Electronic Supporting Information

Reversible formation and cleavage of Pt→Ag dative bonds in a pre-organized cavity of a luminescent heteropolynuclear platinum(II) complex

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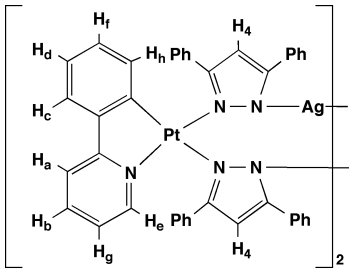
Experimental section

Materials. $[Pt(ppy)(\mu\text{-}Cl)]_2$ (ppy = 2-phenylpyridinate),[1] [PtCl(dfppy)(Hdfppy)] (dfppy = 2-(2,4-difluorophenyl)pyridinate)[2] were prepared by the literature methods. All other commercially available reagents were used as purchased.

Physical Measurement and Instrumentation. The ^{1}H NMR spectra were obtained at 400 MHz with JEOL JNM-AL400 and 500 MHz Varian NMR System 500PS spectrometer. The ^{195}Pt NMR spectra were recorded at JEOL JNM-AL400 spectrometer. UV/Vis spectra were recorded on a Jasco V-560 spectrophotometer at 20°C. Corrected emission spectra were obtained by using a Jasco FP-6500 spectrofluorometer (λ_{ex} = 350 nm). Lifetime measurements were conducted by using a streak camera (Hamamatsu C4334) as a detector and the third-harmonic generation of an Nd:YAG Laser (Continuum Minilite) at 355 nm excitation. Emission quantum yields in the solid state were determined by using a Hamamatsu Photonic Absolute PL Quantum Yield Measurement System C9920-02.

Preparation of Complexes. $[Pt(ppy)(Ph_2pzH)_2]Cl$ (1a). A mixture of $[Pt(ppy)(\mu\text{-}Cl)]_2$ (233 mg, 0.30 mmol) and Ph_2pzH (328 mg, 1.49 mmol) in acetonitrile (20 mL) was refluxed for 3 h with stirring under air, and the solution was concentrated to dryness. The pale yellow-brown solid was dissolved into methanol, and the solution was filtered. The filtrate was again concentrated to dryness, and the solid was extracted with dichloromethane. The extract was concentrated, and *n*-hexane was added to the solution. The resulted pale yellow-brown precipitate was collected, washed with diethyl ether, and dried in vacuum. Yield 266 mg (53%). It was recrystallized from dichloromethane/*n*-hexane. This complex exists as a 1:1 mixture of two isomers in the solution, which have eclipsed and staggered orientation in Ph_2pzH moieties. ^{1}H NMR (500 MHz, $CDCl_3$, r.t., TMS): δ = 15.6 (s, 1H), 15.5 (s, 1H), 13.4 (s, 1H), 9.43 (d, *J* = 5.5 Hz, 1H), 8.38 (d, *J* = 7.1 Hz, 2H), 8.13 (d, *J* = 7.6 Hz, 4H), 7.80-7.91 (m, 4H), 7.70-7.77 (m, 7H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.55 (t, *J* = 6.8 Hz, 2H), 7.38-7.51 (m, 9H), 7.27-7.38 (m, 10H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.12-7.19 (m, 4H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 7.8 Hz, 2H), 6.95-6.98 (m, 1H), 6.89-6.93 (m, 2H), 6.88 (s, 1H), 6.82 (s, 2H), 6.79 (t, *J* = 6.8 Hz, 2H), 6.75 (t, *J* = 6.4 Hz, 1H), 6.40 (d, *J* = 7.6 Hz, 1H), 6.33 ppm (d, *J* = 7.7 Hz, 1H). Anal. Calcd for $C_{41}H_{32}ClN_5Pt$: C, 59.67; H, 3.91; N, 8.49. Found: C, 59.65; H, 3.98; N, 8.51. ESI MS: *m*/*z* 789.2 $[M]^+$.

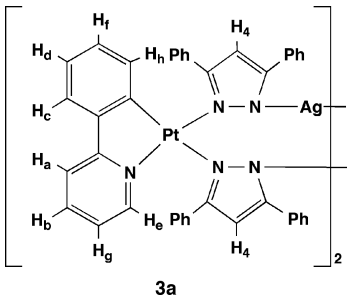
[$Pt_2Ag_2(ppy)_2(Ph_2pz)_4$] (2a). To a solution of **1a** (82 mg, 0.10 mmol) in methanol (10 mL) was added a solution of $AgBF_4$ (21 mg, 0.11 mmol) in methanol (5 mL). The solution was stirred for 1 h at 25 °C in the dark, and resulted precipitate (AgCl) was filtered off. A solution of $AgBF_4$ (19 mg, 0.10 mmol) in methanol (5 mL) and Et_3N (28 μL, 0.20 mmol) were added to the solution, and the mixture was stirred for 3 h in the dark. The resulted yellow precipitate was collected, washed with methanol, and dried in vacuum. Yield 59 mg (67%). It was recrystallized from toluene/*n*-hexane.



2a

^{1}H NMR (500 MHz, $CDCl_3$, r.t., TMS): δ = 7.88 (d, *J* = 7.0 Hz, 2H, Ph), 7.57 (d, *J* = 7.2 Hz, 2H, Ph), 7.42 (d, *J* = 7.2 Hz, 2H, Ph), 7.21-7.25 (m, 1H, H_a), 7.18 (d, *J* = 6.6 Hz, Ph), 7.02-7.13 (m, 5H, Ph), 6.91-7.02 (m, 5H, Ph, H_e, H_c and H_g), 6.83-6.89 (m, 1H, Ph), 6.77-6.83 (m, 2H, Ph), 6.71-6.76 (m, 3H, Ph and H_4 of Ph_2pz), 6.67-6.71 (m, 1H, H_d), 6.64-6.66 (s, 1H, H_4 of Ph_2pz), 6.61 (d, *J* = 7.6 Hz, 1H, H_h), 6.27 (t, *J* = 6.6 Hz, 1H, H_b), 6.00 ppm (t, *J* = 7.4 Hz, 1H, H_f). ^{195}Pt NMR (86 MHz, 90% CH_2Cl_2/10% $CDCl_3$, r.t., H_2PtCl_6): δ = –3073 (s). Anal. Calcd for $C_{82}H_{60}Ag_2N_{10}Pt_2$: C, 54.98; H, 3.38; N, 7.82. Found: C, 54.69; H, 3.38; N, 7.72. ESI MS: *m*/*z* 1791.3 [*M*]$^+$.

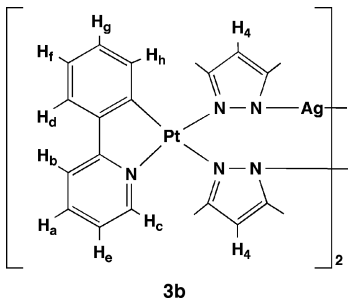
[$Pt_2Ag_3(ppy)_2(Ph_2pz)_4$]$BF_4$ (3a). To a solution of **1a** (168 mg, 0.20 mmol) in methanol (20 mL) was added a solution of $AgBF_4$ (39 mg, 0.20 mmol) in methanol (10 mL). The solution was stirred for 1 h at 25 °C in the dark, and resulted precipitate (AgCl) was filtered off. A solution of $AgBF_4$ (81 mg, 0.42 mmol) in methanol (5 mL) and Et_3N (56 μL, 0.40 mmol) were added to the solution, and the mixture was stirred for 3 h in the dark. The yellow solution was concentrated to dryness, and the resulted oily product was extracted with dichloromethane. The extract was washed with water, dried over anhydrous magnesium sulfate, and concentrated to dryness. The solid was again dissolved into a small amount of dichloromethane, and *n*-hexane was added to the solution. The resulted yellow precipitate was collected, washed with diethyl ether, and dried in vacuum. Yield 136 mg (67%). It was recrystallized from chloroform/*n*-hexane.



3a

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 7.73-7.83 (m, 2H, Ph), 7.54 (d, J = 7.9 Hz, 1H, H_a), 7.43 (t, J = 7.8 Hz, 1H, H_b), 7.37 (d, J = 7.8 Hz, 1H, H_c), 7.27-7.34 (m, 3H, Ph), 7.16-7.30 (m, 3H, Ph), 7.10-7.14 (m, 3H, Ph and H_4 of Ph_2pz), 6.98 (s, 5H, Ph), 6.86-6.94 (m, 4H, H_d and Ph), 6.81 (t, J = 7.4 Hz, 2H, Ph) , 6.65 (d, J = 2.0 Hz, 1H, H_4 of Ph_2pz), 6.60 (d, J = 5.4 Hz, 1H, H_e), 6.31 (t, J = 7.4 Hz, 1H, H_f), 6.20 (t, J = 6.6 Hz, 1H, H_g), 5.91 ppm (d, J = 7.4 Hz, 1H, H_d). ^{195}Pt NMR (86 MHz, 90% CH_2Cl_2/10% $CDCl_3$, r.t., H_2PtCl_6): δ = –2576 (d, $^1J(^{195}Pt–^{107,109}Ag)$ = 766 Hz). Anal. Calcd for $C_{82}H_{60}Ag_3BF_4N_{10}Pt_2$: C, 49.59; H, 3.05; N, 7.05. Found: C, 49.63; H, 3.06; N, 6.99. ESI MS: m/z 1899.2 $[M]^+$.

$[Pt_2Ag_3(ppy)_2(Me_2pz)_4]BF_4$ (3b). To a solution of $[Pt(ppy)(Me_2pzH)_2]Cl$ (**1b**)[3] (115 mg, 0.20 mmol) in methanol (10 mL) was added a solution of $AgBF_4$ (39 mg, 0.20 mmol) in methanol (5 mL). The solution was stirred for 1 h at 25 °C in the dark, and resulted precipitate (AgCl) was filtered off. A solution of $AgBF_4$ (81 mg, 0.42 mmol) in methanol (5 mL) and Et_3N (56 μL, 0.40 mmol) were added to the solution, and the mixture was stirred for 3 h in the dark. The yellow solution was concentrated to dryness, and the resulted oily product was extracted with dichloromethane. The extract was washed with water, dried over anhydrous magnesium sulfate, and concentrated to dryness. The solid was dissolved into a small amount of EtOH, and *n*-hexane was added to the solution. The resulted yellow precipitate was collected, washed with diethyl ether, and dried in vacuum. Yield 91 mg (61%). It was recrystallized from EtOH/*n*-hexane.



3b

^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 8.08 (t, J = 7.9 Hz, 1H, H_a), 7.91 (d, J = 8.2 Hz, 1H, H_b), 7.65 (d, J = 7.8 Hz, 2H, H_c), 7.51 (d, J = 5.7 Hz, 1H, H_d), 7.22 (t, J = 7.8 Hz, 1H, H_e), 7.20 (t, J = 7.5 Hz, 1H, H_f), 6.73 (t, J = 6.9 Hz, 1H, H_g), 6.13 (s, 1H, H_4 of Me_2pz), 5.96 (s, 1H, H_4 of Me_2pz), 5.86-5.95 (br, 1H, H_h) , 2.20 (s, 6H, Me), 2.07 (s, 3H, Me), 1.66 ppm (s, 3H, Me). Anal. Calcd for $C_{42}H_{44}Ag_3BF_4N_{10}Pt_2$: C, 33.87; H, 2.98; N, 9.40. Found: C, 33.96; H, 2.84; N, 9.34. ESI MS: m/z 1402.6 $[M]^+$.

$[Pt(dfppy)(Ph_2pzH)_2]Cl$ (4a). A mixture of [Pt(dfppy)(Hdfppy)Cl] (245 mg, 0.40 mmol) and Ph_2pzH (352 mg, 1.60 mmol) in acetonitrile (50 mL) was refluxed for 3 h with stirring under air, and then the solution was filtered and concentrated to dryness. The yellow solid was dissolved into dichloromethane, and *n*-hexane was added to the solution. The yellow precipitate was

collected, washed with diethyl ether, and dried in vacuum. Yield 184 mg (53%). It was recrystallized from dichloromethane/*n*-hexane. This complex exists as a 4:1 mixture of two isomers in the solution, which have eclipsed and staggered orientation in Ph_2pzH moieties. ^1H NMR (500 MHz, $CDCl_3$, r.t., TMS): δ = 13.7 (s, 1H), 9.41 (d, *J* = 5.6 Hz, 1H), 8.27 (d, *J* = 7.0 Hz, 2H), 8.11 (d, *J* = 5.5 Hz, 2H, H of isomer A), 8.07 (d, *J* = 8.5 Hz, 2H, H of isomer B), 7.77-7.88 (m, 4H), 7.72 (d, *J* = 7.3 Hz, 4H), 7.28-7.65 (m, 16H), 7.13-7.20 (m, 1H), 7.04 (t, *J* = 7.7 Hz, 1H), 6.80-6.93 (m, 3H), 6.66 (t, *J* = 6.1 Hz, 1H, H of isomer A), 6.58 (t, *J* = 10.6 Hz, 1H, H of isomer B), 6.35 (t, *J* = 10.7 Hz, 1H), 5.89 (d, *J* = 8.7 Hz, 1H, H of isomer B), 5.68 ppm (d, *J* = 8.9 Hz, 1H, H of isomer A). Anal. Calcd for $C_{41}H_{30}ClF_2N_5Pt$: C, 57.18; H, 3.51; N, 8.13. Found: C, 57.30; H, 3.33; N, 8.25. ESI MS: *m*/*z* 825.8 $[M]^+$.

$[Pt_2Ag_2(dfppy)_2(\mu\text{-}Ph_2pz)_4]$ (5a). To a solution of **4a** (79 mg, 0.09 mmol) in methanol (10 mL) was added a solution of $AgBF_4$ (23 mg, 0.12 mmol) in methanol (5 mL). The solution was stirred for 1 h at 25 °C in the dark, and resulted precipitate (AgCl) was filtered off. A solution of $AgBF_4$ (20 mg, 0.10 mmol) in methanol (10 mL) and Et_3N (28 μL, 0.20 mmol) were added to the solution, and the mixture was stirred for 3 h in the dark. The resulted pale yellow precipitate was collected, washed with methanol, and dried in vacuum. Yield 54 mg (63%). It was recrystallized from dichloromethane/*n*-hexane. ^1H NMR (500 MHz, $CDCl_3$, r.t., TMS): δ = 7.60 (br, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 7.5 Hz, 2H), 7.27-7.31 (m, 2H), 6.99-7.17 (m, 6H), 6.94 (t, *J* = 7.4 Hz, 2H), 6.82-6.89 (m, 6H), 6.72-6.81 (m, 3H), 6.63 (s, 1H), 6.23 (t, *J* = 9.9 Hz, 1H), 6.07 ppm (br, 1H). Anal. Calcd for $C_{82}H_{56}Ag_2F_4N_{10}Pt_2$: C, 52.86; H, 3.03; N, 7.52. Found: C, 52.60; H, 2.79; N, 7.52. ESI MS: *m*/*z* 1863.3 $[M]^+$.

Abstraction of Ag^+ ion from 3a with *n*-Bu_4NCl. To a $CDCl_3$ solution of **3a** (9.4 mg, 5.0 μmol) was added a $CDCl_3$ solution of *n*-Bu_4NCl (1.4 mg, 5.0 μmol: 1 eq.). After the solution was heated for 30 min at 40 °C and filtered by a membrane filter, the formation of **2a** was confirmed by ^1H NMR spectroscopy.

X-ray Structural Determinations. Crystals suitable for X-ray structural analysis were obtained by recrystallization from dichloromethane/*n*-hexane (**1a**·CH_2Cl_2, **5a**), toluene/*n*-hexane (**2a**·$3C_7H_8$) and chloroform/*n*-hexane (**3a**·$1.4CHCl_3$·$0.4C_6H_{14}$), respectively. Intensity data were collected on a Rigaku Saturn724 diffractometer using multi-layer mirror monochromated Mo Kα (λ = 0.71075 Å) radiation at 93 K. The data were corrected for Lorentz and polarization effects.

An empirical absorption correction was applied.

The crystal structures were solved by direct method (SHELXS-97).[4] The positional and thermal parameters of non-H atoms were refined anisotropically by the full-matrix least-squares method except for disordering solvent molecules and counter anions (one of three toluene molecules in **2a**·$3C_7H_8$ and chloroform and hexane molecules and BF_4 anion in **3a**·$1.4CHCl_3$·$0.4C_6H_{14}$). The minimized function was $\Sigma w(F_o^2-F_c^2)^2$. Hydrogen atoms were included at calculated positions with fixed displacement parameters. In the final cycle of the refinement, parameter shifts were less than 0.1σ. No correction was made for secondary extinction. All calculations were performed using the CrystalStructure[5] crystallographic software package except for refinement, which was performed using SHELXL-97.[4] Listings of the selected bond distances and angles are summarized in Table S2.

