Table S1: Cartesian coordinates of ligand **2a** in the gas phase.

7	2.957240000	1.117782000	-0.134224000
6	1.980176000	2.059920000	-0.047978000
6	2.629438000	-0.158060000	0.016569000
6	2.375778000	3.419717000	-0.171180000
6	0.596265000	1.749150000	0.168986000
6	1.286060000	-0.562339000	0.235892000
6	3.736160000	-1.152066000	-0.051175000
6	1.456854000	4.435159000	-0.046906000
1	3.427566000	3.615309000	-0.351346000
6	-0.316567000	2.824847000	0.330677000
6	0.250145000	0.357016000	0.267589000
1	1.055466000	-1.614066000	0.364591000
6	3.505389000	-2.511916000	-0.314604000
6	0.102032000	4.133881000	0.224423000
1	1.771623000	5.470740000	-0.136385000
1	-1.349809000	2.612033000	0.575211000
6	-1.117291000	-0.165330000	0.402476000
6	4.563723000	-3.418156000	-0.367861000
1	2.498872000	-2.868833000	-0.507422000
6	6.115387000	-1.630834000	0.096538000
1	-0.612004000	4.940444000	0.362068000
1	-1.186683000	-1.092118000	0.969876000
6	-2.230334000	0.313107000	-0.190240000
6	5.872460000	-2.982732000	-0.158419000
1	4.364467000	-4.464530000	-0.580412000
1	7.131368000	-1.282287000	0.258847000
1	-2.141360000	1.178602000	-0.842235000
6	-3.580026000	-0.253786000	-0.102429000
1	6.696311000	-3.689408000	-0.197690000
6	-3.949238000	-1.230297000	0.843758000
6	-4.565865000	0.197684000	-0.999701000
6	-5.238625000	-1.748569000	0.880561000
1	-3.224701000	-1.579633000	1.572133000
6	-5.861994000	-0.310506000	-0.977237000
1	-4.306631000	0.956043000	-1.733334000
6	-6.177520000	-1.281622000	-0.035273000
1	-5.529566000	-2.497314000	1.609188000
1	-6.621561000	0.032662000	-1.670900000

9	-7.429582000	-1.780674000	0.000677000
6	5.060062000	-0.724826000	0.146236000
1	5.237384000	0.327306000	0.337062000

Table S2: Cartesian coordinates of complex **4a** in the gas phase.

77	0.167380000	-0.248842000	1.001674000
6	0.348848000	2.479590000	-0.936039000
6	-1.300013000	2.407775000	0.728054000
6	1.323663000	1.806167000	-1.713177000
6	0.062789000	3.850158000	-1.238382000
6	-1.602749000	3.775108000	0.494755000
6	1.990175000	2.449545000	-2.734363000
1	1.524144000	0.770141000	-1.486172000
6	0.761178000	4.478193000	-2.299607000
6	-0.944938000	4.518531000	-0.461566000
1	-2.326448000	4.262351000	1.134629000
6	1.711035000	3.798807000	-3.032913000
1	2.729640000	1.907278000	-3.316530000
1	0.525814000	5.505907000	-2.553547000
1	2.232671000	4.297477000	-3.844322000
6	-1.994404000	1.617668000	1.747832000
6	-3.146264000	2.095945000	2.404381000
6	-1.447008000	0.341284000	2.058452000
6	-3.765553000	1.340641000	3.389894000
1	-3.575004000	3.056742000	2.135751000
6	-2.095504000	-0.390464000	3.073869000
6	-3.226385000	0.094264000	3.727864000
1	-4.654915000	1.714215000	3.889002000
1	-1.703108000	-1.358438000	3.364190000
1	-3.693841000	-0.503924000	4.506773000
7	-0.319174000	1.787191000	0.050669000
6	-1.238966000	5.943243000	-0.655769000
1	-0.407082000	6.566136000	-0.973601000
6	-2.450180000	6.507803000	-0.472009000
1	-3.287263000	5.856027000	-0.225743000
6	-2.793430000	7.926250000	-0.602268000
6	-1.830021000	8.946670000	-0.733996000
6	-4.150356000	8.301045000	-0.589306000
6	-2.203534000	10.279428000	-0.863445000
1	-0.773355000	8.699546000	-0.720512000
6	-4.542102000	9.631342000	-0.716655000
1	-4.910889000	7.532396000	-0.481752000
6	-3.558256000	10.602913000	-0.854747000

