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Mononuclear (N^N)(P^P) silver(I) complexes based on 2-(pyrazol-3-yl)pyridines and DPEphos

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§1. Materials and Instrumentation

$AgBF_4$ (≥99%, Aldrich), DPEPhos (99%, Dalchem) were used as purchased. 2-(3-Phenyl-1*H*-pyrazol-5-yl)pyridine and 6-methyl-2-(3-phenyl-1*H*-pyrazol-5-yl)pyridine were synthesized according to the published methodology[S1]. All reactions were performed under an argon atmosphere using anhydrous solvents or solvents treated with an appropriate drying reagent.

^1H, ^{19}F and $^{31}P\{^1H\}$ NMR spectra were registered using a Bruker AV-300 spectrometer. Single-crystal X-ray diffraction experiments of all complexes were carried out with a Bruker SMART APEX II diffractometer (Bruker, Billerica, MA, United States)

The photoluminescence spectra of solid samples and lifetime measurements of the phosphorescence were recorded at 77 K and 298 K using a Fluorolog-3 spectrofluorometer system (HORIBA Jobin Yvon S.A.S., Palaiseau France) (the excitation source was a 450 W Xenon lamp with Czerny–Turner double monochromators; the registration channel was a R928 photomultiplier, while a 150 W pulsed Xenon lamp (HORIBA Jobin Yvon S.A.S.) was used for the lifetime measurements). The samples for these measurements were packed in quartz capillaries. The phosphorescence quenching curves were analyzed using the FluoroEssenceTM) software for the calculation of the phosphorescence lifetime values.

Single crystals of **1**·4(CH_2Cl_2) and **2** were obtained at -18 °C from CH_2Cl_2/hexane solutions (v/v = 1/2). A suitable crystal was selected and measured on a Bruker APEX-II CCD diffractometer. The crystal was kept at 120.00 K during data collection. Using Olex2[S2], the structure was solved with the SHELXT[S3] structure solution program using Intrinsic Phasing and refined with the XL[S4] refinement package using Least Squares minimization.

§2. Synthetic procedures and characterization data.

Synthesis of **1**•CH_2Cl_2

In the Schlenk flask in an argon atmosphere, $AgBF_4$ (50.0 mg, 1 eq.) in 1 ml of MeCN was dissolved. Then a solution of 2-(3-phenyl-1*H*-pyrazol-3-yl)pyridine (56.8 mg, 1 eq.) in 2 ml CH_2Cl_2 was slowly added. After stirring for 1 hour, to the resulting mixture was added a solution DPEPhos (138.3 mg, 1eq.) in 2 ml CH_2Cl_2. The mixture was stirred overnight protecting it from light with aluminium foil. The content of the flask was then evaporated to dryness, washed with boiling tetrahydrofuran and slowly crystallized from a mixture of CH_2Cl_2 and hexane (ratio 1 to 2) at -18 °C. After some time, white crystals are formed, which are isolated by filtration, and then dried under the vacuum of an oil pump (~15 Torr). (Note. Vacuum drying of vacuum in oil pump does not remove the last molecule of CH_2Cl_2, which is part of the complex)

Complex **1**•CH_2Cl_2: yield 73% colorless solid. ^1H NMR (300 MHz, DMSO-d_6) δ: 5.75 (br.s, 2H CH_2Cl_2), 6.77 (m, 2H), 6.92 (m, 2H), 7.12 (m, 2H), 7.31–8.06 (m, 31H), 8.39 (br.s, 1H^{Py}). ^{19}F NMR (300 MHz, DMSO-d_6) δ: -148.22 (s, BF_4). $^{31}P\{^1H\}$ NMR (300 MHz, DMSO-d_6) δ: -11.15 – -10.96 (d), -7.75 – -7.56 (d).

Elemental analysis. Found (%): C, 58.68; H, 4.09; N, 4.24. Calc. for $C_{51}H_{41}AgBF_4N_3OP_2Cl_2$ (%): C, 58.93; H, 3.98; N, 4.04.

Synthesis of **1**

Complex **1**•CH_2Cl_2 (70 mg) in a Schlenk flask was subjected to sonication in a ultrasonic bath in an oil pump vacuum (~10^{-2} Torr) at a temperature of 60 °C for 4 hours.

Yield 99% colorless solid. ^{1}H NMR (300 MHz, acetone-d_6) δ: 6.86-6.91 (m, 2H), 6.98–7.01 (m, 2H), 7.14 (t, *J*= 6 Hz, 2H), 7.34-7.59 (m, 27H), 7.84 (d, *J*= 6 Hz, 2H), 8.07 (t, *J*= 6 Hz, 1H), 8.15 (d, *J*= 6 Hz, 1H), 8,45 (d, *J*= 6 Hz, 1H^{Py}). ^{19}F NMR (300 MHz, acetone-d_6) δ: -151.37 (s, BF_4). ^{31}P {^{1}H} NMR (300 MHz, acetone-d_6) δ: -9.72 – -9.95 (d), -6.61 – -6.37 (d).

Elemental analysis. Found (%): C, 62.94; H, 4.21; N, 4.49. Calc. for $C_{50}H_{39}AgBF_4N_3OP_2$ (%): C, 62.92; H, 4.12; N, 4.40.

Synthesis of **2**

The procedure for obtaining complex **2** is similar to the procedure for complex **1**•CH_2Cl_2. However, the resulting crystals do not contain CH_2Cl_2 molecules and the product does not require strict drying conditions as for complex **1**.

Yield 79%, colorless solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 1.96 (s, 3H, CH_3), 6.75 (m, 2H), 6.89 (d, *J*= 6 Hz, 2H), 7.12 (t, *J*= 6 Hz, 3H), 7.28 – 7.44 (m, 23H), 7.58 (m, 3H), 7.83 (d, *J*= 6 Hz, 2H), 7.98 (m, 2H). ^{19}F NMR (300 MHz, DMSO-d_6) δ: -148.22 (s, BF_4). ^{31}P {^{1}H} NMR (300 MHz, DMSO-d_6) δ: -9.75 – -9.51 (d), -6.47 – -6.24 (d).

Elemental analysis. Found (%): C, 62.98; H, 4.52; N, 4.42. Calc. for $C_{51}H_{41}AgBF_4N_3OP_2$ (%): C, 63.25; H, 4.27; N, 4.34.

