Electronic Supporting Information

Unprecedented Ir(III) cationic complexes based on tridentate tetrazolate ligands: synthesis, photophysics and encapsulation in SiO_2 nanoparticles

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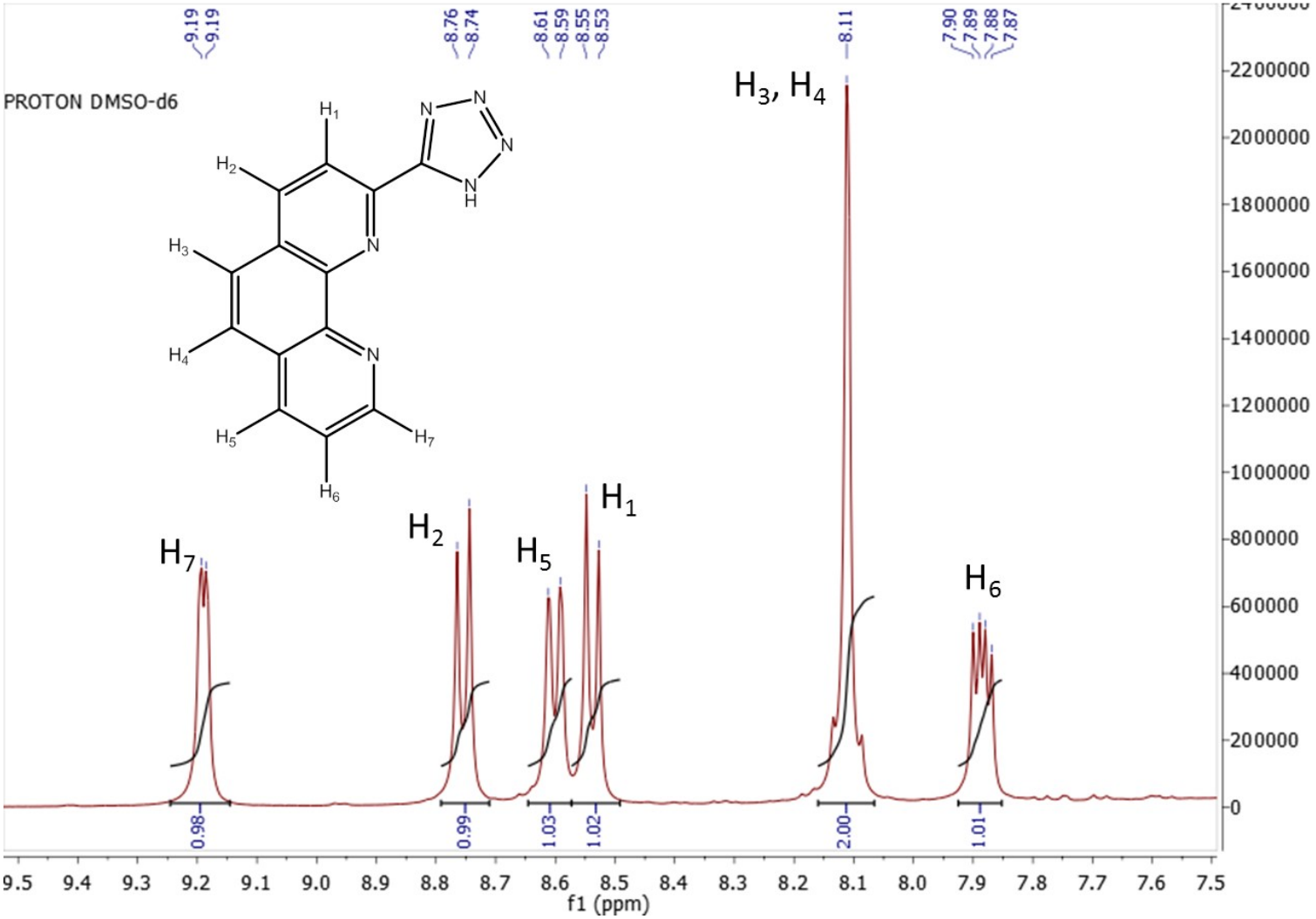
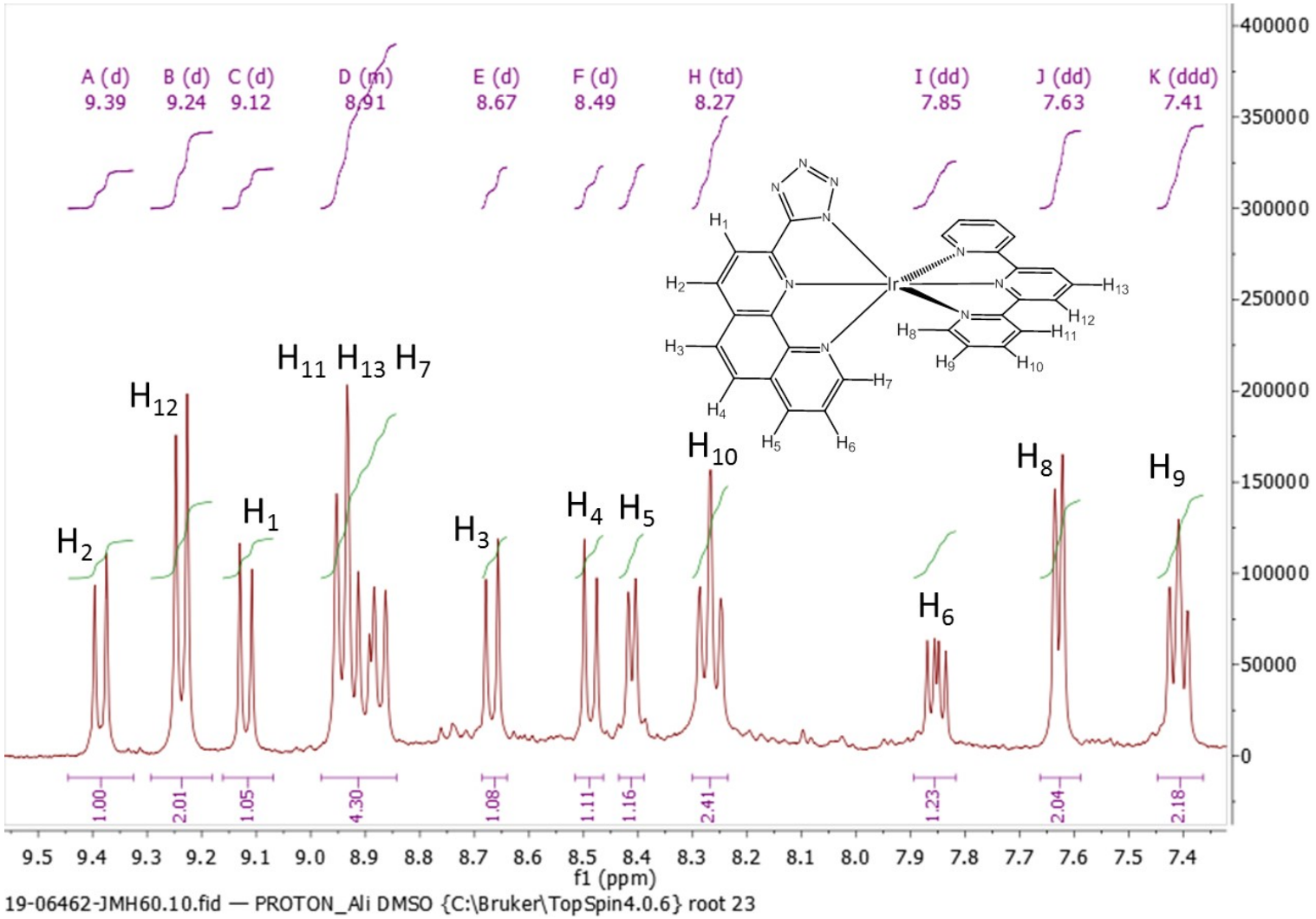
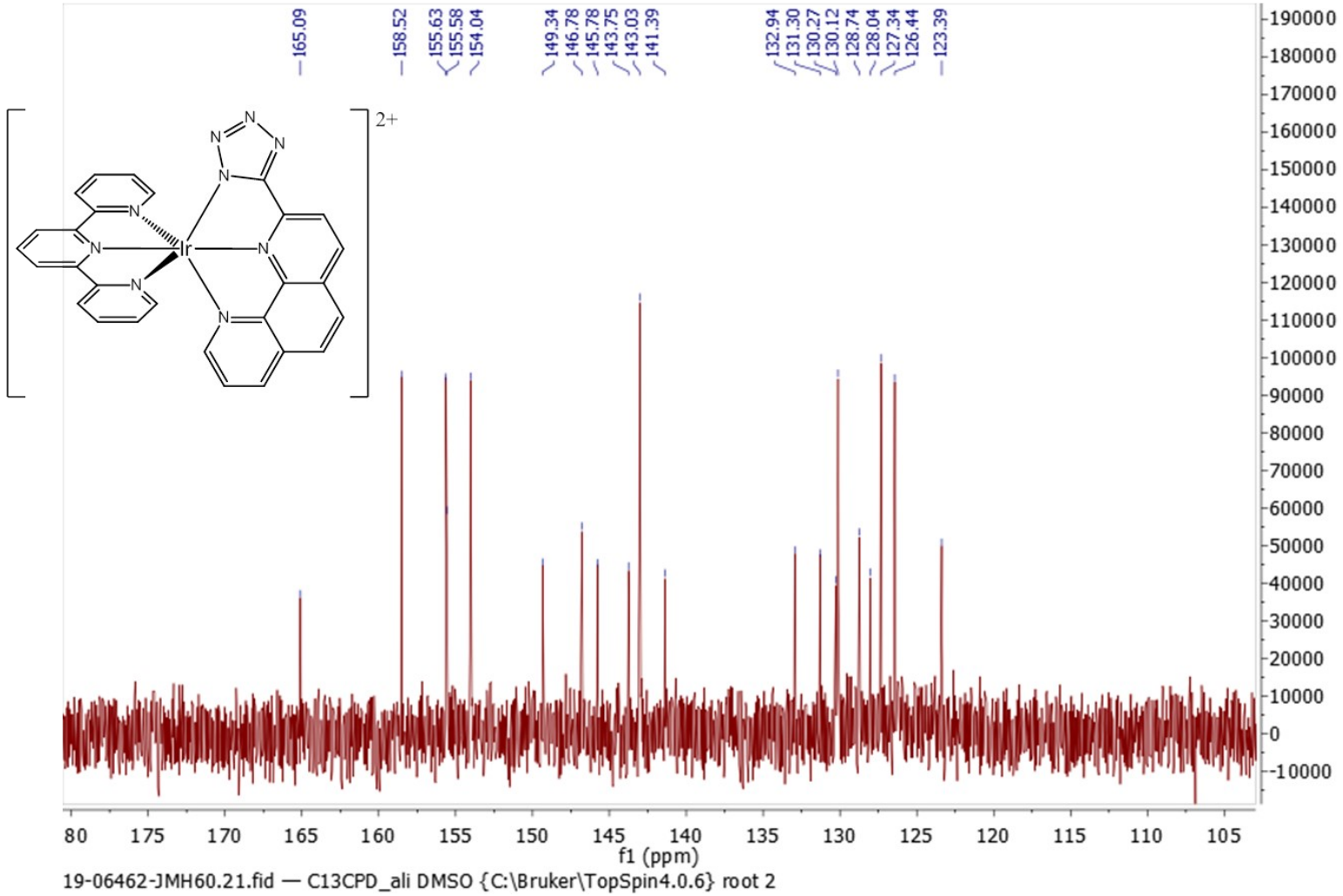
^{1}H NMR of ligand Hphenttz