1	-1.466623000	11.069318000	-0.960971000
1	-5.587028000	9.921606000	-0.709039000
7	2.170998000	-0.801653000	0.020249000
6	2.435342000	-1.685423000	-1.003775000
6	3.201247000	-0.273169000	0.703190000
6	1.357254000	-2.199054000	-1.765437000
6	3.768075000	-2.075084000	-1.356223000
6	4.539815000	-0.654010000	0.423726000
6	2.865497000	0.669762000	1.772683000
6	1.576890000	-3.052084000	-2.826023000
1	0.358199000	-1.898176000	-1.488976000
6	3.958093000	-2.945584000	-2.458258000
6	4.855636000	-1.540464000	-0.583387000
1	5.329441000	-0.281150000	1.062252000
6	3.855071000	1.404085000	2.457477000
6	1.487980000	0.805584000	2.104062000
6	2.888051000	-3.430651000	-3.180275000
1	0.731738000	-3.428049000	-3.395334000
1	4.966378000	-3.217047000	-2.751143000
6	6.244209000	-1.945032000	-0.833320000
6	3.511952000	2.264616000	3.490188000
1	4.900112000	1.318194000	2.175523000
6	1.180213000	1.678043000	3.167644000
1	3.055515000	-4.094172000	-4.023393000
1	6.392514000	-2.955820000	-1.203713000
6	7.317388000	-1.151244000	-0.638474000
6	2.164943000	2.391023000	3.848126000
1	4.279759000	2.829570000	4.010695000
1	0.147672000	1.797392000	3.474997000
1	7.142282000	-0.119358000	-0.337234000
6	8.726815000	-1.506132000	-0.823005000
1	1.881961000	3.052425000	4.663919000
6	9.172160000	-2.827455000	-1.029355000
6	9.694480000	-0.484124000	-0.788911000
6	10.520254000	-3.114491000	-1.210701000
1	8.458792000	-3.645275000	-1.034363000
6	11.048902000	-0.754025000	-0.967616000
1	9.375601000	0.541497000	-0.623893000
6	11.441319000	-2.070185000	-1.179256000
1	10.869142000	-4.129680000	-1.366026000

1	11.795423000	0.032313000	-0.943883000
7	-1.337146000	-1.644359000	-0.035212000
6	-2.223342000	-1.383660000	-1.057326000
6	-1.434952000	-2.809725000	0.626486000
6	-2.031765000	-0.222367000	-1.845697000
6	-3.300889000	-2.270215000	-1.389818000
6	-2.497566000	-3.711092000	0.361687000
6	-0.427419000	-3.064483000	1.658608000
6	-2.841764000	0.046379000	-2.928187000
1	-1.218143000	0.436169000	-1.581514000
6	-4.095153000	-1.976174000	-2.526883000
6	-3.472537000	-3.446970000	-0.578576000
1	-2.589019000	-4.600168000	0.973674000
6	-0.300545000	-4.322033000	2.282349000
6	0.421448000	-1.978054000	2.011901000
6	-3.875965000	-0.843169000	-3.282537000
1	-2.665027000	0.938360000	-3.522239000
1	-4.861768000	-2.680369000	-2.825086000
6	-4.604659000	-4.377853000	-0.667346000
6	0.649704000	-4.528431000	3.272164000
1	-0.933340000	-5.152462000	1.983168000
6	1.367047000	-2.223438000	3.027702000
1	-4.488688000	-0.647123000	-4.157415000
1	-4.362516000	-5.401965000	-0.387802000
6	-5.891097000	-4.065675000	-0.930765000
6	1.480628000	-3.466388000	3.647166000
1	0.745774000	-5.501381000	3.745194000
1	2.025526000	-1.422820000	3.345010000
1	-6.146770000	-3.023717000	-1.107620000
6	-7.029834000	-4.988867000	-0.950072000
1	2.223545000	-3.611244000	4.428287000
6	-6.891325000	-6.391317000	-0.933382000
6	-8.332785000	-4.457390000	-0.994820000
6	-8.002896000	-7.226299000	-0.943558000
1	-5.902425000	-6.838283000	-0.926430000
6	-9.457044000	-5.279148000	-1.005269000
1	-8.464075000	-3.378879000	-1.014346000
6	-9.273178000	-6.656238000	-0.977017000
1	-7.902496000	-8.306260000	-0.934205000
1	-10.461517000	-4.871339000	-1.035531000