§3. NMR Spectra

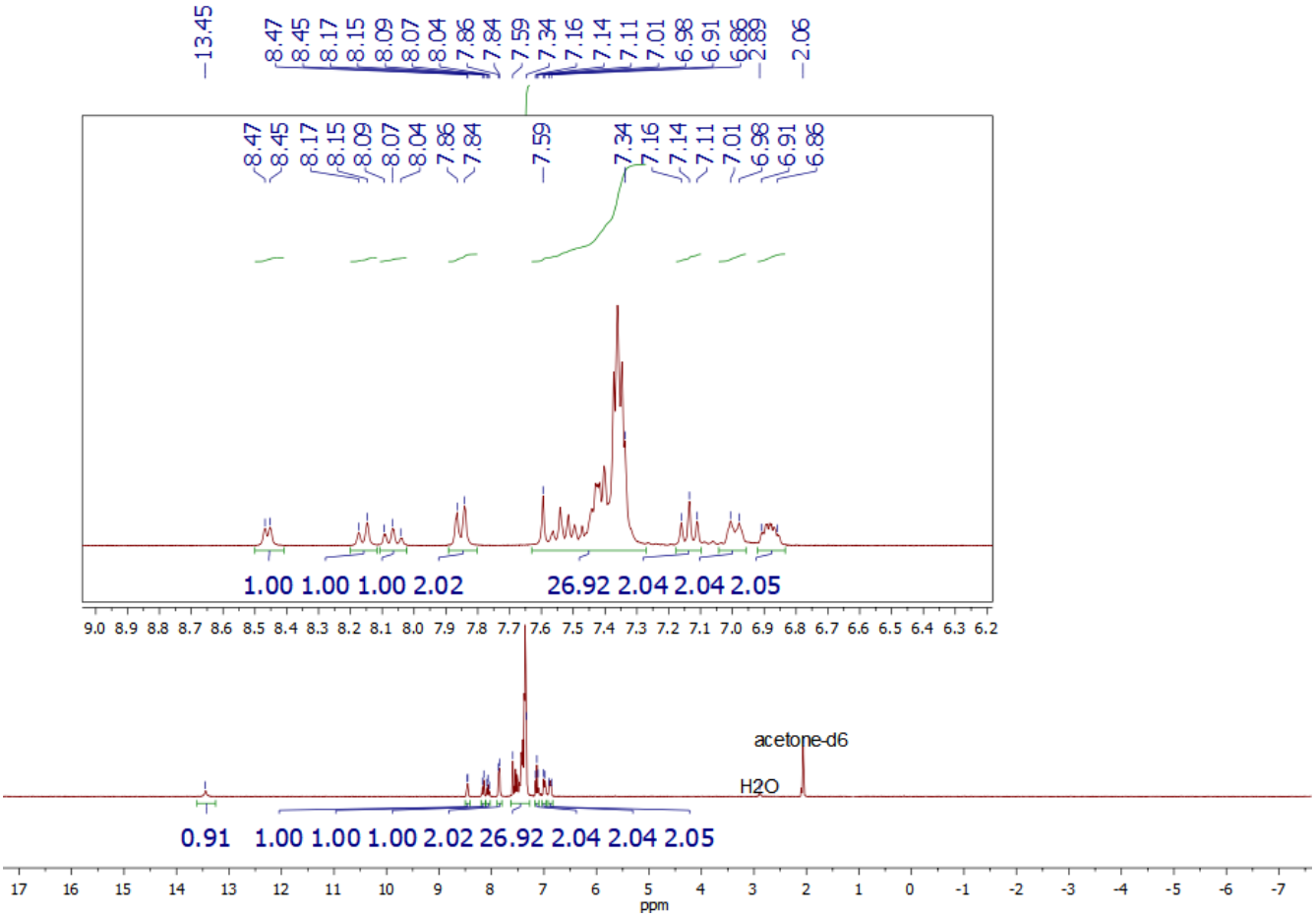


Figure S1. ^{1}H NMR spectrum of **1** in acetone-d_6.

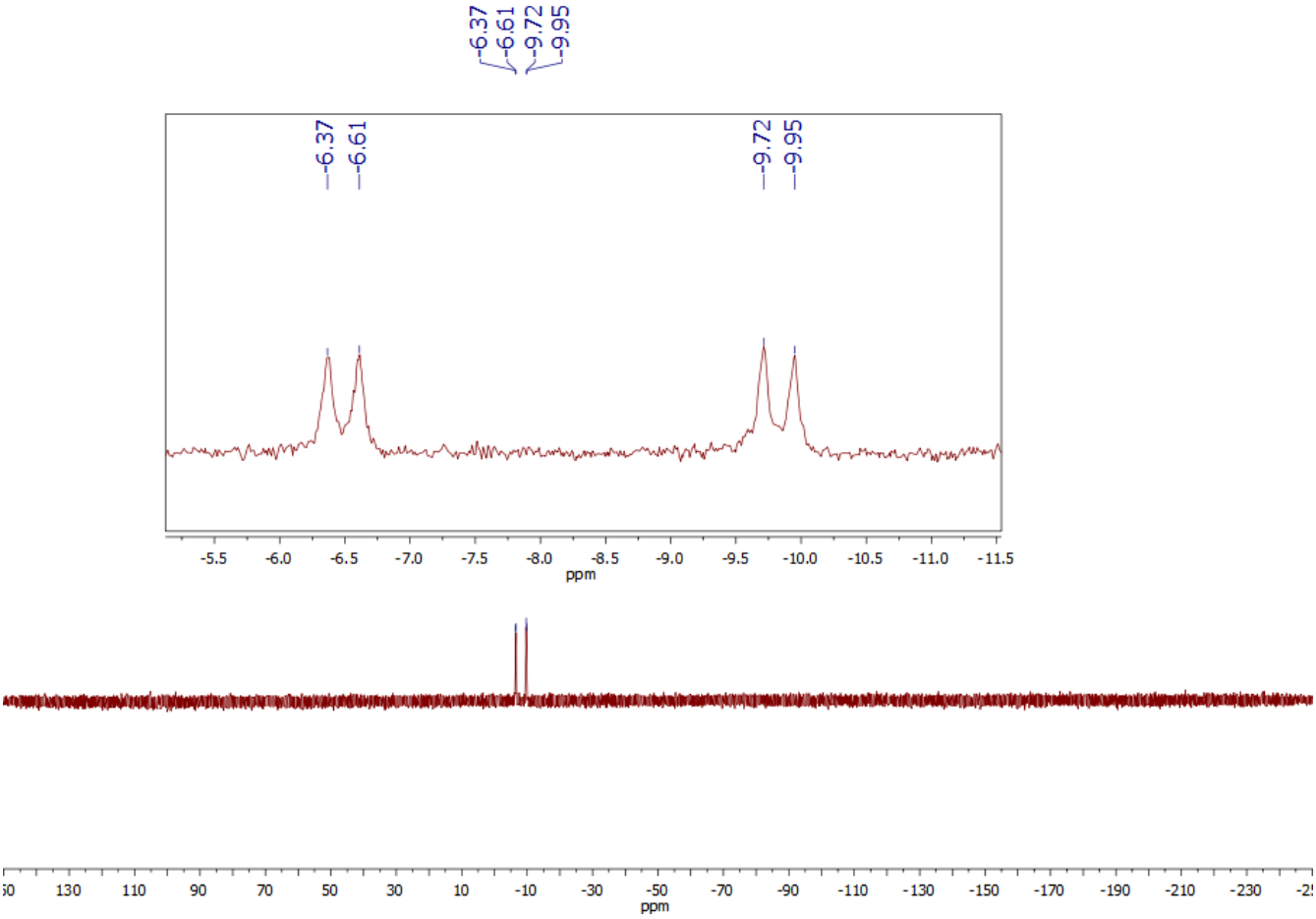


Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum of **1** in acetone-d_6.