Computational methods. The geometries of **2a** and cationic parts of **3a** and **3b** were optimized with the DFT method, where B3LYP functional was employed.[6] X-ray structures were used as initial geometries without any geometrical constraints. In these calculations, for all metals, basis sets with ECPs proposed by Christiansen et al were employed.[7] In details, for Ag and Pt atoms, (541/541/211) and (541/5511/211) basis sets were used, respectively. For C, N, and H atoms, cc-pVDZ basis sets were used.[8] All calculations were carried out using the Gaussian 09 package.[9] Molecular orbitals with the isovalue of 0.02 were drawn by the Gauss View 5.[10]

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Table S1. Crystallographic information for $[Pt(ppy)(Ph_2pzH)_2]Cl{\cdot}CH_2Cl_2$ (**1a**·CH_2Cl_2), $[Pt_2Ag_2(ppy)_2(Ph_2pz)_4]{\cdot}3C_7H_8$ (**2a**·$3C_7H_8$), $[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]BF_4{\cdot}1.4CHCl_3{\cdot}0.4C_6H_{14}$ (**3a**·$1.4CHCl_3{\cdot}0.4C_6H_{14}$) and $[Pt_2Ag_2(dfppy)_2(Ph_2pz)_4]$ (**5a**)

	1a·CH_2Cl_2	**2a**·$3C_7H_8$	**3a**·$1.4CHCl_3{\cdot}0.4C_6H_{14}$
Empirical formula	$C_{42}H_{34}Cl_3N_5Pt$	$C_{103}H_{84}Ag_2N_{10}Pt_2$	$C_{85.8}H_{67}Ag_3BCl_{4.2}F_4N_{10}Pt_2$
Formula weight	910.21	2067.78	2187.63
Temperature (K)	93(1)	93(1)	93(1)
Wavelength (Å)	0.71075	0.71075	0.71075
Crystal system	monoclinic	orthorhombic	triclinic
Space group	$P2_1/c$ (14)	*Pbcn* (60)	$P1-$ (2)
Unit cell dimensions			
a (Å)	15.354(2)	18.6158(16)	14.001(2)
b (Å)	20.314(3)	18.2847(14)	16.562(3)
c (Å)	23.041(4)	24.601(2)	20.395(4)
α (deg)	90	90	101.594(2)
β (deg)	93.005(2)	90	101.990(2)
γ (deg)	90	90	100.392(2)
V (Å^3)	7176.8(19)	8373.8(12)	4408.4(14)
Z	8	4	2
ρ_{calcd} (g/cm^3)	1.685	1.640	1.648
μ(Mo Kα) (mm^{-1})	4.157	3.833	3.985
F(000)	3600	4088	2122.40
Index ranges	-20<=h<=19	-24<=h<=23	-15<=h<=17
	-26<=k<=26	-23<=k<=19	-20<=k<=20
	-31<=l<=31	-31<=l<=31	-25<=l<=25
Reflections collected	65554	66939	33257
Independent reflections	18939 [R_{int} = 0.0697]	9581 [R_{int} = 0.0360]	9717 [R_{int} = 0.0380]
Data / restraints / parameters	18939 / 0 / 919	9581 / 0 / 512	16971 / 20 / 986
Goodness-of-fit on F^2	1.082	1.096	1.061
Final R index [$I>2\sigma(I)$][a]	R_1 = 0.0655	R_1 = 0.0264	R_1 = 0.0698
R indices (all data)[a,b]	R_1 = 0.0909, wR_2 = 0.1340	R_1 = 0.0308, wR_2 = 0.0552	R_1 = 0.0862, wR_2 = 0.1886
Largest diff. peak and hole (e.Å^{-3})	2.84 and –2.04	1.80 and –0.86	3.45 and –2.33
CCDC number	1535614	1535612	1535611

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S1. Crystallographic Information (*continued*)

	5a
Empirical formula	$C_{82}H_{56}Ag_2F_4N_{10}Pt_2$
Formula weight	1863.32
Temperature (K)	93(1)
Wavelength (Å)	0.71075
Crystal system	monoclinic
Space group	$P2_1/c$ (14)
Unit cell dimensions	
a (Å)	23.523(5)
b (Å)	14.927(3)
c (Å)	19.897(5)
α (deg)	90
β (deg)	109.989(3)
γ (deg)	90
V (Å^3)	6565(3)
Z	4
ρ_{calcd} (g/cm^3)	1.885
μ(Mo Kα) (mm^{-1})	4.886
F(000)	3616
Index ranges	-30<=h<=30 -18<=k<=19 -23<=l<=24
Reflections collected	53578
Independent reflections	14744 [R_{int} = 0.0885]
Data / restraints / parameters	14744 / 0 / 901
Goodness-of-fit on F^2	1.164
Final R index [I>2σ(I)][a]	R_1 = 0.0810
R indices (all data)[a,b]	R_1 = 0.1125, wR_2 = 0.1465
Largest diff. peak and hole (e.Å^{-3})	1.23 and –1.84
CCDC number	1535613

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S2. Selected bond lengths [Å] and torsion angles [°] for $[Pt_2Ag_2(ppy)_2(Ph_2pz)_4]$ (**2a**), $[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]BF_4$ (**3a**), and $[Pt_2Ag_2(dfppy)_2(Ph_2pz)_4]$ (**5a**)

	2a	**3a**	**5a**
Pt1···Pt2(Pt1')	4.6707(4)	5.1641(9)	4.596(1)
Pt1···Ag1	3.2028(3)	3.421(1)	3.294(1)
Pt1···Ag2(Ag1')	3.4249(3)	3.327(1)	3.375(1)
Pt1···Ag3		2.820(1)	
Pt2···Ag1		3.301(1)	3.352(1)
Pt2···Ag2		3.443(1)	3.446(1)
Pt2···Ag3		2.801(1)	
Ag1···Ag2(Ag1')	2.9840(4)	3.224(1)	2.962(1)
Ag1···Ag3		2.996(1)	
Ag2···Ag3		3.063(1)	
Ag3···C122		2.41(1)	
Ag3···C422		2.48(1)	
N11–Pt1–Pt2–N41		168.2(4)	26.5(4)
N11–Pt1–Pt1'–N11'	3.0(1)		
C122–Pt1–Pt2–C422		7.3(5)	-139.7(4)
C122–Pt1–Pt1'–C122'	-157.9(1)		
N21–Pt1–Pt2–N61		87.2(3)	-55.3(4)
N21–Pt1–Pt1'–N31'	-77.29(9)		
N31–Pt1–Pt2–N51		88.1(3)	-57.3(4)

Table S3 Photophysical data for $[Pt_2Ag_2(ppy)_2(Ph_2pz)_4]$ (**2a**), $[Pt_2Ag_2(ppy)_2(Me_2pz)_4]$ (**2b**)[a], $[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]BF_4$ (**3a**), $[Pt_2Ag_3(ppy)_2(Me_2pz)_4]BF_4$ (**3b**) and $[Pt_2Ag_2(dfppy)_2(Ph_2pz)_4]$ (**5a**)

Complex	Absorption λ_{max} [nm] (ε_{max} [$dm^3mol^{-1}cm^{-1}$])	Emission λ_{max} [nm] (τ [μs])	Φ_{em}
2a	259 (127000), 331 sh, 368 sh, 410 sh[b]	489, 522 (τ_1 = 0.52 (A_1 = 0.88), τ_2 = 2.24 (A_2 = 0.12))[b,d]	0.05[e]
		498, 530 (τ_1 = 1.20 (A_1 = 0.67), τ_2 = 2.97 (A_2 = 0.33))[c,d]	0.17[f]
2b[a]	259 (42900), 332 sh, 370 (7200), 409 sh[b]	491, 525 (τ = 0.43)[b]	0.04[e]
		497, 531 (τ_1 = 0.69 (A_1 = 0.52), τ_2 = 3.93 (A_2 = 0.48))[c,d]	0.34[f]
3a	251 (111000), 324 (13200), 350 sh, 374 sh, 437 sh[b]	529 (τ = 9.87)[b]	0.03[e]
		533 (τ_1 = 0.66 (A_1 = 0.83), τ_2 = 1.94 (A_2 = 0.17))[c,d]	0.15[f]
3b	255 sh, 282 sh, 321 sh, 360 sh, 405 sh, 433 sh[b]	482, 517, 547 (τ = 9.87)[b]	0.23[e]
		533 (τ_1 = 0.61 (A_1 = 0.63), τ_2 = 1.80 (A_2 = 0.37))[c,d]	0.53[f]
5a	256 (138000), 328 (11300), 361 sh[b]	471, 501 (τ = 0.72)[b]	0.02[e]
		475, 505 (τ_1 = 0.87 (A_1 = 0.48), τ_2 = 2.83 (A_2 = 0.52))[c,d]	0.40[f]

[a] Ref. 3 in SI. [b] In CH_2Cl_2 at 298 K. [c] In the solid state at 298 K. [d] Emission decay curve was analyzed by the equation ($I(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$) using the nonlinear least-squares method.
[e] Emission quantum yield in CH_2Cl_2. [f] Emission quantum yield in the solid state.

Table S4. Mayer bond order[a]

		Pt-Ag	Pt-Ag*	Ag-Ag*	Ag*-C
$[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]^+$ (**3a'**)	S_0	0.03	0.32	0.11	0.18
	T_1	0.01	0.22	0.23	0.11
$[Pt_2Ag_3(ppy)_2(Me_2pz)_4]^+$ (**3b'**)	S_0	0.03	0.32	0.10	0.18
	T_{1a}	0.02	0.21	0.22	0.07
	T_{1b}	0.02	0.31	0.11	0.30
		0.03	0.24	0.11	0.16

[a] Ag* in **3a'** and **3b'** denotes the Ag atom forming Pt→Ag dative bond.

Table S5. Wiberg bond order[a]

		Pt-Ag	Pt-Ag*	Ag-Ag*	Ag*-C
$[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]^+$ (**3a'**)	S_0	0.02	0.11	0.05	0.07
	T_1	0.01	0.08	0.12	0.07
$[Pt_2Ag_3(ppy)_2(Me_2pz)_4]^+$ (**3b'**)	S_0	0.02	0.12	0.05	0.07
	T_{1a}	0.01	0.09	0.11	0.06
	T_{1b}	0.02	0.11	0.05	0.16
		0.02	0.10	0.05	0.08

[a] Ag* in **3a'** and **3b'** denotes the Ag atom forming Pt→Ag dative bond.

Table S6. Bond lengths [Å] optimized by the B3LYP method[a]

		Pt-Ag	Pt-Ag*	Ag-Ag*	Ag-Ag	Ag*-C
$[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]^+$ (**3a'**)	S_0	3.49	2.82	3.11	3.29	2.61
		3.64				
	T_1	3.47	2.91	2.87	3.08	2.81
		3.57				
$[Pt_2Ag_3(ppy)_2(Me_2pz)_4]^+$ (**3b'**)	S_0	3.49	2.81	3.14	3.17	2.64
		3.71				
	T_{1a}	3.61	2.91	2.90	3.08	2.94
		3.65				
	T_{1b}	3.49	2.81	3.12	3.16	2.53
		3.53	2.83	3.13	3.24	2.66
		3.66				
		3.71				

[a] Ag* in **3a'** and **3b'** denotes the Ag atom forming Pt→Ag dative bond.

Table S7. Spin densities by Mulliken population analysis[a]

		Pt	Ag		ppy	Ph_2pz
$[Pt_2Ag_2(ppy)_2(Ph_2pz)_4]$ (**2a**)	T_1	0.21	0.01		1.76	0.02
		Pt	Ag	Ag*	ppy	Ph_2pz
$[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]^+$ (**3a'**)	T_1	0.34	0.18	0.39	0.17	0.93
		Pt	Ag	Ag*	ppy	Me_2pz
$[Pt_2Ag_3(ppy)_2(Me_2pz)_4]^+$ (**3b'**)	T_{1a}	0.43	0.14	0.44	0.17	0.82
	T_{1b}	0.40	0.02	0.20	1.26	0.11

[a] Ag* in **3a'** and **3b'** denotes the Ag atom forming Pt→Ag dative bond.

Table S8. Spin densities by NBO[a]

		Pt	Ag		ppy	Ph2pz
$[Pt_2Ag_2(ppy)_2(Ph_2pz)_4]$ (**2a**)	T_1	0.19	0.01		1.77	0.03
		Pt	Ag	Ag*	ppy	Ph2pz
$[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]^+$ (**3a'**)	T_1	0.28	0.16	0.38	0.21	0.97
		Pt	Ag	Ag*	ppy	Me2pz
$[Pt_2Ag_3(ppy)_2(Me_2pz)_4]^+$ (**3b'**)	T_{1a}	0.38	0.11	0.44	0.21	0.86
	T_{1b}	0.34	0.02	0.19	1.33	0.13

[a] Ag* in **3a'** and **3b'** denotes the Ag atom forming Pt→Ag dative bond.

Table S9. Natural electron configuration by NBO[a]

$[Pt_2Ag_2(ppy)_2(Ph_2pz)_4]$ (**2a**)		S_0		T_1	
Pt	1	[core] $6s^{0.57}$ $5d^{8.74}$	$6p^{0.01}$ $6d^{0.02}$ $7p^{0.01}$	[core] $6s^{0.57}$ $5d^{8.74}$	$6p^{0.01}$ $6d^{0.02}$ $7p^{0.01}$
Pt	2	[core] $6s^{0.57}$ $5d^{8.74}$	$6p^{0.01}$ $6d^{0.02}$ $7p^{0.01}$	[core] $6s^{0.57}$ $5d^{8.64}$	$6p^{0.02}$ $6d^{0.02}$ $7p^{0.01}$
Ag	3	[core] $5s^{0.41}$ $4d^{9.85}$	$5p^{0.01}$ $6p^{0.01}$	[core] $5s^{0.40}$ $4d^{9.85}$	$5p^{0.01}$ $6p^{0.01}$
Ag	4	[core] $5s^{0.41}$ $4d^{9.85}$	$5p^{0.01}$ $6p^{0.01}$	[core] $5s^{0.41}$ $4d^{9.85}$	$5p^{0.01}$ $6p^{0.01}$

$[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]^+$ (**3a'**)		S_0		T_1	
Pt	1	[core] $6s^{0.56}$ $5d^{8.73}$	$6p^{0.01}$ $6d^{0.02}$ $7p^{0.02}$	[core] $6s^{0.55}$ $5d^{8.70}$	$6p^{0.03}$ $6d^{0.03}$ $7p^{0.01}$
Pt	2	[core] $6s^{0.56}$ $5d^{8.73}$	$6p^{0.01}$ $6d^{0.02}$ $7p^{0.02}$	[core] $6s^{0.55}$ $5d^{8.70}$	$6p^{0.03}$ $6d^{0.03}$ $7p^{0.01}$
Ag*	3	[core] $5s^{0.32}$ $4d^{9.94}$	$5p^{0.01}$ $6s^{0.01}$ $6p^{0.01}$	[core] $5s^{0.71}$ $4d^{9.95}$	$5p^{0.05}$ $6p^{0.01}$
Ag	4	[core] $5s^{0.43}$ $4d^{9.84}$	$5p^{0.01}$ $6p^{0.01}$	[core] $5s^{0.43}$ $4d^{9.87}$	$5p^{0.03}$ $6p^{0.01}$
Ag	5	[core] $5s^{0.43}$ $4d^{9.84}$	$5p^{0.01}$ $6p^{0.01}$	[core] $5s^{0.43}$ $4d^{9.87}$	$5p^{0.03}$ $6p^{0.01}$

$[Pt_2Ag_3(ppy)_2(Me_2pz)_4]^+$ (**3b'**)		S_0		T_{1a}		T_{1b}	
Pt	1	[core] $6s^{0.58}$ $5d^{8.73}$	$6d^{0.02}$ $7p^{0.02}$	[core] $6s^{0.57}$ $5d^{8.67}$	$6p^{0.03}$ $6d^{0.02}$ $7p^{0.01}$	[core] $6s^{0.58}$ $5d^{8.72}$	$6p^{0.02}$ $6d^{0.02}$ $7p^{0.01}$
Pt	2	[core] $6s^{0.58}$ $5d^{8.73}$	$6d^{0.02}$ $7p^{0.02}$	[core] $6s^{0.57}$ $5d^{8.67}$	$6p^{0.03}$ $6d^{0.02}$ $7p^{0.01}$	[core] $6s^{0.56}$ $5d^{8.59}$	$6p^{0.04}$ $6d^{0.02}$ $7p^{0.01}$
Ag*	3	[core] $5s^{0.34}$ $4d^{9.95}$	$5p^{0.01}$ $6s^{0.01}$ $6p^{0.01}$	[core] $5s^{0.79}$ $4d^{9.96}$	$5p^{0.05}$ $6p^{0.01}$	[core] $5s^{0.51}$ $4d^{9.91}$	$5p^{0.02}$ $6s^{0.01}$ $6p^{0.01}$
Ag	4	[core] $5s^{0.50}$ $4d^{9.82}$	$6p^{0.02}$	[core] $5s^{0.48}$ $4d^{9.86}$	$5p^{0.03}$	[core] $5s^{0.50}$ $4d^{9.82}$	$5p^{0.02}$
Ag	5	[core] $5s^{0.50}$ $4d^{9.82}$	$6p^{0.02}$	[core] $5s^{0.48}$ $4d^{9.86}$	$5p^{0.03}$	[core] $5s^{0.49}$ $4d^{9.83}$	$5p^{0.02}$

[a] Ag* in **3a'** and **3b'** denotes the Ag atom forming Pt→Ag dative bond.

