	44367
no. of unique reflns	10465	10690
no. of obsd reflns (<i>I</i> > 2 σ (<i>I</i>))	7783	6815
no. of variables	584	548
<i>R</i> 1 ^{<i>a</i>}	0.060	0.037
<i>wR</i> 2 ^{<i>b</i>}	0.145	0.109
<i>GOF</i>	1.095	0.994

^{*a*} $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ (for obsd. refs with *I* > 2 σ (*I*)). ^{*b*} $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ (for all refs).

Table S2. Selected bond lengths (Å) and angles (°) of **3** and **4**.^a

	3	4
Pt1–Pt2	2.7779(2)	2.72840(16)
Pt1–P1	2.342(2)	2.3282(11)
Pt1–P2	2.476(2)	2.3529(12)
Pt1–P3*	2.321(2)	2.3105(11)
Pt1–C1	1.991(8)	1.970(5)
Pt2–P4	2.237(2)	2.2378(11)
C1–N1	1.183(12)	1.050(7)
Pt1–Pt2–Pt1*	180	180
Pt2–Pt1–P1	78.05(4)	82.13(2)
Pt2–Pt1–P2	92.37(4)	86.07(2)
Pt2–Pt1–P3*	84.25(4)	90.24(2)
Pt2–Pt1–C1	165.1(2)	178.79(14)
P1–Pt1–P2	91.98(9)	101.17(4)
P1–Pt1–P3*	141.78(8)	134.00(4)
P2–Pt1–P3*	122.66(8)	123.59(3)
P1–Pt1–C1	98.8(2)	96.76(13)
P2–Pt1–C1	102.4(3)	94.64(16)
P3*–Pt1–C1	89.7(2)	90.20(13)
Pt1–Pt2–P4	83.38(4)	83.23(2)
Pt1–Pt2–P4*	96.68(4)	96.77(2)

^a The atomic numbering schemes are shown in Figure 1.

