Electronic Supplementary Information

Alkyl chain modified cyclometalated iridium complexes as tunable anticancer and imaging agent

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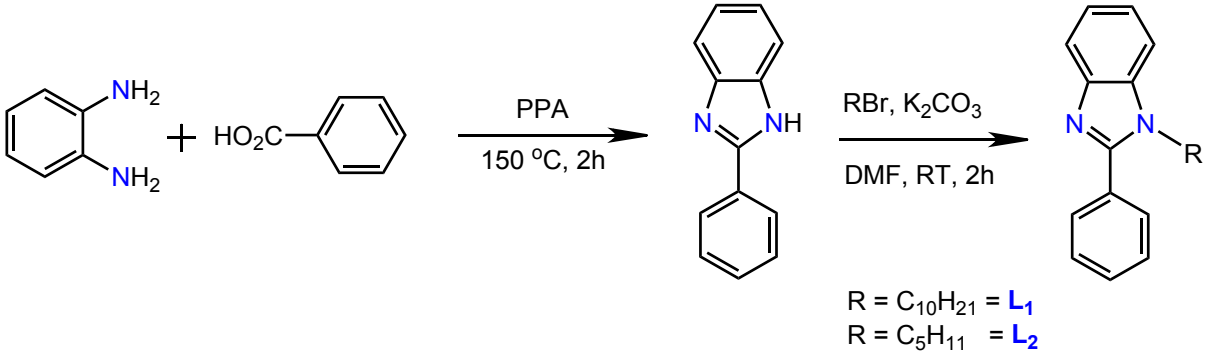
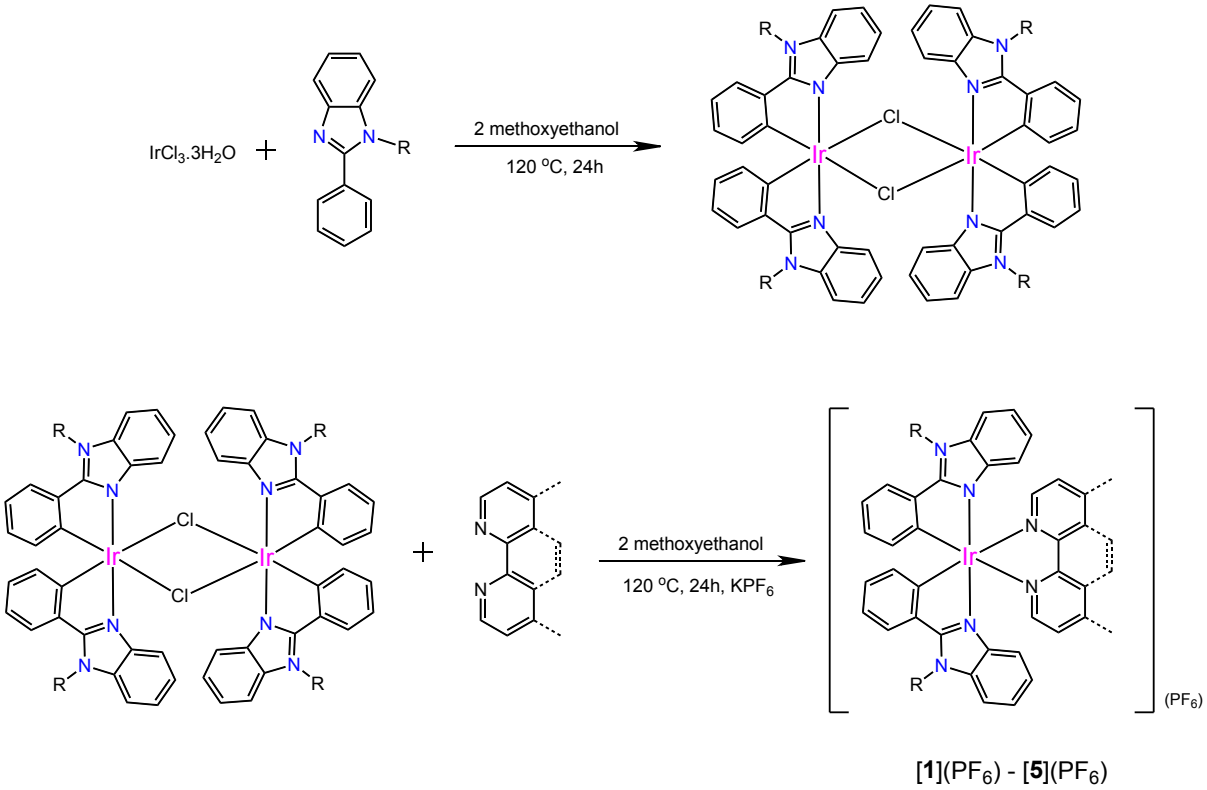
Scheme S1. Synthetic outline for the ligands $\mathbf{L_1}$ and $\mathbf{L_2}$.



Scheme S2. Synthetic scheme for the preparation of complexes [**1**]$^{+}$ - [**5**]$^{+}$.



[**1**](PF$_6$) - [**5**](PF$_6$)

Fig. S1 ^{1}H NMR spectra of the complexes [**1**](PF$_6$) –[**3**](PF$_6$) in CDCl$_3$.

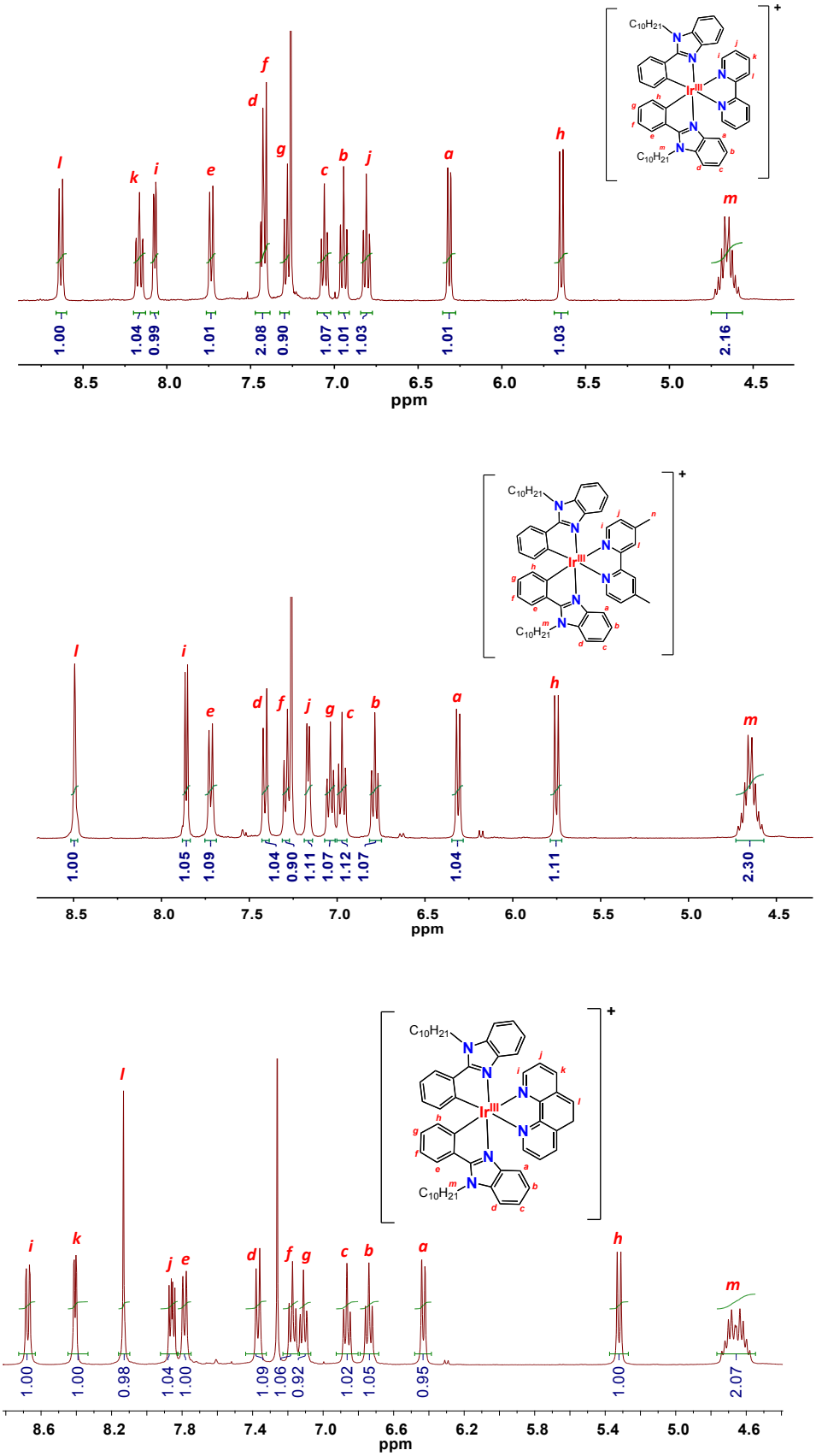


Fig. S2 ^{1}H NMR spectra of the complexes [**4**](PF$_6$) and [**5**](PF$_6$) in CDCl$_3$.

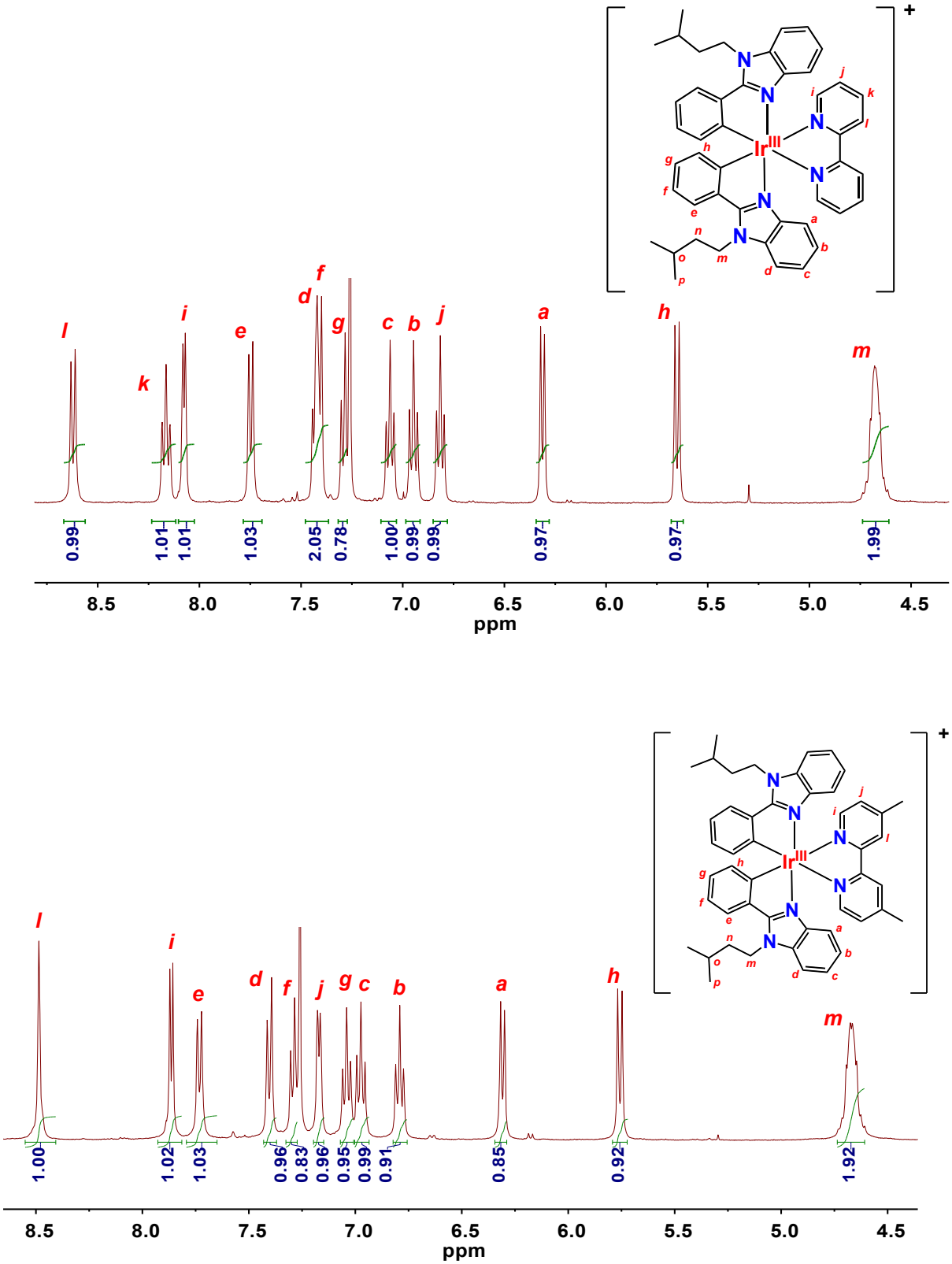


Fig. S3 ^{13}C NMR spectra of the complexes [**1**](PF_6)–[**3**](PF_6) in $CDCl_3$.

