

## Controlling the emission of blue-green Iridium (III) phosphorescent emitters

Muhammad T. Sajjad,<sup>a</sup> Nidhi Sharma,<sup>a,b</sup> Amlan K. Pal,<sup>b</sup> Kamrul Hasan,<sup>c,d</sup> Guohua Xie,<sup>a</sup> Lisa Sophie Kölln,<sup>a</sup> Garry S. Hanan,<sup>\*c</sup> Ifor D. W. Samuel,<sup>\*a</sup> Eli Zysman-Colman<sup>\*b</sup>

<sup>a</sup> Organic Semiconductor Centre, SUPA, School of Physics and Astronomy, University of St. Andrews, St. Andrews, Fife, KY16 9SS, UK; *Tel:* +44-1334 463114;  
*E-mail:* [ids@st-andrews.ac.uk](mailto:ids@st-andrews.ac.uk)

<sup>b</sup> Organic Semiconductor Centre, EaStCHEM School of Chemistry, University of St Andrews, St Andrews, Fife, UK, KY16 9ST, *Fax:* +44-1334 463808; *Tel:* +44-1334 463826;  
*E-mail:* [eli.zysman-colman@st-andrews.ac.uk](mailto:eli.zysman-colman@st-andrews.ac.uk); *URL:* <http://www.zysman-colman.com>

<sup>c</sup> Département de Chimie, Université de Montréal, 2900 Edouard-Montpetit, Montréal, Québec H3T-1J4, Canada.  
*E-mail:* [garry.hanan@umontreal.ca](mailto:garry.hanan@umontreal.ca); *Fax:* +1-514 343-2468; *Tel:* +1-514 343-7056

<sup>d</sup> Department of Chemistry, College of Sciences, University of Sharjah, P. O. Box 27272, Sharjah, United Arab Emirates  
*E-mail:* [khasan@sharjah.ac.ae](mailto:khasan@sharjah.ac.ae); *Fax:* +971 6 5053820; *Tel:* +971 6 5166768

### SUPPORTING INFORMATION

#### Table of contents

	<b>Pages</b>
<sup>1</sup> H, <sup>19</sup> F and <sup>13</sup> C NMR spectra of individual compounds and complexes	S2-S9
Photophysical characterisation	S10-S11
DFT calculations	S12-S20
OLED Device Fabrication	S20