Table S10. Excitation energies of $[Pt_2Ag_2(ppy)_2(Ph_2pz)_4]$ (**2a**) by the TD-B3LYP method

State	Excitation Energy (eV)	Excitation Energy (nm)	Oscillator Strength	Contribution (%)			
1	3.00	413	0.0087	HOMO	→	LUMO+1	21.7%
				HOMO−1	→	LUMO	20.6%
2	3.00	413	0.0068	HOMO	→	LUMO	29.8%
				HOMO−1	→	LUMO+1	14.5%
3	3.12	398	0.0180	HOMO−4	→	LUMO	13.0%
4	3.12	398	0.0162	HOMO−4	→	LUMO+1	11.6%
				HOMO	→	LUMO+1	10.3%
5	3.20	387	0.0001	HOMO−1	→	LUMO	16.0%
				HOMO−3	→	LUMO	13.6%
6	3.22	386	0.0223	HOMO−1	→	LUMO+1	15.9%
				HOMO−4	→	LUMO	12.6%
				HOMO−3	→	LUMO+1	10.4%
7	3.26	381	0.0044	HOMO−2	→	LUMO	17.6%
				HOMO−1	→	LUMO+1	11.2%
8	3.26	381	0.0023	HOMO−2	→	LUMO+1	15.5%
9	3.41	364	0.0096	HOMO−6	→	LUMO	30.1%
10	3.41	363	0.0009	HOMO−6	→	LUMO+1	28.3%
11	3.44	360	0.0001	HOMO−4	→	LUMO+1	19.0%
				HOMO−3	→	LUMO	17.8%
12	3.44	360	0.0003	HOMO−3	→	LUMO+1	23.4%
				HOMO−4	→	LUMO	15.6%
13	3.49	355	0.0058	HOMO−5	→	LUMO	31.6%
14	3.51	354	0.0020	HOMO−5	→	LUMO+1	32.2%

Table S11. Excitation energies of $[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]^+$ (**3a'**) by the TD-B3LYP method

State	Excitation Energy (eV)	Excitation Energy (nm)	Oscillator Strength	Contribution (%)		
1	2.48	500	0.0009	HOMO−1 →	LUMO	47.7%
2	2.48	500	0.0065	HOMO →	LUMO	47.7%
3	2.62	473	0.0026	HOMO−2 →	LUMO	47.8%
4	2.65	468	0.0072	HOMO−3 →	LUMO	46.4%
5	2.80	443	0.0035	HOMO−4 →	LUMO	46.5%
6	2.82	439	0.0033	HOMO−5 →	LUMO	47.8%
7	2.91	426	0.0130	HOMO−8 →	LUMO	41.6%
8	2.96	419	0.0011	HOMO−6 →	LUMO	46.8%
9	3.01	412	0.0029	HOMO−7 →	LUMO	47.4%
10	3.09	401	0.0008	HOMO →	LUMO+1	45.3%
11	3.09	401	0.0219	HOMO−1 →	LUMO+1	47.0%
12	3.12	398	0.0084	HOMO−11→	LUMO	35.9%
13	3.19	388	0.0197	HOMO−9 →	LUMO	40.9%
14	3.23	384	0.0075	HOMO−2 →	LUMO+1	37.7%
15	3.23	384	0.0743	HOMO−10→	LUMO	30.8%
16	3.25	381	0.0013	HOMO−3 →	LUMO+1	43.6%
17	3.33	372	0.0175	HOMO−13→	LUMO	30.3%
18	3.38	367	0.0018	HOMO−4 →	LUMO+1	27.2%
19	3.39	366	0.0001	HOMO−12→	LUMO	18.9%
				HOMO−4 →	LUMO+1	16.5%
20	3.40	364	0.0104	HOMO−5 →	LUMO+1	44.4%
21	3.45	360	0.0115	HOMO−14→	LUMO	38.0%
22	3.49	356	0.0040	HOMO−15→	LUMO	21.2%
				HOMO−8 →	LUMO+1	10.7%
23	3.51	354	0.0003	HOMO−8 →	LUMO+1	28.0%
				HOMO−15→	LUMO	14.7%

Table S12. Excitation energies of $[Pt_2Ag_3(ppy)_2(Me_2pz)_4]^+$ (**3b'**) by the TD-B3LYP method

State	Excitation Energy (eV)	Excitation Energy (nm)	Oscillator Strength	Contribution (%)		
1	2.55	487	0.0013	HOMO	→ LUMO	46.5%
2	2.57	483	0.0020	HOMO−1	→ LUMO	44.6%
3	2.77	448	0.0034	HOMO−2	→ LUMO	45.6%
4	2.77	447	0.0224	HOMO−3	→ LUMO	43.3%
5	2.82	440	0.0101	HOMO−4	→ LUMO	42.0%
6	2.91	427	0.0026	HOMO−5	→ LUMO	41.7%
7	2.93	423	0.0042	HOMO−6	→ LUMO	39.1%
8	2.98	416	0.0000	HOMO−7	→ LUMO	46.6%
9	3.03	410	0.0090	HOMO−8	→ LUMO	42.3%
10	3.11	398	0.0065	HOMO−9	→ LUMO	41.1%
11	3.17	391	0.0010	HOMO	→ LUMO+1	46.8%
12	3.19	389	0.0001	HOMO−1	→ LUMO+1	45.2%
13	3.35	371	0.0015	HOMO−2	→ LUMO+1	27.9%
				HOMO−10	→ LUMO	12.9%
14	3.35	370	0.0467	HOMO−11	→ LUMO	38.8%
15	3.36	370	0.0012	HOMO−3	→ LUMO+1	29.4%
				HOMO−2	→ LUMO+1	11.3%
16	3.36	369	0.0110	HOMO−10	→ LUMO	28.8%
17	3.42	363	0.0198	HOMO−4	→ LUMO+1	41.2%
18	3.49	355	0.0127	HOMO−5	→ LUMO+1	40.3%
19	3.52	353	0.0005	HOMO−6	→ LUMO+1	34.4%
20	3.56	349	0.0010	HOMO−7	→ LUMO+1	43.5%
21	3.58	346	0.0461	HOMO−14	→ LUMO	35.1%
22	3.58	346	0.0505	HOMO−12	→ LUMO	38.4%

Table S13. Orbital composition percentages of selected orbitals in $[Pt_2Ag_2(ppy)_2(Ph_2pz)_4]$ (**2a**), $[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]^+$ (**3a'**) and $[Pt_2Ag_3(ppy)_2(Me_2pz)_4]^+$ (**3b'**) by the B3LYP method[a]

	$[Pt_2Ag_2(ppy)_2(Ph_2pz)_4]$ (**2a**)				$[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]^+$ (**3a'**)					$[Pt_2Ag_3(ppy)_2(Me_2pz)_4]^+$ (**3b'**)				
	Pt	Ag	ppy	Ph_2pz	Pt	Ag	Ag*	ppy	Ph_2pz	Pt	Ag	Ag*	ppy	Me_2pz
LUMO+2	0.6	0.2	97.2	2.0	6.7	6.4	11.1	68.1	7.8	7.3	5.2	14.9	66.6	6.0
LUMO+1	2.8	0.4	94.3	2.4	3.3	0.2	0.7	93.2	2.6	3.6	0.2	0.6	94.1	1.6
LUMO	3.4	2.7	90.4	3.5	11.4	6.9	23.1	48.2	10.4	11.5	5.1	24.2	51.2	8.1
HOMO	18.2	2.7	7.0	72.1	6.9	0.8	0.1	1.1	91.0	16.2	0.1	0.2	1.8	81.7
HOMO−1	16.0	0.6	11.8	71.5	7.6	1.3	0.1	0.8	90.2	15.4	0.2	0.1	2.6	81.6
HOMO−2	18.0	2.6	3.5	75.9	3.8	1.2	0.2	1.4	93.4	0.9	7.1	0.1	0.2	91.7
HOMO−3	16.4	0.3	19.7	63.6	4.1	0.4	0.6	7.4	87.6	11.3	0.2	1.4	18.6	68.6
HOMO−4	29.5	5.1	37.0	28.4	4.7	1.1	0.3	2.4	91.4	6.5	0.2	0.1	4.0	89.2
HOMO−5	22.6	1.2	24.9	51.2	4.5	0.4	0.2	1.3	93.6	1.4	4.4	0.2	1.2	92.7
HOMO−6	45.9	16.9	5.4	31.8	0.8	3.7	0.0	0.4	95.0	9.6	1.8	1.8	25.2	61.7
HOMO−7	8.3	1.2	17.0	73.6	0.9	1.6	0.1	0.8	96.6	3.8	3.5	0.7	0.8	91.1
HOMO−8	14.2	0.9	25.3	59.7	20.4	0.3	5.0	52.0	22.4	8.9	3.9	2.3	26.1	58.9
HOMO−9	23.2	8.8	2.6	65.5	10.7	7.7	1.4	2.3	77.9	22.0	1.3	0.7	69.6	6.5
HOMO−10					8.9	2.0	0.0	7.6	81.4	37.9	25.3	6.8	7.1	22.9
HOMO−11					19.4	3.0	0.7	63.8	13.1	29.0	31.7	2.8	9.8	26.7
HOMO−12					7.1	6.0	1.0	6.6	79.4	15.6	3.7	1.3	74.9	4.5
HOMO−13					3.0	11.6	0.6	3.5	81.4	3.1	7.8	0.9	82.6	5.5
HOMO−14					5.7	0.3	0.1	1.6	92.4	51.6	17.2	3.7	10.0	17.5

[a] Ag* in **3a'** and **3b'** denotes the Ag atom forming Pt→Ag dative bond. The contribution of Ag* atom is separated from that of other Ag atoms.

Table S14. Optimized geometries of $[Pt_2Ag_2(ppy)_2(Ph_2pz)_4]$ (**2a**) by the B3LYP method

	S_0				T_1		
	x	*y*	*z*		*x*	*y*	*z*
Pt	2.533243	-0.859865	-0.770299	Pt	-2.514624	0.833710	-0.819241
Pt	-2.533231	0.858888	-0.771447	Pt	2.510450	-0.916865	-0.734184
Ag	-0.297744	-1.618515	0.801573	Ag	0.305726	1.665268	0.724349
Ag	0.297318	1.618644	0.799435	Ag	-0.322802	-1.555564	0.906536
N	2.238027	-0.953209	-2.807264	N	-2.200031	0.814149	-2.855187
C	2.131173	-2.218150	-3.321300	C	-2.085913	2.048150	-3.437612
C	1.950801	-2.394380	-4.702240	C	-1.888974	2.147670	-4.823386
C	1.863337	-1.290886	-5.543063	C	-1.790411	0.999187	-5.600490
C	1.941631	-0.008749	-4.992971	C	-1.876012	-0.250061	-4.981311
C	2.127427	0.114530	-3.621204	C	-2.080052	-0.296997	-3.607471
C	2.207851	-3.285569	-2.324408	C	-2.170974	3.169435	-2.501832
C	2.343123	-2.852021	-0.974382	C	-2.315660	2.811133	-1.131172
C	2.429031	-3.850386	0.012520	C	-2.408047	3.861816	-0.200890
C	2.372585	-5.207855	-0.319113	C	-2.351715	5.199285	-0.606457
C	2.234923	-5.614586	-1.651864	C	-2.205783	5.531907	-1.958600
C	2.155758	-4.651601	-2.654112	C	-2.117742	4.515077	-2.905764
H	1.879364	-3.403125	-5.107198	H	-1.809546	3.132319	-5.282582
H	1.729325	-1.429003	-6.618203	H	-1.639431	1.077209	-6.679311
H	1.866454	0.888065	-5.607620	H	-1.785918	-1.179450	-5.542971
H	2.197727	1.087366	-3.138986	H	-2.156908	-1.242201	-3.074413
H	2.540297	-3.572401	1.060498	H	-2.524775	3.641324	0.860088
H	2.432243	-5.957868	0.473516	H	-2.418287	5.991806	0.143174
H	2.191129	-6.675723	-1.905024	H	-2.162702	6.577514	-2.270003
H	2.056658	-4.969581	-3.694605	H	-2.011103	4.774927	-3.961469
N	-2.237307	0.950406	-2.808362	N	2.217850	-1.082305	-2.743179
C	-2.130273	2.214888	-3.323516	C	2.081087	-2.420302	-3.209330
C	-1.949390	2.389852	-4.704542	C	1.910406	-2.655716	-4.608216
C	-1.861689	1.285594	-5.544344	C	1.850238	-1.613112	-5.498125
C	-1.940228	0.003962	-4.993127	C	1.948633	-0.280213	-4.993925
C	-2.126470	-0.118068	-3.621302	C	2.127985	-0.078209	-3.631165
C	-2.207386	3.283205	-2.327625	C	2.120429	-3.390854	-2.197856
C	-2.343198	2.850868	-0.977272	C	2.312011	-2.876667	-0.810838
C	-2.429569	3.850098	0.008712	C	2.400581	-3.823562	0.230971
C	-2.373069	5.207268	-0.324115	C	2.289705	-5.186278	-0.010761
C	-2.234875	5.612815	-1.657175	C	2.072727	-5.665690	-1.348028
C	-2.155234	4.648947	-2.658533	C	1.988864	-4.803987	-2.410932

H	-1.877731	3.398225	-5.110394	H	1.831612	-3.685890	-4.957524
H	-1.727303	1.422749	-6.619561	H	1.728952	-1.795784	-6.566950
H	-1.864935	-0.893419	-5.606930	H	1.889298	0.584877	-5.653916
H	-2.196929	-1.090481	-3.138251	H	2.205266	0.927039	-3.220466
H	-2.541276	3.573043	1.056891	H	2.553171	-3.480818	1.254095
H	-2.433107	5.957996	0.467810	H	2.351513	-5.900646	0.811528
H	-2.191040	6.673730	-1.911256	H	1.974166	-6.741081	-1.515823
H	-2.055702	4.965995	-3.699267	H	1.827069	-5.195113	-3.416654
N	2.654129	-0.975858	1.282863	N	-2.649328	1.062958	1.223569
N	1.528296	-1.373240	1.940606	N	-1.527961	1.493088	1.869194
C	1.861710	-1.684574	3.216607	C	-1.871555	1.867475	3.125680
C	3.241436	-1.480321	3.379860	C	-3.252617	1.671434	3.287975
C	3.705802	-1.025776	2.140574	C	-3.707346	1.155251	2.069437
C	0.890787	-2.177445	4.211390	C	-0.909180	2.406868	4.104610
C	-0.453092	-1.759979	4.222196	C	0.434667	1.991559	4.146380
C	-1.345787	-2.250473	5.178560	C	1.318529	2.524193	5.088190
C	-0.914753	-3.160388	6.148320	C	0.878441	3.475900	6.012773
C	0.420840	-3.576357	6.154083	C	-0.457323	3.890653	5.987840
C	1.312709	-3.091724	5.195873	C	-1.340253	3.363578	5.043908
C	5.093637	-0.626153	1.809686	C	-5.093089	0.740100	1.747852
C	5.417318	0.717219	1.556688	C	-5.418422	-0.614585	1.567473
C	6.742219	1.094598	1.325367	C	-6.742304	-1.001151	1.345734
C	7.761116	0.137391	1.343067	C	-7.758767	-0.042214	1.301469
C	7.449113	-1.201830	1.595606	C	-7.445161	1.308294	1.481487
C	6.124673	-1.580935	1.830731	C	-6.121645	1.696896	1.706318
H	3.827228	-1.585484	4.288189	H	-3.845837	1.822199	4.184976
H	-0.801673	-1.026959	3.493359	H	0.789943	1.227529	3.453712
H	-2.381686	-1.903942	5.170882	H	2.354653	2.178628	5.105261
H	-1.613334	-3.539143	6.897818	H	1.569907	3.887820	6.751288
H	0.770250	-4.287466	6.906544	H	-0.813902	4.633985	6.704958
H	2.348338	-3.438077	5.195164	H	-2.375976	3.708692	5.018959
H	4.624186	1.465762	1.548172	H	-4.627928	-1.364837	1.608914
H	6.976989	2.142880	1.128613	H	-6.978204	-2.058230	1.205716
H	8.796308	0.434563	1.159856	H	-8.793151	-0.346809	1.126131
H	8.239634	-1.955984	1.610525	H	-8.233663	2.063933	1.447423
H	5.879561	-2.626251	2.030852	H	-5.875457	2.751180	1.849996
N	2.958775	1.262086	-0.764968	N	-2.959501	-1.283599	-0.701758
N	2.195216	2.144749	-0.070103	N	-2.207251	-2.131173	0.046342
C	2.699993	3.393607	-0.245351	C	-2.711219	-3.386985	-0.072776

C	3.815899	3.310865	-1.086419	C	-3.816508	-3.344991	-0.930714
C	3.958142	1.948128	-1.388897	C	-3.952228	-1.998600	-1.302755
C	2.132645	4.598929	0.388012	C	-2.148076	-4.557938	0.625402
C	2.127279	5.820663	-0.310658	C	-2.131319	-5.813206	-0.010935
C	1.622030	6.980275	0.279270	C	-1.626104	-6.939493	0.640917
C	1.106401	6.942521	1.579076	C	-1.121556	-6.834387	1.941543
C	1.107091	5.735716	2.284868	C	-1.134015	-5.593699	2.585817
C	1.620589	4.576374	1.698174	C	-1.647918	-4.467914	1.937413
C	4.996968	1.346139	-2.250406	C	-4.979401	-1.437135	-2.204385
C	5.464686	2.074504	-3.362945	C	-5.438722	-2.217920	-3.284261
C	6.457688	1.558166	-4.196781	C	-6.421081	-1.739450	-4.152579
C	7.005081	0.297067	-3.940218	C	-6.965693	-0.465208	-3.963901
C	6.553085	-0.434651	-2.838286	C	-6.521889	0.318308	-2.894732
C	5.564733	0.083701	-1.998089	C	-5.544072	-0.161663	-2.020208
H	4.481656	4.118706	-1.375388	H	-4.480424	-4.165197	-1.187387
H	2.510572	5.852263	-1.332847	H	-2.506524	-5.897905	-1.033117
H	1.624861	7.917892	-0.281946	H	-1.621939	-7.904484	0.128054
H	0.710834	7.850350	2.040687	H	-0.726842	-7.716233	2.451692
H	0.718795	5.692095	3.304920	H	-0.754907	-5.496918	3.605666
H	1.646126	3.651050	2.275548	H	-1.682994	-3.515098	2.467753
H	5.029152	3.051909	-3.582310	H	-5.005153	-3.206594	-3.450764
H	6.800952	2.141511	-5.054767	H	-6.757976	-2.362839	-4.984510
H	7.781429	-0.110066	-4.592329	H	-7.733441	-0.087760	-4.643471
H	6.980964	-1.415307	-2.617691	H	-6.947686	1.310299	-2.727213
H	5.240485	-0.487714	-1.128390	H	-5.226168	0.450671	-1.176419
N	-2.654591	0.976810	1.281654	N	2.639809	-0.916979	1.335440
N	-1.528683	1.374719	1.938985	N	1.512180	-1.261154	2.020754
C	-1.862177	1.688273	3.214421	C	1.849901	-1.516273	3.307574
C	-3.242036	1.484995	3.377734	C	3.234386	-1.327615	3.451455
C	-3.706410	1.028650	2.139107	C	3.696912	-0.942828	2.188448
C	-0.891184	2.182156	4.208633	C	0.878201	-1.946526	4.330410
C	0.452536	1.764207	4.220171	C	-0.462427	-1.518939	4.320717
C	1.345311	2.255690	5.175949	C	-1.356935	-1.950497	5.303335
C	0.914520	3.167117	6.144395	C	-0.930942	-2.810518	6.319783
C	-0.420920	3.583587	6.149436	C	0.401396	-3.236029	6.345699
C	-1.312872	3.097955	5.191809	C	1.295045	-2.810141	5.361549
C	-5.094338	0.629042	1.808771	C	5.088919	-0.583401	1.830765
C	-5.418053	-0.714215	1.555164	C	5.430786	0.737966	1.498038
C	-6.743057	-1.091586	1.324436	C	6.760261	1.081916	1.242305