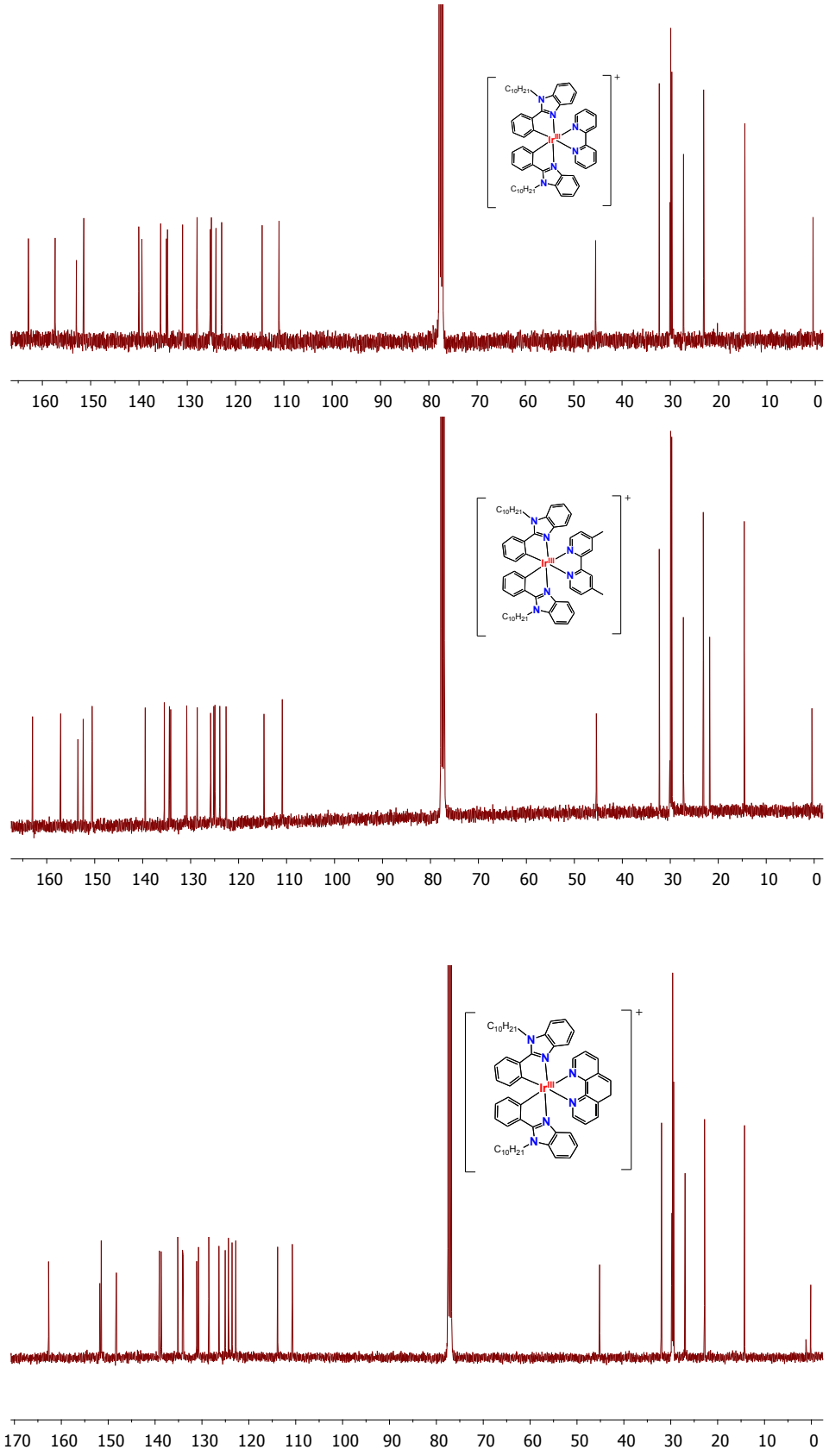


Fig. S4 ^{13}C NMR spectra of the complexes [**4**](PF_6) –[**5**](PF_6) in $CDCl_3$.

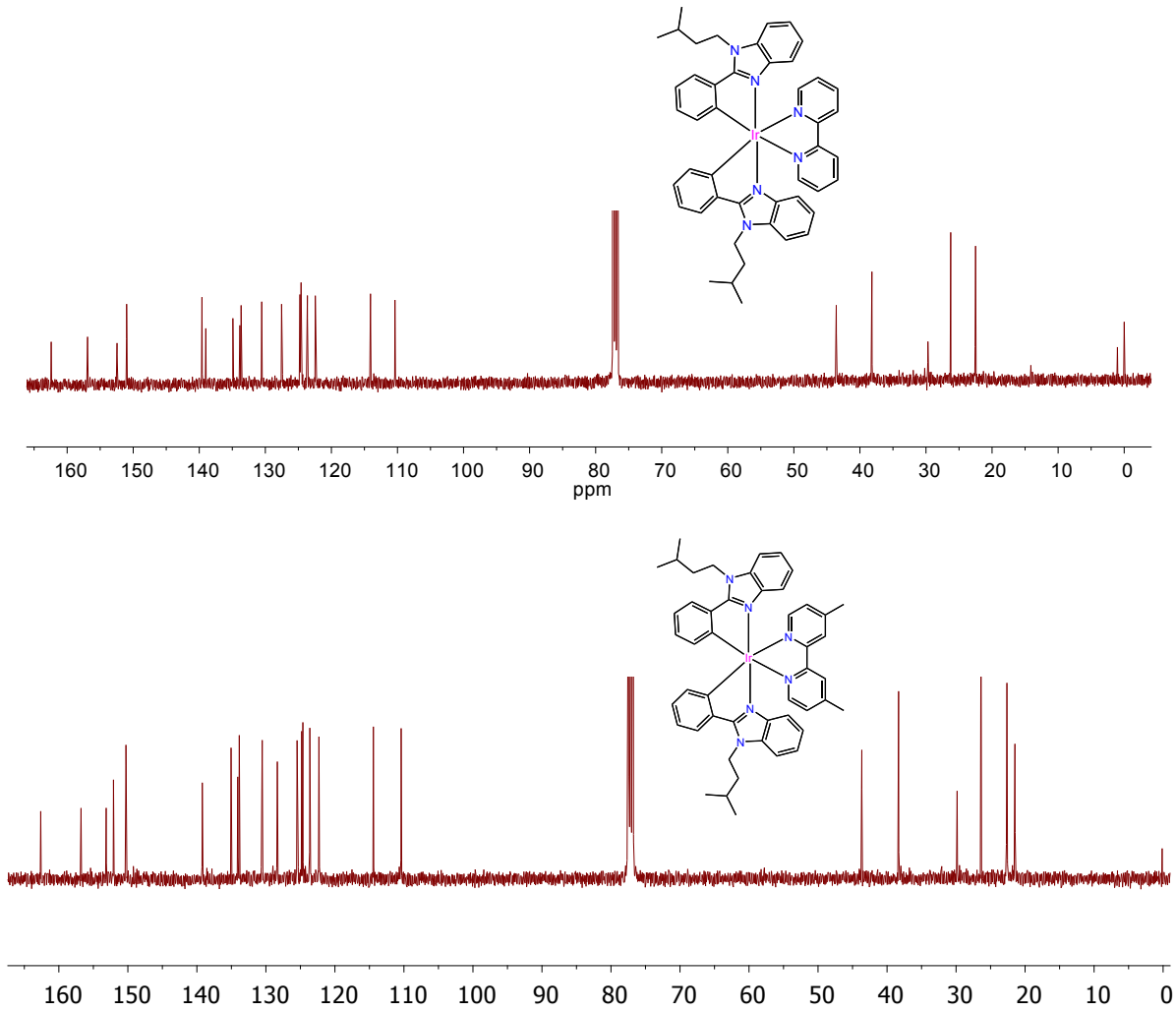


Fig. S5 Positive ion ESI mass spectra of the complexes $[\mathbf{1}]^+$ – $[\mathbf{5}]^+$ in CH_3OH.

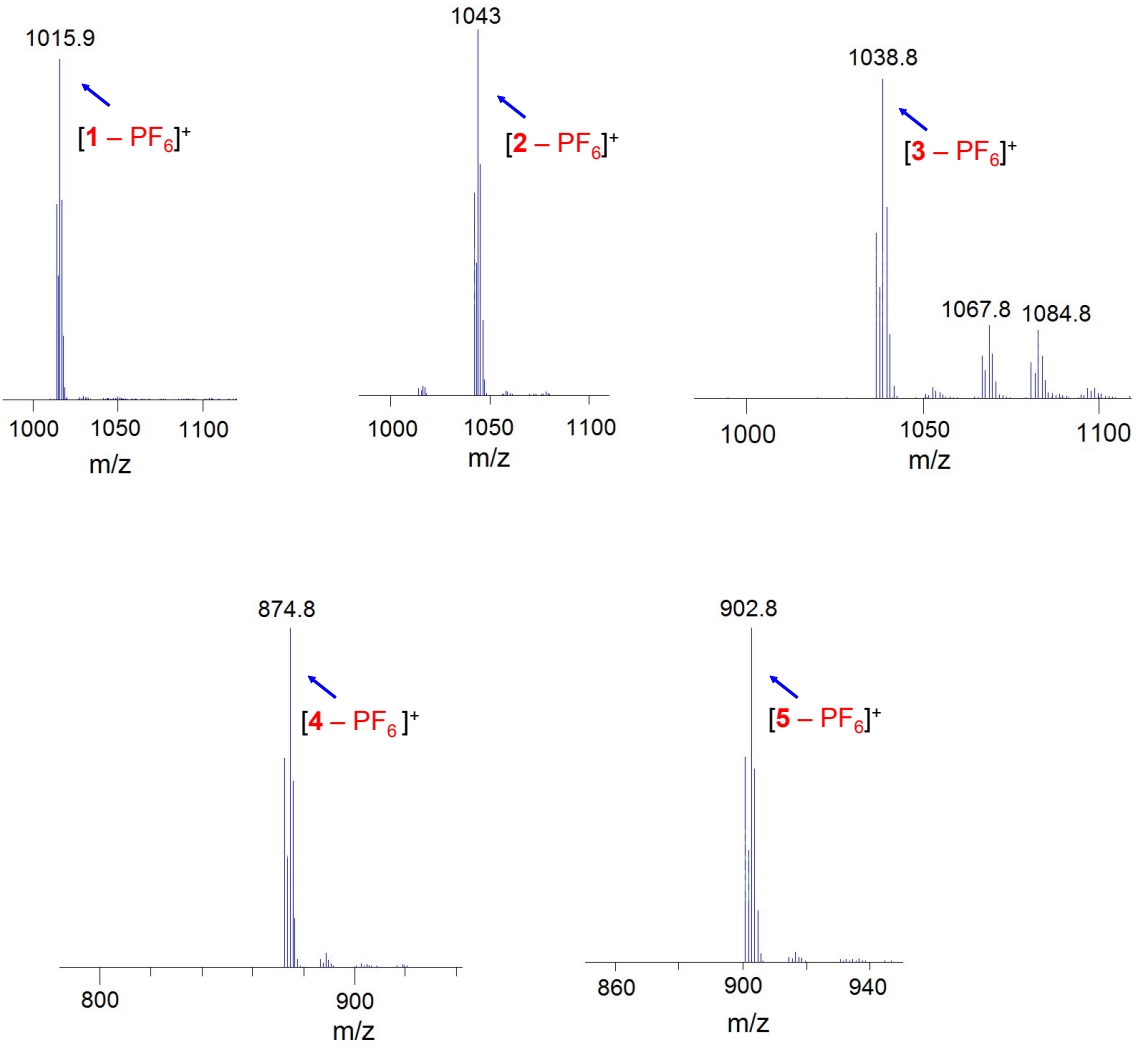


Table TS1. Important crystallographic bond parameters of [**2**](PF_6), [**3**](PF_6) and [**4**](PF_6).

Complex	[**2**](PF_6)	[**3**](PF_6). [$(CH_3)_2SO$]	[**4**](PF_6)
Empirical formula	C_{58} H_{70} F_6 Ir N_6 P	C_{60} H_{72} F_6 Ir N_6 O P S	$C_{46}H_{46}F_6IrN_6P$
Fw	1188.37	1262.46	1020.08
Radiation	MoK_α	MoK_α	MoK_α
Wavelength (Å)	0.71073	0.71073	0.71073
Temp(K)	150(2)	150(2)	298(2)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	C 2/c	P 21/n	I b c a
a/Å	17.724(2)	15.2226(10)	17.2258(6)
b/Å	23.066(2)	21.0932(14)	19.4733(8)
c/Å	15.945(3)	18.1419(11)	25.4230(10)
α (^{0})	90	90	90
β (^{0})	113.863(3)	104.978(2)	90
γ (^{0})	90	90	90
V/ Å^3	5961.3(15)	5627.3(6)	8528.0(6)
Crystal size (mm)	0.25 x 0.22 x 0.20	0.25 x 0.22 x 0.20	0.24 x 0.22 x 0.20
Z	4	4	8
μ / mm^{-1}	2.325	2.505	3.236
D_{calcd} / g cm^{-3}	1.324	1.490	1.589
F(000)	2424	2576	4080
θ range	2.7 – 28.3	2.243 – 28.344	2.53 – 26.27
Data/restraints/parameters	5232/7/294	13992/2/689	3653/24/274
R1,wR2 [I>2σ(I)]	0.0463	0.0408	0.0367
R1,wR2 (all data)	0.1433	0.1060	0.0767
Largest diff. peak hole (eÅ^{-3})	0.98, -0.72	1.93, -1.34	0.822, -0.688

Table TS2. Selected bond angle (°) and bond distances (Å) of [**2**](PF_6), [**3**](PF_6) and [**4**](PF_6).

[**2**](PF_6)			[**3**](PF_6)			[**4**](PF_6)		
Bond Length(Å)								
	Crystal	DFT		Crystal	DFT		Crystal	DFT
Ir1-N1	2.048(6)	2.079	Ir1-N1	2.043(3)	2.080	Ir1-N1	2.138(5)	2.208
Ir1-N3	2.140(5)	2.207	Ir1-N2	2.125(3)	2.215	Ir1-N2	2.048(5)	2.079
Ir1-C7	2.013(6)	2.030	Ir1-N3	2.132(3)	2.215	Ir1-C11	2.029(6)	2.030
			Ir1-N4	2.042(3)	2.080			
			Ir1-C13	2.011(4)	2.029			
			Ir1-C36	2.011(4)	2.029			
Bond angle(^{0})								
	Crystal	DFT		Crystal	DFT		Crystal	DFT
N3-Ir1-N3	75.9(3)	74.6	N3-Ir1-N2	78.0(14)	75.6	N1-Ir1-N1	76.5(3)	74.7
N1-Ir1-N3	90.8(2)	87.3	N4-Ir1-N1	171.9(13)	170.8	N2-Ir1-N1	89.8(19)	87.3
N1-Ir1-N1	168.6(3)	171.0	N2-Ir1-N1	88.1(12)	87.5	N2-Ir1-N1	99.1(2)	99.9
C7-Ir1-C7	87.5(4)	89.5	C13-Ir1-C36	93.3(15)	90.6	C11-Ir1-C11	86.6(3)	89.5

Table TS3. The B3LYP optimised coordinates for [**1**]$^{+}$.