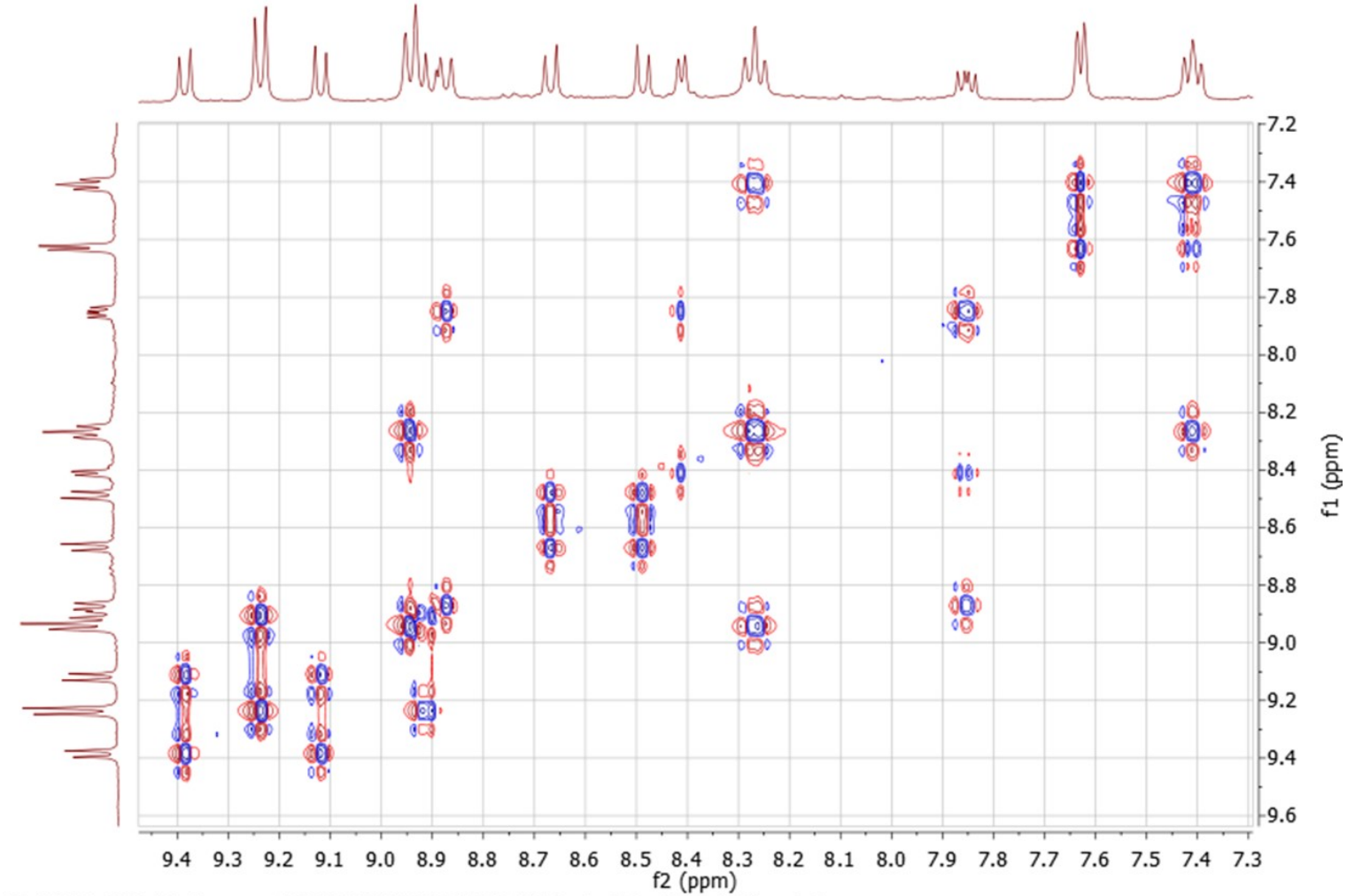
^{1}H NMR of complex **1**



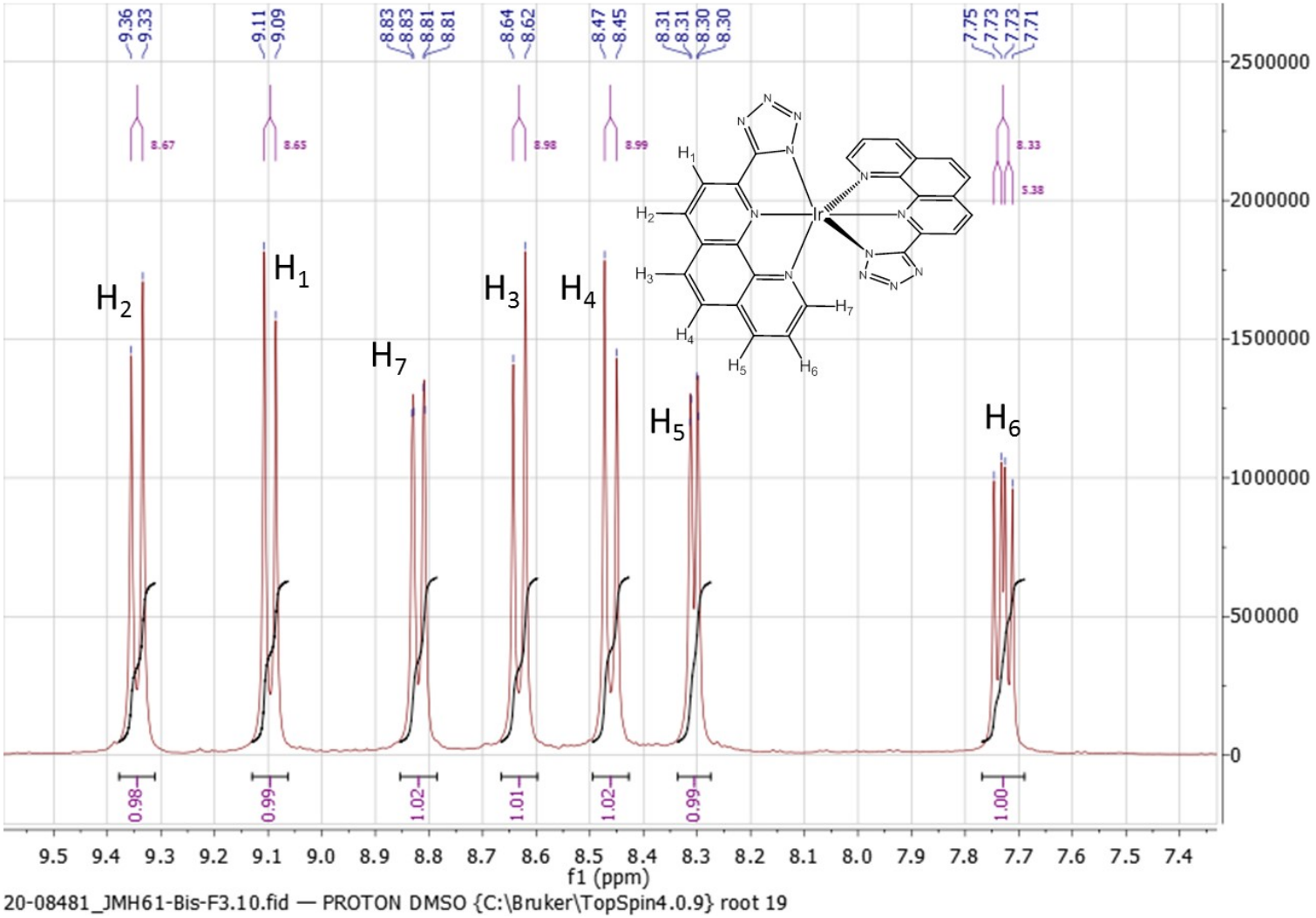
^{13}C NMR of complex **1**



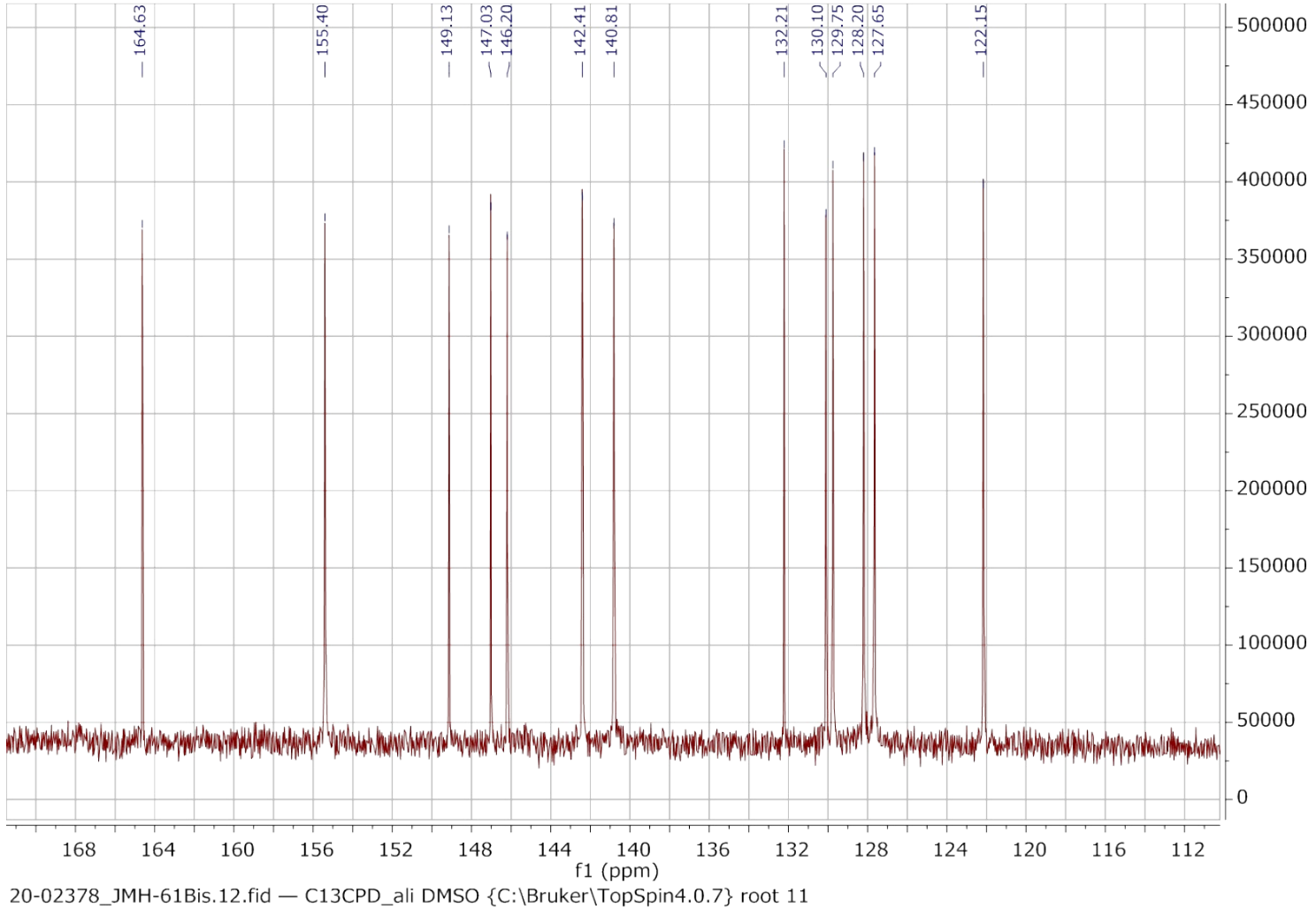
2D HH-COSY of complex **1**



^{1}H NMR of complex **2**



^{13}C NMR of complex **2**



^{13}C DEPT of complex **2**

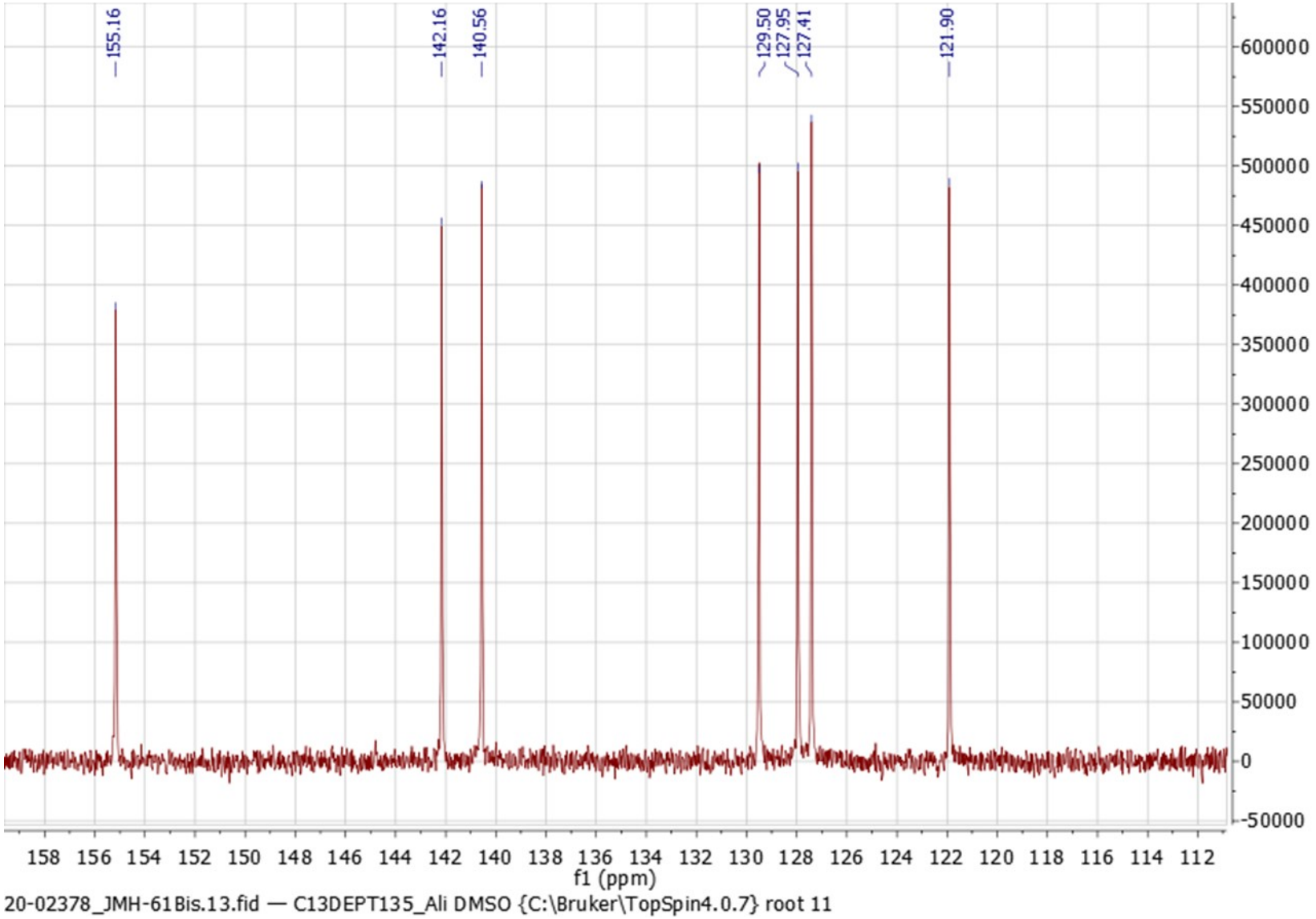


Table S1. Crystallographic data for complexes 1-2.

	1	**2**
Formula	$C_{30}H_{21}F_{12}IrN_{10}P_2$	$C_{34}H_{26}F_6IrN_{16}P$
Mw ($g \cdot mol^{-1}$)	1003.71	995.88
T (K)	100	100.0
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	C2/c
a/Å	13.6360(5)	18.841(3)
b/Å	11.6774(4)	12.3097(19)
c/Å	20.3107(7)	18.522(4)
α/°	90	90
β/°	91.2258(12)	120.168(3)
γ/°	90	90
Z	4	4
ρ_{calc} ($g \cdot cm^{-3}$)	2.062	1.781
M (mm^{-1})	4.341	3.720
F(000)	1944.0	1952.0
Crystal size/mm^3	0.339 × 0.31 × 0.239	0.304 × 0.183 × 0.145
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.592 to 61.304	5.002 to 56.844
Reflections collected	74808	55479
Independent reflections	9938 [R_{int} = 0.0534, R_{sigma} = 0.0270]	4647 [R_{int} = 0.0510, R_{sigma} = 0.0221]
Data/restraints/parameters	9938/52/534	4647/0/266
Goodness-of-fit on F^2	1.175	1.119
Final R indexes [I>=2σ (I)]	R_1 = 0.0241, wR_2 = 0.0513	R_1 = 0.0151, wR_2 = 0.0386
Final R indexes [all data]	R_1 = 0.0320, wR_2 = 0.0542	R_1 = 0.0164, wR_2 = 0.0390
Largest diff. peak/hole /e $Å^{-3}$	1.38/-1.16	0.61/-1.00

Table S2. Selected bond distances (Å) and angles (º) for complex **1**. The theoretical values have been calculated at the CAM-B3LYP/6-31G**+LANL2DZ and B3LYP/6-31G**+LANL2DZ levels in the presence of the solvent (acetonitrile) in the singlet ground state (S_0) and in the lowest-energy (T_1) triplet state.

Bond distances (Å)					
	Exp. (RX)	**Theor. S_0 CAM-B3LYP**	**Theor. T_1 CAM-B3LYP**	**Theor. S_0 B3LYP**	**Theor. T_1 B3LYP**
Ir1-N1	2.045(2)	2.075	2.076	2.087	2.088
Ir1-N2	1.972(2)	1.993	1.992	2.000	2.004
Ir1-N3	2.060(2)	2.076	2.076	2.087	2.088
Ir1-N4	2.069(2)	2.111	2.111	2.128	2.130
Ir1-N5	2.0007(19)	2.012	2.011	2.022	2.005
Ir1-N6	2.047(2)	2.051	2.039	2.062	2.048

Bond angles (º)					
	Exp. (RX)	**Theor. S_0 CAM-B3LYP**	**Theor. T_1 CAM-B3LYP**	**Theor. S_0 B3LYP**	**Theor. T_1 B3LYP**
N1-Ir-N2	79.83(8)	79.83	79.81	79.68	79.60
N1-Ir-N3	159.63(8)	159.65	159.60	159.35	159.18
N1-Ir-N4	93.43(8)	92.16	92.50	92.19	92.61
N1-Ir-N5	99.71(8)	100.17	100.18	100.32	100.39
