Supporting Information

Cyclometalated Ir(III) Complexes Bridged by μ-OH and μ-3,5-Bis(4-methoxyphenyl)-Pyrazole Ligands

Mausami[a1], Harshita Trivedi[a1],Ranjan Patra[b], Ravi Prakash Behere[c], Biplab Kuila[c], Sandeep Kumar Singh Patel[a], Mrituanjay D. Pandey[c], Biswajit Maiti[c], Bani Mahanti, [*a]

[a] Department of Chemistry, Mahila Mahavidyalaya, Banaras Hindu University, Varanasi-221005, India

[b]Amity Institute of Click Chemistry Research and Studies, Amity University, Noida, Uttar Pradesh, India

[c]Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi-221005, India

[1] Equal contribution

Table of Contents

Figure S1. IR spectrum (KBr cm^{-1}) of complex **1**
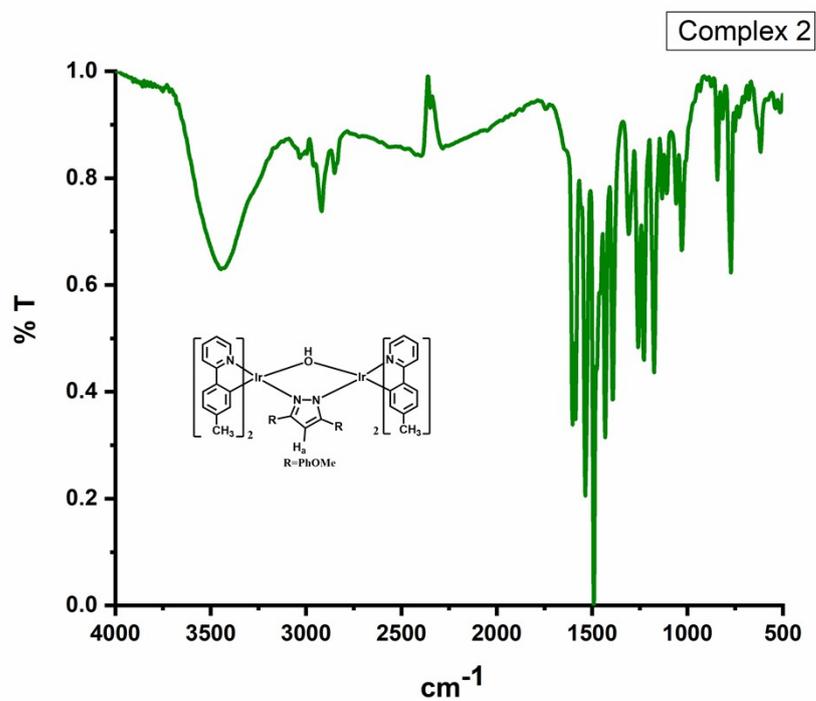