# $^1\text{H}$ , $^{19}\text{F}$ and $^{13}\text{C}$ NMR spectra of individual compounds and complexes

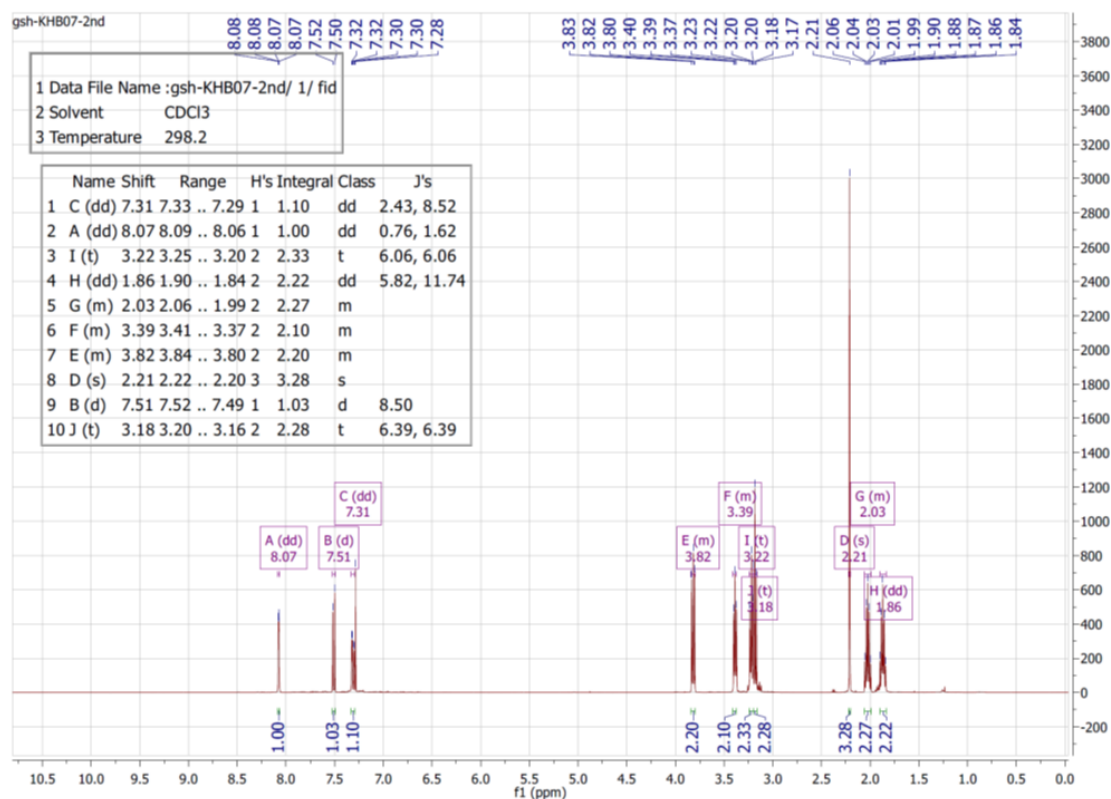


Figure S1.  $^1\text{H}$  NMR spectrum of L1 (**Me-gpy**) in CDCl<sub>3</sub> at 400 MHz.

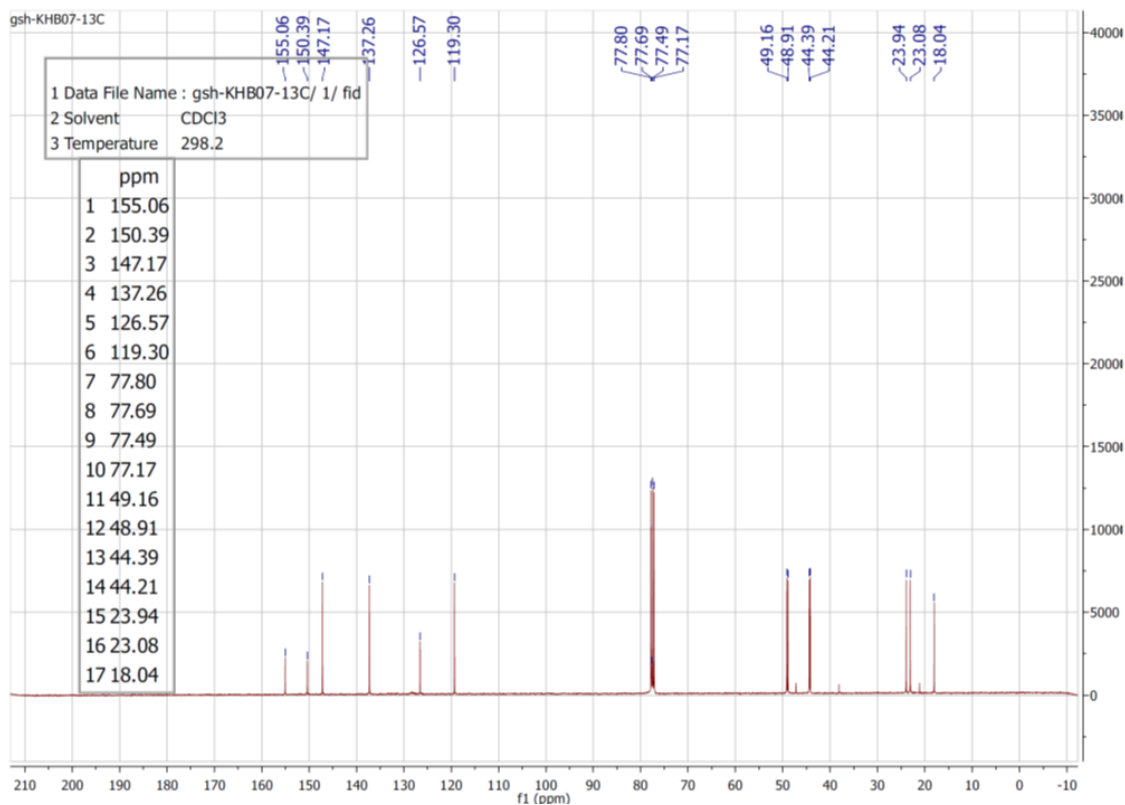


Figure S2.  $^{13}\text{C}$  NMR spectrum of L1 (**Me-gpy**) in CDCl<sub>3</sub> at 400 MHz.

