Electronic Supplementary Information (ESI)

Heteropolynuclear $PdAg_4$ Complexes with Self-Assembled Trans-Chelating $\{(Ar_2pz)_3Ag_2\}$ Units

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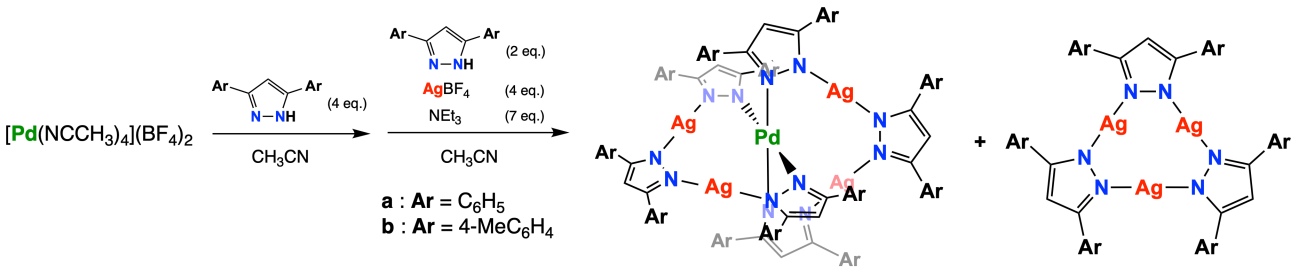
Materials. All other commercially available reagents were used as purchased. The complexes were synthesized under a N_2 atmosphere, unless otherwise noted.

Physical Measurement and Instrumentation. 1D (^{1}H, ^{13}C{^{1}H}) and 2D (^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, and ^{1}H-^{13}C HMBC) NMR spectra were obtained using a 500 MHz Varian NMR System 500PS spectrometer. UV/Vis spectra were recorded on a Jasco V-560 spectrophotometer at room temperature. The corrected emission spectra were obtained using a Hamamatsu PMA-12 multichannel photodetector (excitation wavelength = 355 nm). The emission quantum yields of the complexes in the crystalline state were determined using a Hamamatsu Photonic Absolute PL Quantum Yield Measurement System C9920-02 with an integrating sphere and PMA-12 multichannel photodetector (excitation wavelength = 355 nm). Emission lifetime measurements were conducted using a Hamamatsu C11200 streak camera as a photodetector by excitation at 355 nm using a nanosecond Q-switched Nd:YAG laser (Continuum® Minilite™, fwhm ≈ 10–12 ns, repetition rate = 10 Hz).

Preparation of Complexes.



[PdAg$_4$(Ph$_2$pz)$_6$] (1a): A mixture of [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ (50.6 mg, 0.114 mmol) and Ph$_2$pzH (100.9 mg, 0.458 mmol) in CH$_3$CN (20 mL) was stirred at room temperature for 1 h. After a CH$_3$CN solution (10 mL) of a mixture of Ph$_2$pzH (50.8 mg, 0.231 mmol), AgBF$_4$ (88.3 mg, 0.454 mmol), and Et$_3$N (108.8 μL, 0.781 mmol) was added to the solution, the mixture was stirred at room temperature for 3 h in the dark to give a white precipitate containing PdAg$_4$ complex **1a** and Ag$_3$ complex **2a**. The precipitate was collected by filtration and dried under vacuum. The solid was recrystallized from a CH$_2$Cl$_2$/CH$_3$CN solution. The PdAg$_4$ complex **1a** was isolated as a yellow block-shaped crystal from the CH$_2$Cl$_2$/CH$_3$CN solution. Yield: 55.8 mg (27.6 μmol, 28%). ^{1}H NMR (500 MHz, CDCl$_3$, 298 K) of **1a**: δ = 7.45 (d, J = 7.5 Hz, 8H, *Ph*$_2$pz), 7.94 (t, J = 7.5 Hz, 2H, *Ph*$_2$pz), 7.29 (d, J = 7.5 Hz, 4H, *Ph*$_2$pz), 7.22 (t, J = 7.5 Hz, 4H, *Ph*$_2$pz), 7.14 (t, J =7.5 Hz, 2H, *Ph*$_2$pz), 6.93 (t, J = 7.5 Hz, 4H, *Ph*$_2$pz), 6.82 (d, J = 7.5 Hz, 4H, *Ph*$_2$pz), 6.66 (t, J = 7.5 Hz, 2H, *Ph*$_2$pz), 6.63 (d, J = 2.0 Hz, 2H, Ph$_2$*pz*), 6.48 ppm (d, J = 2.0 Hz, 4H, Ph$_2$*pz*). ^{13}C NMR (125 MHz, CDCl$_3$, 298 K) of **1a**: δ = 155.8 ($C_{4,pz}$), 155.1 ($C_{4,pz}$), 151.5 ($C_{4,pz}$), 134.1 ($C_{4,Ph}$), 134.0 ($C_{4,Ph}$), 133.4 ($C_{4,Ph}$), 129.5 (C_{Ph}), 128.9 (C_{Ph}), 128.7 (C_{Ph}), 128.4 (C_{Ph}), 128.1 (C_{Ph}), 127.6 (C_{Ph}), 126.7 (C_{Ph}), 126.4 (C_{Ph}), 125.3 (C_{Ph}), 105.7 (C_{pz})), 100.0 ppm

(C_{pz})). FAB-MS for **1a**: *m*/*z* calcd for $[C_{90}H_{66}N_{12}Ag_4Pd]^+$: 1853.5 $[M]^+$; found: 1854.1. Elemental analysis calcd (%) for $C_{90}H_{66}N_{12}Ag_4Pd$: C, 58.32; H, 3.59; N, 9.07; found: C, 58.42; H, 3.66; N, 8.69.

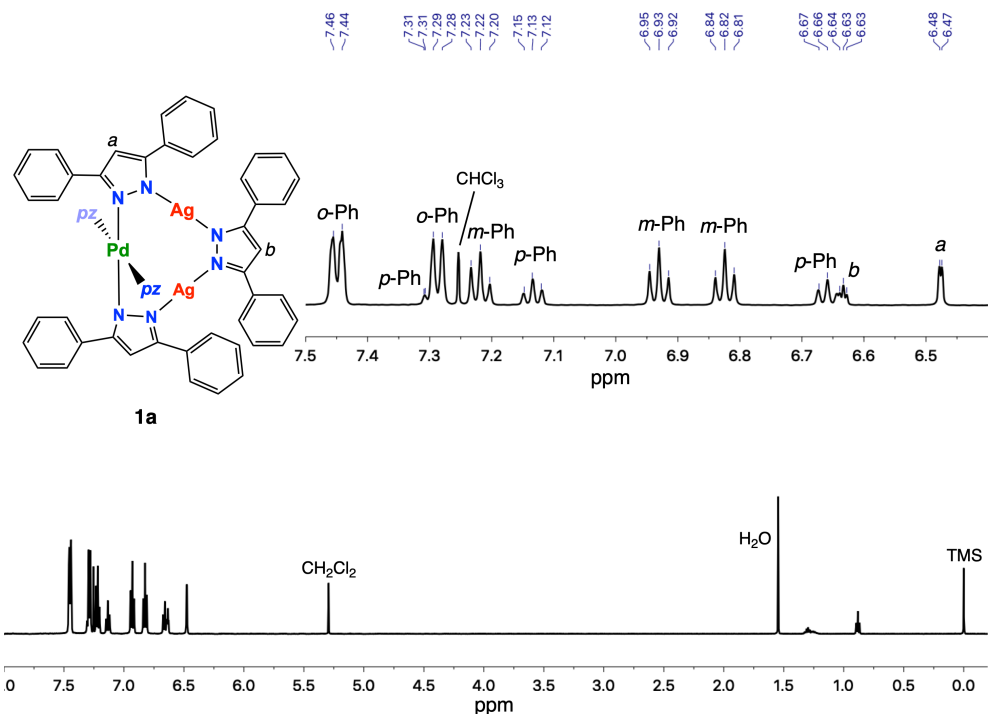


Fig. S1 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1a**.

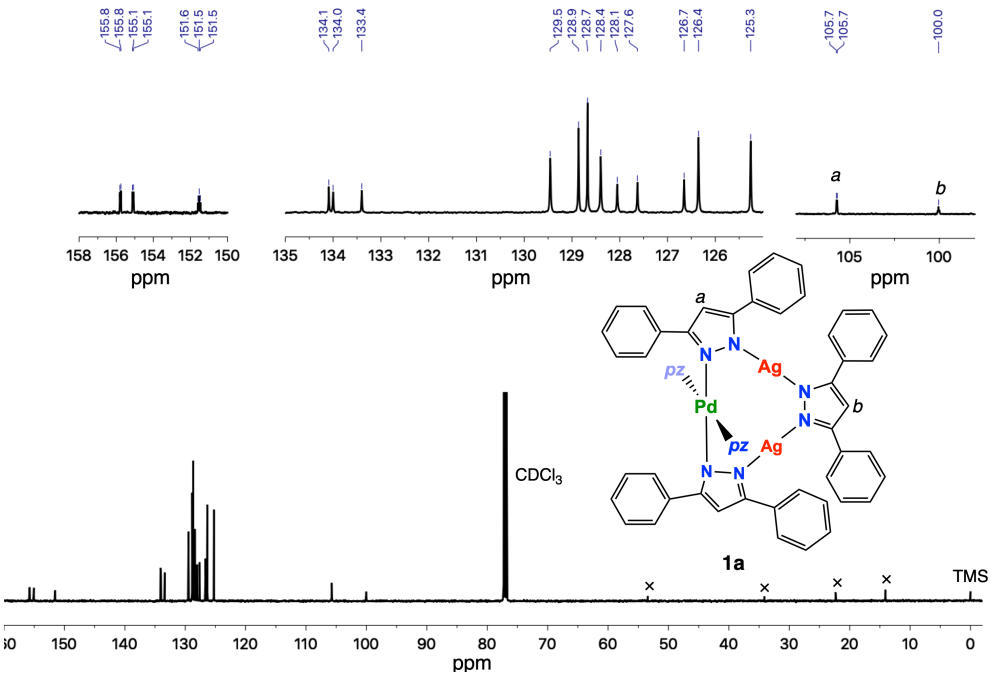


Fig. S2 $^{13}C\{^1H\}$ NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1a**.