N1-Ir-N6	88.33(8)	91.83	91.41	91.92	91.50
N2-Ir-N3	80.09(8)	79.83	79.81	79.68	79.60
N2-Ir-N4	97.33(8)	101.71	102.54	101.94	102.44
N2-Ir-N5	177.76(8)	178.54	178.53	178.57	178.76
N2-Ir-N6	104.82(8)	101.01	99.70	101.12	100.50
N3-Ir-N4	92.43(8)	92.16	92.50	92.18	92.61
N3-Ir-N5	100.49(8)	100.17	100.18	100.32	100.39
N3-Ir-N6	93.56(8)	91.83	91.41	91.92	91.50
N4-Ir-N5	80.49(8)	79.75	78.93	79.49	78.80
N4-Ir-N6	157.73(8)	157.28	157.76	156.93	157.06
N5-Ir-N6	77.33(8)	77.52	78.83	77.44	78.26

Table S3. Selected bond distances (Å) and angles (º) for complex **2**. The theoretical values have been calculated at the CAM-B3LYP/6-31G**+LANL2DZ and B3LYP/6-31G**+LANL2DZ levels in the presence of the solvent (acetonitrile) in the singlet ground state (S_0) and in the lowest-energy (T_1) triplet state.

Bond distances (Å)					
	Exp. (RX)	**Theor. S_0 CAM-B3LYP**	**Theor. T_1 CAM-B3LYP**	**Theor. S_0 B3LYP**	**Theor. T_1 B3LYP**
Ir1-N1	2.0812(13)	2.112	2.113	2.125	2.128
Ir1-N2	1.9933(15)	2.008	2.008	2.017	2.020
Ir1-N3	2.0388(14)	2.049	2.049	2.060	2.060

Bond angles (º)					
	Exp. (RX)	**Theor. S_0 CAM-B3LYP**	**Theor. T_1 CAM-B3LYP**	**Theor. S_0 B3LYP**	**Theor. T_1 B3LYP**
N1-Ir-N1’	90.63(7)	93.23	93.72	93.01	93.52
N1-Ir-N2	80.12(6)	79.80	79.77	79.55	79.48
N1-Ir-N2’	101.83(5)	101.49	101.68	102.00	101.89
N1-Ir-N3	157.87(5)	157.42	157.37	157.10	156.95
N1-Ir-N3’	94.68(5)	91.72	91.20	91.95	91.47
N1’-Ir-N2	101.83(5)	101.67	102.33	102.00	102.61
N1’-Ir-N2’	80.12(6)	79.80	79.00	79.55	78.85
N1’-Ir-N3	94.68(5)	91.73	91.80	91.95	92.26
N1’-Ir-N3’	157.87(5)	157.42	157.93	157.10	157.36
N2-Ir-N2’	177.28(8)	178.02	178.01	177.79	177.97
N2-Ir-N3	77.77(6)	77.63	77.61	77.55	77.48
N2-Ir-N3’	100.25(5)	100.89	99.72	100.89	100.02
N3-Ir-N3’	88.44(8)	92.10	91.87	92.12	91.73

Table S4. Continuous Shape Measures[1] of the coordination sphere geometry for the Ir(III) centre in the complexes reported in this work.

Compound	JPPY-6	TPR-6	OC-6	PPY-6	HP6
1	26.366	11.585	**2.394**	22.307	33.383
2	27.095	12.118	**2.570**	23.088	33.967
$[Ir(tpy)_2]^{3+}$	27.575	12.166	**2.032**	23.636	34.185

JPPY-6	5 C5v	Johnson pentagonal pyramid J2
TPR-6	4 D3h	Trigonal prism
OC-6	3 Oh	Octahedron
PPY-6	2 C5v	Pentagonal pyramid
HP-6	1 D6h	Hexagon

[1] a) S. Alvarez, P. Alemany, D. Casanova, J. Cirera, M. Llunell, D. Avnir, *Coord. Chem. Rev.* **2005**, *249*, 1693-1708, b) J. Cirera, E. Ruiz, S. Alvarez, *Organometallics*, **2005**, *24*, 1556-1562.