Figure S2. IR spectrum (KBr cm^{-1}) of complex **2**
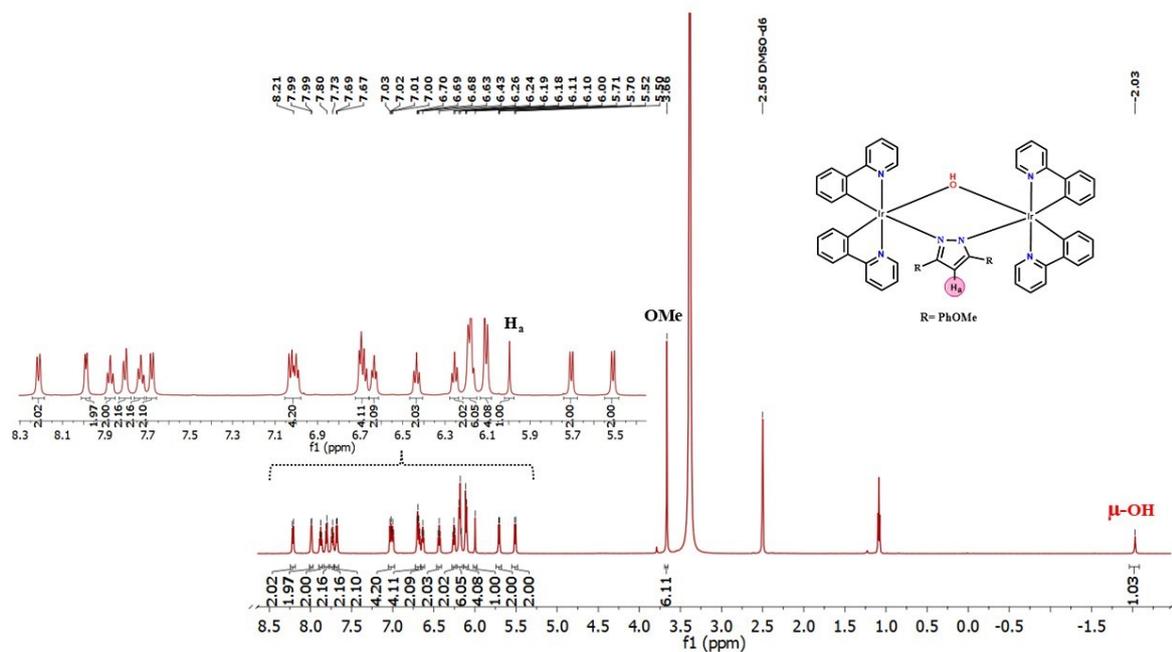
Figure S3. ^{1}H NMR (600MHz, DMSO-d$_6$, 298 K) spectrum of complex **1.**
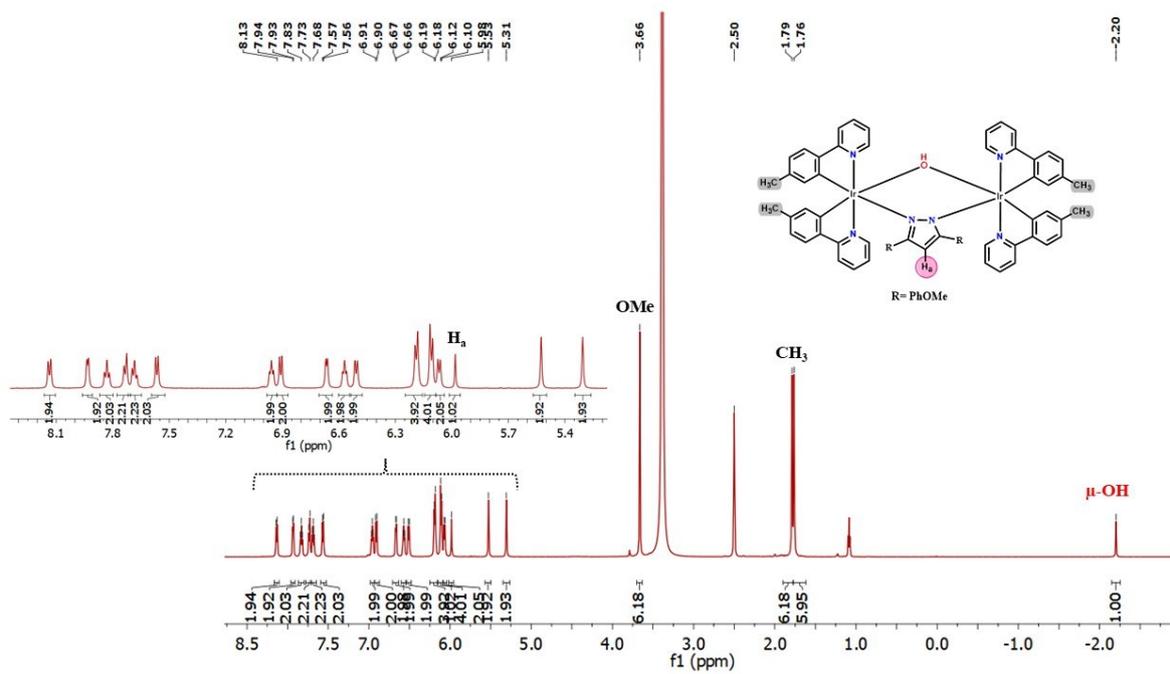
Figure S4. ^{1}H NMR (600MHz, DMSO-d$_6$, 298 K) spectrum of complex **2.**
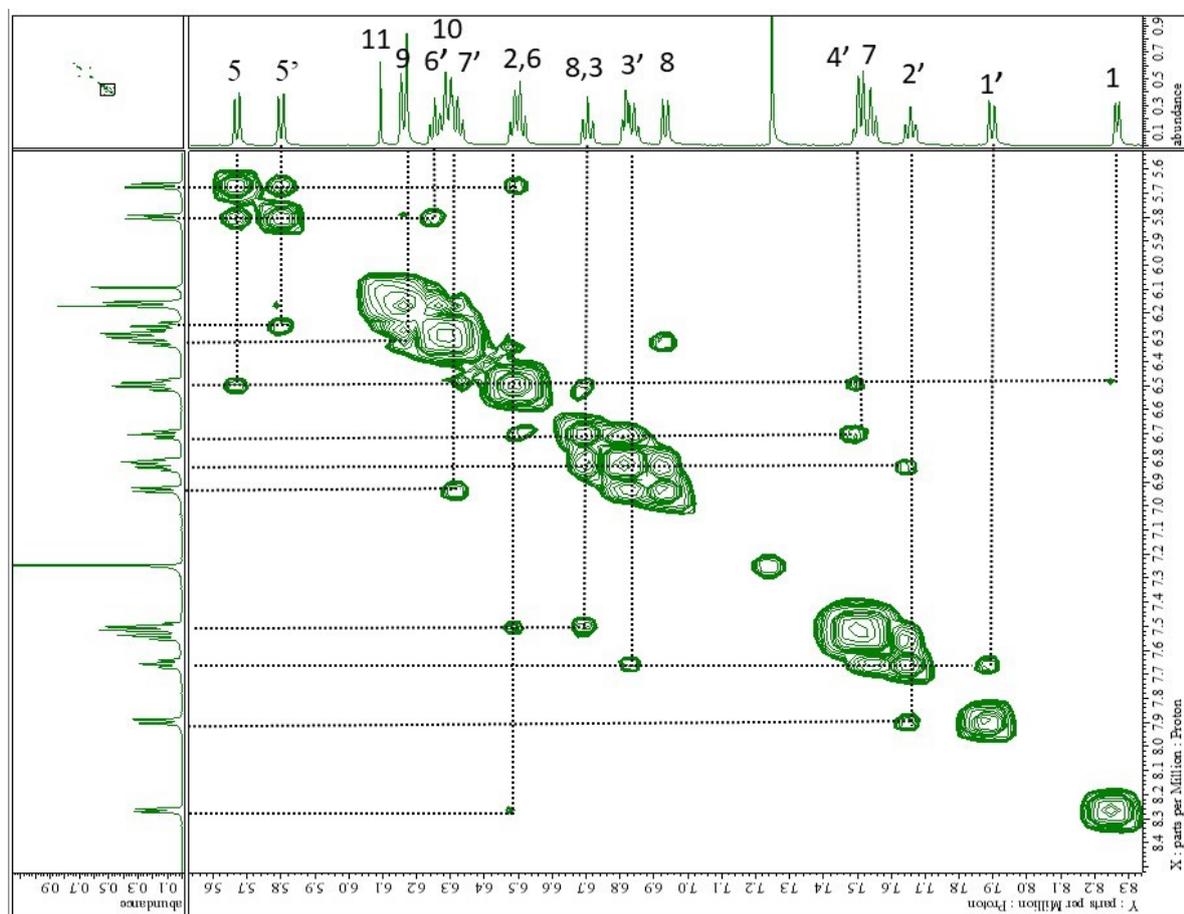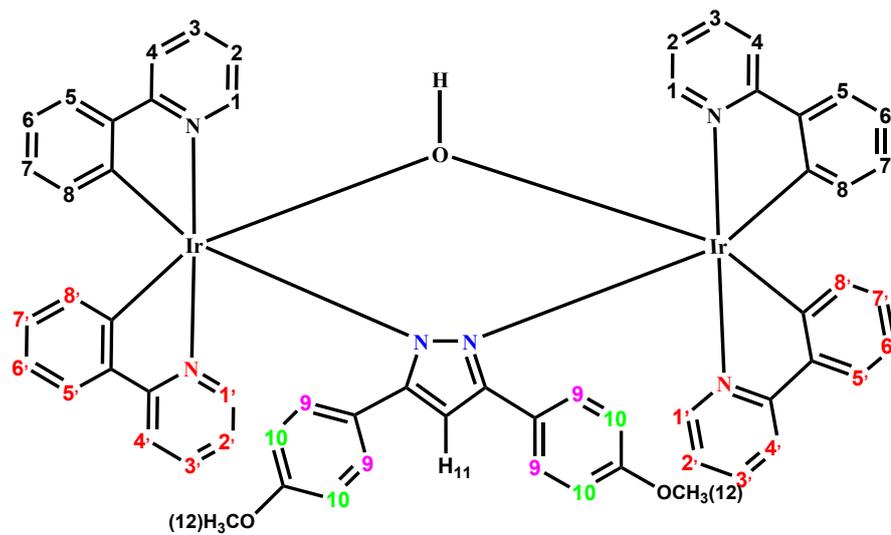
Figure S5. COSY NMR (H^1-H^1) (500MHz, CDCl$_3$, 298 K) spectrum of complex **1**
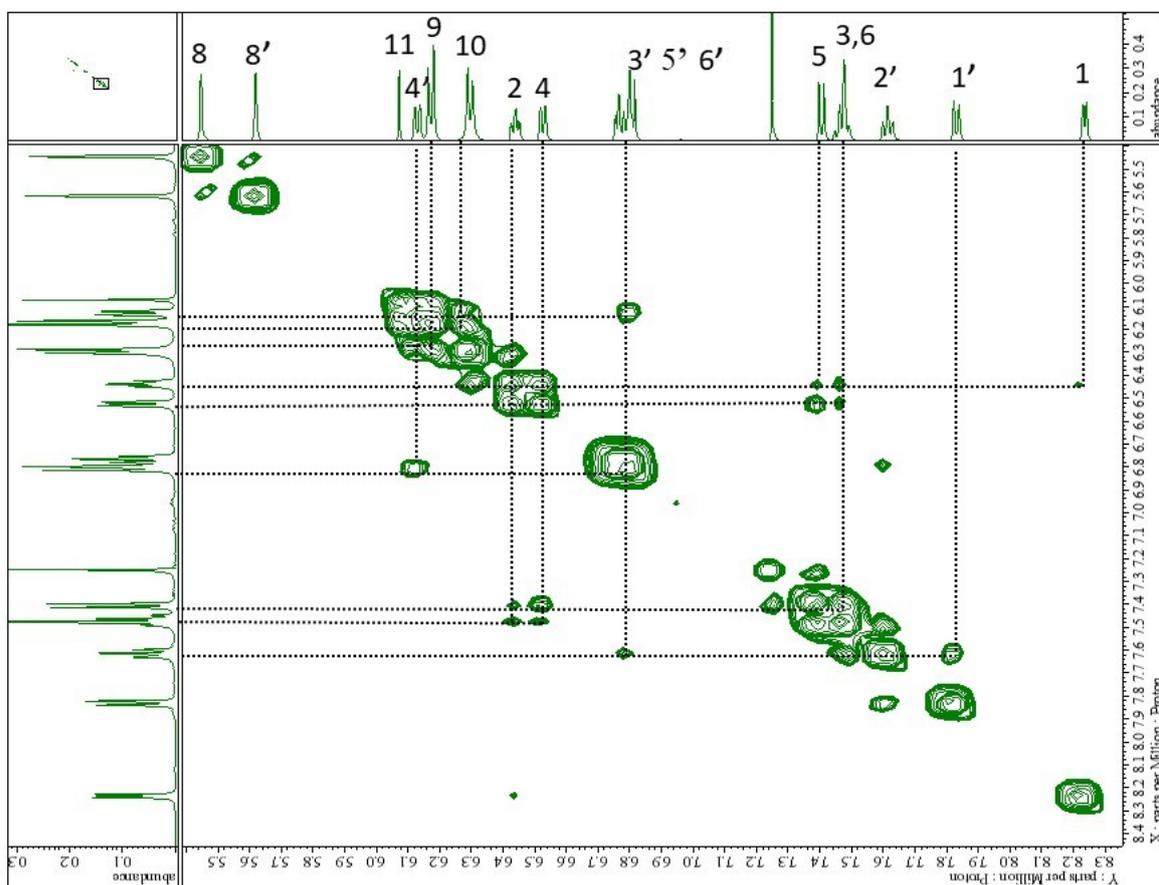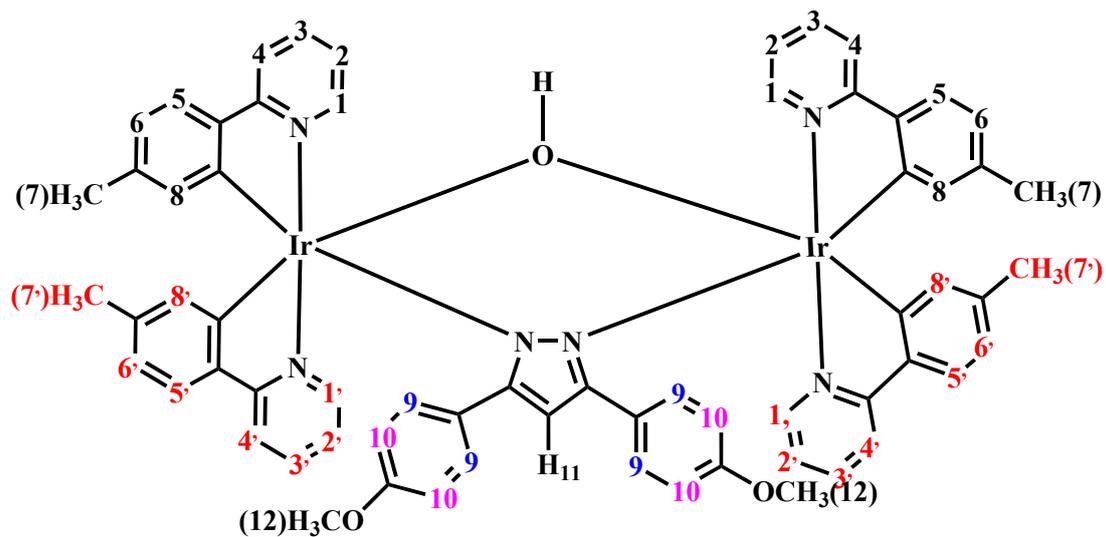
Figure S6. COSY NMR (H^1-H^1) (500MHz, $CDCl_3$, 298 K) spectrum of complex **2**
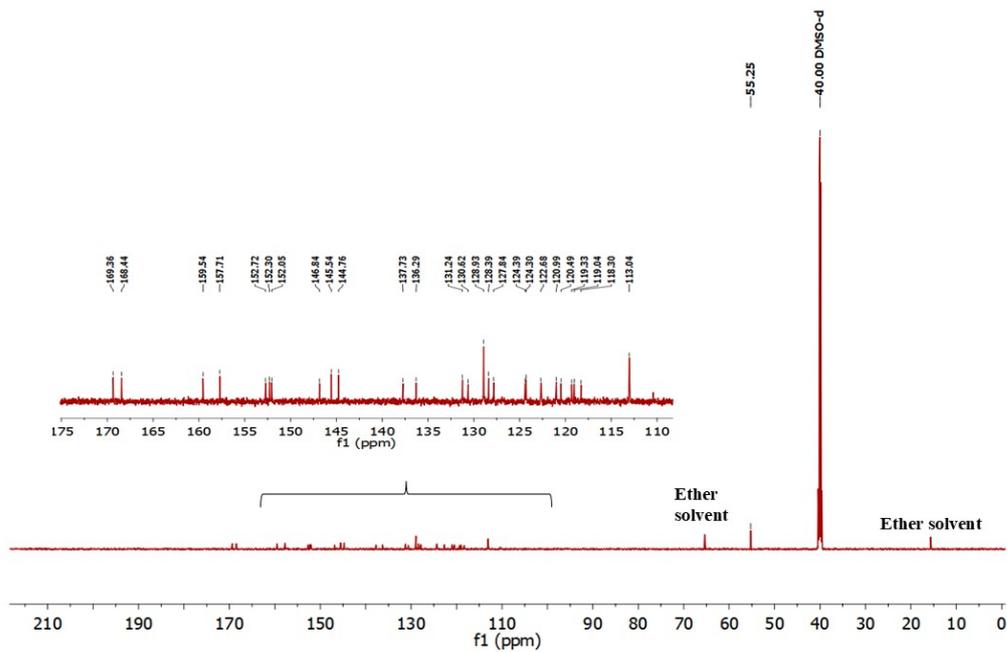
Figure S7.^{13}C NMR (150MHz, DMSO-d$_6$, 298 K) spectrum of complex **1**
