Supporting Information

Four cyclometalated Ir(III) complexes and Insights into their luminescence, cytotoxicity and DNA/BSA binding performance

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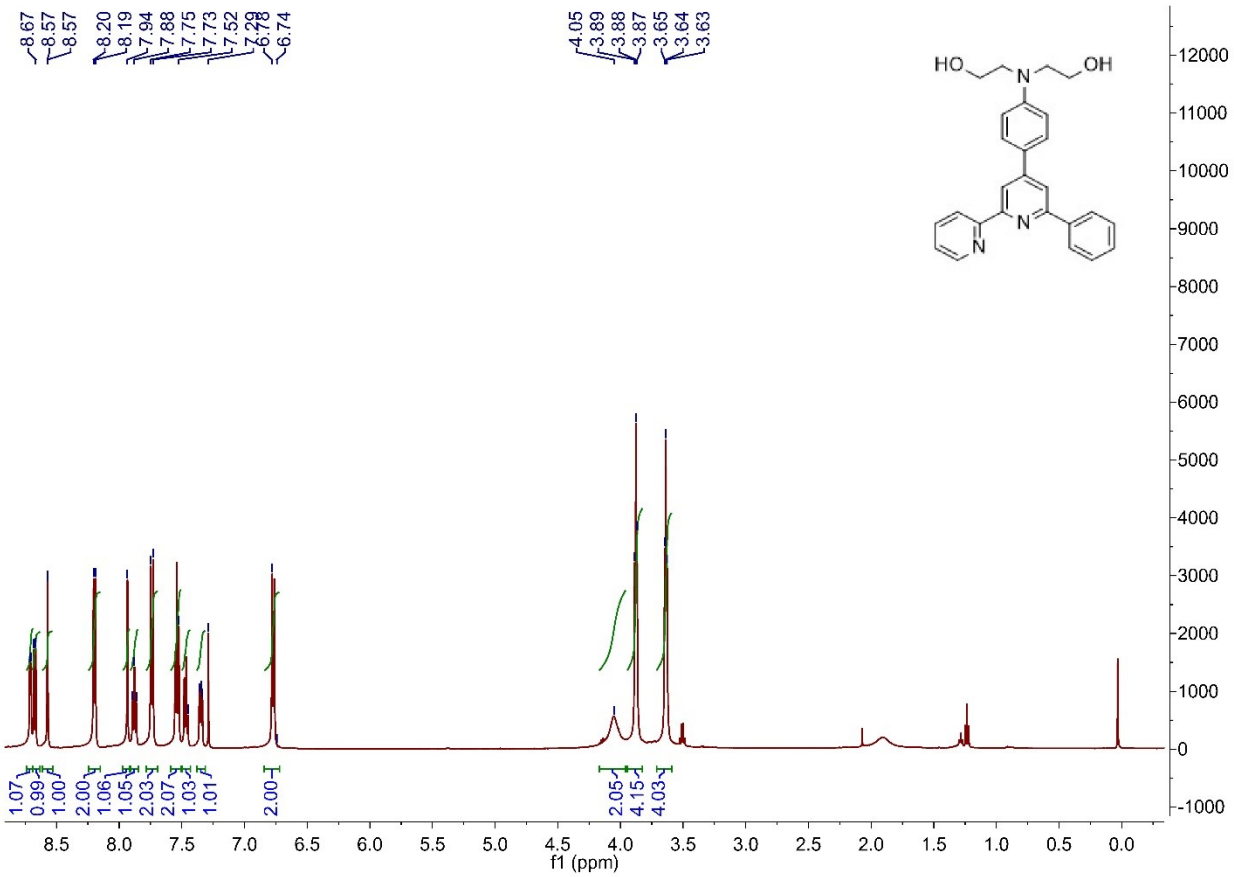