Table S5. List of the computed electronic transitions for complex **1** with their character obtained using CAM-B3LYP with the 6-31G** + LANL2DZ basis sets. Only the transitions with character greater than 5% are reported.

Excited state	E (eV)	Wavelength (nm)	f	Assignments	Character (%)
T_1	2.6319	471.09	0	HOMO-2 ->LUMO+1	14.0
				HOMO-1 ->LUMO+1	7.7
				HOMO ->LUMO+1	15.2
				HOMO ->LUMO+2	12.6
				HOMO ->LUMO+3	26.7
T_2	2.8783	430.75	0	HOMO-6 ->LUMO	6.8
				HOMO-3 ->LUMO	12.9
				HOMO-2 ->LUMO+2	7.8
				HOMO-1 ->LUMO+2	30.8
				HOMO-1 ->LUMO+3	14.8
T_3	3.1009	399.84	0	HOMO ->LUMO+1	62.9
				HOMO ->LUMO+3	7.2
T_4	3.1408	394.75	0	HOMO-2 ->LUMO	8.6
				HOMO-1 ->LUMO	52.8
				HOMO ->LUMO	5.4
T_5	3.5135	352.88	0	HOMO-2 ->LUMO+1	40.9
				HOMO-2 ->LUMO+3	5.3
				HOMO-1 ->LUMO+1	9.4
				HOMO ->LUMO+2	5.5
				HOMO ->LUMO+3	11.0
T_6	3.7463	330.95	0	HOMO-19 ->LUMO+7	7.5
				HOMO-4 ->LUMO+7	38.3
				HOMO-1 ->LUMO+7	12.7
				HOMO ->LUMO+7	27.0
T_7	3.7614	329.62	0	HOMO-11 ->LUMO+5	6.0
				HOMO-8 ->LUMO	12.8
				HOMO-3 ->LUMO	35.2
T_8	3.8081	325.58	0	HOMO-7 ->LUMO+1	5.2
				HOMO-2 ->LUMO+1	7.3
				HOMO-2 ->LUMO+2	13.1
				HOMO-2 ->LUMO+3	26.6
				HOMO-1 ->LUMO+3	6.3
S_1	3.8862	319.04	0.0542	HOMO ->LUMO+1	86.2
T_9	3.8962	318.22	0	HOMO-4 ->LUMO	24.1
				HOMO-2 ->LUMO	12.4
				HOMO-1 ->LUMO	6.4
				HOMO ->LUMO	5.6
T_{10}	3.9667	312.57	0	HOMO-5 ->LUMO+1	19.4
				HOMO ->LUMO+4	7.8
				HOMO ->LUMO+6	10.9

S_2	4.0508	306.08	0.0743	HOMO-1 ->LUMO	55.7
				HOMO ->LUMO	26.0
S_3	4.1796	296.64	0.0099	HOMO-19 ->LUMO+7	6.1
				HOMO-4 ->LUMO+7	36.5
				HOMO-1 ->LUMO+7	13.0
				HOMO ->LUMO+7	29.5
S_4	4.1817	296.49	0.0269	HOMO-2 ->LUMO+1	33.7
				HOMO-1 ->LUMO+1	13.3
				HOMO ->LUMO+2	15.5
				HOMO ->LUMO+3	27.7
S_5	4.2865	289.24	0.2412	HOMO-3 ->LUMO	5.4
				HOMO-2 ->LUMO+1	14.8
				HOMO-2 ->LUMO+2	6.4
				HOMO-2 ->LUMO+3	6.5
				HOMO-1 ->LUMO+1	13.2
				HOMO-1 ->LUMO+3	6.6
				HOMO ->LUMO+2	9.8
				HOMO ->LUMO+3	20.6
S_6	4.2946	288.70	0.225	HOMO-5 ->LUMO	5.9
				HOMO-4 ->LUMO	14.2
				HOMO-2 ->LUMO	9.4
				HOMO-1 ->LUMO	19.0
				HOMO ->LUMO	44.0
S_7	4.3458	285.30	0.0018	HOMO-3 ->LUMO	53.1
				HOMO-2 ->LUMO+3	6.9
				HOMO-1 ->LUMO+2	19.9
S_8	4.4108	281.09	0.0476	HOMO-5 ->LUMO	20.9
				HOMO-4 ->LUMO	18.7
				HOMO-2 ->LUMO	41.0
				HOMO-1 ->LUMO	7.1
				HOMO ->LUMO	5.0
S_9	4.4507	278.57	0.2729	HOMO-3 ->LUMO+7	32.8
				HOMO-3 ->LUMO+9	7.1
				HOMO-2 ->LUMO+1	6.0
				HOMO-1 ->LUMO+3	8.5
				HOMO ->LUMO+3	12.5
S_{10}	4.4712	277.3	0.0257	HOMO-5 ->LUMO+7	42.9
				HOMO-5 ->LUMO+9	6.7
				HOMO-2 ->LUMO+7	13.2
				HOMO-1 ->LUMO+7	7.4
				HOMO ->LUMO+7	7.8

Table S6. List of the computed electronic transitions for complex **1** with their character obtained using B3LYP with the 6-31G** + LANL2DZ basis sets. Only the transitions with character greater than 5% are reported.

Excited state	E (eV)	Wavelength (nm)	f	Assignments	Character (%)
T_1	2.6365	470.27	0	HOMO-2 ->LUMO+1	6.6
				HOMO-1 ->LUMO+1	11.9
				HOMO ->LUMO+1	28.9
				HOMO ->LUMO+3	38.7
T_2	2.8533	434.53	0	HOMO ->LUMO+1	58.8
				HOMO ->LUMO+3	27.7
T_3	2.8737	431.44	0	HOMO-3 ->LUMO	14.1
				HOMO-2 ->LUMO+2	21.4
				HOMO-1 ->LUMO+2	39.5
				HOMO ->LUMO+2	5.1
T_4	2.9680	417.74	0	HOMO-2 ->LUMO	12.9
				HOMO-1 ->LUMO	48.5
				HOMO ->LUMO	25.4
T_5	3.2205	384.98	0	HOMO-2 ->LUMO+1	37.1
				HOMO-1 ->LUMO+1	31.2
				HOMO ->LUMO+3	15.4
S_1	3.2627	380.01	0	HOMO-1 ->LUMO	5.9
				HOMO ->LUMO	91.4
T_6	3.3088	374.71	0	HOMO-4 ->LUMO	5.7
				HOMO-2 ->LUMO	12.7
				HOMO-1 ->LUMO	12.8
				HOMO ->LUMO	63.1
S_2	3.3350	371.77	0.0273	HOMO ->LUMO+1	90.8
T_7	3.4174	362.80	0	HOMO-3 ->LUMO	61.6
				HOMO-1 ->LUMO+2	9.4
				HOMO ->LUMO+2	10.1
T_8	3.5341	350.82	0	HOMO-4 ->LUMO+3	9.3
				HOMO-2 ->LUMO+3	39.2
				HOMO-1 ->LUMO+3	28.9
T_9	3.5796	346.36	0	HOMO-4 ->LUMO+6	20.7
				HOMO-1 ->LUMO+6	17.5
				HOMO ->LUMO+6	39.8

S_3	3.5978	344.61	0.0278	HOMO-1 ->LUMO	87.0
				HOMO ->LUMO	6.1
T_{10}	3.6091	343.54	0	HOMO-4 ->LUMO	16.6
				HOMO-2 ->LUMO	42.0
				HOMO-1 ->LUMO	18.8
				HOMO ->LUMO+6	5.5
S_4	3.6823	336.70	0.007	HOMO ->LUMO+2	91.9
S_5	3.6866	336.31	0.0666	HOMO-2 ->LUMO+1	11.4
				HOMO-1 ->LUMO+1	12.7
				HOMO ->LUMO+3	67.4
S_6	3.7120	334.00	0.0772	HOMO-3 ->LUMO	9.7
				HOMO-1 ->LUMO+1	60.1
				HOMO-1 ->LUMO+3	5.3
				HOMO ->LUMO+3	13.5
S_7	3.8046	325.88	0.1166	HOMO-2 ->LUMO	87.0
S_8	3.8313	323.61	0.0014	HOMO-3 ->LUMO+1	87.7
S_9	3.8959	318.24	0.0312	HOMO-3 ->LUMO	68.8
				HOMO-1 ->LUMO+2	8.3
S_{10}	3.9029	317.67	0.0009	HOMO-4 ->LUMO+6	16.2
				HOMO-3 ->LUMO+1	9.1
				HOMO-1 ->LUMO+6	15.2
				HOMO ->LUMO+6	49.8

Table S7. List of the computed electronic transitions for complex **2** with their character, obtained using CAM-B3LYP with the 6-31G** + LANL2DZ basis sets. Only the transitions with character greater than 5% are reported.

Excited state	E (eV)	Wavelength (nm)	f	Assignments	Character (%)
T_1	2.6192	473.37	0	HOMO-3 ->LUMO+1	6.5
				HOMO-2 ->LUMO	12.8
				HOMO-1 ->LUMO+1	11.3
				HOMO-1 ->LUMO+2	19.1
				HOMO ->LUMO	5.2
				HOMO ->LUMO+3	20.6
T_2	2.6212	473.01	0	HOMO-3 ->LUMO	6.6
				HOMO-2 ->LUMO+1	12.6
				HOMO-1 ->LUMO	11.4
				HOMO-1 ->LUMO+3	19.0
				HOMO ->LUMO+1	5.2
				HOMO ->LUMO+2	20.9
T_3	3.1153	397.98	0	HOMO-1 ->LUMO	26.6
				HOMO ->LUMO+1	35.9
				HOMO ->LUMO+2	7.2
T_4	3.1181	397.63	0	HOMO-1 ->LUMO+1	26.6
				HOMO ->LUMO	36.1
				HOMO ->LUMO+3	7.3
T_5	3.5212	352.1	0	HOMO-3 ->LUMO	26.2
				HOMO-2 ->LUMO+1	23.0
				HOMO-2 ->LUMO+2	6.6
				HOMO-1 ->LUMO+3	9.3
				HOMO ->LUMO+1	5.5
				HOMO ->LUMO+2	7.6
T_6	3.5226	351.97	0	HOMO-3 ->LUMO+1	25.5
				HOMO-2 ->LUMO	22.7
				HOMO-2 ->LUMO+3	7.1
				HOMO-1 ->LUMO+2	9.6
				HOMO ->LUMO	5.3
				HOMO ->LUMO+3	7.5
T_7	3.6538	339.33	0	HOMO-21 ->LUMO+6	5.6
				HOMO-6 ->LUMO+6	6.8
				HOMO-4 ->LUMO+6	24.1
				HOMO-2 ->LUMO+6	12.3
				HOMO ->LUMO+6	42.5
T_8	3.8124	325.22	0	HOMO-4 ->LUMO+2	5.4
				HOMO-3 ->LUMO+3	25.0
				HOMO-2 ->LUMO+1	5.2
				HOMO-2 ->LUMO+2	21.6