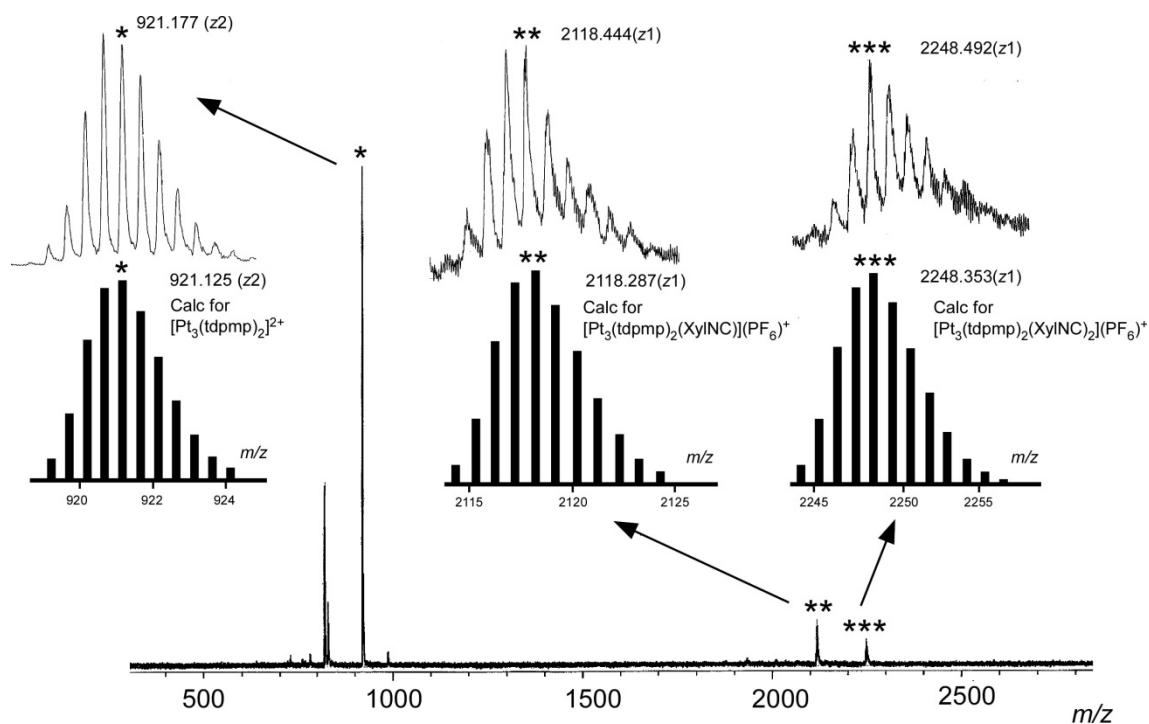
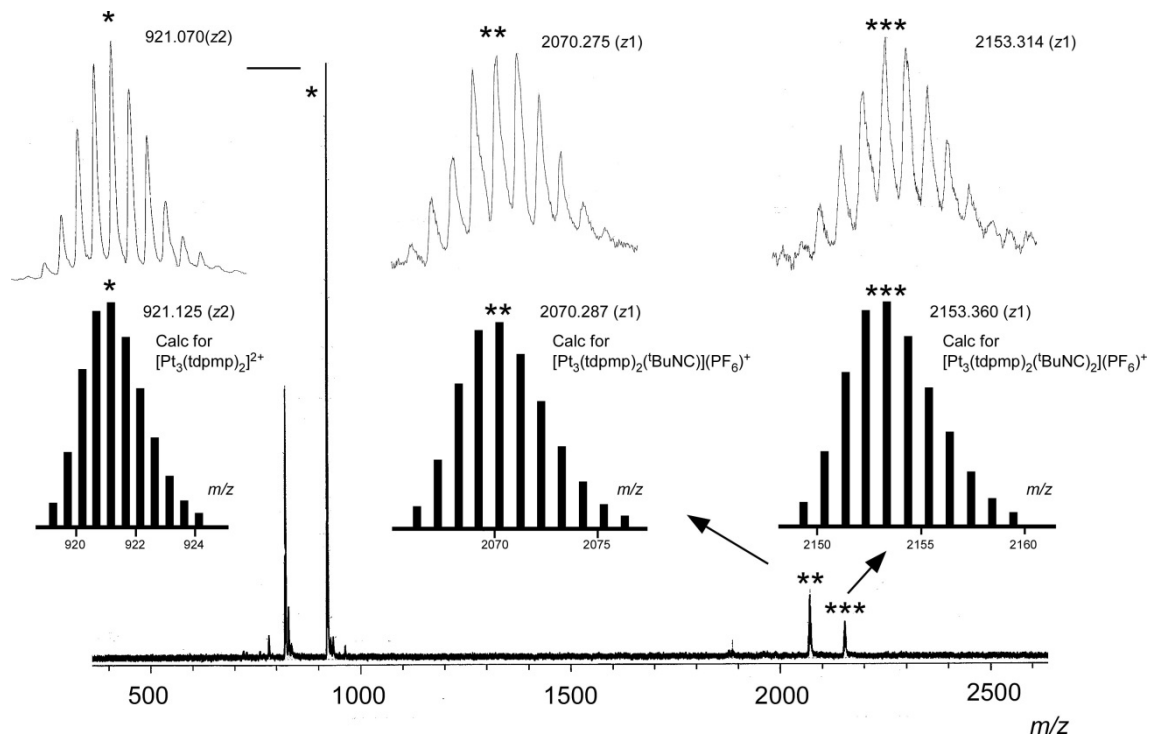
Figure S1. ESI-TOF mass spectra of **3** in CH₃OH.**Figure S2.** ESI-TOF mass spectra of **4** in CH₃OH.

Figure S3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **4** at (a) 60 °C, (b) 20 °C, and (c) –30 °C in CD_3CN and the assignments.