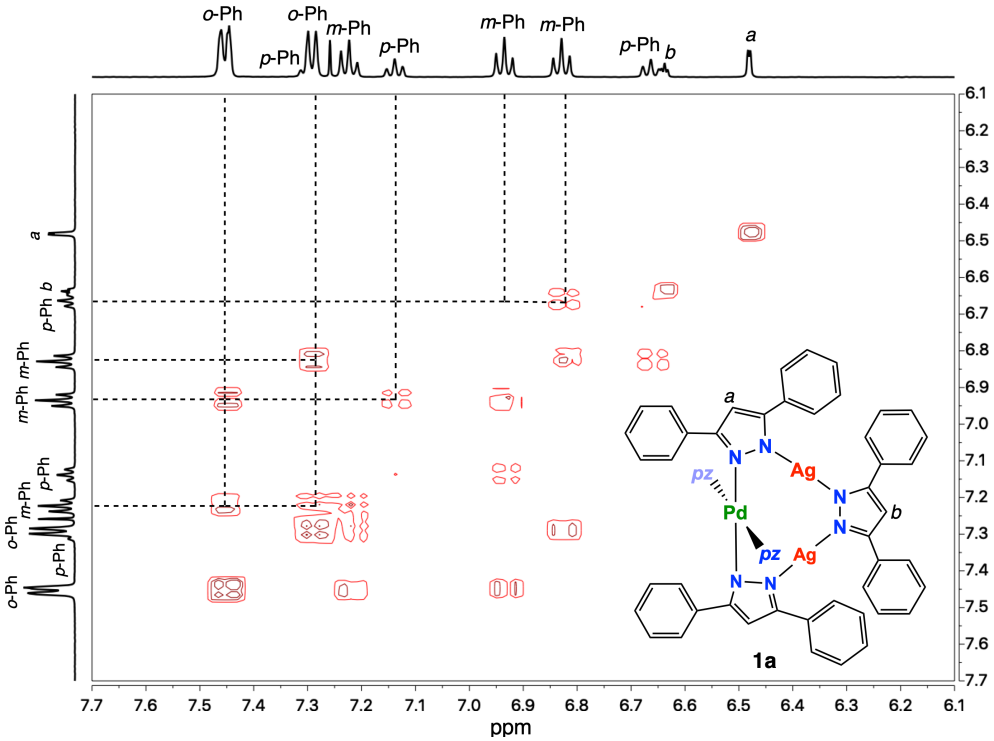


Fig. S3 ^{1}H-^{1}H COSY spectrum (500 MHz, $CDCl_3$, 298 K) of **1a**.

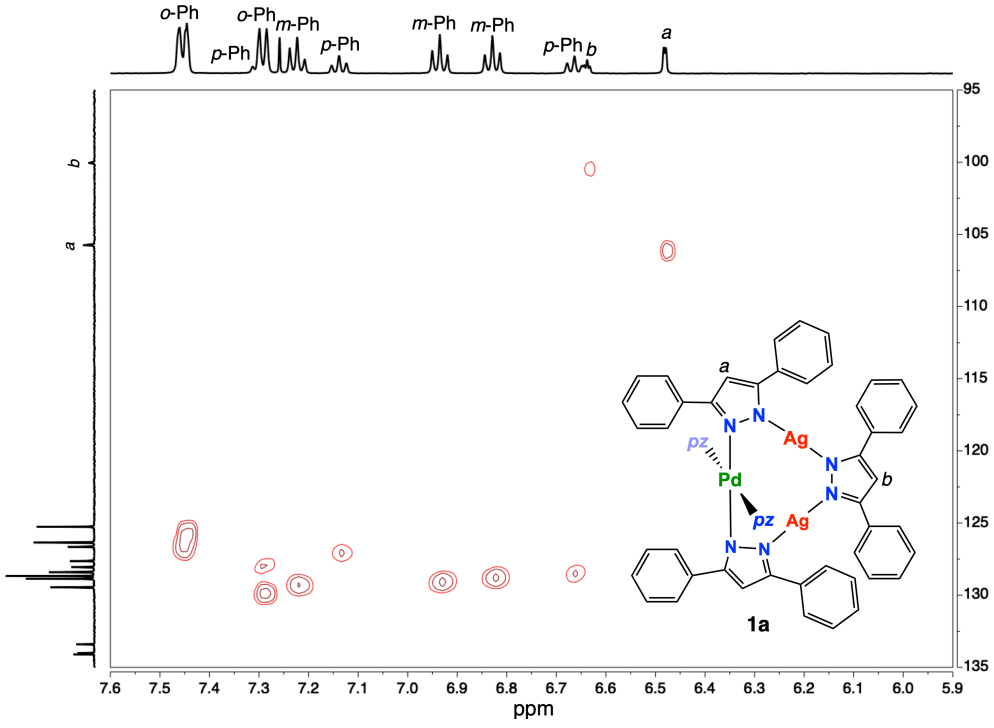


Fig. S4 ^{1}H-^{13}C HSQC spectrum (500 MHz, $CDCl_3$, 298 K) of **1a**.

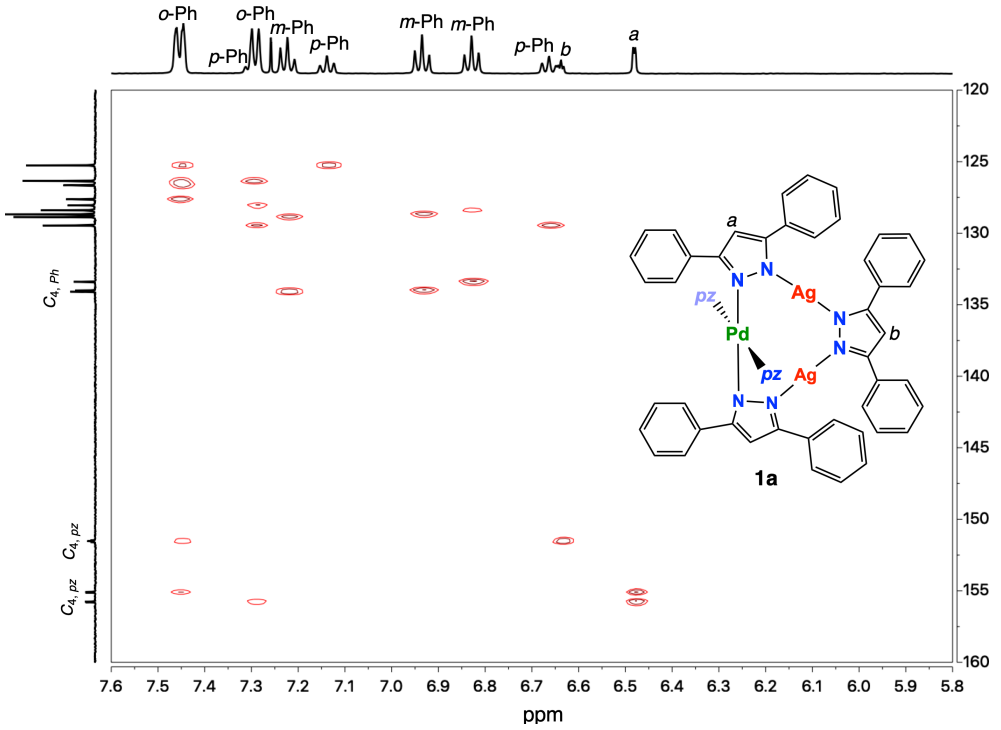


Fig. S5 ^{1}H-^{13}C HMBC spectrum (500 MHz, $CDCl_3$, 298 K) of **1a**. Correlations between protons and carbons, with two or three bonds apart from each other, gave cross-peaks in the spectrum.

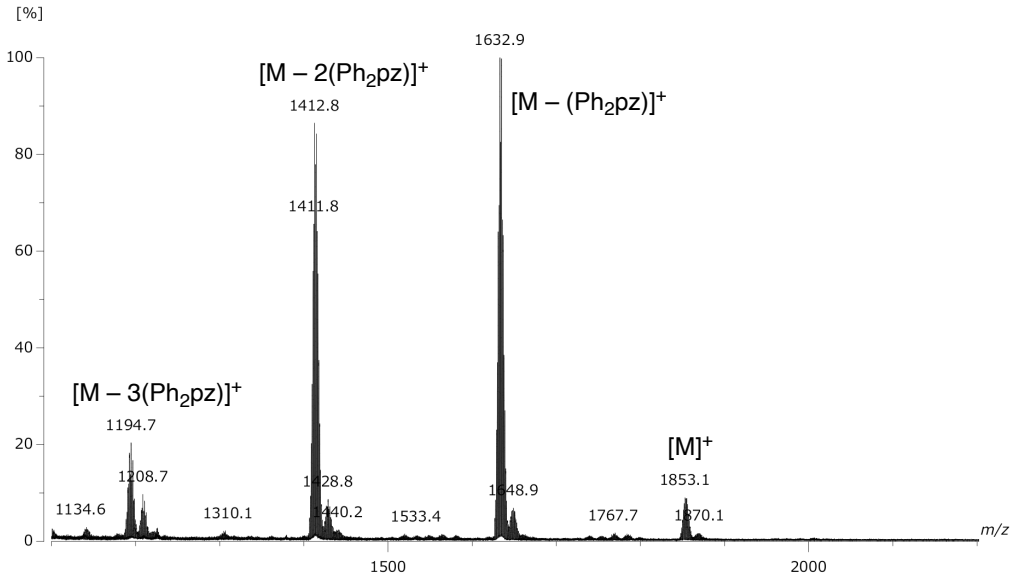


Fig. S6 FAB-MS spectrum of **1a**. In addition to the parent peak of **1a**, fragment peaks were also observed, corresponding to the consecutive losses of Ph_2pz ligands from the parent ion $[M]^+$.