Fig. S1 ^{1}HNMR spectrum of PhbpyOH in $CDCl_3$

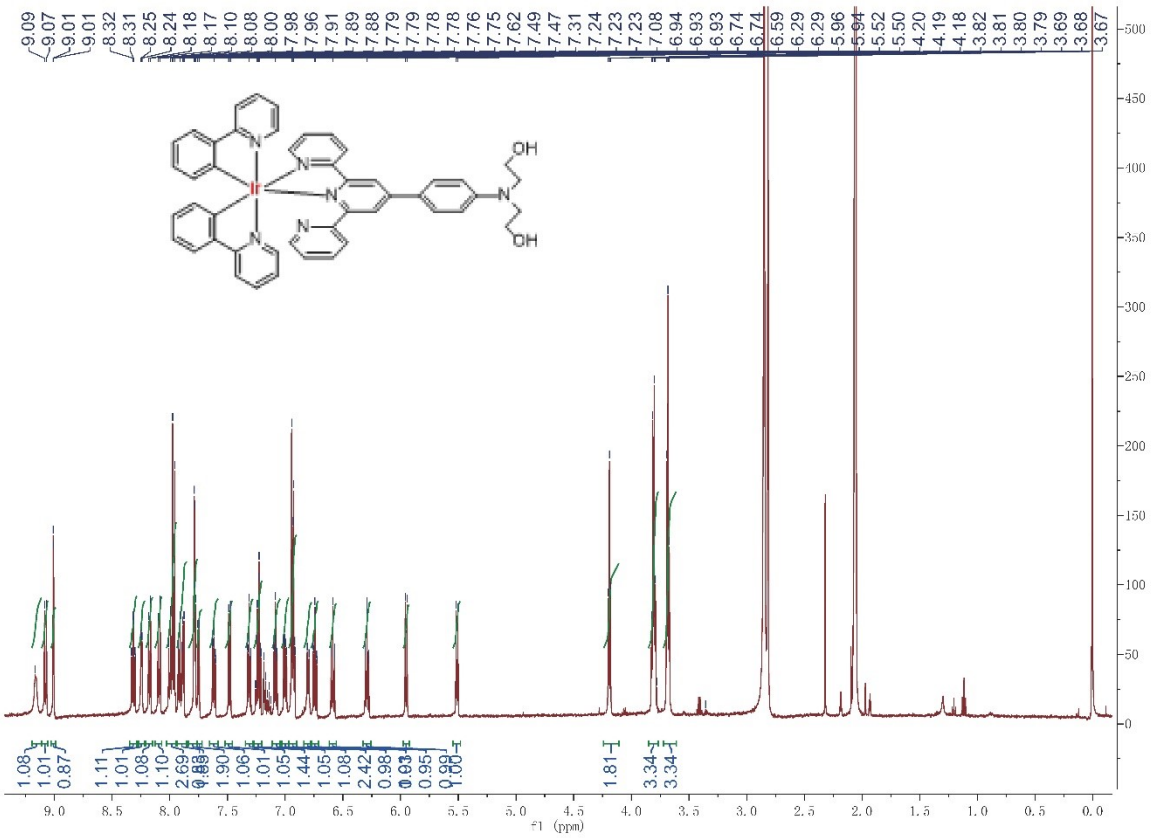


Fig. S2 ^{1}HNMR spectrum of Ir1A in d_6-acetone

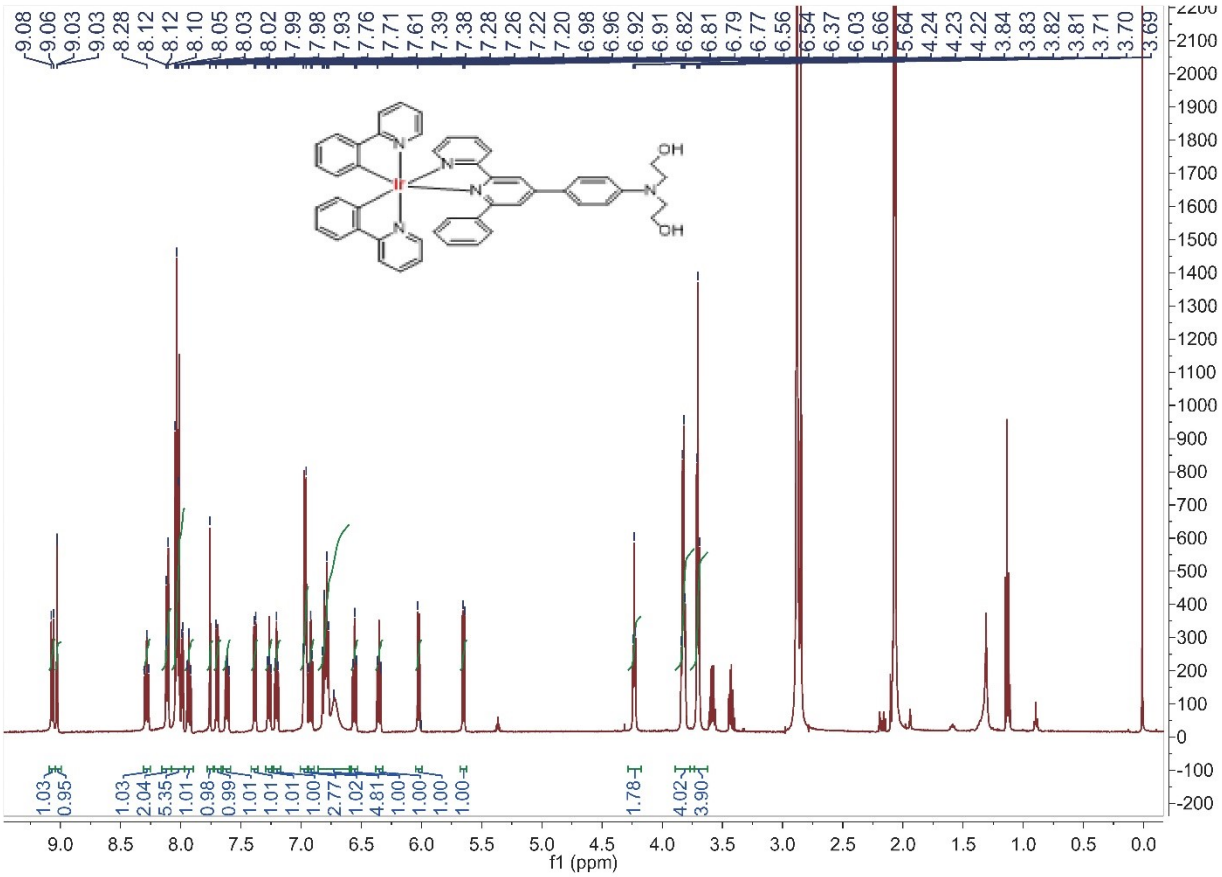


Fig. S3 ^{1}HNMR spectrum of Ir1B in d_6-acetone

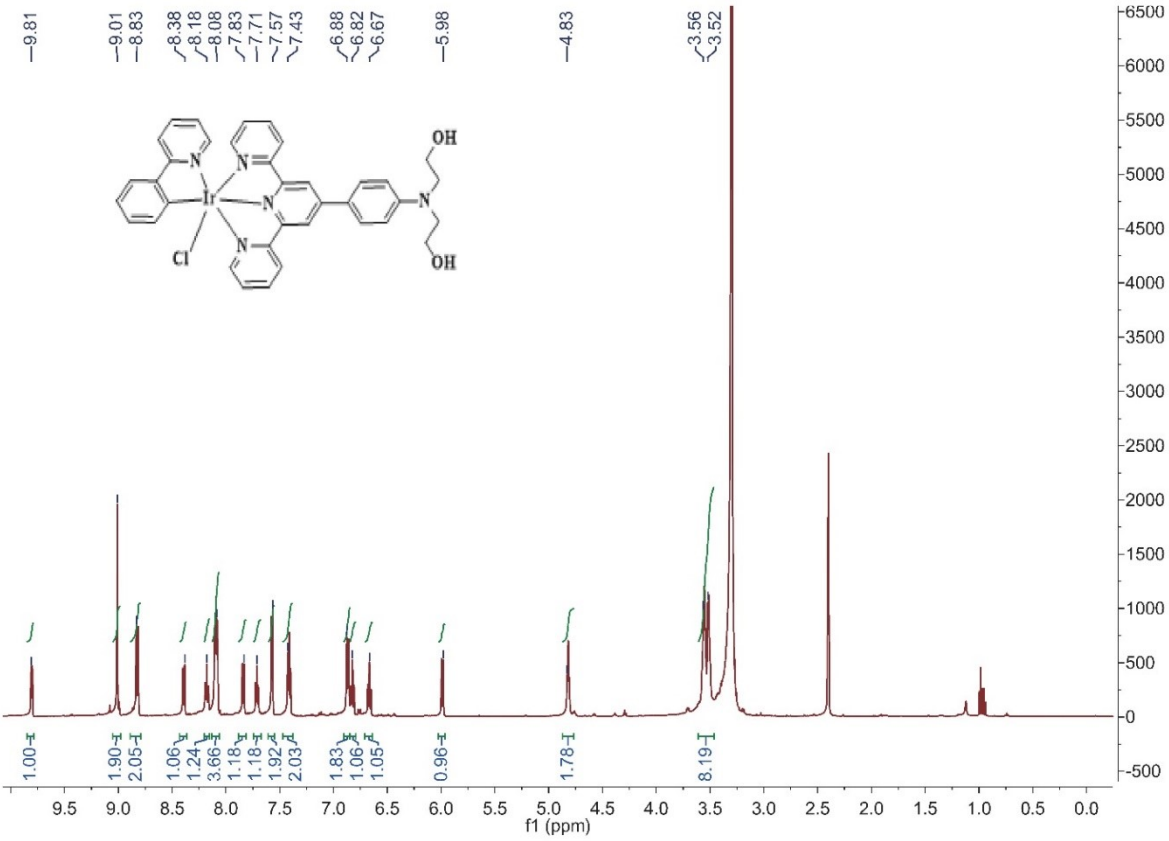


Fig. S4 ^{1}HNMR spectrum of Ir2A in d_6-DMSO

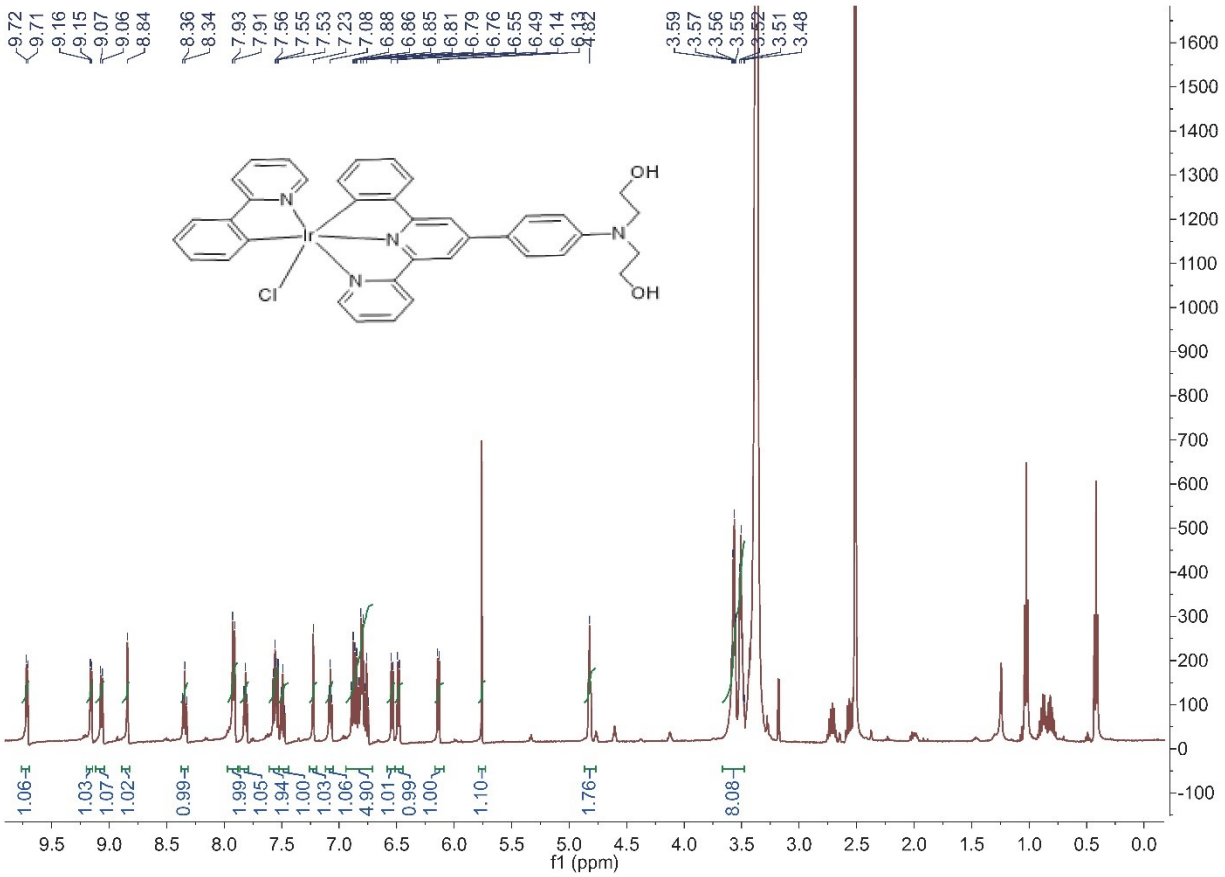


Fig. S5 ^{1}HNMR spectrum of Ir2B in d_6-DMSO

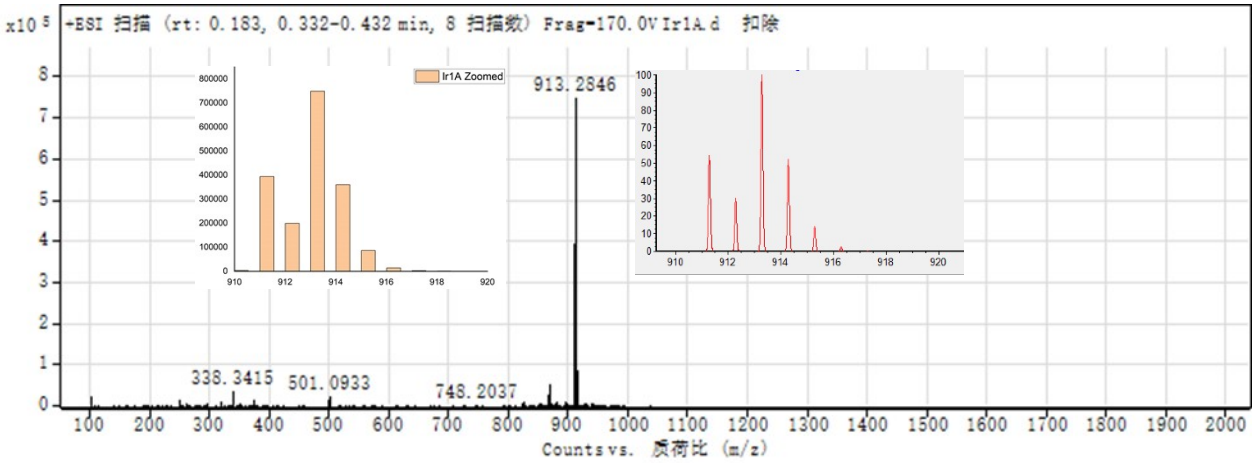


Fig.S6 ESI-MS for complex Ir1A. Inserted are the zoomed mass spectrum (yellow) and simulated isotope distribution using IsoPro 3.0 (red)