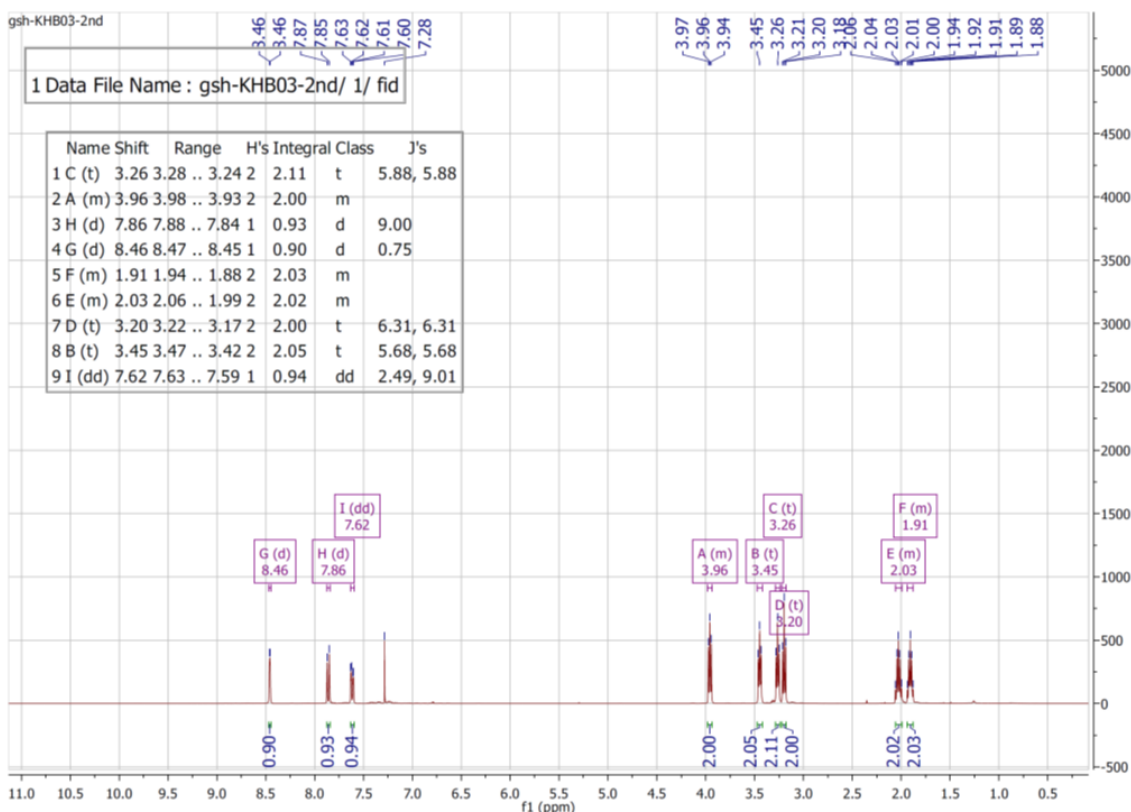


Figure S3.  $^1\text{H}$  NMR spectrum of **L2** ( $\text{CF}_3\text{-gpy}$ ) in  $\text{CDCl}_3$  at 400 MHz at r.t.