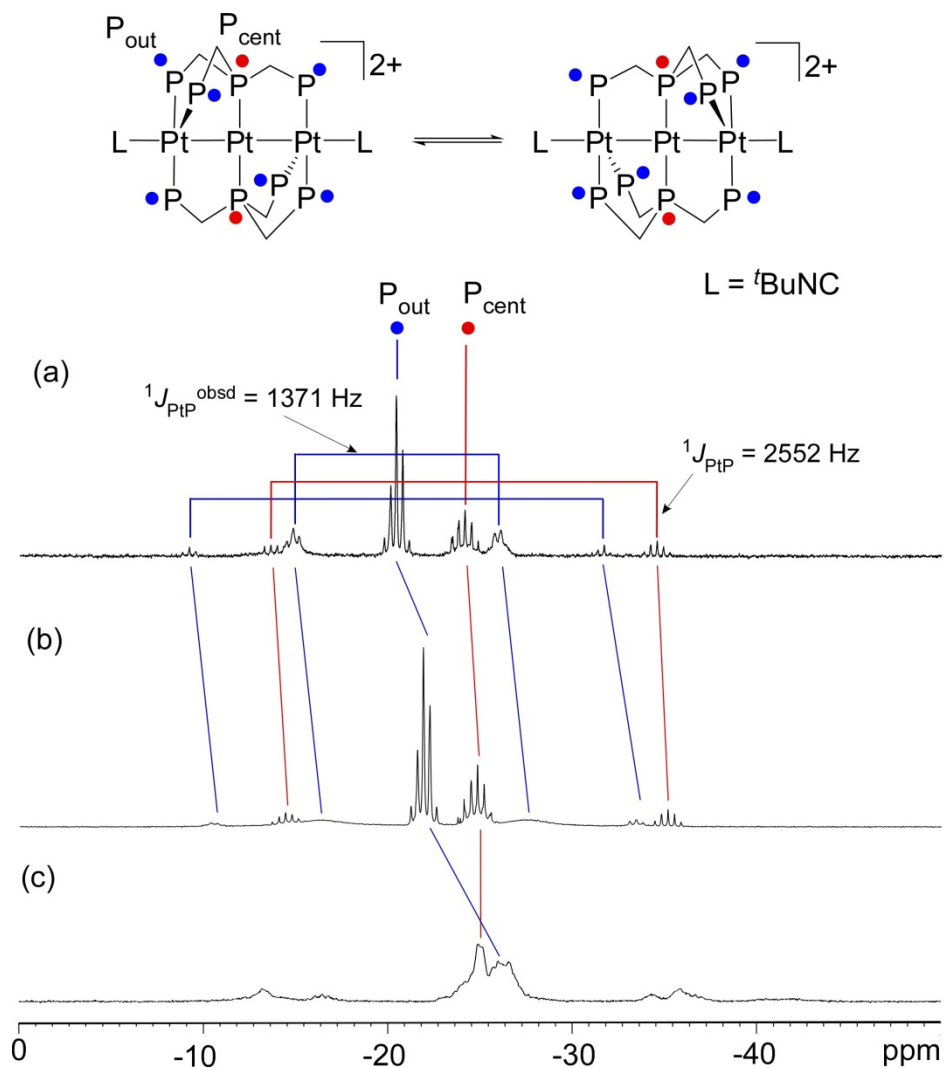


Figure S4. Variable temperature UV–vis absorption spectra of **3** in CD₃CN; (a) from 20 °C to –30 °C, and (b) from 20 °C to 60 °C.