C	-7.762051	-0.134500	1.343353	C	7.765587	0.113023	1.314238
C	-6.125485	1.583686	1.831098	C	6.106626	-1.549738	1.906518
C	-7.450026	1.204590	1.596564	C	7.435517	-1.204347	1.646203
H	-8.240610	1.958656	1.612480	H	8.215313	-1.967506	1.704203
H	-3.827915	1.591696	4.285825	H	3.825006	-1.397063	4.360119
H	0.800931	1.030065	3.492397	H	-0.806460	-0.822995	3.554350
H	2.381081	1.908762	5.168847	H	-2.390028	-1.596468	5.278983
H	1.613161	3.546663	6.893437	H	-1.630964	-3.143105	7.089534
H	-0.770146	4.295867	6.900875	H	0.746838	-3.908642	7.134468
H	-2.348371	3.444693	5.190531	H	2.327930	-3.164211	5.377861
H	-4.624871	-1.462688	1.545841	H	4.648528	1.496139	1.446203
H	-6.977841	-2.139781	1.127238	H	7.009256	2.113269	0.983394
H	-5.880377	2.628910	2.031709	H	5.847902	-2.577777	2.169320
N	-2.958612	-1.263161	-0.764262	N	2.963208	1.195944	-0.832928
N	-2.195421	-2.145073	-0.068064	N	2.223890	2.113713	-0.155949
C	-2.700106	-3.394125	-0.242217	C	2.745183	3.346738	-0.383960
C	-3.815579	-3.312299	-1.083933	C	3.847957	3.216639	-1.237334
C	-3.957673	-1.949886	-1.387969	C	3.965294	1.843395	-1.494067
C	-2.132980	-4.598727	0.392723	C	2.205101	4.582767	0.212047
C	-2.126596	-5.821079	-0.304854	C	2.215161	5.779911	-0.527977
C	-1.621484	-6.979991	0.286564	C	1.733802	6.967088	0.025915
C	-1.107029	-6.940900	1.586800	C	1.227592	6.981916	1.329881
C	-1.108766	-5.733476	2.291521	C	1.213859	5.800057	2.076686
C	-1.622129	-4.574829	1.703330	C	1.703252	4.613170	1.525909
C	-4.996098	-1.348884	-2.250644	C	4.988979	1.197580	-2.341886
C	-5.463647	-2.078730	-3.362292	C	5.432382	1.867383	-3.499949
C	-6.456288	-1.563366	-4.197159	C	6.415667	1.312767	-4.320622
C	-7.003498	-0.301786	-3.942567	C	6.976161	0.071476	-4.004070
C	-6.551666	0.431407	-2.841552	C	6.547920	-0.602080	-2.856442
C	-5.563670	-0.085960	-2.000330	C	5.569422	-0.045295	-2.029794
H	-4.481203	-4.120460	-1.372307	H	4.522514	4.002425	-1.564111
H	-2.508973	-5.853705	-1.327353	H	2.590173	5.770365	-1.553632
H	-1.623493	-7.918113	-0.273813	H	1.747392	7.884903	-0.566910
H	-0.711570	-7.848185	2.049568	H	0.850225	7.911288	1.762928
H	-0.721396	-5.688817	3.311882	H	0.832575	5.797435	3.100280
H	-1.648522	-3.649003	2.279862	H	1.718002	3.707471	2.133756
H	-5.028285	-3.056547	-3.580152	H	4.985373	2.828219	-3.764450
H	-6.799418	-2.147871	-5.054410	H	6.739944	1.849720	-5.215376
H	-7.779567	0.104575	-4.595492	H	7.744374	-0.366094	-4.645987

H	-6.979387	1.412474	-2.622486	H	6.987126	-1.566249	-2.590278
H	-5.239501	0.486664	-1.131384	H	5.264915	-0.569090	-1.124144
H	-8.797326	-0.431678	1.160616	H	8.804300	0.384129	1.111668

Table S15. Optimized geometries of $[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]^+$ (**3a'**) by the B3LYP method

	S_0				T_1		
	x	*y*	*z*		*x*	*y*	*z*
Pt	-2.522967	0.838529	-0.735476	Pt	-2.654860	0.783044	-0.736250
Pt	2.522977	-0.840352	-0.733080	Pt	2.654679	-0.782934	-0.735928
Ag	-0.000447	-0.003973	-1.664332	Ag	-0.000290	-0.000474	-1.636783
Ag	0.418825	1.590136	0.975398	Ag	0.374380	1.495001	0.788375
Ag	-0.419060	-1.587311	0.979678	Ag	-0.374416	-1.494839	0.789432
N	2.194696	-2.872528	-1.015168	N	2.429421	-2.812729	-1.106751
C	2.034040	-2.150736	-3.286351	C	2.357596	-2.019337	-3.354656
C	2.228857	-0.848196	-2.737223	C	2.477816	-0.732953	-2.750645
C	2.200403	0.245505	-3.626868	C	2.445810	0.389855	-3.603043
C	2.019076	0.055349	-5.003882	C	2.325511	0.246511	-4.988982
C	1.863300	-1.230893	-5.525352	C	2.227634	-1.025467	-5.565957
C	1.868601	-2.332152	-4.667045	C	2.239618	-2.153860	-4.749011
C	2.040148	-3.256006	-2.320001	C	2.351311	-3.154202	-2.432255
C	2.239561	-3.806488	-0.042705	C	2.438137	-3.779841	-0.163811
C	2.114301	-5.164859	-0.309365	C	2.362790	-5.129373	-0.481254
C	1.943866	-5.574520	-1.632958	C	2.274721	-5.498447	-1.827564
C	1.911537	-4.613893	-2.639295	C	2.268606	-4.505643	-2.800225
H	2.354685	1.256839	-3.248886	H	2.530430	1.393348	-3.182985
H	2.011577	0.920089	-5.670951	H	2.311703	1.135375	-5.624174
H	1.737929	-1.379404	-6.599418	H	2.140621	-1.135592	-6.648364
H	1.744942	-3.332554	-5.086175	H	2.155877	-3.142131	-5.205602
H	2.371301	-3.439273	0.972078	H	2.503552	-3.442894	0.868001
H	2.142494	-5.878017	0.513811	H	2.370458	-5.870038	0.318184
H	1.839895	-6.632714	-1.879144	H	2.214690	-6.549989	-2.114344
H	1.792278	-4.912454	-3.679898	H	2.207976	-4.770420	-3.855095
N	-2.193727	2.869751	-1.023220	N	-2.430361	2.812811	-1.107419
C	-2.032991	2.141490	-3.292307	C	-2.358629	2.019068	-3.355200
C	-2.228888	0.840634	-2.739614	C	-2.478619	0.732787	-2.750963
C	-2.201176	-0.255537	-3.626255	C	-2.446553	-0.390160	-3.603161
C	-2.019445	-0.069327	-5.003770	C	-2.326372	-0.247033	-4.989141
C	-1.862531	1.215340	-5.528744	C	-2.228710	1.024854	-5.566341
C	-1.867129	2.318956	-4.673464	C	-2.240806	2.153386	-4.749582
C	-2.038607	3.249468	-2.329076	C	-2.352551	3.154096	-2.432981
C	-2.238329	3.806472	-0.053399	C	-2.439352	3.780060	-0.164625
C	-2.112301	5.164018	-0.323866	C	-2.364603	5.129577	-0.482296
C	-1.941244	5.569854	-1.648560	C	-2.276830	5.498466	-1.828676

C	-1.909114	4.606376	-2.652170	C	-2.270412	4.505509	-2.801179
H	-2.356440	-1.265714	-3.245570	H	-2.531065	-1.393582	-3.182929
H	-2.012551	-0.935915	-5.668447	H	-2.312505	-1.136001	-5.624184
H	-1.736851	1.360803	-6.603192	H	-2.141808	1.134810	-6.648773
H	-1.742566	3.318095	-5.095333	H	-2.157272	3.141599	-5.206342
H	-2.370461	3.442170	0.962380	H	-2.504494	3.443231	0.867246
H	-2.140329	5.879515	0.497281	H	-2.372526	5.870378	0.317016
H	-1.836606	6.627292	-1.897692	H	-2.217271	6.549989	-2.115635
H	-1.789316	4.901905	-3.693575	H	-2.210029	4.770132	-3.856103
N	-3.032895	-1.138341	-0.655197	N	-3.177122	-1.192996	-0.564835
N	-2.267439	-2.055548	0.000998	N	-2.407088	-2.078286	0.079479
C	-2.821444	-3.280042	-0.185926	C	-2.954620	-3.326768	-0.085114
C	-3.963358	-3.141222	-0.983880	C	-4.111141	-3.211997	-0.864949
C	-4.077178	-1.771802	-1.260136	C	-4.248573	-1.850462	-1.148701
C	-2.262184	-4.517367	0.391587	C	-2.370939	-4.536361	0.498369
C	-1.737404	-4.556891	1.696324	C	-1.658760	-4.506116	1.715004
C	-1.227294	-5.746747	2.223867	C	-1.130257	-5.677874	2.257973
C	-1.245046	-6.919673	1.462948	C	-1.303803	-6.900408	1.599972
C	-1.776663	-6.895169	0.168764	C	-2.014153	-6.944981	0.393184
C	-2.277770	-5.705550	-0.362839	C	-2.544474	-5.777544	-0.151232
C	-5.127327	-1.114150	-2.062179	C	-5.320630	-1.213419	-1.917264
C	-5.658536	0.146371	-1.735542	C	-5.812107	0.076398	-1.626587
C	-6.660915	0.720686	-2.520512	C	-6.847335	0.626337	-2.382052
C	-7.159467	0.045453	-3.638110	C	-7.418390	-0.096419	-3.434005
C	-6.648989	-1.214566	-3.965536	C	-6.949853	-1.384321	-3.725093
C	-5.643657	-1.787660	-3.185683	C	-5.916924	-1.937620	-2.973841
H	-4.668167	-3.919196	-1.260752	H	-4.813629	-3.999878	-1.117259
H	-1.761778	-3.663581	2.323094	H	-1.551204	-3.568683	2.261130
H	-0.836857	-5.755684	3.243767	H	-0.597775	-5.632477	3.210045
H	-0.860759	-7.852630	1.881420	H	-0.896878	-7.818304	2.029852
H	-1.803549	-7.808717	-0.429724	H	-2.154268	-7.896242	-0.124608
H	-2.680912	-5.690047	-1.377730	H	-3.083824	-5.817389	-1.099542
H	-5.312555	0.665960	-0.841518	H	-5.405004	0.631340	-0.782358
H	-7.066664	1.696176	-2.243741	H	-7.222248	1.621309	-2.134053
H	-7.946929	0.494913	-4.246858	H	-8.231024	0.336662	-4.021106
H	-7.032174	-1.752662	-4.835305	H	-7.388894	-1.954650	-4.546206
H	-5.238528	-2.764460	-3.458497	H	-5.541414	-2.932169	-3.221664
N	-2.602160	1.026732	1.420112	N	-2.651638	1.065012	1.409842
N	-1.446127	1.431892	2.030719	N	-1.476822	1.462878	1.986206

C	-1.734133	1.821696	3.299419	C	-1.732839	1.876380	3.252115
C	-3.112261	1.668361	3.508422	C	-3.111915	1.755966	3.493180
C	-3.621660	1.155171	2.308454	C	-3.653107	1.232216	2.313622
C	-0.716280	2.324921	4.242084	C	-0.688311	2.352905	4.177837
C	0.586897	1.795311	4.288924	C	0.603438	1.793390	4.196881
C	1.528513	2.295450	5.192720	C	1.568183	2.255599	5.096311
C	1.184732	3.326367	6.071768	C	1.261264	3.279203	5.997372
C	-0.111685	3.851719	6.044216	C	-0.022245	3.836369	5.995589
C	-1.052192	3.357009	5.138819	C	-0.986527	3.378597	5.095743
C	-5.025169	0.763158	2.041712	C	-5.069082	0.861298	2.079695
C	-6.051090	1.720857	2.125145	C	-6.068271	1.849973	2.086046
C	-7.386365	1.348599	1.948746	C	-7.414427	1.502340	1.942655
C	-7.714556	0.013390	1.695166	C	-7.781060	0.160852	1.798405
C	-6.701558	-0.947096	1.618166	C	-6.795105	-0.830529	1.797337
C	-5.365661	-0.576645	1.789710	C	-5.448843	-0.484303	1.936523
H	-3.666873	1.839780	4.426362	H	-3.644243	1.954419	4.419038
H	0.861593	0.960272	3.641950	H	0.849397	0.966783	3.528159
H	2.530287	1.861224	5.219921	H	2.559550	1.797153	5.102382
H	1.919439	3.711958	6.781650	H	2.014105	3.634458	6.704113
H	-0.392331	4.653110	6.731279	H	-0.274279	4.632816	6.699393
H	-2.057857	3.782096	5.114786	H	-1.982680	3.826289	5.093792
H	-5.796454	2.762720	2.332849	H	-5.783908	2.897371	2.210381
H	-8.172984	2.103574	2.014155	H	-8.179558	2.281870	1.949680
H	-8.758334	-0.278546	1.561446	H	-8.833217	-0.111696	1.692074
H	-6.951033	-1.992604	1.425847	H	-7.075175	-1.880969	1.693246
H	-4.578112	-1.329653	1.740890	H	-4.682491	-1.260882	1.951551
N	3.032490	1.136793	-0.658443	N	3.177517	1.192901	-0.564962
N	2.267218	2.055712	-0.004490	N	2.407800	2.078453	0.079116
C	2.821286	3.279678	-0.194613	C	2.955587	3.326866	-0.085960
C	3.963053	3.138750	-0.992417	C	4.112027	3.211617	-0.865881
C	4.076744	1.768629	-1.265178	C	4.249188	1.850007	-1.149219
C	2.262335	4.518494	0.379983	C	2.372233	4.536675	0.497224
C	1.737746	4.561242	1.684685	C	1.659180	4.506682	1.713381
C	1.227961	5.752457	2.209467	C	1.130986	5.678667	2.256124
C	1.245846	6.923564	1.445752	C	1.305642	6.901173	1.598345
C	1.777305	6.895867	0.151568	C	2.016810	6.945496	0.392015
C	2.278075	5.704872	-0.377271	C	2.546881	5.777850	-0.152152
C	5.126885	1.108865	-2.065496	C	5.320959	1.212467	-1.917651
C	5.658270	-0.150679	-1.735369	C	5.811793	-0.077614	-1.626967

C	6.660728	-0.727032	-2.518738	C	6.846805	-0.628037	-2.382366
C	7.159192	-0.054824	-3.638194	C	7.418285	0.094470	-3.434263
C	6.648551	1.204222	-3.969107	C	6.950403	1.382622	-3.725370
C	5.643136	1.779342	-3.190849	C	5.917706	1.936415	-2.974191
H	4.667877	3.915951	-1.271419	H	4.814632	3.999292	-1.118511
H	1.761993	3.669393	2.313545	H	1.550701	3.569250	2.259320
H	0.837656	5.763904	3.229394	H	0.597837	5.633454	3.207829
H	0.861802	7.857594	1.862046	H	0.898900	7.819247	2.028021
H	1.804324	7.807981	-0.449098	H	2.157742	7.896734	-0.125598
H	2.681073	5.686874	-1.392178	H	3.086878	5.817523	-1.100103
H	5.312399	-0.667833	-0.839894	H	5.404367	-0.632381	-0.782775
H	7.066620	-1.701693	-2.239261	H	7.221212	-1.623197	-2.134359
H	7.946721	-0.505858	-4.245693	H	8.230749	-0.338993	-4.021321
H	7.031676	1.739956	-4.840358	H	7.389782	1.952740	-4.546450
H	5.237882	2.755338	-3.466338	H	5.542695	2.931143	-3.222056
N	2.602050	-1.022459	1.423023	N	2.651822	-1.064639	1.410082
N	1.445949	-1.426104	2.034496	N	1.476963	-1.461783	1.986820
C	1.733714	-1.812221	3.304381	C	1.733087	-1.875063	3.252782
C	3.111751	-1.658043	3.513286	C	3.112278	-1.755117	3.493528
C	3.621358	-1.148220	2.311965	C	3.653444	-1.232072	2.313660
C	0.715734	-2.313122	4.248142	C	0.688525	-2.350989	4.178757
C	-0.587479	-1.783457	4.293398	C	-0.603184	-1.791356	4.197448
C	-1.529257	-2.281431	5.198228	C	-1.568013	-2.253068	5.097030
C	-1.185602	-3.310164	6.079873	C	-1.261225	-3.276278	5.998589
C	0.110843	-3.835531	6.053875	C	0.022235	-3.833557	5.997148
C	1.051511	-3.343001	5.147458	C	0.986608	-3.376283	5.097150
C	5.024872	-0.756857	2.044341	C	5.069549	-0.861995	2.079164
C	5.365184	0.582196	1.788149	C	5.450034	0.483377	1.935732
C	6.701049	0.952321	1.615680	C	6.796437	0.828815	1.795933
C	7.714197	-0.007739	1.695973	C	7.781821	-0.163139	1.796653
C	7.386182	-1.342186	1.953750	C	7.414466	-1.504406	1.941143
C	6.050933	-1.714111	2.131046	C	6.068166	-1.851250	2.085120
H	3.666176	-1.826814	4.431827	H	3.644738	-1.953490	4.419329
H	-0.862057	-0.950024	3.644297	H	-0.849040	-0.965048	3.528327
H	-2.531063	-1.847198	5.224152	H	-2.559347	-1.794553	5.102813
H	-1.920435	-3.694034	6.790557	H	-2.014149	-3.631156	6.705430
H	0.391380	-4.635220	6.742961	H	0.274153	-4.629708	6.701325
H	2.057199	-3.768099	5.124636	H	1.982716	-3.824077	5.095450
H	4.577508	1.334904	1.736792	H	4.684135	1.260409	1.951047

H	6.950391	1.997253	1.420069	H	7.077078	1.879088	1.691664
H	8.757955	0.283950	1.561549	H	8.834093	0.108790	1.689866
H	8.172917	-2.096812	2.021752	H	8.179146	-2.284383	1.947898
H	5.796434	-2.755363	2.341964	H	5.783252	-2.898479	2.209627