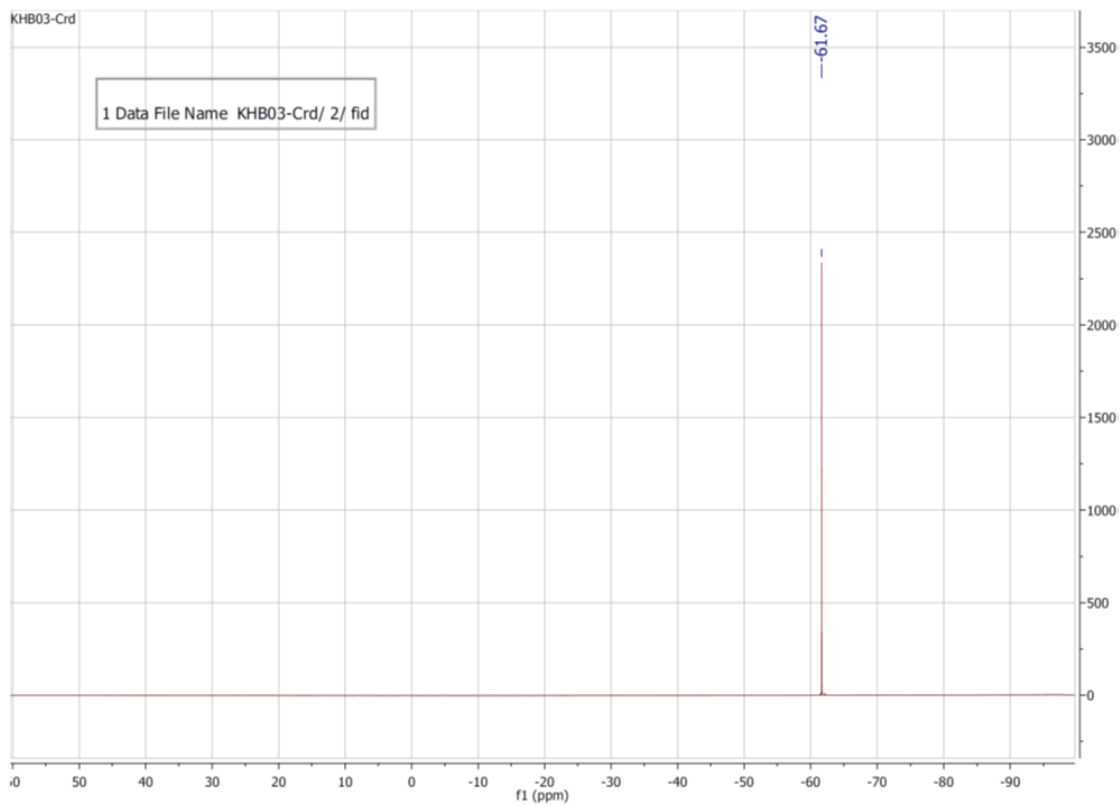


Figure S4.  $^{19}\text{F}$  NMR spectrum of **L2** ( $\text{CF}_3\text{-gpy}$ ) in  $\text{CDCl}_3$  at 400 MHz at r.t.