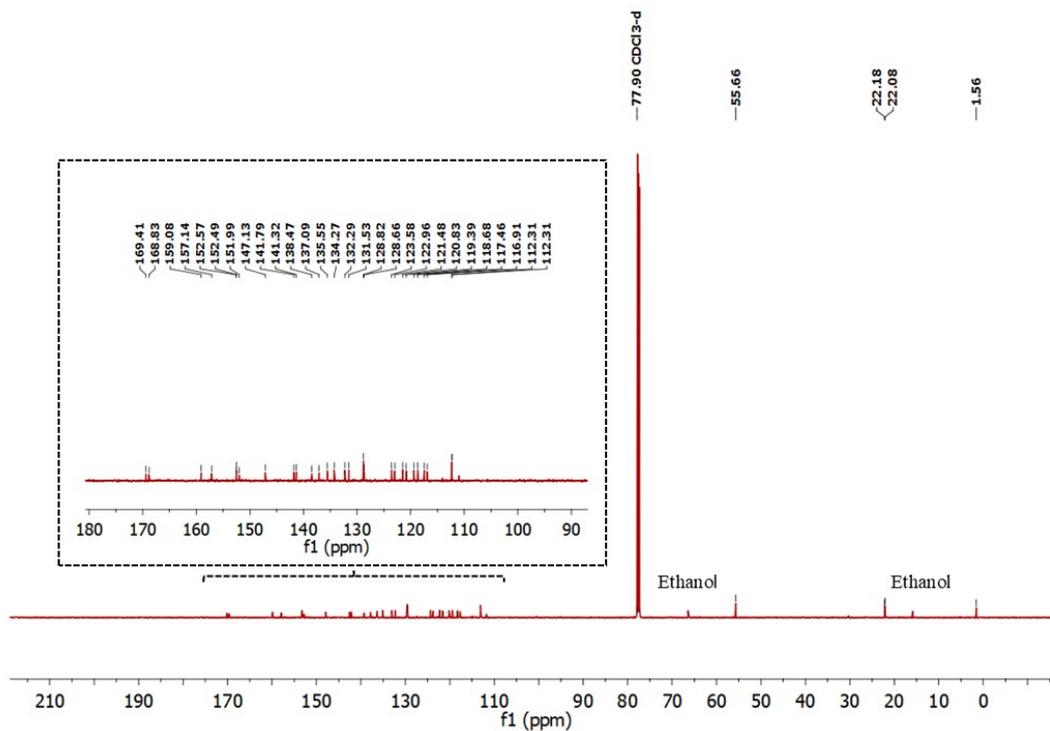
Figure S8.^{13}C NMR (150 MHz, CDCl$_3$, 298 K) spectrum of complex **2**.
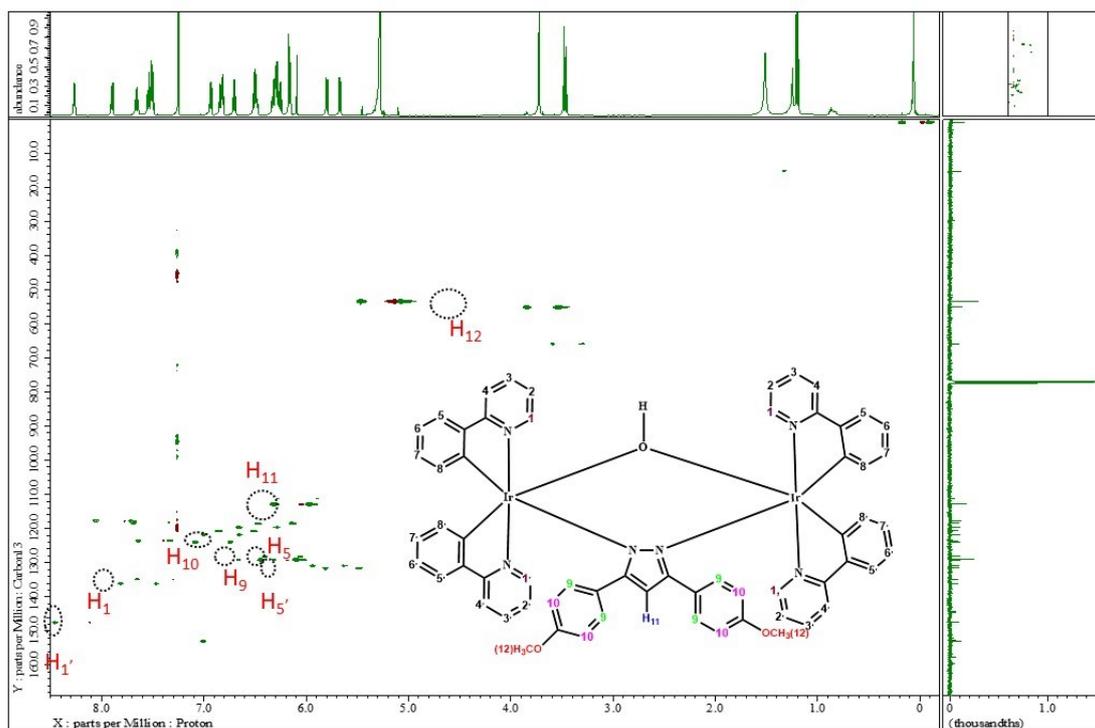
Figure S9. HSQC NMR (H^1-^{13}C) (500MHz, CDCl$_3$, 298 K) spectrum of complex **1**
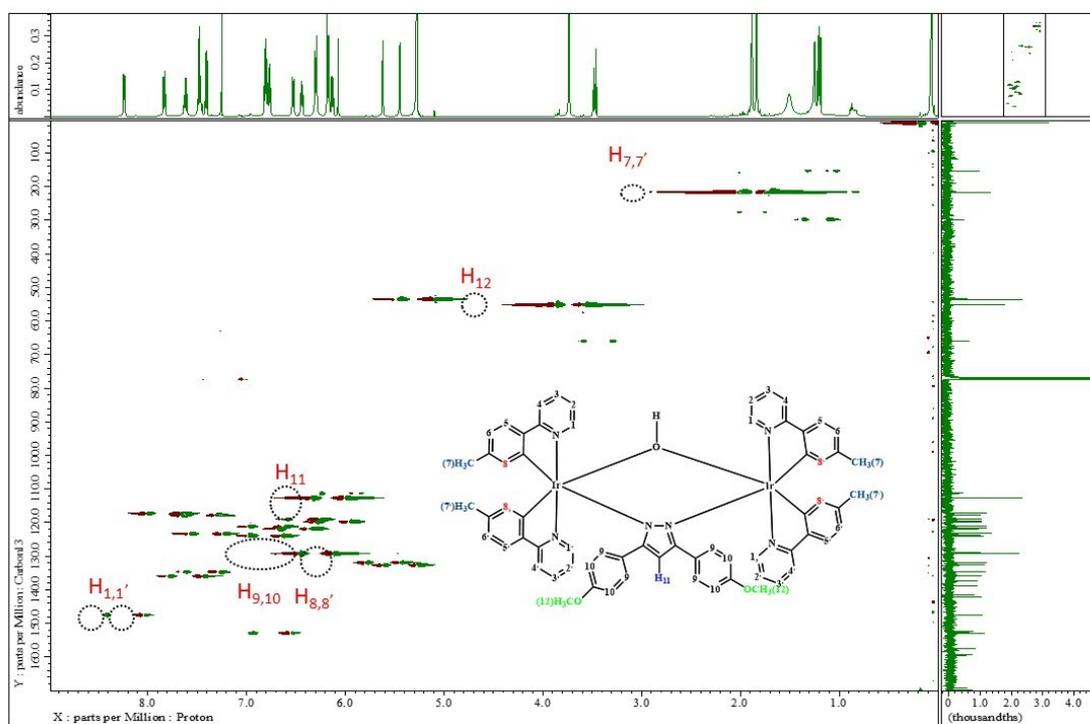
Figure S10: HSQC NMR (H^1-^{13}C) (500MHz, CDCl$_3$, 298 K)spectrum of complex **2**
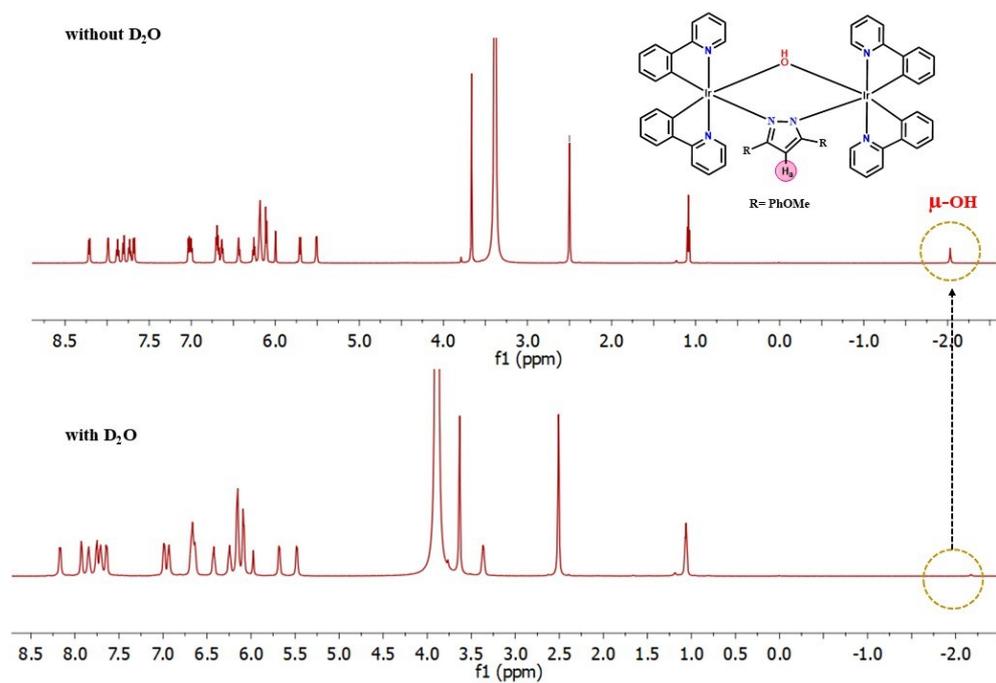
Figure S11: ^{1}H NMR spectra (600 MHz, DMSO-d$_6$) of the complex recorded (top) without D$_2$O and (bottom) after addition of 100 μl D$_2$O for complex **1**.
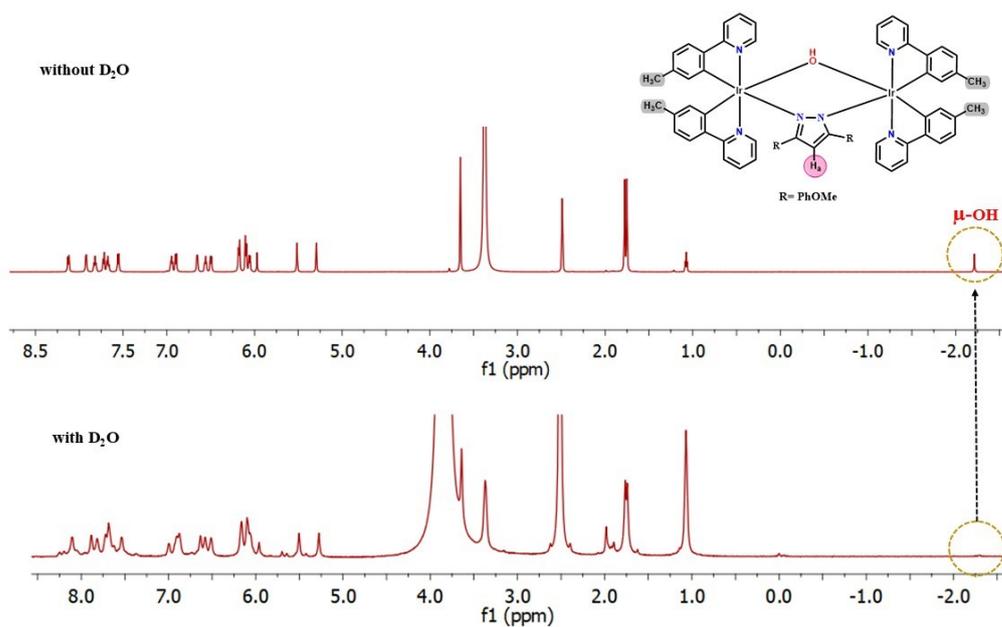
Figure S12: ^{1}H NMR spectra (600 MHz, DMSO-d6) of the complex recorded (top) without D$_2$O and (bottom) after addition of 100 μl D$_2$O for complex **2**.
