Supporting Information

Bimolecular Fusion of $[Pd_3(\mu\text{-}CN\text{-}C_6H_3Me_2\text{-}2,6)_3(CN\text{-}C_6H_3Me_2\text{-}2,6)_3]$ Induced by Ph_2GeH_2: Formation of Redox-Active Pd_6Ge_2 Complex†

Take-aki Koizumi,[1] Kimiya Tanaka,[1] Yoshitaka Tsuchido,[1] Makoto Tanabe,[1] Tomohito Tomohito Ide[2] and Kohtaro Osakada*,[1]

[1] *Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, 4259-R1-3 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

[2] *Department of Chemistry, National Institute of Technology, Tokyo College, 1220-2 Kunugida-machi, Hachioji-shi, Tokyo, 193-0997, Japan.*

Figure S23. UV-vis spectra and calculated peak positions.

1. Experimental Section

General considerations

All the procedures for synthesis, purification, and characterization were done under inert gas atmosphere, using Schlenk-type flask and glove-box. $[Pd_3(CN(C_6H_4\text{-}2,6\text{-}Me_2))_6]$ [1] and $[Pd(dba)_2]$ [2] were prepared according to the literature method. All other commercially available reagents were used as purchased. ^1H, $^{13}C\{^1H\}$, and ^1H–^1H COSY NMR spectra were recorded on a JEOL GX-500 spectrometer. Electrochemical measurements were performed with ALS/chi Electrochemical Analyzer 660A. A conventional three-electrode configuration was used, with glassy carbon working (BAS PFCE carbon electrode) and platinum wire auxiliary electrode (Nilaco special order) and 0.01 M $AgNO_3$/Ag reference (BAS RE-5). Cyclic voltammograms were recorded at a scan rate of 100 mV s^{-1}. Elemental analyses were carried out at the Suzukakedai Materials Analysis Division, Technical Department, Tokyo Institute of Technology.

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Synthesis of $[Pd_6(GePh_2)(CN(2,6\text{-dimethylphenyl})_{10})]$ (**2**)

Method A. To a THF (2 mL) solution of $[Pd_3(CN(C_6H_4\text{-}2,6\text{-}Me_2)_6]$ (96 mg, 0.087 mmol) was added H_2GePh_2 (20 mg, 0.087 mmol) and stirred at rt. After 2 h, diethyl ether (20 mL) was added to the solution, and the solution was cooled at –25 ºC. The solution was removed by cannula filtration and resulting black crystals were dried under the vacuum. Yield: 86 mg (82%). ^1H NMR (400 MHz, [D$_6$]benzene, RT): δ = 8.45 (d, 8H, *J*(H-H) = 7.0 Hz, $GeC_6\underline{H}_5$ *ortho*), 7.17 (t, 8H, *J*(H-H) = 7.0 Hz, $GeC_6\underline{H}_5$ *meta*), 7.10 (t, 4H, *J*(H-H) = 7.0 Hz, $GeC_6\underline{H}_5$ *para*), 6.65-6.28 (m, 16H; $CNC_6\underline{H}_3(CH_3)_2$-4,6), 6.57 (d, 8H *J*(H-H) = 7.6 Hz, $CNC_6\underline{H}_3(CH_3)_2$-4,6), 6.42 (d, 4H *J*(H-H) = 7.5 Hz, $CNC_6\underline{H}_3(CH_3)_2$-4,6), 6.30 (t, 2H *J*(H-H) = 7.6 Hz, $CNC_6\underline{H}_3(CH_3)_2$-4,6), 2.32 (s, 24H; $CNC_6H_3(C\underline{H}_3)_2$-4,6), 1.99 (s, 12H; $CNC_6H_3(C\underline{H}_3)_2$-4,6), 1.92 (s, 24H; $CNC_6H_3(C\underline{H}_3)_2$-4,6); $^{13}C\{^1H\}$ NMR (126 MHz, [D$_6$]benzene, RT): δ = 172.9 (N$\underline{C}$), 166.0 (N$\underline{C}$), 162.0 (Ge$\underline{C}_6H_5$ *ipso*), 136.2, 135.7 (N$\underline{C}$), 134.8, 133.3, 130.8, 129.3, 129.0, 128.6, 127.5, 127.5, 127.3, 126.9, 126.8, 125.9, 123.2, 19.5 (-$\underline{C}H_3$), 18.7 (-$\underline{C}H_3$), 18.6 (-$\underline{C}H_3$); elemental analysis calcd (%) for $C_{114}H_{110}Ge_2N_{10}Pd_6$: C 56.96, H 4.61, N 5.83; found: C 56.62, H 5.01, N 5.55. IR (KBr, cm^{-1}): 3036, 2977, 2054, 2033, 1997, 1915, 1586, 1460, 1426, 1380, 1261, 1188, 1164, 1089, 1072, 765, 727, 719, 694, 659. UV-vis (THF, RT): λ (nm) = 445,

559 (sh), 670, 770 (sh).

Method B. To a THF (1mL) solution of $Pd(dba)_2$ (100 mg, 0.17 mmol) was added 2,6-dimethylphenylisocyanide (48 mg, 0.366 mmol) and stirred at rt. After 5 min., H_2GePh_2 (11 mg, 0.48 mmol) was added to the solution and stirred at rt for 12 h. Recrystallization from THF/hexane (1:10) and washing with MeCN and diethyl ether gave **2** as black crystals (53 mg, 0.022 mmol, 76%).

Synthesis of $[Pd_6(GePh_2)(CN(2,6\text{-dimethylphenyl})_8)(S(C_6H_4\text{-}4\text{-}NO_2)_2]$ (**3**)
To a THF (1mL) solution of **2** (42 mg, 17 μmol) was added bis(4-nitrophenyl)disulfide (6.0 mg, 20 mmol) and stirred at rt. After 2 h, diethyl ether (20 mL) was added to the solution, and the solution was cooled at –25 °C. The solution was removed by cannula filtration and resulting deep green crystals were dried under the vacuum. Yield: 22 mg (9.1 μmol, 52%). ^{1}H NMR (500 MHz, [D_6]benzene, RT): δ = 8.36 (d, 8H; *J*(H-H) = 7.3 Hz, $GeC_6\underline{H}_5$ *ortho*), 7.84 (d, 4H, *J*(H-H) = 8.5 Hz, $SC_6\underline{H}_4\text{-}NO_2$), 7.30 (d, 4H, *J*(H-H) = 8.5 Hz, $SC_6\underline{H}_4\text{-}NO_2$), 7.07 (t, 8H; *J*(H-H) = 7.6 Hz, $GeC_6\underline{H}_5$ *meta*), 6.99 (t, 4H; $GeC_6\underline{H}_5$ *para*), 6.79 (t, 4H, *J*(H-H) = 7.6 Hz, $CNC_6\underline{H}_3(CH_3)_2$-4,6 *para*), 6.69 (t, 4H, *J*(H-H) = 7.6 Hz, $CNC_6\underline{H}_3(CH_3)_2$-4,6 *para*), 6.67 (d, 8H, *J*(H-H) = 7.6 Hz, $CNC_6\underline{H}_3(CH_3)_2$-4,6 *meta*), 6.57 (d, 8H, *J*(H-H) = 7.6 Hz, $CNC_6\underline{H}_3(CH_3)_2$-4,6 *meta*), 2.09 (s, 24H; $CNC_6H_3(C\underline{H}_3)_2$-4,6), 1.93 (s, 24H; $CNC_6H_3(C\underline{H}_3)_2$-4,6), $^{13}C\{^1H\}$ NMR (126 MHz, [D_6]benzene, RT): δ = 165.6, 154.1, 152.4, 143.0, 136.0, 134.8, 133.4, 132.3, 129.0, 128.2, 127.3, 127.1, 127.0, 126.8, 126.3, 121.7, 18.8 ($-\underline{C}H_3$), 18.4 ($-\underline{C}H_3$); elemental analysis: Found(%): C 52.70, H 4.23, N 5.48, S 2.33; calcd (%) for $C_{114}H_{110}Ge_2N_{10}Pd_6$: C 52.95, H 4.11, N 5.72, S 2.82. IR (KBr, cm^{-1}): 3059, 2921, 2098, 2057, 1995, 1587, 1566, 1496, 1465, 1315, 1183, 1080, 849, 768, 743, 730, 720, 697, 660. UV-vis (THF, RT): λ (nm) = 458 (sh), 640.

2. X-ray results

Crystal structure determination

Crystals for X-ray analyses were obtained as described in the preparations. Suitable crystals were mounted on glass fibers or sealed in thin-walled glass capillaries. Data collection for **2** was performed at -180 ^{o}C on a Rigaku/XtaLAB Synergy-DW diffractometer with graphite monochromated Cu Kα radiation (λ = 1.54184 Å). The structure was solved by using the OLEX2 software package [3]. Refinements were performed anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. Hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. Selected bond lengths of complex **2** are summarized in Table S1. Crystal data and processing parameters are summarized in Table S2.

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Table S1. Selected bond lengths (Å) and angles (^{o}) of **2**.

Molecule A		Molecule B	
Pd1-Pd2	2.8053(5)	Pd7-Pd8	2.8060(5)
Pd1-Pd3	2.9434(5)	Pd7-Pd9	2.8698(6)
Pd1-Pd4	2.7570(6)	Pd7-Pd10	2.7587(6)
Pd1-Pd5	2.8797(5)	Pd7-Pd11	2.8414(6)
Pd1-Pd6	2.7929(6)	Pd7-Pd12	2.7829(6)
Pd2-Pd3	2.7239(5)	Pd8-Pd9	2.8085(6)
Pd2-Pd4	3.0369(5)	Pd8-Pd10	2.8953(6)
Pd2-Pd5	2.8053(5)	Pd8-Pd11	2.8504(6)
Pd2-Pd6	2.9333(6)	Pd8-Pd12	2.8676(6)
Pd3-Pd4	2.7049(5)	Pd9-Pd10	2.6788(5)
Pd5-Pd6	2.6962(5)	Pd11-Pd12	2.6872(6)
Pd1-Ge1	2.9687(7)	Pd7-Ge3	2.9759(7)
Pd1-Ge2	2.8328(7)	Pd7-Ge4	2.9444(8)

Pd2-Ge1	2.9281(8)	Pd8-Ge3	2.9895(8)
Pd2-Ge2	3.0859(7)	Pd8-Ge4	3.0866(7)
Pd3-Ge1	2.4629(8)	Pd9-Ge3	2.4460(7)
Pd4-Ge2	2.4631(7)	Pd10-Ge4	2.4400(8)
Pd5-Ge2	2.4375(7)	Pd11-Ge4	2.4510(7)
Pd6-Ge1	2.4545(8)	Pd12-Ge3	2.4515(8)
Pd1-C25	1.993(6)	Pd7-C139	1.972(7)
Pd1-C34	1.986(8)	Pd7-C148	1.966(6)
Pd2-C52	1.975(6)	Pd8-C157	1.972(7)
Pd2-C9FA	1.966(6)	Pd8-C166	1.979(7)
Pd3-C61	2.137(6)	Pd9-C175	2.098(6)
Pd3-C70	1.959(6)	Pd9-C184	1.949(6)
Pd4-C61	2.118(6)	Pd10-C175	2.124(6)
Pd4-C79	1.957(6)	Pd10-C193	1.944(6)
Pd5-C88	2.128(6)	Pd11-C202	2.101(6)
Pd5-C97	1.962(6)	P11-C211	1.931(6)
Pd6-C88	2.096(6)	Pd12-C202	2.121(6)
Pd6-C106	1.959(6)	Pd12-C220	1.951(6)
Ge1-C1	1.990(7)	Ge3-C115	1.996(6)
Ge1-C7	2.010(6)	Ge3-C121	1.990(6)
Ge2-C13	2.002(5)	Ge4-C127	1.993(6)
Ge2-C19	1.992(6)	Ge4-C133	2.012(6)
C61-N5-C62	163.5(6)	C175-N15-C176	149.5(6)
C88-N8-C89	160.5(7)	C202-N18-C203	150.3(6)

Table S2. X-ray crystallographic details.