				HOMO ->LUMO+2	6.6
T_9	3.8147	325.02	0	HOMO-4 ->LUMO+3	5.6
				HOMO-3 ->LUMO+2	24.9
				HOMO-2 ->LUMO	5.6
				HOMO-2 ->LUMO+3	20.9
				HOMO ->LUMO+3	6.4
S_1	3.8661	320.69	0.0458	HOMO-1 ->LUMO+1	21.1
				HOMO ->LUMO	63.8
S_2	3.879	319.63	0.047	HOMO-1 ->LUMO	20.8
				HOMO ->LUMO+1	64.0
T_{10}	4.0634	305.12	0	HOMO-6 ->LUMO+1	5.1
				HOMO-5 ->LUMO	7.9
				HOMO-5 ->LUMO+6	5.6
				HOMO-1 ->LUMO+4	10.1
				HOMO ->LUMO+5	7.5
S_3	4.0742	304.31	0.0023	HOMO-6 ->LUMO+6	6.3
				HOMO-4 ->LUMO+6	22.1
				HOMO-2 ->LUMO+6	11.7
				HOMO ->LUMO+6	45.2
S_4	4.0882	303.27	0.042	HOMO-3 ->LUMO	15.5
				HOMO-2 ->LUMO+1	22.0
				HOMO-1 ->LUMO	7.5
				HOMO-1 ->LUMO+3	13.9
				HOMO ->LUMO+2	33.5
S_5	4.1212	300.84	0.0316	HOMO-3 ->LUMO+1	17.5
				HOMO-2 ->LUMO	25.2
				HOMO-1 ->LUMO+1	7.2
				HOMO-1 ->LUMO+2	13.4
				HOMO ->LUMO+3	28.8
S_6	4.2238	293.54	0.2203	HOMO-2 ->LUMO	15.3
				HOMO-2 ->LUMO+3	9.6
				HOMO-1 ->LUMO+1	9.4
				HOMO-1 ->LUMO+2	21.0
				HOMO ->LUMO	5.3
				HOMO ->LUMO+3	15.9
S_7	4.2771	289.88	0.0922	HOMO-3 ->LUMO+3	8.6
				HOMO-2 ->LUMO+1	10.1
				HOMO-2 ->LUMO+2	17.7
				HOMO-1 ->LUMO	10.6
				HOMO-1 ->LUMO+3	18.1
				HOMO ->LUMO+1	6.3
				HOMO ->LUMO+2	7.5

S_8	4.285	289.35	0.3179	HOMO-6 ->LUMO	8.2
				HOMO-3 ->LUMO+1	8.1
				HOMO-2 ->LUMO	16.9
				HOMO-1 ->LUMO+1	14.5
				HOMO ->LUMO	11.8
				HOMO ->LUMO+3	18.8
S_9	4.4004	281.75	0.1531	HOMO-6 ->LUMO+1	7.6
				HOMO-5 ->LUMO	7.2
				HOMO-2 ->LUMO+1	16.7
				HOMO-1 ->LUMO	32.3
				HOMO ->LUMO+1	12.8
S_{10}	4.4231	280.31	0.1845	HOMO-5 ->LUMO+1	8.6
				HOMO-3 ->LUMO+1	6.7
				HOMO-3 ->LUMO+2	6.3
				HOMO-2 ->LUMO+3	16.5
				HOMO-1 ->LUMO+1	22.8
				HOMO ->LUMO+3	7.2

Table S8. List of the computed electronic transitions for complex **2** with their character, obtained using B3LYP with the 6-31G** + LANL2DZ basis sets. Only the transitions with character greater than 5% are reported.

Excited state	E (eV)	Wavelength (nm)	f	Assignments	Character (%)
T_1	2.6272	471.93	0	HOMO-2 ->LUMO	11.3
				HOMO-1 ->LUMO+1	17.5
				HOMO-1 ->LUMO+3	19.1
				HOMO ->LUMO	10.7
				HOMO ->LUMO+2	23.4
T_2	2.6289	471.62	0	HOMO-2 ->LUMO+1	11.1
				HOMO-1 ->LUMO	18.1
				HOMO-1 ->LUMO+2	19.2
				HOMO ->LUMO+1	10.0
				HOMO ->LUMO+3	23.6
T_3	2.8476	435.40	0	HOMO-1 ->LUMO	18.5
				HOMO-1 ->LUMO+2	8.3
				HOMO ->LUMO+1	44.8
				HOMO ->LUMO+3	15.9
T_4	2.8515	434.81	0	HOMO-1 ->LUMO+1	18.4
				HOMO-1 ->LUMO+3	7.9
				HOMO ->LUMO	44.9
				HOMO ->LUMO+2	16.2
T_5	3.1951	388.05	0	HOMO-3 ->LUMO+1	19.7
				HOMO-2 ->LUMO	32.3
				HOMO-1 ->LUMO+1	5.5
				HOMO-1 ->LUMO+3	5.9
				HOMO ->LUMO	15.3
				HOMO ->LUMO+2	10.6
T_6	3.1962	387.91	0	HOMO-3 ->LUMO	21.0
				HOMO-2 ->LUMO+1	31.9
				HOMO-1 ->LUMO+2	6.2
				HOMO ->LUMO+1	15.7
				HOMO ->LUMO+3	10.2
S_1	3.2442	382.17	0.0144	HOMO ->LUMO	92.4
S_2	3.2531	381.13	0.0122	HOMO ->LUMO+1	92.2
T_7	3.4488	359.50	0	HOMO-6 ->LUMO+6	5.3
				HOMO-4 ->LUMO+6	6.4

				HOMO-2 ->LUMO+6	7.7
				HOMO-1 ->LUMO+1	10.6
				HOMO ->LUMO+4	6.0
				HOMO ->LUMO+6	41.0
T_8	3.4831	355.96	0	HOMO-4 ->LUMO+1	5.2
				HOMO-3 ->LUMO	6.3
				HOMO-3 ->LUMO+2	5.0
				HOMO-2 ->LUMO+3	8.7
				HOMO-1 ->LUMO	37.9
				HOMO ->LUMO+1	20.2
T_9	3.4965	354.60	0	HOMO-3 ->LUMO+3	8.0
				HOMO-2 ->LUMO+2	13.1
				HOMO-1 ->LUMO+1	22.6
				HOMO ->LUMO	13.3
				HOMO ->LUMO+6	13.6
T_{10}	3.5125	352.98	0	HOMO-3 ->LUMO+2	16.0
				HOMO-2 ->LUMO+3	23.1
				HOMO-1 ->LUMO	7.6
				HOMO-1 ->LUMO+2	6.4
				HOMO ->LUMO+3	15.3
S_3	3.5182	352.41	0.0215	HOMO-1 ->LUMO+1	80.9
				HOMO ->LUMO+2	7.2
S_4	3.5800	346.33	0.0278	HOMO-1 ->LUMO	75.3
				HOMO ->LUMO+3	14.0
S_5	3.5878	345.57	0.0752	HOMO-1 ->LUMO+1	7.0
				HOMO ->LUMO+2	84.2
S_6	3.6030	344.12	0.0203	HOMO-2 ->LUMO+1	12.8
				HOMO-1 ->LUMO	11.3
				HOMO ->LUMO+3	67.3
S_7	3.6316	341.40	0.0656	HOMO-2 ->LUMO	84.3
S_8	3.7262	332.73	0.0107	HOMO-3 ->LUMO	12.9
				HOMO-2 ->LUMO+1	54.1
				HOMO-2 ->LUMO+3	8.6
				HOMO-1 ->LUMO+2	9.4
S_9	3.7674	329.09	0.0247	HOMO-2 ->LUMO+1	12.6
				HOMO-1 ->LUMO+2	73.0

S_{10}	3.8016	326.14	0.0274	HOMO-3 ->LUMO+1	8.1
				HOMO-1 ->LUMO+3	52.7
				HOMO ->LUMO+6	18.1

Table S9. Calculated wavelengths and orbital transition analyses of the lowest energy emission band of complex **1** obtained using CAM-B3LYP and B3LYP with the 6-31G** + LANL2DZ basis sets. Only the transitions with character greater than 5% are reported.

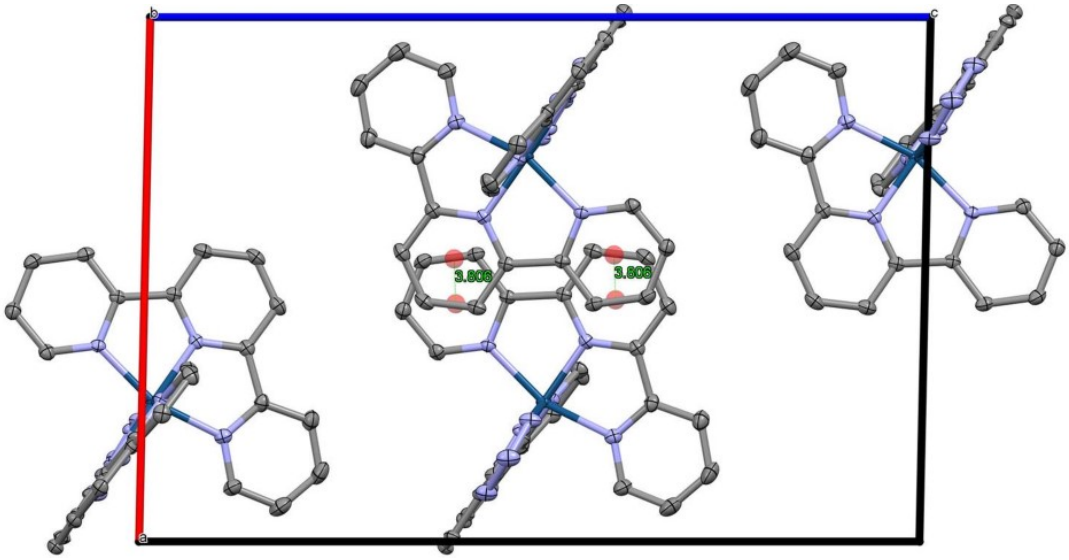
Functional	Excited state	E (eV)	Wavelength (nm)	f	Assignments	Character (%)
CAM-B3LYP	T_1	1.2189	1017.20	0	HOMO → LUMO	79.3
B3LYP	T_1	1.8678	663.80	0	HOMO → LUMO	86.2

Table S10. Calculated wavelengths and orbital transition analyses of the lowest energy emission band of complex **2** obtained using CAM-B3LYP and B3LYP with the 6-31G** + LANL2DZ basis sets. Only the transitions with character greater than 5% are reported.

Functional	Excited state	E (eV)	Wavelength (nm)	f	Assignments	Character (%)
CAM-B3LYP	T_1	2.5508	486.06	0	HOMO → LUMO	79.4
B3LYP	T_1	2.5700	482.09	0	HOMO → LUMO	81.2
					HOMO-1 → LUMO	6.4

Figure S1.- Unit cell content of compounds **1** and **2** highlighting intermolecular π-π interactions between neighbour complexes (crystallization solvent molecules and counter-ions have been omitted).