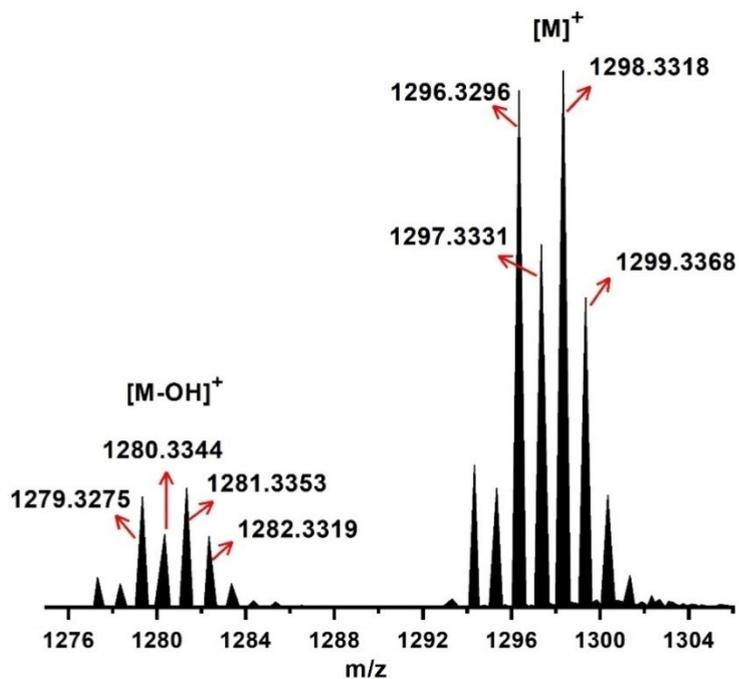
Figure S13: ESI-MS spectrum ofcomplex**1** showing [M-OH]$^+$, [M]$^+$ peaks
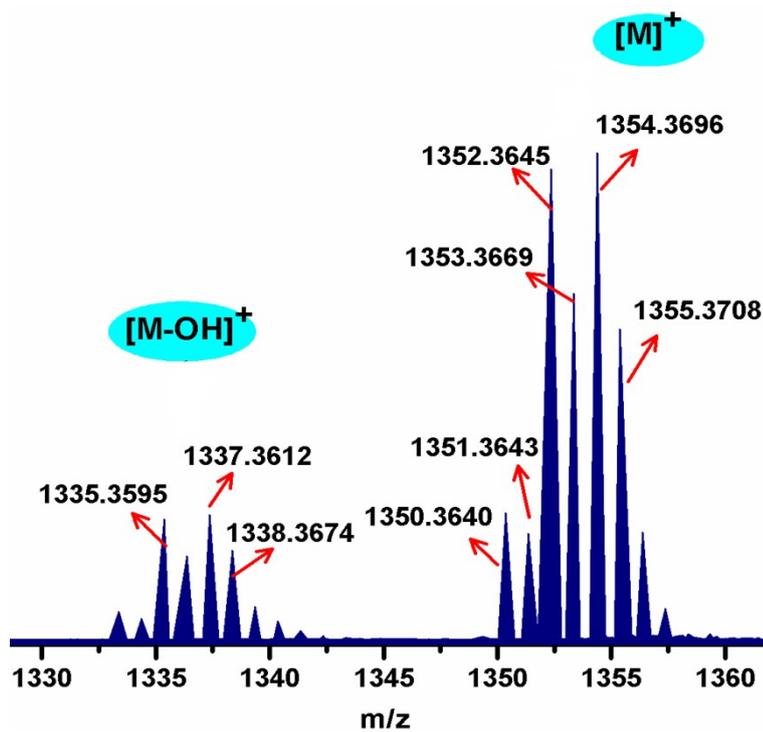
Figure S14: ESI-MS spectrum of complex **2** showing [M-OH]$^+$, [M]$^+$ peaks.
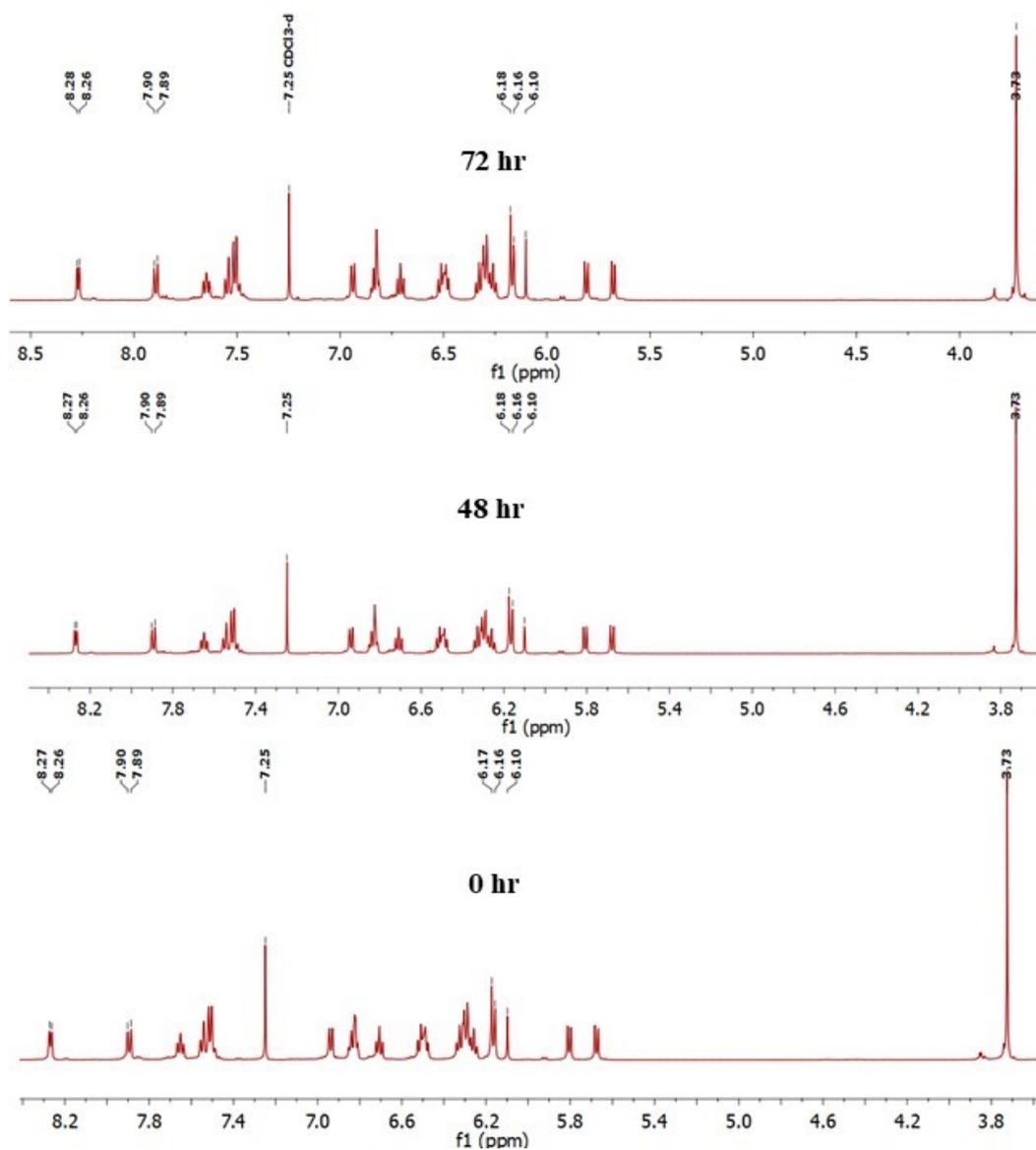
Figure S15: ¹H NMR spectra of complex 1 in CDCl₃, measured immediately after preparation (bottom), after 48 hours (middle), and after 72 hours(top).
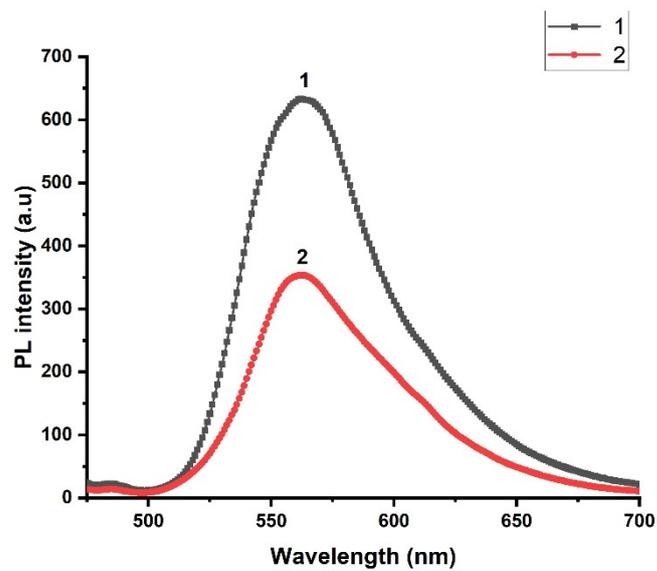
Figure S16. Solid state emission spectra complexes**1, 2** at room temperature (λ_{ex}=450 nm)
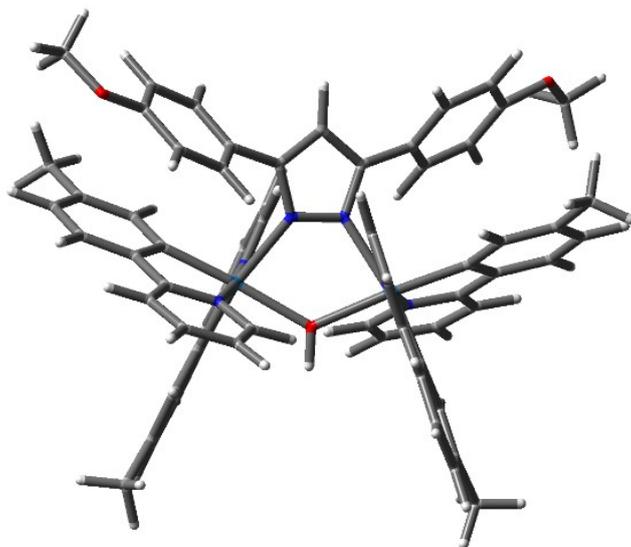
Figure S17: DFT Optimized structure of complex **2** in the ground state (S0) at the PBE0/LANL2TZ/D95V level.