Compound	Complex **2**
Empirical formula	$C_{238}H_{240}Ge_4N_{20}OPd_{12}$
Formula weight	4963.62
Crystal system	triclinic
Space group	*P*1 (No. 1)

a/Å	15.27410(10)
b/Å	16.00210(10)
c/Å	26.7383(3)
α/°	83.0180(10)
β/°	74.7000(10)
γ/°	62.5470(10)
Volume/Å^3	5593.82(10)
Z	1
D_{calc} g/cm^3	1.473
μ/mm^{-1}	8.589
F(000)	2496.0
Reflections collected	69463
Data/restraints/parameters	32657/3/2538
R [all data]	0.0287
R_1 [$I > 2\sigma(I)$]	0.0278
$_wR2$ [all data]	0.0705
GOF on F^2	1.057
ρ_{max}/hole / e Å^{-3}	0.68/-0.79

Disordered solvent molecules were removed by SQUEEZE program and the result was attached to the CIF file.[1-6]

1. Rigaku CrystalStructure, Version 4.2 (2015).
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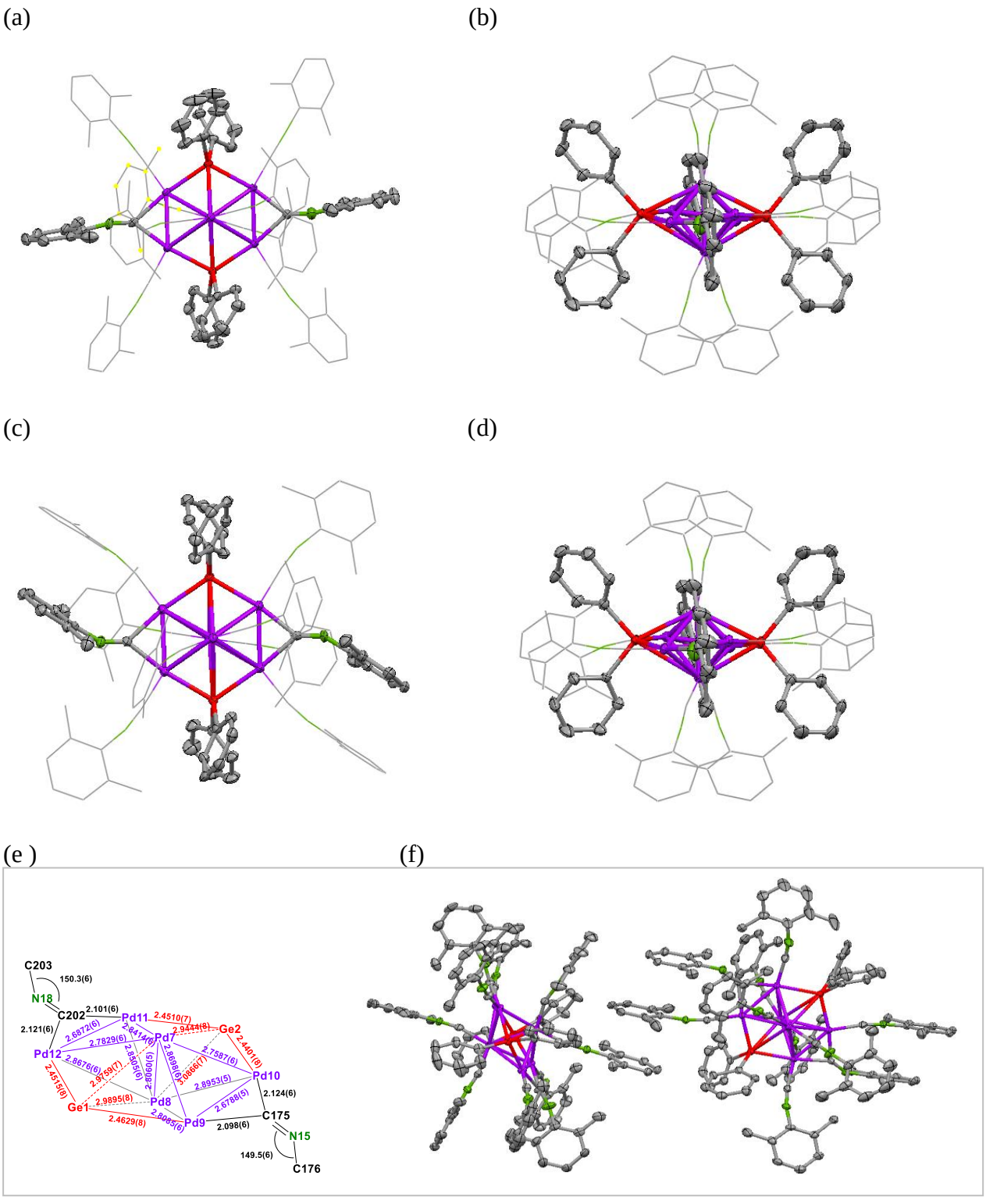

Figure S1. ORTEP drawing of complex **2**. Molecule A: (a) Top view, (b) side view, Molecule B: (c) Top view, (d) side view. (e) Atomic numbering of molecule B. (f) Packing of the molecules.

3. NMR spectra

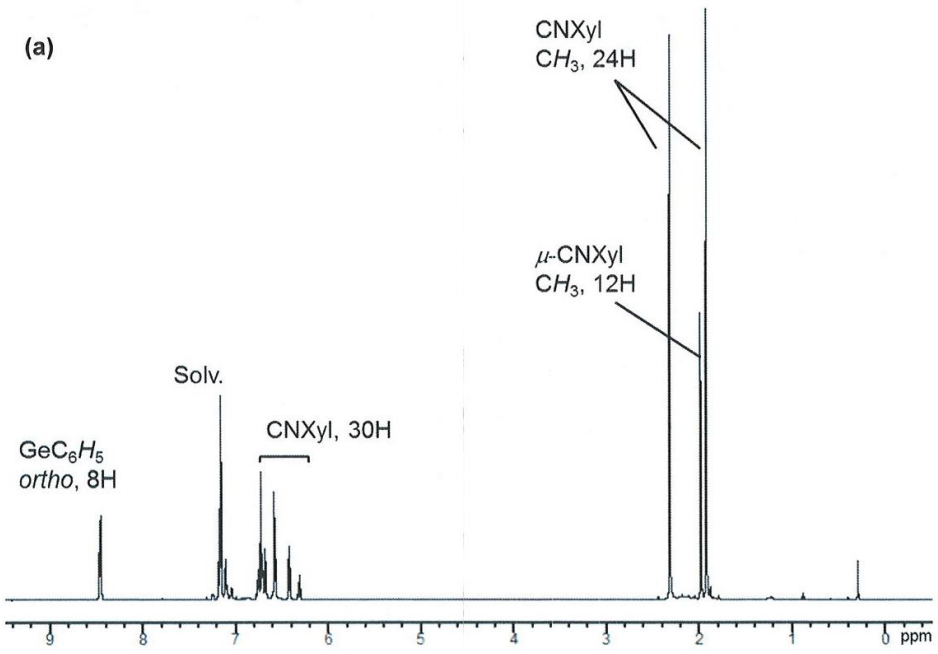

Figure S2. ^{1}H-NMR spectrum of **2** in C_6D_6.

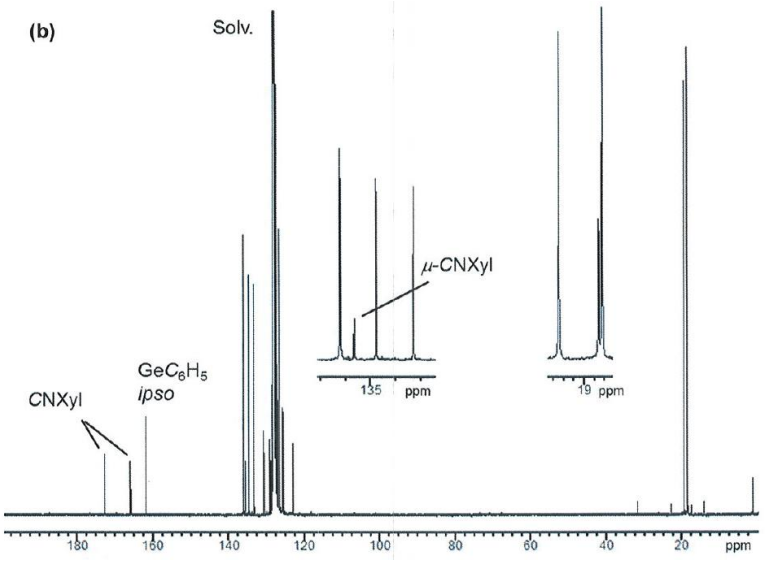

Figure S3. ^{13}C{^{1}H}-NMR spectrum of **2** in C_6D_6.

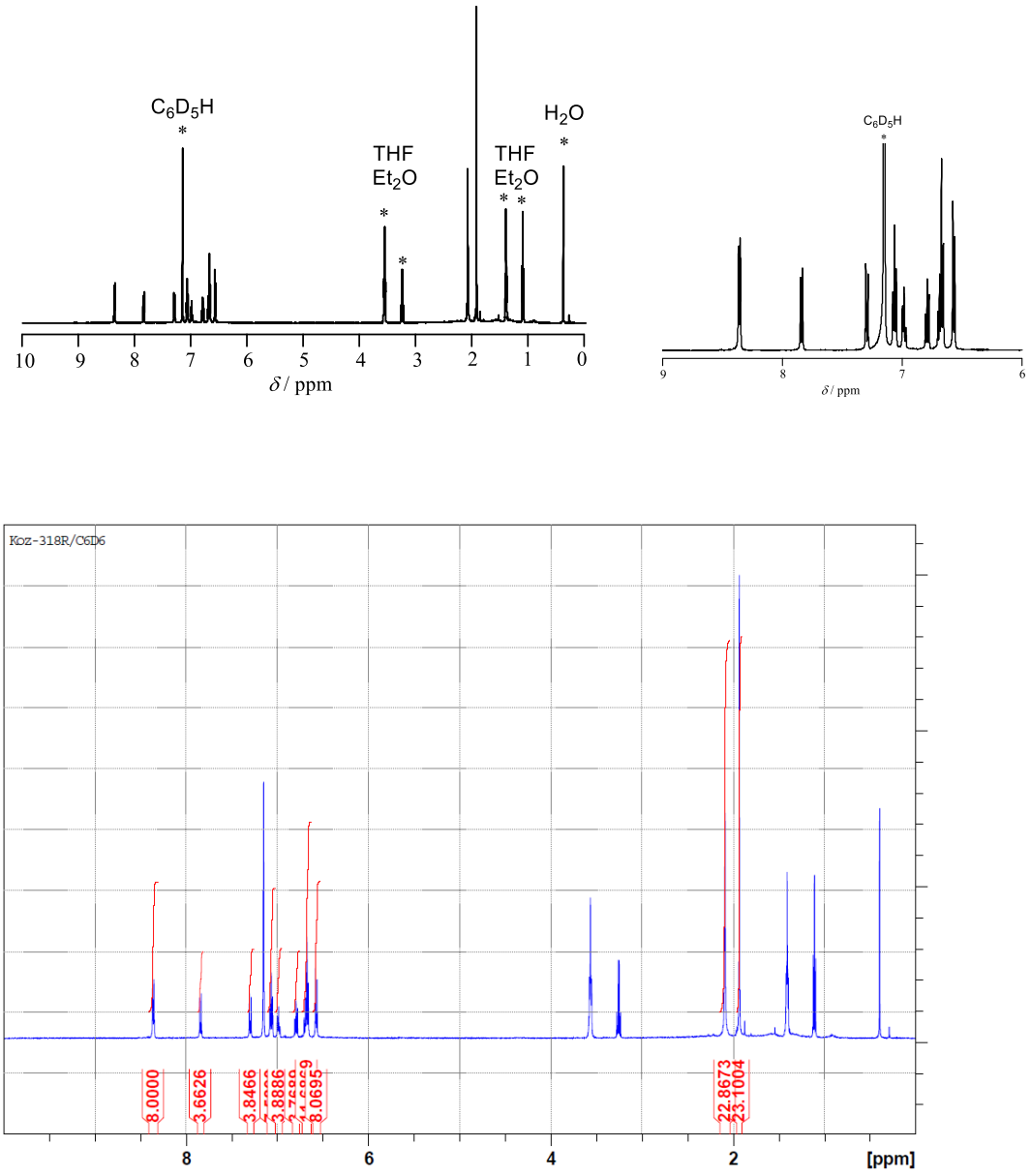

Figure S4 ^{1}H-NMR spectrum of **3** with the original spectrum with data of signal integration (in C_6D_6).