Ir	0.000000	0.658190	0.000000
N	-0.981280	2.412620	-0.913860
N	3.580310	-0.510920	-1.779850
C	2.566810	-0.430000	-0.861610
C	3.315140	0.425640	-2.777000
C	2.307070	-1.146970	0.378120
C	-0.564320	3.630020	-0.480570
N	0.981280	2.412620	0.913870
C	0.564320	3.630020	0.480570
N	-3.580310	-0.510920	1.779850
C	-2.566810	-0.430010	0.861610
C	-3.315140	0.425630	2.777000
C	-2.307070	-1.146970	-0.378120
C	-1.055720	-0.783950	-0.963170
C	1.055720	-0.783950	0.963180
N	1.664440	0.494610	-1.236070
N	-1.664440	0.494610	1.236080
C	2.097460	1.049510	-2.428920
C	-2.097460	1.049510	2.428930
C	-1.550740	-2.346740	-2.776420
H	-1.250020	-2.815180	-3.710270
C	-2.778850	-2.677370	-2.198170
H	-3.438180	-3.395340	-2.676510
C	-3.159550	-2.075440	-1.003260
H	-4.124940	-2.326800	-0.581900
C	-0.708350	-1.413050	-2.167850
H	0.233160	-1.168390	-2.649260
C	-4.017310	0.766080	3.935390

H	-4.957830	0.292540	4.197420
C	-3.461300	1.750240	4.748280
H	-3.977980	2.042030	5.657340
C	-2.242880	2.372120	4.414880
H	-1.837860	3.131520	5.077060
C	-1.546320	2.033500	3.259030
H	-0.604890	2.507850	3.011630
C	-4.744020	-1.403740	1.795640
H	-4.995450	-1.569380	2.847560
H	-4.436430	-2.373450	1.398280
C	-5.956180	-0.841610	1.041990
H	-5.679310	-0.654020	-0.003810
H	-6.220330	0.132950	1.473300
C	-7.164120	-1.786710	1.101940
H	-7.424010	-1.981290	2.152720
H	-6.888980	-2.760970	0.671480
C	-2.003250	2.335550	-1.782930
H	-2.285450	1.333740	-2.086890
C	-2.657560	3.461690	-2.273050
H	-3.474850	3.347910	-2.977070
C	-2.239580	4.717880	-1.836640
H	-2.727160	5.620910	-2.190420
C	2.239570	4.717880	1.836640
H	2.727150	5.620910	2.190420
C	2.657550	3.461690	2.273050
H	3.474840	3.347920	2.977070
C	2.003250	2.335560	1.782940
H	2.285450	1.333750	2.086890
C	2.242880	2.372130	-4.414880
H	1.837860	3.131520	-5.077050

C	3.461300	1.750250	-4.748280
H	3.977980	2.042040	-5.657340
C	4.017300	0.766090	-3.935390
H	4.957830	0.292550	-4.197420
C	1.546320	2.033500	-3.259030
H	0.604890	2.507850	-3.011620
C	3.159560	-2.075430	1.003260
H	4.124940	-2.326790	0.581900
C	2.778860	-2.677370	2.198180
H	3.438180	-3.395330	2.676510
C	1.550750	-2.346740	2.776420
H	1.250020	-2.815180	3.710270
C	0.708350	-1.413050	2.167850
H	-0.233150	-1.168390	2.649260
C	4.744020	-1.403740	-1.795640
H	4.995450	-1.569380	-2.847560
H	4.436430	-2.373450	-1.398280
C	5.956180	-0.841600	-1.041990
H	5.679310	-0.654020	0.003810
H	6.220330	0.132960	-1.473300
C	7.164120	-1.786700	-1.101950
H	7.424010	-1.981280	-2.152720
H	6.888980	-2.760970	-0.671480
C	-8.395120	-1.237040	0.368130
C	-9.605920	-2.178180	0.423270
H	-8.133630	-1.040740	-0.682110
H	-8.669770	-0.264000	0.801030
C	-10.838690	-1.628290	-0.306680
H	-9.329940	-3.150660	-0.010450
H	-9.863850	-2.376220	1.474040

C	-12.050320	-2.568450	-0.253000
H	-11.113800	-0.655860	0.128040
H	-10.579690	-1.428980	-1.357220
H	-11.774970	-3.540450	-0.688540
H	-12.307620	-2.768830	0.797660
C	-13.284140	-2.018430	-0.980610
H	-13.027310	-1.817440	-2.031550
H	-13.560090	-1.046480	-0.544850
C	8.395120	-1.237040	-0.368130
C	9.605920	-2.178170	-0.423270
H	8.133630	-1.040750	0.682110
H	8.669770	-0.263990	-0.801020
C	10.838690	-1.628290	0.306680
H	9.329940	-3.150660	0.010440
H	9.863850	-2.376210	-1.474040
C	12.050320	-2.568450	0.252990
H	11.113800	-0.655860	-0.128030
H	10.579690	-1.428980	1.357220
H	11.774970	-3.540460	0.688530
H	12.307620	-2.768820	-0.797660
C	13.284140	-2.018430	0.980610
C	14.496300	-2.957920	0.927780
H	13.027310	-1.817450	2.031550
H	13.560090	-1.046480	0.544860
C	15.723970	-2.400590	1.655910
H	14.220830	-3.928660	1.364010
H	14.752750	-3.158610	-0.122180
H	16.570720	-3.093840	1.599800
H	16.045080	-1.446820	1.219260
H	15.509130	-2.222640	2.716900

C	-14.496300	-2.957920	-0.927790
C	-15.723970	-2.400580	-1.655920
H	-14.752740	-3.158610	0.122180
H	-14.220830	-3.928660	-1.364030
H	-16.570720	-3.093830	-1.599800
H	-16.045080	-1.446820	-1.219260
H	-15.509130	-2.222630	-2.716900
C	1.185330	4.800700	0.931300
H	0.859450	5.770000	0.574230
C	-1.185340	4.800700	-0.931300
H	-0.859450	5.770000	-0.574230

Table TS4. The B3LYP optimised coordinates for [**2**]$^{+}$.

Ir	0.000010	0.448590	0.000010
N	-0.960800	2.166990	-0.923860
N	3.594960	-0.733430	-1.759350
C	2.574600	-0.655790	-0.833550
C	3.331900	0.209620	-2.764450
C	2.307150	-1.369910	0.401480
C	-0.551350	3.398070	-0.490010
N	0.960810	2.166840	0.924150
C	0.551390	3.397990	0.490480
N	-3.594950	-0.733710	1.759170
C	-2.574590	-0.655900	0.833390
C	-3.331880	0.209160	2.764450
C	-2.307170	-1.369790	-0.401790
C	-1.049660	-1.001250	-0.982550
C	1.049660	-1.001430	0.982320
N	1.668720	0.278760	-1.219650
N	-1.668700	0.278570	1.219650
C	2.109880	0.839220	-2.420790
C	-2.109850	0.838800	2.420900
C	-1.525760	-2.576620	-2.796830
H	-1.217740	-3.048270	-3.725270
C	-2.759240	-2.911430	-2.222920
H	-3.409650	-3.634320	-2.703240
C	-3.152770	-2.306850	-1.029830
H	-4.118510	-2.562620	-0.613440
C	-0.689830	-1.633700	-2.186270
H	0.253700	-1.386120	-2.659290
C	-4.038830	0.545990	3.922330

H	-4.976730	0.068790	4.181960
C	-3.488570	1.533670	4.740970
H	-4.007650	1.822050	5.648200
C	-2.269000	2.162190	4.410640
H	-1.869900	2.921830	5.074030
C	-1.565660	1.825730	3.253770
H	-0.627470	2.304450	3.010970
C	-4.767810	-1.624020	1.767250
H	-5.027250	-1.795000	2.816940
H	-4.468960	-2.592960	1.360930
C	-5.976850	-1.045730	1.012590
H	-5.700030	-0.860060	-0.034150
H	-6.232380	-0.069840	1.447460
C	-7.199970	-1.979350	1.072050
H	-7.446130	-2.194840	2.122950
H	-6.949040	-2.946220	0.609820
C	-1.974380	2.087170	-1.820970
H	-2.256020	1.089090	-2.127720
C	-2.609820	3.216630	-2.324670
H	-3.413580	3.099840	-3.042890
C	-2.209850	4.496370	-1.898860
C	2.609760	3.216250	2.325220
H	3.413420	3.099340	3.043530
C	1.974330	2.086870	1.821320
H	2.255910	1.088750	2.127980
C	2.269030	2.162950	-4.410300
H	1.869940	2.922710	-5.073560
C	3.488600	1.534480	-4.740740
H	4.007690	1.823010	-5.647920
C	4.038860	0.546660	-3.922270

H	4.976750	0.069500	-4.181990
C	1.565700	1.826290	-3.253490
H	0.627500	2.304970	-3.010620
C	3.152710	-2.307140	1.029310
H	4.118420	-2.562890	0.612840
C	2.759170	-2.911940	2.222290
H	3.409550	-3.634960	2.702450
C	1.525720	-2.577170	2.796280
H	1.217690	-3.048990	3.724640
C	0.689820	-1.634090	2.185930
H	-0.253690	-1.386570	2.659000
C	4.767830	-1.623730	-1.767540
H	5.027400	-1.794400	-2.817240
H	4.468930	-2.592800	-1.361540
C	5.976780	-1.045650	-1.012590
H	5.699870	-0.860270	0.034180
H	6.232350	-0.069640	-1.447170
C	7.199910	-1.979250	-1.072190
H	7.446120	-2.194510	-2.123120
H	6.948960	-2.946220	-0.610180
C	-8.439170	-1.388110	0.374720
C	-9.667310	-2.314930	0.424920
H	-8.194520	-1.165210	-0.675000
H	-8.691850	-0.425290	0.844150
C	-10.913790	-1.707470	-0.244180
H	-9.422370	-3.271140	-0.061860
H	-9.899710	-2.553690	1.473980
C	-12.144230	-2.631640	-0.199570
H	-11.159340	-0.753400	0.247030
H	-10.681410	-1.463280	-1.292210

H	-11.903620	-3.581790	-0.700550
H	-12.370390	-2.884680	0.847650
C	-13.394270	-2.014970	-0.852990
H	-13.169200	-1.758910	-1.899930
H	-13.636480	-1.066090	-0.349860
C	8.439080	-1.388150	-0.374690
C	9.667230	-2.314950	-0.425040
H	8.194390	-1.165460	0.675060
H	8.691770	-0.425240	-0.843920
C	10.913710	-1.707580	0.244160
H	9.422300	-3.271250	0.061590
H	9.899630	-2.553540	-1.474130
C	12.144160	-2.631740	0.199400
H	11.159240	-0.753440	-0.246900
H	10.681330	-1.463560	1.292230
H	11.903560	-3.581960	0.700260
H	12.370290	-2.884630	-0.847860
C	13.394200	-2.015130	0.852870
C	14.626330	-2.937800	0.811470
H	13.169150	-1.759220	1.899860
H	13.636390	-1.066190	0.349860
C	15.870930	-2.309490	1.458480
H	14.386340	-3.883970	1.318490
H	14.847800	-3.197440	-0.234240
H	16.730510	-2.987700	1.412950
H	16.152010	-1.378640	0.950070
H	15.689160	-2.070250	2.513850
C	-14.626390	-2.937660	-0.811740
C	-15.870970	-2.309280	-1.458700
H	-14.847880	-3.197430	0.233940

H	-14.386370	-3.883750	-1.318870
H	-16.730550	-2.987510	-1.413280
H	-16.152090	-1.378500	-0.950180
H	-15.689180	-2.069910	-2.514030
C	1.165350	4.563220	0.968030
H	0.841580	5.532850	0.611410
C	-1.165320	4.563380	-0.967360
H	-0.841580	5.532950	-0.610550
C	2.209880	4.496050	1.899520
C	2.882890	5.739560	2.422290
H	3.954820	5.732220	2.191960
H	2.451270	6.645240	1.988350
H	2.788660	5.808990	3.512510
C	-2.882450	5.739990	-2.421880
H	-2.781660	5.812880	-3.511330
H	-3.955720	5.729720	-2.198170
H	-2.455310	6.645290	-1.982730

Table TS5. The B3LYP optimised coordinates for [**3**]$^{+}$.

Ir	0.000000	0.465380	0.000000
N	0.966830	2.214860	0.954960
N	-3.618370	-0.714010	1.694130
C	-2.588900	-0.619980	0.795330
C	-3.372280	0.209540	2.707640
C	-2.308380	-1.320830	-0.448810
C	0.519080	3.419690	0.498010
N	-0.966840	2.214860	-0.954930
C	-0.519080	3.419690	-0.497970
C	-1.034410	4.650380	-0.975380
N	3.618380	-0.713970	-1.694140
C	2.588910	-0.619960	-0.795330
C	3.372280	0.209590	-2.707640
C	2.308390	-1.320820	0.448800
C	1.040540	-0.962120	0.999320
C	-1.040540	-0.962110	-0.999330
N	-1.692870	0.298800	1.198480
N	1.692870	0.298830	-1.198480
C	-2.149320	0.839020	2.389650
C	2.149320	0.839060	-2.389640
C	1.505300	-2.498530	2.842460
H	1.185830	-2.959860	3.773640
C	2.752260	-2.820600	2.300740
H	3.407900	-3.523620	2.805660
C	3.156410	-2.229530	1.108070
H	4.136490	-2.471980	0.716090
C	0.668730	-1.581140	2.201940
H	-0.286800	-1.340290	2.656590

C	4.096420	0.533780	-3.857080
H	5.040370	0.054680	-4.095910
C	3.558120	1.509070	-4.692200
H	4.092080	1.788590	-5.595110
C	2.335860	2.138110	-4.388170
H	1.945390	2.891380	-5.065920
C	1.617200	1.814690	-3.241570
H	0.673820	2.295500	-3.016860
C	4.782590	-1.606190	-1.680370
H	5.034590	-1.806040	-2.726460
H	4.476990	-2.562430	-1.250990
C	5.993260	-1.014840	-0.946830
H	5.719840	-0.803650	0.095470
H	6.244340	-0.048680	-1.404040
C	7.212170	-1.946610	-0.990770
H	7.453180	-2.183420	-2.037430
H	6.960310	-2.904420	-0.512250
C	1.941540	2.194480	1.863400
H	2.264750	1.212820	2.193050
C	2.516910	3.367610	2.382280
H	3.305770	3.290660	3.122890
C	2.061560	4.596070	1.943850
H	2.482860	5.518970	2.332530
C	1.034410	4.650370	0.975430
C	0.497600	5.880540	0.465680
H	0.900870	6.816290	0.841790
C	-0.497610	5.880550	-0.465620
H	-0.900880	6.816300	-0.841730
C	-2.061570	4.596080	-1.943800
H	-2.482870	5.518990	-2.332480

C	-2.516920	3.367630	-2.382240
H	-3.305770	3.290690	-3.122850
C	-1.941550	2.194500	-1.863370
H	-2.264760	1.212840	-2.193040
C	-2.335870	2.138050	4.388190
H	-1.945400	2.891310	5.065950
C	-3.558130	1.509000	4.692210
H	-4.092080	1.788500	5.595130
C	-4.096420	0.533710	3.857080
H	-5.040370	0.054610	4.095900
C	-1.617210	1.814640	3.241580
H	-0.673830	2.295450	3.016880
C	-3.156400	-2.229540	-1.108090
H	-4.136470	-2.472000	-0.716120
C	-2.752240	-2.820590	-2.300780
H	-3.407880	-3.523600	-2.805700
C	-1.505290	-2.498500	-2.842490
H	-1.185820	-2.959810	-3.773680
C	-0.668720	-1.581120	-2.201960
H	0.286800	-1.340250	-2.656610
C	-4.782590	-1.606230	1.680340
H	-5.034590	-1.806090	2.726430
H	-4.476990	-2.562470	1.250960
C	-5.993250	-1.014870	0.946810
H	-5.719840	-0.803680	-0.095490
H	-6.244330	-0.048720	1.404030
C	-7.212160	-1.946640	0.990740
H	-7.453180	-2.183450	2.037410
H	-6.960320	-2.904440	0.512210
C	8.450250	-1.346320	-0.310270