Figure S18: Relevant molecular orbitals of complex **2** (iso value=0.04) obtained from DFT calculations at the PBE0/LANL2TZ/D95V level.
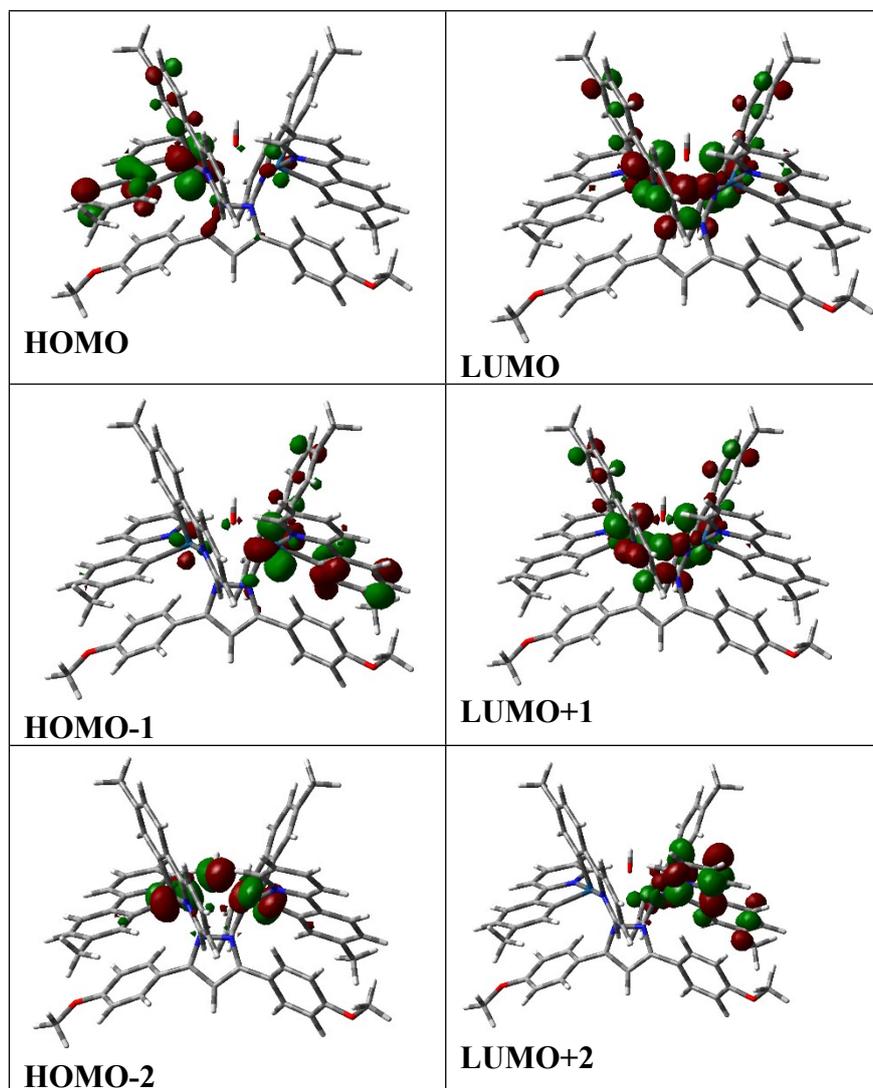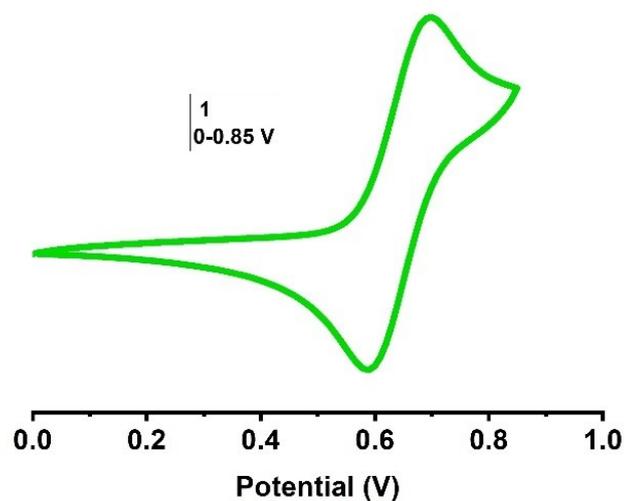
Figure S19: Cyclic voltammogram of complex 1(By switching the potential window from 0 to 0.8 V) recorded at room temperature, scan rate 100mVs^{-1}, starting voltage 0.0V, in deaerated dichloromethane solution (1 mM) with 0.1 M TBAPF$_6$
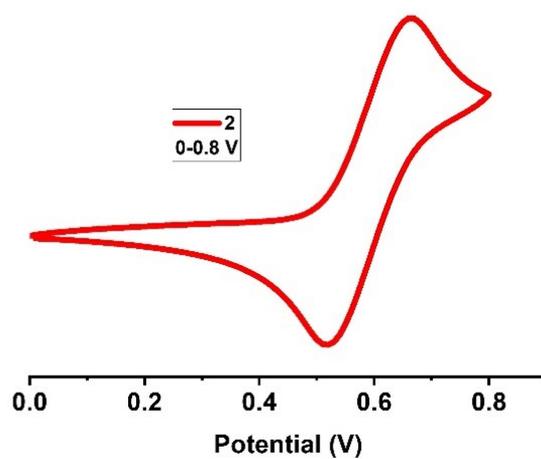
Figure S20: Cyclic voltammogram of complex 2 (By switching the potential window from 0 to 0.8 V) recorded at room temperature, scan rate 100mVs^{-1}, starting voltage 0.0V, in deaerated dichloromethane solution (1 mM) with 0.1 M TBAPF$_6$