[PdAg$_4${(4-MeC$_6$H$_4$)$_2$pz}$_6$] (1b): A mixture of [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ (25.4 mg, 57.2 μmol) and (4-MePh)$_2$pzH (54.9 mg, 221 μmol) in CH$_3$CN (10 mL) was stirred at room temperature for 1 h. After a CH$_3$CN solution (10 mL) of a mixture of (4-MePh)$_2$pzH (27.8 mg, 112 μmol), AgBF$_4$ (43.5 mg, 223 μmol), and Et$_3$N (53.7 μL, 385 μmol) was added to the solution, the mixture was stirred for 2 h in the dark to yield a pale-yellow precipitate containing PdAg$_4$ complex **1b** and Ag$_3$ complex **2b**. The precipitate was collected by filtration, dried in vacuo, and recrystallized from a CHCl$_3$/*n*-pentane solution. The PdAg$_4$ complex **1b** was isolated as a yellow block-shaped crystal from a CHCl$_3$/*n*-pentane solution. Yield: 23.2 mg (11.5 μmol, 20%). ^{1}H NMR (500 MHz, CDCl$_3$, 298 K) of **1b**: δ = 7.42 ((Me*Ph*)$_2$pz), 7.37 ((Me*Ph*)$_2$pz), 7.14 ((Me*Ph*)$_2$pz), 7.05 ((Me*Ph*)$_2$pz), 6.79 ((Me*Ph*)$_2$pz), 6.63–6.58 ((Me*Ph*)$_2$pz and H$_b$), 6.39 (d, J = 3.0 Hz, 4H, (MePh)$_2$*pz*), 2.42 ((*Me*Ph)$_2$pz), 2.35 ((*Me*Ph)$_2$pz), 1.63 ppm ((*Me*Ph)$_2$pz). ^{13}C NMR (125 MHz, CDCl$_3$, 298 K) of **1b**: δ = 155.4 ($C_{4,\,pz}$), 154.9 ($C_{4,\,pz}$), 150.9 ($C_{4,\,pz}$), 138.0 ($C_{4,\,Ph}$), 136.6 ($C_{4,\,Ph}$), 135.8 ($C_{4,\,Ph}$), 131.6 ($C_{4,\,Ph}$), 131.3 ($C_{4,\,Ph}$), 130.6 ($C_{4,\,Ph}$), 129.5 (C_{Ph}), 129.3 (C_{Ph}), 129.3 (C_{Ph}), 129.2 (C_{Ph}), 126.5 (C_{Ph}), 125.0 (C_{Ph}), 105.5 (C_{pz}), 99.5 (C_{pz}), 21.4 (C_{Me}), 21.3 (C_{Me}), 20.8 ppm (C_{Me}). FAB-MS for **1b**: *m*/*z* calcd for [C$_{102}$H$_{90}$N$_{12}$Ag$_4$Pd]$^+$: 2021.8 [*M*]$^+$; found: 2021.3. Elemental analysis calcd (%) for [C$_{102}$H$_{90}$N$_{12}$Ag$_4$Pd]·0.2CHCl$_3$: C, 60.01; H, 4.44; N, 8.22; found: C, 60.08; H, 4.35; N, 8.33.

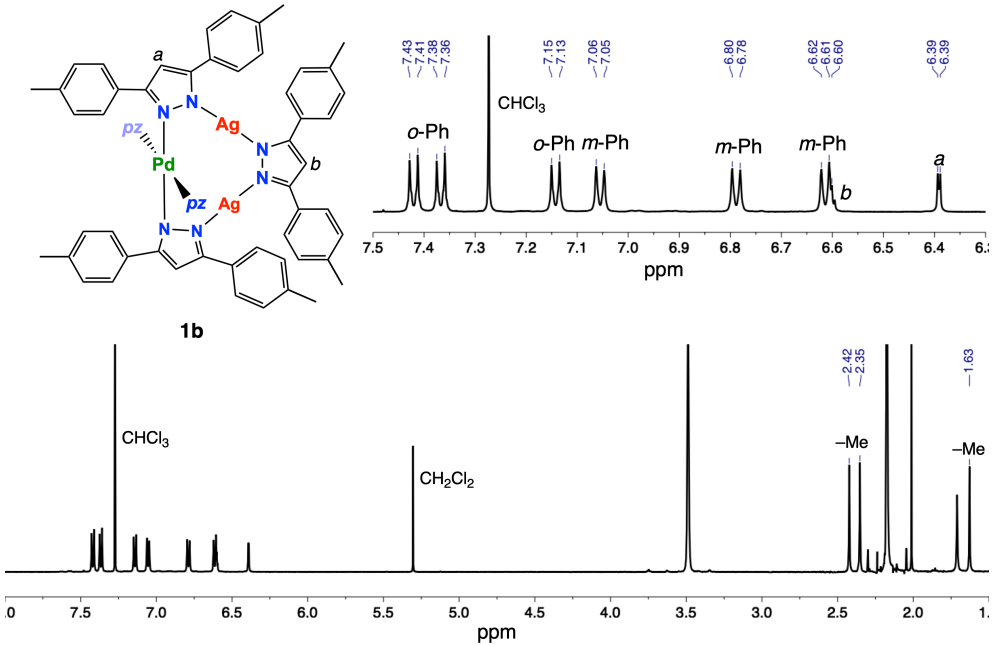


Fig. S7 ^{1}H NMR spectrum (500 MHz, CDCl$_3$, 298 K) of **1b**.

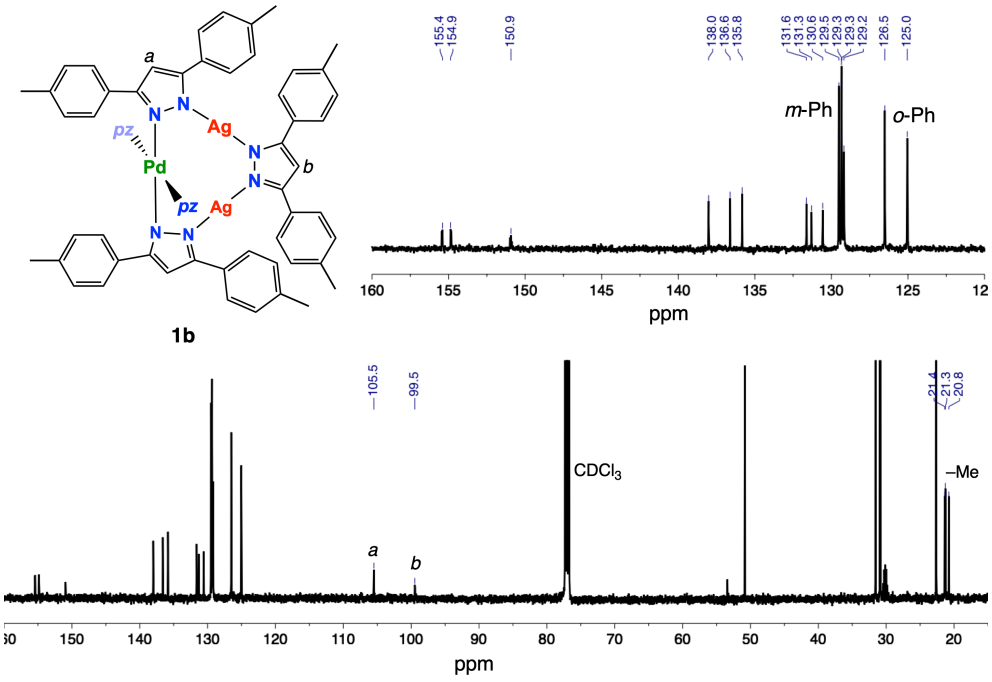


Fig. S8 $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1b**.

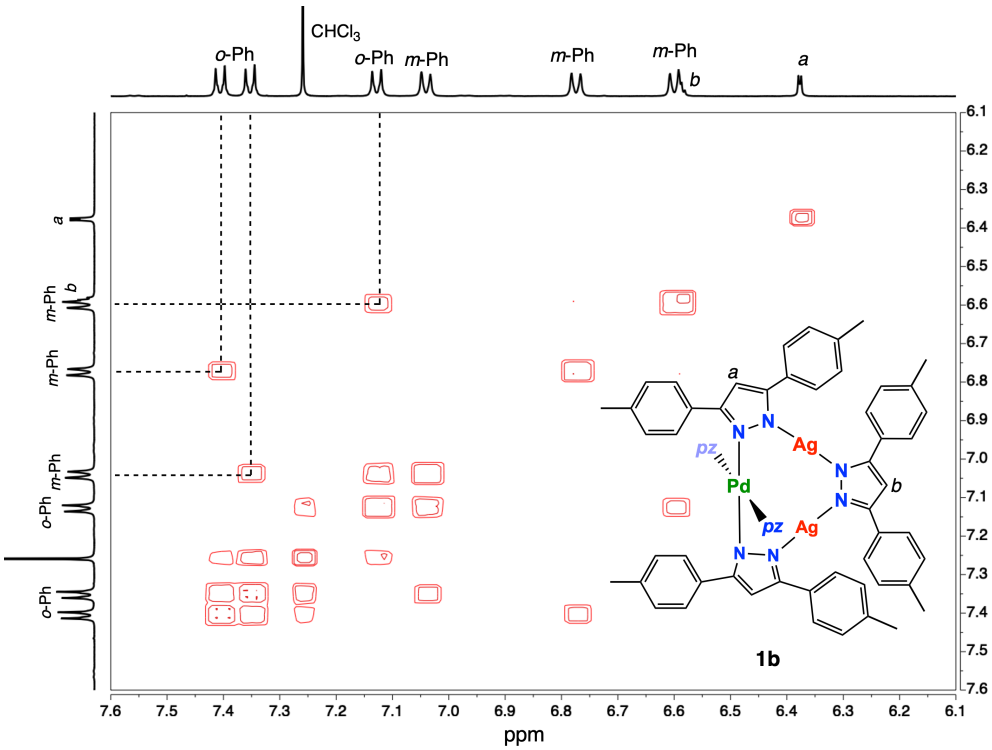


Fig. S9 ^{1}H-^{1}H COSY spectrum (500 MHz, $CDCl_3$, 298 K) of **1b**.