Table S16. Optimized geometries of $[Pt_2Ag_3(ppy)_2(Me_2pz)_4]^+$ (**3b'**) by the B3LYP method

	S_0				T_{1a}		
	x	*y*	*z*		*x*	*y*	*z*
Pt	-2.651717	0.273363	-0.304425	Pt	-2.811020	0.262038	-0.117815
Pt	2.651629	0.276143	0.305118	Pt	2.811040	0.260751	0.117602
Ag	-0.000535	1.157644	-0.000408	Ag	0.000501	1.020490	-0.001550
Ag	-0.321470	-1.553701	1.551302	Ag	-0.096407	-1.438809	1.535605
Ag	0.324298	-1.550492	-1.553237	Ag	0.094853	-1.441912	-1.533582
N	3.197691	0.694383	-1.648040	N	3.142401	0.909164	-1.829677
C	2.738887	2.919533	-0.911223	C	2.886831	3.033552	-0.779837
C	2.364711	2.281793	0.310423	C	2.642664	2.258364	0.390519
C	1.897573	3.100757	1.358658	C	2.331167	2.948413	1.578475
C	1.829300	4.494028	1.214171	C	2.287630	4.345614	1.611750
C	2.224686	5.100352	0.018993	C	2.544498	5.093791	0.455518
C	2.677134	4.314109	-1.043157	C	2.838666	4.438071	-0.737740
C	3.206739	2.022321	-1.977784	C	3.170186	2.269309	-1.994746
C	3.627720	-0.226119	-2.534423	C	3.386363	0.097646	-2.881216
C	4.081586	0.121628	-3.802109	C	3.666796	0.588181	-4.149328
C	4.091363	1.471509	-4.162148	C	3.695344	1.974339	-4.340716
C	3.651824	2.422073	-3.244780	C	3.444668	2.811254	-3.259719
H	1.609323	2.647298	2.309404	H	2.124294	2.387129	2.491577
H	1.473774	5.107445	2.045239	H	2.052487	4.856403	2.548771
H	2.182824	6.185739	-0.088171	H	2.513614	6.184312	0.485965
H	2.985552	4.801122	-1.970345	H	3.032205	5.027489	-1.636161
H	3.596671	-1.260635	-2.196209	H	3.351563	-0.970541	-2.675144
H	4.422799	-0.656792	-4.484812	H	3.864419	-0.107748	-4.964869
H	4.443668	1.781933	-5.147644	H	3.915026	2.396199	-5.323261
H	3.660998	3.480100	-3.503590	H	3.466677	3.893021	-3.385710
N	-3.198567	0.687252	1.649427	N	-3.141383	0.913538	1.828588
C	-2.745354	2.914637	0.915966	C	-2.883865	3.036204	0.775763
C	-2.369452	2.279678	-0.306543	C	-2.640821	2.259120	-0.393576
C	-1.904384	3.101319	-1.353548	C	-2.329111	2.947170	-1.582650
C	-1.839737	4.494551	-1.207070	C	-2.284222	4.344281	-1.617920
C	-2.236800	5.098136	-0.011054	C	-2.539943	5.094342	-0.462650
C	-2.687260	4.309180	1.049919	C	-2.834336	4.440614	0.731646
C	-3.210888	2.014666	1.981196	C	-3.167694	2.273941	1.991797
C	-3.626360	-0.235648	2.534397	C	-3.385929	0.103722	2.881305
C	-4.081030	0.109032	3.802630	C	-3.665520	0.596289	4.148813
C	-4.094075	1.458330	4.164747	C	-3.692560	1.982738	4.338307

C	-3.656889	2.411371	3.248826	C	-3.441282	2.817906	3.256098
H	-1.614850	2.649953	-2.304910	H	-2.123130	2.384356	-2.495021
H	-1.485740	5.110095	-2.037222	H	-2.048917	4.853518	-2.555744
H	-2.197806	6.183475	0.097660	H	-2.508014	6.184790	-0.494655
H	-2.997067	4.794032	1.977778	H	-3.027019	5.031504	1.629284
H	-3.592880	-1.269553	2.194568	H	-3.352232	-0.964783	2.676702
H	-4.420339	-0.671271	4.484131	H	-3.863668	-0.098312	4.965360
H	-4.447094	1.766380	5.150733	H	-3.911541	2.406174	5.320330
H	-3.668614	3.468969	3.509273	H	-3.462117	3.899868	3.380613
N	-2.266548	0.024647	-2.291803	N	-2.724105	-0.187681	-2.092403
N	-1.162082	-0.627663	-2.763385	N	-1.694109	-0.875567	-2.652335
C	-1.229293	-0.643639	-4.113917	C	-1.981310	-1.070054	-3.956204
C	-2.399077	0.010300	-4.516462	C	-3.238005	-0.491055	-4.242484
C	-3.032842	0.419793	-3.337912	C	-3.680965	0.058661	-3.047282
C	-0.189228	-1.319372	-4.952583	C	-1.058724	-1.803015	-4.871589
C	-4.324392	1.160579	-3.181004	C	-4.949116	0.799661	-2.768012
H	-2.756815	0.159270	-5.531834	H	-3.756431	-0.481007	-5.197659
H	-4.164930	2.194624	-2.836657	N	-2.988022	-1.795616	0.392861
H	-4.850934	1.201435	-4.144883	N	-1.956248	-2.450768	1.006793
H	-4.987233	0.673371	-2.449846	C	-2.323610	-3.734766	1.202663
H	-0.456281	-2.370306	-5.156675	C	-3.636116	-3.911201	0.717336
H	-0.081298	-0.812591	-5.923110	C	-4.020651	-2.668399	0.219772
H	0.792112	-1.315091	-4.452007	C	-1.406600	-4.738255	1.821371
N	-2.899017	-1.835706	-0.106967	C	-5.310273	-2.275434	-0.427392
N	-1.955345	-2.535931	0.598485	H	-4.225088	-4.824796	0.727036
C	-2.274738	-3.850507	0.557174	N	2.723564	-0.186059	2.092842
C	-3.445721	-4.000650	-0.194680	N	1.692603	-0.871542	2.653853
C	-3.806791	-2.707275	-0.597710	C	1.979365	-1.064048	3.958133
C	-1.463760	-4.883001	1.277507	C	3.236705	-0.486071	4.243579
C	-4.968190	-2.276595	-1.438197	C	3.680552	0.060905	3.047461
H	-3.974793	-4.924517	-0.414185	C	1.056077	-1.794850	4.874543
H	-4.656334	-2.052676	-2.471476	C	4.949480	0.800169	2.767174
H	-5.725314	-3.072307	-1.480000	H	3.754909	-0.474823	5.198858
H	-5.446370	-1.372022	-1.030586	N	2.986435	-1.797807	-0.390275
H	-1.884726	-5.104581	2.273249	N	1.954090	-2.453685	-1.002462
H	-1.440756	-5.828303	0.715062	C	2.321142	-3.738012	-1.196850
H	-0.425918	-4.543389	1.420004	C	3.633972	-3.913951	-0.712287
N	2.267151	0.023489	2.292148	C	4.019060	-2.670495	-0.216783
N	1.163712	-0.631100	2.762875	C	1.403647	-4.742288	-1.813580

C	1.231037	-0.648867	4.113389	C	5.309197	-2.276811	0.428902
C	2.399819	0.006334	4.516767	H	4.222789	-4.827653	-0.721106
C	3.032879	0.418431	3.338735	H	-1.532934	-2.719653	-5.260717
C	0.192092	-1.327450	4.951146	H	-0.791554	-1.183134	-5.743314
C	4.323135	1.161634	3.182670	H	-0.131758	-2.087570	-4.351392
H	2.757373	0.154483	5.532324	H	-4.755411	1.858561	-2.537109
H	4.161819	2.195842	2.839653	H	-5.608566	0.754167	-3.646035
H	4.849716	1.202191	4.146540	H	-5.487200	0.375144	-1.907529
H	4.986744	0.676519	2.450820	H	-5.180477	-2.112138	-1.509574
H	0.459878	-2.378796	5.152145	H	-6.059225	-3.068622	-0.294186
H	0.084787	-0.823359	5.923137	H	-5.712913	-1.345395	0.003186
H	-0.789719	-1.322332	4.451499	H	-0.510318	-4.251744	2.235503
N	2.902395	-1.832142	0.104138	H	-1.910028	-5.292484	2.629690
N	1.959866	-2.532406	-0.602814	H	-1.074075	-5.483397	1.078443
C	2.281118	-3.846601	-0.563819	H	1.525504	-2.716952	5.256652
C	3.452181	-3.996448	0.187970	H	0.798004	-1.177434	5.750669
C	3.811341	-2.703290	0.593426	H	0.124478	-2.070204	4.357680
C	1.471683	-4.878962	-1.286083	H	4.756851	1.858940	2.534772
C	4.971903	-2.272448	1.434984	H	5.608841	0.755255	3.645292
H	3.982529	-4.919961	0.405884	H	5.487176	0.373907	1.907321
H	1.892809	-5.097888	-2.282346	H	5.180226	-2.112205	1.510981
H	1.450330	-5.825411	-0.725510	H	6.058020	-3.070184	0.296081
H	0.433253	-4.540768	-1.427696	H	5.711520	-1.347298	-0.003101
H	4.659710	-2.052330	2.468985	H	0.505959	-4.256629	-2.225652
H	5.730902	-3.066502	1.474293	H	1.905735	-5.295984	-2.623113
H	5.447852	-1.365532	1.029993	H	1.073569	-5.487820	-1.069967

Table S16 (*Continued*). Optimized geometries of $[Pt_2Ag_3(ppy)_2(Me_2pz)_4]^+$ (**3b'**) by the B3LYP method

		T_{1b}	
	x	*y*	*z*
Pt	2.674119	0.183604	0.200052
Pt	-2.661776	0.358641	-0.203021
Ag	0.044067	1.159952	-0.010065
Ag	0.156822	-1.524547	-1.588010
Ag	-0.324795	-1.489103	1.613235
N	-3.108144	0.826399	1.753241
C	-2.489622	2.994067	1.017651
C	-2.204464	2.286036	-0.257305
C	-1.839070	3.093204	-1.386038
C	-1.720372	4.460167	-1.282188
C	-1.959691	5.118364	-0.024425
C	-2.334439	4.402638	1.091285
C	-2.944142	2.170531	2.087839
C	-3.526027	-0.044510	2.697160
C	-3.813181	0.344936	3.997533
C	-3.644819	1.698523	4.364868
C	-3.210075	2.598450	3.411946
H	-1.656870	2.601758	-2.342966
H	-1.441881	5.057471	-2.152293
H	-1.856702	6.203515	0.037095
H	-2.537499	4.931137	2.024026
H	-3.632863	-1.078870	2.374602
H	-4.174124	-0.397232	4.709837
H	-3.857190	2.028422	5.382775
H	-3.068763	3.647784	3.670098
N	3.143284	0.613230	-1.770147
C	2.818818	2.842014	-0.977255
C	2.483077	2.197598	0.253460
C	2.108931	3.018100	1.338901
C	2.091073	4.413396	1.219704
C	2.442625	5.025162	0.011771
C	2.804632	4.240206	-1.085293
C	3.193205	1.945551	-2.079674
C	3.489387	-0.308883	-2.691146
C	3.893718	0.041413	-3.974634
C	3.942420	1.395942	-4.314713

C	3.590156	2.347910	-3.362021
H	1.849934	2.558640	2.294920
H	1.809843	5.026808	2.078979
H	2.440651	6.113196	-0.075872
H	3.081231	4.730458	-2.020834
H	3.433027	-1.346675	-2.366222
H	4.167845	-0.738662	-4.685133
H	4.258007	1.708134	-5.312017
H	3.631495	3.408954	-3.605059
N	2.402102	-0.088115	2.204277
N	1.310455	-0.708689	2.740327
C	1.476826	-0.765718	4.080822
C	2.700444	-0.171177	4.411291
C	3.260784	0.245973	3.199172
C	0.474012	-1.421300	4.978766
C	4.564426	0.942629	2.960460
H	3.137768	-0.064941	5.400625
H	4.421466	2.011249	2.732700
H	5.198675	0.869901	3.855266
H	5.111077	0.501579	2.113395
H	0.747978	-2.468810	5.191153
H	0.409951	-0.896205	5.943714
H	-0.528427	-1.423338	4.522269
N	2.807008	-1.929980	-0.050133
N	1.792126	-2.574924	-0.707990
C	2.047046	-3.904071	-0.694851
C	3.249141	-4.120657	-0.011864
C	3.695741	-2.851495	0.381661
C	1.144820	-4.889548	-1.371525
C	4.923372	-2.492423	1.159636
H	3.742338	-5.071997	0.170661
H	4.677876	-2.234848	2.202769
H	5.623364	-3.339717	1.177821
H	5.445196	-1.629738	0.716115
H	1.496965	-5.128812	-2.389665
H	1.104450	-5.835065	-0.810091
H	0.119374	-4.496553	-1.455693
N	-2.442913	0.064579	-2.226207
N	-1.397009	-0.636292	-2.754249

C	-1.557741	-0.682654	-4.095042
C	-2.729249	0.006058	-4.435348
C	-3.265056	0.465672	-3.227723
C	-0.601352	-1.414261	-4.984778
C	-4.509339	1.266180	-2.999748
H	-3.147090	0.148620	-5.428549
H	-4.280387	2.299671	-2.693160
H	-5.100934	1.312597	-3.924898
H	-5.138806	0.826153	-2.211606
H	-0.956563	-2.435601	-5.203643
H	-0.484825	-0.893508	-5.947148
H	0.391947	-1.499167	-4.516791
N	-2.975710	-1.728303	0.042113
N	-2.082359	-2.429904	0.810451
C	-2.431761	-3.733623	0.788257
C	-3.581408	-3.877968	-0.007770
C	-3.889451	-2.595660	-0.466636
C	-1.667581	-4.770967	1.547938
C	-5.015916	-2.168435	-1.353999
H	-4.128475	-4.794160	-0.214726
H	-2.140051	-4.983045	2.522583
H	-1.630572	-5.718776	0.990434
H	-0.634502	-4.441373	1.738426
H	-4.655377	-1.890922	-2.357171
H	-5.737797	-2.989113	-1.468053
H	-5.551138	-1.300471	-0.938256

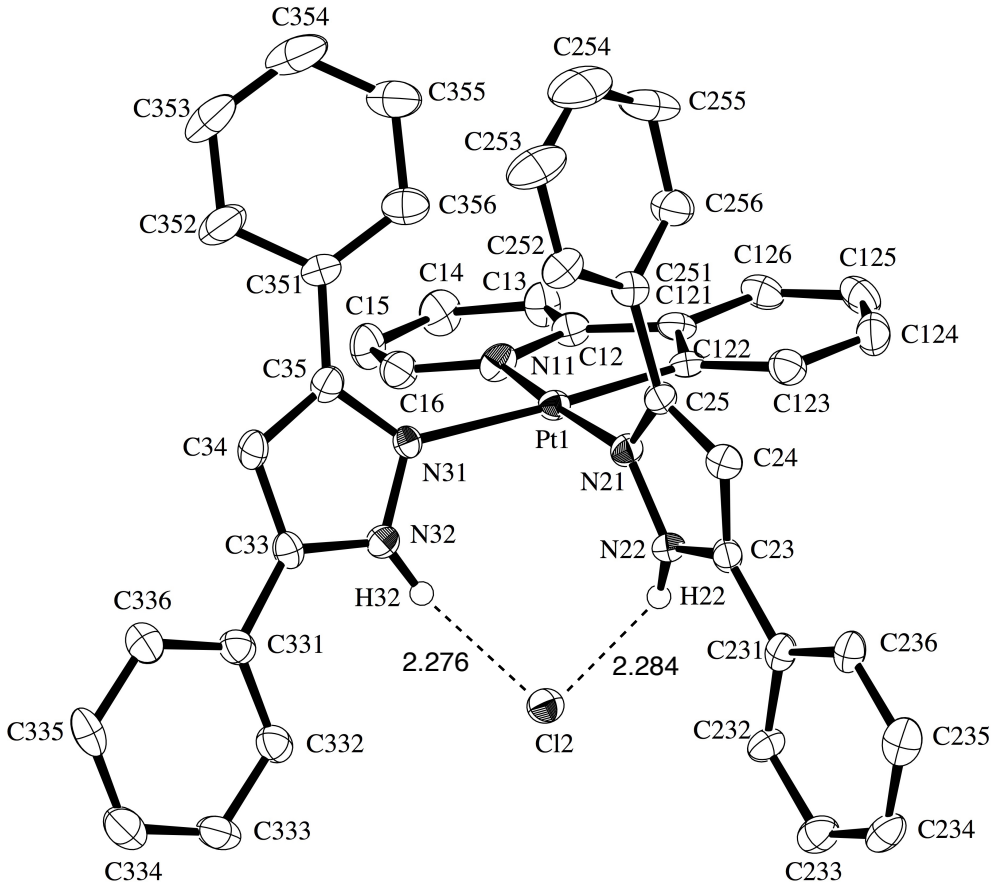
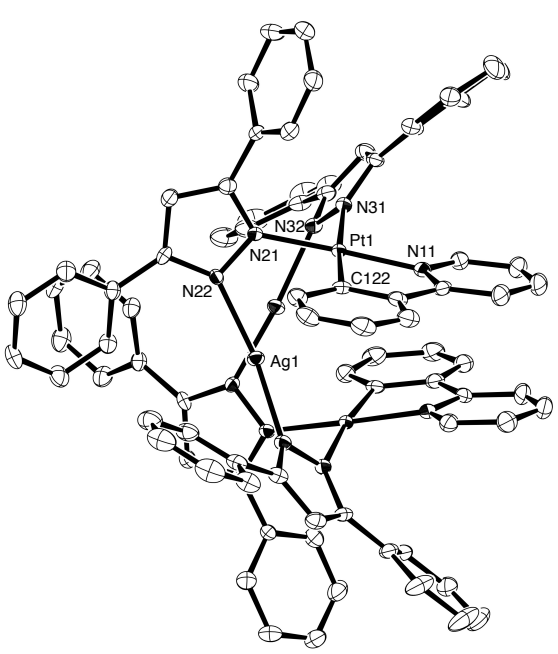
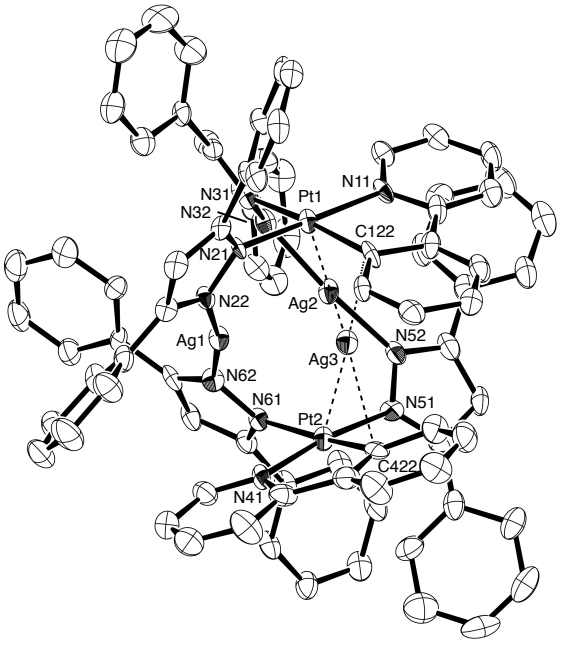


Fig. S1 ORTEP drawing of [Pt(ppy)(Ph_2pzH)$_2$]Cl (**1a**) with the atom numbering scheme (50% probability ellipsoids). Dahed lines show hydrogen bonding.