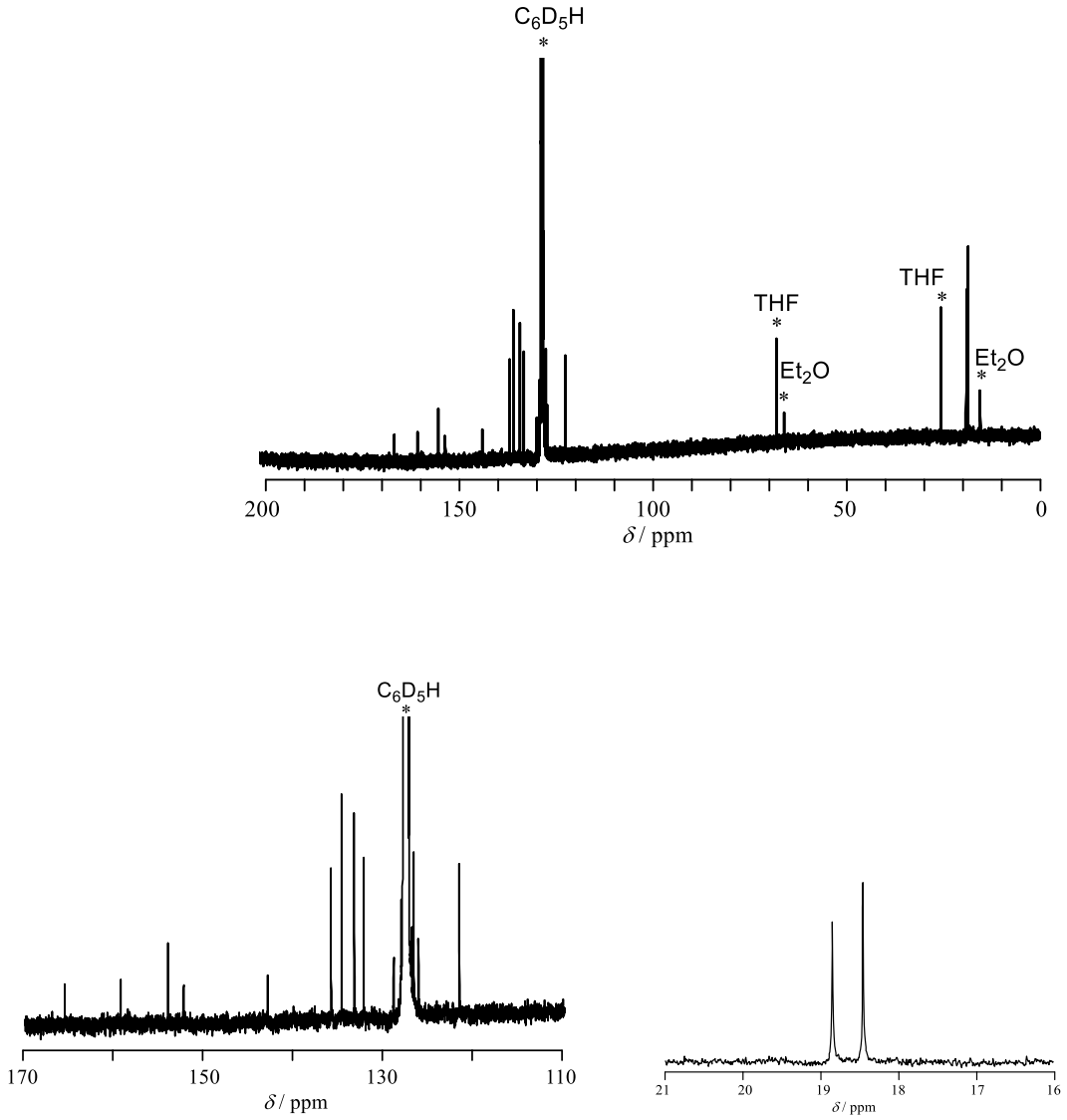

Figure S5. $^{13}C\{^{1}H\}$-NMR spectrum of **3** in C_6D_6.

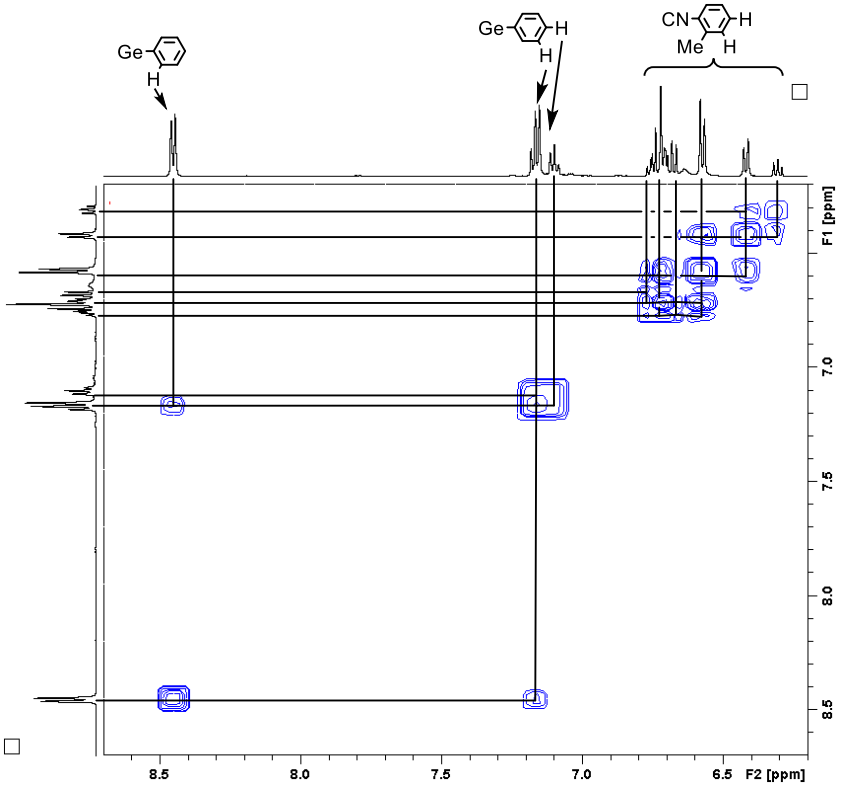

Figure S6. ^{1}H-^{1}H COSY spectrum of **3** in C_6D_6.

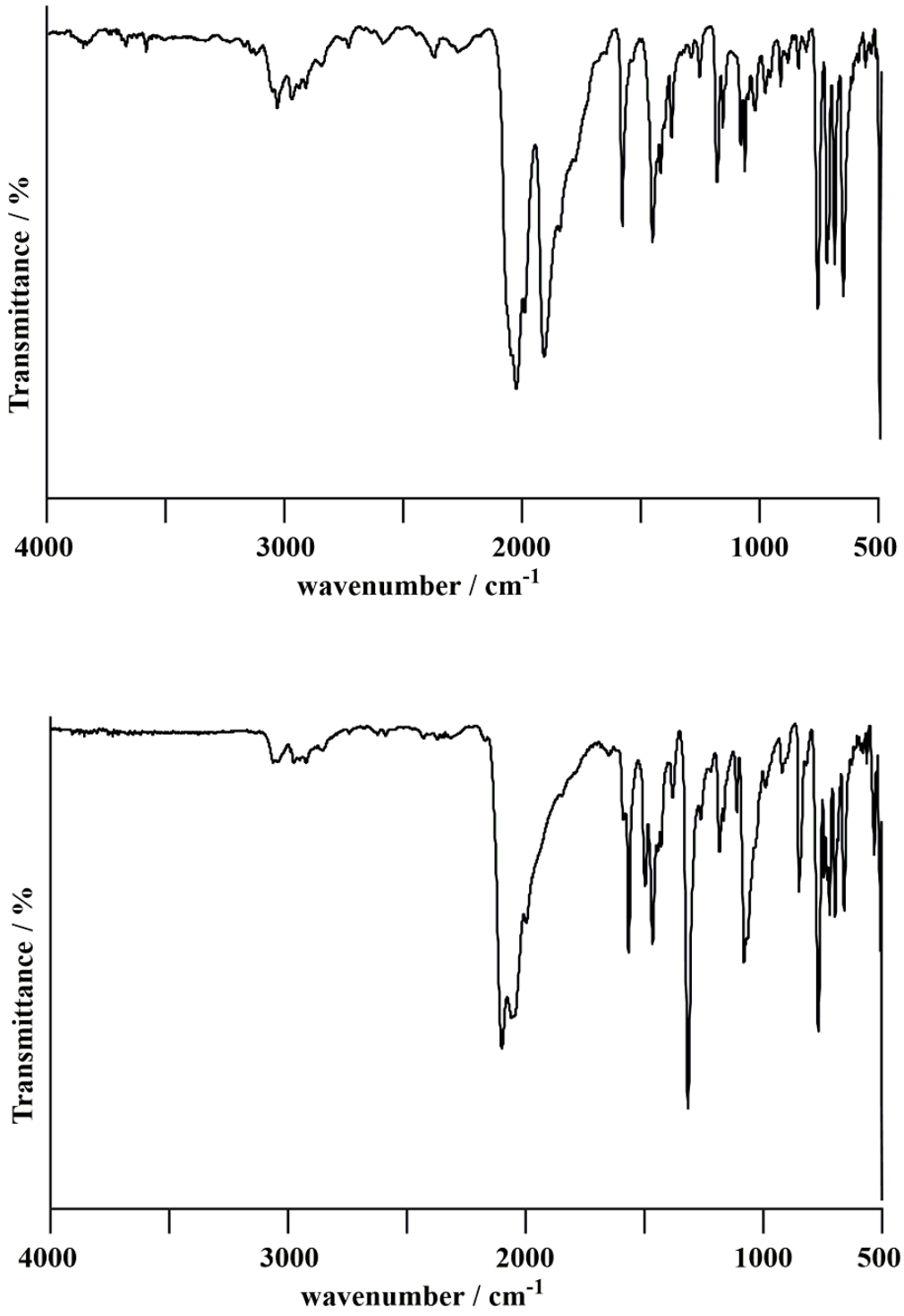

Figure S7. IR spectra of **2** (upper) and **3** (lower) in KBr disks.

4. Computation

Computational Details

The geometries of **2** and **3** were optimized by the PBE-D3(BJ)[S1][S2] functional in conjunction with the def2-SV(P)[S3] basis set and effective core potential (for Pd). Vibrational frequency analyses were carried out to confirm the stationary point at the same level of theory. The density fitting approximation[S4] was applied for geometry optimization and frequency calculations in combination with the W06[S5] auxiliary basis set. Those calculations were carried out with the Gaussian 16, Revision B.01 package.[S6] The natural bond orbital analysis was performed based on wave function obtained from the single point calculation by the ωB97X-D3[S7] functional with the def2-TZVP[S3] basis set and effective core potential (for Pd) using NBO 7.0 program.[S8] Single point calculation at the ωB97X-D3/def2-TZVP level of theory was carried out with ORCA 4.1.0 package.[S9] The RIJCOSX approximation[S10] was applied for single point calculation in combination with the def2/J[S5] auxiliary basis set. Molecular orbitals (Kohn–Sham (KS) orbitals) were obtained at the ωB97X-D3/def2-TZVP level of theory. The orbitals were visualized by VESTA program.[S11]

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Table S3 The Cartesian coordinate of **2**.