Table S1: The main optimized geometry parameters for **1** and **2** in the ground state (S0) at the PBE0 level together with the experimental value for **1**.

Bond Specification	X-Ray Structure (Complex 1)	PBE0/LANL2TZ/D-95V (Complex 1)	PBE0/LANL2TZ/D-95V (Complex 2)
Ir(1)- N(5)	2.201(6)	2.172	2.177
Ir(1)-O(1)	2.147(6)	2.119	2.117
Ir(2)-O(1)	2.143(6)	2.118	2.116
Ir(2)-N(6)	2.187(6)	2.170	2.165
Ir1….Ir2	3.798	3.782	3.781
N(4)-Ir(2)- N(3) (trans bond length)	2.038(7) … 1.997(8)	2.032…2.021	2.034….2.022
N(2)-Ir(1)- N(1) (trans bond length)	2.050(6) … 2.064(6)	2.020…2.032	2.022….2.033
Ir(1)-C(11)	2.011(9)	2.000	2.001
Ir(2)-C(33)	2.007(9)	1.999	2.000
Bond Angle	(º)		
N(4)-Ir(2)-N(3) (trans bond angle)	171.3(3)	171.9	171.9
N(2)-Ir(1)-N(1) (trans bond angle)	172.3(3)	171.9	172.0
Ir(1)-O(1)-Ir(2)	124.6(3)	126.4	126.5
N(6)-Ir(2)-O(1)	81.4(2)	80.8	80.9
N(5)-Ir(1)-O(1)	81.0(2)	80.5	80.3
N(3)-Ir(2)-C(33)	80.1(4)	80.9	80.9
N(4)-Ir(2)-C(44)	80.7(3)	80.9	80.9
N(2)-Ir(1)-C(12)	80.2(3)	80.9	80.9
C(11)-Ir(1)-N(1)	79.9(3)	80.9	80.9

Table S2: Singlet excited states calculated at the PBE0/LANL2DZ/D95V level using pcm solvation model for complex**1**

States	Participating MO	E(eV)	λ (nm)	f	Transition Character
S1	HOMO $\rightarrow$ LUMO (38%)	2.749	450.97	0.005	$Ir(d) + L_C \rightarrow L_C$
	HOMO $-$ 1 $\rightarrow$ LUMO (27%)				$Ir(d) + L_C \rightarrow L_C$
	HOMO $\rightarrow$ LUMO+1 (24%)				$Ir(d) + L_C \rightarrow L_C$
S2	HOMO $-$ 1 $\rightarrow$ LUMO (30%)	2.778	446.25	0.005	$Ir(d) + L_C \rightarrow L_C$
	HOMO$-$ 1 $\rightarrow$ LUMO +1(31%)				$Ir(d) + L_C \rightarrow L_C$
	HOMO $\rightarrow$ LUMO (25%)				$Ir(d) + L_C \rightarrow L_C$
S3	HOMO $-$ 2 $\rightarrow$ LUMO (72%)	2.908	426.32	0.096	$Ir(d) + L_C + L_{OH} \rightarrow L_C$
S4	HOMO$-$ 1 $\rightarrow$ LUMO +2 (62%)	2.951	420.16	0.001	$Ir(d) + L_C \rightarrow L_C$
S5	HOMO $\rightarrow$ LUMO +3 (57%)	2.965	418.12	0.011	$Ir(d) + L_C \rightarrow L_C$
	HOMO $-$ 1$\rightarrow$ LUMO +3 (20%)				$Ir(d) + L_C \rightarrow L_C$