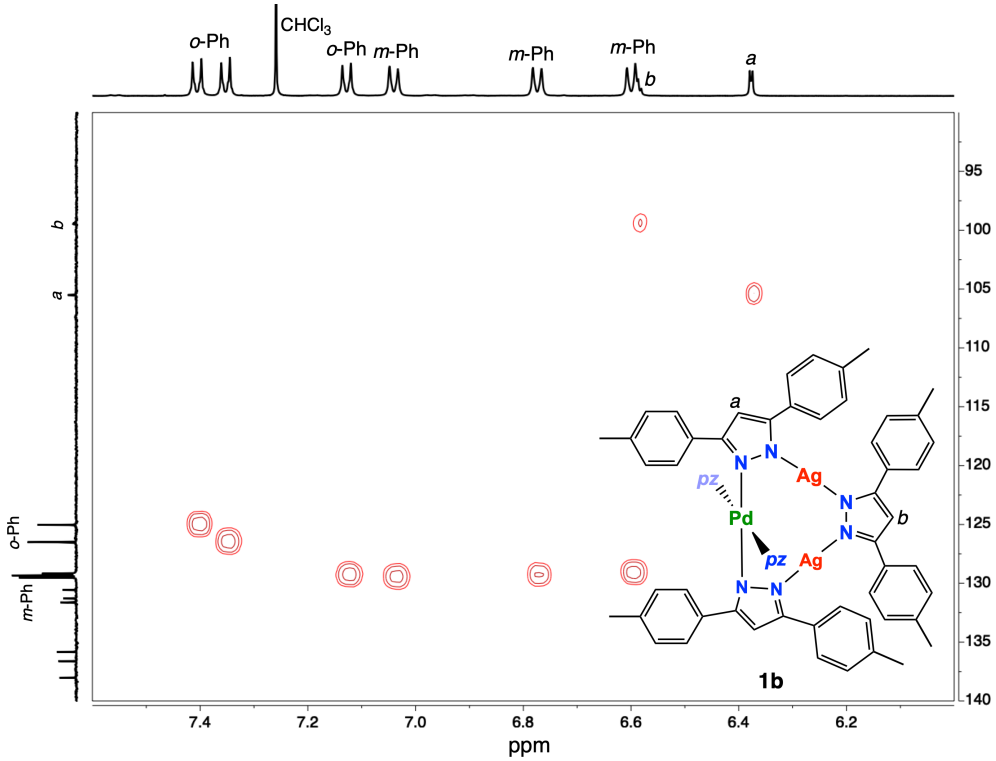


Fig. S10 ^{1}H-^{13}C HSQC spectrum (500 MHz, $CDCl_3$, 298 K) of **1b**.

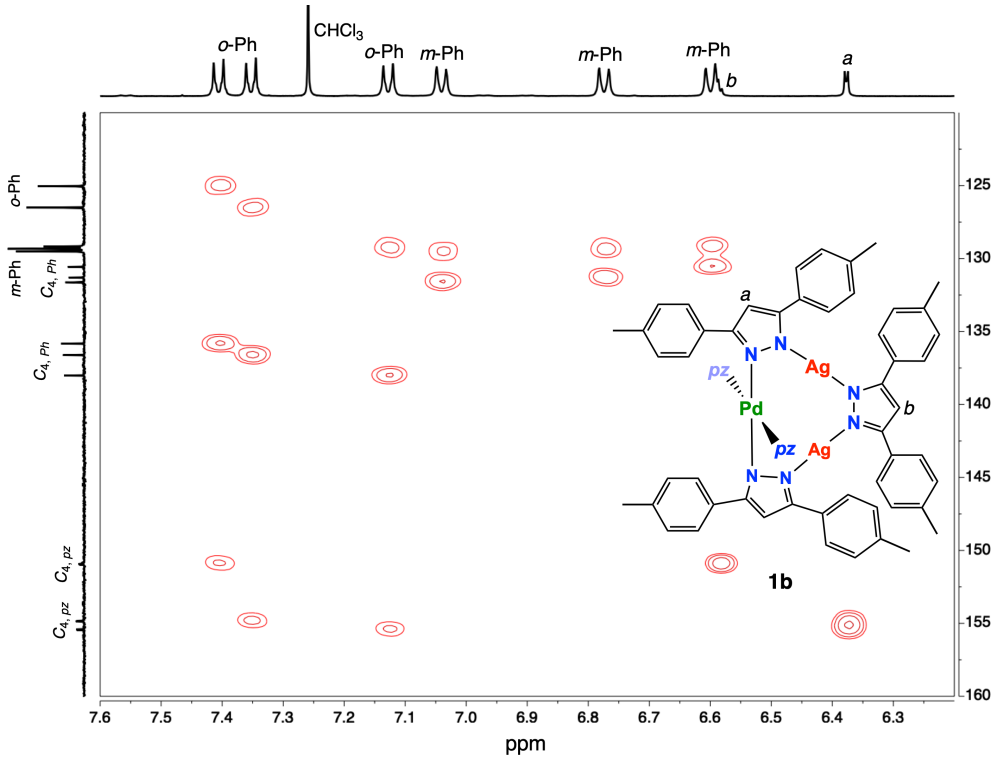


Fig. S11 ^{1}H-^{13}C HMBC spectrum (500 MHz, $CDCl_3$, 298 K) of **1b**. Correlations between protons and carbons, with two or three bonds apart from each other, gave cross peaks in the spectrum.

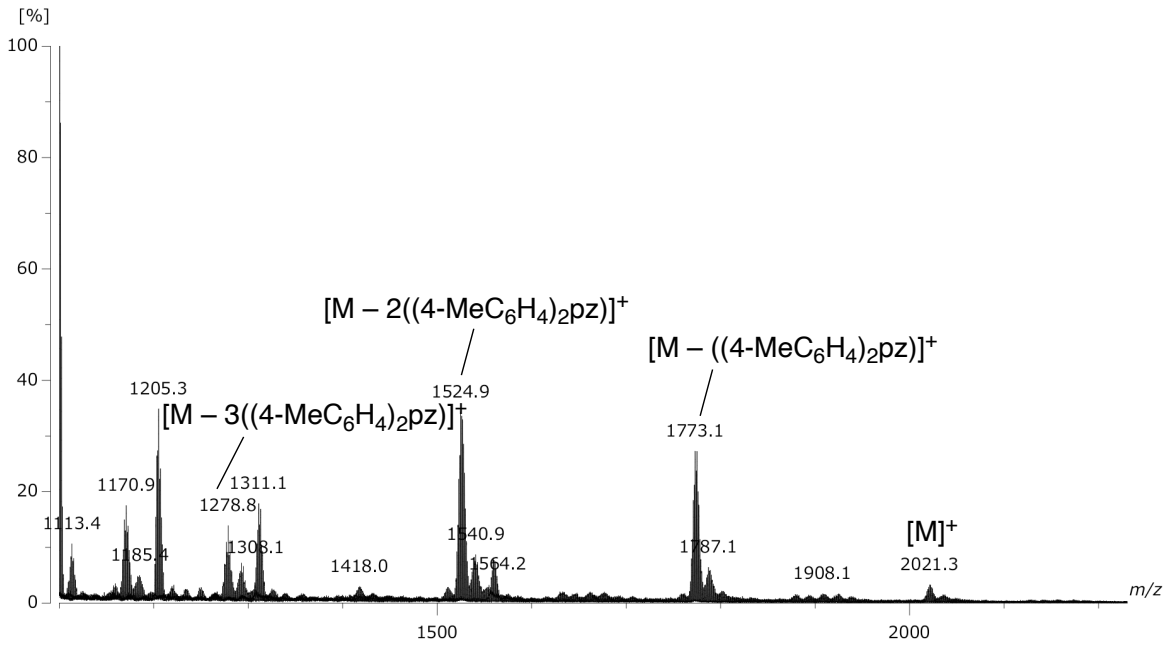
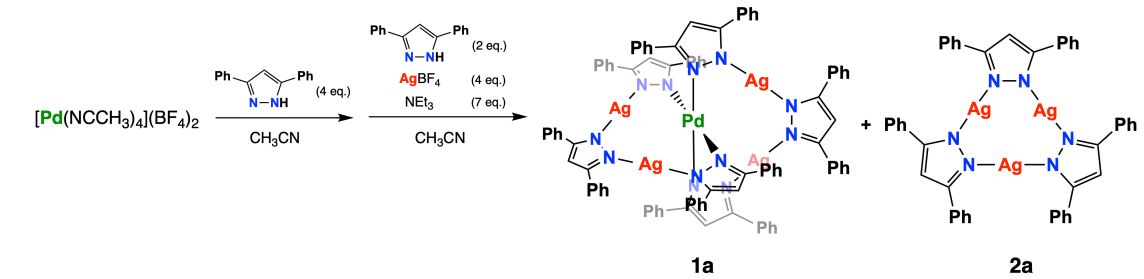


Fig. S12 FAB-MS spectrum of **1b**. In addition to the parent peak of **1b**, fragment peaks were also observed, corresponding to the consecutive losses of $(4\text{-MeC}_6\text{H}_4)_2\text{pz}$ ligands from the parent ion $[\text{M}]^+$.

Reactivities of the complexes



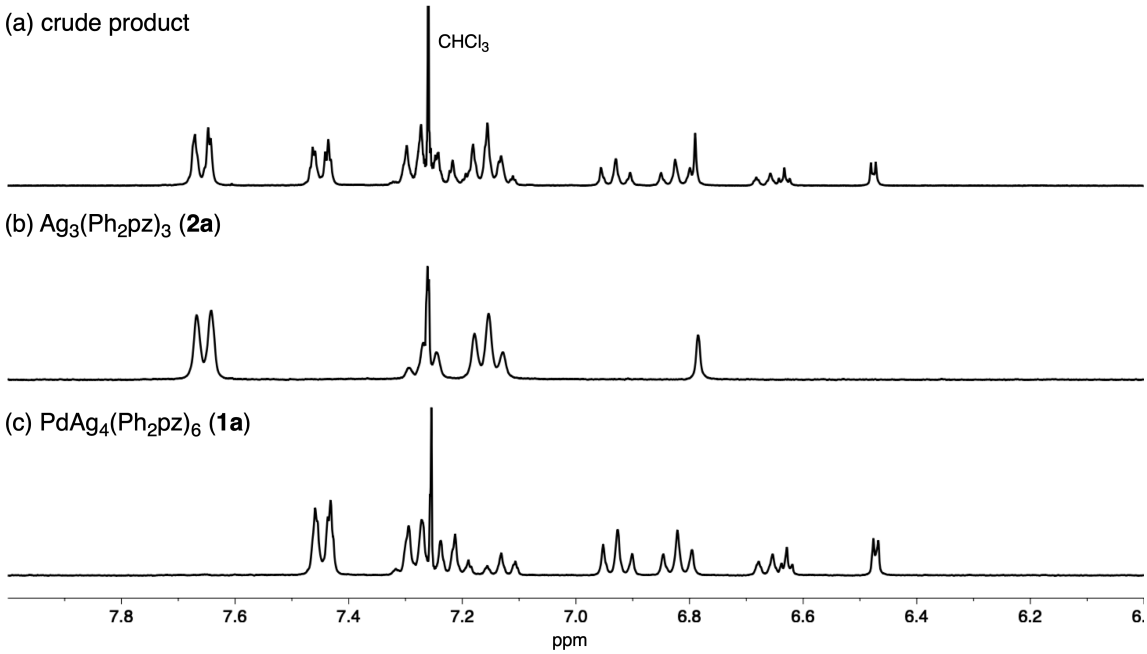
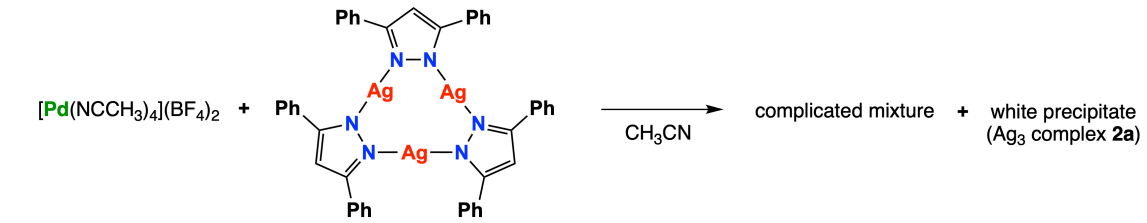


Fig. S13 ^{1}H NMR spectra (500 MHz, $CDCl_3$, r.t.) of (a) crude product, (b) Ag_3 complex **2a**, and (c) $PdAg_4$ complex **1a**.