1



2

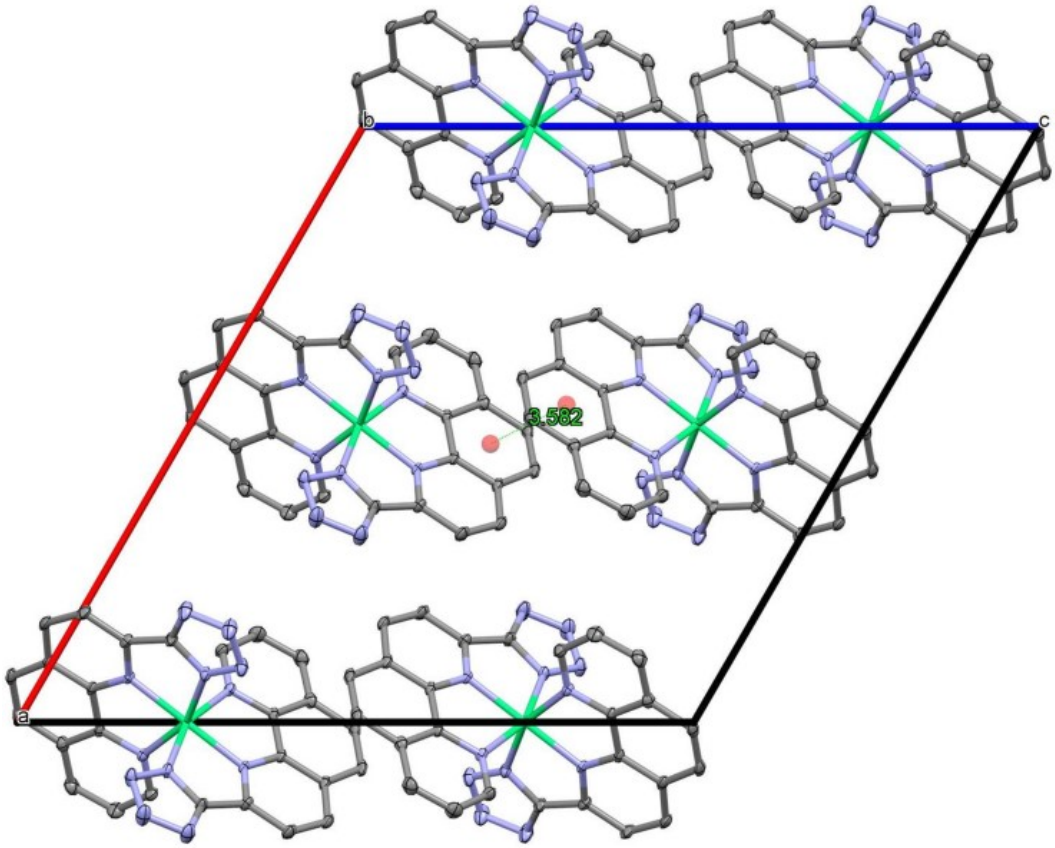


Figure S2.- Experimental (black dots) and fitting decay (red line) of the excited **1** at 293K in aerated acetonitrile solution. Excitation at 375 nm. Emission at 532 nm.

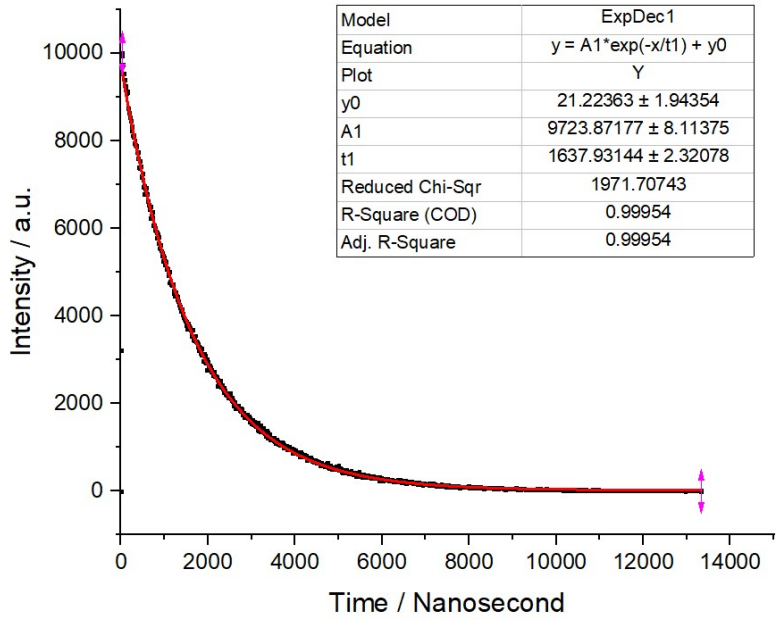


Figure S3.- Experimental (black dots) and fitting decay (red line) of the excited **2** at 293K in aerated acetonitrile solution. Excitation at 370 nm. Emission at 532 nm.

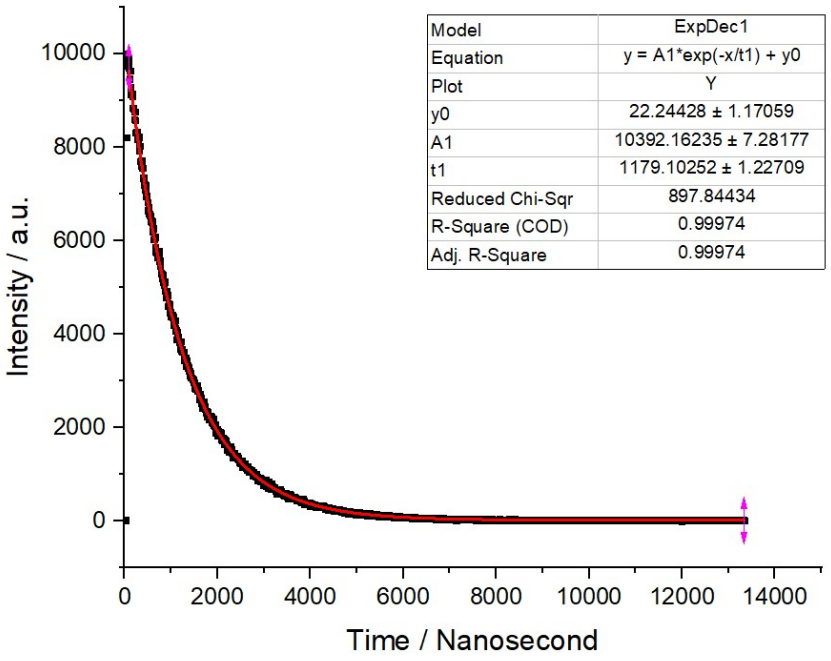


Figure S4.- Experimental (black dots) and fitting decay (red line) of the excited **1** at 293K in deaerated acetonitrile solution. Excitation at 375 nm. Emission at 532 nm.

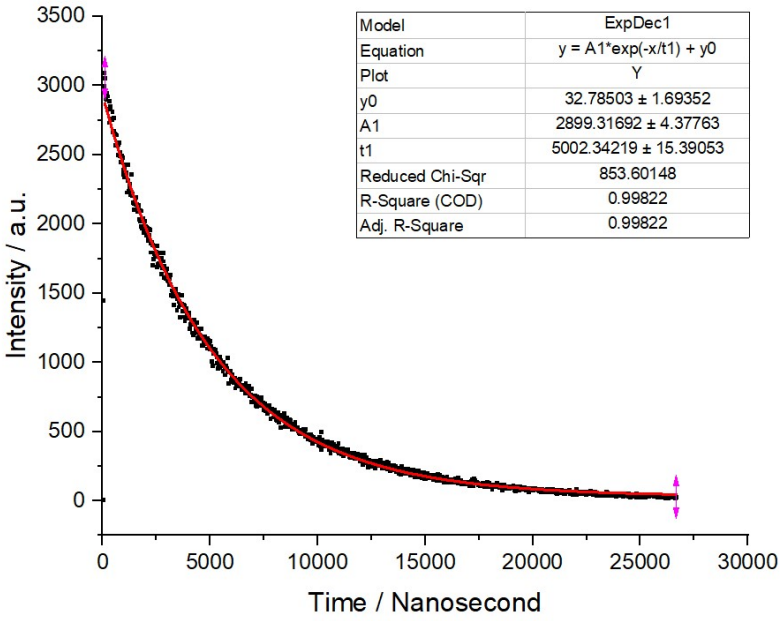


Figure S5.- Experimental (black dots) and fitting decay (red line) of the excited **2** at 293K in deaerated acetonitrile solution. Excitation at 370 nm. Emission at 532 nm.

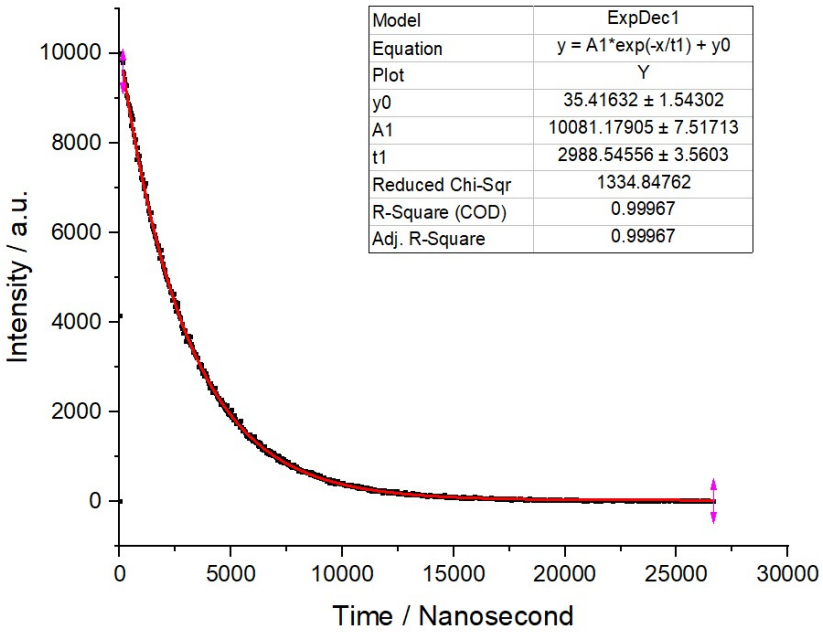


Figure S6.- Experimental (black dots) and fitting decay (red line) of the excited **1** at 77K in frozen acetonitrile solution. Excitation at 375 nm. Emission at 532 nm.

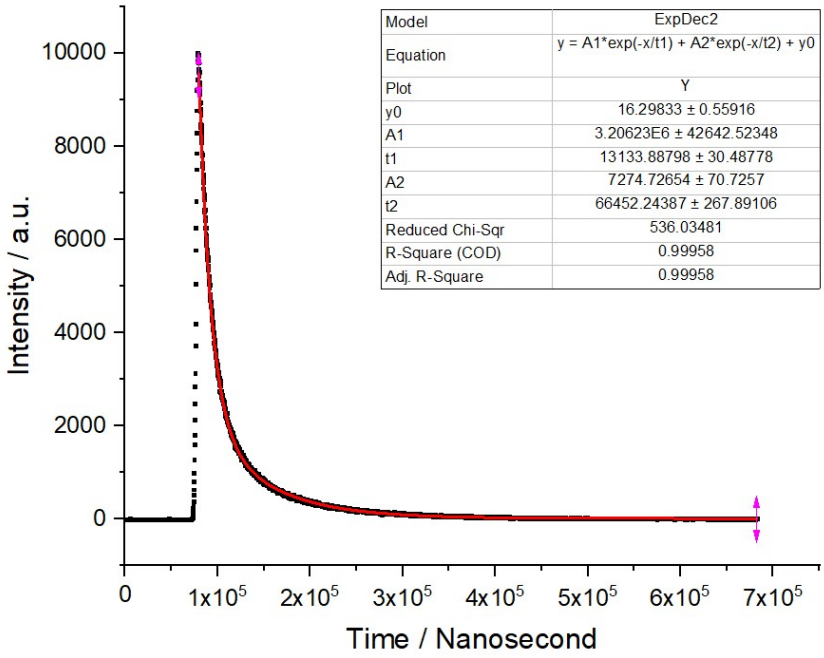


Figure S7.- Experimental (black dots) and fitting decay (red line) of the excited **2** at 77K in frozen acetonitrile solution. Excitation at 375 nm. Emission at 580 nm.