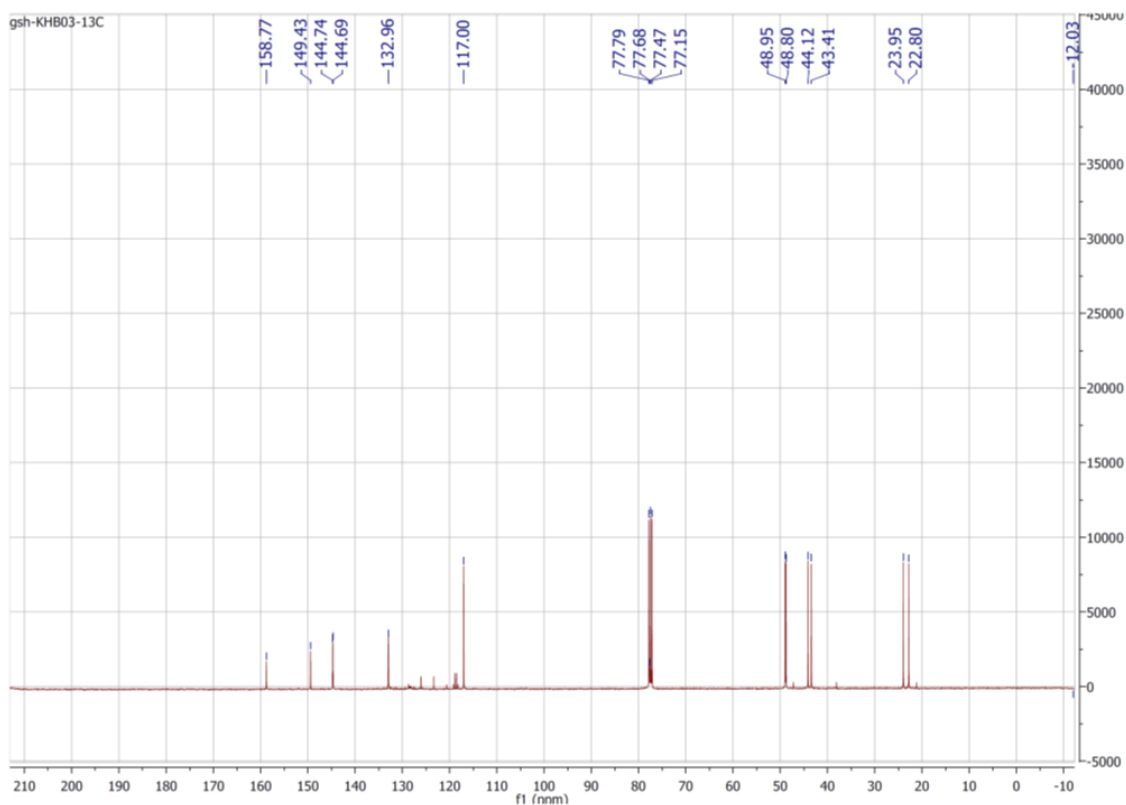


Figure S5.  $^{13}\text{C}$  NMR spectrum of **L2** ( $\text{CF}_3\text{-gpy}$ ) in  $\text{CDCl}_3$  at 400 MHz at r.t.

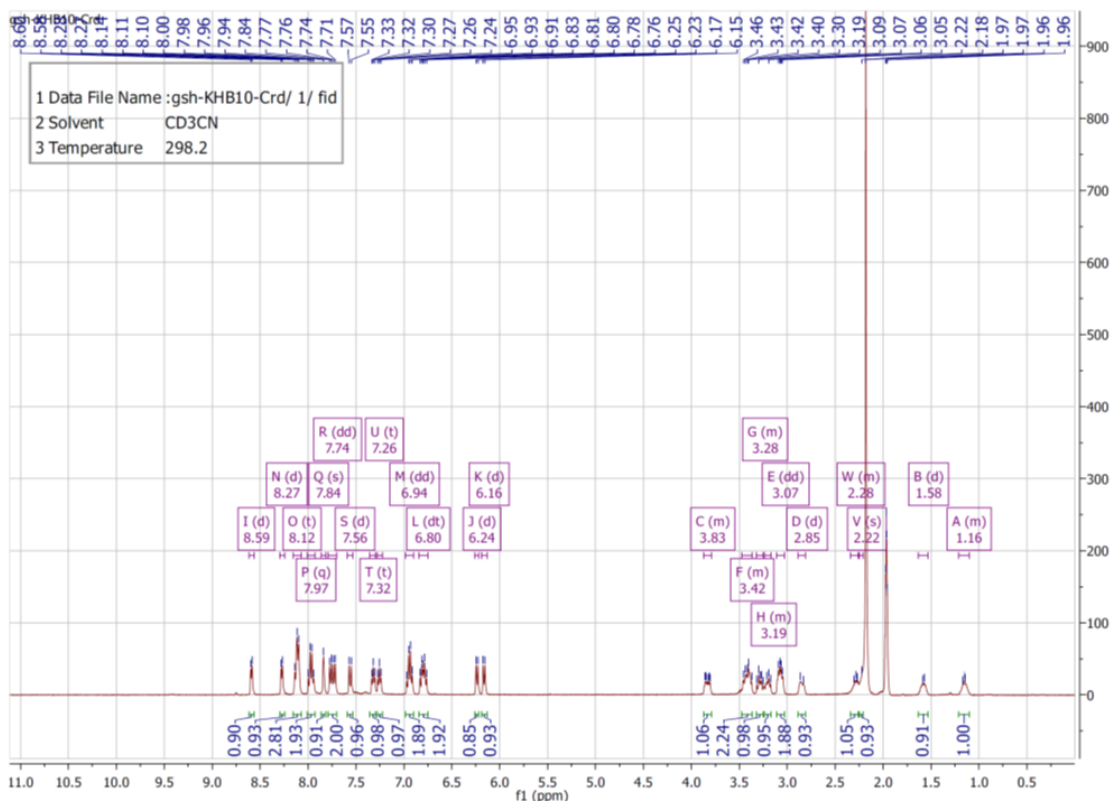


Figure S6.  $^1\text{H}$  NMR spectrum of  $[\text{Ir}(\text{ppy})_2(\text{CF}_3\text{-gpy})]\text{PF}_6$ , **1a** in Acetonitrile- $d_3$  at 400 MHz.