C	9.675240	-2.269720	-0.348980
H	8.208860	-1.104260	0.735200
H	8.699380	-0.390900	-0.794710
C	10.919500	-1.656170	0.307130
H	9.430890	-3.219440	0.149120
H	9.904480	-2.524510	-1.394180
C	12.147140	-2.576240	0.271960
H	11.162270	-0.707730	-0.194570
H	10.689310	-1.397150	1.351320
H	11.907550	-3.521350	0.781380
H	12.371260	-2.842280	-0.771710
C	13.394300	-1.955190	0.914800
H	13.170510	-1.686530	1.958140
H	13.634310	-1.010940	0.403500
C	-8.450240	-1.346330	0.310250
C	-9.675240	-2.269730	0.348950
H	-8.208850	-1.104280	-0.735220
H	-8.699370	-0.390920	0.794690
C	-10.919500	-1.656170	-0.307150
H	-9.430900	-3.219450	-0.149140
H	-9.904480	-2.524520	1.394160
C	-12.147140	-2.576230	-0.271980
H	-11.162260	-0.707730	0.194560
H	-10.689310	-1.397150	-1.351340
H	-11.907560	-3.521340	-0.781400
H	-12.371260	-2.842280	0.771690
C	-13.394310	-1.955170	-0.914820
C	-14.623570	-2.873140	-0.882360
H	-13.170520	-1.686510	-1.958150
H	-13.634310	-1.010920	-0.403510

C	-15.865300	-2.240730	-1.519800
H	-14.386030	-3.814670	-1.397600
H	-14.844950	-3.144450	0.159650
H	-16.724710	-2.919360	-1.479750
H	-16.147680	-1.314900	-1.003550
H	-15.687140	-1.990760	-2.573030
C	14.623560	-2.873170	0.882350
C	15.865300	-2.240770	1.519790
H	14.844950	-3.144480	-0.159670
H	14.386010	-3.814690	1.397590
H	16.724700	-2.919400	1.479740
H	16.147690	-1.314940	1.003550
H	15.687140	-1.990790	2.573020

Table TS6. The B3LYP optimised coordinates for [**4**]$^{+}$.

Ir	0.000000	0.253660	0.000000
N	-0.713810	2.008050	1.134890
N	1.925290	0.089220	0.768880
N	3.915410	-0.918630	0.806190
C	2.648780	0.643440	1.811830
C	0.773890	-1.188090	-1.201870
C	3.914160	0.018060	1.837880
C	2.701360	-0.836260	0.176480
C	-0.421980	3.225550	0.609370
C	2.133170	-1.551600	-0.956670
N	0.713810	2.008060	-1.134880
C	0.421980	3.225560	-0.609350
N	-1.925290	0.089220	-0.768880
N	-3.915410	-0.918630	-0.806190
C	-2.648780	0.643450	-1.811830
C	-0.773890	-1.188100	1.201860
C	-3.914160	0.018070	-1.837880
C	-2.701360	-0.836260	-0.176490
C	-2.133170	-1.551610	0.956660
C	7.016180	-3.461650	-1.267720
H	6.542510	-3.366700	-2.253890
H	7.941600	-4.032060	-1.402510
H	6.356630	-4.063450	-0.631700
C	7.314910	-2.077940	-0.667920
H	7.766540	-2.228180	0.324990
C	8.331500	-1.319900	-1.535080
H	9.258180	-1.893790	-1.644130
H	7.932340	-1.139760	-2.541530
H	8.588050	-0.348260	-1.097050

C	6.042670	-1.226290	-0.478990
H	6.326920	-0.224380	-0.131550
H	5.543720	-1.088450	-1.448340
C	5.045100	-1.813360	0.529910
H	4.643080	-2.774200	0.207260
H	5.540790	-1.992700	1.489210
C	-5.045100	-1.813350	-0.529920
H	-4.643080	-2.774200	-0.207280
H	-5.540800	-1.992680	-1.489220
C	-6.042660	-1.226300	0.479000
H	-6.326910	-0.224380	0.131570
H	-5.543710	-1.088470	1.448340
C	-7.314900	-2.077940	0.667930
H	-7.766540	-2.228170	-0.324980
C	-8.331480	-1.319910	1.535100
H	-9.258170	-1.893800	1.644150
H	-7.932320	-1.139780	2.541550
H	-8.588040	-0.348260	1.097080
C	-7.016170	-3.461660	1.267710
H	-6.542500	-3.366730	2.253880
H	-7.941600	-4.032070	1.402500
H	-6.356630	-4.063450	0.631680
C	-2.797650	-2.478490	1.780520
H	-3.839030	-2.729060	1.621730
C	-2.123840	-3.079050	2.839040
H	-2.639050	-3.795910	3.471250
C	-0.788520	-2.748610	3.083270
H	-0.258900	-3.216160	3.909620
C	-0.129820	-1.815930	2.278280
H	0.903550	-1.571050	2.502420

C	-4.888700	0.356310	-2.779580
H	-5.863980	-0.119200	-2.793560
C	-4.559700	1.340640	-3.707710
H	-5.291270	1.630880	-4.455410
C	-3.297580	1.964460	-3.695740
H	-3.075720	2.723970	-4.439440
C	-2.328950	1.627600	-2.755400
H	-1.356430	2.103700	-2.756760
C	-1.477890	1.930800	2.237560
H	-1.672270	0.928870	2.603590
C	-1.984150	3.056830	2.879620
H	-2.592880	2.942940	3.770140
C	-1.692390	4.313120	2.350640
H	-2.072580	5.216070	2.818060
C	-0.906200	4.396160	1.204820
H	-0.682850	5.365530	0.776240
C	0.906200	4.396160	-1.204790
H	0.682850	5.365540	-0.776210
C	1.692390	4.313140	-2.350610
H	2.072590	5.216090	-2.818030
C	1.984150	3.056850	-2.879610
H	2.592880	2.942970	-3.770120
C	1.477880	1.930820	-2.237550
H	1.672260	0.928890	-2.603590
C	2.328940	1.627580	2.755410
H	1.356430	2.103690	2.756770
C	3.297580	1.964430	3.695750
H	3.075710	2.723940	4.439460
C	4.559700	1.340610	3.707720
H	5.291260	1.630850	4.455420

C	4.888690	0.356290	2.779580
H	5.863970	-0.119220	2.793560
C	2.797660	-2.478470	-1.780540
H	3.839030	-2.729040	-1.621760
C	2.123840	-3.079030	-2.839070
H	2.639060	-3.795880	-3.471290
C	0.788530	-2.748580	-3.083290
H	0.258910	-3.216130	-3.909650
C	0.129830	-1.815920	-2.278300
H	-0.903550	-1.571030	-2.502440

Table TS7. The B3LYP optimised coordinates for [**5**]$^{+}$.

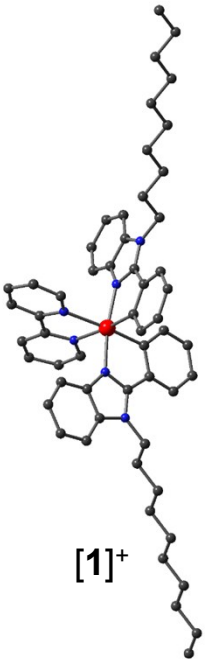
Ir	0.000000	0.048660	0.000000
N	-0.741170	1.804280	1.113670
N	1.903660	-0.114630	0.820870
N	3.893690	-1.119760	0.911010
C	2.598450	0.440230	1.882630
C	0.807250	-1.391920	-1.180670
C	3.863610	-0.183490	1.942490
C	2.696350	-1.038670	0.249020
C	-0.437490	3.021680	0.598910
C	2.159990	-1.754210	-0.899250
N	0.741170	1.804280	-1.113670
C	0.437490	3.021680	-0.598910
N	-1.903660	-0.114630	-0.820870
N	-3.893690	-1.119760	-0.911010
C	-2.598450	0.440230	-1.882630
C	-0.807250	-1.391920	1.180670
C	-3.863610	-0.183490	-1.942490
C	-2.696350	-1.038670	-0.249030
C	-2.159990	-1.754210	0.899250
C	7.051990	-3.662140	-1.075520
H	6.605550	-3.568390	-2.074410
H	7.981250	-4.231920	-1.184200
H	6.375500	-4.263820	-0.457480
C	7.332810	-2.277670	-0.468870
H	7.757130	-2.426730	0.536210
C	8.372300	-1.519570	-1.308390
H	9.302150	-2.092740	-1.391490
H	8.000740	-1.340630	-2.325580
H	8.615870	-0.547310	-0.864320

C	6.055140	-1.427040	-0.315710
H	6.328890	-0.424640	0.038760
H	5.582950	-1.290270	-1.298500
C	5.030490	-2.014040	0.665780
H	4.637760	-2.975040	0.332260
H	5.500160	-2.193270	1.638150
C	-5.030490	-2.014040	-0.665780
H	-4.637750	-2.975040	-0.332260
H	-5.500160	-2.193270	-1.638160
C	-6.055140	-1.427040	0.315710
H	-6.328890	-0.424640	-0.038760
H	-5.582950	-1.290280	1.298500
C	-7.332810	-2.277670	0.468870
H	-7.757130	-2.426730	-0.536210
C	-8.372300	-1.519570	1.308390
H	-9.302150	-2.092740	1.391490
H	-8.000740	-1.340630	2.325580
H	-8.615870	-0.547310	0.864320
C	-7.051990	-3.662140	1.075510
H	-6.605550	-3.568390	2.074410
H	-7.981250	-4.231920	1.184200
H	-6.375500	-4.263820	0.457480
C	-2.847860	-2.679990	1.705060
H	-3.884930	-2.929200	1.518230
C	-2.203860	-3.281160	2.781550
H	-2.736910	-3.997180	3.399820
C	-0.875060	-2.952330	3.061570
H	-0.368590	-3.420420	3.902070
C	-0.193740	-2.020780	2.274550
H	0.833510	-1.777050	2.526650

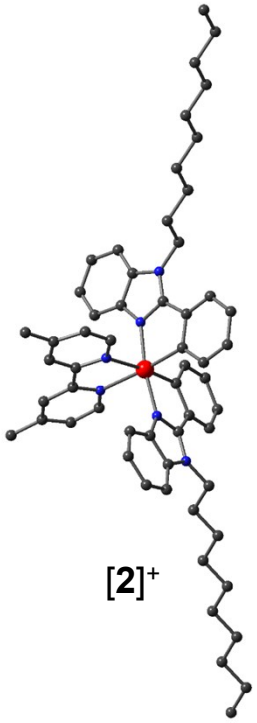
C	-4.812030	0.155630	-2.910130
H	-5.787190	-0.318700	-2.950160
C	-4.456890	1.139180	-3.829520
H	-5.167700	1.429950	-4.596830
C	-3.194740	1.761290	-3.783710
H	-2.951990	2.520210	-4.521550
C	-2.252050	1.423660	-2.817540
H	-1.279180	1.898360	-2.792270
C	-1.533660	1.737550	2.197890
H	-1.742120	0.738870	2.565300
C	-2.050610	2.864710	2.821570
H	-2.681500	2.747680	3.697540
C	-1.755440	4.136730	2.312190
C	-0.935260	4.191760	1.182600
H	-0.695320	5.157990	0.754270
C	0.935260	4.191760	-1.182590
H	0.695330	5.157990	-0.754260
C	1.755450	4.136730	-2.312180
C	2.050610	2.864710	-2.821570
H	2.681510	2.747680	-3.697530
C	1.533670	1.737550	-2.197890
H	1.742120	0.738870	-2.565300
C	2.252050	1.423660	2.817540
H	1.279180	1.898350	2.792270
C	3.194740	1.761290	3.783710
H	2.951990	2.520200	4.521550
C	4.456890	1.139170	3.829520
H	5.167700	1.429950	4.596830
C	4.812030	0.155630	2.910130
H	5.787190	-0.318700	2.950160

C	2.847860	-2.679990	-1.705060
H	3.884930	-2.929200	-1.518230
C	2.203860	-3.281160	-2.781550
H	2.736910	-3.997180	-3.399820
C	0.875060	-2.952320	-3.061570
H	0.368590	-3.420410	-3.902070
C	0.193740	-2.020780	-2.274550
H	-0.833510	-1.777050	-2.526650
C	2.305600	5.384410	-2.952400
H	1.947630	6.287980	-2.451580
H	3.401500	5.388590	-2.917790
H	2.016840	5.442170	-4.008230
C	-2.305610	5.384410	2.952400
H	-1.947470	6.287980	2.451710
H	-3.401500	5.388690	2.917570
H	-2.017050	5.442070	4.008290

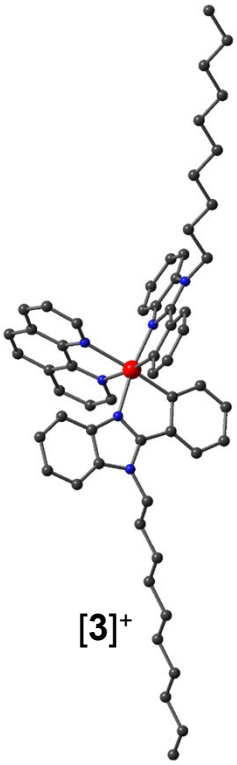
Fig. S6 Optimised structures of complexes [**1**]$^{+}$-[**5**]$^{+}$.



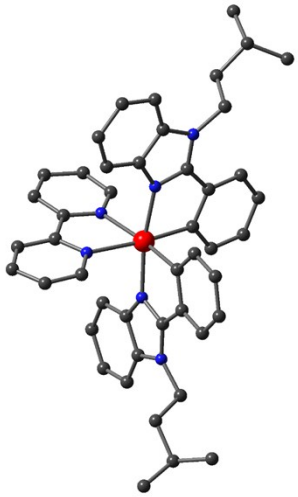
$[\mathbf{1}]^+$



$[\mathbf{2}]^+$



$[\mathbf{3}]^+$



$[\mathbf{4}]^+$

$[\mathbf{5}]^+$

Table TS8. Calculated energies of Kohn-Sham molecular orbitals (MO) at the B3LYP Level and the contributions of various molecular groups to the MOs of [**1**]$^+$, [**2**]$^+$ and [**3**]$^+$.