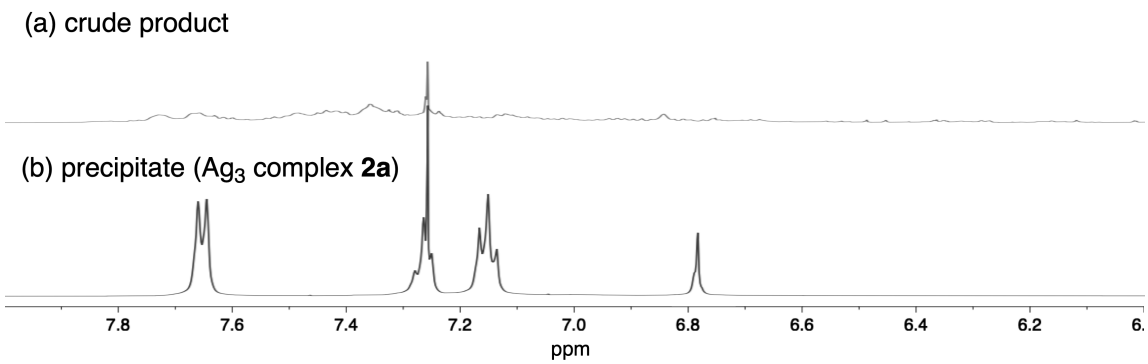


Fig. S14 ^{1}H NMR spectra (500 MHz, $CDCl_3$, r.t.) of the crude product from the reaction of $[Pd(NCCH_3)_4](BF_4)_2$ and Ag_3 complex **2a** indicated that the Pd-pyrazole adduct was a key intermediate in the formation of $PdAg_4$ complex **1a**.

Photophysical data

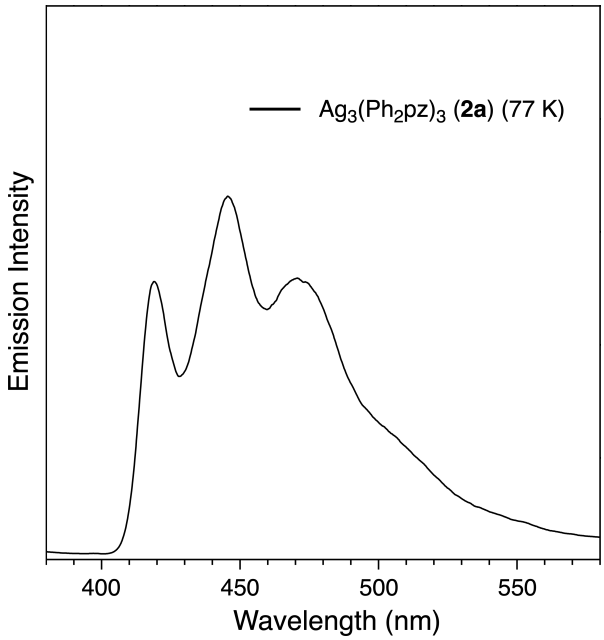


Fig. S15 Emission spectrum of crystalline Ag_3 complex **2a** at 77 K.

X-ray Structural Analysis.

Crystals suitable for X-ray structural analysis were obtained by recrystallization from CH_2Cl_2/MeCN (**1a**•$(MeCN)_4$) and $CHCl_3$/*n*-pentane (**1b**•$(CHCl_3)_2$). The crystal structures were solved using a direct method (SHELXS-97). The positional and thermal parameters of the non-H atoms were refined anisotropically using the full-matrix least-squares method, except for the disordered solvent molecules. All calculations were performed using the CrystalStructure crystallographic software package, except for the refinement, which was performed using SHELXL-97.

Table S1. Crystallographic data for $[PdAg_4(Ph_2pz)_6]$ (**1a**•4MeCN) and $[PdAg_4\{(4\text{-}MeC_6H_4)_2pz\}_6]$ (**1b**•$2CHCl_3$).

	1a·4MeCN	**1b**·$2CHCl_3$
Empirical formula	$C_{98}H_{78}Ag_4N_{16}Pd$	$C_{104}H_{94}Ag_4Cl_6N_{12}Pd$
Formula weight	2017.67	2262.56
Temperature (K)	93(1)	93(1)
Wavelength (Å)	0.71075	0.71075
Crystal system	orthorhombic	orthorhombic
Space group	*Pbcn* (#60)	*Fddd* (#70)
Unit cell dimensions		
a (Å)	23.946(3)	22.207(6)
b (Å)	19.482(3)	23.351(5)
c (Å)	18.327(2)	36.8272(10)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
V (Å^3)	8550.1(19)	19097(7)
Z	4	8
ρ_{calcd} (g/cm^3)	1.567	1.572
μ(Mo Kα) (mm^{-1})	1.164	1.213
F(000)	4048	9088
Index ranges	-31<=h<=30	-28<=h<=28
	-25<=k<=25	-28<=k<=30
	-19<=l<=23	-47<=l<=46
Reflections collected	67668	38064
Independent reflections	9759 [R_{int} = 0.0568]	5439 [R_{int} = 0.0642]
Data / restraints / parameters	9759 / 0 / 539	5439 / 24 / 309
Goodness-of-fit on F^2	1.190	1.132
Final *R* index [$I>2\sigma(I)$][a]	R_1 = 0.0487	R_1 = 0.0601
R indices (all data)[a,b]	R_1 = 0.0561, wR_2 = 0.1123	R_1 = 0.0696, wR_2 = 0.01469
Largest diff. peak and hole (e.Å^{-3})	0.94 and –1.85	1.55 and –1.65
CCDC number	2431540	2431541

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

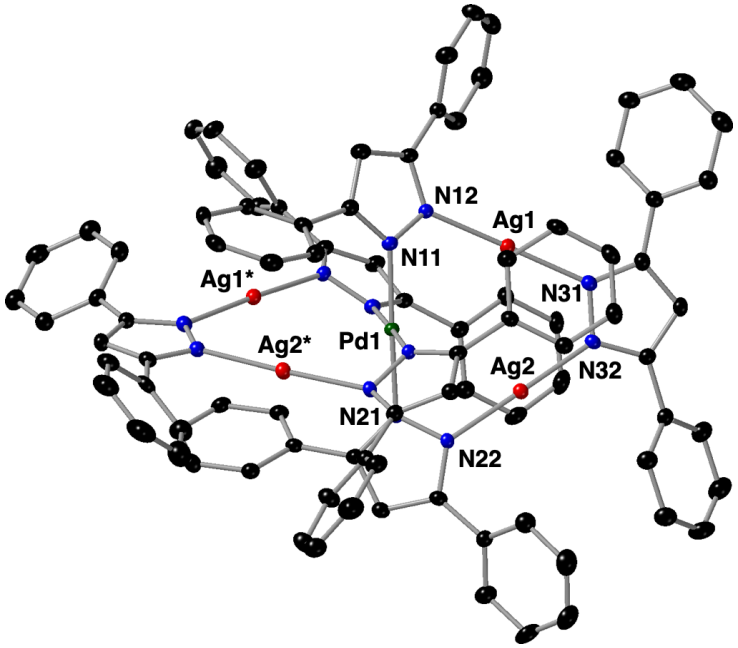


Fig. S16 ORTEP drawing (50% probability ellipsoids) of **1a**. Hydrogen atoms and solvent molecules are omitted for clarity.

Table S2. Selected interatomic distances (Å) for **1a**.

Pd1–N11	2.035(3)	Pd1···Ag1	3.3611(6)
Pd1–N21	2.032(3)	Pd1···Ag2	3.3864(6)
Ag1–N12	2.105(3)	Ag1···Ag2	3.3788(7)
Ag1–N31	2.101(3)		
Ag2–N22	2.098(3)		
Ag2–N32	2.095(3)		

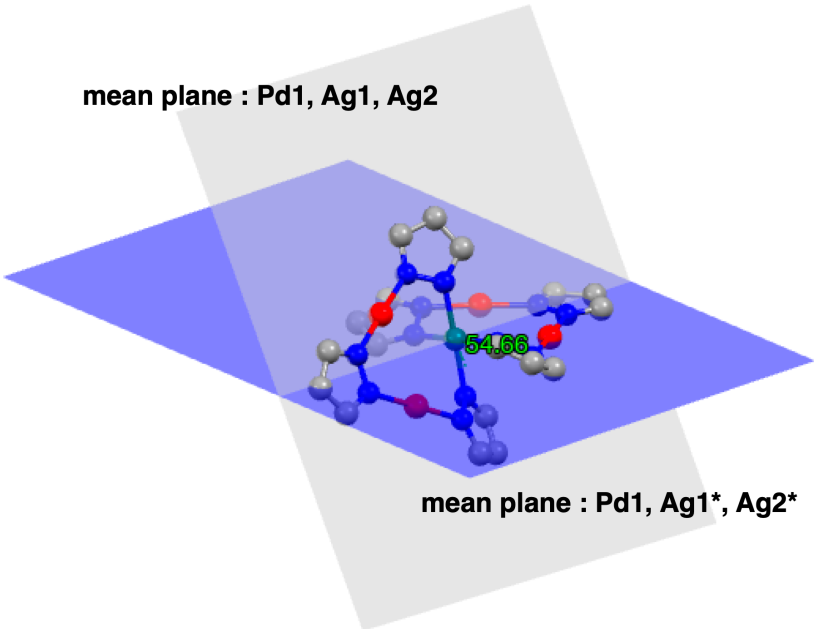


Fig. S17 Dihedral angle between the two $PdAg_2$ planes of **1a**.