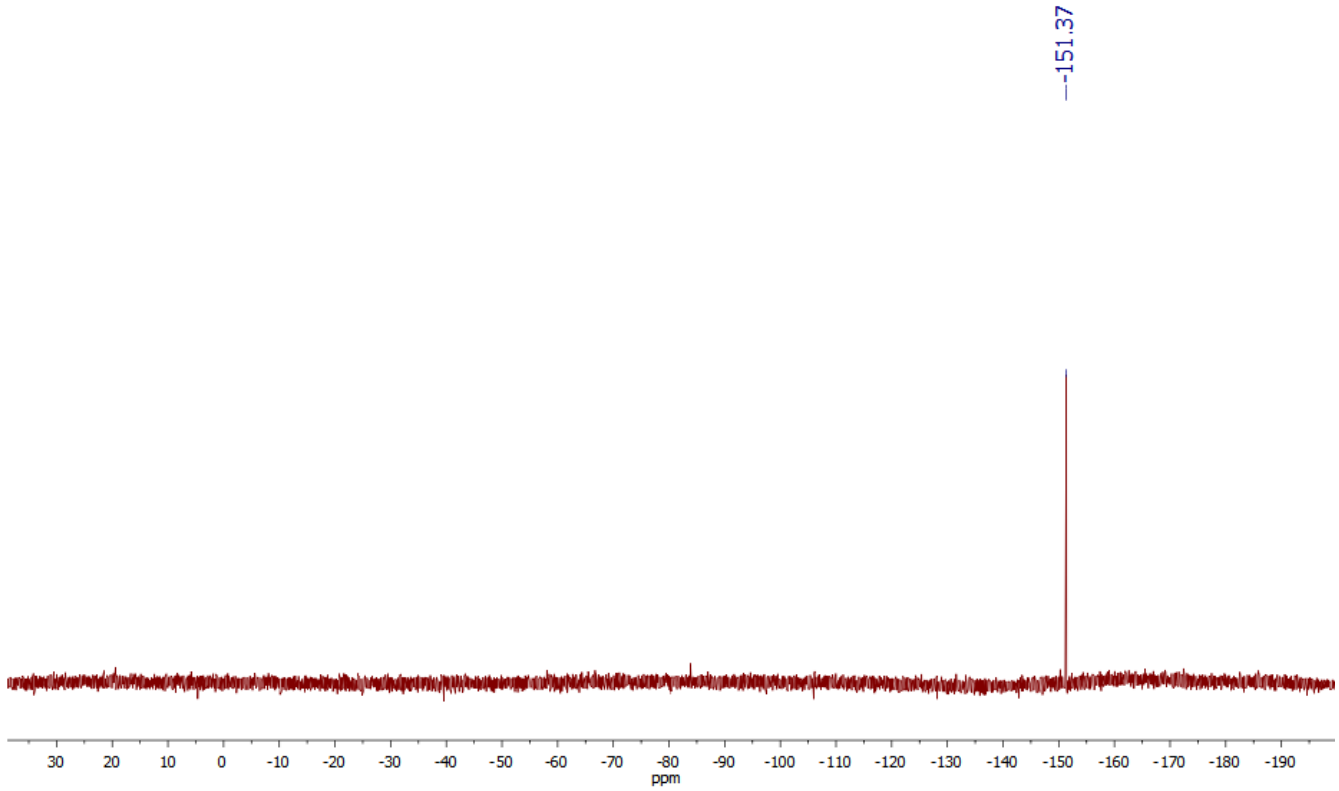


Figure S3. ^{19}F NMR spectrum of **1** in acetone-d_6.