Pd	6.542547785	10.178473571	9.239610785
Pd	6.640718000	7.750710571	10.920104785
Pd	8.823919000	9.307514785	10.611919000
Ge	8.677945000	11.821865785	10.556540644
N	8.250172429	8.054823429	7.728950571
N	5.096422142	11.491989571	6.814343215
N	4.932055571	5.177851785	11.240715927
N	9.389390000	6.335848785	11.489902000
N	11.950188000	9.441362429	10.638840571
C	9.757414429	12.539728000	9.024544073
C	9.541428429	12.028083429	7.726802858
H	8.830032429	11.192643215	7.593518644
C	10.197039429	12.571219644	6.610544073
H	10.016499644	12.149820858	5.605829858
C	11.077566429	13.656940644	6.768035502
H	11.587311429	14.090306858	5.890297502
C	11.291170215	14.192548429	8.047461502
H	11.961963215	15.057864429	8.183595717
C	10.638587215	13.633913000	9.160589288
H	10.816465215	14.078338785	10.154510502
C	9.653178356	12.515651785	12.161483073
C	8.913889927	12.967598785	13.275488858
H	7.813395927	12.924288571	13.234964429
C	9.550074283	13.460379000	14.426410073
H	8.948239068	13.813204785	15.278620644
C	10.954314283	13.498605215	14.490007502
H	11.459641854	13.883303215	15.391502717
C	11.708709712	13.027212215	13.401647717
H	12.811188712	13.038005429	13.446594146
C	11.062600356	12.540513000	12.251862502
H	11.674874571	12.175292000	11.410986717
C	7.864439215	8.841049000	8.561361571

C	8.914547858	7.091816429	7.016023571
C	8.398333644	5.765282644	6.975144927
C	7.120324000	5.419066644	7.688937854
H	6.988152142	4.318697644	7.761025781
H	6.232705429	5.831982932	7.153959639
H	7.089950785	5.849184785	8.716129283
C	9.125304858	4.800824644	6.255905142
H	8.741796644	3.768251858	6.222477498
C	10.321128502	5.127235644	5.596630000
H	10.875540717	4.352117644	5.043265215
C	10.809857502	6.441930644	5.650354644
H	11.752914932	6.702396644	5.140031288
C	10.124809288	7.443923429	6.353196429
C	10.632225502	8.857600429	6.435343288
H	9.943949932	9.562968644	5.913798644
H	11.637143932	8.953484215	5.973722146
H	10.689957644	9.212530215	7.487362288
C	5.599622356	10.988454571	7.774553215
C	4.475547356	12.156792785	5.792873429
C	3.107045356	11.878497000	5.526511000
C	2.385814142	10.842293785	6.342654571
H	2.813389927	9.826427785	6.185337142
H	1.307624142	10.803561000	6.083542356
H	2.485893142	11.037227142	7.432816571
C	2.487432571	12.603939215	4.494487000
H	1.424142571	12.411612429	4.274247785
C	3.197473785	13.562656429	3.753841429
H	2.690709000	14.120819644	2.949719429
C	4.549710785	13.815296215	4.036935858
H	5.103380000	14.573078215	3.457984073
C	5.217633571	13.122011785	5.059164644
C	6.654315571	13.386359785	5.420878073
H	7.286099571	12.480834571	5.265352073
H	6.760251356	13.641986356	6.500239288
H	7.079792785	14.214821785	4.817847288
C	5.628009785	6.136230785	11.087850142

C	4.049451785	4.170364785	11.536336142
C	3.937656000	3.745543000	12.887025142
C	4.761200215	4.414239215	13.953095927
H	4.472546429	5.485352215	14.050641712
H	5.847898215	4.397394000	13.707635712
H	4.616064429	3.925593429	14.939511142
C	3.008212000	2.731218000	13.173907571
H	2.902183215	2.386076215	14.214988571
C	2.219490000	2.166346785	12.160331785
H	1.496109000	1.371322785	12.405988000
C	2.341687571	2.614473785	10.836225785
H	1.715317571	2.173548571	10.042182785
C	3.257117571	3.624899785	10.491736356
C	3.391440142	4.149007571	9.088837356
H	3.098244712	5.221169356	9.023672142
H	2.754251142	3.576912356	8.381987356
H	4.445482142	4.098832785	8.732812142
C	8.635271000	7.237456785	11.201533785
C	10.466547215	5.533720215	11.740113215
C	11.410726215	5.279881215	10.701057215
C	11.214264000	5.875375785	9.335163000
H	10.302190000	5.473422785	8.843361429
H	12.076668785	5.659972571	8.671694785
H	11.076632215	6.976878785	9.385634785
C	12.517722644	4.468613644	11.006662429
H	13.260027644	4.270969644	10.215391429
C	12.693792858	3.924249073	12.287266429
H	13.572618073	3.296090502	12.504162644
C	11.747321858	4.179915073	13.291830429
H	11.879247073	3.750986502	14.299734644
C	10.617567429	4.977324644	13.041778215
C	9.592484429	5.269996429	14.100386215
H	9.791012644	4.697436858	15.029429429
H	8.562873429	5.031143000	13.745350215
H	9.585388000	6.350995644	14.368519000
C	10.755752000	9.425634215	10.624003785

C	13.323719000	9.474059215	10.673667142
C	14.014869000	10.259096215	9.708767142
C	13.254980000	11.019576644	8.658283571
H	12.536097215	11.745438644	9.100122000
H	12.644062785	10.338461073	8.025849356
H	13.943386000	11.582568858	7.993824571
C	15.418237000	10.278497571	9.772039498
H	15.973803000	10.881720571	9.035013498
C	16.112340215	9.549945356	10.750395283
H	17.213465215	9.579342712	10.781570854
C	15.406867215	8.779344571	11.686890498
H	15.952102215	8.204821356	12.453490283
C	14.003067215	8.721181000	11.672708927
C	13.229886215	7.894392429	12.662873356
H	12.689996356	7.060249858	12.160920571
H	12.457130858	8.500249858	13.182574785
H	13.903191429	7.451821000	13.425433927
Pd	6.527179785	10.484869571	12.001441785
Pd	6.432458000	12.912633571	10.320948785
Pd	4.249259000	11.359276785	10.632579000
Ge	4.395230000	8.844924785	10.698301644
N	4.829900429	12.622309429	13.508653571
N	7.962957142	9.171352571	14.433607215
N	8.134226571	15.488938785	9.986550927
N	3.683787000	14.330941785	9.754596000
N	1.122990000	11.235765429	10.598769571
C	3.322652429	8.130511000	12.237191073
C	3.538637429	8.649050429	13.531484858
H	4.250033429	9.481045215	13.661321644
C	2.883025429	8.109362644	14.651190073
H	3.067010644	8.534209858	15.652456858
C	2.002498429	7.023641644	14.500592502
H	1.492751429	6.593723858	15.378330502
C	1.785449215	6.484585429	13.221167502
H	1.114657215	5.619269429	13.088480717
C	2.438034215	7.036326000	12.104592288

H	2.260157215	6.588451785	11.114118502
C	3.409657356	8.151137785	9.100252073
C	4.142051927	7.699189785	7.982799858
H	5.242545927	7.739051571	8.016431429
C	3.495527283	7.209854000	6.835327073
H	4.093916068	6.853579785	5.976222644
C	2.091287283	7.175075215	6.778623502
H	1.579065854	6.790376215	5.880575717
C	1.343785712	7.646468215	7.870428717
H	0.241306712	7.639122429	7.832377146
C	2.000235356	8.129722000	9.016767502
H	1.391408571	8.494946000	9.861088717
C	5.212185215	11.829192000	12.676241571
C	4.172419858	13.585315429	14.221583571
C	4.685186644	14.915295644	14.252122927
C	5.952855000	15.261514644	13.521093854
H	6.071237142	16.361884644	13.431771781
H	6.847368429	14.869279932	14.052623639
H	5.979779785	14.817608785	12.500796283
C	3.961663858	15.879752644	14.974813142
H	4.341725644	16.915771858	14.997901498
C	2.776182502	15.553340644	15.647877000
H	2.225217717	16.328457644	16.204691215
C	2.287453502	14.238645644	15.604492644
H	1.351289932	13.978178644	16.125158288
C	2.969053288	13.233207429	14.898200429
C	2.465083502	11.819530429	14.829838288
H	3.160253932	11.117607644	15.341039644
H	1.467059932	11.720199215	15.305249146
H	2.393559644	11.461157215	13.777819288
C	7.463204356	9.674888571	13.473396215
C	8.587280356	8.509996785	15.458522429
C	9.955784356	8.791736000	15.717985000
C	10.673567142	9.824491785	14.894946571
H	10.242544927	10.840357785	15.045370142
H	11.751758142	9.866672000	15.150610356

H	10.573486142	9.619218142	13.804785571
C	10.578846571	8.069738215	16.750006000
H	11.642138571	8.265509429	16.966793785
C	9.872254785	7.114467429	17.497546429
H	10.382469000	6.559750644	18.301666429
C	8.520015785	6.858384215	17.221350858
H	7.969794000	6.100602215	17.803751073
C	7.848642571	7.544777785	16.195679644
C	6.411959571	7.280430785	15.840864073
H	5.780177571	8.182511571	15.996391073
H	6.302572356	7.017910356	14.764951288
H	5.989928785	6.451971785	16.447344288
C	7.441718785	14.530559785	10.142862142
C	9.020275785	16.496427785	9.694378142
C	9.135522000	16.924691000	8.343687142
C	8.315432215	16.259433215	7.274168927
H	8.607535429	15.188321215	7.173183712
H	7.228732215	16.272832000	7.516176712
H	8.464018429	16.751521429	6.291198142
C	10.064965000	17.939018000	8.063698571
H	10.174444215	18.287602215	7.022615571
C	10.853680000	18.500448785	9.080721785
H	11.577060000	19.295473785	8.838512000
C	10.724585571	18.052325785	10.404827785
H	11.350951571	18.489810571	11.198872785
C	9.809157571	17.041898785	10.742424356
C	9.667937142	16.514349571	12.145325356
H	9.954241712	15.438741356	12.207050142
H	10.305122142	17.083002356	12.852175356
H	8.613893142	16.567969785	12.497899142
C	4.437905000	13.429331785	10.039516785
C	2.610073215	15.139960215	9.507834215
C	1.665897215	15.393797215	10.546895215
C	1.858920000	14.791410785	11.909343000
H	2.769267785	15.193373785	12.408035429
H	0.993067785	15.003358571	12.569364785

H	2.000011215	13.689909785	11.855422785
C	0.565789644	16.211953644	10.244740429
H	-0.176512356	16.409595644	11.036015429
C	0.393158858	16.763211073	8.964137429
H	-0.482222927	17.398258502	8.750690644
C	1.339625858	16.507546073	7.959569429
H	1.211141073	16.943366502	6.955111644
C	2.462491429	15.703247644	8.206170215
C	3.487570429	15.407131429	7.147557215
H	3.292487644	15.986588858	6.221964429
H	4.517182429	15.639086000	7.502591215
H	3.487768000	14.329579644	6.875973000
C	2.317426000	11.248048215	10.617049785
C	-0.250541000	11.199622215	10.557051142
C	-0.941691000	10.414586215	11.521952142
C	-0.181802000	9.660999644	12.579328571
H	0.540526215	8.935136644	12.144383000
H	0.425669785	10.349009073	13.208314356
H	-0.870208000	9.101455858	13.243787571
C	-2.345059000	10.384846571	11.448340498
H	-2.900625000	9.781624571	12.185367498
C	-3.035714785	11.109951356	10.466537283
H	-4.136840785	11.070214712	10.428468854
C	-2.330241785	11.883997571	9.533487498
H	-2.875477785	12.455074356	8.763441283
C	-0.926442785	11.949054000	9.554561927
C	-0.153261785	12.782734429	8.571290356
H	0.372842356	13.623769858	9.076689571
H	0.629833858	12.183769858	8.058481785
H	-0.823119571	13.218413000	7.801835927

Table S4 The Cartesian coordinate of **3**.