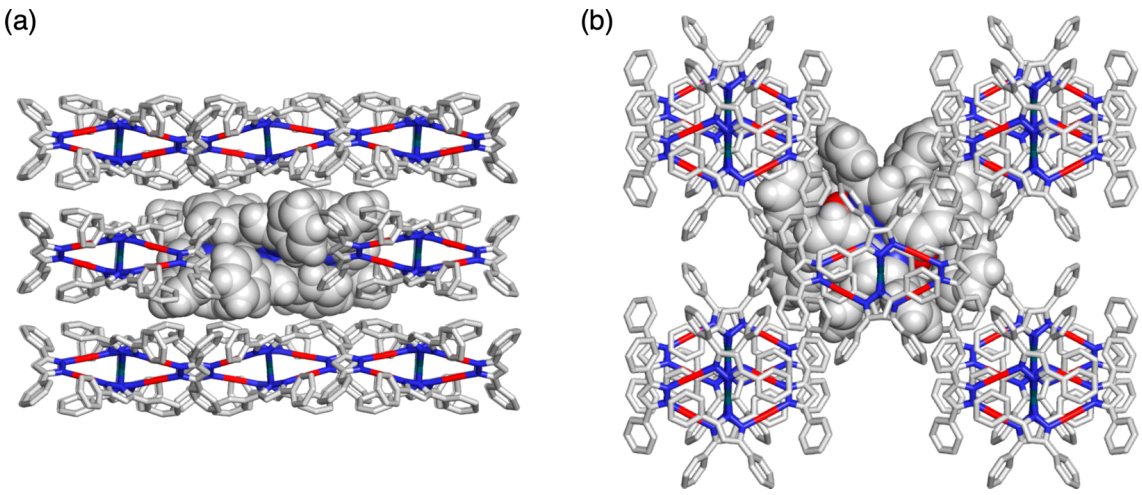


Fig. S18 Packing structures of **1a** viewed from (a) the *b*-axis and (c) the *c*-axis. One $PdAg_4$ complex is highlighted with a space-filling model and solvent molecules are omitted for clarity.

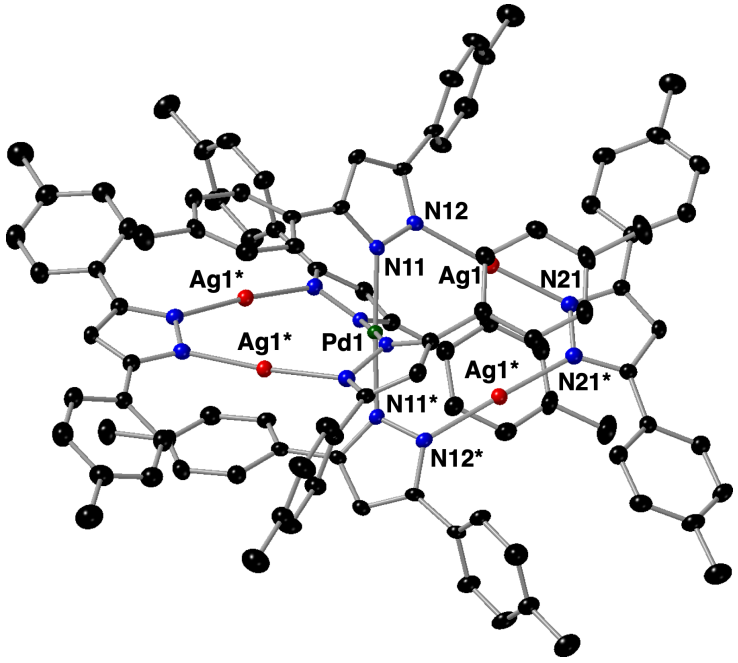


Fig. S19 ORTEP drawing (50% probability ellipsoids) of **1b**. Hydrogen atoms and solvent molecules are omitted for clarity.

Table S3. Selected interatomic distances (Å) for **1b**.

Pd1–N11	2.034(4)	Pd1···Ag1	3.3556(8)
Ag1–N12	2.107(4)	Ag1···Ag1*	3.3133(10)
Ag1–N21	2.104(4)		

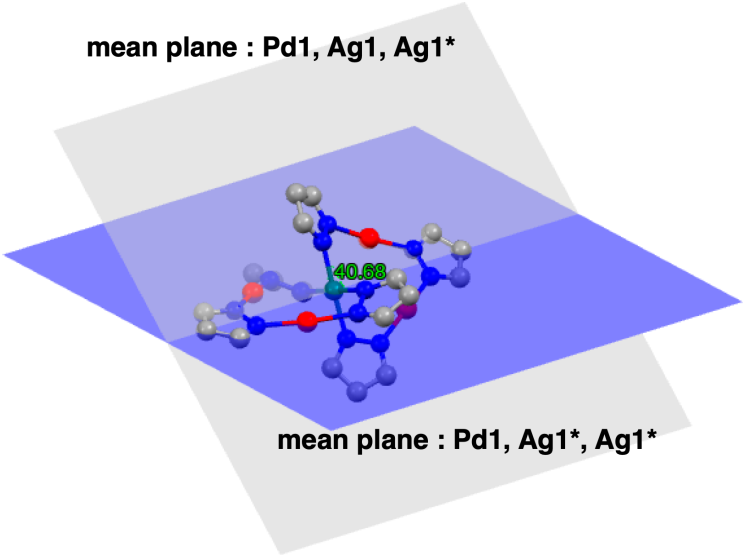


Fig. S20 Dihedral angle between the two $PdAg_2$ planes of **1b**.

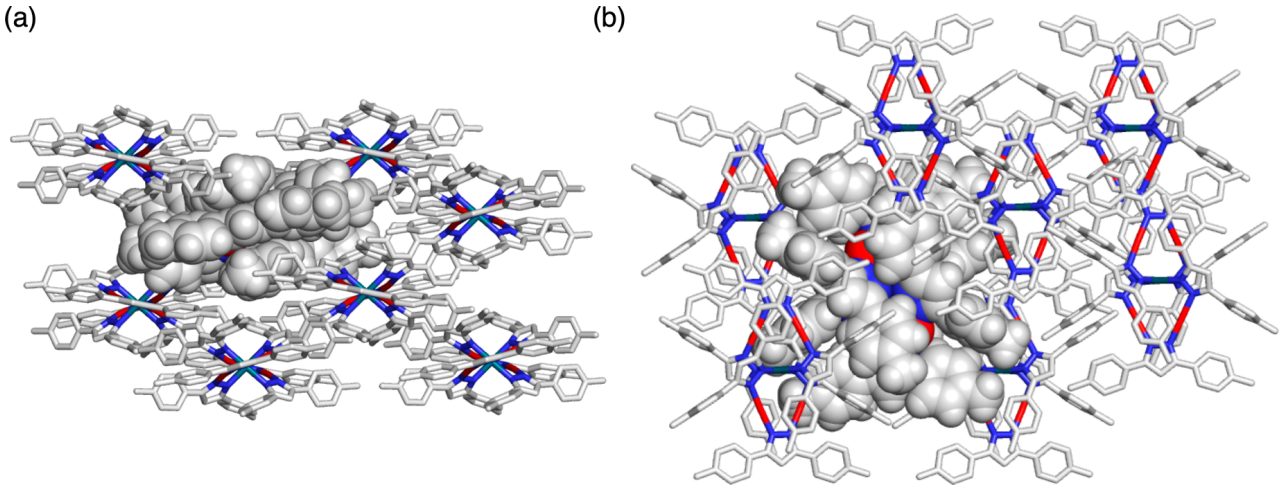


Fig. S21 Packing structures of **1b** viewed from (a) the *b*-axis and (c) the *a*-axis. One $PdAg_4$ complex is highlighted with a space-filling model and solvent molecules are omitted for clarity.

Computational methods.

The geometry of **1a** was optimized with the DFT method, where B3LYP functional was employed.[1] X-ray structure was used as an initial geometry without any geometrical constraints. In these calculations, for all metals, basis sets with ECPs proposed by Christiansen et al were employed.[2] In details, for Ag and Pd atoms, (541/541/211) basis sets were used. For F, C, N, and H atoms, cc-pVDZ basis sets were used.[3] All calculations were carried out using the Gaussian 09 package.[4] Molecular orbitals with the isovalue of 0.02 were drawn by the Gauss View 5.[5]