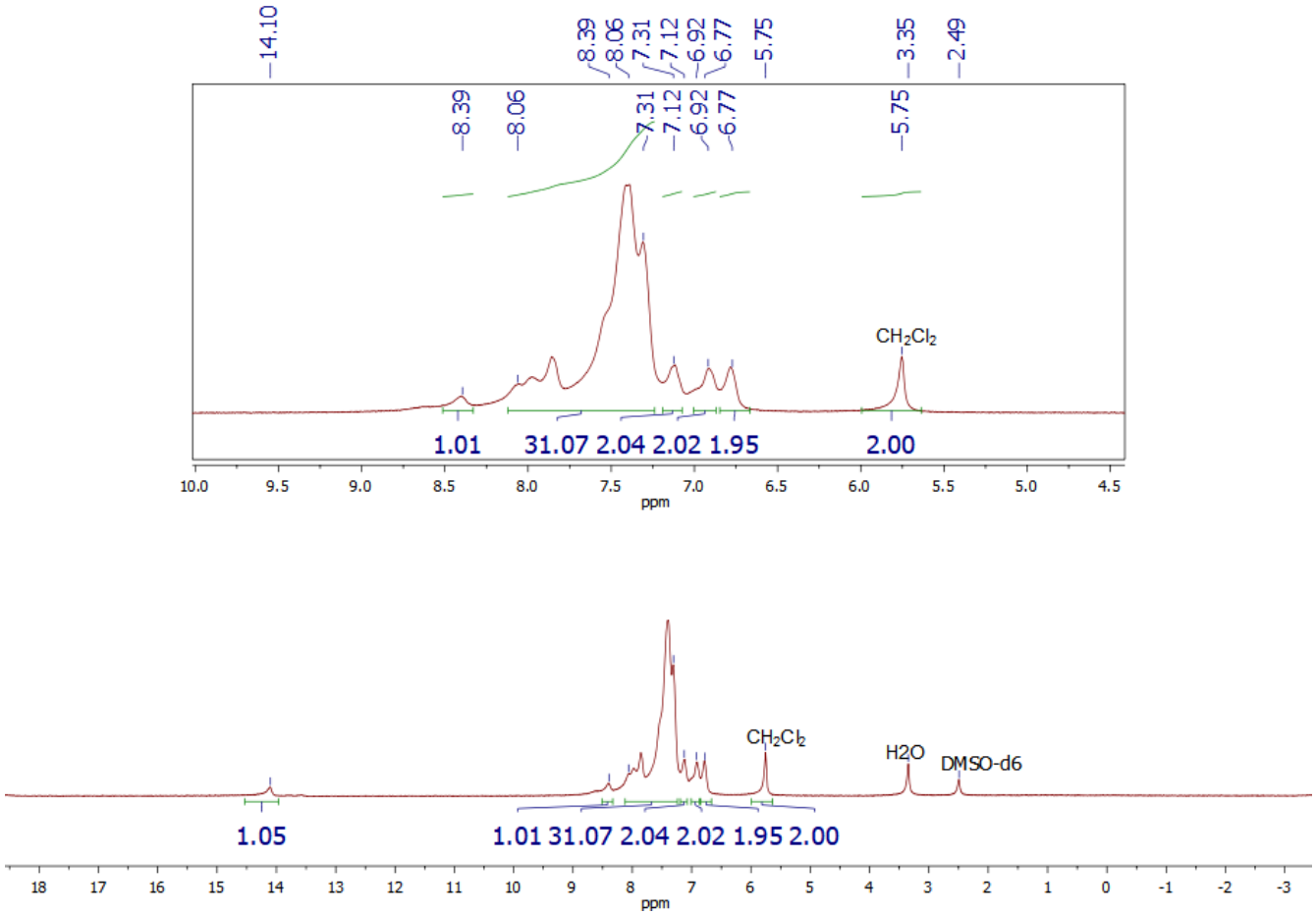


Figure S4. ^{1}H NMR spectrum of **1**•CH_2Cl_2 in DMSO-d_6.

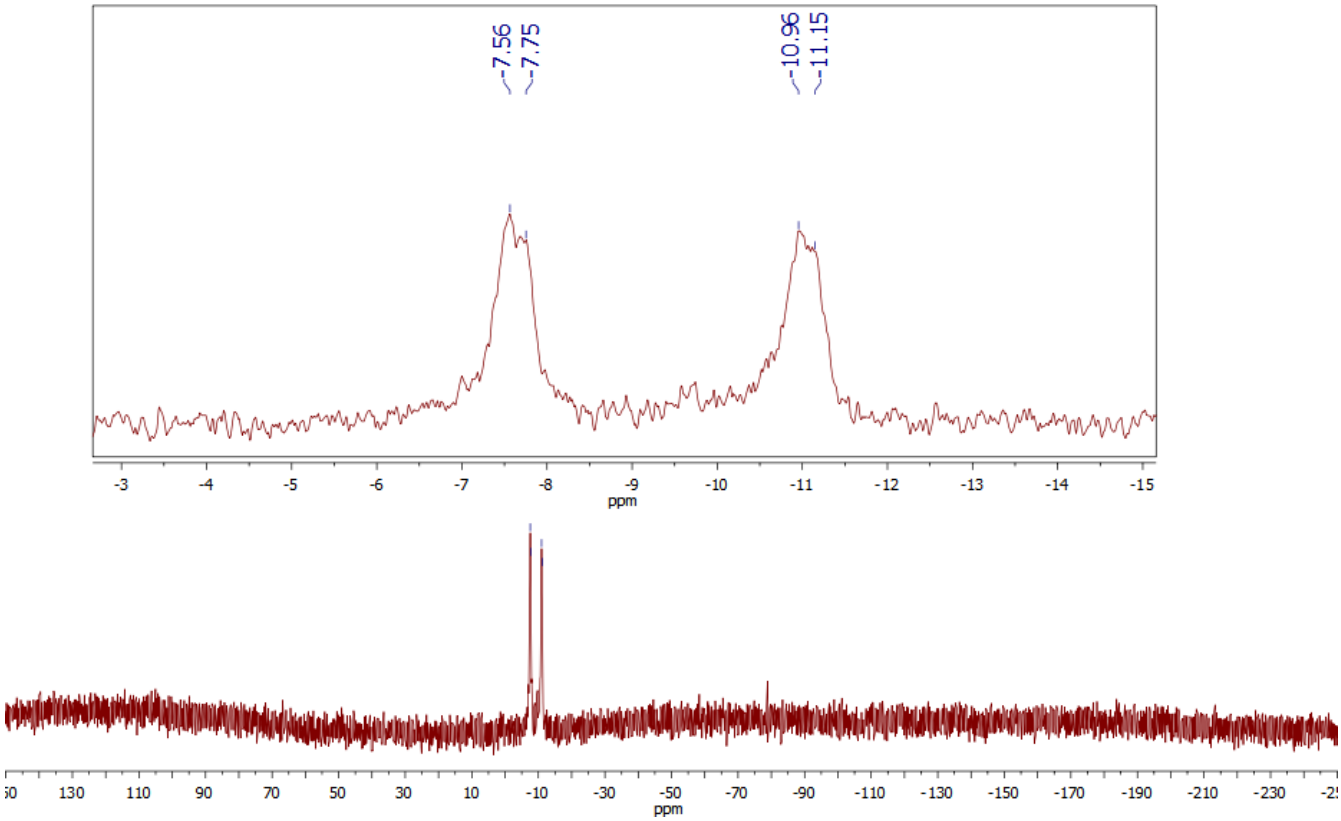


Figure S5. ^{31}P{^{1}H} NMR spectrum of **1**•CH_2Cl_2 in DMSO-d_6.