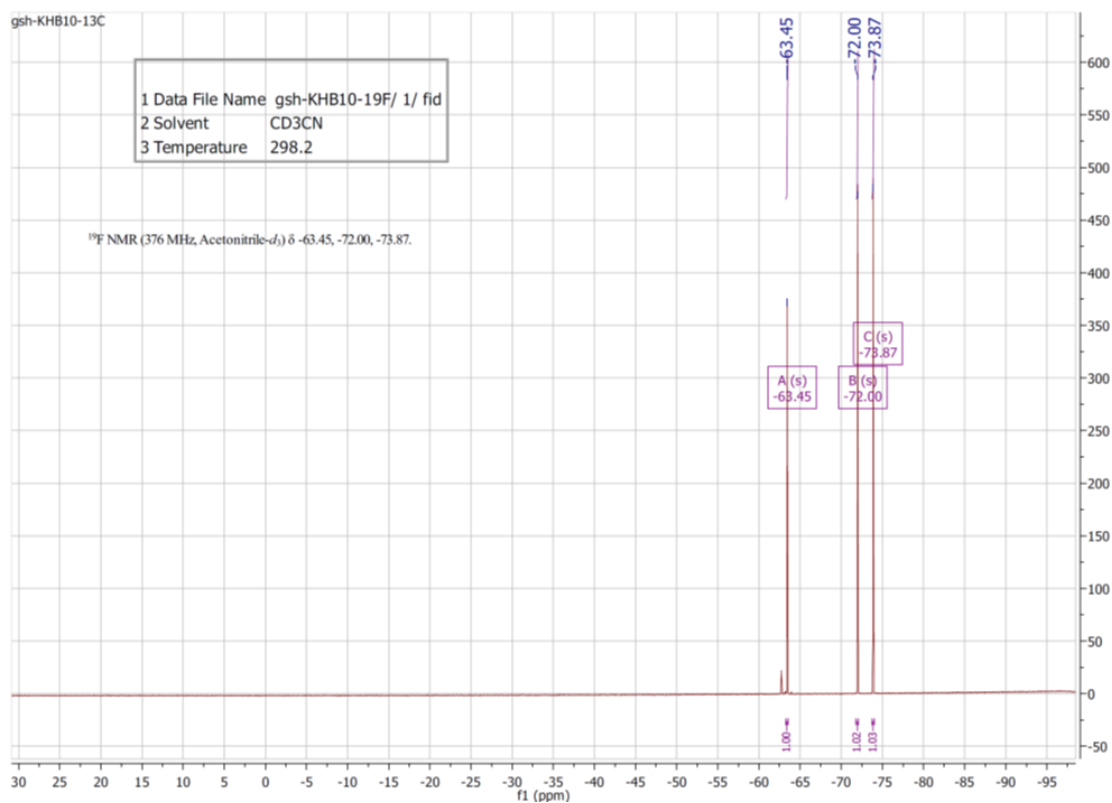


Figure S7.  $^{19}\text{F}$  NMR spectrum of  $[\text{Ir}(\text{ppy})_2(\text{CF}_3\text{-gpy})]\text{PF}_6$ , **1a** in Acetonitrile- $d_3$  at 400 MHz.