9	12.749077000	-2.347163000	-1.351219000
9	-3.922120000	11.894933000	-0.976522000
9	-10.351809000	-7.464502000	-0.990483000

Table S3: Summary of Physico-chemical properties of ligands (**2a-d**) and (**3a-d**) and complexes (**4a-d**) and (**5a-d**).

Compd.	R	R'	% Yield	Colour
2a	4-H	-F	42	Yellow solid
2b	4-F	-F	38	Yellow solid
2c	4-Cl	-F	48	Yellow solid
2d	4-OCH_3	-F	48	Brilliant Yellow solid
3a	4-H	-OCH_3	67	Yellow Oil
3b	4-F	-OCH_3	42	Brilliant Yellow solid
3c	4-Cl	-OCH_3	41	White solid
3d	4-OCH_3	-OCH_3	47	Bright Yellow solid
4a	4-H	-F	27	Brown solid
4b	4-F	-F	30	Brown Solid
4c	4-Cl	-F	25	Pink Solid
4d	4-OCH_3	-F	28	Dark Brown solid
5a	4-H	-OCH_3	53	Brown solid
5b	4-F	-OCH_3	57	Brown solid
5c	4-Cl	-OCH_3	42	Brown solid
5d	4-OCH_3	-OCH_3	45	Dark Brown solid

Table S4: Summary of photophysical data of ligands (**2a-d**) and (**3a-d**).

	Abs. λ_{max} (nm)[a]	(ε) × 10^4 Mol^{-1} cm^{-1}	λ_{em} (nm)[b] $CHCl_3$	λ_{em} (nm) DMF	λ_{em} (nm) CH_3OH	Quantum Yield (Φ)[c] $CHCl_3$	Quantum Yield (Φ) DMF	Quantum Yield (Φ) CH_3OH	Stokes Shift [d] ($CHCl_3$)
2a	265, 335	0.42, 0.29	449	409	449	0.23	0.11	0.23	184, 114
2b	278, 337	0.78, 0.25	454	411	439	0.27	0.14	0.27	176, 117
2c	267, 328	0.66, 0.25	454	406	462	0.30	0.27	0.30	187, 126
2d	293, 338	0.57, 0.45	478	442	482	0.16	0.15	0.16	185, 140
3a	261, 340	0.52, 0.24	465	452	450	0.31	0.14	0.30	204, 125
3b	262, 354	0.28, 0.17	470	438	480	0.45	0.14	0.23	208, 116
3c	266, 348	0.43, 0.35	460	454	440	0.23	0.06	0.47	193, 111
3d	278, 338	0.51, 0.19	455	389	470	0.40	0.35	0.25	177, 117

[a] Absorption spectra, [b]emission spectra, [c]luminescence quantum yields (Φ) and [d]Stokes-shifts were measured relative to chloroform solutions at 298 K. Wavelengths of excitation light are in the range of 350 – 385 nm.

Table S5: Summary of photophysical and electrochemical data of [Ir(**4a-d**)$_3$] and [Ir(**5a-d**)$_3$].