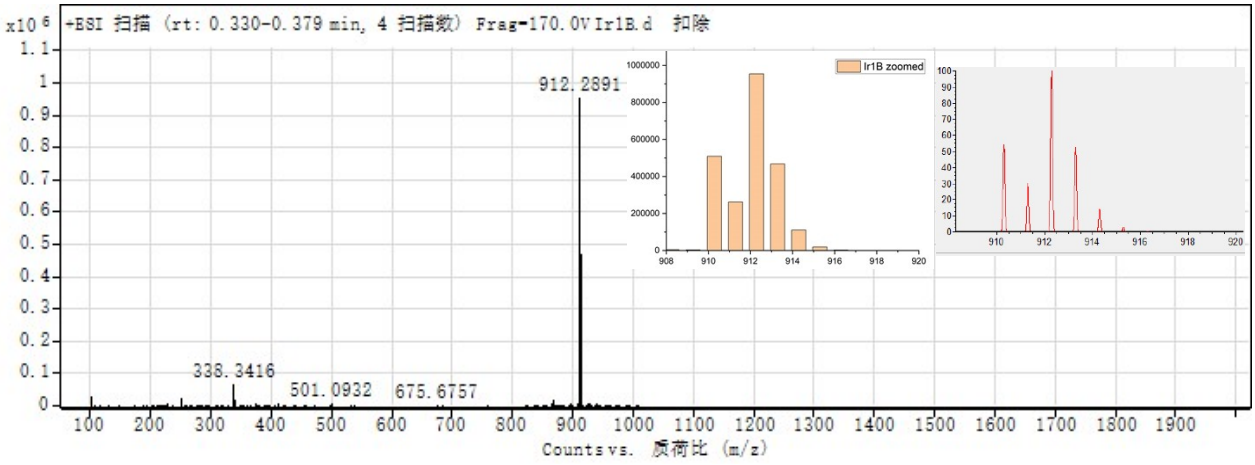


Fig.S7 ESI-MS for complex Ir1B. Inserted are the zoomed mass spectrum (yellow) and simulated isotope distribution using IsoPro 3.0 (red)

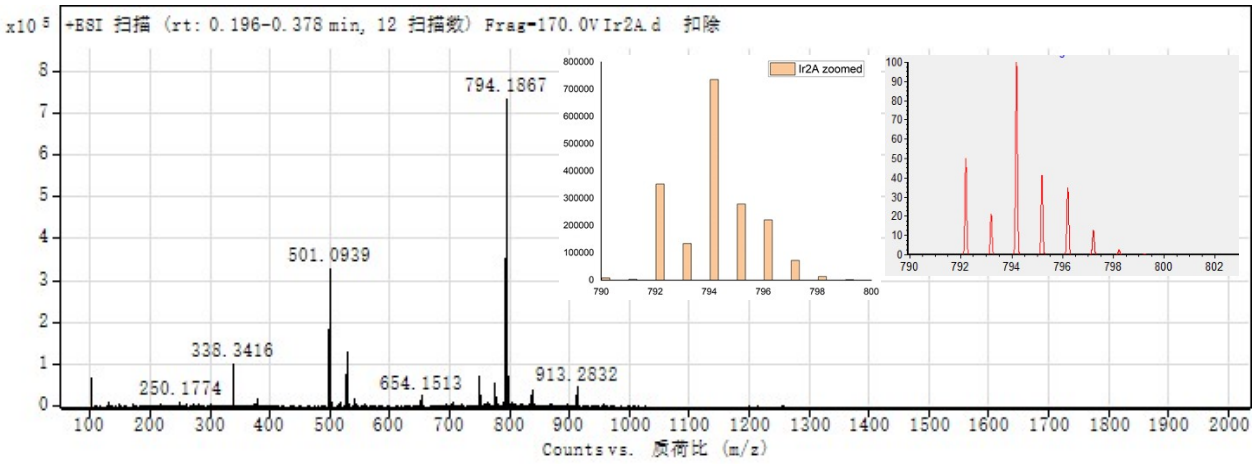


Fig.S8 ESI-MS for complex Ir2A. Inserted are the zoomed mass spectrum (yellow) and simulated isotope distribution using IsoPro 3.0 (red)

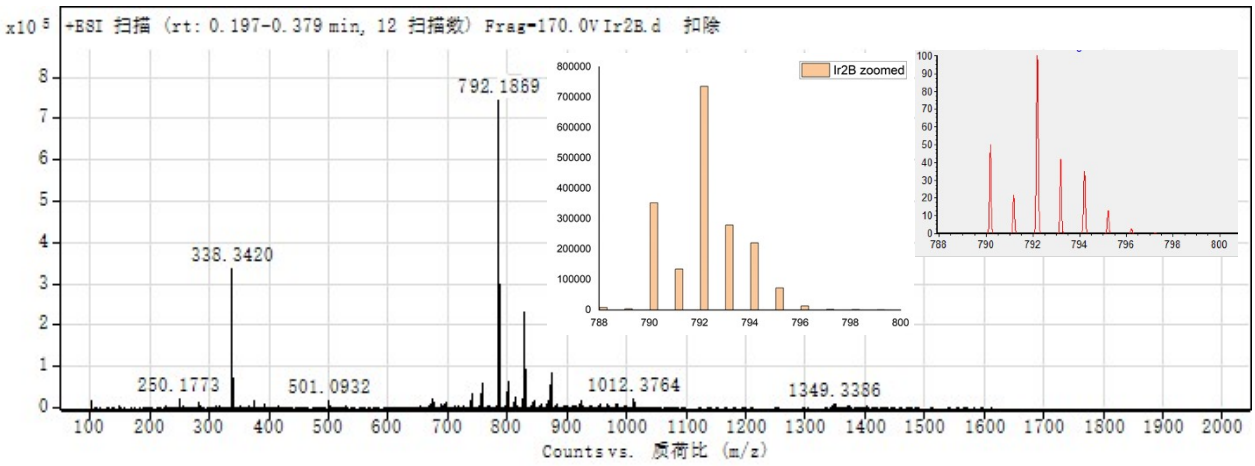


Fig.S9 ESI-MS for complex Ir2B. Inserted are the zoomed mass spectrum (yellow) and simulated isotope distribution using IsoPro 3.0 (red)