TableS3: Triplet excited states calculated at the PBE0/LANL2DZ/D95V level using pcm solvation model for complex**1**

States	Participating MO	E(eV)	λ(nm)	Transition character
T1	HOMO $-$ 2 $\rightarrow$ LUMO (25%)	2.497	496.37	$Ir(d) + L_C + L_{OH} \rightarrow L_C$
	HOMO$-$ 1 $\rightarrow$ LUMO (23%)			$Ir(d) + L_C \rightarrow L_C$
	HOMO $\rightarrow$ LUMO+1 (11%)			$Ir(d) + L_C \rightarrow L_C$
	HOMO $\rightarrow$ LUMO (10%)			$Ir(d) + L_C \rightarrow L_C$
T2	HOMO $\rightarrow$ LUMO (25%)	2.524	491.04	$Ir(d) + L_C \rightarrow L_C$
	HOMO$-$ 1 $\rightarrow$ LUMO+1 (22%)			$Ir(d) + L_C \rightarrow L_C$

Table S4: Singlet excited states calculated at the PBE0/LANL2DZ/D95V level using pcm solvation model for complex **2**

States	Participating MO	E(eV)	λ (nm)	f	Transition Character
S1	HOMO $\to$ LUMO (44%)	2.791	444.12	0.006	$Ir(d) + L_C \to L_C$
	HOMO $-$ 1 $\to$ LUMO (21%)				$Ir(d) + L_C \to L_C$
	HOMO $\to$ LUMO+1 (26%)				$Ir(d) + L_C \to L_C$
S2	HOMO $-$ 1 $\to$ LUMO (46%)	2.821	439.45	0.005	$Ir(d) + L_C \to L_C$
	HOMO $-$ 1 $\to$ LUMO +1 (29%)				$Ir(d) + L_C \to L_C$
	HOMO $\to$ LUMO (19%)				$Ir(d) + L_C \to L_C$
S3	HOMO $-$ 2 $\to$ LUMO (80%)	2.936	422.25	0.100	$Ir(d) + L_C + L_{OH} \to L_C$
S4	HOMO $-$ 1 $\to$ LUMO +2 (69%)	2.979	416.12	0.001	$Ir(d) + L_C \to L_C$
S5	HOMO $\to$ LUMO +3 (62%)	2.988	414.81	0.010	$Ir(d) + L_C \to L_C$
	HOMO $-$ 1 $\to$ LUMO +2 (12%)				$Ir(d) + L_C \to L_C$

Table S5: Triplet excited states calculated at the PBE0/LANL2DZ/D95V level using pcm solvation model for complex **2**

States	Participating MO	E(eV)	λ(nm)	Transition character
T1	HOMO $-$ 2 $\to$ LUMO (24%)	2.463	503.39	$Ir(d) + L_C + L_{OH} \to L_C$
	HOMO $-$ 1 $\to$ LUMO (18%)			$Ir(d) + L_C \to L_C$
	HOMO $\to$ LUMO+1 (8%)			$Ir(d) + L_C \to L_C$
	HOMO $\to$ LUMO (12%)			$Ir(d) + L_C \to L_C$
T2	HOMO $\to$ LUMO (10%)	2.501	495.65	$Ir(d) + L_C \to L_C$
	HOMO $-$ 1 $\to$ LUMO+1 (22%)			$Ir(d) + L_C \to L_C$

Table S6: Optimized coordinates for complex **1** at the PBE0/LANL2TZ/D95V level

	X	Y	Z
Ir	-1.78337500	-0.69409100	-0.62460900
Ir	1.74281400	-0.60276100	0.74036800
O	-0.03361600	-1.59834400	0.15722400
O	6.33589200	3.77876300	-2.32459200
O	-6.09494100	4.73216400	1.01506800
N	1.00320200	-0.04205200	2.54805100
N	2.72228900	-1.20979200	-0.92110200
N	-2.77377800	-0.82873800	1.13117700
N	-1.03029600	-0.65048600	-2.51175700
N	0.71977600	1.04125800	-0.24076000
N	-0.67532300	1.09718900	-0.09123000
C	0.45362800	1.17067600	2.82078400
H	0.37447900	1.85925600	1.99255100
C	0.02391000	1.52713400	4.09669700
H	-0.40774000	2.50875800	4.25632400
C	0.16673200	0.60376000	5.14503400
H	-0.15791400	0.85228000	6.15074400
C	0.75236900	-0.63355700	4.87619900
H	0.90340500	-1.35371200	5.67217600
C	1.17887900	-0.94976700	3.57416900
C	1.85381700	-2.17892300	3.17291600
C	2.07751500	-3.26565400	4.04105800
H	1.72997000	-3.23672700	5.07140600
C	2.75098500	-4.39870600	3.58002300
H	2.92616800	-5.24125400	4.24283800
C	3.20042400	-4.43741400	2.24671900
H	3.72812000	-5.31600700	1.88228400
C	2.97575000	-3.35606400	1.38396300
H	3.33921200	-3.42048000	0.36207300
C	2.29541300	-2.19575800	1.81592400
C	2.14567000	-1.91929400	-1.92294000
H	1.08808000	-2.11049200	-1.79707700
C	2.87157300	-2.37449600	-3.01985300
H	2.36747500	-2.93770300	-3.79693600
C	4.24666500	-2.08827600	-3.08710700
H	4.84168000	-2.43140700	-3.92806300
C	4.83954200	-1.35821500	-2.05722900
H	5.89704700	-1.12315200	-2.08895200
C	4.06956300	-0.91669700	-0.96541300
C	4.54595300	-0.13764300	0.16815800
C	5.88580700	0.26573500	0.32645000
H	6.63669400	-0.00025600	-0.41403900
C	6.26155300	1.01613900	1.44145500
H	7.29493400	1.32395700	1.57439600
C	5.28494600	1.36391900	2.39452100
H	5.57005900	1.94574600	3.26889900

C	3.95264800	0.96466200	2.23453000
H	3.23216300	1.24886900	2.99663700
C	3.53572900	0.20305500	1.11899600
C	-2.21610200	-1.27500500	2.28389400
H	-1.16166900	-1.50858100	2.22281400
C	-2.95435400	-1.43030700	3.45357400
H	-2.46365300	-1.78978600	4.35080500
C	-4.32454200	-1.11441200	3.43438000
H	-4.93068500	-1.23282600	4.32751200
C	-4.89794700	-0.65026800	2.25056500
H	-5.95234300	-0.40172800	2.21132900
C	-4.11467300	-0.50353600	1.09027200
C	-4.56601700	-0.00982400	-0.20127000
C	-5.89212200	0.38491700	-0.46439600
H	-6.65576500	0.31515700	0.30749600
C	-6.23835900	0.86962100	-1.72578100
H	-7.25826600	1.17771100	-1.93693900
C	-5.24666000	0.95736200	-2.72236500
H	-5.50911900	1.33476600	-3.70851900
C	-3.93007200	0.56004600	-2.46186200
H	-3.19750500	0.63344200	-3.26138300
C	-3.54265700	0.06560700	-1.19552600
C	-0.43535100	0.42791500	-3.08541400
H	-0.33912000	1.30874500	-2.46770100
C	0.01403500	0.42015700	-4.40362900
H	0.48312300	1.30886200	-4.81047100
C	-0.15731300	-0.74206900	-5.17287300
H	0.18166500	-0.77898200	-6.20353800
C	-0.79165400	-1.84295700	-4.59680000
H	-0.96681500	-2.74114700	-5.17779200
C	-1.23769800	-1.78850500	-3.26430800
C	-1.96597200	-2.84159900	-2.56466700
C	-2.24108500	-4.10384600	-3.12569000
H	-1.89371100	-4.35700900	-4.12483000
C	-2.96762700	-5.04735600	-2.39608100
H	-3.18317100	-6.02332100	-2.82141900
C	-3.41969400	-4.71894800	-1.10446000
H	-3.98894500	-5.44829200	-0.53237900
C	-3.14536800	-3.46211800	-0.54769800
H	-3.51459500	-3.24318900	0.45054100
C	-2.40926900	-2.48628100	-1.25544100
C	1.16460900	2.31015100	-0.50097600
C	0.07760000	3.19987400	-0.44920100
H	0.10648900	4.26960000	-0.58967500
C	-1.05362400	2.41174400	-0.17212000
C	2.53872000	2.65759300	-0.89783700
C	3.14121400	2.03211500	-2.00909800
H	2.61036700	1.23507900	-2.52156200
C	4.39719800	2.43020000	-2.46368100
H	4.86600900	1.95226600	-3.31791800