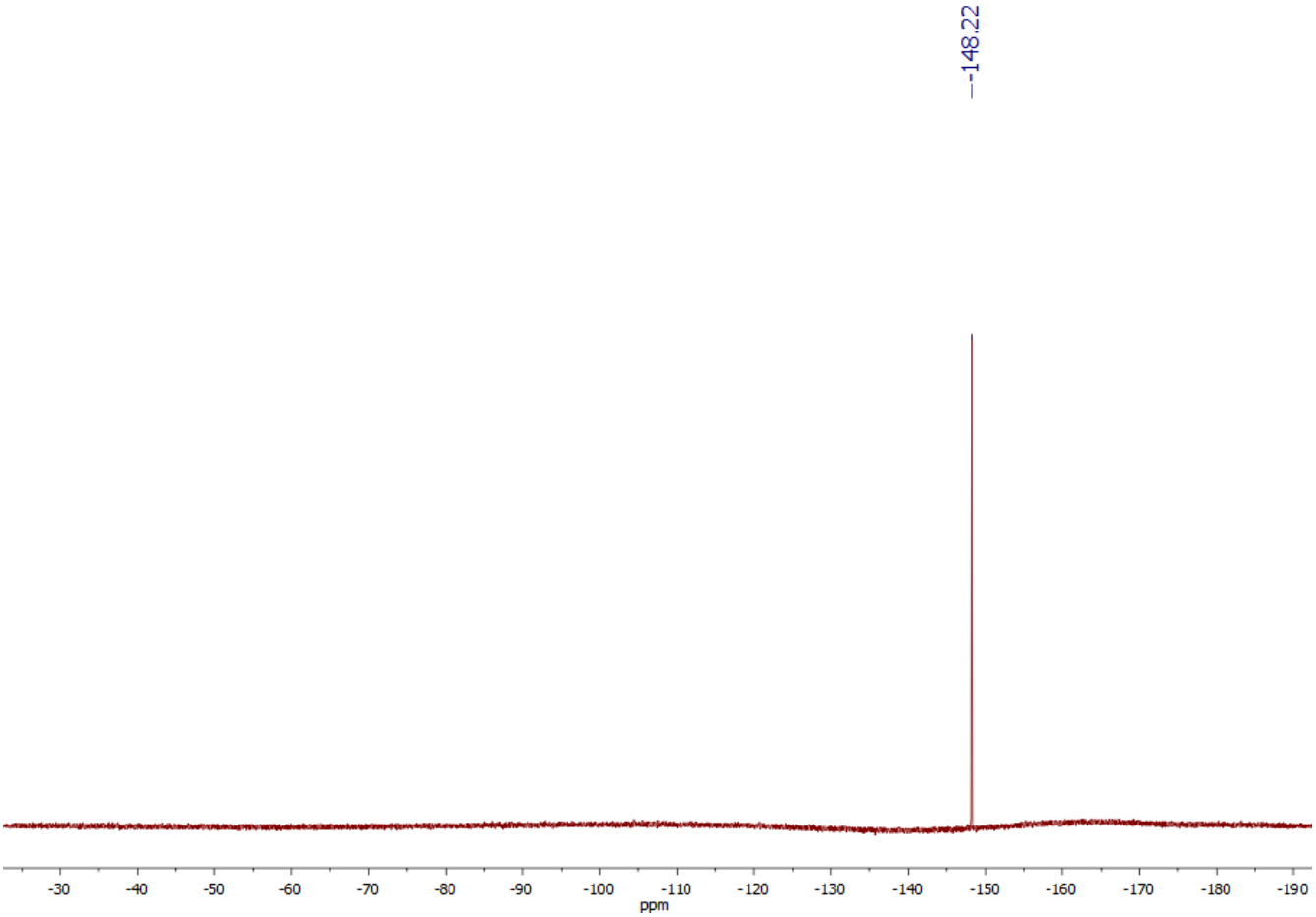


Figure S6. ^{19}F NMR spectrum of **1**•CH_2Cl_2 in DMSO-d_6.

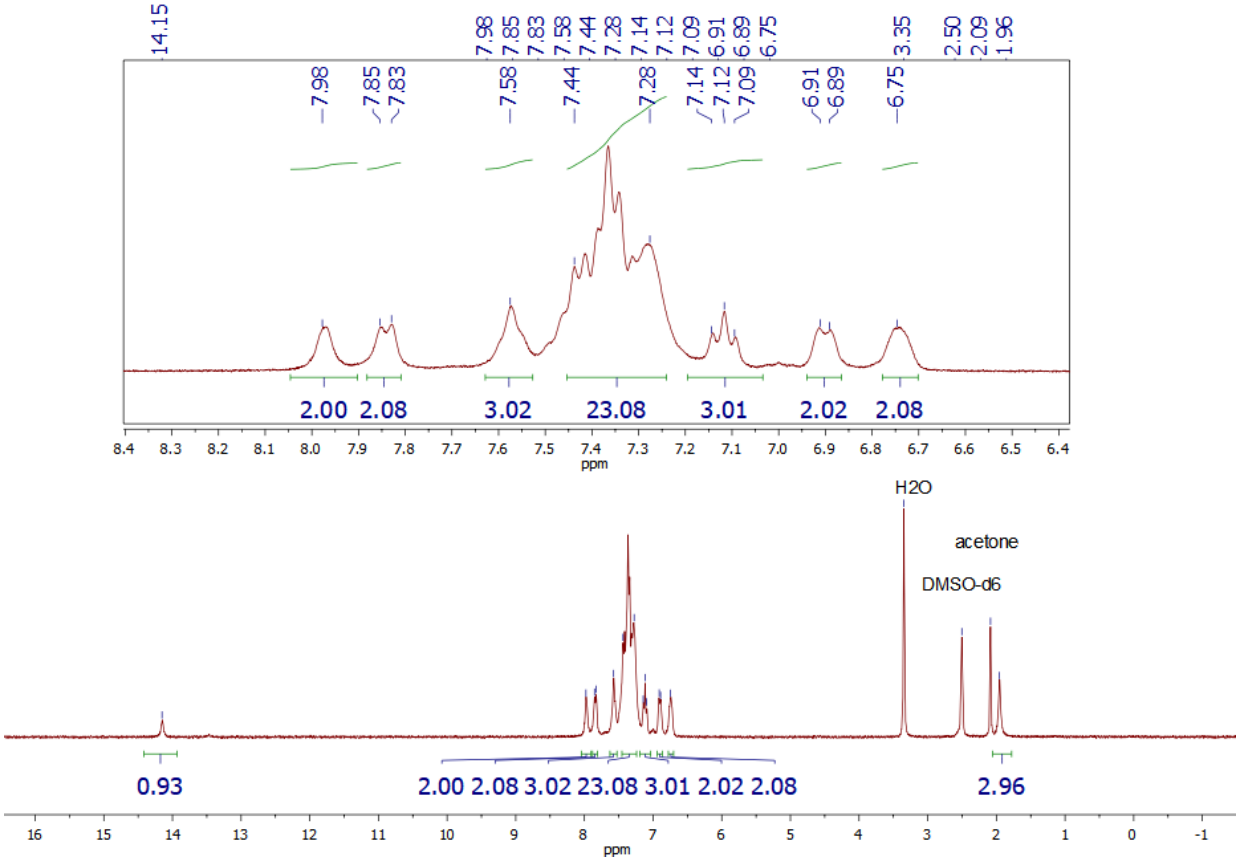


Figure S7. ^{1}H NMR spectrum of **2** in DMSO-d_6.