	[**1**]$^+$				[**2**]$^+$				[**3**]$^+$			
MO's	**E(eV)**	**Ir**	**bpy**	**L_1**	**E(eV)**	**Ir**	**mebpy**	**L_1**	**E(eV)**	**Ir**	**phen**	**L_1**
L+10	-1.71	1	0	99	-1.64	3	1	96	-1.69	1	0	99
L+9	-1.82	9	2	88	-1.69	4	1	95	-1.8	10	2	88
L+8	-1.97	6	1	93	-1.87	8	4	88	-1.95	7	1	92
L+7	-2.04	4	1	94	-1.9	3	1	96	-2.02	4	2	94
L+6	-2.07	14	4	82	-1.98	5	0	95	-2.04	13	3	84
L+5	-2.31	1	98	1	-2.24	0	98	2	-2.53	1	99	0
L+4	-3.38	2	12	86	-3.3	1	33	66	-3.25	2	97	1
L+3	-3.52	2	1	97	-3.45	2	67	31	-3.37	2	1	96
L+2	-3.62	1	88	11	-3.46	2	1	97	-3.49	2	1	98
L+1	-3.8	2	97	0	-3.58	3	96	0	-4.5	0	99	0
LUMO	**-4.69**	**3**	**97**	**0**	**-4.57**	**3**	**96**	**0**	**-4.62**	**3**	**96**	**0**
HOMO	**-7.51**	**34**	**2**	**64**	**-7.39**	**38**	**2**	**60**	**-7.48**	**34**	**2**	**66**
H-1	-7.83	15	2	82	-7.74	25	3	72	-7.81	16	2	82
H-2	-8.02	35	2	62	-7.87	44	3	74	-8	35	2	62
H-3	-8.26	22	3	76	-8.16	21	4	75	-8.23	22	3	76
H-4	-8.32	13	1	86	-8.28	12	1	87	-8.3	13	1	86
H-5	-8.55	1	1	98	-8.49	1	1	98	-8.54	1	1	98
H-6	-8.89	37	4	60	-8.79	27	5	68	-8.86	30	21	49
H-7	-8.95	38	7	56	-8.83	29	8	64	-8.86	37	5	58
H-8	-9.29	3	1	76	-9.28	4	1	95	-9.27	3	0	97
H-9	-9.38	0	0	100	-9.39	0	0	100	-9.37	0	6	94
H-10	-9.39	0	0	100	-9.39	0	0	100	-9.38	0	0	100

Table TS9. Calculated energies of Kohn-Sham molecular orbitals (MO) at the B3LYP Level and the contributions of various molecular groups to the MOs of [**4**]$^+$ and [**5**]$^+$.

	[**4**]$^+$				[**5**]$^+$			
MO's	**E(eV)**	**Ir**	**bpy**	**L_2**	**E(eV)**	**Ir**	**mebpy**	**L_2**
L+10	-1.73	1	0	99	-1.66	1	0	99
L+9	-1.83	9	2	87	-1.75	9	2	88
L+8	-1.99	6	1	93	-1.91	5	1	94
L+7	-2.05	4	2	93	-1.97	6	3	91
L+6	-2.08	14	4	82	-2	11	2	87
L+5	-2.32	1	98	1	-2.24	0	98	2
L+4	-3.39	2	12	86	-3.27	1	44	56
L+3	-3.53	2	1	97	-3.42	2	57	42
L+2	-3.63	1	88	10	-3.45	2	1	97
L+1	-3.81	2	97	0	-3.57	3	96	0
LUMO	**-4.70**	**3**	**97**	**0**	**-4.54**	**3**	**97**	**0**
HOMO	**-7.52**	**34**	**2**	**64**	**-7.42**	**34**	**2**	**64**
H-1	-7.85	15	2	82	-7.76	18	2	80
H-2	-8.03	35	2	62	-7.94	37	2	60
H-3	-8.27	22	3	76	-8.18	23	3	74
H-4	-8.33	14	1	86	-8.25	14	1	86
H-5	-8.56	1	1	98	-8.48	1	1	98
H-6	-8.90	36	4	60	-8.8	33	6	61
H-7	-8.96	38	7	56	-8.85	34	8	48
H-8	-9.31	3	1	97	-9.23	3	2	95
H-9	-9.44	0	0	100	-9.37	0	0	100
H-10	-9.62	1	98	1	-9.46	1	96	2

Fig. S7 Pictorial representation of frontiers molecular orbitals of [**2**]$^{+}$.

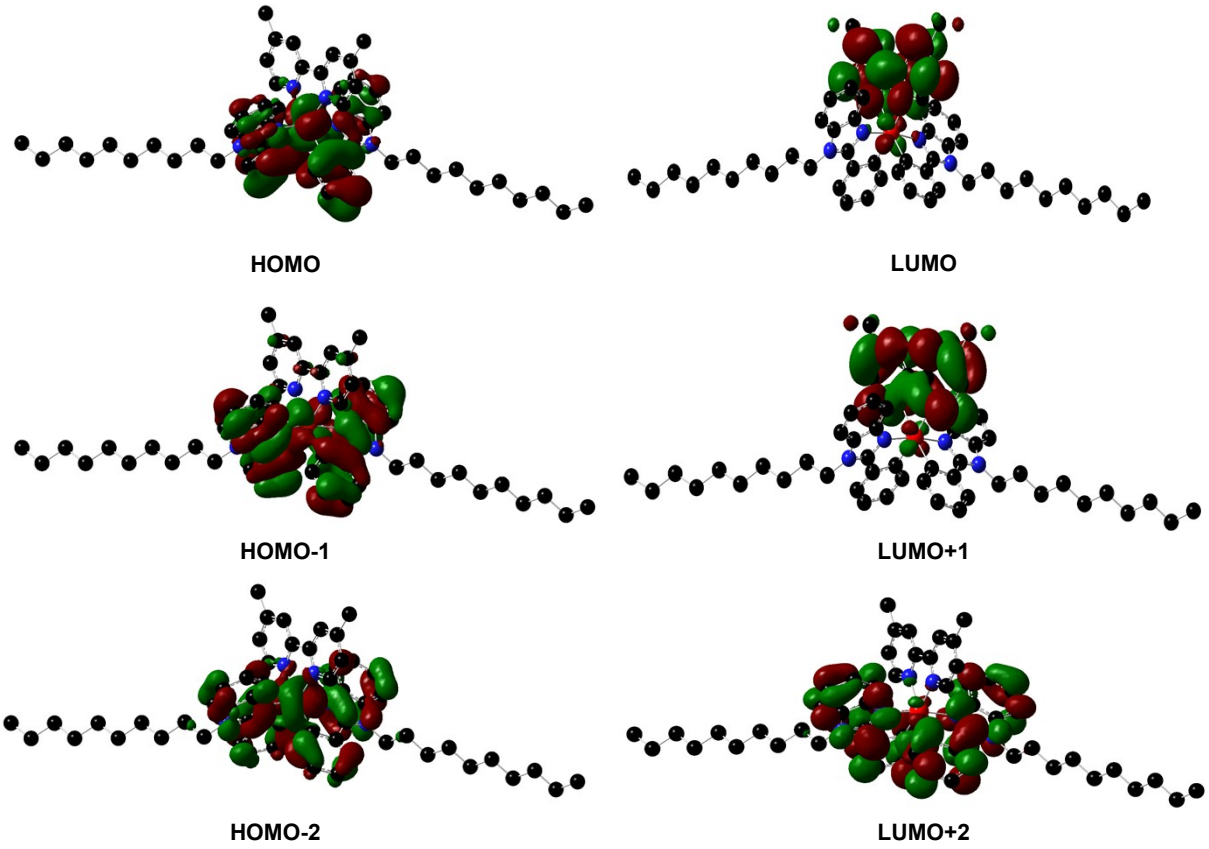


Fig. S8 Pictorial representation of frontiers molecular orbitals of [**3**]$^{+}$.

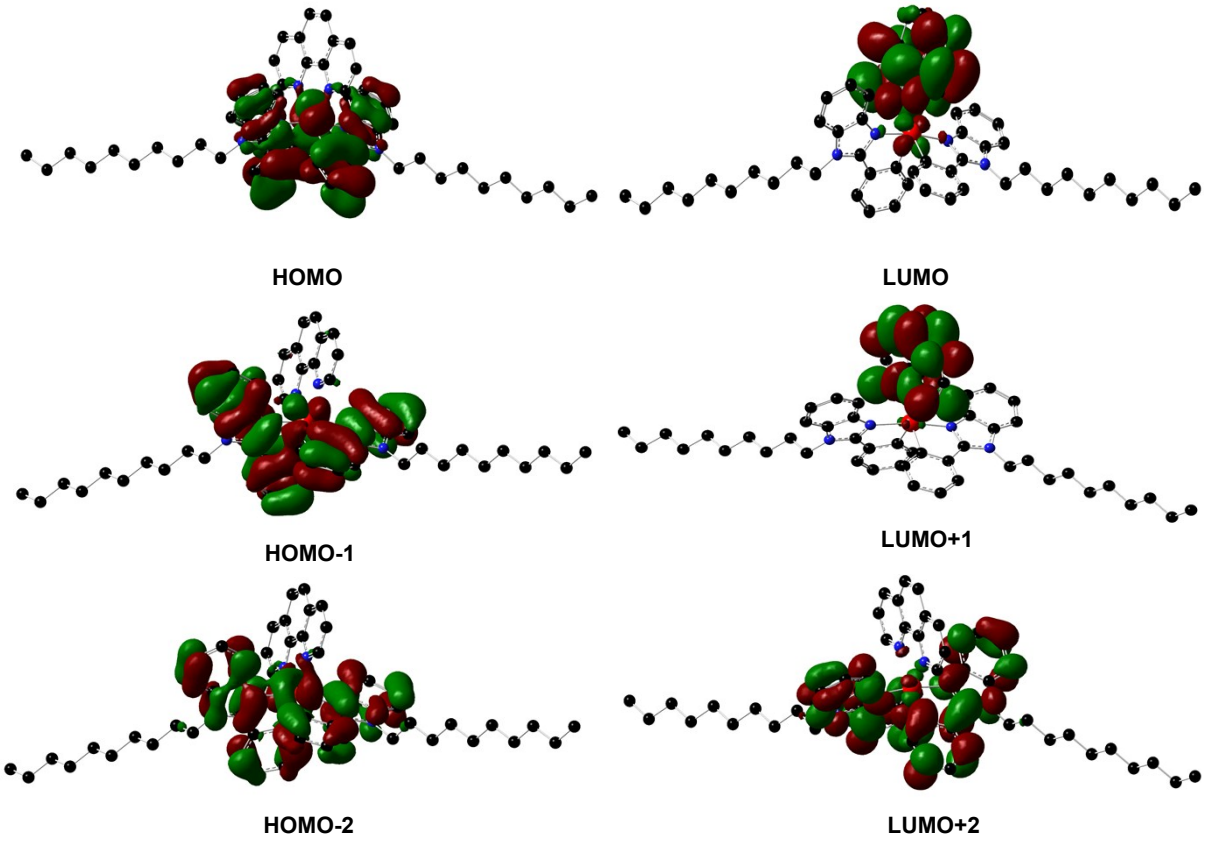


Fig. S9 Pictorial representation of frontiers molecular orbitals of [**4**]$^{+}$.

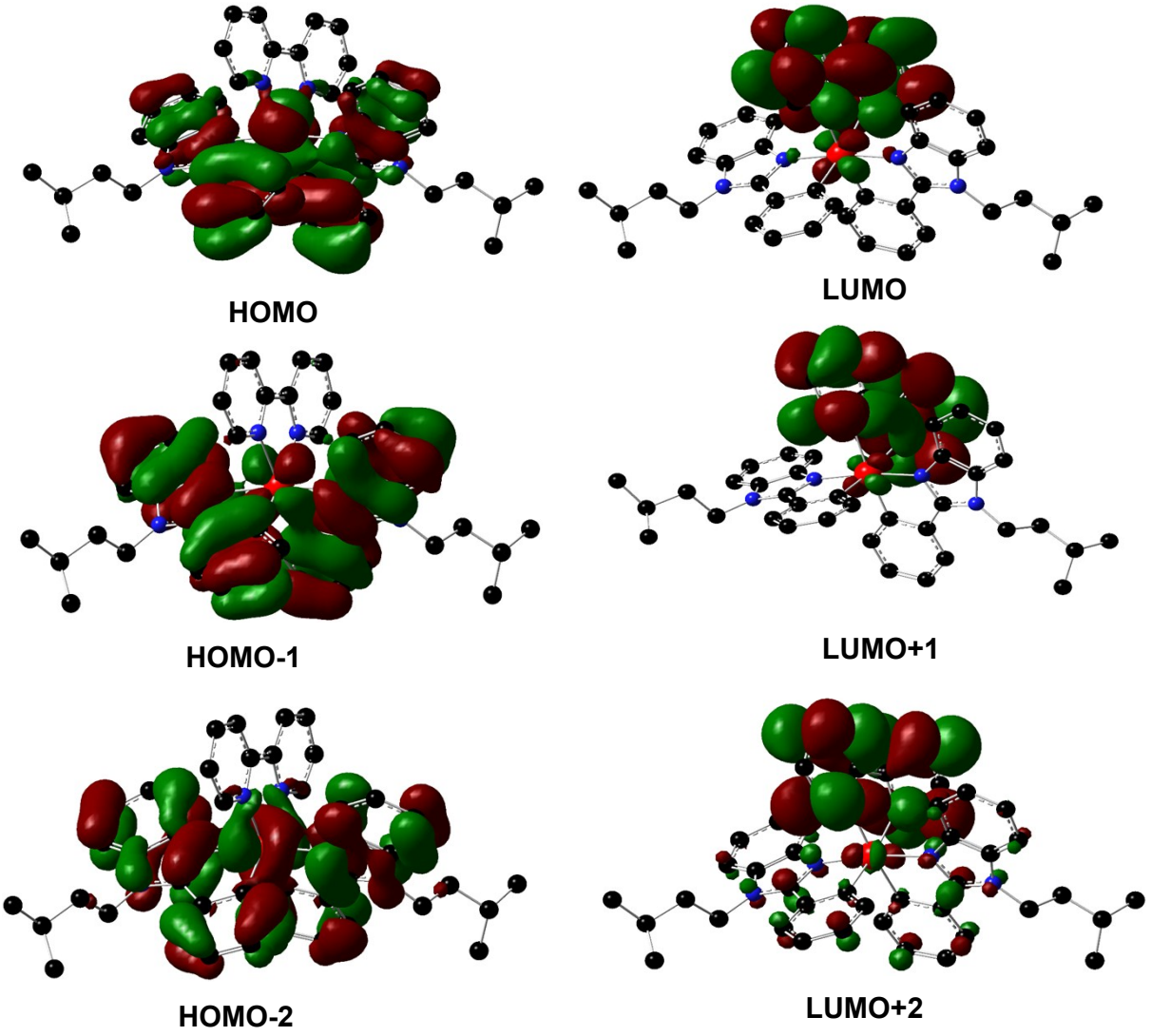


Fig. S10 Pictorial representation of frontiers molecular orbitals of [**5**]$^{+}$.