Pd	0.159886000	1.672036000	-0.025216000
Pd	-0.163806000	-1.097745000	-0.233813000
Pd	0.617988000	0.103606000	2.313343000
Pd	2.504675000	-0.125275000	0.161644000
Pd	-0.614491000	0.830993000	-2.540485000
Pd	-2.584778000	0.254995000	-0.495052000
Ge	1.738182000	0.253873000	-2.115271000
Ge	-1.777089000	0.218042000	1.842728000
S	3.048842000	-0.085835000	2.548109000
S	-3.093898000	0.878431000	-2.848581000
O	4.007848000	-6.238039000	5.064590000
O	5.716648000	-6.126029000	3.705775000
O	-4.785502000	7.239405000	-4.111537000
O	-4.826010000	7.295385000	-1.925894000
N	4.701617000	-5.652144000	4.226294000
N	-4.687015000	6.704295000	-3.003380000
N	-0.594564000	3.957370000	-1.998629000
N	1.673526000	3.348674000	2.149894000
N	1.476876000	-3.604809000	0.651608000
N	-2.508997000	-2.707745000	-1.517825000
N	-0.261498000	-0.304922000	5.256108000
N	5.361455000	0.125468000	-1.025100000
N	-0.179828000	-0.500278000	-5.314454000
N	-5.332061000	0.301315000	0.951956000
C	3.465582000	-1.746103000	3.008583000
C	2.750647000	-2.449863000	4.008098000
H	1.867779000	-1.980726000	4.466562000
C	3.157600000	-3.722736000	4.411890000
H	2.613869000	-4.283700000	5.185550000
C	4.283882000	-4.309065000	3.812384000
C	5.008555000	-3.635954000	2.815212000
H	5.880930000	-4.130436000	2.365524000
C	4.599037000	-2.361519000	2.419342000
H	5.156794000	-1.817355000	1.640640000
C	-3.621284000	2.568805000	-2.849555000

C	-3.965085000	3.270509000	-1.668139000
H	-3.921423000	2.741560000	-0.703965000
C	-4.337766000	4.613889000	-1.718553000
H	-4.598021000	5.174459000	-0.809274000
C	-4.362781000	5.274911000	-2.957978000
C	-4.059042000	4.596603000	-4.149494000
H	-4.096785000	5.146764000	-5.099833000
C	-3.696156000	3.249538000	-4.091429000
H	-3.444579000	2.705508000	-5.015841000
C	2.660063000	1.836737000	-2.902010000
C	2.801774000	3.012648000	-2.133721000
H	2.494979000	3.003356000	-1.073660000
C	3.299065000	4.196277000	-2.702125000
H	3.384288000	5.106963000	-2.085561000
C	3.692148000	4.218803000	-4.051896000
H	4.083769000	5.146389000	-4.501274000
C	3.575915000	3.051593000	-4.824992000
H	3.878710000	3.058721000	-5.885856000
C	3.054214000	1.876311000	-4.255248000
H	2.935187000	0.981658000	-4.887491000
C	2.293998000	-1.345022000	-3.167889000
C	3.587383000	-1.457373000	-3.720210000
H	4.314257000	-0.636845000	-3.593827000
C	3.967363000	-2.600234000	-4.448349000
H	4.981315000	-2.662856000	-4.879132000
C	3.056591000	-3.653478000	-4.634731000
H	3.348008000	-4.544179000	-5.215455000
C	1.769629000	-3.563229000	-4.075754000
H	1.045668000	-4.383451000	-4.217503000
C	1.400778000	-2.423142000	-3.344634000
H	0.391294000	-2.359660000	-2.902321000
C	-2.443823000	1.883441000	2.725363000
C	-2.592618000	3.064459000	1.966577000
H	-2.334976000	3.046762000	0.893297000
C	-3.045056000	4.257293000	2.554136000
H	-3.156668000	5.165876000	1.938890000

C	-3.354344000	4.294733000	3.924573000
H	-3.716076000	5.227974000	4.387120000
C	-3.189616000	3.136327000	4.701466000
H	-3.417256000	3.155171000	5.780857000
C	-2.731922000	1.946435000	4.106716000
H	-2.599861000	1.055117000	4.741750000
C	-2.745242000	-1.304824000	2.702945000
C	-3.886120000	-1.125816000	3.514531000
H	-4.258757000	-0.112404000	3.733069000
C	-4.587551000	-2.225735000	4.040353000
H	-5.478548000	-2.053748000	4.666942000
C	-4.170064000	-3.532866000	3.745519000
H	-4.723214000	-4.398151000	4.147087000
C	-3.041646000	-3.729778000	2.929940000
H	-2.709807000	-4.753828000	2.690323000
C	-2.334859000	-2.627131000	2.423093000
H	-1.448333000	-2.788307000	1.786053000
C	-0.412163000	2.888399000	-1.485862000
C	-0.850498000	5.125580000	-2.664147000
C	-1.304800000	6.244439000	-1.913597000
C	-1.446363000	6.133061000	-0.420699000
H	-0.458712000	5.979898000	0.072405000
H	-2.065113000	5.250726000	-0.148990000
H	-1.920516000	7.040919000	0.005683000
C	-1.624972000	7.418181000	-2.614409000
H	-2.012394000	8.285378000	-2.056211000
C	-1.496436000	7.479997000	-4.010041000
H	-1.780301000	8.399800000	-4.545130000
C	-1.020367000	6.370549000	-4.725990000
H	-0.917487000	6.425468000	-5.822449000
C	-0.682979000	5.171991000	-4.075441000
C	-0.181833000	3.965264000	-4.815859000
H	-0.211362000	4.128470000	-5.913303000
H	-0.783933000	3.060749000	-4.571121000
H	0.864748000	3.718500000	-4.527883000
C	1.041960000	2.665085000	1.398810000

C	2.380843000	3.973351000	3.145124000
C	3.801094000	3.964255000	3.092438000
C	4.512760000	3.288297000	1.952732000
H	5.603802000	3.489622000	1.988892000
H	4.121739000	3.626972000	0.967127000
H	4.360352000	2.183773000	1.985730000
C	4.490677000	4.589534000	4.145269000
H	5.593155000	4.593094000	4.128764000
C	3.801905000	5.197667000	5.205844000
H	4.364985000	5.677640000	6.022676000
C	2.398304000	5.201775000	5.226283000
H	1.857848000	5.687480000	6.055820000
C	1.656943000	4.598565000	4.196945000
C	0.154111000	4.608141000	4.166003000
H	-0.267651000	5.041807000	5.095717000
H	-0.265234000	3.586504000	4.033064000
H	-0.228455000	5.201999000	3.304823000
C	-1.829414000	-1.841716000	-1.029662000
C	-3.137648000	-3.808895000	-2.036573000
C	-4.414902000	-3.655270000	-2.642624000
C	-5.057515000	-2.298073000	-2.714067000
H	-4.520294000	-1.628079000	-3.423385000
H	-5.016179000	-1.773524000	-1.735894000
H	-6.115780000	-2.370754000	-3.040613000
C	-5.022144000	-4.802446000	-3.181992000
H	-6.013793000	-4.706920000	-3.654690000
C	-4.388390000	-6.053289000	-3.125150000
H	-4.883081000	-6.939602000	-3.554769000
C	-3.128776000	-6.181118000	-2.518958000
H	-2.634480000	-7.165681000	-2.472755000
C	-2.478026000	-5.068353000	-1.961016000
C	-1.129165000	-5.170215000	-1.302147000
H	-1.169590000	-4.826325000	-0.244297000
H	-0.377722000	-4.515142000	-1.797879000
H	-0.749104000	-6.212367000	-1.316843000
C	0.958063000	-2.587800000	0.302336000

C	2.130323000	-4.764921000	0.982418000
C	1.620623000	-5.570822000	2.034409000
C	0.373149000	-5.154993000	2.762660000
H	0.449673000	-4.111260000	3.140903000
H	0.164701000	-5.826631000	3.621009000
H	-0.509720000	-5.177443000	2.084041000
C	2.321170000	-6.745927000	2.354105000
H	1.959911000	-7.373955000	3.183923000
C	3.483071000	-7.107320000	1.655918000
H	4.034292000	-8.016312000	1.942855000
C	3.963102000	-6.295097000	0.617267000
H	4.883424000	-6.575554000	0.079071000
C	3.300548000	-5.111074000	0.255298000
C	3.787404000	-4.212383000	-0.844383000
H	3.909715000	-3.166112000	-0.483940000
H	3.061008000	-4.156711000	-1.686821000
H	4.756918000	-4.567804000	-1.248616000
C	0.051021000	-0.177562000	4.112872000
C	-0.638555000	-0.399810000	6.573741000
C	-0.492521000	0.743241000	7.406254000
C	0.062301000	2.023771000	6.844145000
H	1.043983000	1.864356000	6.343665000
H	0.196582000	2.785470000	7.639776000
H	-0.615406000	2.447733000	6.069118000
C	-0.893695000	0.619669000	8.747260000
H	-0.790553000	1.490562000	9.415410000
C	-1.414361000	-0.587035000	9.239203000
H	-1.721673000	-0.661317000	10.294985000
C	-1.540941000	-1.701158000	8.395453000
H	-1.945996000	-2.648600000	8.787360000
C	-1.155601000	-1.636232000	7.045956000
C	-1.277202000	-2.809119000	6.112601000
H	-0.291327000	-3.082732000	5.671241000
H	-1.949285000	-2.579082000	5.256438000
H	-1.679499000	-3.699085000	6.638630000
C	4.256377000	0.033267000	-0.585584000

C	6.620701000	0.199057000	-1.576870000
C	7.311350000	-1.010162000	-1.864395000
C	6.669636000	-2.335877000	-1.566072000
H	6.395919000	-2.423990000	-0.490497000
H	7.348366000	-3.176300000	-1.819829000
H	5.724485000	-2.463218000	-2.139879000
C	8.590965000	-0.910586000	-2.435620000
H	9.142945000	-1.836605000	-2.666351000
C	9.166167000	0.339257000	-2.708802000
H	10.171807000	0.395431000	-3.156123000
C	8.466206000	1.517561000	-2.410922000
H	8.920337000	2.499272000	-2.623805000
C	7.182763000	1.477791000	-1.839806000
C	6.410181000	2.726097000	-1.522789000
H	6.082954000	2.743424000	-0.459218000
H	5.482370000	2.793600000	-2.132993000
H	7.018225000	3.633326000	-1.718086000
C	-0.306666000	0.120467000	-4.303009000
C	-0.191284000	-1.484141000	-6.278107000
C	-1.263702000	-2.418442000	-6.260184000
C	-2.351788000	-2.299665000	-5.230942000
H	-2.872299000	-1.317363000	-5.296380000
H	-1.938245000	-2.351533000	-4.198831000
H	-3.101540000	-3.109691000	-5.340154000
C	-1.245566000	-3.446089000	-7.217798000
H	-2.064318000	-4.184392000	-7.219135000
C	-0.208391000	-3.540071000	-8.158200000
H	-0.214323000	-4.352648000	-8.902812000
C	0.836574000	-2.604291000	-8.153242000
H	1.652842000	-2.683691000	-8.890068000
C	0.871137000	-1.559210000	-7.214565000
C	2.011640000	-0.580892000	-7.154492000
H	2.663407000	-0.806230000	-6.279210000
H	1.652715000	0.464277000	-7.030911000
H	2.635709000	-0.637125000	-8.070538000
C	-4.292994000	0.399364000	0.376921000