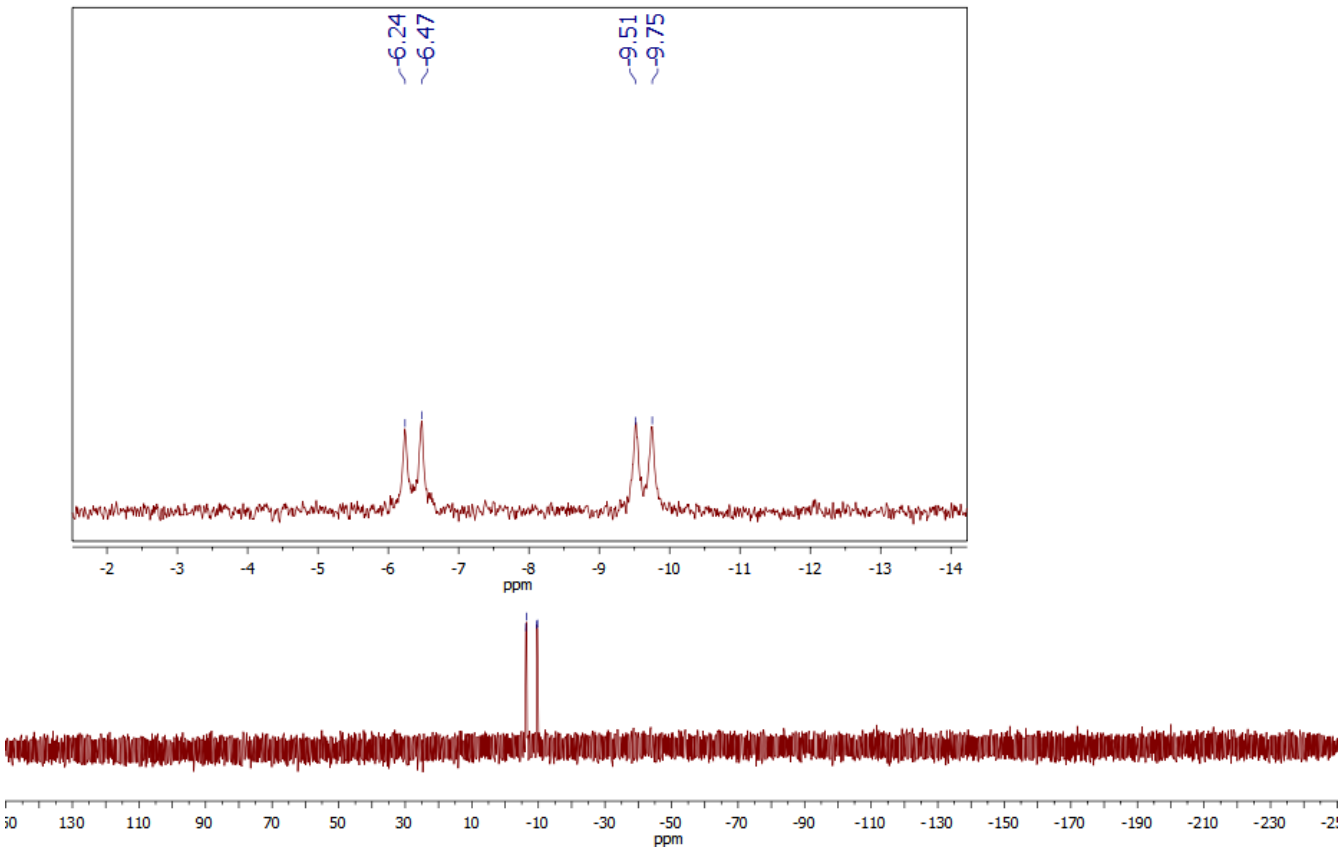


Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum of **2** in DMSO-d_6.

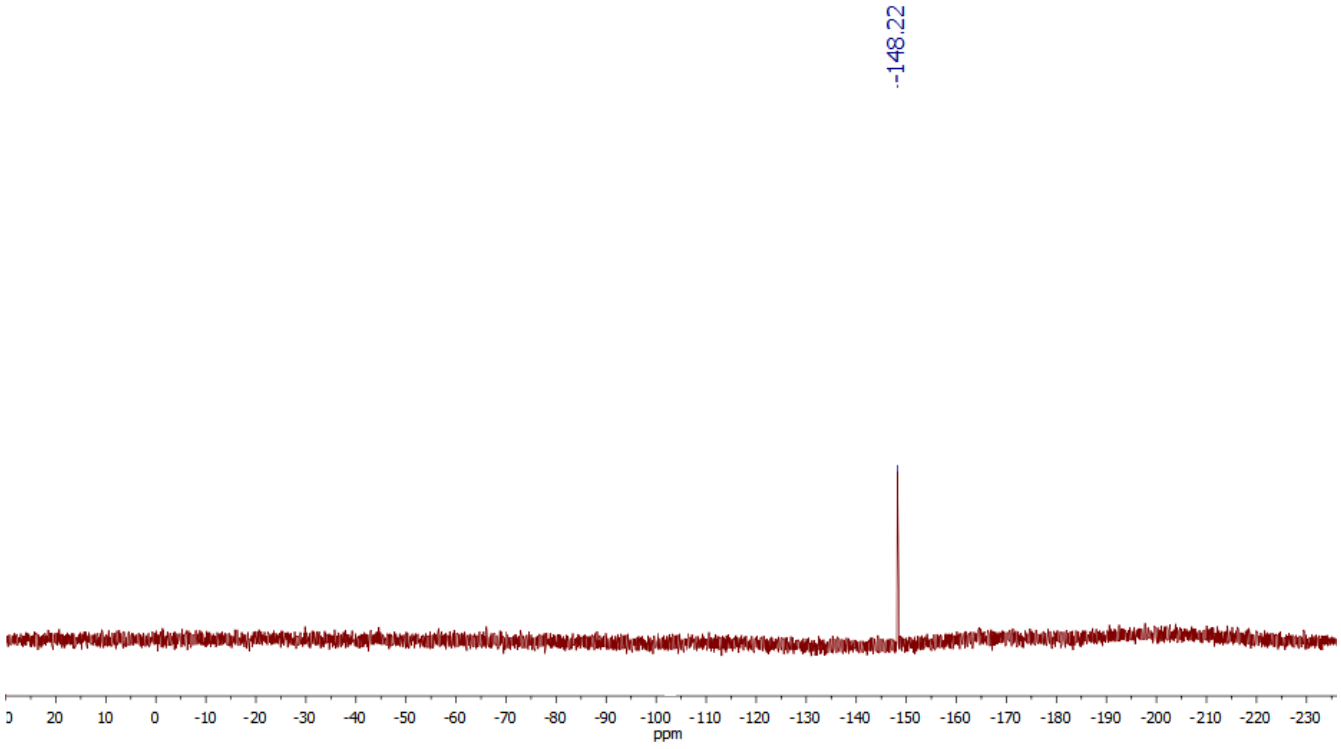
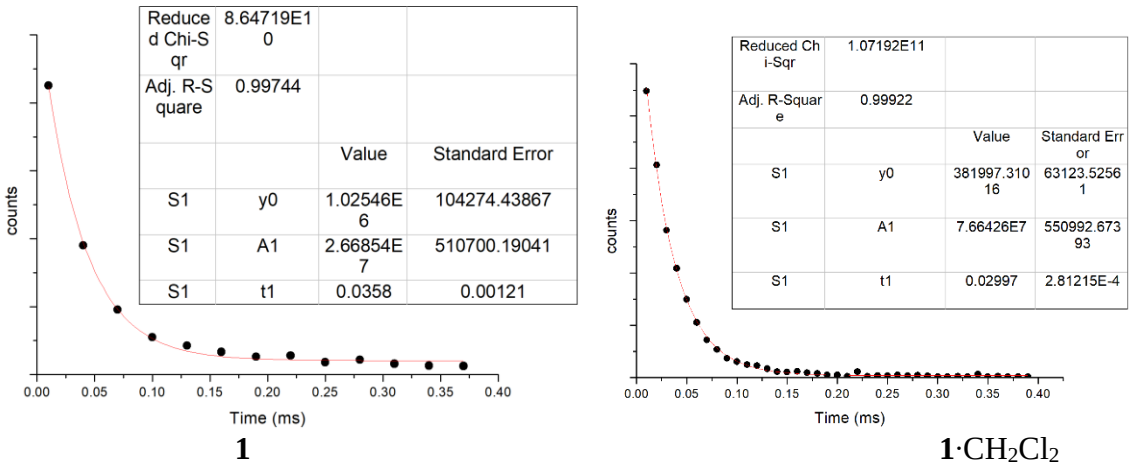