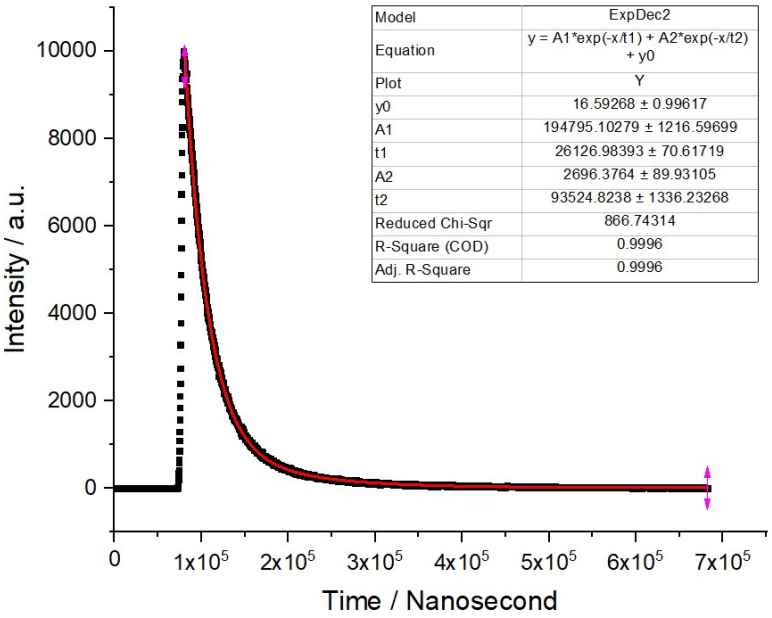
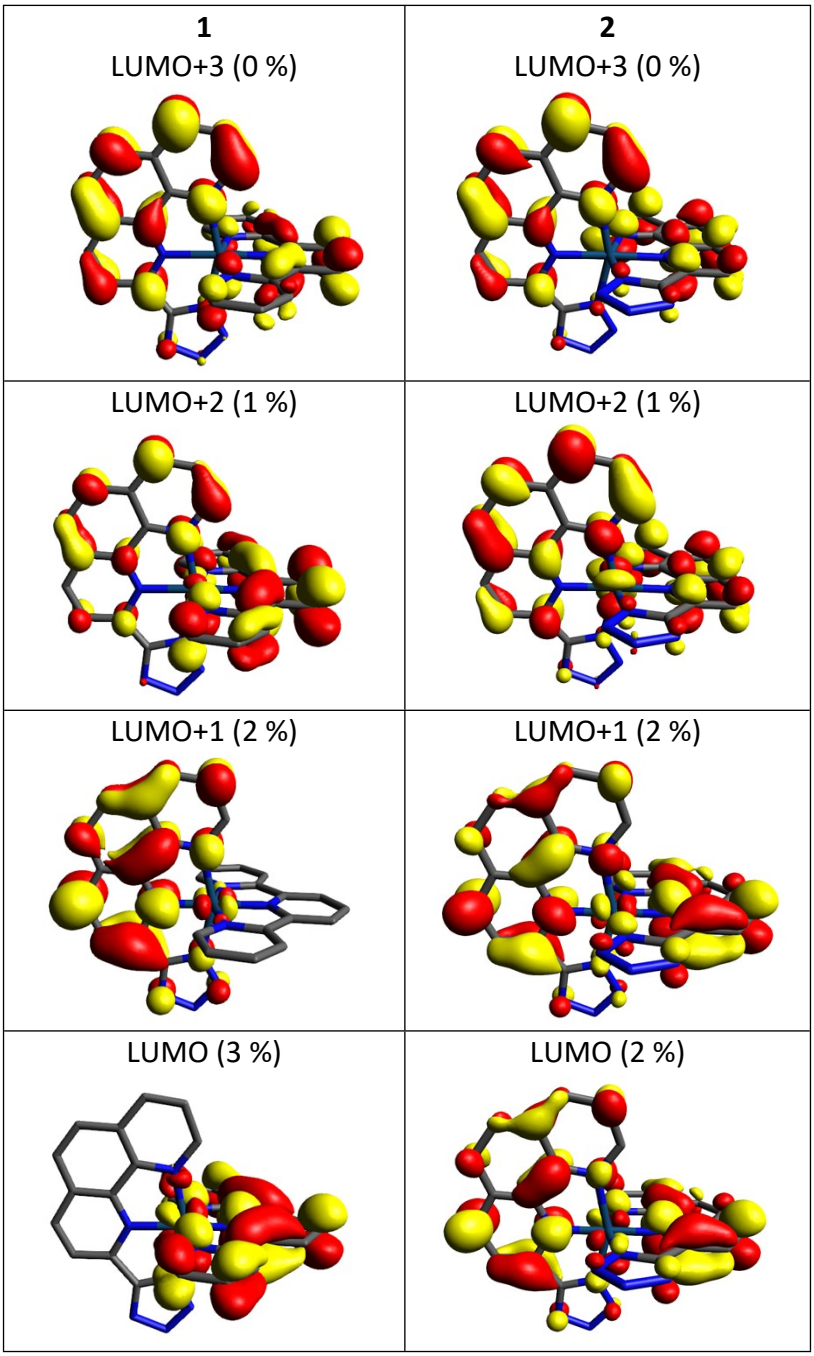


Figure S8.- Localization of the HOMO, LUMO, HOMO-1, HOMO-2, HOMO-3, LUMO+1, LUMO+2 and LUMO+3 orbitals for the ground state S_0 of **1** and **2** Ir(III) complexes at the CAM-B3LYP/6-31G** + LANL2DZ level of theory. The relative electron density distribution at the Ir atoms is placed between the parentheses. Hydrogen atoms are omitted for clarity.



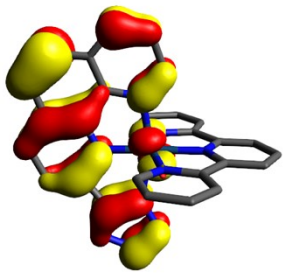
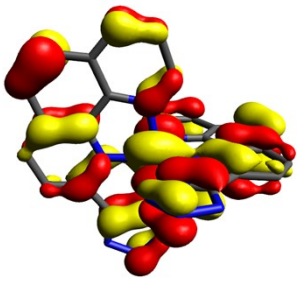
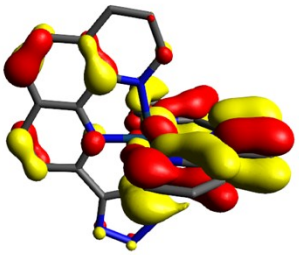
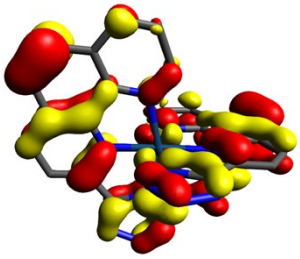
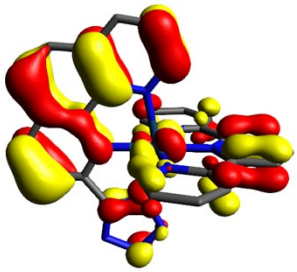
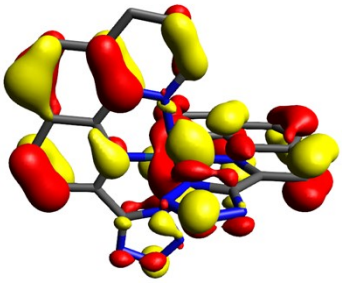
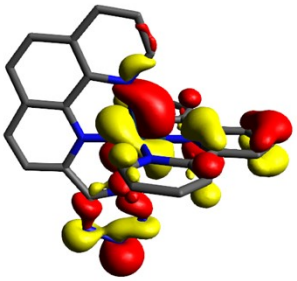
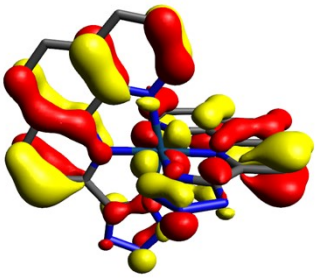
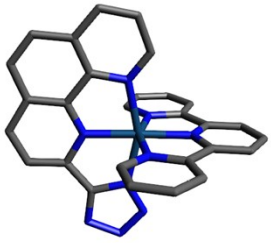
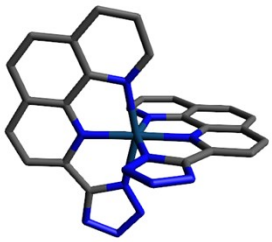
HOMO (11 %) 	HOMO (17 %) 
HOMO-1 (9 %) 	HOMO-1 (4 %) 
HOMO-2 (8 %) 	HOMO-2 (20 %) 
HOMO-3 (40 %) 	HOMO-3 (10 %) 
Optimized structure 	Optimized structure 

Figure S9.- Localization of the HOMO and LUMO orbitals for the excited state T_1 of **1** and **2** Ir(III) complexes at the CAM-B3LYP/6-31G** + LANL2DZ level of theory. The relative electron density distribution at the Ir atoms is placed between the parentheses. Hydrogen atoms are omitted for clarity.

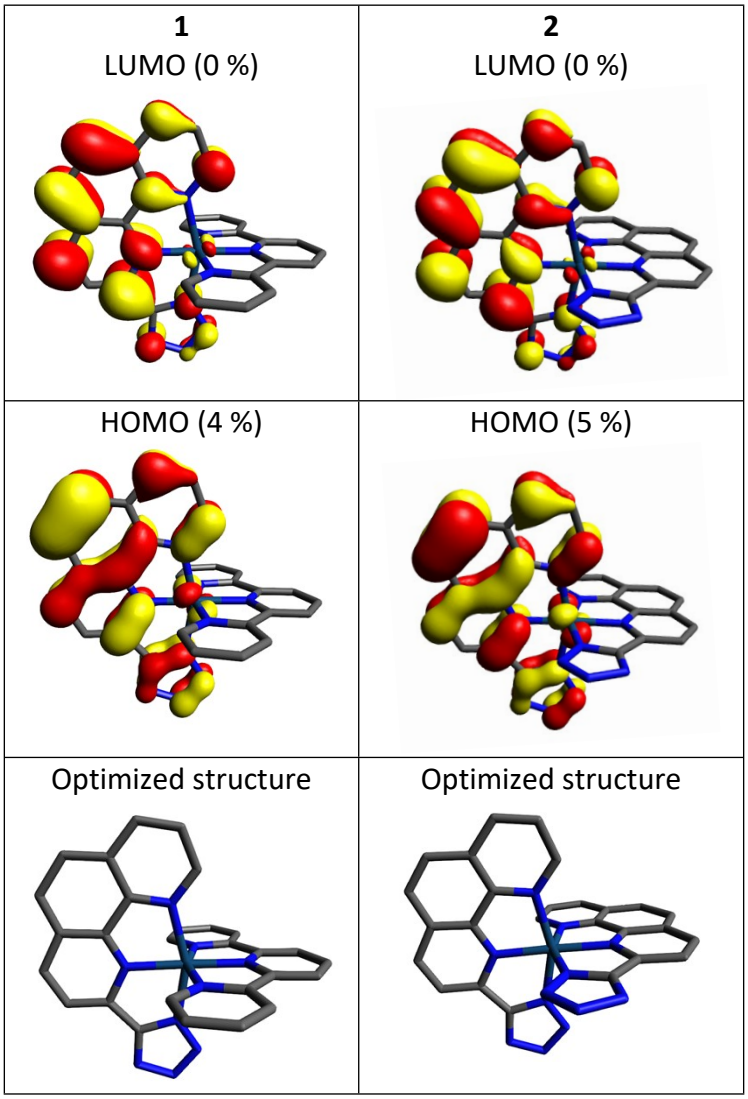


Figure S8.- Experimental (black dots) and fitting decay (red line) of the excited **1@SiO$_2$** at 293K in aerated acetonitrile solution. Excitation at 375 nm. Emission at 535 nm.