	Abs. λ_{max} (nm)[a]	(ε) × 10^4 Mol^{-1} cm^{-1}	λ_{em} (nm)[b] CH_3OH	Quantum Yield (Φ)[c] CH_3OH	E_{ox} (V)[d]	E_{re} (V)[e]
4a	258, 335, 396	1.65, 0.55, 0.13	499	0.59	0.41, 0.81	–0. 63
4b	260, 329, 392	1.90, 0.70, 0.11	530	0.47	0.22, 0.41, 0.76	–0.64
4c	265, 342	2.17, 0.43	489	0.70	0.21, 0.42, 0.76	–0.54, –0.73
4d	277, 340, 398	2.43, 0.62, 0.23	470	0.56	0.20, 0.41, 0.81	–0.67, –0.82
5a	258, 275, 336	0.71, 053, 0.27	500	0.62	0.17, 0.45, 0.77	–0.89
5b	260, 280, 324	1.53, 1.07, 0.60	530	0.57	0.42, 0.75	–0.57
5c	264, 324, 381	1.71, 0.62, 0.16	489	0.50	0.15, 0.42, 0.80	– 0.54, – 0.79
5d	284, 349, 380	1.11, 0.55, 0.61	545	0.58	0.20, 0.43, 0.78	–0.62

[a] Absorption spectra, [b]emission spectra, [c]luminescence quantum yields (Φ) were measured in methanol solutions at 298 K. Wavelengths of excitation light are in the range of 350 – 450 nm. [d&e]Electrochemical data versus Fc^+/Fc (Fc is Ferrocene) as internal standard.

Fig. S1: Cyclic voltammograms of [Ir(**4a-d**)$_3$] showing the quasi-reversible oxidation potential against ferrocene/ferrocenium.