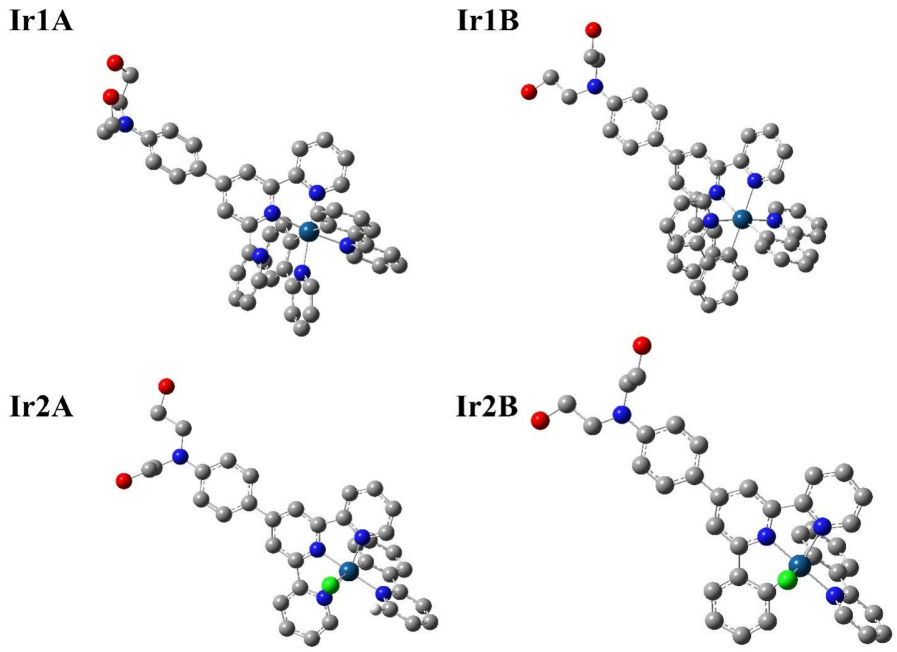


Fig.S10 Three-dimensional molecular structure of four iridium (III) complexes (Ir1A~Ir2B) optimized via Gaussian calculations.

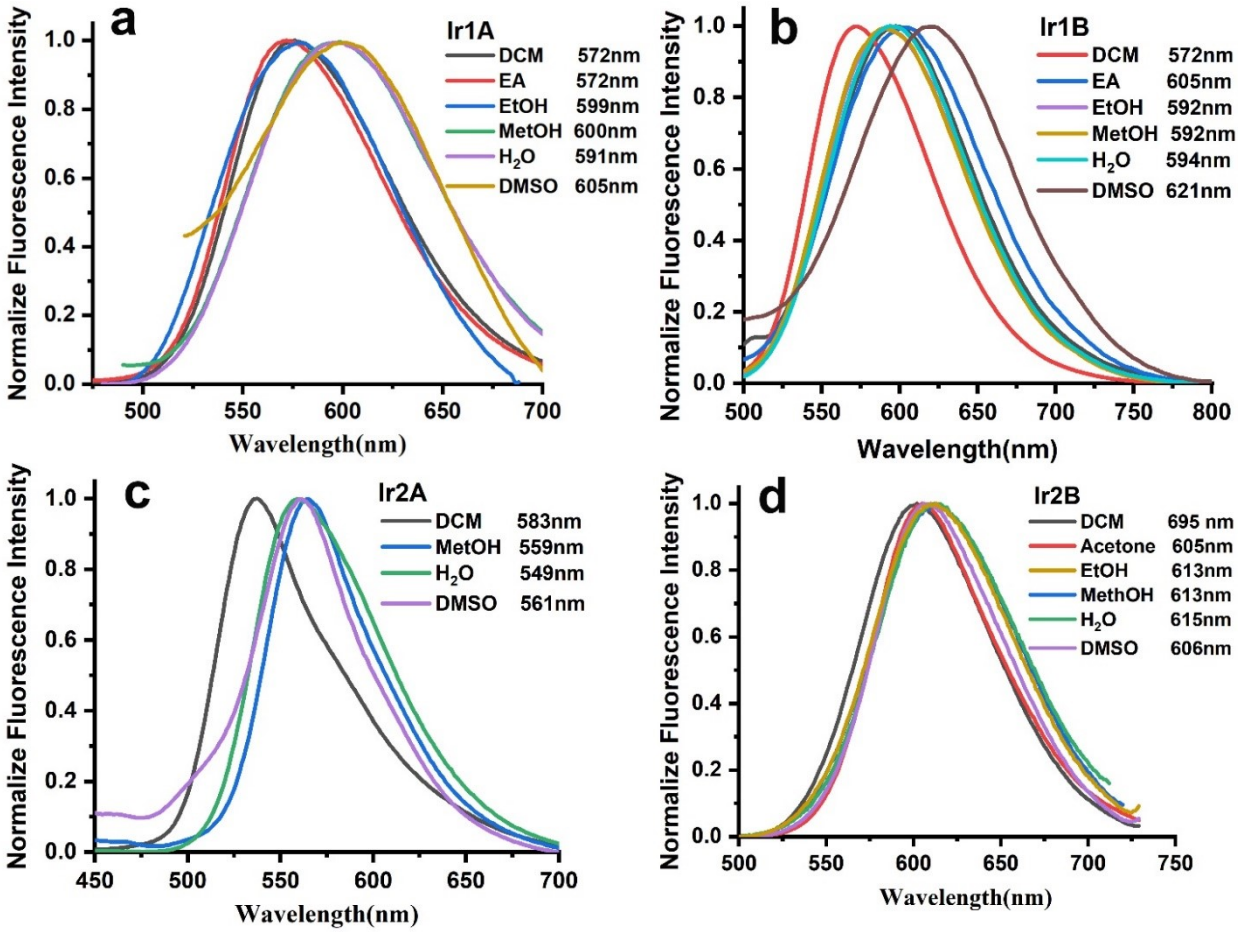
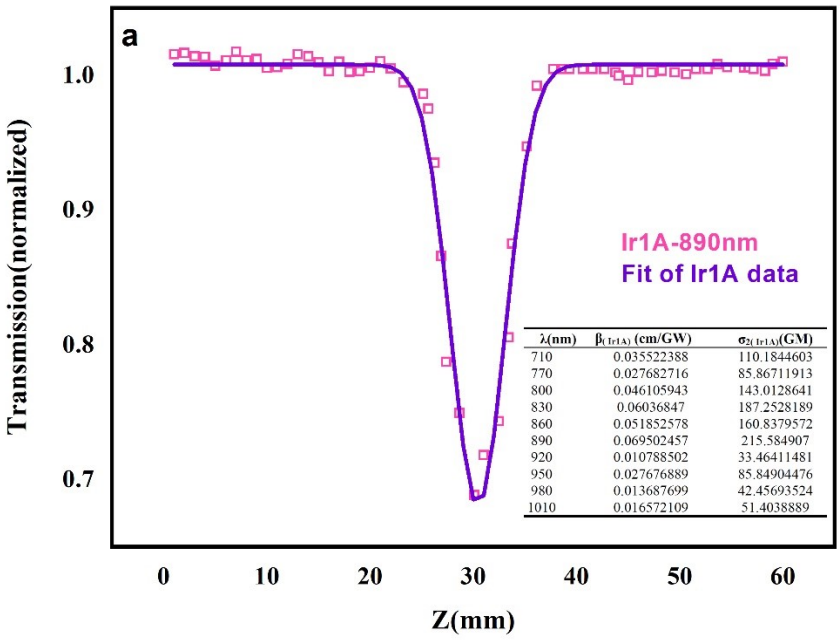


Fig.S11 Normalized one-photon excited fluorescence spectra of four iridium(III) complexes (Ir1A~Ir2B) in different solvents.