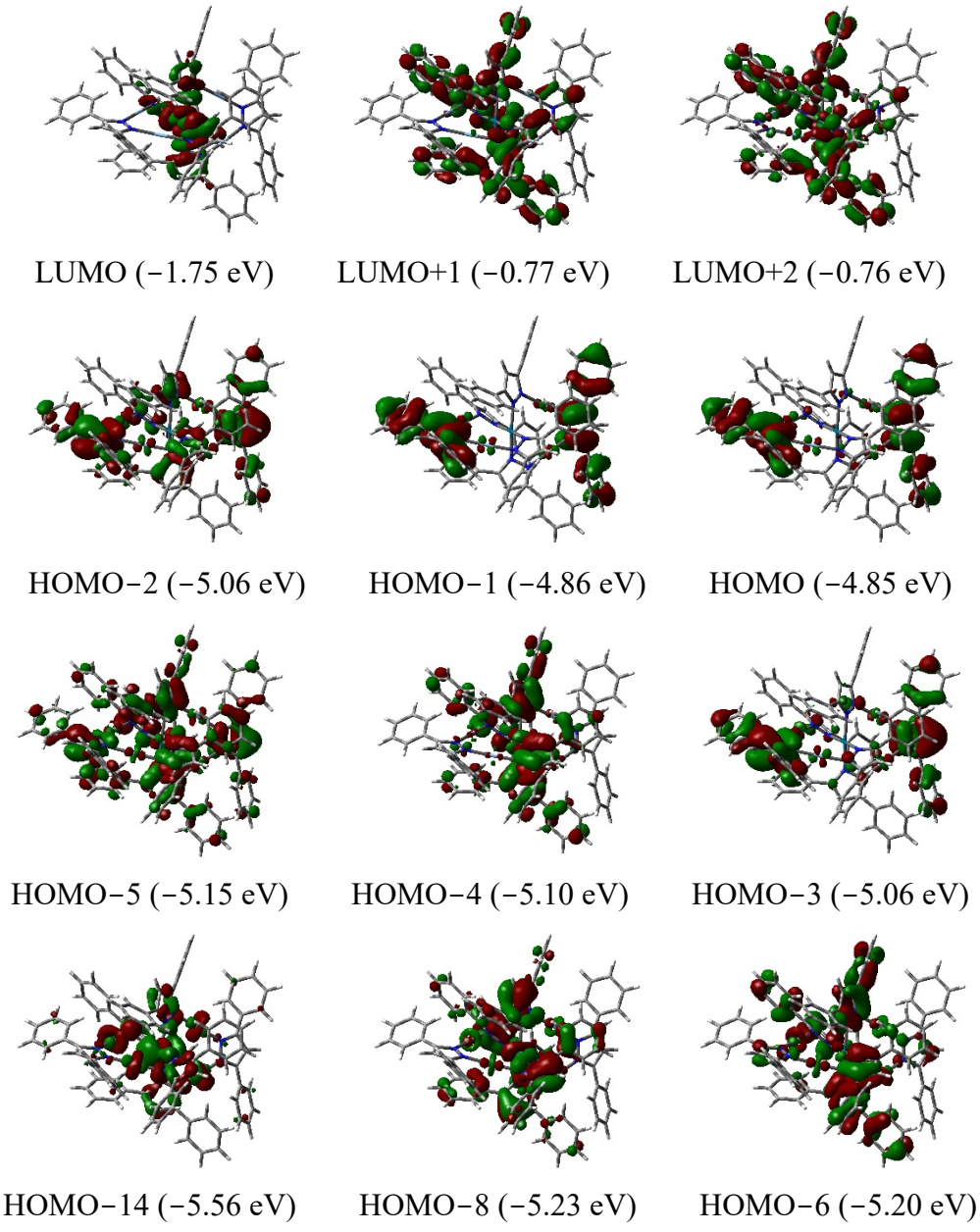


Fig. S22 Molecular orbitals of the singlet state for **1a** by the B3LYP method.

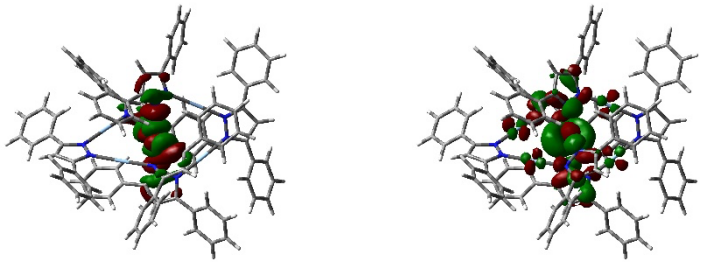


Fig. S23 Singly occupied molecular orbitals of the triplet states of **1a** by the B3LYP method.

Table S4. Emission energies of **1a** by the B3LYP method.

Compound	Singlet optimized geometry		Triplet optimized geometry	
	Emission (eV)	Emission (nm)	Emission (eV)	Emission (nm)
1a	2.43	509	1.28	970

Table S5. Excitation energies of **1a** by the TD-B3LYP method.

Compound	State	Excitation Energy (eV)	Excitation Energy (nm)	Oscillator Strength	Contribution (%)		
1a	1	2.81	441	0.0017	HOMO−4	→ LUMO	28%
					HOMO−8	→ LUMO	10%
	2	2.97	417	0.0022	HOMO−14	→ LUMO	31%
	3	3.15	394	0.0021	HOMO−5	→ LUMO	23%
					HOMO−2	→ LUMO	21%
	4	3.16	392	0.0015	HOMO	→ LUMO	40%
					HOMO−8	→ LUMO	9%
	5	3.19	388	0.0000	HONO−1	→ LUMO	49%
	6	3.21	386	0.0409	HOMO−6	→ LUMO	32%
					HOMO−3	→ LUMO	10%

Table S6. Orbital composition percentage (%) of selected molecular orbitals in **1a**.

	1a			
	Pd	Ag	$Ph_2pz(1)$	$Ph_2pz(2)$
LUMO+2	1	8	88	3
LUMO+1	0	4	94	2
LUMO	45	1	54	0
HOMO	0	3	7	90
HOMO−1	0	3	1	96
HOMO−2	0	4	30	66
HOMO−3	0	4	14	82
HOMO−4	5	2	87	6
HOMO−5	1	5	62	32
HOMO−6	2	7	91	0
HOMO−8	6	7	87	0
HOMO−14	38	18	44	0

$Ph_2pz(1)$ denotes four diphenylpyrazole ligands between Pd and Ag ions. $Ph_2pz(2)$ denotes the two diphenylpyrazole ligands between two Ag ions.

Table S7. Optimized Geometries of $[PdAg_4(Ph_2pz)_6]$ (**1a**) by the B3LYP method.

	Singlet				Triplet		
	x	*y*	*z*		*x*	*y*	*z*
Pd	0.000000	0.000000	0.000821	Pd	0.000000	0.000000	0.021243
Ag	0.791928	3.075562	1.502536	Ag	-2.165356	2.172001	-1.538705
Ag	-0.797705	3.075327	-1.504022	Ag	-0.694988	3.012925	1.521423
Ag	-0.791928	-3.075562	1.502536	Ag	2.165356	-2.172001	-1.538705
Ag	0.797705	-3.075327	-1.504022	Ag	0.694988	-3.012925	1.521423
N	-1.420100	0.098021	-1.523254	N	1.334134	0.803350	1.643884
N	-1.249777	1.150585	-2.372338	N	0.629703	1.620316	2.465109
N	1.420003	0.099747	1.525446	N	-1.386285	-0.727067	-1.600503
N	1.248605	1.153215	2.373367	N	-1.692736	0.291143	-2.443071
N	-0.383579	4.958867	-0.565599	N	-1.985430	4.403617	0.533667
N	0.378264	4.958383	0.561993	N	-2.656538	4.023115	-0.586869
N	1.420100	-0.098021	-1.523254	N	-1.334134	-0.803350	1.643884
N	1.249777	-1.150585	-2.372338	N	-0.629703	-1.620316	2.465109
N	-1.420003	-0.099747	1.525446	N	1.386285	0.727067	-1.600503
N	-1.248605	-1.153215	2.373367	N	1.692736	-0.291143	-2.443071
N	0.383579	-4.958867	-0.565599	N	1.985430	-4.403617	0.533667
N	-0.378264	-4.958383	0.561993	N	2.656538	-4.023115	-0.586869
C	-1.956591	0.908036	-3.502529	C	1.264752	1.698946	3.663313

C	-2.601064	-0.328529	-3.375281	C	2.424972	0.913931	3.602578
C	-2.239579	-0.815189	-2.111715	C	2.439789	0.368259	2.311103
C	-1.953764	1.809480	-4.669511	C	0.737902	2.452467	4.813007
C	-0.766145	2.429893	-5.099718	C	-0.642105	2.479309	5.089310
C	-0.753758	3.220553	-6.251074	C	-1.128775	3.143596	6.217524
C	-1.924526	3.402290	-6.995299	C	-0.248315	3.789343	7.092050
C	-3.110746	2.791914	-6.574996	C	1.125388	3.768122	6.827090
C	-3.125830	2.003931	-5.422273	C	1.613924	3.106604	5.699168
C	-2.730270	-2.081744	-1.524918	C	3.496457	-0.480712	1.729163
C	-2.703139	-3.256190	-2.300943	C	4.147023	-1.441043	2.527346
C	-3.274465	-4.440896	-1.831865	C	5.216897	-2.184765	2.025657
C	-3.893189	-4.474651	-0.579730	C	5.663462	-1.980886	0.716873
C	-3.931618	-3.315044	0.199923	C	5.027294	-1.029937	-0.086377
C	-3.354742	-2.128890	-0.264764	C	3.951726	-0.288232	0.410870
C	1.954722	0.912084	3.504206	C	-2.088641	-0.223084	-3.635847
C	2.599904	-0.324369	3.378703	C	-2.042996	-1.621928	-3.551920
C	2.239162	-0.812486	2.115541	C	-1.602568	-1.904375	-2.250874
C	1.950480	1.814206	4.670633	C	-2.435754	0.604883	-4.803256
C	0.762193	2.434226	5.099516	C	-1.710954	1.773562	-5.103768
C	0.748380	3.225231	6.250638	C	-2.005857	2.518506	-6.248069
C	1.918341	3.407717	6.995927	C	-3.025208	2.109620	-7.114469
C	3.105227	2.797747	6.576912	C	-3.751308	0.949161	-6.825230
C	3.121744	2.009443	5.424423	C	-3.459811	0.204090	-5.681280
C	2.730150	-2.079528	1.529982	C	-1.457631	-3.243767	-1.648972
C	3.353133	-2.127701	0.269154	C	-1.900608	-3.514645	-0.340265
C	3.930773	-3.313895	-0.194545	C	-1.854796	-4.814743	0.172295
C	3.894430	-4.472443	0.586769	C	-1.361713	-5.865834	-0.606430
C	3.276942	-4.437689	1.839490	C	-0.915054	-5.608137	-1.905642
C	2.704950	-3.252925	2.307659	C	-0.965178	-4.312144	-2.422302
C	0.631888	6.243505	0.916171	C	-3.496457	5.024654	-0.951764
C	0.000000	7.092330	-0.002758	C	-3.348151	6.083695	-0.046777
C	-0.633830	6.244222	-0.921017	C	-2.381552	5.656574	0.872890
C	1.475727	6.626806	2.062453	C	-4.427223	4.934169	-2.091293
C	2.312111	7.755706	1.959347	C	-5.721663	5.476805	-1.973849
C	3.124658	8.146757	3.024423	C	-6.629052	5.401103	-3.031489
C	3.124941	7.414419	4.216122	C	-6.265626	4.774770	-4.228445
C	2.297698	6.294121	4.334307	C	-4.982983	4.235796	-4.360940
C	1.475863	5.909358	3.271761	C	-4.070343	4.322947	-3.306183
C	-1.476730	6.628063	-2.067849	C	-1.822224	6.410854	2.009247
C	-1.478616	5.908749	-3.276077	C	-1.518634	5.801503	3.239458