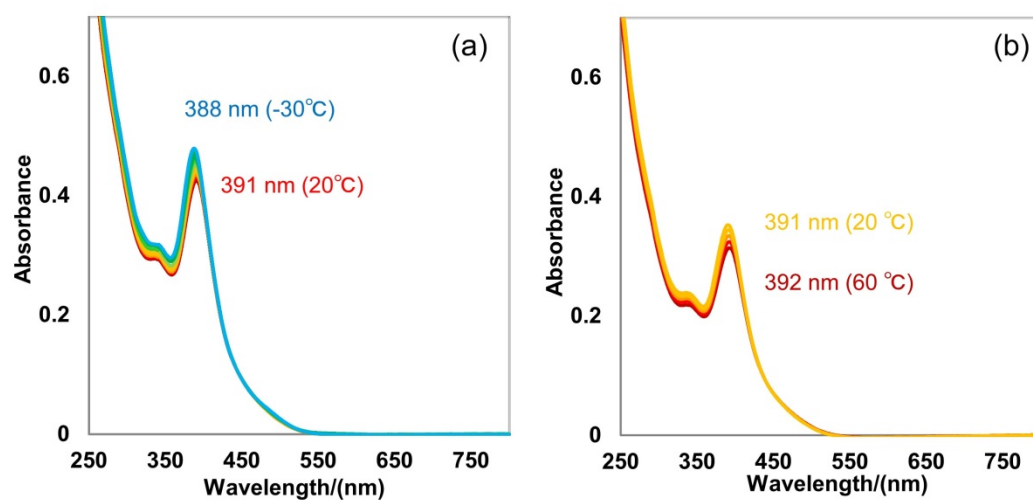
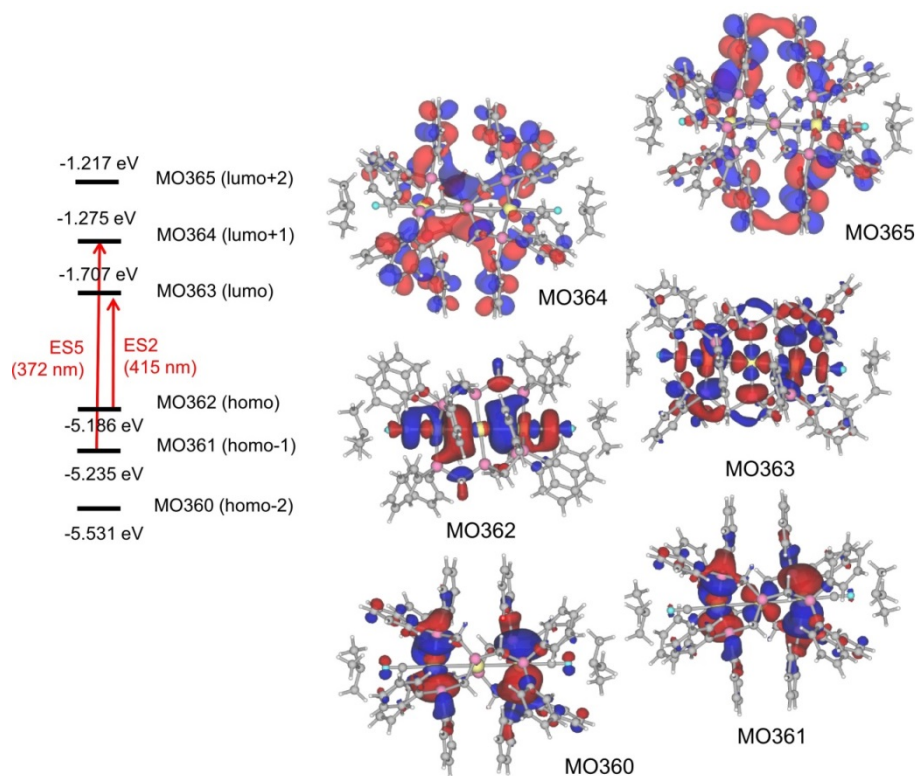


Figure S5. (a) Representative MO diagrams for the DFT calculations on $[\text{Pt}_3(\mu\text{-tdpmp})_2(\text{tBuNC})_2]^{2+}$ (**4**) by B3LYP methods with lanl2dz and PCM (CH_2Cl_2), and (b) the results of TD-DFT calculations.