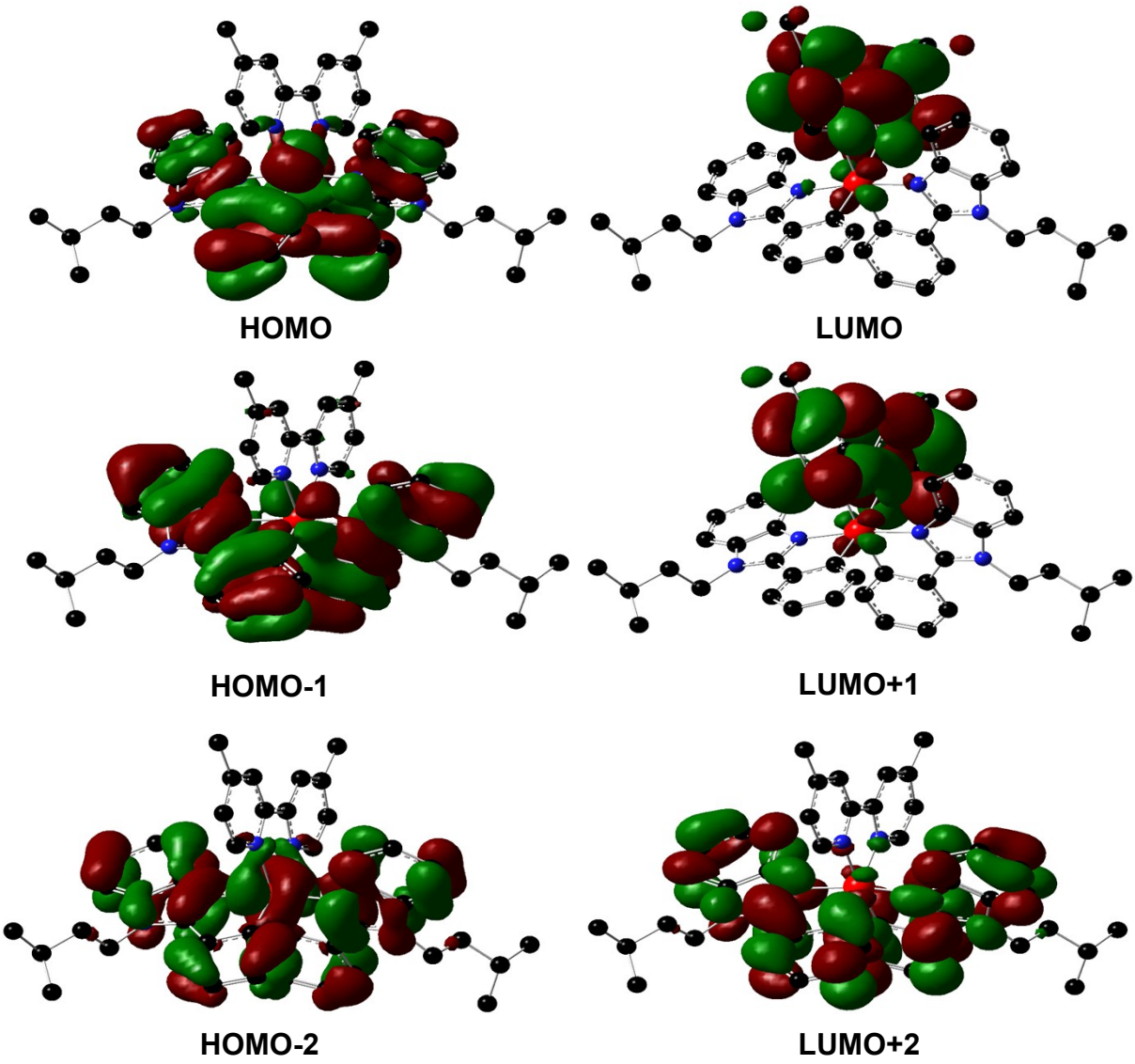


Table TS10. TD-DFT calculated electronic transitions for [**1**]$^{+}$.

λ/nm (DFT)	**λ/nm (Exp)**	***f***	**Major contribution**	**Characters**
375	374	0.115	HOMO→L+3 (96%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)
339	374	0.033	H-7→LUMO (79%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ Bpy(π*)
331	374	0.051	H-1→L+3 (82%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)
323	374	0.048	H-2→L+3 (59%) H-1→L+4 (34%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)
317	304	0.074	H-2→L+3 (32%) H-1→L+4 (56%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)
316	304	0.021	H-3→L+1 (91%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ Bpy(π*)
309	304	0.035	H-2→L+4 (87%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)
306	304	0.026	H-3→L+2 (84%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ Bpy(π*)
296	293	0.028	H-4→L+2 (49%) H-3→L+3 (36%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ Bpy(π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)
290	293	0.039	H-4→L+3 (24%) H-3→L+4 (63%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)
288	293	0.353	H-4→L+3 (62%) H-3→L+4 (20%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)
281	293	0.033	H-4→L+4 (87%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)
280	293	0.084	H-12→LUMO (26%) H-6→L+1 (43%)	Bpy(π)→ Bpy(π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ Bpy(π*)
271	293	0.122	H-12→LUMO (30%) H-6→L+1 (28%)	Bpy(π)→ Bpy(π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ Bpy(π*)
267	240	0.115	H-5→L+4 (31%) HOMO→L+6 (40%)	$\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)
265	240	0.063	H-6→L+2 (88%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ Bpy(π*)
261	240	0.042	H-7→L+2 (57%) H-6→L+3 (20%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ Bpy(π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)
259	240	0.088	H-7→L+2 (15%) H-6→L+3 (68%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ Bpy(π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)

Table TS11. TD-DFT calculated electronic transitions for [**2**]$^{+}$.

λ/nm (DFT)	λ/nm (Exp)	*f*	Major contributions	Character
481	n.o	0.0277	H-1→LUMO (98%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ Mebpy(π*)
383	381	0.0976	HOMO→L+2 (95%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)
339	338	0.0271	H-1→L+3 (66%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ Mebpy(π*)/ $\mathbf{L_1}$ (π*)
337	338	0.0803	H-7→LUMO (39%) H-1→L+2 (49%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ Mebpy(π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)
331	338	0.0674	H-2→L+2 (66%) H-1→L+4 (19%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ Mebpy(π*)/ $\mathbf{L_1}$ (π*)
323		0.0436	H-1→L+4 (73%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ Mebpy(π*)/ $\mathbf{L_1}$ (π*)
316		0.0512	H-2→L+4 (90%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ Mebpy(π*)/ $\mathbf{L_1}$ (π*)
300	304	0.0746	H-3→L+3 (85%)	$\mathbf{L_1}$ (π)→ Mebpy(π*)/ $\mathbf{L_1}$ (π*)
289	294	0.0614	H-3→L+4 (79%)	$\mathbf{L_1}$ (π)→ Mebpy(π*)/ $\mathbf{L_1}$ (π*)
287	294	0.0550	H-4→L+3 (87%)	$\mathbf{L_1}$ (π)→ Mebpy(π*)/ $\mathbf{L_1}$ (π*)
286	294	0.3115	H-4→L+2 (80%)	$\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)
278	294	0.0210	H-5→L+2 (79%)	$\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)
277	294	0.0331	H-4→L+4 (79%)	$\mathbf{L_1}$ (π)→ Mebpy(π*)/ $\mathbf{L_1}$ (π*)
274	294	0.1287	H-1→LUMO (40%) H-6→L+1 (36%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ Mebpy(π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ Mebpy(π*)
265	294	0.0275	H-19→LUMO (69%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ Mebpy(π*)
262	294	0.1181	HOMO→L+6 (22%) HOMO→L+8 (41%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ Mebpy(π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ Mebpy(π*)
260	240	0.0933	H-6→L+3 (78%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ Mebpy(π*)/ $\mathbf{L_1}$ (π*)
257	240	0.0936	H-7→L+3 (60%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ Mebpy(π*)/ $\mathbf{L_1}$ (π*)
255	240	0.0363	HOMO→L+6 (68%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ Mebpy(π*)
250	240	0.0845	H-7→L+4 (66%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ Mebpy(π*)/ $\mathbf{L_1}$ (π*)
238	240	0.0313	H-8→L+2 (15%) HOMO→L+11 (40%)	$\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)

Table TS12. TD-DFT calculated electronic transitions for [**3**]$^{+}$.

λ/nm (DFT)	**λ/nm (Exp)**	***f***	**Major contributions**	**Character**
405	n.o	0.0232	H-3→LUMO (95%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ phen(π*)
375	368	0.1189	HOMO→L+2 (97%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)
341	368	0.0355	H-6→LUMO (80%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ phen(π*)
331	368	0.0341	H-1→L+2 (90%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)
326	368	0.0367	H-7→L+1 (83%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ phen(π*)
325	305	0.0240	H-6→L+1 (50%) H-2→L+2 (20%) H-1→L+3 (23%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ phen(π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)
324	305	0.0258	H-6→L+1 (44%) H-1→L+3 (32%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ phen(π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)
317	305	0.0883	H-2→L+2 (53%) H-1→L+3 (35%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)
310	305	0.0533	H-2→L+3 (39%) H-1→L+4 (53%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ phen(π*)
291	293	0.0981	H-3→L+3 (76%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)

Table TS13. TD-DFT calculated electronic transitions for [**4**]$^{+}$.

λ/nm (DFT)	λ/nm (Exp)	*f*	Major contributions	Character
376	370	0.114	HOMO→L+3 (96%)	Ir(dπ)/ $\mathbf{L_2}$ (π)→ $\mathbf{L_2}$ (π*)
340	370	0.033	H-7→LUMO (79%)	Ir(dπ)/ $\mathbf{L_2}$ (π)→bpy(π*)
331	370	0.051	H-1→L+3 (83%)	Ir(dπ)/ $\mathbf{L_2}$ (π)→ $\mathbf{L_2}$ (π*)
324	370	0.046	H-2→L+3 (59%) H-1→L+4 (34%)	Ir(dπ)/ $\mathbf{L_2}$ (π)→ $\mathbf{L_2}$ (π*) Ir(dπ)/ $\mathbf{L_2}$ (π)→ $\mathbf{L_2}$ (π*)
318	370	0.071	H-2→L+3 (32%) H-1→L+4 (56%)	Ir(dπ)/ $\mathbf{L_2}$ (π)→ $\mathbf{L_2}$ (π*) Ir(dπ)/ $\mathbf{L_2}$ (π)→ $\mathbf{L_2}$ (π*)
317	370	0.022	H-3→L+1 (91%)	Ir(dπ)/ $\mathbf{L_2}$ (π)→ bpy(π*)
309	283	0.035	H-2→L+4 (87%)	Ir(dπ)/ $\mathbf{L_2}$ (π)→ $\mathbf{L_2}$ (π*)
306	283	0.026	H-3→L+2 (83%)	Ir(dπ)/ $\mathbf{L_2}$ (π)→ bpy(π*)
296	283	0.029	H-4→L+2 (51%) H-3→L+3 (34%)	Ir(dπ)/ $\mathbf{L_2}$ (π)→ bpy(π*) Ir(dπ)/ $\mathbf{L_2}$ (π)→ $\mathbf{L_2}$ (π*)
290	283	0.034	H-4→L+3 (26%) H-3→L+4 (62%)	Ir(dπ)/ $\mathbf{L_2}$ (π)→ $\mathbf{L_2}$ (π*) Ir(dπ)/ $\mathbf{L_2}$ (π)→ $\mathbf{L_2}$ (π*)
289	283	0.355	H-4→L+3 (60%) H-3→L+4 (21%)	Ir(dπ)/ $\mathbf{L_2}$ (π)→ $\mathbf{L_2}$ (π*) Ir(dπ)/ $\mathbf{L_2}$ (π)→ $\mathbf{L_2}$ (π*)

Table TS14. TD-DFT calculated electronic transitions for [**5**]$^{+}$.

λ/nm (DFT)	λ/nm (Exp)	*f*	Major contributions	Character
377	403	0.1054	HOMO→L+2 (94%)	Ir(dπ)/ **L₂** (π)→ **L₂** (π*)
332	354	0.0933	H-7→LUMO (38%) H-1→L+2 (51%)	Ir(dπ)/ **L₂** (π)→Mebpy(π*) Ir(dπ)/ **L₂** (π)→ **L₂** (π*)
331	381	0.0302	H-1→L+3 (72%)	Ir(dπ)/ **L₂** (π)→ **L₂** (π*)/ Mebpy(π*)
323	354	0.0570	H-2→L+2 (70%)	Ir(dπ)/ **L₂** (π)→ **L₂** (π*)
317	302	0.0382	H-1→L+4 (76%)	Ir(dπ)/ **L₂** (π)→ **L₂** (π*)/ Mebpy(π*)
308	302	0.0478	H-2→L+4 (92%)	Ir(dπ)/ **L₂** (π)→ **L₂** (π*)/ Mebpy(π*)
297	302	0.0552	H-8→LUMO (22%) H-3→L+3 (57%)	**L₂** (π)→ Mebpy(π*) Ir(dπ)/ **L₂** (π)→ **L₂** (π*)/ Mebpy(π*)
296	302	0.0362	H-8→LUMO (70%) H-3→L+3 (24%)	**L₂** (π)→ Mebpy(π*) Ir(dπ)/ **L₂** (π)→ **L₂** (π*)/ Mebpy(π*)
289	302	0.1450	H-4→L+2 (80%)	**L₂** (π)→ **L₂** (π*)
287	305	0.0338	H-9→LUMO (29%) H-4→L+3 (61%)	**L₂** (π)→ Mebpy(π*) **L₂** (π)→ **L₂** (π*)/ Mebpy(π*)
287	279	0.1905	H-3→L+4 (73%)	Ir(dπ)/ **L₂** (π)→ **L₂** (π*)/ Mebpy(π*)
286	279	0.0264	H-9→LUMO (63%) H-4→L+3 (30%)	**L₂** (π)→ Mebpy(π*) **L₂** (π)→ **L₂** (π*)/ Mebpy(π*)
279	279	0.0323	H-5→L+2 (78%)	**L₂** (π)→ **L₂** (π*)
276	279	0.0983	H-10→LUMO (29%) H-5→L+3 (31%)	Mebpy(π)→ Mebpy(π*) **L₂** (π)→ **L₂** (π*)/ Mebpy(π*)
276	279	0.0684	H-10→LUMO (25%) H-5→L+3 (40%)	Mebpy(π)→ Mebpy(π*) **L₂** (π)→ **L₂** (π*)/ Mebpy(π*)
268	279	0.1143	HOMO→L+6 (29%) HOMO→L+7 (24%)	Ir(dπ)/ **L₂** (π)→ **L₂** (π*) Ir(dπ)/ **L₂** (π)→ **L₂** (π*)
265	240	0.0220	H-6→L+1 (30%) H-5→L+4 (48%)	Ir(dπ)/ **L₂** (π)→ Mebpy(π*) **L₂** (π)→ **L₂** (π*)/ Mebpy(π*)
265	240	0.1061	H-6→L+1 (41%) H-5→L+4 (26%)	Ir(dπ)/ **L₂** (π)→ Mebpy(π*) **L₂** (π)→ **L₂** (π*)/ Mebpy(π*)

Table TS15. TDDFT vertical gas phase energies of the ten lowest lying triplet state for $[\mathbf{1}]^+$ [oscillator strengths (*f*) =0.0000, not list here].