2a



Cationic part of **3a**

Fig. S2 ORTEP drawings of $[Pt_2Ag_2(ppy)_2(Ph_2pz)_4]$ (**2a**) and cationic part of $[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]BF_4$ (**3a**) with the atom numbering scheme (50% probability ellipsoids). Dahed lines in **3a** show Pt→Ag dative bonds and Ag-C bonds.

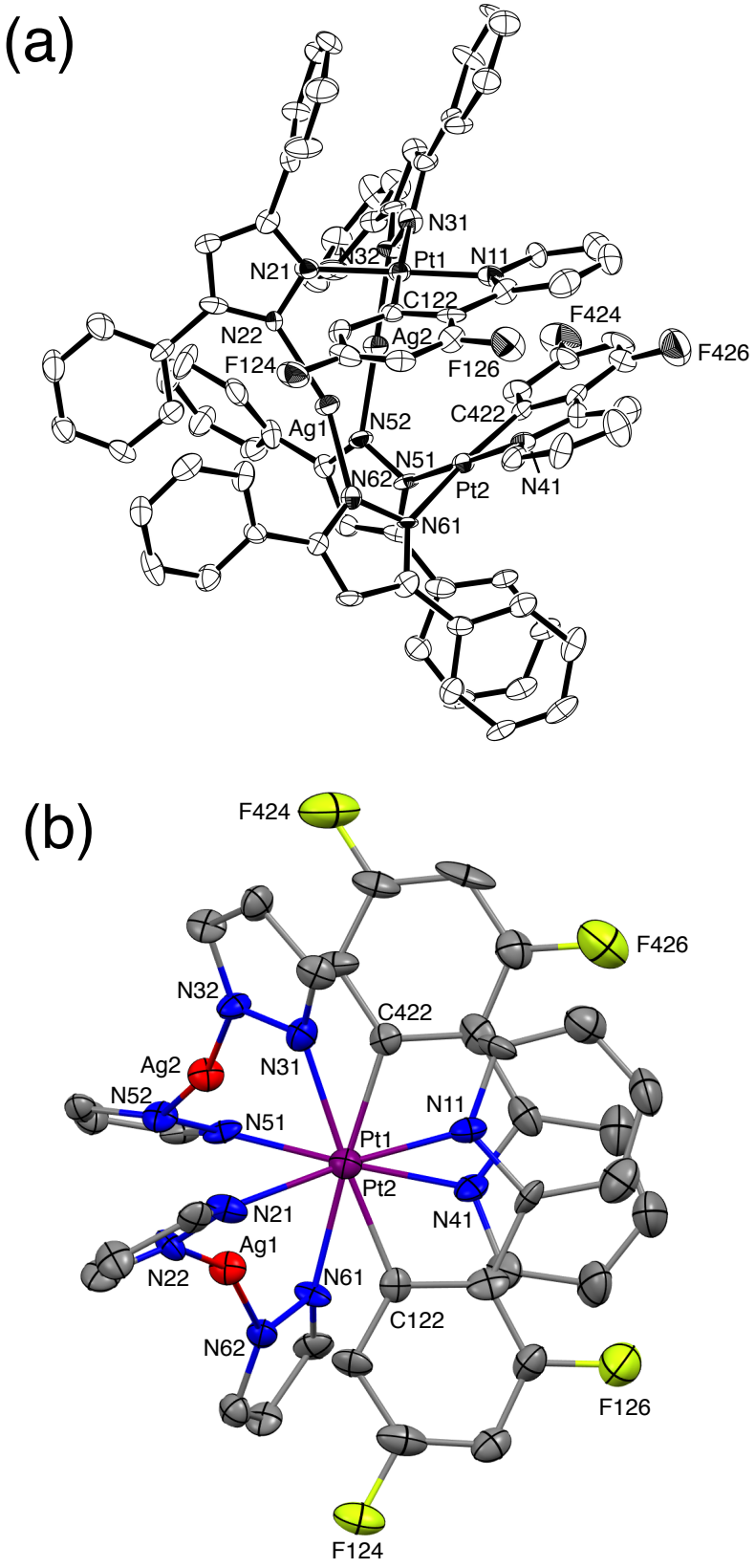


Fig. S3 (a) ORTEP drawing of $[Pt_2Ag_2(dfppy)_2(Ph_2pz)_4]$ (**5a**) with the atom numbering scheme (50% probability ellipsoids). (b) Molecular structure viewed along the Pt···Pt axis. Phenyl groups are omitted for clarity.

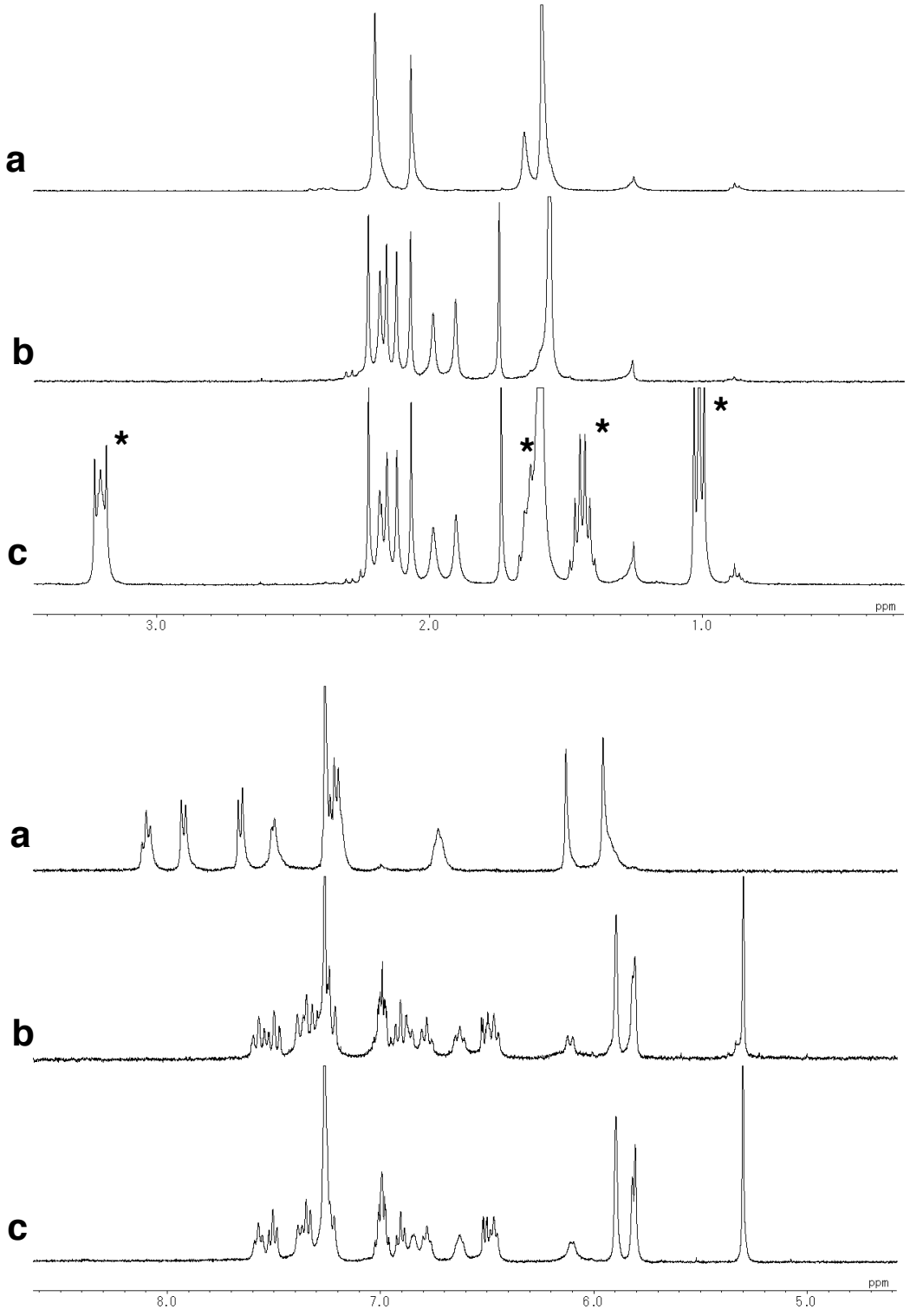


Fig. S4 ^{1}H NMR spectra (400 MHz, $CDCl_3$, 296 K) ((*top*) high field region, (*bottom*) aromatic region) of (a) $[Pt_2Ag_3(ppy)_2(Me_2pz)_4]BF_4$ (**3b**), (b) $[Pt_2Ag_2(ppy)_2(Me_2pz)_4]$ (**2b**) and (c) reaction product obtained by the treatment of **3b** with Bu_4NCl at 40 ºC. Asterisks denote the signals of coexisting Bu_4N^+ ion.

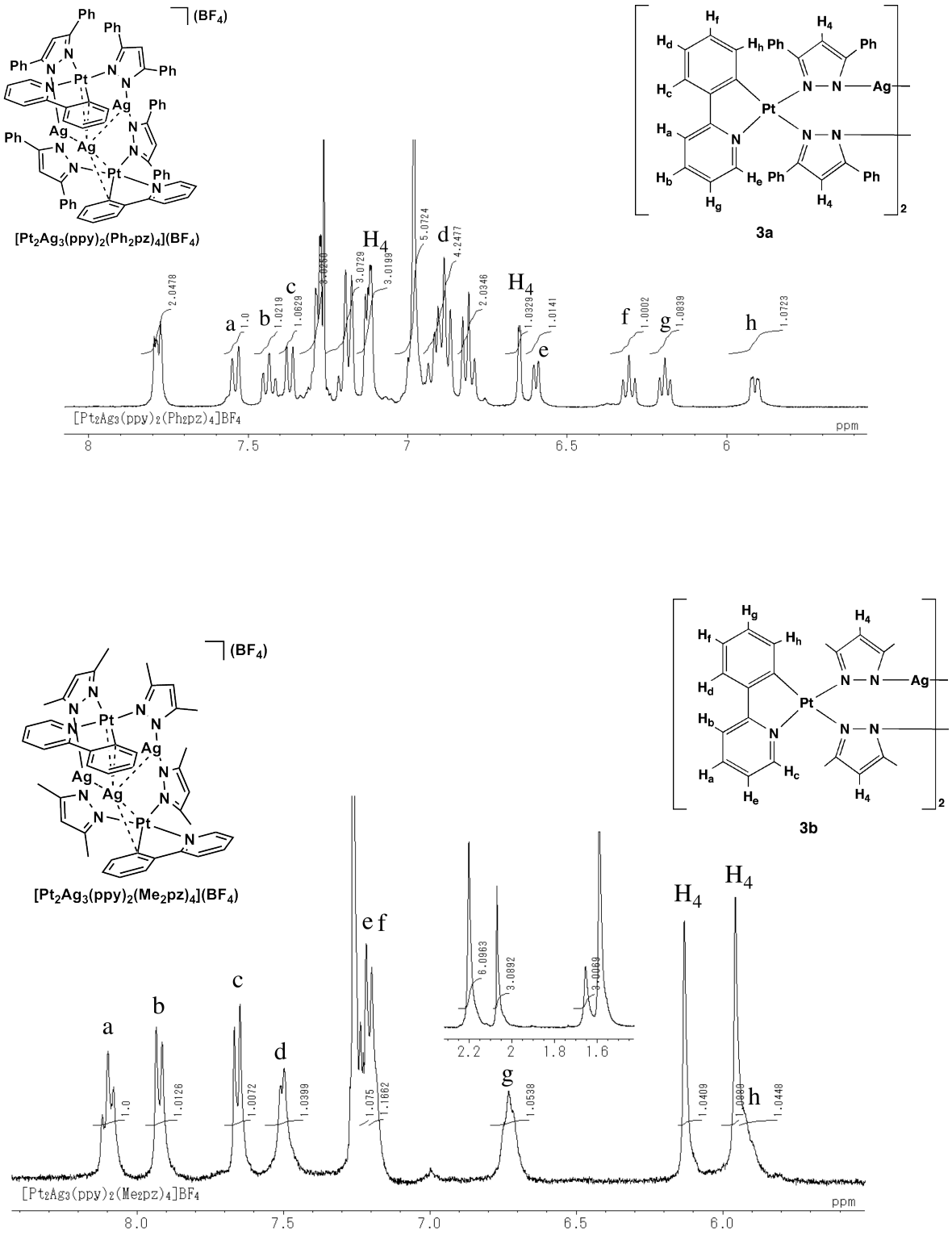
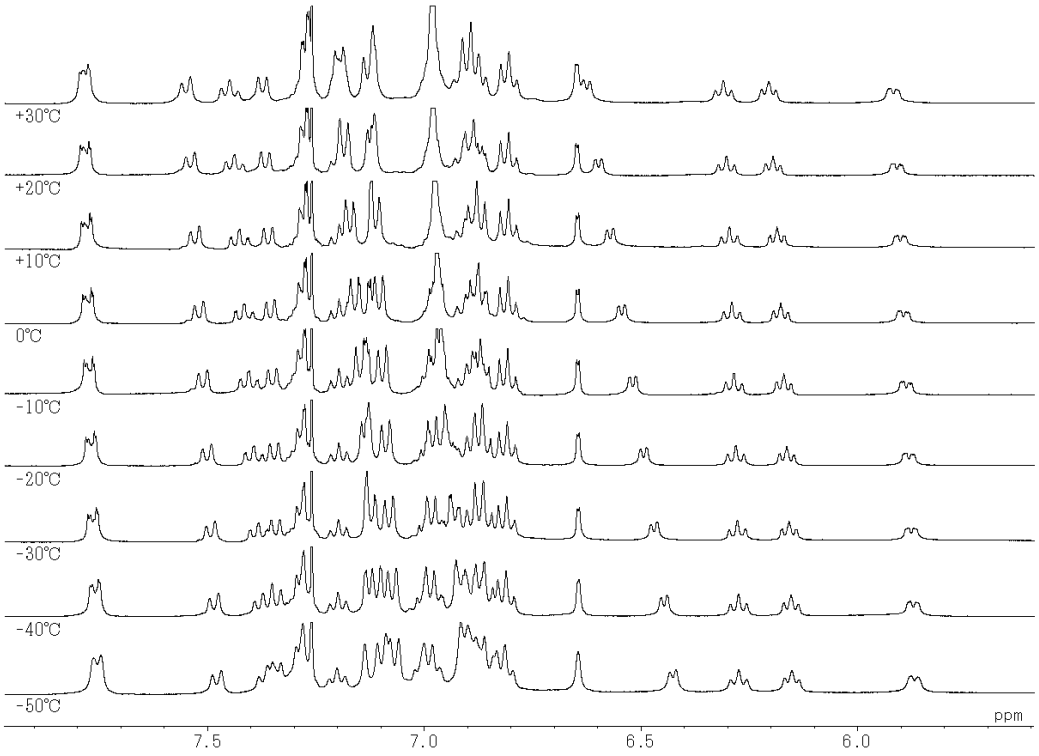


Fig. S5 ^{1}H NMR spectra (400 MHz, $CDCl_3$, 296 K) and their assignment of $[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]BF_4$ (**3a**) (*top*) and $[Pt_2Ag_3(ppy)_2(Me_2pz)_4]BF_4$ (**3b**) (*bottom*).