Figure S9. ^{19}F NMR spectrum of **2** in DMSO-d_6.

§4. Photoluminescence.

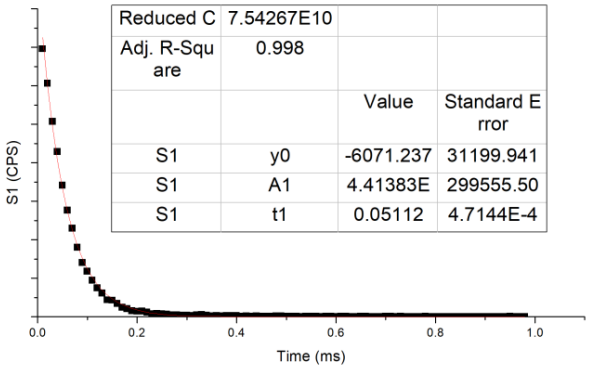


Reduced Chi-Sqr	8.64719E10		
Adj. R-Square	0.99744		
		Value	Standard Error
S1	y0	1.02546E6	104274.43867
S1	A1	2.66854E7	510700.19041
S1	t1	0.0358	0.00121

1

Reduced Chi-Sqr	1.07192E11		
Adj. R-Square	0.99922		
		Value	Standard Error
S1	y0	381997.31016	63123.52561
S1	A1	7.66426E7	550992.67393
S1	t1	0.02997	2.81215E-4

1·CH_2Cl_2



Reduced C	7.54267E10		
Adj. R-Square	0.998		
		Value	Standard Error
S1	y0	-6071.237	31199.941
S1	A1	4.41383E	299555.50
S1	t1	0.05112	4.7144E-4

2

Figure S10. Phosphorescence decays of complexes **1**, **1**·CH_2Cl_2 and **2** in the solid state at 298 K.

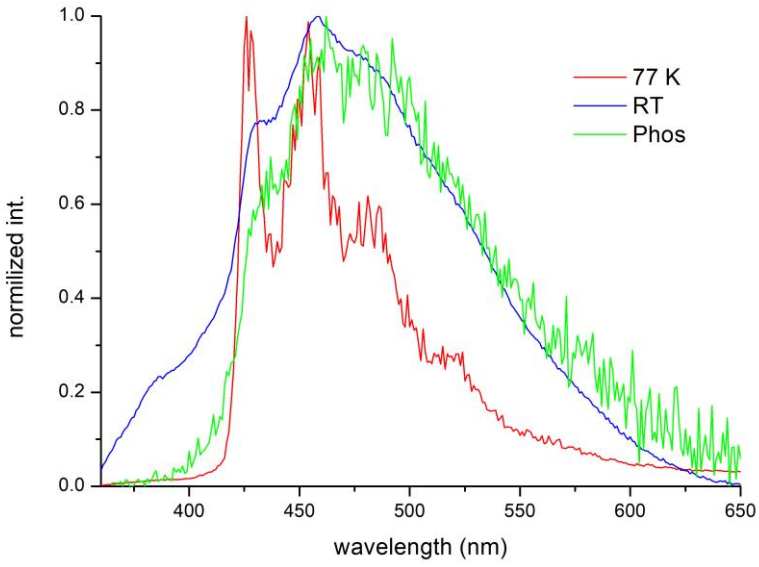


Figure S11. Emission spectra of complex **1** in PMMA matrix: steady state and phosphorescence (sample window 0.2 ms, flash delay 0.05 ms).

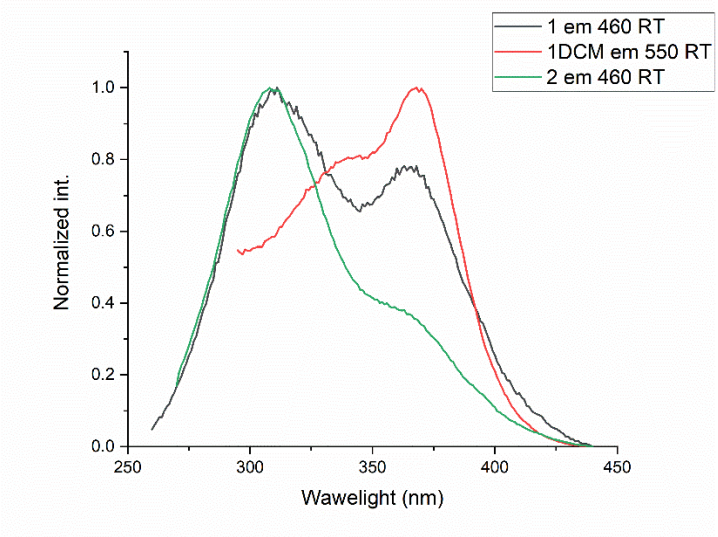


Figure S12. Excitation spectra of complexes **1**, **1**·CH_2Cl_2 and **2** in the solid state at 298 K.

§5. Computational details

The DFT computations performed with ORCA 5.04 package[S5,S6] applying ωB97X-D3 functional[S7,S8] and ZORA-TZVP basis set with ZORA relativistic Hamiltonian. Basis set for Ag atoms was the relativistic SARC-ZORA-TZVP[S9] Ground states of complexes were fully optimized without any contrains. RIJCOSX procedure was used in order to speedup calculations. 20 lowest energy exited states were considered under Tamm–Dancoff approximation (TDA). The quantitative analysis of excitations (natural transition orbitals, fragment impacts) was performed with the Multiwfn v3.8 program[S10].