C	-2.299854	6.293651	-4.339036	C	-0.973523	6.542240	4.291700
C	-3.124728	7.415867	-4.222336	C	-0.737902	7.911548	4.140957
C	-3.122619	8.150024	-3.031773	C	-1.050033	8.534563	2.927933
C	-2.310686	7.758846	-1.966255	C	-1.582369	7.792026	1.872948
C	1.956591	-0.908036	-3.502529	C	-1.264752	-1.698946	3.663313
C	2.601064	0.328529	-3.375281	C	-2.424972	-0.913931	3.602578
C	2.239579	0.815189	-2.111715	C	-2.439789	-0.368259	2.311103
C	1.953764	-1.809480	-4.669511	C	-0.737902	-2.452467	4.813007
C	0.766145	-2.429893	-5.099718	C	0.642105	-2.479309	5.089310
C	0.753758	-3.220553	-6.251074	C	1.128775	-3.143596	6.217524
C	1.924526	-3.402290	-6.995299	C	0.248315	-3.789343	7.092050
C	3.110746	-2.791914	-6.574996	C	-1.125388	-3.768122	6.827090
C	3.125830	-2.003931	-5.422273	C	-1.613924	-3.106604	5.699168
C	2.730270	2.081744	-1.524918	C	-3.496457	0.480712	1.729163
C	2.703139	3.256190	-2.300943	C	-4.147023	1.441043	2.527346
C	3.274465	4.440896	-1.831865	C	-5.216897	2.184765	2.025657
C	3.893189	4.474651	-0.579730	C	-5.663462	1.980886	0.716873
C	3.931618	3.315044	0.199923	C	-5.027294	1.029937	-0.086377
C	3.354742	2.128890	-0.264764	C	-3.951726	0.288232	0.410870
C	-1.954722	-0.912084	3.504206	C	2.088641	0.223084	-3.635847
C	-2.599904	0.324369	3.378703	C	2.042996	1.621928	-3.551920
C	-2.239162	0.812486	2.115541	C	1.602568	1.904375	-2.250874
C	-1.950480	-1.814206	4.670633	C	2.435754	-0.604883	-4.803256
C	-0.762193	-2.434226	5.099516	C	1.710954	-1.773562	-5.103768
C	-0.748380	-3.225231	6.250638	C	2.005857	-2.518506	-6.248069
C	-1.918341	-3.407717	6.995927	C	3.025208	-2.109620	-7.114469
C	-3.105227	-2.797747	6.576912	C	3.751308	-0.949161	-6.825230
C	-3.121744	-2.009443	5.424423	C	3.459811	-0.204090	-5.681280
C	-2.730150	2.079528	1.529982	C	1.457631	3.243767	-1.648972
C	-3.353133	2.127701	0.269154	C	1.900608	3.514645	-0.340265
C	-3.930773	3.313895	-0.194545	C	1.854796	4.814743	0.172295
C	-3.894430	4.472443	0.586769	C	1.361713	5.865834	-0.606430
C	-3.276942	4.437689	1.839490	C	0.915054	5.608137	-1.905642
C	-2.704950	3.252925	2.307659	C	0.965178	4.312144	-2.422302
C	-0.631888	-6.243505	0.916171	C	3.496457	-5.024654	-0.951764
C	0.000000	-7.092330	-0.002758	C	3.348151	-6.083695	-0.046777
C	0.633830	-6.244222	-0.921017	C	2.381552	-5.656574	0.872890
C	-1.475727	-6.626806	2.062453	C	4.427223	-4.934169	-2.091293
C	-2.312111	-7.755706	1.959347	C	5.721663	-5.476805	-1.973849
C	-3.124658	-8.146757	3.024423	C	6.629052	-5.401103	-3.031489

C	-3.124941	-7.414419	4.216122	C	6.265626	-4.774770	-4.228445
C	-2.297698	-6.294121	4.334307	C	4.982983	-4.235796	-4.360940
C	-1.475863	-5.909358	3.271761	C	4.070343	-4.322947	-3.306183
C	1.476730	-6.628063	-2.067849	C	1.822224	-6.410854	2.009247
C	1.478616	-5.908749	-3.276077	C	1.518634	-5.801503	3.239458
C	2.299854	-6.293651	-4.339036	C	0.973523	-6.542240	4.291700
C	3.124728	-7.415867	-4.222336	C	0.737902	-7.911548	4.140957
C	3.122619	-8.150024	-3.031773	C	1.050033	-8.534563	2.927933
C	2.310686	-7.758846	-1.966255	C	1.582369	-7.792026	1.872948
H	-3.247513	-0.817600	-4.098348	H	3.161867	0.766822	4.386820
H	0.156442	2.252012	-4.544226	H	-1.324963	1.938879	4.431723
H	0.180042	3.683897	-6.579238	H	-2.201727	3.143846	6.424177
H	-1.910890	4.012732	-7.901451	H	-0.630013	4.300808	7.978640
H	-4.030972	2.930887	-7.147609	H	1.821101	4.271530	7.502466
H	-4.056347	1.535310	-5.093933	H	2.686214	3.101658	5.492332
H	-2.229298	-3.235055	-3.284633	H	3.807484	-1.605196	3.552242
H	-3.232338	-5.342215	-2.447640	H	5.702201	-2.929507	2.660563
H	-4.338636	-5.400432	-0.209510	H	6.498865	-2.562609	0.321979
H	-4.421702	-3.327912	1.176252	H	5.373008	-0.858325	-1.108356
H	-3.413143	-1.225131	0.340673	H	3.471072	0.462530	-0.215521
H	3.246047	-0.812426	4.102725	H	-2.304636	-2.336863	-4.326671
H	-0.159810	2.255806	4.543197	H	-0.886102	2.068282	-4.452862
H	-0.185937	3.688285	6.577743	H	-1.424923	3.416061	-6.473559
H	1.903596	4.018424	7.901883	H	-3.248295	2.688733	-8.013484
H	4.024873	2.937319	7.150334	H	-4.551141	0.622767	-7.494057
H	4.052766	1.541145	5.097076	H	-4.036338	-0.695489	-5.455306
H	3.409800	-1.224720	-0.337632	H	-2.304040	-2.703919	0.265619
H	4.419828	-3.327602	-1.171370	H	-2.213678	-5.006619	1.186129
H	4.340646	-5.398199	0.217417	H	-1.321885	-6.878489	-0.200109
H	3.236322	-5.338294	2.456387	H	-0.521382	-6.420183	-2.521112
H	2.232047	-3.230824	3.291784	H	-0.615452	-4.121029	-3.438988
H	0.001291	8.178513	-0.003215	H	-3.871779	7.035157	-0.055862
H	2.335058	8.317907	1.023217	H	-6.019328	5.944702	-1.033110
H	3.768076	9.024043	2.919605	H	-7.629374	5.825720	-2.916837
H	3.764565	7.717078	5.048703	H	-6.977772	4.710303	-5.054327
H	2.280770	5.714959	5.259574	H	-4.680291	3.750840	-5.290960
H	0.809769	5.052653	3.394541	H	-3.059679	3.932416	-3.440414
H	-0.814467	5.050332	-3.397613	H	-1.733458	4.741247	3.386669
H	-2.284366	5.713016	-5.263439	H	-0.742485	6.042080	5.234128
H	-3.763943	7.718610	-5.055194	H	-0.315714	8.491346	4.964962

H	-3.764113	9.028866	-2.928166	H	-0.869329	9.604502	2.798829
H	-2.332175	8.322552	-1.030997	H	-1.801573	8.278559	0.920192
H	3.247513	0.817600	-4.098348	H	-3.161867	-0.766822	4.386820
H	-0.156442	-2.252012	-4.544226	H	1.324963	-1.938879	4.431723
H	-0.180042	-3.683897	-6.579238	H	2.201727	-3.143846	6.424177
H	1.910890	-4.012732	-7.901451	H	0.630013	-4.300808	7.978640
H	4.030972	-2.930887	-7.147609	H	-1.821101	-4.271530	7.502466
H	4.056347	-1.535310	-5.093933	H	-2.686214	-3.101658	5.492332
H	2.229298	3.235055	-3.284633	H	-3.807484	1.605196	3.552242
H	3.232338	5.342215	-2.447640	H	-5.702201	2.929507	2.660563
H	4.338636	5.400432	-0.209510	H	-6.498865	2.562609	0.321979
H	4.421702	3.327912	1.176252	H	-5.373008	0.858325	-1.108356
H	3.413143	1.225131	0.340673	H	-3.471072	-0.462530	-0.215521
H	-3.246047	0.812426	4.102725	H	2.304636	2.336863	-4.326671
H	0.159810	-2.255806	4.543197	H	0.886102	-2.068282	-4.452862
H	0.185937	-3.688285	6.577743	H	1.424923	-3.416061	-6.473559
H	-1.903596	-4.018424	7.901883	H	3.248295	-2.688733	-8.013484
H	-4.024873	-2.937319	7.150334	H	4.551141	-0.622767	-7.494057
H	-4.052766	-1.541145	5.097076	H	4.036338	0.695489	-5.455306
H	-3.409800	1.224720	-0.337632	H	2.304040	2.703919	0.265619
H	-4.419828	3.327602	-1.171370	H	2.213678	5.006619	1.186129
H	-4.340646	5.398199	0.217417	H	1.321885	6.878489	-0.200109
H	-3.236322	5.338294	2.456387	H	0.521382	6.420183	-2.521112
H	-2.232047	3.230824	3.291784	H	0.615452	4.121029	-3.438988
H	-0.001291	-8.178513	-0.003215	H	3.871779	-7.035157	-0.055862
H	-2.335058	-8.317907	1.023217	H	6.019328	-5.944702	-1.033110
H	-3.768076	-9.024043	2.919605	H	7.629374	-5.825720	-2.916837
H	-3.764565	-7.717078	5.048703	H	6.977772	-4.710303	-5.054327
H	-2.280770	-5.714959	5.259574	H	4.680291	-3.750840	-5.290960
H	-0.809769	-5.052653	3.394541	H	3.059679	-3.932416	-3.440414
H	0.814467	-5.050332	-3.397613	H	1.733458	-4.741247	3.386669
H	2.284366	-5.713016	-5.263439	H	0.742485	-6.042080	5.234128
H	3.763943	-7.718610	-5.055194	H	0.315714	-8.491346	4.964962
H	3.764113	-9.028866	-2.928166	H	0.869329	-9.604502	2.798829
H	2.332175	-8.322552	-1.030997	H	1.801573	-8.278559	0.920192

One imaginary frequency (−5.26 cm^{-1}) at the triplet optimized geometry could not be eliminated because of the large molecules. It is considered that a small frequency does not affect the estimation of emission energy.

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