State	λ (nm)	Energy (eV)	Major contribution	Transitions	Nature
T_1	585.7	2.11	HOMO→LUMO (97%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ bpy(π*)	^{3}MLLCT
T_2	507.6	2.44	H-1→LUMO (86%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ bpy(π*)	^{3}MLLCT
T_3	482.8	2.56	H-2→LUMO (88%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ bpy(π*)	^{3}MLLCT
T_4	441.9	2.80	H-1→L+4 (23%) HOMO→L+3 (54%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)	^{3}MLLCT ^{3}MLLCT
T_5	438.1	2.82	H-1→L+3 (39%) HOMO→L+4 (31%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ $\mathbf{L_1}$ (π*)	^{3}MLLCT ^{3}MLLCT
T_6	425.9	2.91	H-3→LUMO (80%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ bpy(π*)	^{3}MLLCT
T_7	413.3	2.99	H-12→LUMO (18%) H-4→LUMO (45%)	bpy(π)→ bpy(π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ bpy(π*)	^{3}LC ^{3}MLLCT
T_8	402.8	3.07	HOMO→L+1 (89%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ bpy(π*)	^{3}MLLCT
T_9	393.2	3.15	H-12→LUMO (37%) H-4→LUMO (45%)	Bpy(π)→ bpy(π*) Ir(dπ)/ $\mathbf{L_1}$ (π)→ bpy(π*)	^{3}LC ^{3}MLLCT
T_{10}	386.3	3.20	HOMO→L+2 (65%)	Ir(dπ)/ $\mathbf{L_1}$ (π)→ bpy(π*)	^{3}MLLCT

Table TS16. TDDFT vertical gas phase energies of the ten lowest lying triplet state for [**2**]$^{+}$ [oscillator strengths (*f*) =0.0000, not list here].

State	λ (nm)	Energy (eV)	Major contributions	Transitions	nature
T_1	594.9	2.08	HOMO→LUMO (96%)	Ir(dπ)/ **L**$_1$ (π)→ Mebpy(π*)	^{3}MLLCT
T_2	521.3	2.37	H-1→LUMO (85%)	Ir(dπ)/ **L**$_1$ (π)→ Mebpy(π*)	^{3}MLLCT
T_3	498.6	2.48	H-2→LUMO (89%)	Ir(dπ)/ **L**$_1$ (π)→ Mebpy(π*)	^{3}MLLCT
T_4	445.1	2.78	HOMO→L+2 (55%)	Ir(dπ)/ **L**$_1$ (π)→ **L**$_1$ (π*)	^{3}MLLCT
T_5	441.2	2.81	H-1→L+2 (37%) HOMO→L+4 (22%)	Ir(dπ)/ **L**$_1$ (π)→ **L**$_1$ (π*) Ir(dπ)/ **L**$_1$ (π)→ Mebpy(π*)/ **L**$_1$ (π*)	^{3}MLLCT ^{3}MLLCT
T_6	419.9	2.95	H-3→LUMO (82%)	**L**$_1$ (π)→ Mebpy(π*)	^{3}LLCT
T_7	407.3	3.04	H-12→LUMO (24%) H-4→LUMO (34%)	Mebpy(π) → Mebpy(π*) **L**$_1$ (π)→ Mebpy(π*)	^{3}LC ^{3}LLCT
T_8	393.9	3.14	HOMO→L+1 (75%)	Ir(dπ)/ **L**$_1$ (π)→ Mebpy(π*)	^{3}MLLCT
T_9	389.9	3.18	H-2→L+2 (27%) HOMO→L+1 (16%) HOMO→L+2 (26%)	Ir(dπ)/ **L**$_1$ (π)→ **L**$_1$ (π*) Ir(dπ)/ **L**$_1$ (π)→ Mebpy(π*) Ir(dπ)/ **L**$_1$ (π)→ **L**$_1$ (π*)	^{3}MLLCT ^{3}MLLCT ^{3}MLLCT
T_{10}	388.7	3.18	H-1→L+2 (17%) HOMO→L+3 (41%)	Ir(dπ)/ **L**$_1$ (π)→ **L**$_1$ (π*) Ir(dπ)/ **L**$_1$ (π)→ Mebpy(π*)/ **L**$_1$ (π*)	^{3}MLLCT ^{3}MLLCT

Table TS17. TDDFT vertical gas phase energies of the ten lowest lying triplet state for [**3**]$^{+}$ [oscillator strengths (*f*) =0.0000, not list here].

State	λ (nm)	Energy (eV)	Major contribution	Transitions	Nature
T_1	574.0	2.16	HOMO→LUMO (97%)	Ir(dπ)/ **L**$_1$ (π)→ phen(π*)	^{3}MLLCT
T_2	521.6	2.37	HOMO→L+1 (96%)	Ir(dπ)/ **L**$_1$ (π)→ phen(π*)	^{3}MLLCT
T_3	499.8	2.48	H-1→LUMO (82%)	Ir(dπ)/ **L**$_1$ (π)→ phen(π*)	^{3}MLLCT
T_4	482.4	2.56	H-2→LUMO (48%) H-1→L+1 (17%)	Ir(dπ)/ **L**$_1$ (π)→ phen(π*) Ir(dπ)/ **L**$_1$ (π)→ phen(π*)	^{3}MLLCT ^{3}MLLCT
T_5	460.3	2.69	H-2→LUMO (36%) H-1→L+1 (52%)	Ir(dπ)/ **L**$_1$ (π)→ phen(π*) Ir(dπ)/ **L**$_1$ (π)→ phen(π*)	^{3}MLLCT ^{3}MLLCT
T_6	441.7	2.80	H-1→L+3 (24%) HOMO→L+2 (49%)	Ir(dπ)/ **L**$_1$ (π)→ **L**$_1$ (π*) Ir(dπ)/ **L**$_1$ (π)→ **L**$_1$ (π*)	^{3}MLLCT ^{3}MLLCT
T_7	438.4	2.82	H-2→L+1 (22%) H-1→L+2 (31%) HOMO→L+3 (27%)	Ir(dπ)/ **L**$_1$ (π)→ phen(π*) Ir(dπ)/ **L**$_1$ (π)→ **L**$_1$ (π*) Ir(dπ)/ **L**$_1$ (π)→ **L**$_1$ (π*)	^{3}MLLCT ^{3}MLLCT ^{3}MLLCT
T_8	431.9	2.87	H-2→L+1 (61%)	Ir(dπ)/ **L**$_1$ (π)→ phen(π*)	^{3}MLLCT
T_9	430.5	2.87	H-6→L+1 (14%) H-1→L+1 (29%)	Ir(dπ)/ **L**$_1$ (π)→ phen(π*) Ir(dπ)/ **L**$_1$ (π)→ phen(π*)	^{3}MLLCT ^{3}MLLCT
T_{10}	420.1	2.95	H-3→LUMO (68%)	Ir(dπ)/ **L**$_1$ (π)→ phen(π*)	^{3}MLLCT

Table TS18. TDDFT vertical gas phase energies of the ten lowest lying triplet state for [**4**]$^{+}$ [oscillator strengths (*f*) =0.0000, not list here].

State	λ (nm)	Energy (eV)	Major contribution	Transitions	Nature
T_1	585.9	2.11	HOMO→LUMO (97%)	Ir(dπ)/**L$_2$**(π)→ bpy(π*)	^{3}MLLCT
T_2	507.6	2.44	H-1→LUMO (86%)	Ir(dπ)/**L$_2$**(π)→ bpy(π*)	^{3}MLLCT
T_3	482.8	2.56	H-2→LUMO (88%)	Ir(dπ)/**L$_2$**(π)→ bpy(π*)	^{3}MLLCT
T_4	442.0	2.80	H-1→L+4 (23%), HOMO→L+3 (54%)	Ir(dπ)/**L$_2$**(π)→ **L$_2$**(π*) Ir(dπ)/**L$_2$**(π)→ **L$_2$**(π*)	^{3}MLLCT ^{3}MLLCT
T_5	438.2	2.82	H-1→L+3 (39%), HOMO→L+4 (31%)	Ir(dπ)/**L$_2$**(π)→ **L$_2$**(π*) Ir(dπ)/**L$_2$**(π)→ **L$_2$**(π*)	^{3}MLLCT ^{3}MLLCT
T_6	425.7	2.91	H-3→LUMO (80%)	Ir(dπ)/**L$_2$**(π)→ bpy(π*)	^{3}MLLCT
T_7	413.3	3.00	H-4→LUMO (45%)	Ir(dπ)/**L$_2$**(π)→ bpy(π*)	^{3}MLLCT
T_8	402.8	3.07	HOMO→L+1 (89%)	Ir(dπ)/**L$_2$**(π)→ bpy(π*)	^{3}MLLCT
T_9	393.0	3.15	H-10→LUMO (37%) H-4→LUMO (45%)	Ir(dπ)/**L$_2$**(π)→ bpy(π*) Ir(dπ)/**L$_2$**(π)→ bpy(π*)	^{3}MLLCT ^{3}MLLCT
T_{10}	386.4	3.20	HOMO→L+2 (65%)	Ir(dπ)/**L$_2$**(π)→ bpy(π*)	^{3}MLLCT

Table TS19. TDDFT vertical gas phase energies of the ten lowest lying triplet state for [**5**]$^{+}$ [oscillator strengths (*f*) =0.0000, not list here].

State	λ (nm)	Energy (eV)	Major Contributions	Transitions	Nature
T_1	566.6	2..18	HOMO→LUMO (97%)	Ir(dπ)/**L$_2$**(π)→ Mebpy(π*)	^{3}MLLCT
T_2	493.7	2.51	H-1→LUMO (86%)	Ir(dπ)/**L$_2$**(π)→ Mebpy(π*)	^{3}MLLCT
T_3	471.0	2.63	H-2→LUMO (87%)	Ir(dπ)/**L$_2$**(π)→ Mebpy(π*)	^{3}MLLCT
T_4	443.0	2.79	HOMO→L+2 (55%)	Ir(dπ)/**L$_2$**(π)→ **L$_2$**(π*)	^{3}MLLCT
T_5	438.7	2.82	H-1→L+2 (39%) HOMO→L+3 (23%),	Ir(dπ)/**L$_2$**(π)→ **L$_2$**(π*) Ir(dπ)/**L$_2$**(π)→ **L$_2$**(π*)/Mebpy(π*)	^{3}MLLCT ^{3}MLLCT
T_6	414.6	2.99	H-3→LUMO (81%)	Ir(dπ)/**L$_2$**(π)→ Mebpy(π*)	^{3}MLLCT
T_7	406.6	3.04	H-10→LUMO (34%) H-4→LUMO (28%),	Mebpy(π)→ Mebpy(π*) **L$_2$**(π)→ Mebpy(π*)	^{3}LC ^{3}LLCT
T_8	388.2	3.19	HOMO→L+1 (42%)	Ir(dπ)/**L$_2$**(π)→ Mebpy(π*)	^{3}MLLCT
T_9	385.9	3.21	H-4→LUMO (38%)	**L$_2$**(π)→ Mebpy(π*)	^{3}LLCT
T_{10}	384.7	3.22	H-4→LUMO (23%) HOMO→L+1 (49%)	**L$_2$**(π)→ Mebpy(π*) Ir(dπ)/ **L$_2$**(π)→ Mebpy(π*)	^{3}LLCT ^{3}MLLCT

Fig. S11 UV-Vis spectra of the complexes $[\mathbf{1}]^+$-$[\mathbf{5}]^+$ in water at room temperature.

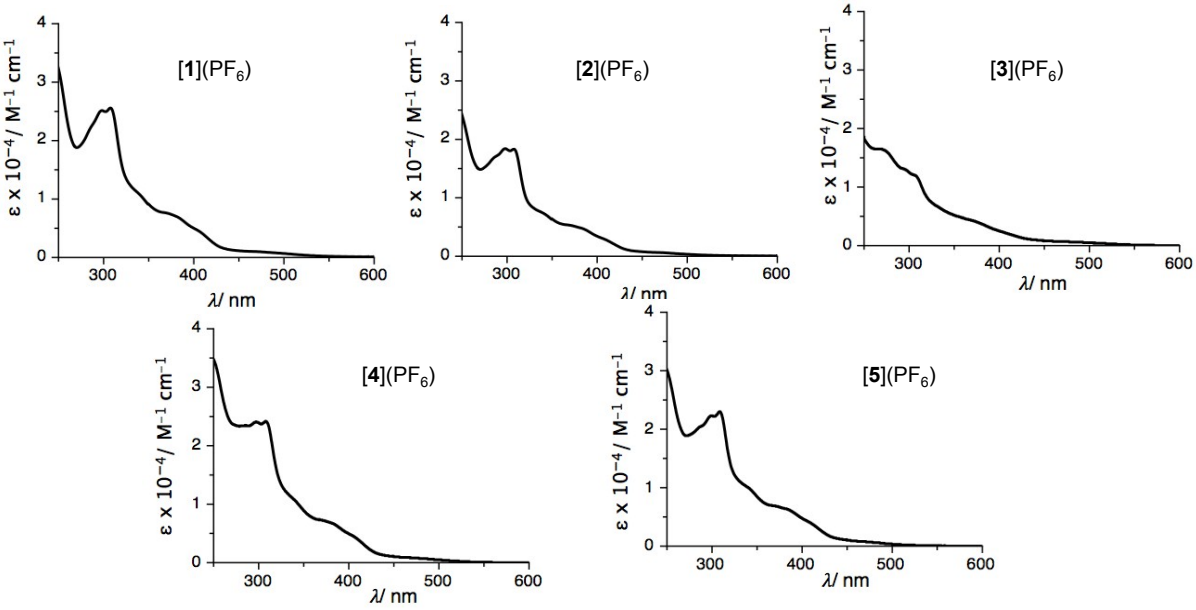


Fig. S12 Emission spectra of the complexes $[\mathbf{1}]^+$-$[\mathbf{5}]^+$ in Water at room temperature.