λ(nm)	$\beta_{(Ir1A)}$ (cm/GW)	$\sigma_{2(Ir1A)}$(GM)
710	0.035522388	110.1844603
770	0.027682716	85.86711913
800	0.046105943	143.0128641
830	0.06036847	187.2528189
860	0.051852578	160.8379572
890	0.069502457	215.584907
920	0.010788502	33.46411481
950	0.027676889	85.84904476
980	0.013687699	42.45693524
1010	0.016572109	51.4038889

Fig. S12 Open-aperture Z-scan experimental data and fitting curves for Complexes Ir1A in DMSO solution. (1.0×10^{-3} M)

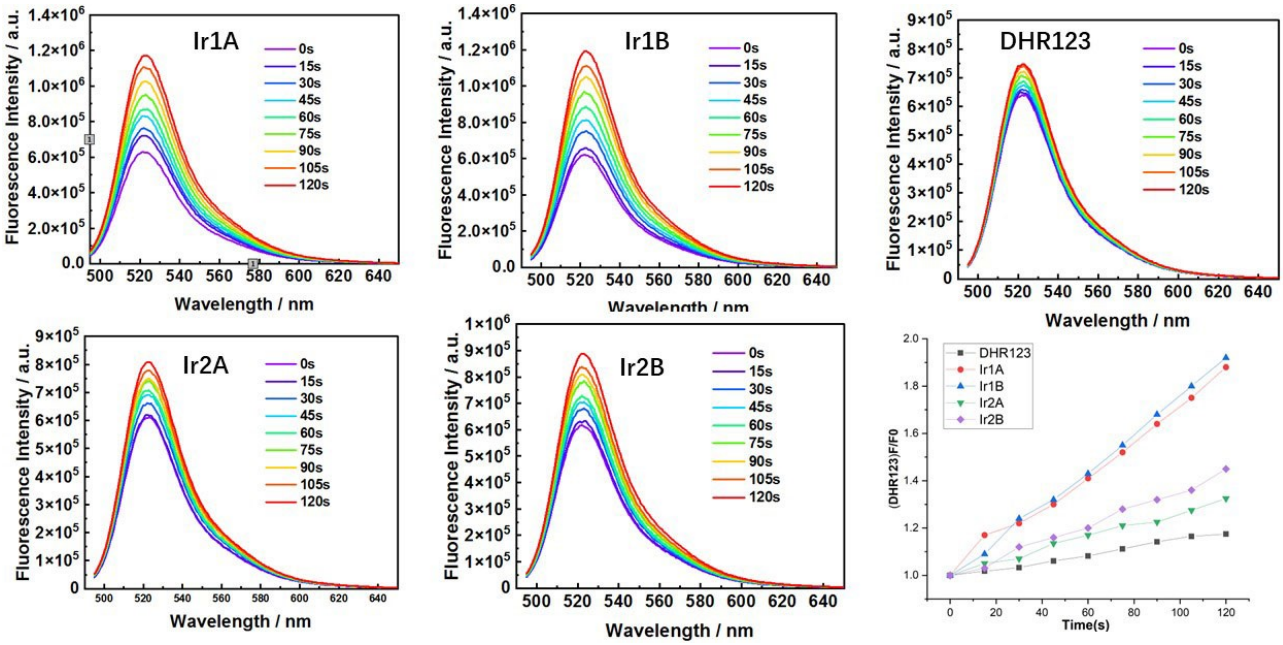


Fig.S13 One-photon excited fluorescence spectra of DHR123 in the absence and presence of iridium(III) complexes Ir1A~Ir2B. (solvent: acetonitrile).

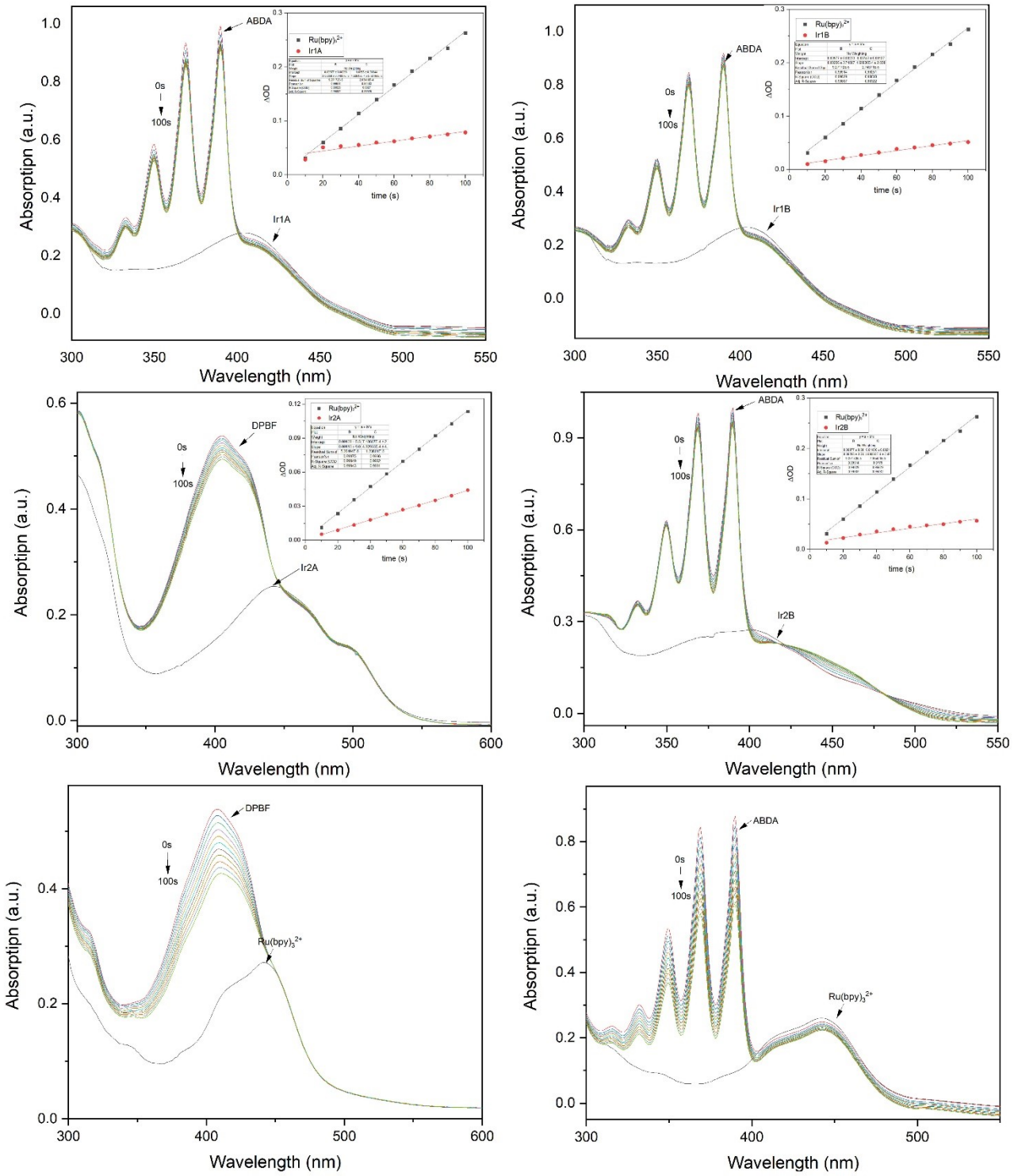


Fig.S14 Absorption spectra of DHR123 in the absence and presence of iridium(III) complexes Ir1A~Ir2B. (Solvent: acetonitrile).