$[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]BF_4$ (**3a**)



$[Pt_2Ag_3(ppy)_2(Me_2pz)_4]BF_4$ (**3b**)

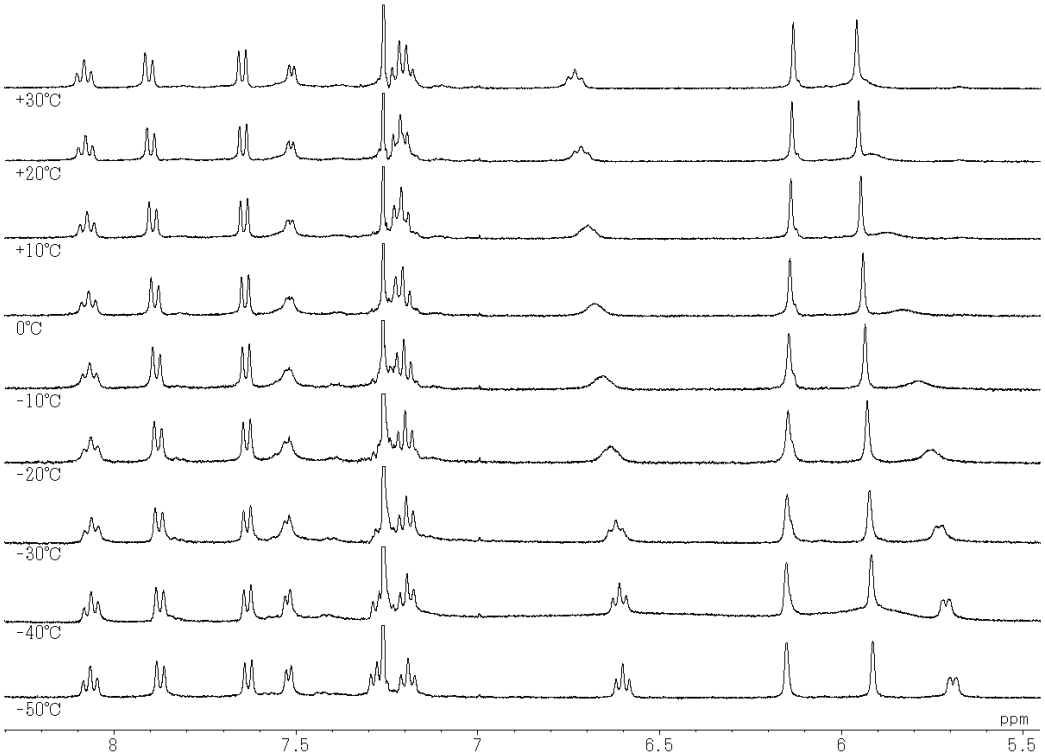
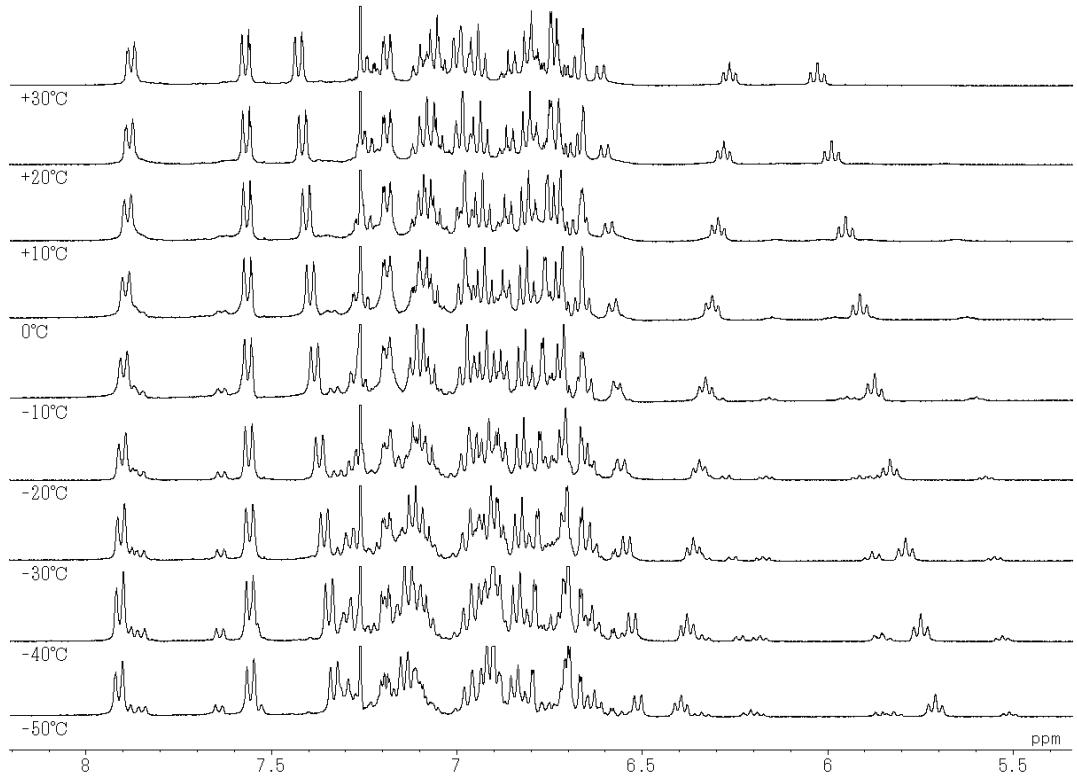
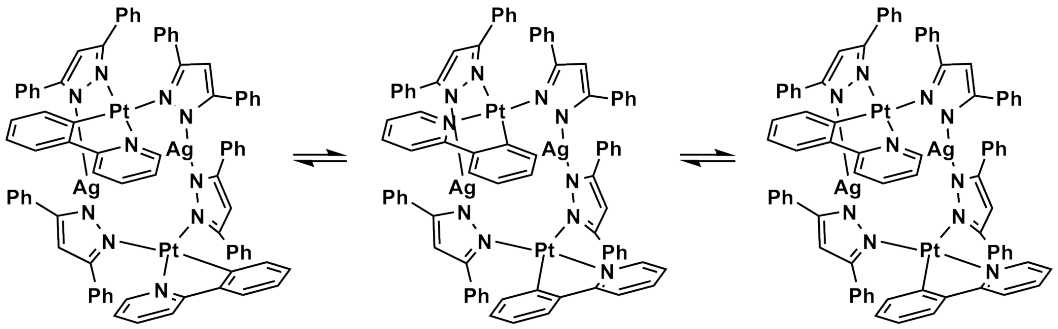


Fig. S6 Variable-temperature ^{1}H NMR spectra (400 MHz, $CDCl_3$) of $[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]BF_4$ (**3a**) (*top*) and $[Pt_2Ag_3(ppy)_2(Me_2pz)_4]BF_4$ (**3b**) (*bottom*).





***C*$_2$ isomer** ***C*$_2$ isomer** ***C*$_s$ isomer**

Fig. S7 Variable-temperature ^{1}H NMR spectra (400 MHz, $CDCl_3$) of $[Pt_2Ag_2(ppy)_2(Ph_2pz)_4]$ (**2a**) showing the splitting of resonances of ppy ligands with decreasing temperature (*top*) and possible geometrical isomers existing in the solution (*bottom*).

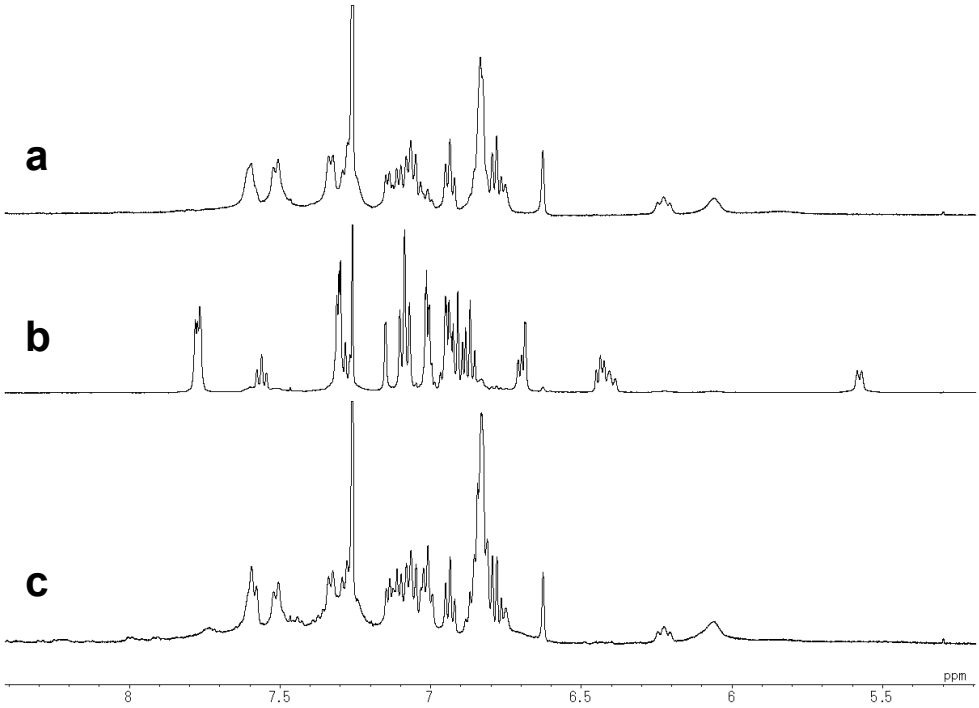


Fig. S8 ^{1}H NMR spectra (500 MHz, $CDCl_3$, 296 K) of (a) $[Pt_2Ag_2(dfppy)_2(Ph_2pz)_4]$ (**5a**), (b) **5a** in the presence of an equivalent amount of $AgBF_4$ and (c) reaction product obtained by the treatment of the mixture of **5a** and $AgBF_4$ with Bu_4NCl at 40 ºC.

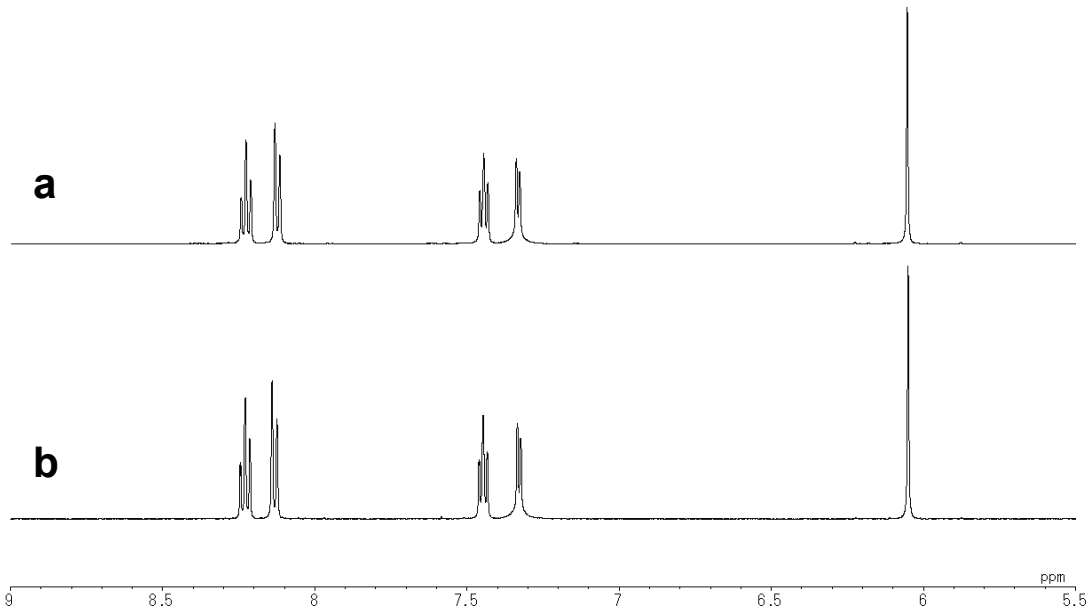


Fig. S9 ^{1}H NMR spectra (500 MHz, CD_3CN, 296 K, aromatic region) of $[Pt_2Ag_2(bpy)_2(Me_2pz)_4](PF_6)_2$ (a) before and (b) after addition of an equivalent amount of $AgBF_4$ into the sample solution.

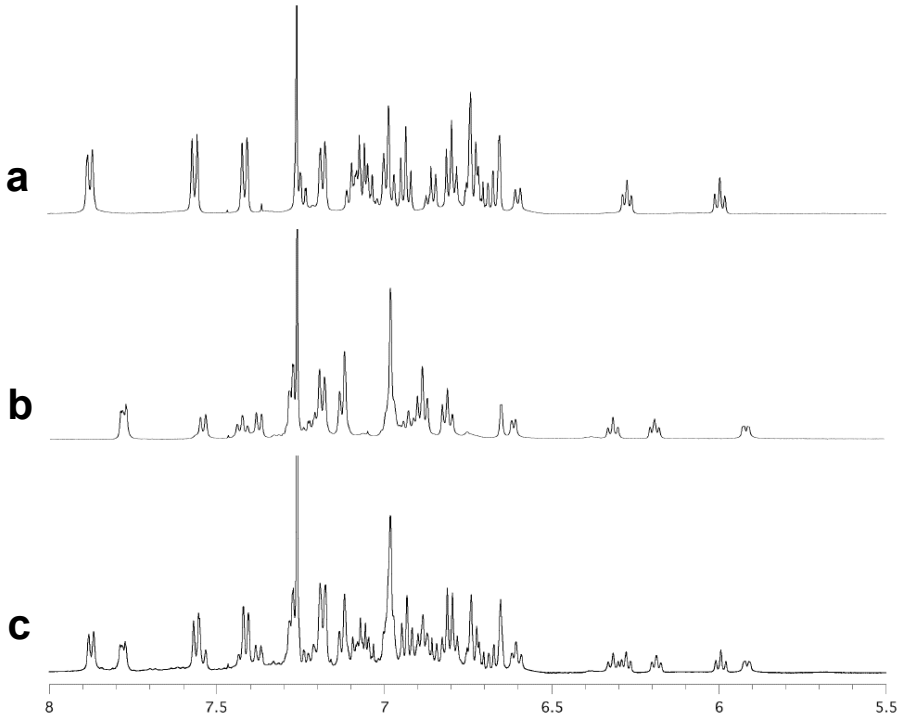


Fig. S10 ^{1}H NMR spectra (500 MHz, $CDCl_3$, 296 K, aromatic region) of a) $[Pt_2Ag_2(ppy)_2(Ph_2pz)_4]$ (**2a**), b) $[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]BF_4$ (**3a**) and c) a 1:1 mixture of **2a** and **3a**.

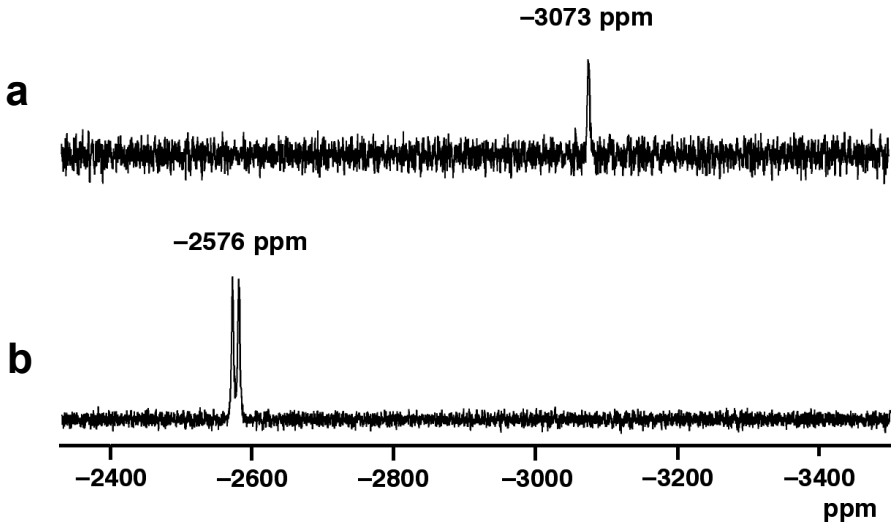


Fig. S11 ^{195}Pt NMR spectra of a) $[Pt_2Ag_2(ppy)_2(Ph_2pz)_4]$ (**2a**) and b) $[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]BF_4$ (**3a**) in 9:1 (v/v) mixture of CH_2Cl_2 and $CDCl_3$ at room temperature. H_2PtCl_6 in D_2O was used as an external standard (δ = 0 ppm).

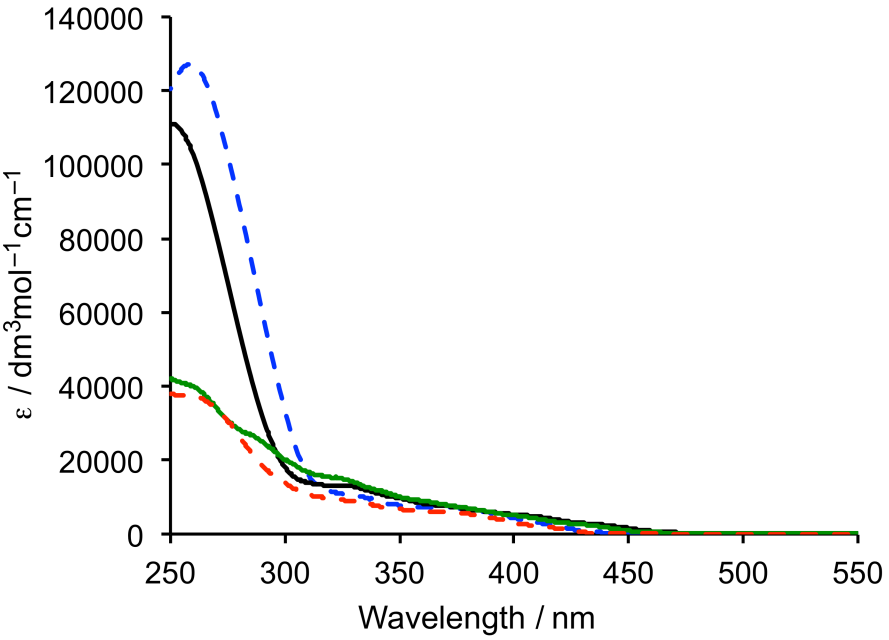


Fig. S12 Electronic absorption spectra of **2a** (- - -), **2b** (- - -)[a], **3a** (———) and **3b** (———) in CH_2Cl_2 at 298 K. [a] Ref. 3 in SI.