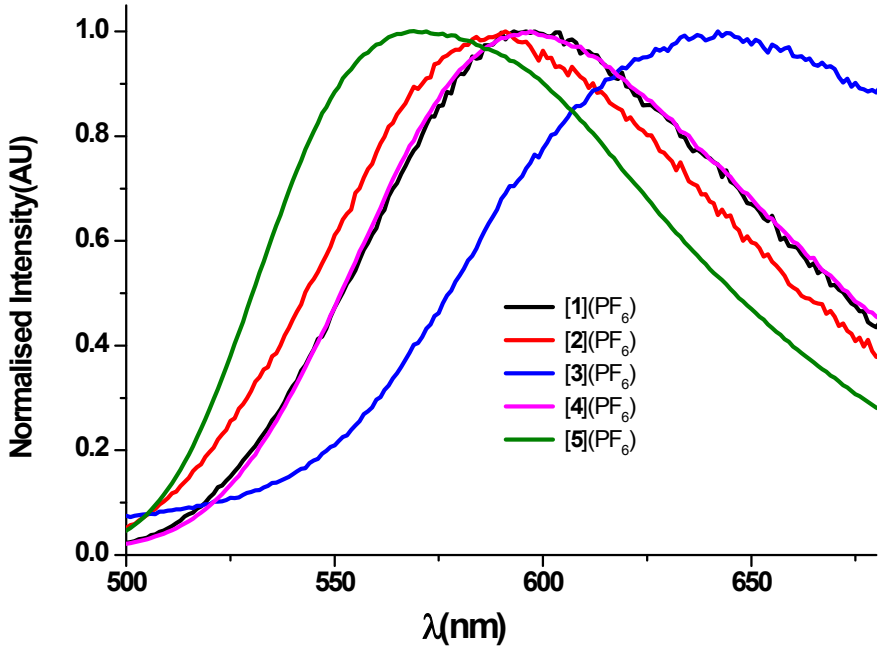


Fig. S13 Flow cytometry analysis of complexes $[\mathbf{1}]^+$ - $[\mathbf{5}]^+$ treated MCF-7 cells. The emission spectra were taken at 555 nm by exciting complexes at 488 nm after 3 h of treatment of complexes.

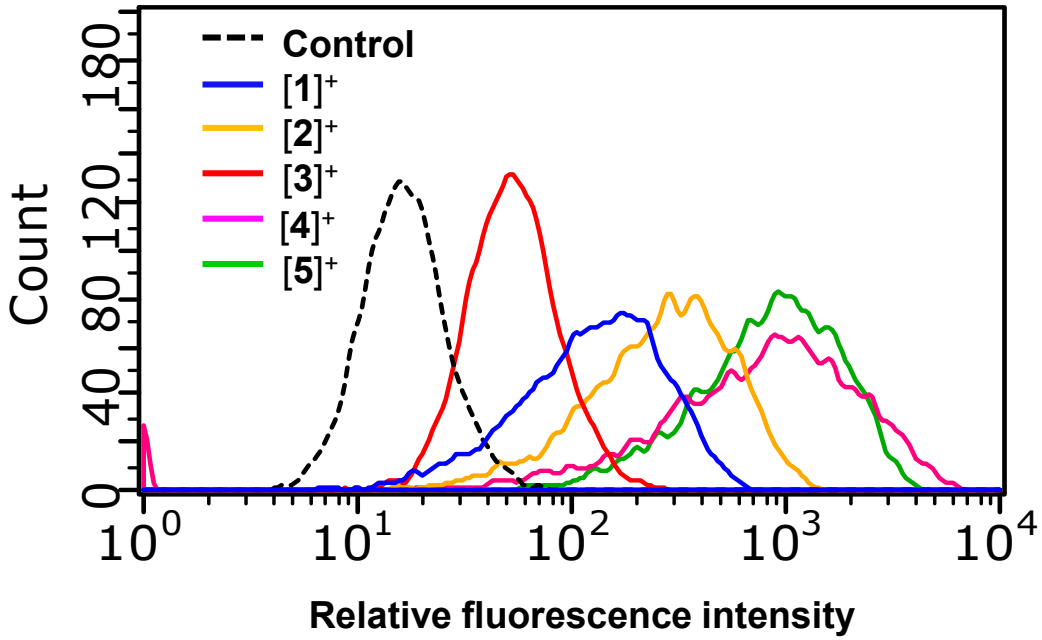


Fig. S14 Fluorescence microscopic images of the complexes $[\mathbf{2}]^+$, $[\mathbf{3}]^+$ and $[\mathbf{4}]^+$ treated MCF-7 cells. The images were taken by exciting at 488 nm and 555 nm after 2 h of treatment of complexes.

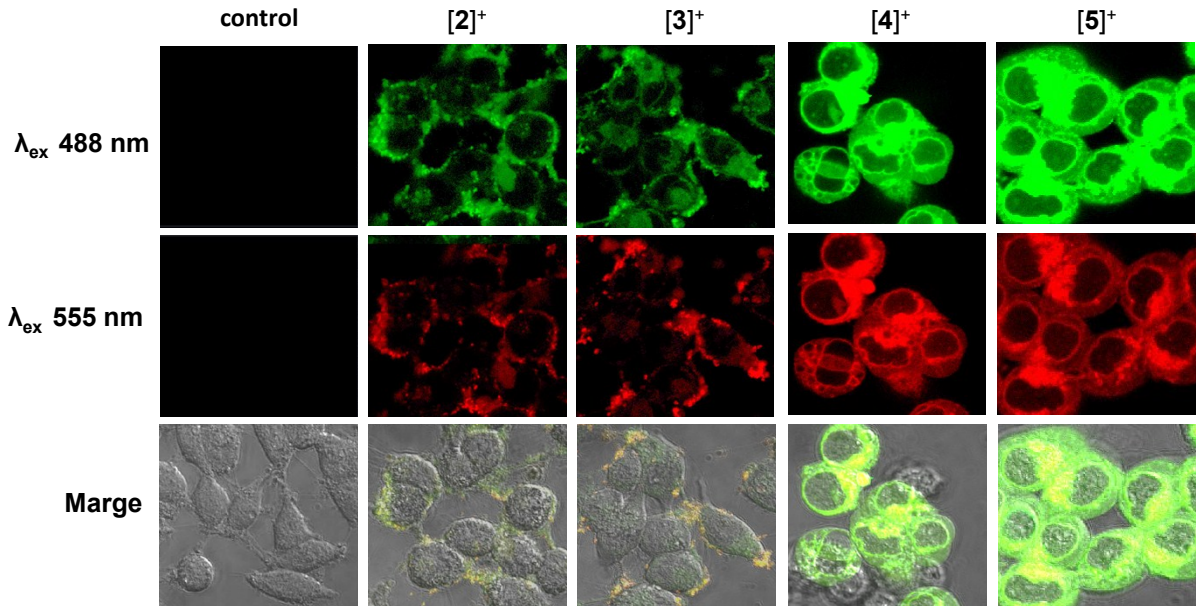


Fig. S15 Cell viability assay of synthesised complexes [**1**]$^{+}$ - [**5**]$^{+}$ against human normal breast cell (MCF-10) line at indicated concentration after 48 h.

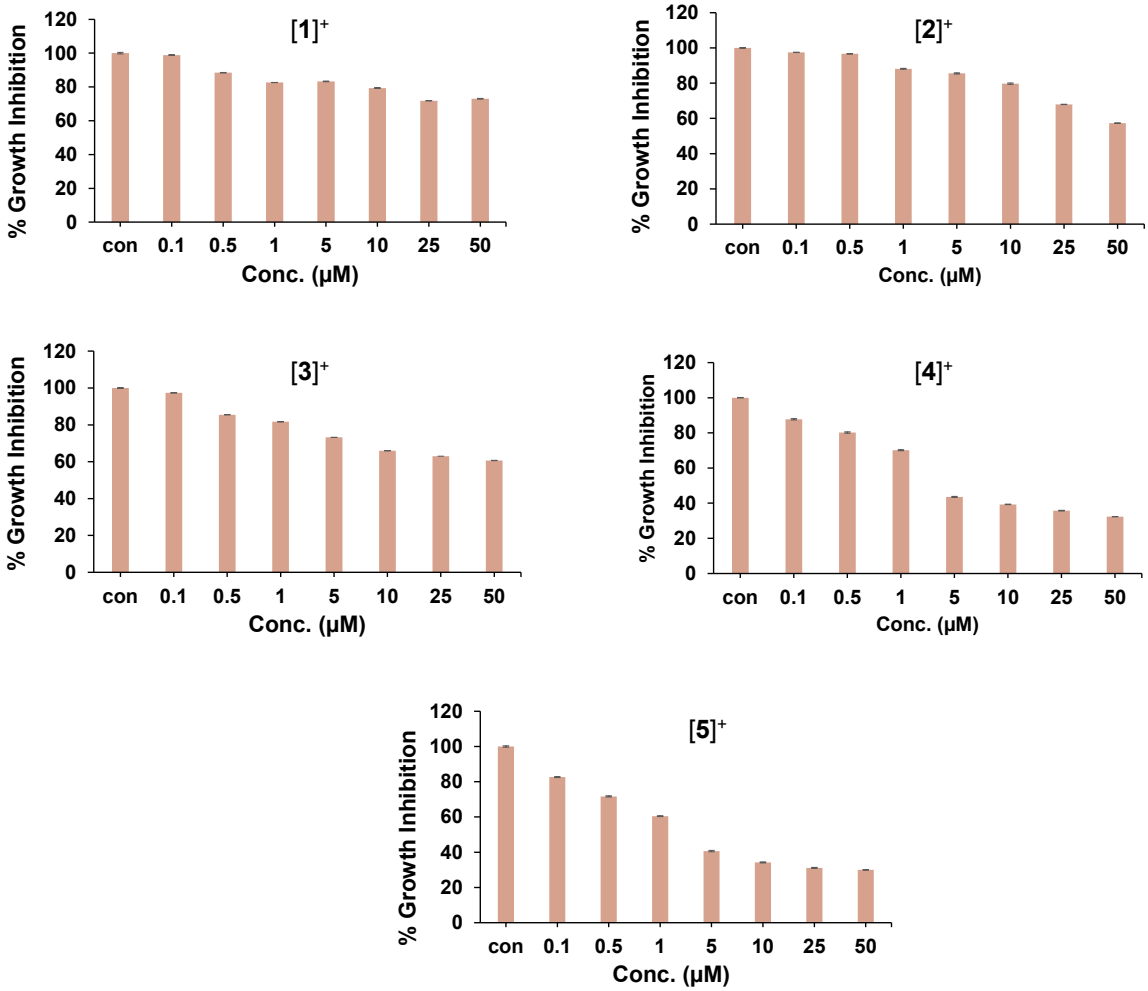


Fig. S16 Western blot analysis of the protein expression related to apoptosis of human breast cancer MCF-7 cells after the treatment of complex [**4**]$^{+}$ and cisplatin at indicated concentration. The incubation time was 48 after the drug treatment.

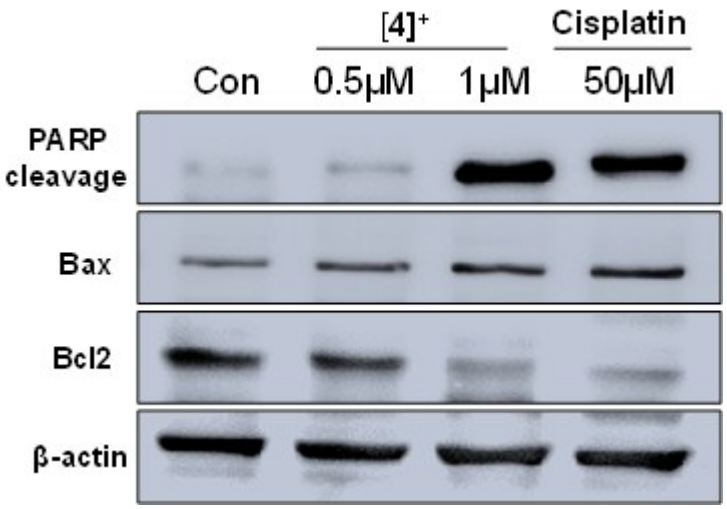


Fig. S17 Light microscopy images of complex $[\mathbf{4}]^+$ (5 μM), complex $[\mathbf{4}]^+$ + 3-MA treated human breast (MCF-7) cancer cells after 48 h incubation.

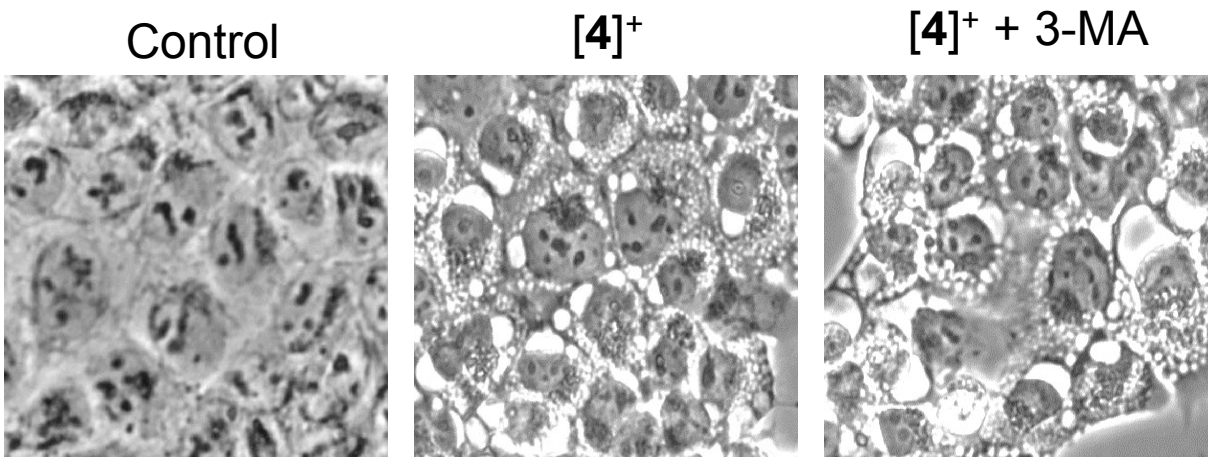


Fig. S18 Fluorescence microscopic images of acridine orange stained human breast (MCF7) cancer cells after the treatment of complex [**4**]$^{+}$ after 3h incubation.