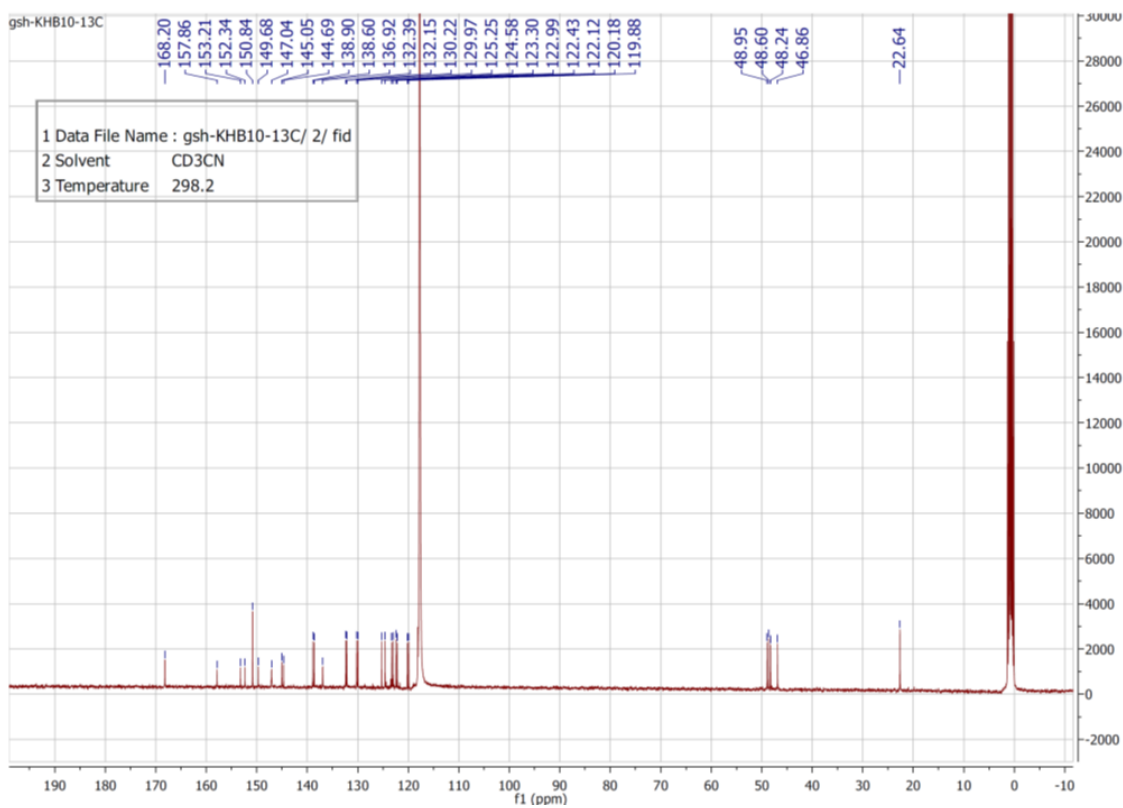


Figure S8.  $^{13}\text{C}$  NMR spectrum of  $[\text{Ir}(\text{ppy})_2(\text{CF}_3\text{-gpy})]\text{PF}_6$ , **1a** in Acetonitrile- $d_3$  at 400 MHz.