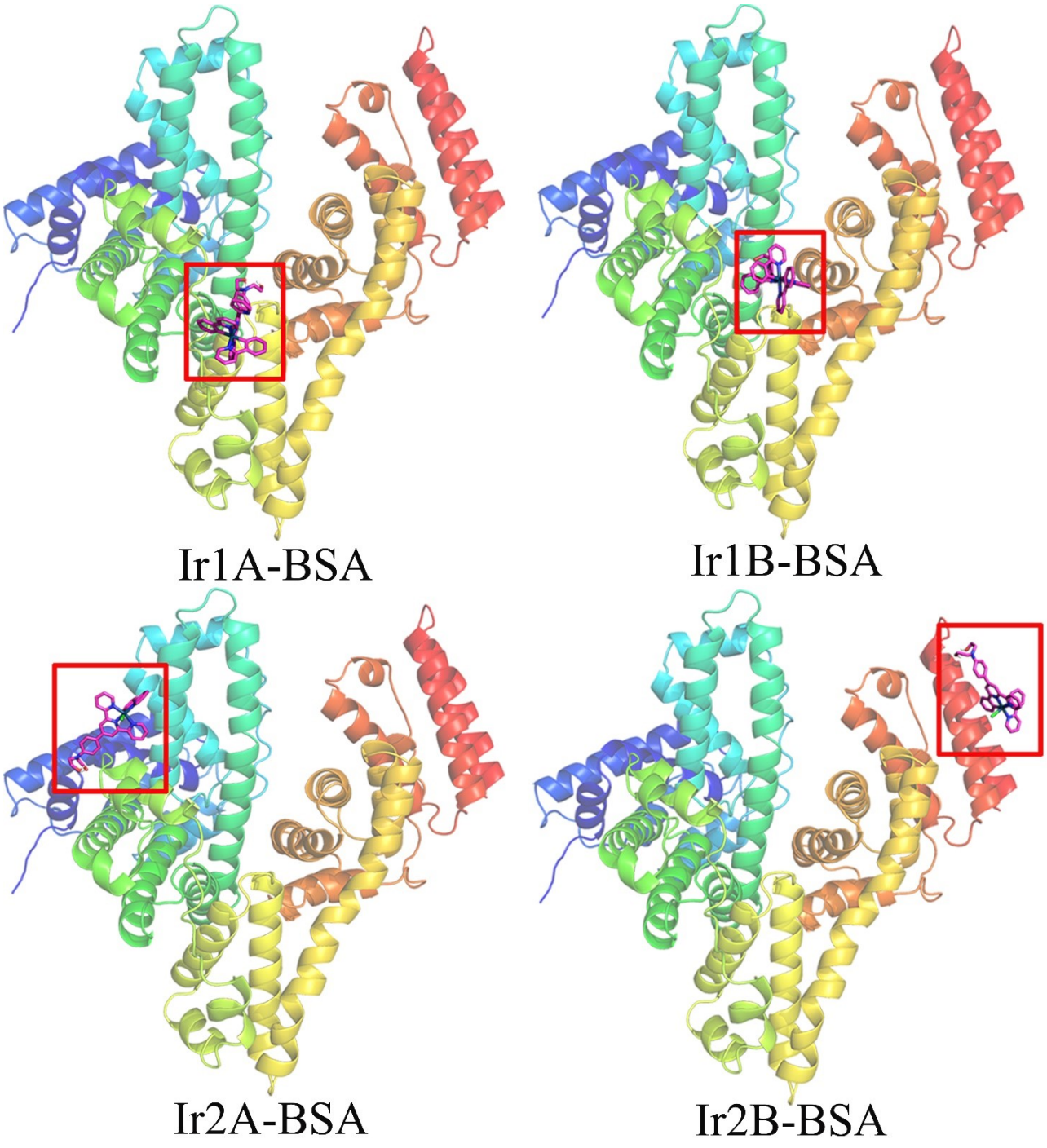


Fig. S15 Theoretical simulation of the interaction mode between the Ir(III) complex with BSA.

Complex	DNA	
	Autodock scores（kcal/mol）	Hydrogen bonding
Ir1A	-4.68	(Ir1A)H57···OP2(DA-18) (1.9 Å) (Ir1A)H58···OP2(DA-18) (1.8 Å) (Ir1A)N14···H7(DA-17) (2.0 Å)
Ir1B	-4.59	(Ir1B)O56···H42(DC-9) (2.0 Å)
Ir2A	-4.33	(Ir2A)H72···OP2(DC-21) (1.8 Å) (Ir2A)H77···OP2(DC-21) (2.3 Å)
Ir2B	-4.76	(Ir2B)O40···H21(DG-10) (1.8 Å) (Ir2B)H72···O2(DC-11) (2.1 Å)
Complex	BSA	
	Autodock scores（kcal/mol）	Hydrogen bonding
Ir1A	-2.41	(Ir1A)H57···O(PRO-338) (2.1 Å)
Ir1B	-2.99	(Ir1B)O56···H11(ARG-217) (2.2 Å)
Ir2A	-3.19	(Ir2A)N27···OE2(GLU-284) (3.0 Å)
Ir2B	-3.34	—

Table S1 Autodock results for the binding of the four Ir(III) complexes with DNA or BSA

Interaction with DNA or BSA	isobestic point	Hypochromism of MLCT band
Ir1A-DNA	/	λ_{405} 23.6%
Ir1B-DNA	/	λ_{425} 14.3% with
Ir2A-DNA	324 and 486nm	λ_{445} 42.5%
Ir2B-DNA	284nm	λ_{423} 9.8%
Ir1A-BSA	293nm	λ_{405} 27.8%
Ir1B-BSA	297nm	λ_{425} 5.6%
Ir2A-BSA	303nm	λ_{445} 10.0%
Ir2B-BSA	297nm	λ_{423} 8.9%

Table S2 Interaction of the Ir(III) complexes with DNA or BSA studied by UV-vis titration experiments.

Ir	2.17414	-0.41517	0.08432	C	6.23112	-1.31668	1.33392
O	-10.1024	0.17545	-2.06799	C	3.86317	-1.29675	-2.18406
O	-10.6467	-1.70798	-0.16007	C	2.40704	1.97496	3.68086
N	-8.41165	0.4223	0.47079	C	-4.89805	1.22126	-0.40391
N	0.11154	-0.07709	-0.07127	C	1.7507	1.27316	4.68887
N	1.44465	-2.30363	0.3346	C	1.31752	-0.53742	3.13236
N	3.05708	1.49385	0.06748	C	-9.55761	-1.81255	0.74631
N	4.16875	-0.97719	0.1689	C	1.69347	-4.65683	0.67501
C	1.96918	0.14197	2.0929	H	-9.86853	-0.19595	-2.93413
C	-6.31316	-0.71493	0.99664	H	-10.3833	-1.0869	-0.87741
C	4.63447	3.76614	0.29996	H	-6.82801	-1.49039	1.54869
C	2.53428	-0.87183	-1.9258	H	5.25355	4.65267	0.39726
C	1.19436	3.51746	-2.36125	H	1.48987	3.55052	-3.40761
N	0.59653	2.39079	-1.95335	H	0.10042	3.23926	1.28038
C	0.22596	2.31745	-0.66449	H	1.23338	5.33582	0.50026
C	0.42067	3.35306	0.2504	H	1.93669	5.48973	-1.9088
C	1.05131	4.51638	-0.18827	H	-6.76566	2.13026	-0.82995
C	1.44274	4.60407	-1.5225	H	7.90265	-1.94309	0.11481
C	-6.27895	1.30272	-0.33136	H	-2.58764	-2.03582	0.45965
C	6.85177	-1.67127	0.13426	H	0.69542	-0.53716	5.1999
C	-2.03507	-1.12543	0.27379	H	4.11451	3.70038	2.38462

C	1.20755	0.01282	4.41323	H	-4.43035	-1.59932	1.4203
C	4.75464	-1.32151	-1.01951	H	5.30101	-1.99447	-3.6591
C	0.09306	-2.43494	0.36466	H	3.6915	-1.92918	-5.52674
C	3.99235	3.23733	1.41279	H	-8.56439	-0.64232	2.26804
C	-4.93268	-0.78434	0.90841	H	-10.0643	0.0535	1.67546
C	3.20484	2.08749	1.29062	H	-2.35303	2.18354	-0.32097
C	4.28022	-1.67284	-3.47272	H	4.94601	3.52309	-1.83511
C	-2.7193	0.08749	0.10707	H	-1.5748	-3.78647	0.56982
C	3.37426	-1.63816	-4.52913	H	-8.69601	2.44372	-0.06493
C	-0.53367	1.09443	-0.27632	H	-10.1578	1.48786	0.12477
C	-9.15547	-0.46903	1.36274	H	6.5791	-1.94222	-1.97848
C	-1.915	1.20345	-0.1769	H	-9.55943	2.17595	-2.23929
C	-0.6509	-1.18317	0.18698	H	-8.20782	1.02543	-2.17923
C	4.47212	3.14334	-0.93698	H	3.50901	1.49172	-1.94409
C	-4.17952	0.17638	0.20675	H	-0.14179	-5.78631	0.85346
C	2.51823	1.41349	2.39769	H	4.35452	-0.68995	2.20455
C	-0.49711	-3.68742	0.55133	H	3.29324	-3.22531	0.45239
C	-9.13657	1.45858	-0.26236	H	1.34313	-1.21397	-5.11898
C	6.11034	-1.67231	-1.03985	H	0.61713	-0.54582	-2.85958
C	-9.19876	1.24913	-1.77228	H	6.77058	-1.30223	2.27421
C	3.67214	2.01208	-1.01055	H	2.81823	2.95736	3.897
C	-7.03975	0.33646	0.3784	H	-4.37313	1.9793	-0.97677
C	0.30724	-4.80929	0.70896	H	1.65897	1.70584	5.68129
C	4.88864	-0.97411	1.30783	H	0.88016	-1.51732	2.9477
C	2.22585	-3.39115	0.48475	H	-8.68429	-2.27756	0.26416
C	2.0539	-1.23498	-4.2955	H	-9.88453	-2.48051	1.55183
C	1.6468	-0.86023	-3.012	H	2.36175	-5.50247	0.79208