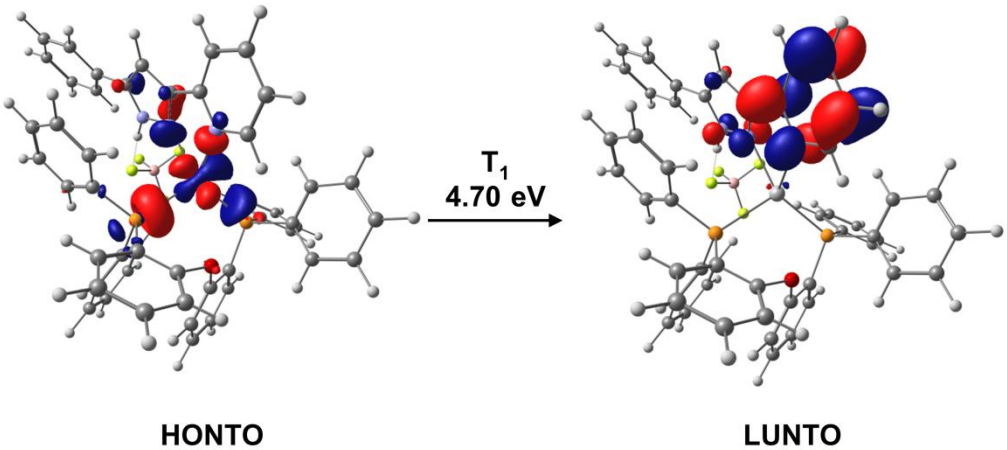


Figure S13. Natural transition orbitals HONTO and LUNTO for the $S_0 \rightarrow S_1$ excitation of **1** as an isosurface at 0.05 a.u.

Table S1. Optimized XYZ coordinates of complex **1**
Optimized ground states, E -8660.423233491987

Ag	1.073759633	8.104548640	10.719514389	C	-2.416363134	8.760112250	9.723215288
P	0.195426284	6.897731203	8.653620425	C	1.552930467	5.978002478	7.835267800
P	-0.762761069	9.100061511	11.956034144	C	1.606178685	4.588942212	7.869275119
O	-1.389673165	9.439454492	9.105179708	H	0.778412662	4.023188863	8.278659924
N	3.576171832	5.988373098	10.761210924	C	2.736953998	3.923920997	7.414662674
H	2.885365455	5.278271626	11.032650689	H	2.777890763	2.842714015	7.466520269
N	3.190867418	7.253242428	10.722464885	C	3.815030431	4.637347028	6.917358625
N	2.792516337	9.826272976	9.932917776	H	4.699968059	4.114705340	6.574569952
C	4.842684239	5.823580699	10.339180318	C	3.768302477	6.025232831	6.885206581
C	5.306623588	7.086912032	10.009781194	H	4.615897099	6.590470676	6.515666999
H	6.283784657	7.338832894	9.633180389	C	2.650729420	6.692935428	7.354566846
C	4.223427620	7.944897894	10.253452246	H	2.637328395	7.778458977	7.363378242
C	4.053875630	9.380443407	9.988823841	C	-1.172035243	5.691074923	8.815465693
C	5.139209481	10.225278355	9.776114026	C	-1.975994982	5.319367609	7.738803235
H	6.147511854	9.837266052	9.841862998	H	-1.813711458	5.755322555	6.759383825
C	4.904284301	11.558286257	9.493052887	C	-2.994439560	4.399727661	7.919954538
H	5.733341305	12.234761563	9.321711818	H	-3.619944776	4.116774124	7.081171560
C	3.597043282	12.017676203	9.439806889	C	-3.210970841	3.838512326	9.173493483
H	3.368002140	13.052986356	9.223590419	H	-4.005107095	3.113654201	9.311266873
C	2.576005333	11.111673694	9.670732970	C	-2.409579148	4.199719858	10.243898943
H	1.536293559	11.421619803	9.646904771	H	-2.553905306	3.761491661	11.223670584
C	5.458343012	4.495433397	10.246717750	C	-1.395589342	5.131168560	10.068191776
C	4.969009219	3.426479605	10.996295731	H	-0.770217336	5.392266019	10.913204507
H	4.151629647	3.565233165	11.695419466	C	-1.064255038	8.648415891	13.700627232
C	5.530262357	2.167193501	10.858285671	C	-0.542383370	7.442846824	14.158677636
H	5.135938487	1.345359770	11.443454240	H	0.063241914	6.813841793	13.515772669
C	6.587805961	1.962034855	9.984378515	C	-0.795325492	7.027516524	15.458519504
H	7.025949400	0.976160186	9.882173197	H	-0.388641547	6.082599463	15.796978033
C	7.083468660	3.024593286	9.241093549	C	-1.554282654	7.820547244	16.304374644
H	7.906353184	2.870438542	8.552805930	H	-1.748289334	7.498304811	17.320945120
C	6.518504693	4.282195237	9.367773890	C	-2.063499479	9.033455488	15.854699747
H	6.886822205	5.103562921	8.763712806	H	-2.652479109	9.656416703	16.517650086
C	-0.414811985	8.072147557	7.369530123	C	-1.821912406	9.447653446	14.555738761
C	-0.157349551	7.916548206	6.009165677	H	-2.221689358	10.392812606	14.205098490
H	0.407065360	7.054131441	5.674318481	C	-0.761678597	10.935292239	11.959004514
C	-0.591780119	8.852331883	5.083114889	C	0.395689426	11.569847936	12.406406423
H	-0.378003515	8.706350561	4.031283980	H	1.244368171	10.974983720	12.729186905
C	-1.289548050	9.973686496	5.505178395	C	0.471509204	12.952549147	12.433795220
H	-1.623078042	10.713237173	4.787151529	H	1.374849917	13.434006370	12.789466369
C	-1.561653323	10.149442947	6.852478541	C	-0.604754518	13.715431771	12.000680273
H	-2.103733607	11.014441216	7.214722327	H	-0.545105163	14.797408333	12.016890345
C	-1.136249055	9.201262783	7.767007990	C	-1.756001296	13.089485790	11.547290291
C	-2.321393006	8.617527426	11.110112130	H	-2.599070727	13.680904281	11.209496510
C	-3.347159864	7.950080607	11.771214826	C	-1.836737331	11.703831499	11.528602134
H	-3.280205556	7.805466360	12.842066813	H	-2.740757064	11.221127041	11.175355668
C	-4.431712301	7.436810744	11.077028765	F	1.530939642	4.335391166	11.320606405
H	-5.209650167	6.904490321	11.609411400	F	1.767307114	2.994015600	13.177612387
C	-4.500937693	7.587699399	9.702757345	F	-0.120144481	4.301740302	12.929790679
H	-5.334871082	7.173554223	9.149162277	F	1.910706712	5.285258132	13.371724423
C	-3.498618949	8.258313277	9.020103449	B	1.262273612	4.206927778	12.743675840
H	-3.542721022	8.365658242	7.943975965				

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§6. References

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