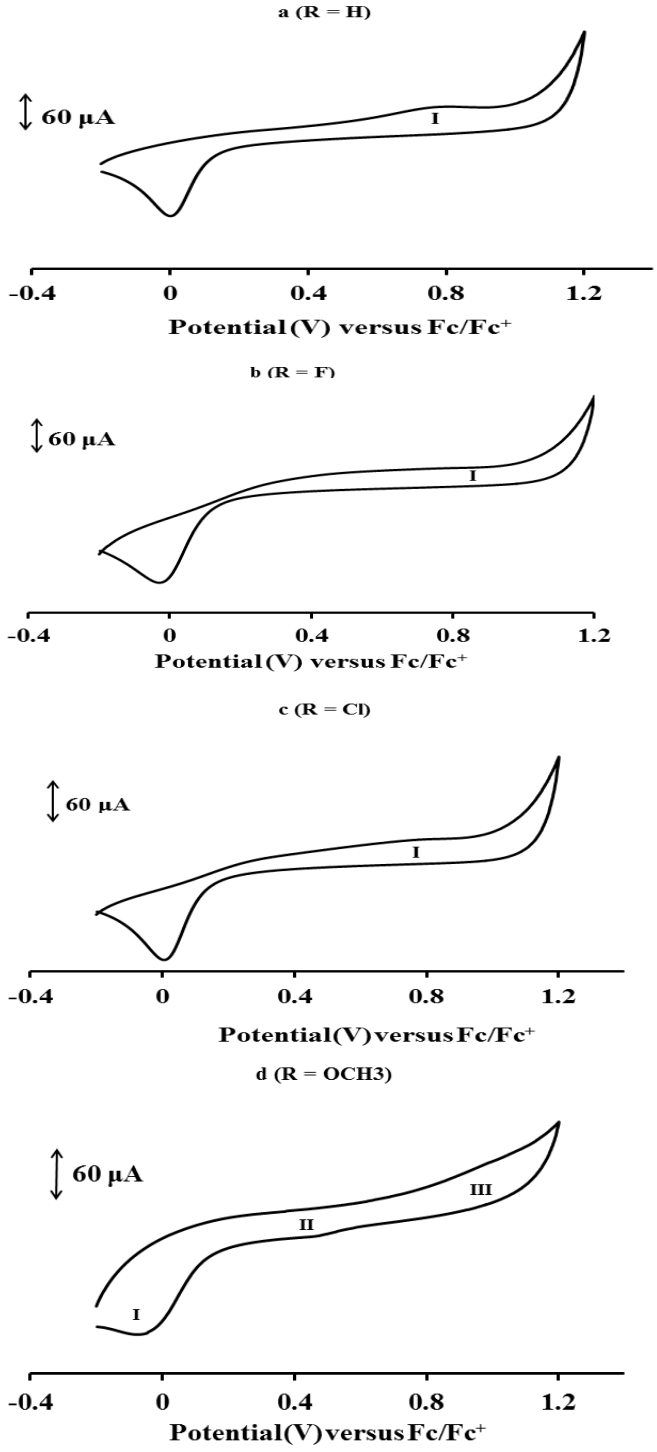

Fig. S2: Cyclic voltammograms of [Ir(**4a-d**)$_3$] showing the reversible reduction potential against ferrocene/ferrocenium.