Table S3 The xyz coordinates for complex Ir1A

C	-3.91092	4.1347	1.12162	N	8.36659	-0.01772	-0.4561
C	-4.27942	3.56176	-0.10183	C	9.11879	-1.26619	-0.33976
C	-3.81627	2.29482	-0.46262	C	9.10272	-1.83959	1.07539
C	-2.9683	1.5624	0.3804	O	9.90154	-3.02228	1.05419
C	-2.60654	2.15829	1.61726	C	9.03147	1.22346	-0.05232
C	-3.07261	3.43152	1.98087	C	10.51912	1.26793	-0.38368
C	-4.53391	-0.90043	2.17754	O	10.91912	2.62168	-0.16953
C	-5.84791	-1.23685	2.51378	H	-4.27641	5.11896	1.40054
C	-6.7976	-1.48304	1.51534	H	-4.93227	4.10909	-0.77807
C	-6.42611	-1.39644	0.17622	H	-4.11896	1.87639	-1.41853
C	-5.10658	-1.06103	-0.16424	H	-2.79145	3.87222	2.93309
C	-4.133	-0.8063	0.83788	H	-3.81771	-0.7069	2.97113
C	-1.73602	1.34905	2.46646	H	-6.13564	-1.30405	3.56043
C	-4.61629	-0.99231	-1.54191	H	-7.81878	-1.74162	1.78052
N	-1.481	0.09687	1.97974	H	-7.16282	-1.59333	-0.59741
C	-0.7073	-0.75526	2.67875	H	-0.56251	-1.73777	2.24872
C	-0.12948	-0.40748	3.88981	H	0.48743	-1.12689	4.41652
C	-0.36249	0.87328	4.39722	H	0.07867	1.18318	5.33952
C	-1.16952	1.74913	3.68298	H	-1.36169	2.74643	4.06038
C	-5.36822	-1.22278	-2.69898	H	-6.42646	-1.44184	-2.61702
C	-4.75582	-1.17635	-3.94566	H	-5.3376	-1.35177	-4.84529
C	-3.38509	-0.9191	-4.02511	H	-2.86307	-0.89534	-4.97508

C	-2.68494	-0.69058	-2.85012	H	-1.62031	-0.50013	-2.84407
N	-3.28513	-0.69965	-1.64655	H	6.78532	-2.15545	-0.98171
Ir	-2.31254	-0.3366	0.1357	H	4.38599	-2.17547	-1.0633
C	6.26252	-1.23737	-0.74575	H	4.28821	1.96802	0.10962
C	4.87847	-1.2499	-0.78198	H	6.69135	2.01446	0.18045
C	4.11389	-0.1007	-0.50144	H	2.41918	-2.24473	-0.25529
C	4.82486	1.06473	-0.16407	H	2.38456	1.99914	-0.95063
C	6.21084	1.09285	-0.11997	H	-2.54277	-5.59325	0.07893
C	6.98144	-0.05506	-0.43312	H	-3.38965	-3.26384	0.37223
C	1.9112	-1.30716	-0.43569	H	1.31983	-3.92048	-0.81659
C	0.52312	-1.28754	-0.48211	H	-0.12103	-5.91874	-0.52868
N	-0.18769	-0.13536	-0.62821	H	-0.91739	1.5295	-3.05273
C	0.50354	1.01272	-0.81176	H	0.36892	3.28855	0.65014
C	1.8962	1.04957	-0.76977	H	-0.7123	5.42767	0.0094
C	2.64736	-0.11708	-0.55986	H	-1.8934	5.62097	-2.17012
C	-1.87329	-4.74956	-0.04694	H	-1.99418	3.66173	-3.69977
C	-2.35468	-3.45699	0.11779	H	8.72712	-2.0039	-1.04339
N	-1.56943	-2.37611	-0.02289	H	10.15166	-1.08936	-0.64084
C	-0.26319	-2.53194	-0.34178	H	9.5087	-1.10042	1.78132
C	0.28091	-3.80524	-0.53346	H	8.07069	-2.06273	1.38021
C	-0.53105	-4.92483	-0.38092	H	9.90267	-3.39288	1.9518
C	-0.88724	2.37683	-2.37668	H	8.57202	2.05077	-0.60055
C	-0.22156	2.26407	-1.14938	H	8.89531	1.4274	1.02065
C	-0.1494	3.37486	-0.30031	H	11.09947	0.59415	0.2595
C	-0.75636	4.57689	-0.6644	H	10.68077	0.97027	-1.43002
C	-1.42242	4.68368	-1.88749	H	11.8809	2.66284	-0.2981
C	-1.48386	3.58224	-2.74391				

Table S4 The xyz coordinates for complex Ir1B

C	2.42887	1.03375	-3.80988	O	-9.53713	-2.26863	1.96664
C	2.00128	0.68095	-2.52666	Ir	2.51663	-0.09063	0.39136
C	2.92882	0.42483	-1.51113	Cl	2.17326	-0.75224	2.82999
C	4.30981	0.53182	-1.81134	O	-10.4691	2.43202	-1.31624
C	4.73308	0.88614	-3.10203	C	-8.65779	-1.1907	0.04132
C	3.79362	1.13636	-4.09904	C	-8.78802	-1.12391	1.56145
C	6.62284	0.30106	-0.76007	H	4.12282	1.41088	-5.09705
C	5.22622	0.2565	-0.70169	H	7.11649	0.55645	-1.69008
N	4.60642	-0.0666	0.47272	H	4.75975	-0.58315	2.46081
C	5.33155	-0.3394	1.5734	H	7.26649	-0.53428	2.47278
C	6.71833	-0.30812	1.56496	H	8.45713	0.0516	0.33305
C	7.37281	0.018	0.37533	H	-6.23156	2.03129	-0.86315
C	-5.74691	1.10022	-0.60206	H	-3.83199	2.01818	-0.70315
C	-4.36414	1.09456	-0.49547	H	-3.90634	-2.15285	0.36628
C	-3.64939	-0.0693	-0.1623	H	-6.30258	-2.16801	0.19712
C	-4.40433	-1.23502	0.06843	H	-1.94111	-2.14874	-0.60498
C	-5.78608	-1.24289	-0.02314	H	-2.02865	2.0071	0.5595
C	-6.50908	-0.07425	-0.37732	H	3.59395	-5.02499	-0.86426
C	-1.44014	-1.24099	-0.29412	H	4.16412	-2.69426	-0.16305
C	-0.05806	-1.22395	-0.16363	H	-0.54833	-3.84332	-0.94188
N	0.55914	-0.07735	0.19166	H	1.17974	-5.6042	-1.26029
C	-1.48688	1.09874	0.32884	H	-0.69846	3.71661	1.04085

C	-0.10319	1.07281	0.43778	H	4.05926	2.50611	1.22011
C	-2.18567	-0.06923	-0.0441	H	3.39588	4.85844	1.74104
C	2.8086	-4.2887	-0.73597	H	0.95911	5.46944	1.64651
C	3.13976	-2.99539	-0.34553	H	-8.41598	1.86388	0.17064
N	2.20628	-2.04916	-0.17079	H	-8.11769	1.71334	-1.56367
C	0.88238	-2.34233	-0.3823	H	-10.238	0.41895	-1.82844
C	0.4989	-3.62064	-0.7753	H	-10.6112	0.73779	-0.1164
C	1.46993	-4.60465	-0.95398	H	-11.4359	2.42041	-1.40543
C	0.3572	3.47844	1.09116	H	-9.65247	-1.19664	-0.40616
C	0.79202	2.18646	0.81321	H	-8.19847	-2.13847	-0.24775
N	2.12745	1.87562	0.87132	H	-7.79189	-1.11748	2.02551
C	3.02283	2.81967	1.19487	H	-9.29801	-0.19348	1.8506
C	2.63994	4.12549	1.48314	H	-9.62598	-2.23466	2.93306
C	1.28887	4.45883	1.4296	H	1.69496	1.22936	-4.58781
N	-7.88734	-0.07991	-0.5142	H	0.93649	0.60885	-2.32408
C	-8.56253	1.20818	-0.7008	H	5.79087	0.96811	-3.334
C	-10.0559	1.10476	-0.98874				