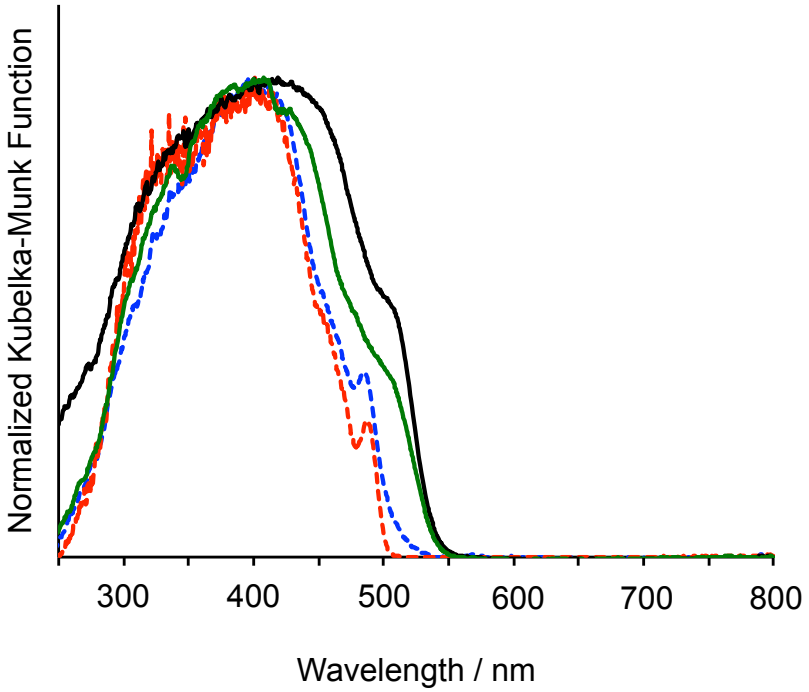


Fig. S13 UV-Vis diffuse reflectance spectra of **2a** (▬ ▬), **2b** (▬ ▬)[a], **3a** (▬) and **3b** (▬) in the solid state at 295 K. [a] Ref. 3 in SI.

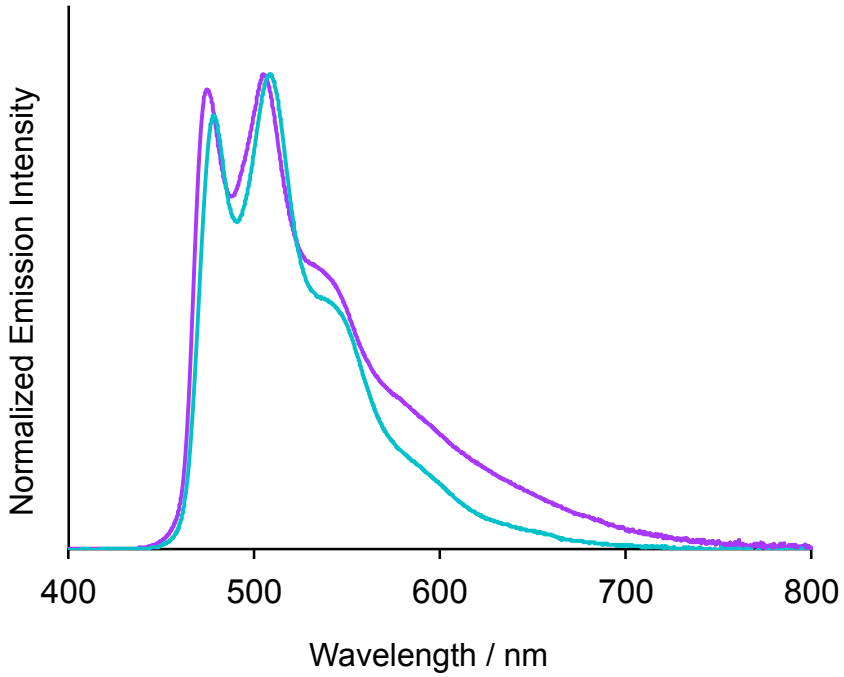


Fig. S14 Normalized emission spectra of **5a** (▬) and $[Pt_2Ag_2(dfppy)_2(Me_2pz)_4]$[a] (▬) in the solid state at 295 K (λ_{ex} = 350 nm). [a] Ref. 3 in SI.

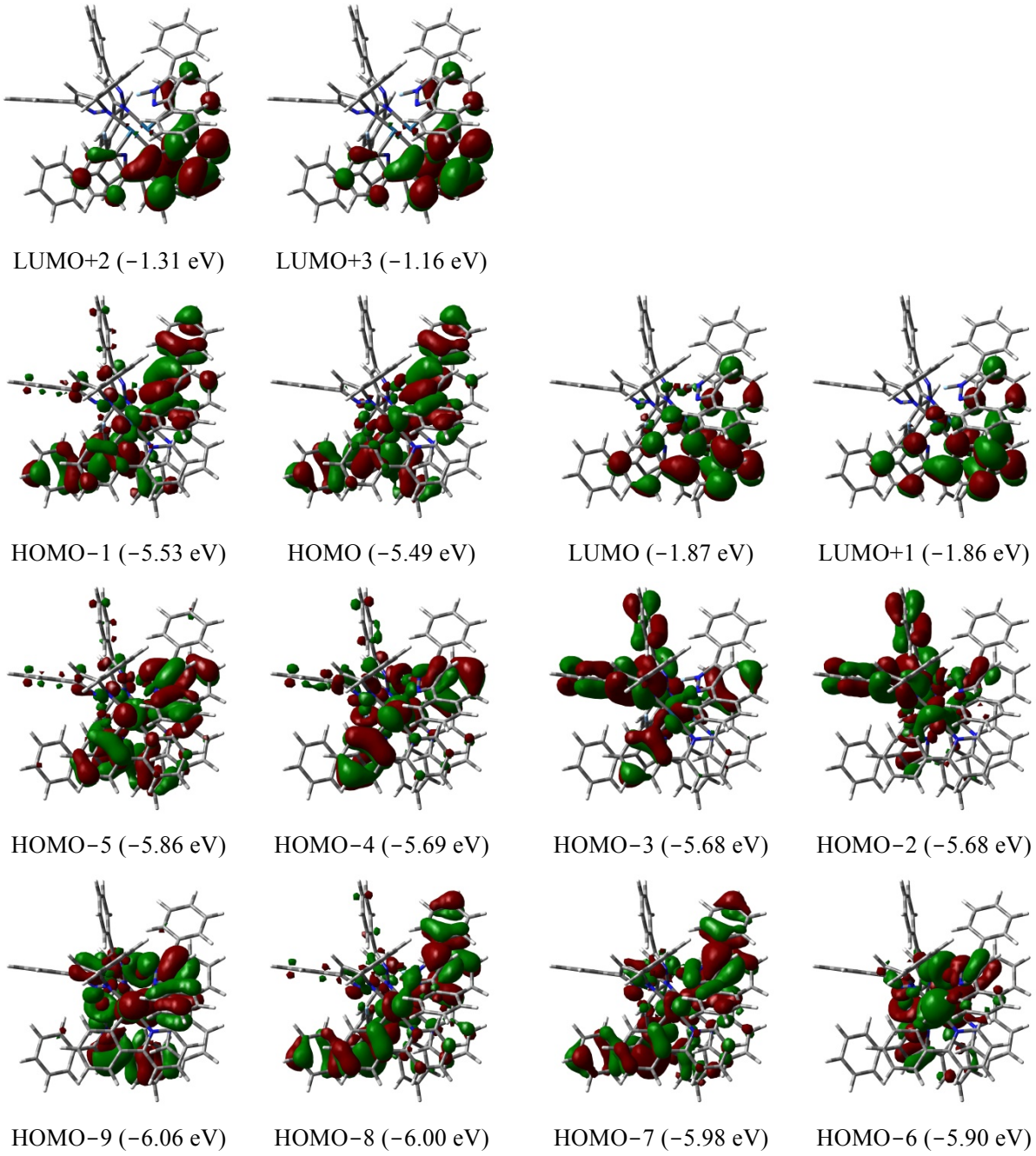


Fig. S15 Molecular orbitals of the singlet state for $[Pt_2Ag_2(ppy)_2(Ph_2pz)_4]$ (**2a**) by the B3LYP method.

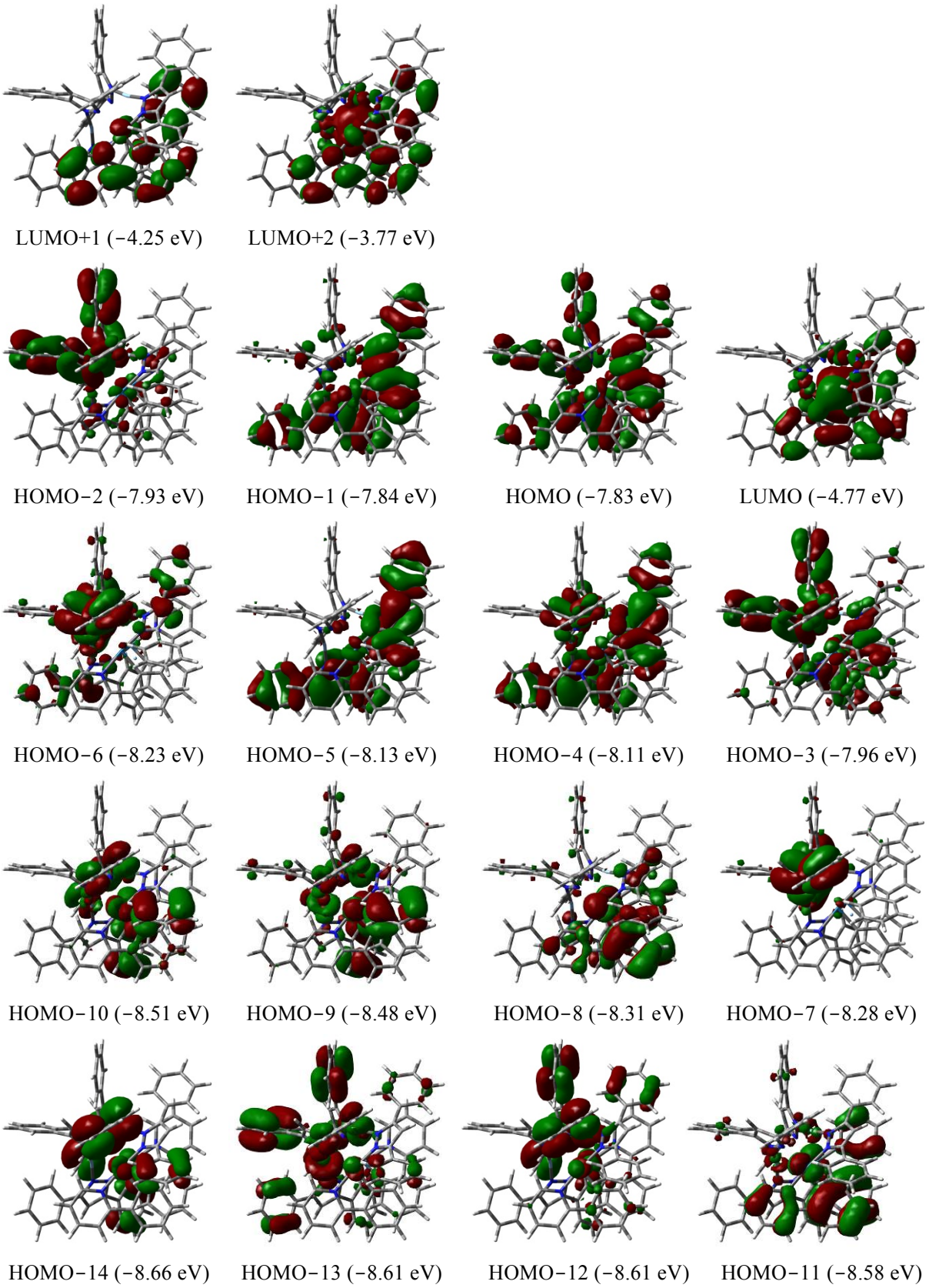


Fig. S16 Molecular orbitals of the singlet state for $[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]^+$ (**3a'**) by the B3LYP method.

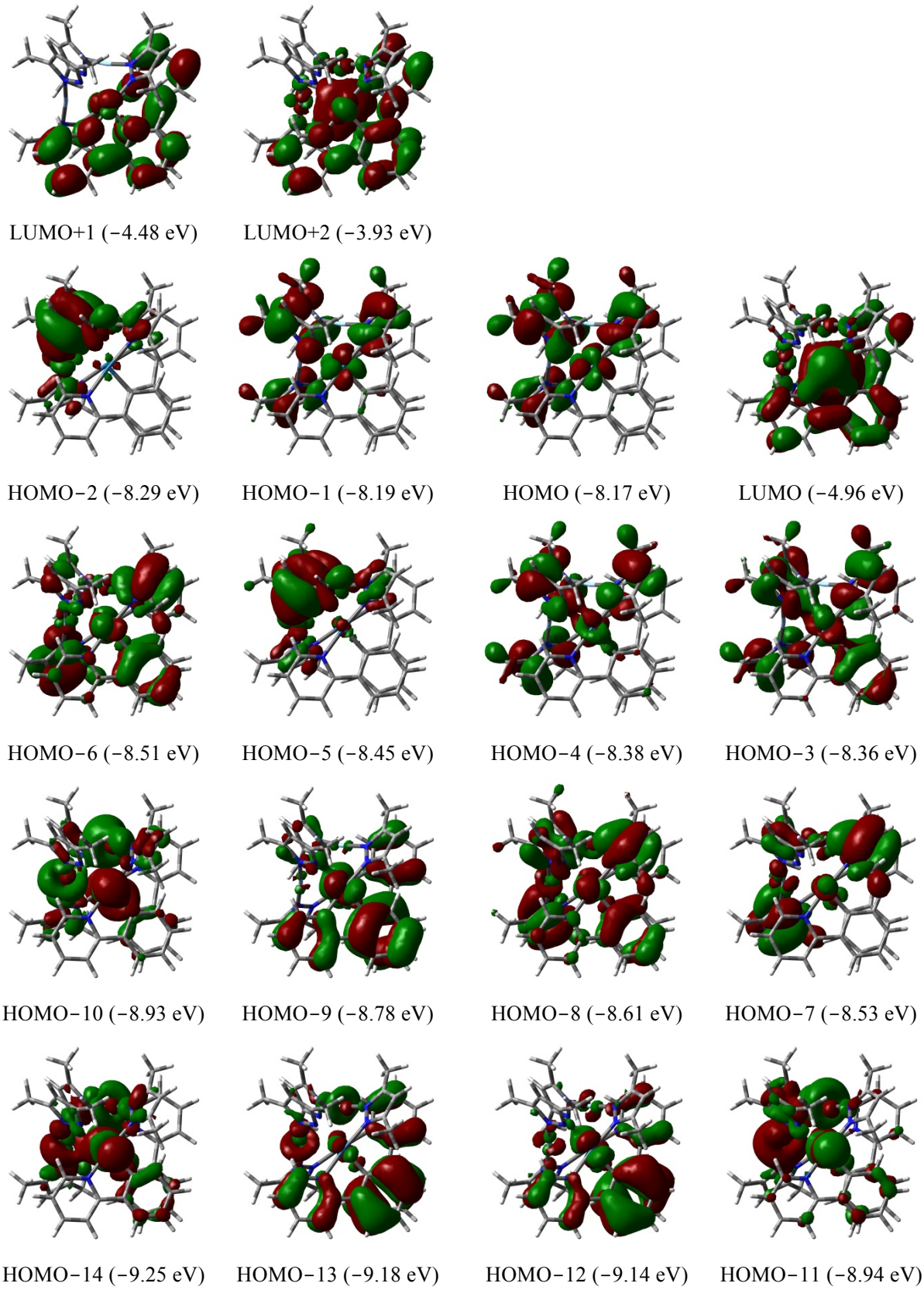


Fig. S17 Molecular orbitals of the singlet state for $[Pt_2Ag_3(ppy)_2(Me_2pz)_4]^+$ (**3b'**) by the B3LYP method.

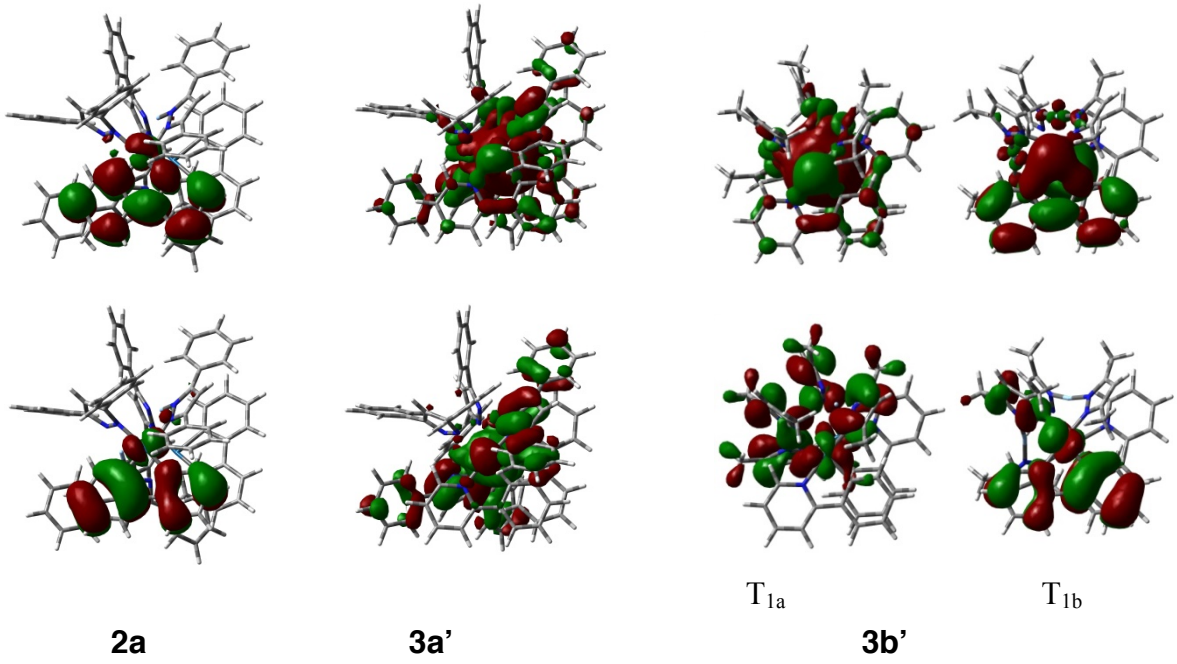


Fig. S18 Singly occupied molecular orbitals of the triplet states for $[Pt_2Ag_2(ppy)_2(Ph_2pz)_4]$ (**2a**), $[Pt_2Ag_3(ppy)_2(Ph_2pz)_4]^+$(**3a'**) and $[Pt_2Ag_3(ppy)_2(Me_2pz)_4]^+$ (**3b'**) by the B3LYP method.