C	-6.455108000	0.080944000	1.712802000
C	-6.987544000	-1.235377000	1.775251000
C	-6.352580000	-2.351748000	0.993000000
H	-6.805143000	-3.329752000	1.255732000
H	-5.258387000	-2.412273000	1.186502000
H	-6.480349000	-2.196701000	-0.101999000
C	-8.110680000	-1.437385000	2.594931000
H	-8.540439000	-2.450225000	2.665570000
C	-8.680795000	-0.378782000	3.318583000
H	-9.561826000	-0.561238000	3.955169000
C	-8.133758000	0.910851000	3.236461000
H	-8.582979000	1.740030000	3.807467000
C	-7.010055000	1.171458000	2.434101000
C	-6.379598000	2.534094000	2.344787000
H	-6.281686000	2.869452000	1.287761000
H	-5.349438000	2.531898000	2.767418000
H	-6.976109000	3.288667000	2.897533000

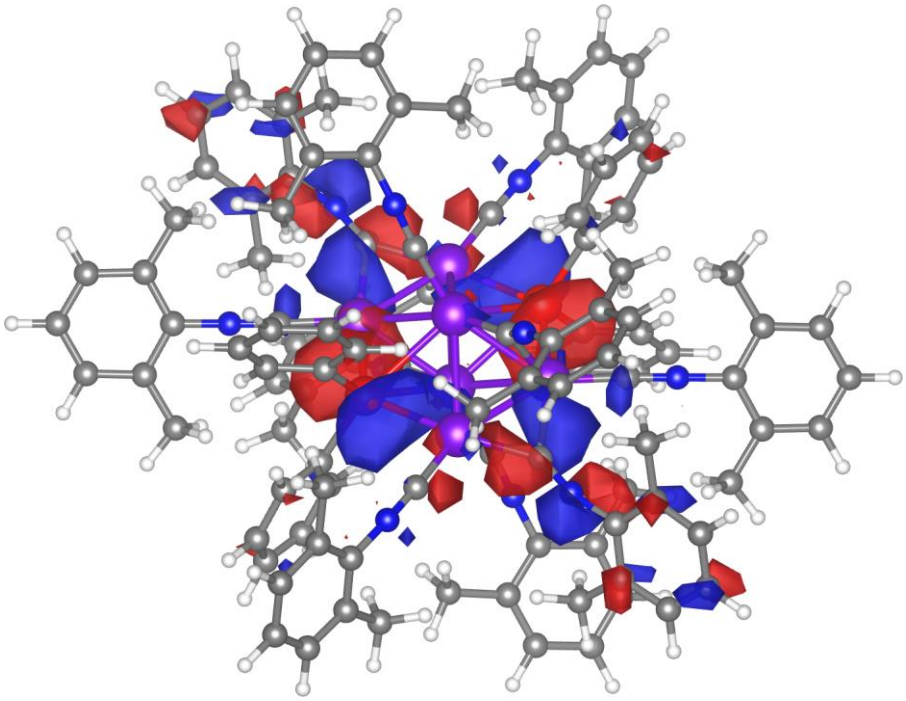


Figure S8. LUMO of complex **2**.

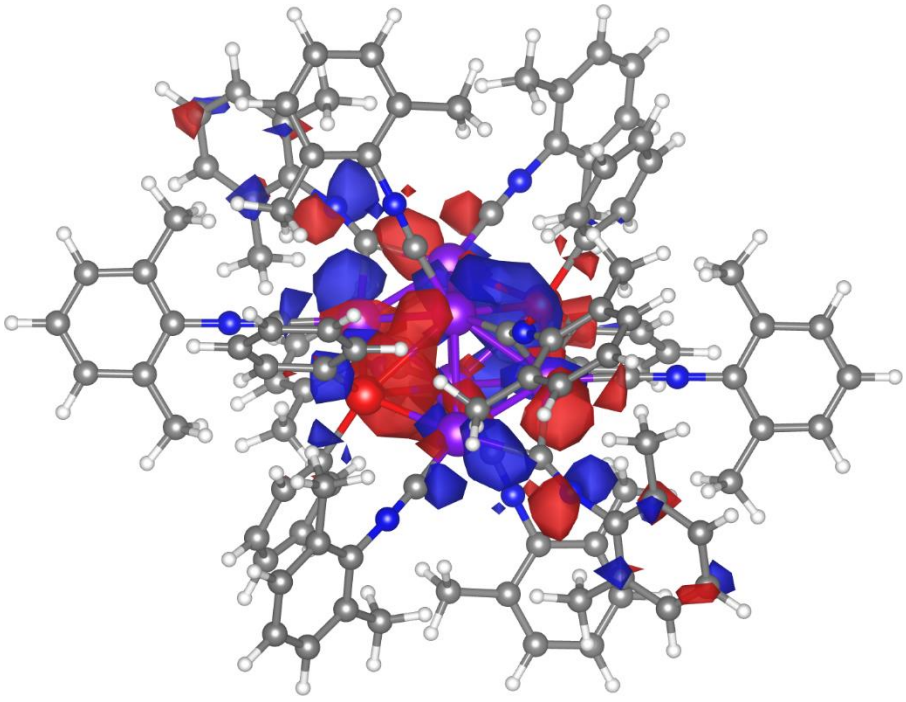


Figure S9. Expanded HOMO of complex **2**.

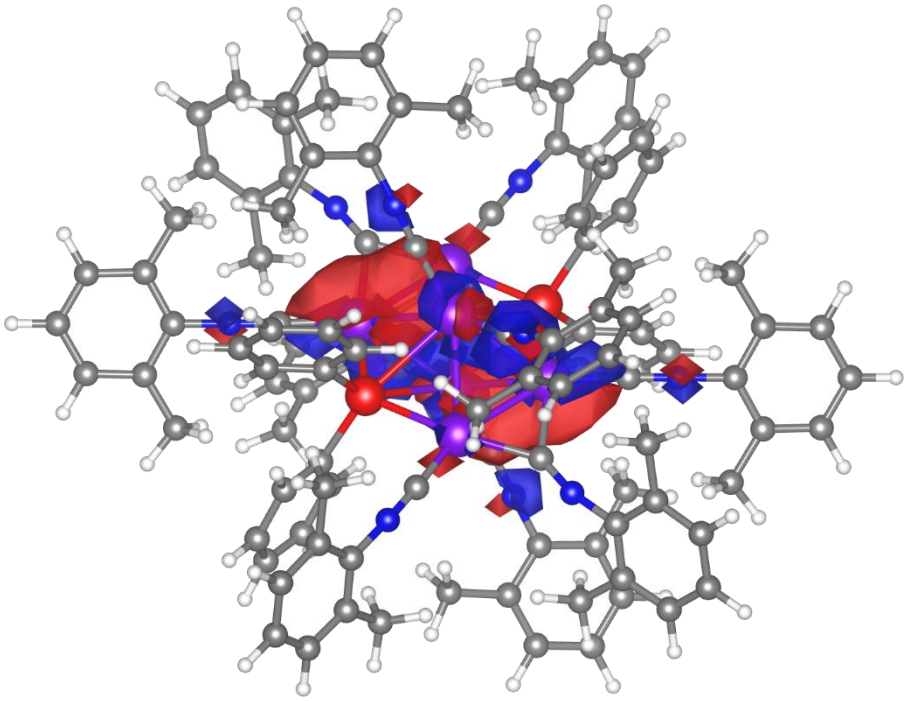


Figure S10. HOMO-1 of complex **2**.

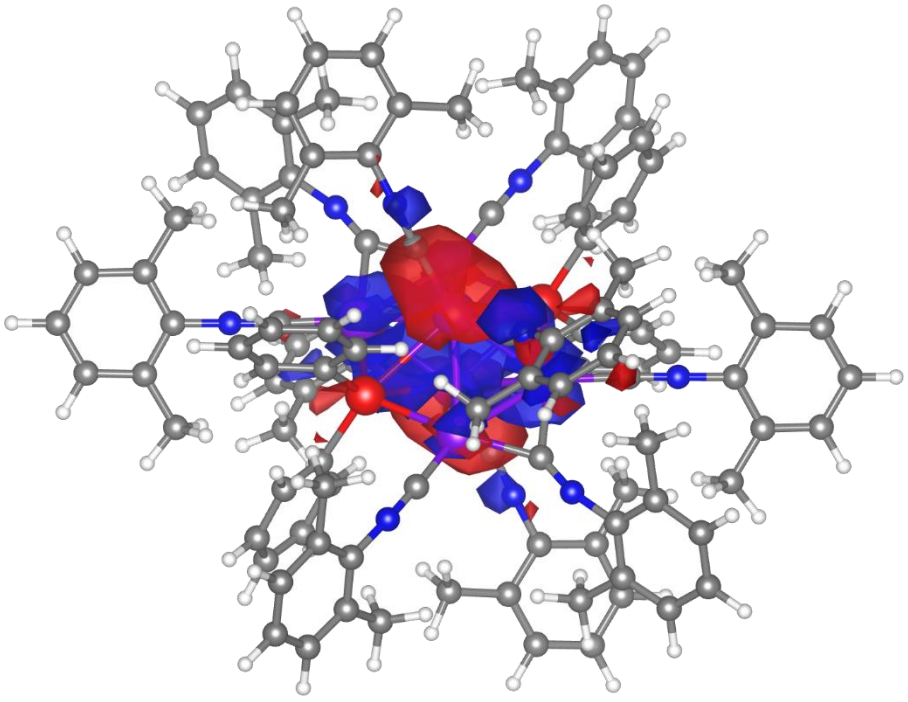


Figure S11. HOMO-2 of complex **2**.

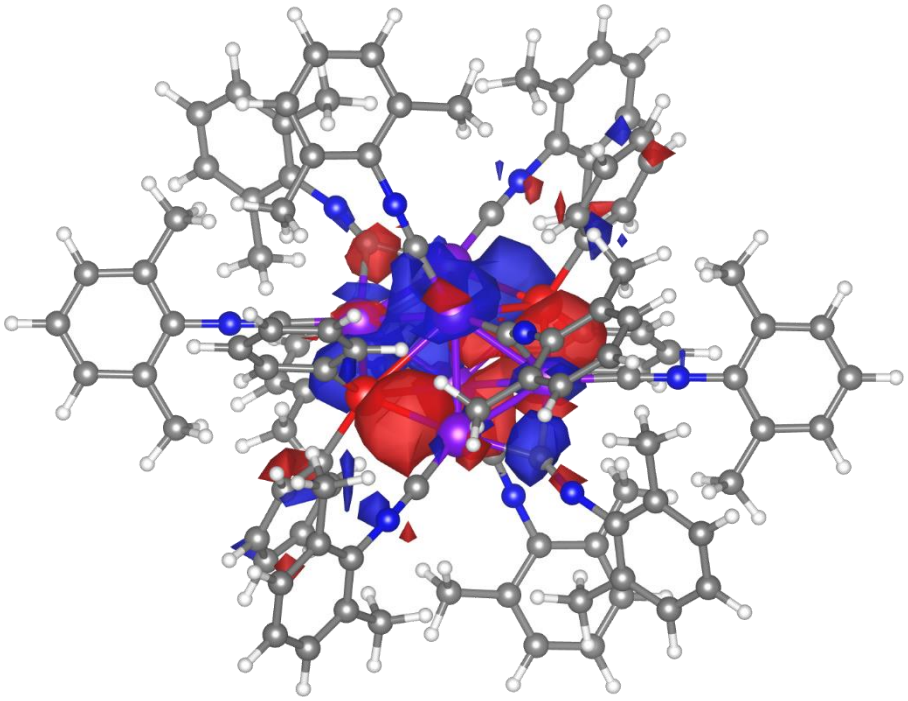


Figure S12. HOMO-3 of complex **2**.