Table S5 The xyz coordinates for complex Ir2A

C	2.45973	-0.26386	3.92223	C	-8.61161	1.30546	-0.16221
C	2.03256	-0.15494	2.59707	C	-10.0976	1.38118	0.16955
C	2.95578	-0.09024	1.54204	O	-10.5523	2.60697	-0.40569
C	4.33798	-0.13331	1.86678	Ir	2.54712	0.03895	-0.41537
C	4.76259	-0.24276	3.20081	Cl	2.22098	0.11076	-2.96609
C	3.82542	-0.30823	4.22823	O	-9.43782	-3.09027	-0.11797
C	6.65062	-0.06725	0.79492	H	0.96716	-0.1198	2.38665
C	5.25283	-0.05447	0.72762	H	5.82168	-0.2749	3.44094
N	4.62784	0.042	-0.48554	H	4.15461	-0.3917	5.26017
C	5.35853	0.1293	-1.61344	H	7.14092	-0.14892	1.75806
C	6.74573	0.12592	-1.59814	H	4.78736	0.20075	-2.53143
C	7.40291	0.02422	-0.36961	H	7.29276	0.20056	-2.53164
C	-5.74667	-0.91666	0.84668	H	8.48759	0.01667	-0.32078
C	-4.36487	-0.93088	0.73655	H	-6.22712	-1.7642	1.31834
C	-3.65432	0.13084	0.14745	H	-3.82658	-1.78201	1.14344
C	-4.41228	1.2113	-0.33301	H	-3.91661	2.03913	-0.83159
C	-5.79748	1.23598	-0.23958	H	-6.31942	2.08362	-0.66316
C	-6.51335	0.17542	0.36805	H	-1.92954	2.24553	0.15809
C	-1.43476	1.29047	0.03123	H	-2.04738	-2.04966	-0.15277
C	-0.04762	1.2517	-0.09658	H	3.55133	5.20105	-0.13594
N	0.56761	0.04651	-0.21582	H	4.26887	2.84927	-0.36103
C	-0.11286	-1.12219	-0.22175	H	-0.55393	3.96743	0.12606
C	-1.49738	-1.1186	-0.10803	H	1.14232	5.76923	0.10466
C	-2.18706	0.10336	0.02447	H	-0.81223	-3.81046	-0.22589
C	2.80619	4.40837	-0.12997	H	3.97542	-2.85333	-0.7212
C	3.20998	3.07523	-0.2566	H	3.22008	-5.23985	-0.71667
C	2.27832	2.02852	-0.25489	H	0.76306	-5.7146	-0.46339
C	0.89798	2.37799	-0.10688	H	-8.1515	-1.58223	1.56046
C	0.49806	3.71565	0.01828	H	-9.62979	-0.79658	1.08796
C	1.4517	4.7324	0.00631	H	-9.21851	-1.38312	-1.30696
C	0.24929	-3.62805	-0.34278	H	-7.7006	-2.18082	-0.8456
C	0.74215	-2.32264	-0.35896	H	-9.49945	-3.66276	-0.89989

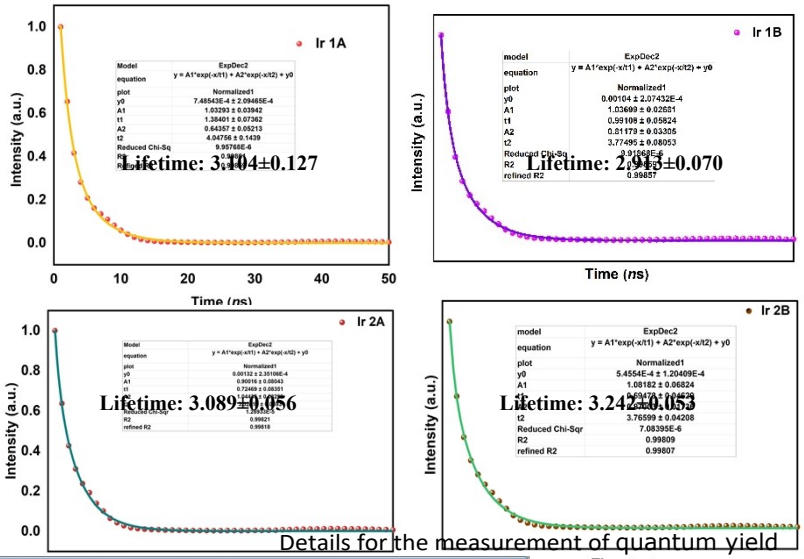
N	2.07741	-2.08615	-0.49599	H	-8.17537	2.25498	0.16279
C	2.92736	-3.11364	-0.61772	H	-8.49627	1.25367	-1.25586
C	2.49792	-4.43723	-0.61406	H	-10.6504	0.53392	-0.25553
C	1.1353	-4.6952	-0.47383	H	-10.2473	1.37887	1.25892
N	-7.89595	0.21513	0.50534	H	-11.5173	2.63549	-0.30185
C	-8.62192	-1.03137	0.74313	H	1.72511	-0.31241	4.72298
C	-8.70933	-1.92202	-0.49472				

Table S6 The xyz coordinates for complex Ir2B

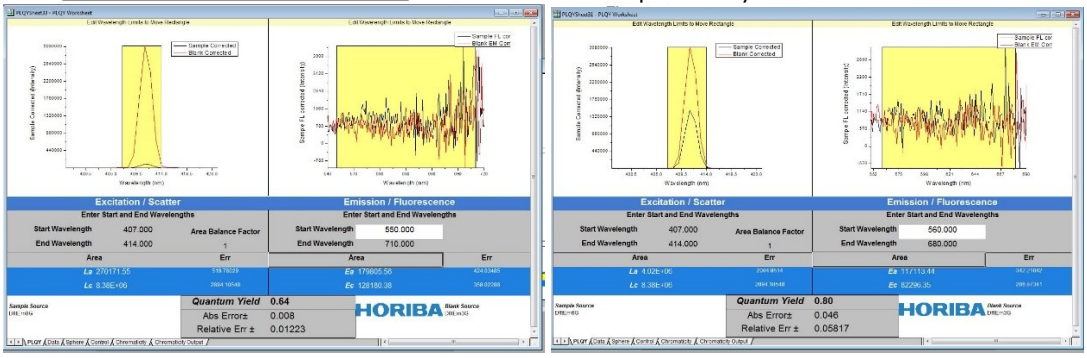
Complex	Ir1A	Ir1B	Ir2A	Ir2B
Lifetime(ns)	3.104±0.127	2.913±0.070	3.089±0.056	3.242±0.053
quantum yield	0.64	0.80	0.54	0.90

Table S7 The lifetime and quantum yield for the four complexes

Details for the fit of emission decay curve

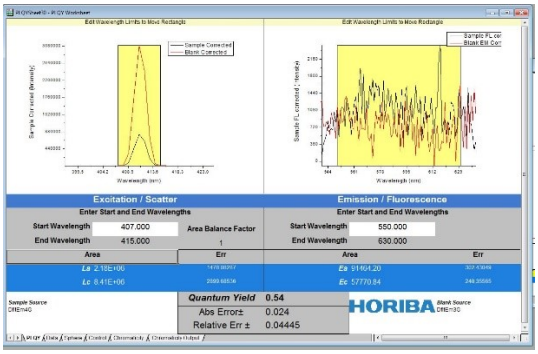


Details for the measurement of quantum yield

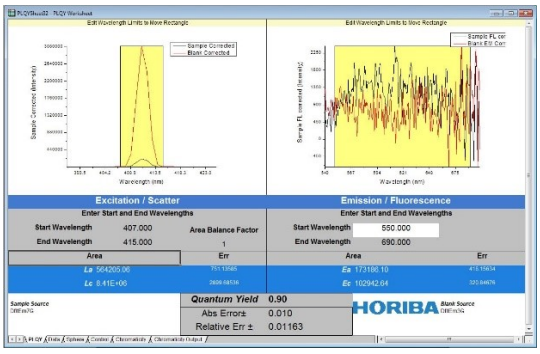


Ir1A

Ir1B



Ir2A



Ir2B