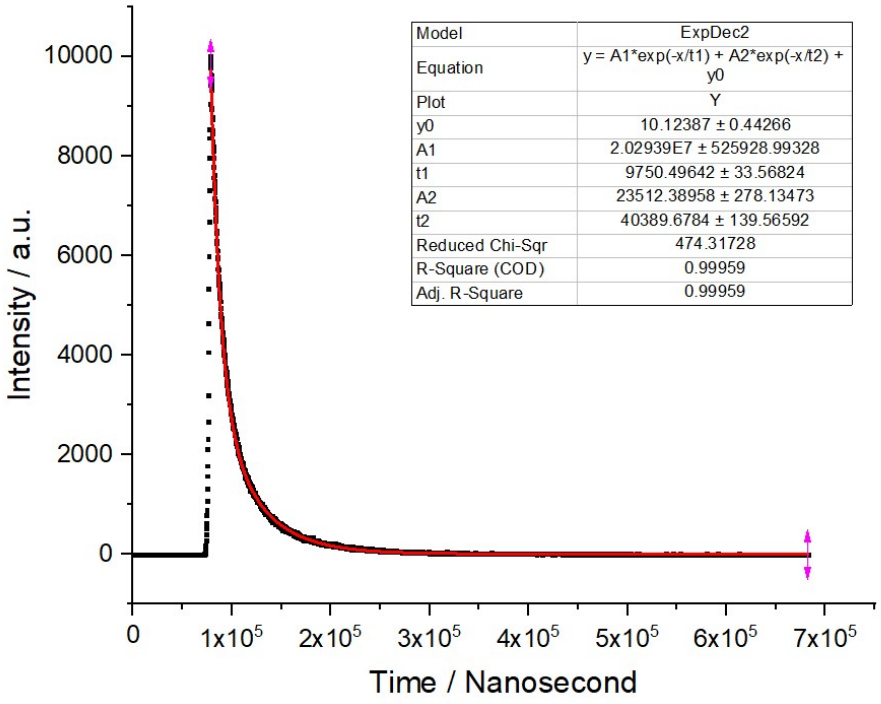


Figure S9.- Experimental (black dots) and fitting decay (red line) of the excited **1@SiO$_2$** at 293K in deaerated acetonitrile solution. Excitation at 375 nm. Emission at 535 nm.

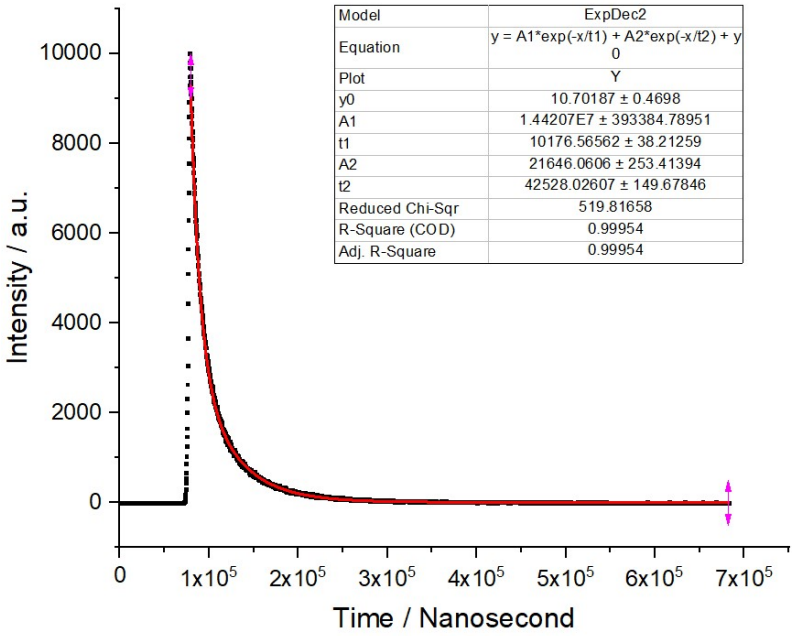


Figure S10.- Experimental (black dots) and fitting decay (red line) of the excited **1@SiO$_2$** at 77K in frozen acetonitrile solution. Excitation at 375 nm. Emission at 532 nm.

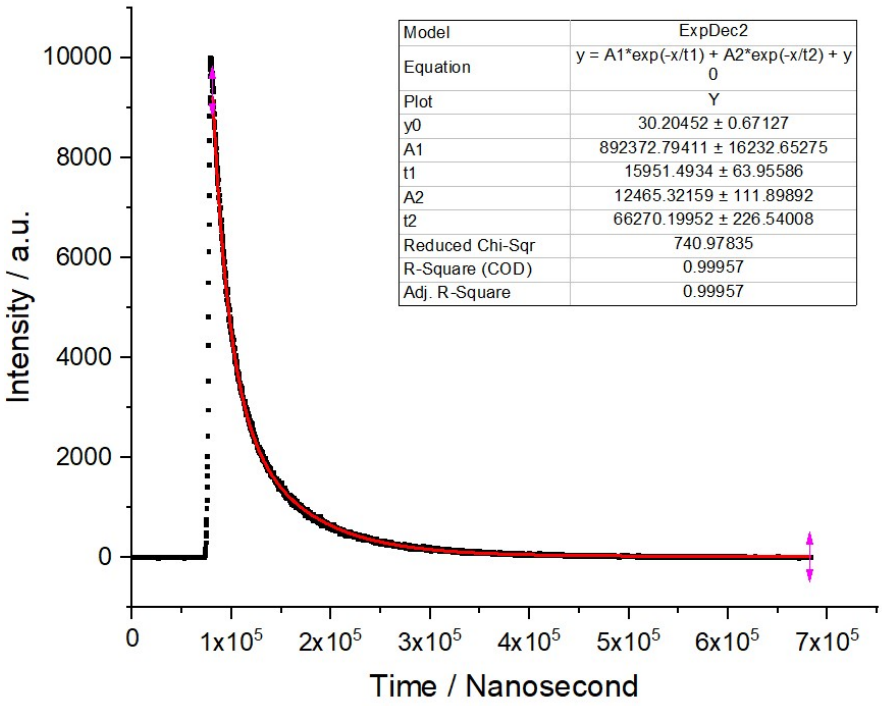


Figure S11.- TEM images of sample **1@SiO$_2$**.

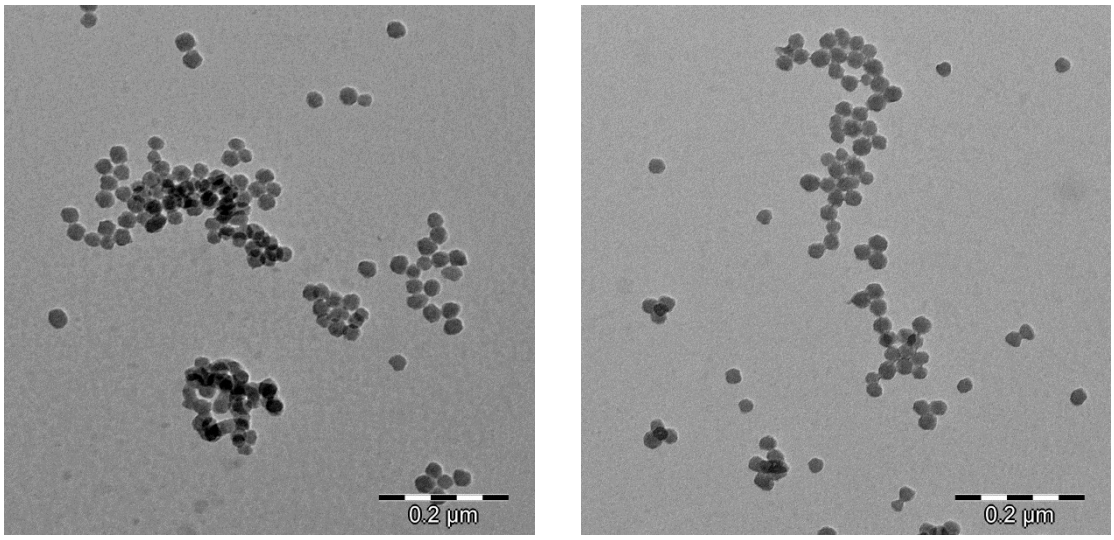
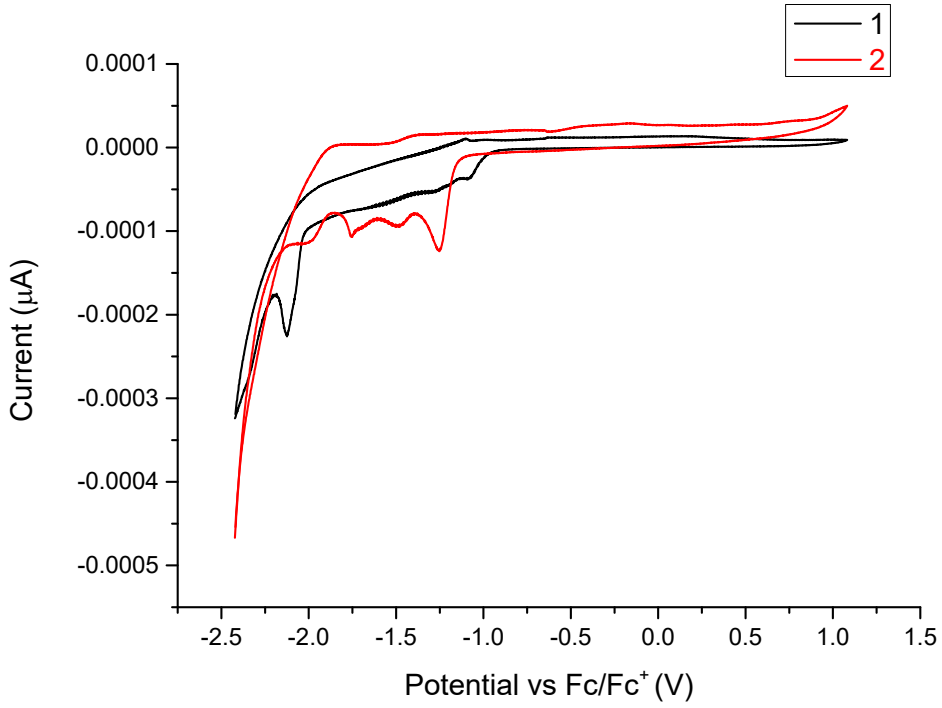


Figure S12.- Reduction range of the cyclic voltammograms for 1 mM solutions of complexes **1** (black) and **2** (red) in 0.1 M Bu_4NPF_6 CH_3CN.



Cyclic voltammetry experiments show irreversible ligand-ligand centred reductions. The metal centred oxidation $Ir^{III/IV}$ is not observed, probably because it appears out of the explored potential range. Thus, the HOMO-LUMO energy gaps for both complexes cannot be determined experimentally and, therefore, compared with those calculated theoretically.