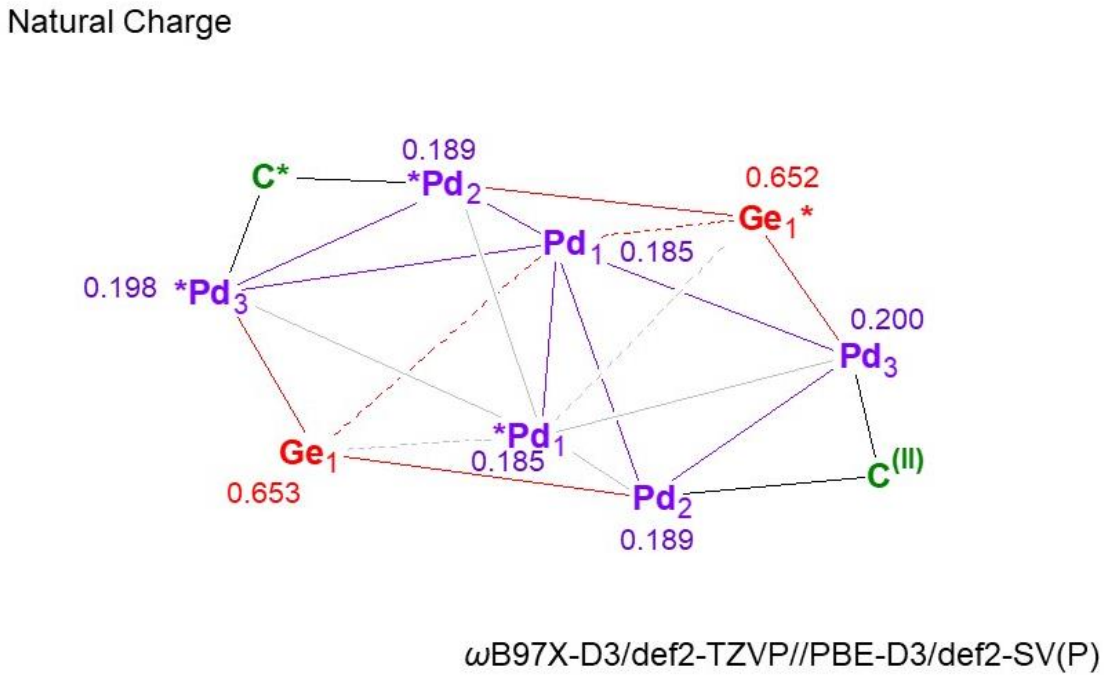


Figure S13. Natural charge of complex **2**.

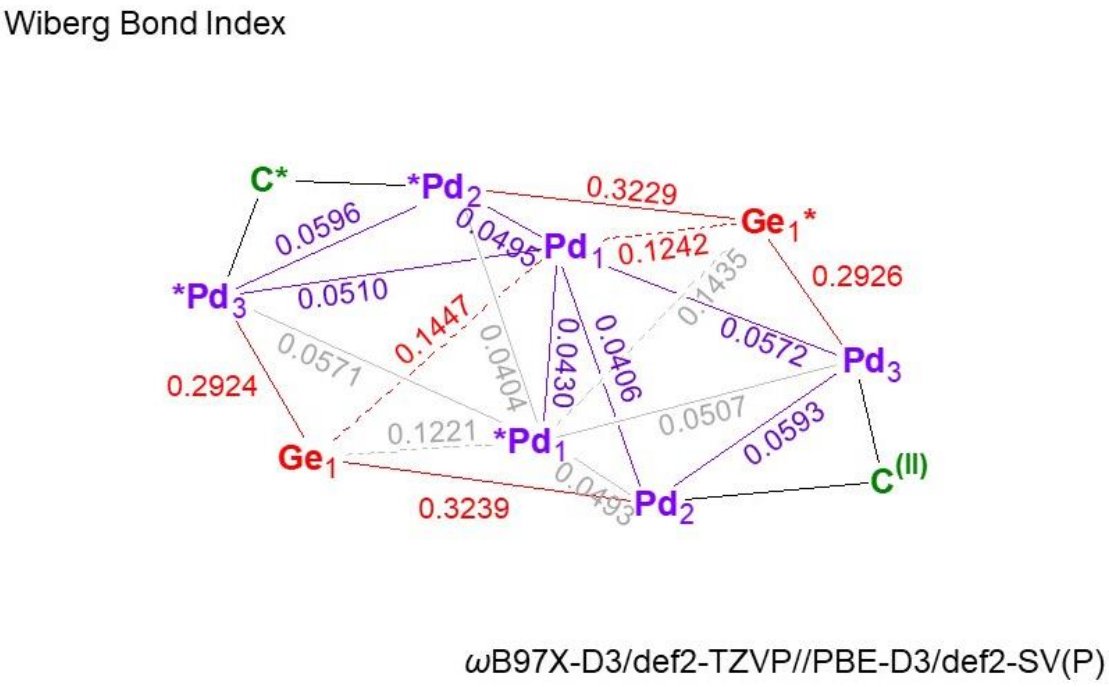


Figure S14. Wiberg bond index of complex **2**.

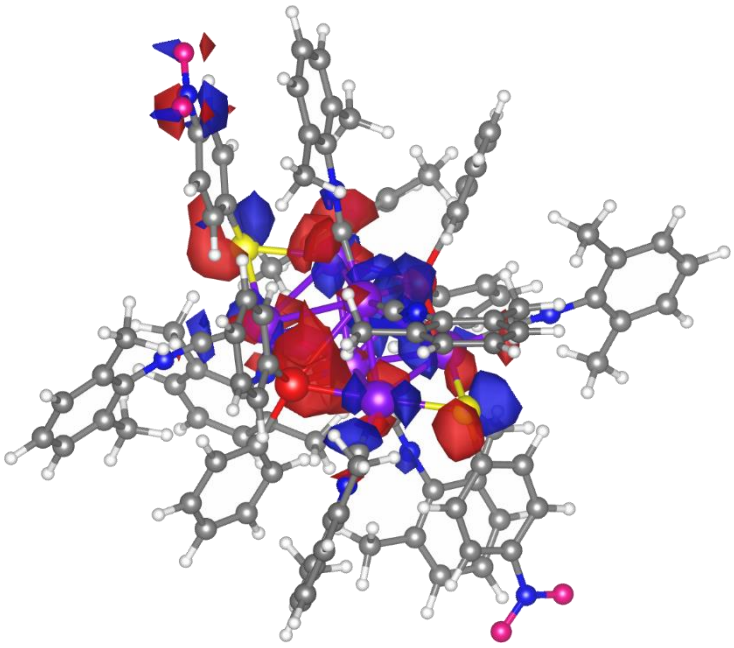


Figure S15. LUMO of complex **3**.

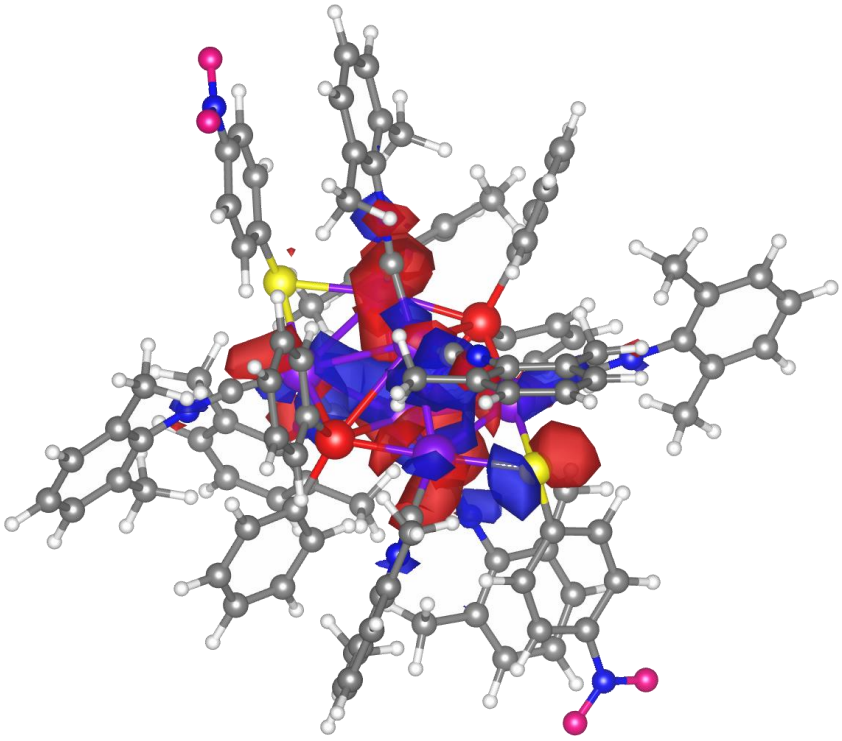


Figure S16. HOMO of complex **3**.

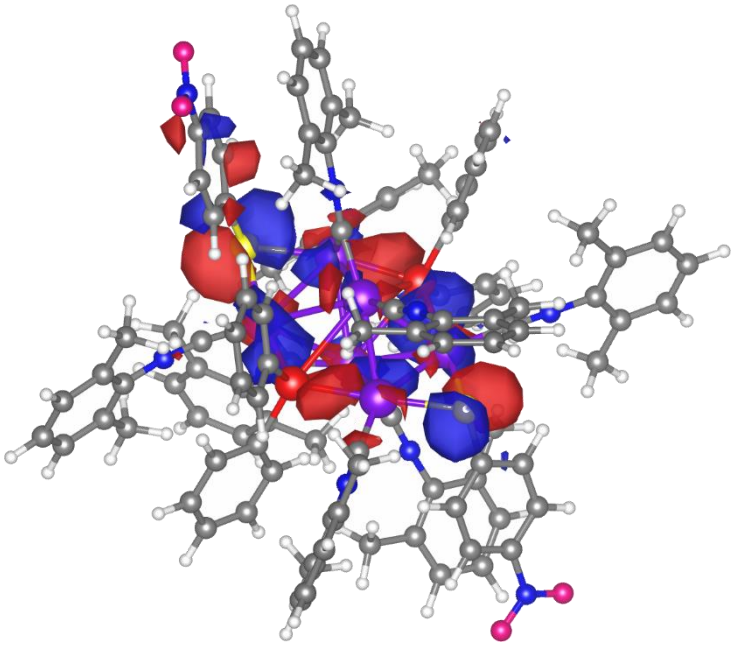


Figure S17. HOMO-1 of complex **3**.

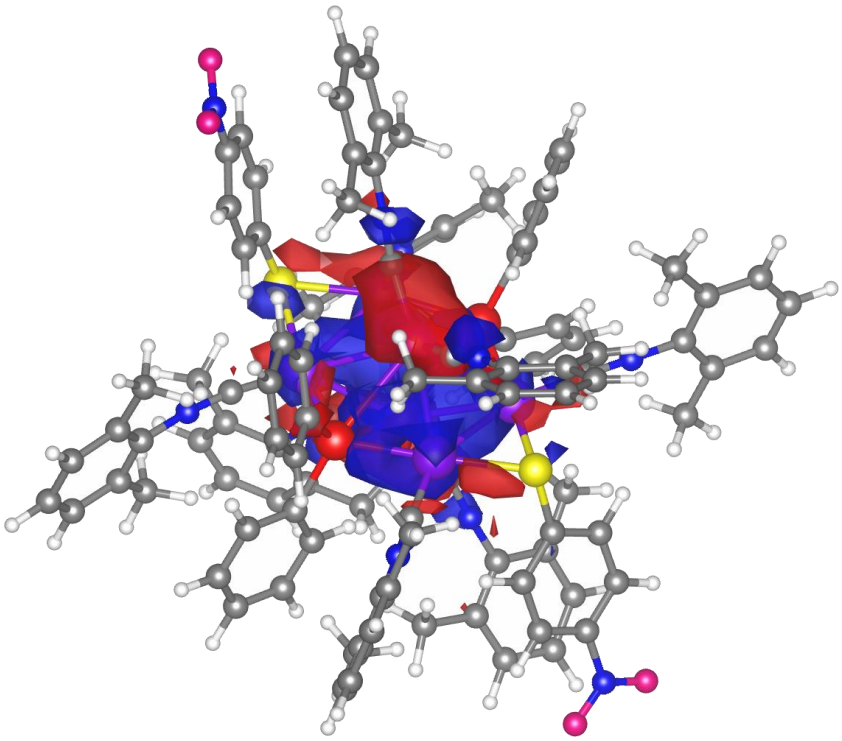


Figure S18. HOMO-2 of complex **3**.