(a)

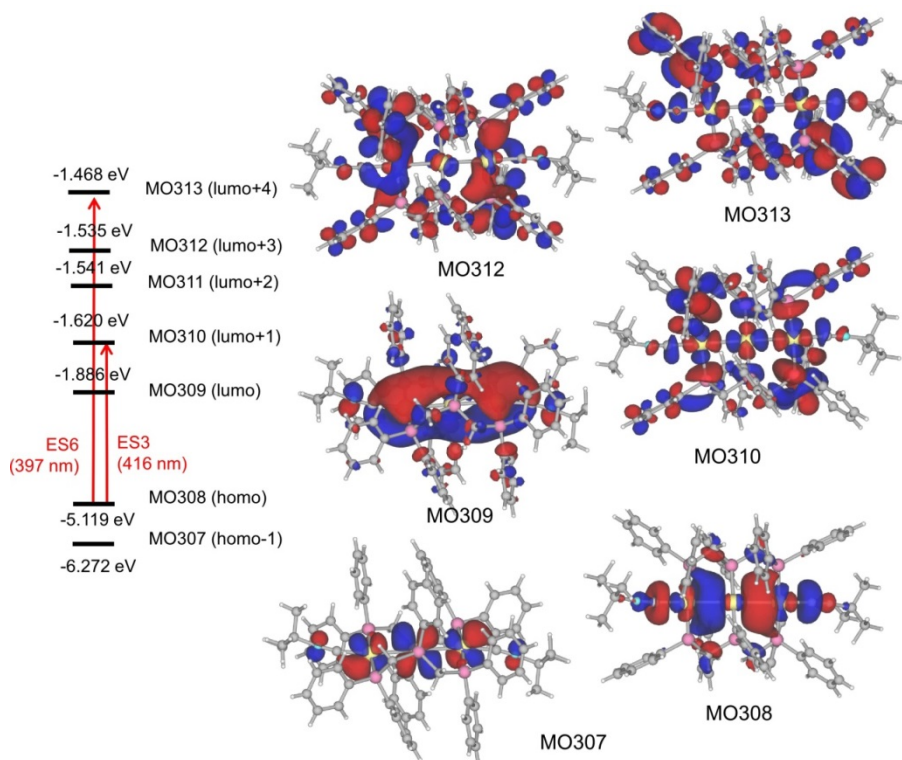


(b)

Excited States	TD-DFT data				obsd (CH_2Cl_2)
	energy/eV	λ/nm	f	transitions	λ/nm
E1	2.682	462	0.0001	361→363 (0.67)	
E2	2.986	415	0.4943	361→364 (0.11) 362→363 (0.64)	392
E3	3.044	407	0.036	360→363 (0.67)	
E4	3.276	379	0.0001	362→364 (0.68)	
E5	3.333	372	0.0926	361→364 (0.66) 361→366 (-0.11)	342
E6	3.428	362	0.0244	362→365 (0.67)	
E7	3.433	361	0.0001	361→365 (0.65)	
E8	3.459	358	0.0001	362→366 (0.67)	

Figure S6. (a) Representative MO diagrams for the DFT calculations on $[\text{Pt}_3(\mu\text{-dpmp})_2(\text{tBuNC})_2]^{2+}$ (**2**) by B3LYP methods with lanl2dz and PCM (CH_2Cl_2), and (b) the results of TD-DFT calculations.

(a)



(b)

Excited States	TD-DFT data				obsd (CH_2Cl_2)
	energy/eV	λ /nm	f	transitions	λ /nm
E1	2.491	498	0.0001	308→309 (0.69)	496
E2	2.916	425	0.0153	308→310 (0.20) 308→312 (0.55) 308→313 (-0.36)	429
E3	2.981	416	0.2103	307→309 (-0.11) 308→310 (0.61) 308→312 (-0.30)	386
E4	3.039	408	0.0001	308→311 (0.69)	
E5	3.116	398	0.0001	308→314 (0.69)	
E6	3.121	397	0.1255	307→309 (-0.13) 308→310 (0.15) 308→312 (0.31) 308→313 (0.58)	360
E7	3.222	385	0.0001	308→315 (0.70)	
E8	3.269	379	0.0083	308→316 (0.69)	