C	5.08414700	3.46489500	-1.80834300
C	4.49756700	4.10924500	-0.70797100
H	5.01227300	4.90697800	-0.18292900
C	3.23064700	3.70292600	-0.26847100
H	2.78285400	4.19397400	0.59142200
C	7.10122600	4.81520200	-1.67257700
H	6.57947600	5.78106400	-1.70854900
H	8.03476300	4.88476900	-2.23253300
H	7.31650300	4.55423500	-0.62786900
C	-2.40127500	2.92586200	0.11577600
C	-3.00278400	3.87783900	-0.73296800
H	-2.50811800	4.15030100	-1.66128800
C	-4.22801100	4.45776400	-0.41105500
H	-4.70368600	5.18017200	-1.06600200
C	-4.87903500	4.10028200	0.78161100
C	-4.29416600	3.16247400	1.64597500
H	-4.77668900	2.87306500	2.57405400
C	-3.06269200	2.58611100	1.30625000
H	-2.60166600	1.87231100	1.98265800
C	-6.81668800	4.39864500	2.21885400
H	-7.06918200	3.32991400	2.25066800
H	-7.73308000	4.98926000	2.18351300
H	-6.24331900	4.66497100	3.11724100
H	-0.08212000	-2.55090400	0.34045300

Table S7: Optimized coordinates for complex **2** at the PBE0/LANL2TZ/D95V level

	X	Y	Z
Ir	1.83637644	0.53139889	-0.52420821
Ir	-1.80175419	0.57587721	0.50650192
O	0.01918915	1.50576114	-0.04189304
O	-6.12994861	-4.06218669	-2.47853042
O	5.96260139	-4.69995187	2.02267231
N	-1.21781360	0.27450790	2.43070266
N	-2.63217882	0.94563938	-1.29984972
N	2.64053757	0.93021877	1.28818140
N	1.27574578	0.22532068	-2.45541117
N	-0.69591244	-1.16093107	-0.16323540
N	0.68019397	-1.19891513	0.11544119
C	-0.67947757	-0.87800589	2.90884244
H	-0.52105627	-1.66801038	2.18967482
C	-0.35534172	-1.05158040	4.25211109
H	0.07323545	-1.99267554	4.57778212
C	-0.59706044	0.00048660	5.15083610
H	-0.35555534	-0.10411074	6.20418869
C	-1.16979485	1.17795861	4.67028129
H	-1.39376146	1.99548258	5.34616112

C	-1.48807500	1.30843827	3.30618049
C	-2.13541580	2.45701099	2.68766918
C	-2.45184617	3.64573793	3.37297871
H	-2.19717911	3.76801400	4.42365627
C	-3.09529953	4.68724301	2.70494898
H	-3.33671731	5.60709223	3.23268927
C	-3.43754054	4.55396192	1.34120523
C	-3.10965264	3.36375205	0.66913792
H	-3.37828511	3.27873228	-0.38150367
C	-2.45635409	2.28838152	1.30798689
C	-1.97095788	1.51922109	-2.33566390
H	-0.92680689	1.73362593	-2.14967707
C	-2.59932960	1.81623629	-3.54157150
H	-2.02940750	2.27387152	-4.34220166
C	-3.96468841	1.50999841	-3.68568807
H	-4.48538337	1.73182149	-4.61244505
C	-4.64373254	0.91570188	-2.62282937
H	-5.69418760	0.66443578	-2.71344588
C	-3.96992982	0.62907484	-1.42053487
C	-4.53771633	-0.00385750	-0.24204712
C	-5.88111698	-0.41398558	-0.14188997
H	-6.56979635	-0.26518036	-0.97073494
C	-6.34193458	-1.02094195	1.02418532
H	-7.38137264	-1.33214032	1.10460333
C	-5.46133766	-1.23078852	2.10986816
C	-4.12423510	-0.82138821	1.99429749
H	-3.46612927	-0.98820699	2.84411191
C	-3.61649548	-0.20175538	0.83025295
C	1.97114841	1.53222599	2.30232693
H	0.92910861	1.74230295	2.10325025
C	2.58791223	1.86541181	3.50491465
H	2.00953734	2.34490031	4.28630994
C	3.95259370	1.56782957	3.66945542
H	4.46509979	1.82018050	4.59303730
C	4.64242101	0.94729107	2.62830140
H	5.69585843	0.71232376	2.73001298
C	3.98061810	0.62573725	1.42753095
C	4.56024139	-0.03612523	0.27290752
C	5.90509400	-0.44720181	0.19697578
H	6.59275100	-0.25004282	1.01715559
C	6.36998182	-1.11211440	-0.93456525
H	7.40766687	-1.43240885	-0.99456733
C	5.49191897	-1.37939779	-2.01012983
C	4.15869494	-0.94989406	-1.92768794
H	3.50522401	-1.15232171	-2.77350239
C	3.64656751	-0.27341344	-0.79849174
C	0.73304074	-0.92296387	-2.93801862
H	0.57373349	-1.71714969	-2.22347383
C	0.41024933	-1.09101519	-4.28235212
H	-0.02085766	-2.02954947	-4.61211778

C	0.65678450	-0.03693081	-5.17713141
H	0.41487479	-0.13664797	-6.23082752
C	1.23532870	1.13565188	-4.69202572
H	1.46327173	1.95454400	-5.36479525
C	1.55365897	1.25933375	-3.32728704
C	2.21046699	2.40145885	-2.70637829
C	2.54486989	3.58432090	-3.39271022
H	2.29698610	3.70699503	-4.44485719
C	3.19819097	4.61972053	-2.72441771
H	3.45344609	5.53500707	-3.25349799
C	3.53220218	4.48540056	-1.35929507
C	3.18604233	3.30078756	-0.68594667
H	3.44854958	3.21737435	0.36622278
C	2.52273992	2.23197616	-1.32498908
C	-1.12897786	-2.44876238	-0.32825633
C	-0.06084180	-3.32864463	-0.08548764
H	-0.08920197	-4.40720911	-0.11278164
C	1.05012183	-2.51621245	0.20500599
C	-2.46498397	-2.82961261	-0.81753250
C	-2.92083128	-2.36322453	-2.06814664
H	-2.30948679	-1.66133307	-2.62797419
C	-4.13583348	-2.79590327	-2.59669340
H	-4.49278227	-2.43866987	-3.55735424
C	-4.92761728	-3.70570807	-1.87800125
C	-4.48680058	-4.19292062	-0.63774917
H	-5.08531107	-4.89191827	-0.06306935
C	-3.25909320	-3.75418617	-0.12369189
H	-2.92468412	-4.12070611	0.84311901
C	-6.99835621	-4.97577817	-1.77483278
H	-6.51535375	-5.95043804	-1.62222592
H	-7.87277875	-5.09937202	-2.41525691
H	-7.30728740	-4.56469969	-0.80446943
C	2.36341336	-3.00248466	0.65137209
C	2.98874968	-4.08142221	-0.00760280
H	2.53940182	-4.48520672	-0.91099600
C	4.18075585	-4.62351757	0.46879283
H	4.67428882	-5.44515960	-0.03987116
C	4.77399874	-4.09637027	1.62830919
C	4.16196106	-3.03214515	2.30732717
H	4.59964036	-2.61150785	3.20697007
C	2.96473437	-2.49693974	1.81405583
H	2.48352780	-1.68218772	2.34666674
C	6.64080299	-4.17490304	3.18274051
H	6.91184335	-3.11963202	3.04272636
H	7.54632210	-4.77399379	3.28809388
H	6.02626601	-4.27734135	4.08755516
H	0.03873278	2.47662277	-0.02558380
C	4.27313725	5.59013770	-0.64469186
H	4.11853578	5.53897447	0.43829158
H	5.35407470	5.51521578	-0.82713916

H	3.95164539	6.57965058	-0.98999046
C	5.98933590	-2.13231786	-3.22039720
H	5.28062063	-2.06424355	-4.05231150
H	6.95652453	-1.74544364	-3.56423953
H	6.12931471	-3.19693929	-2.98710400
C	-4.16753933	5.66693947	0.62821075
H	-4.03406971	5.60100769	-0.45669732
H	-5.24626529	5.61772488	0.83120291
H	-3.81836237	6.65284347	0.95680260
C	-5.96733340	-1.87471018	3.37913175
H	-5.15065141	-2.06219723	4.08396161
H	-6.70212474	-1.23201851	3.88241298
H	-6.46330186	-2.83202222	3.17220752