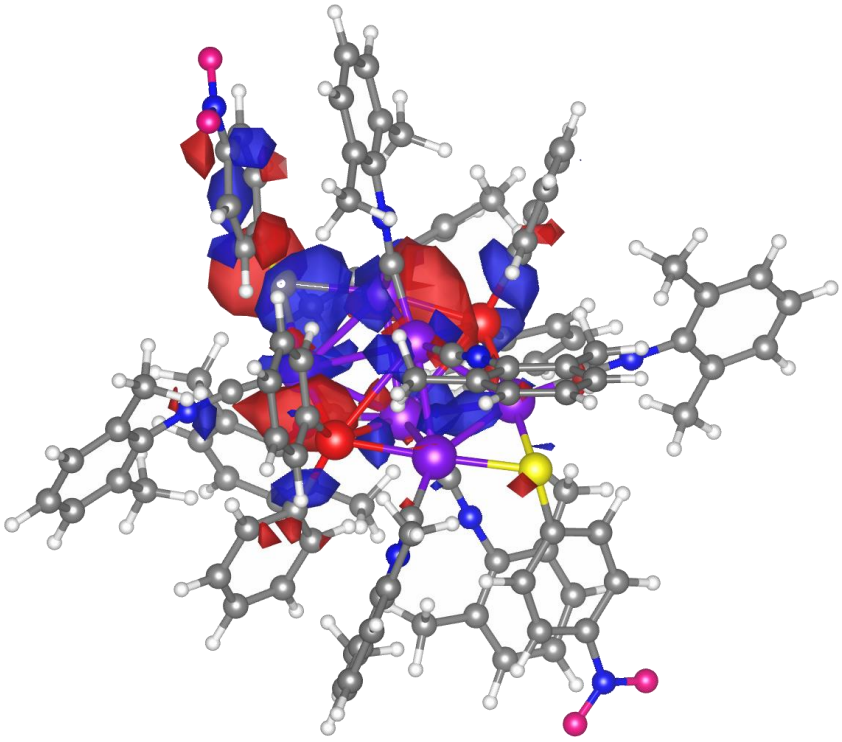


Figure S19. HOMO-3 of complex **3**.

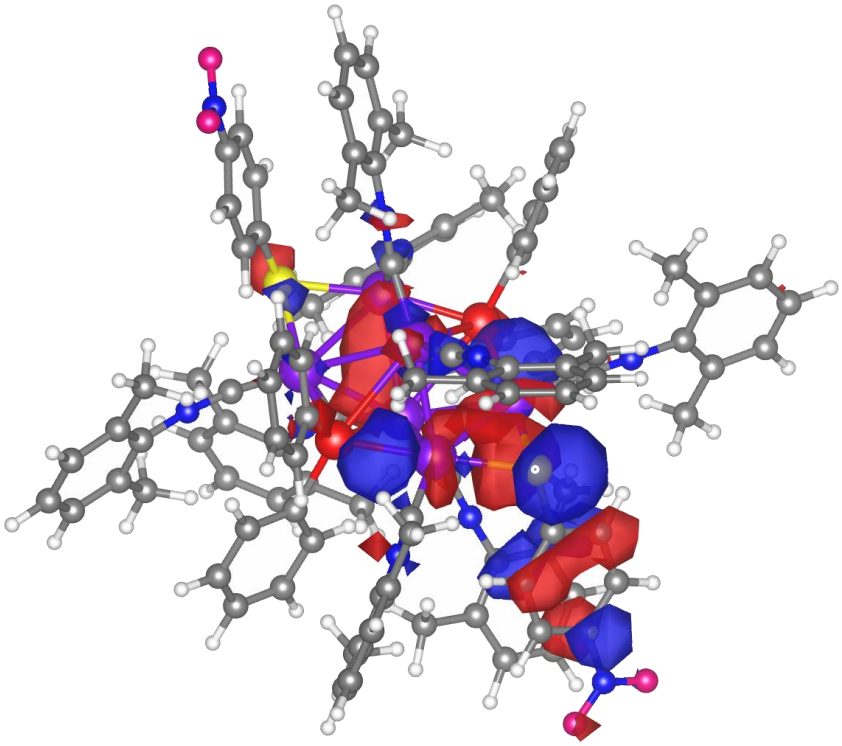
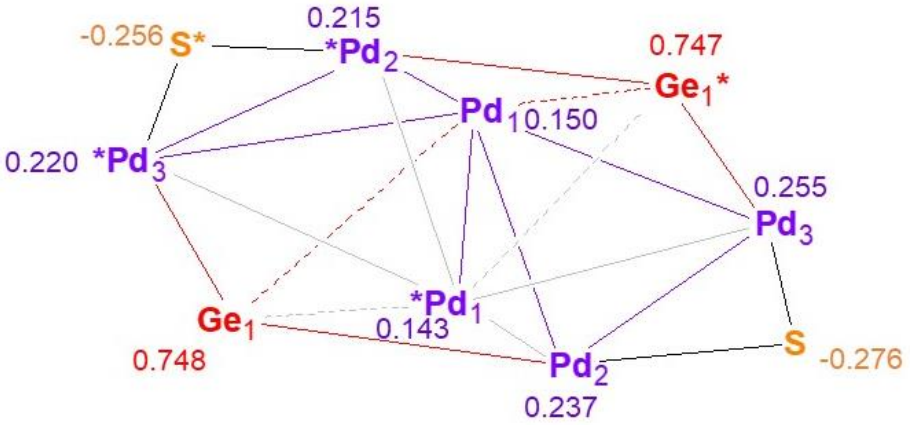


Figure S20. HOMO-4 of complex **3**.

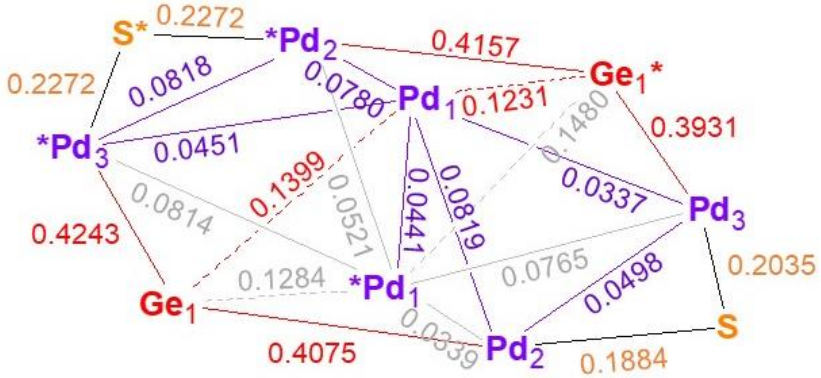
Natural Charge



ωB97X-D3/def2-TZVP//PBE-D3/def2-SV(P)
NBO 7.0

Figure S21. Natural charge of complex **3**.

Wiberg Bond Index



ωB97X-D3/def2-TZVP//PBE-D3/def2-SV(P)
NBO 7.0

Figure S22. Wiberg bond index of complex **3**.

5. DFT calculation results and absorption spectra

Time-dependent DFT (TDDFT) calculation with Tamm-Dancoff approximation (TDA) was carried out by ORCA 4.1.0 at the B3LYP/def2-SVP level of theory. The RIJCOSX approximation was applied for the calculation in combination with the def2-SVP/C auxiliary basis set.

Complex **2**

State	Wavelength (nm)	Oscillator strength (au^2)	Electronic transitions (ratio)
1	781.9	0.000024	HOMO−1 → LUMO (99%)
2	717.7	0.18	HOMO−1 → LUMO+1 (16%) HOMO → LUMO (80%)
3	672.7	0.000040	HOMO → LUMO+1 (98%)
4	583.2	0.000072	HOMO−2 → LUMO (98%)
5	572.8	0.56	HOMO−1 → LUMO+1 (70%) HOMO → LUMO (11%) HOMO → LUMO+2 (10%)
6	545.1	0.11	HOMO−1 → LUMO+1 (7%) HOMO → LUMO+2 (76%)

Complex **3**

State	Wavelength (nm)	Oscillator strength (au^2)	Electronic transitions (ratio)
1	736.0	0.00097	HOMO → LUMO (89%) HOMO → LUMO+2 (6%)
2	646.4	0.013	HOMO−2 → LUMO (35%) HOMO−1 → LUMO (52%)
3	594.9	0.0011	HOMO → LUMO+1 (95%)
4	559.6	0.011	HOMO−2 → LUMO (5%) HOMO → LUMO (6%) HOMO → LUMO+2 (74%)
5	557.5	0.21	HOMO−2 → LUMO (43%) HOMO−1 → LUMO (31%) HOMO → LUMO+2 (11%)
6	540.5	0.0068	HOMO−3 → LUMO (64%) HOMO−3 → LUMO+2 (5%) HOMO → LUMO+2 (5%) HOMO → LUMO+3 (15%)

Absorbance at 646 nm is assigned to the second exited state.

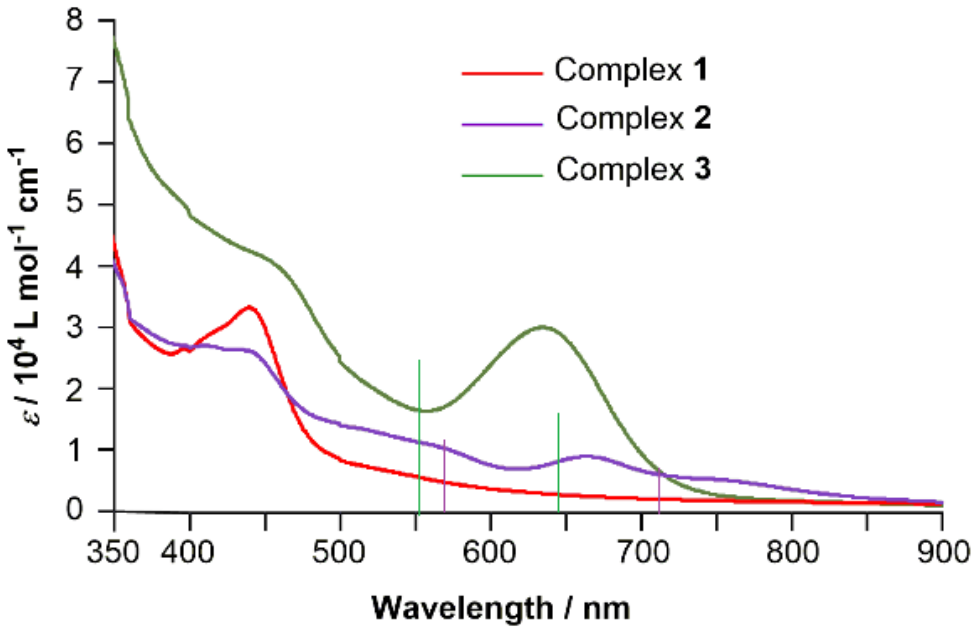


Figure S23. UV-vis spectra and calculated peak positions.