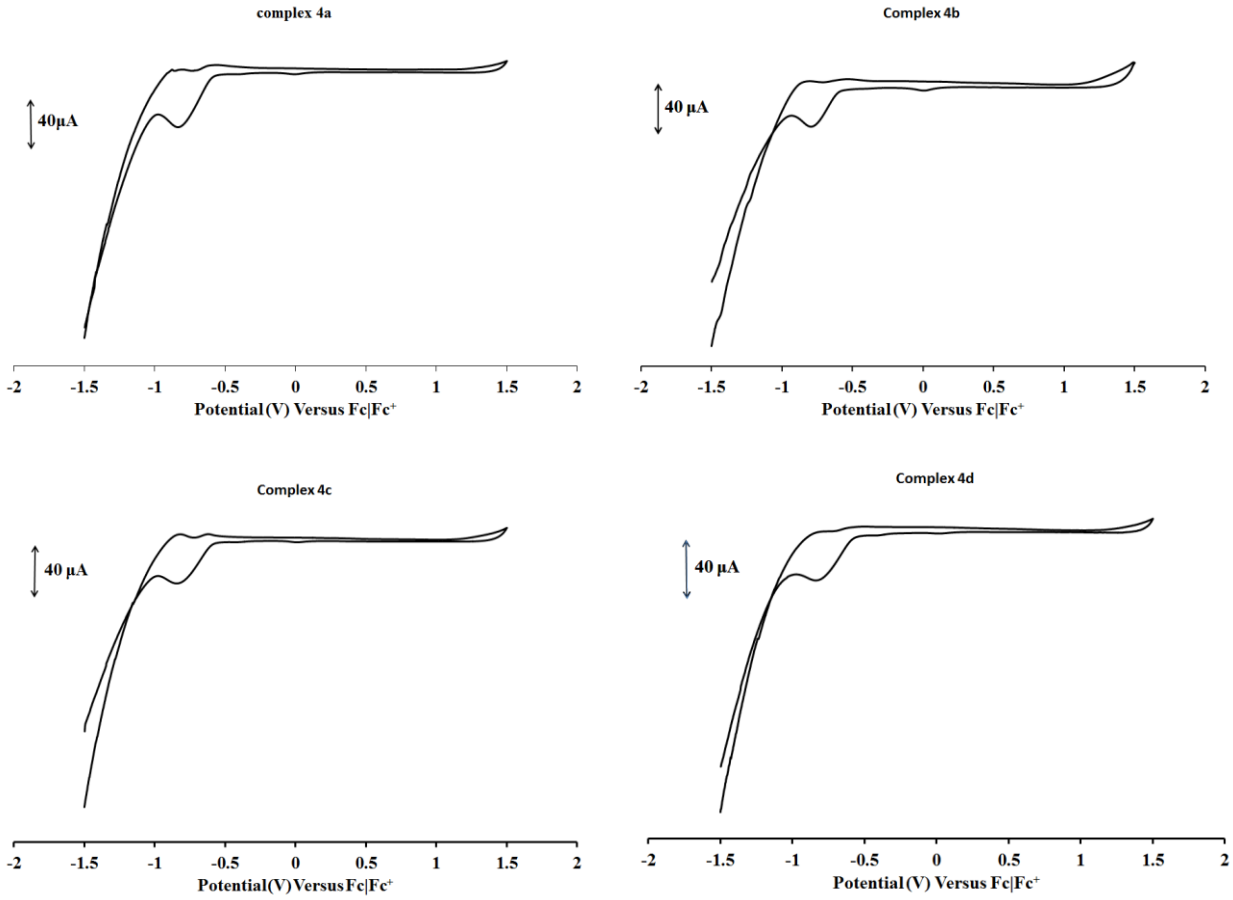

Fig. S3: Cyclic voltammograms of [Ir(**5a-d**)$_3$] showing the quasi-reversible oxidation potential against ferrocene/ferrocenium.

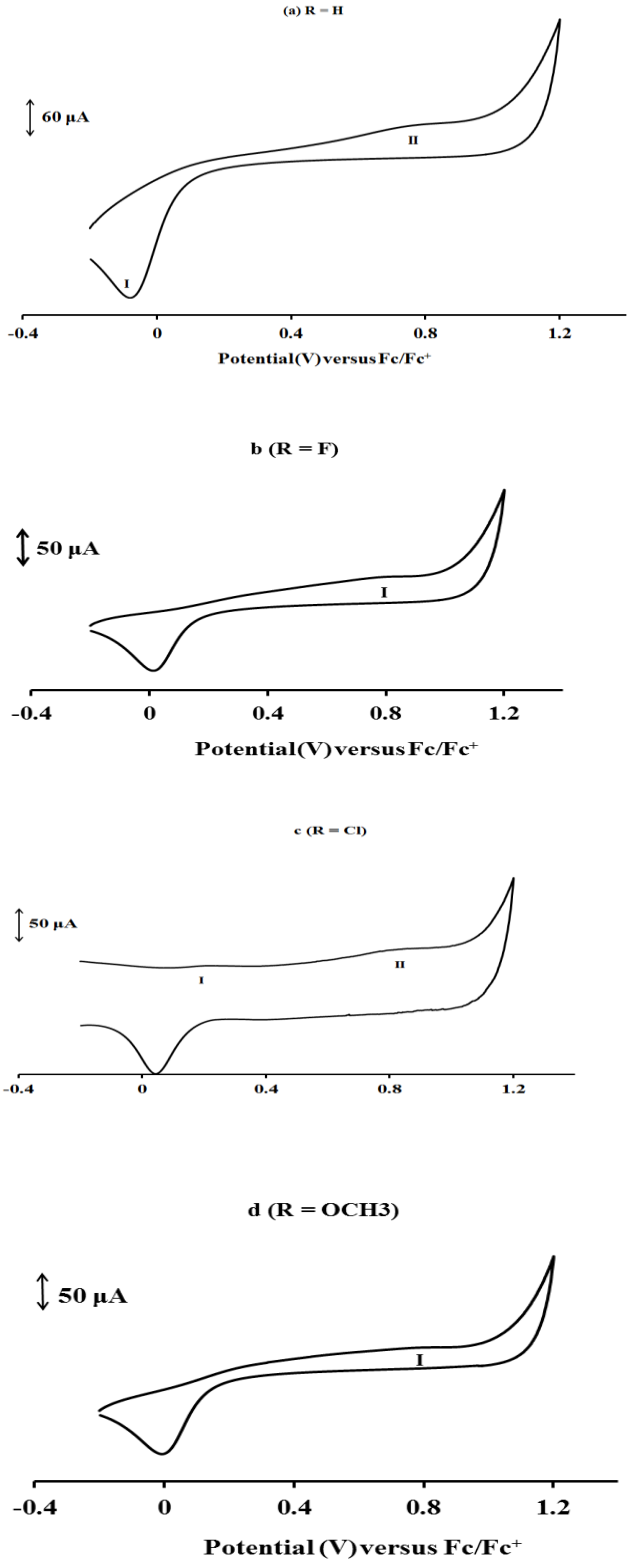

Fig. S4: Cyclic voltammograms of [Ir(**5a-d**)$_3$] showing the reversible reduction potential against ferrocene/ferrocenium.