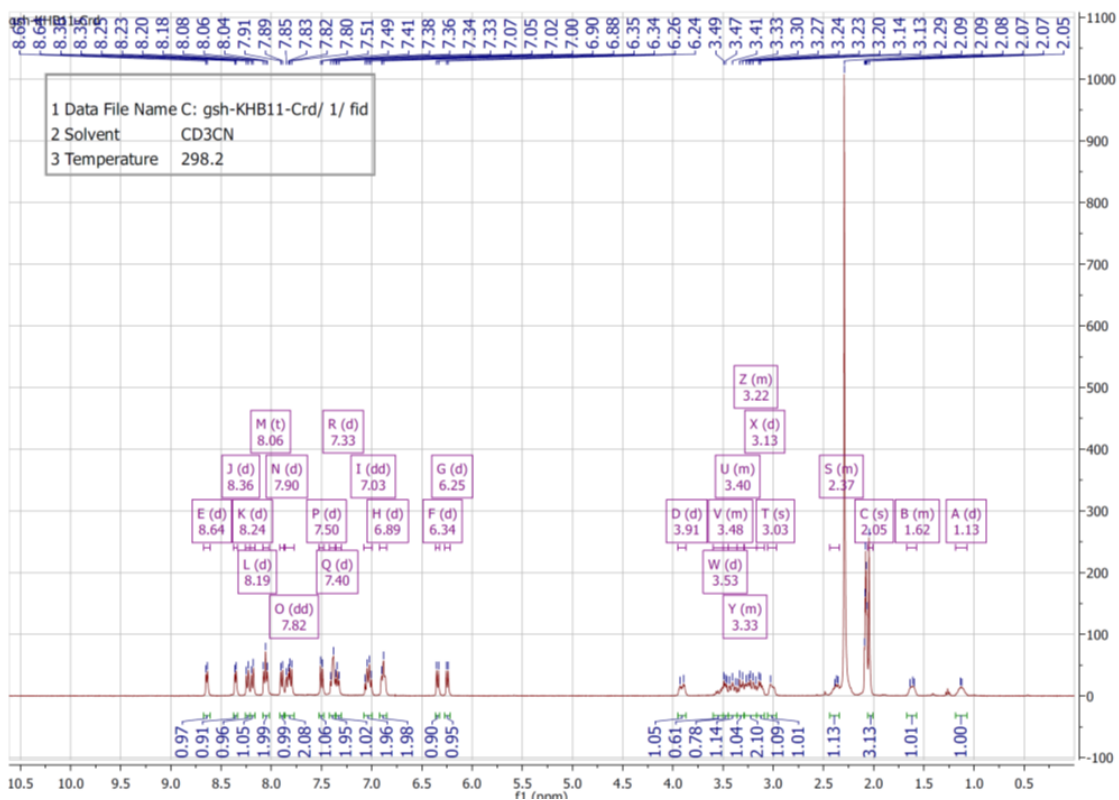


Figure S9.  $^1\text{H}$  NMR spectrum of  $[\text{Ir}(\text{ppy})_2(\text{Me-gpy})]\text{PF}_6$ , **1b** in Acetonitrile- $d_3$  at 400 MHz.

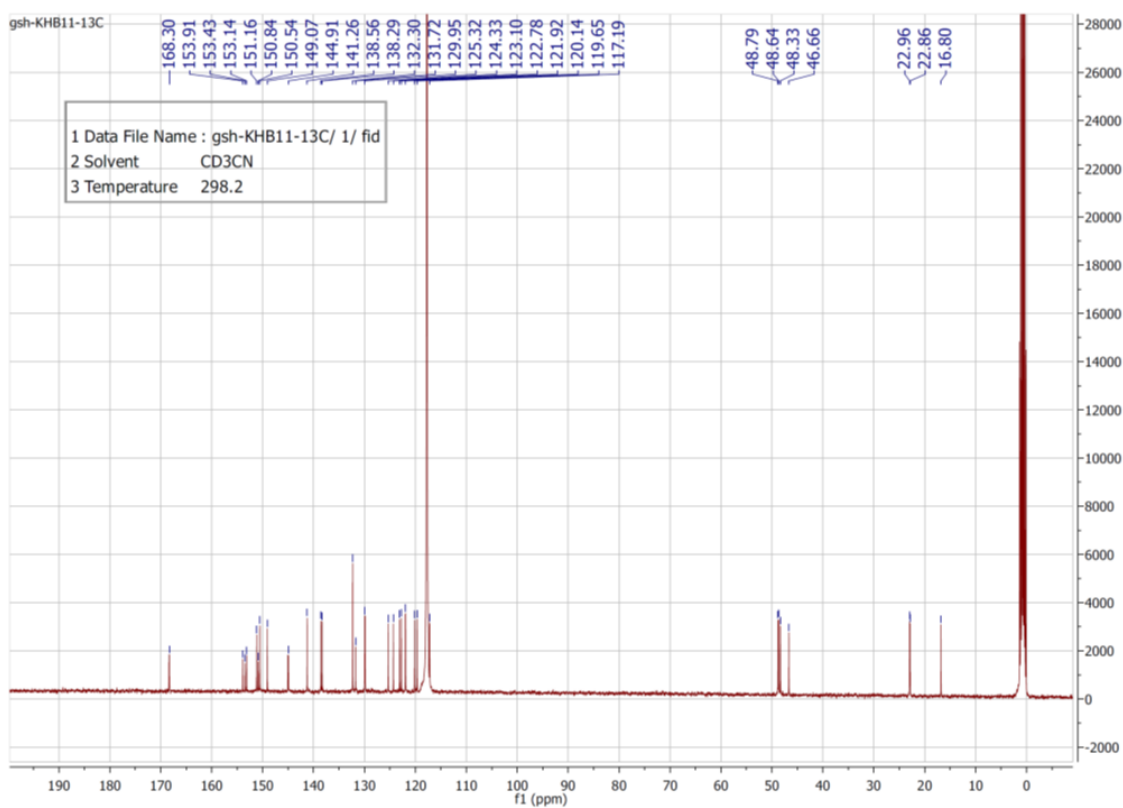


Figure S10.  $^{13}\text{C}$  NMR spectrum of  $[\text{Ir}(\text{ppy})_2(\text{Me-gpy})]\text{PF}_6$ , **1b** in Acetonitrile- $d_3$  at 400 MHz.

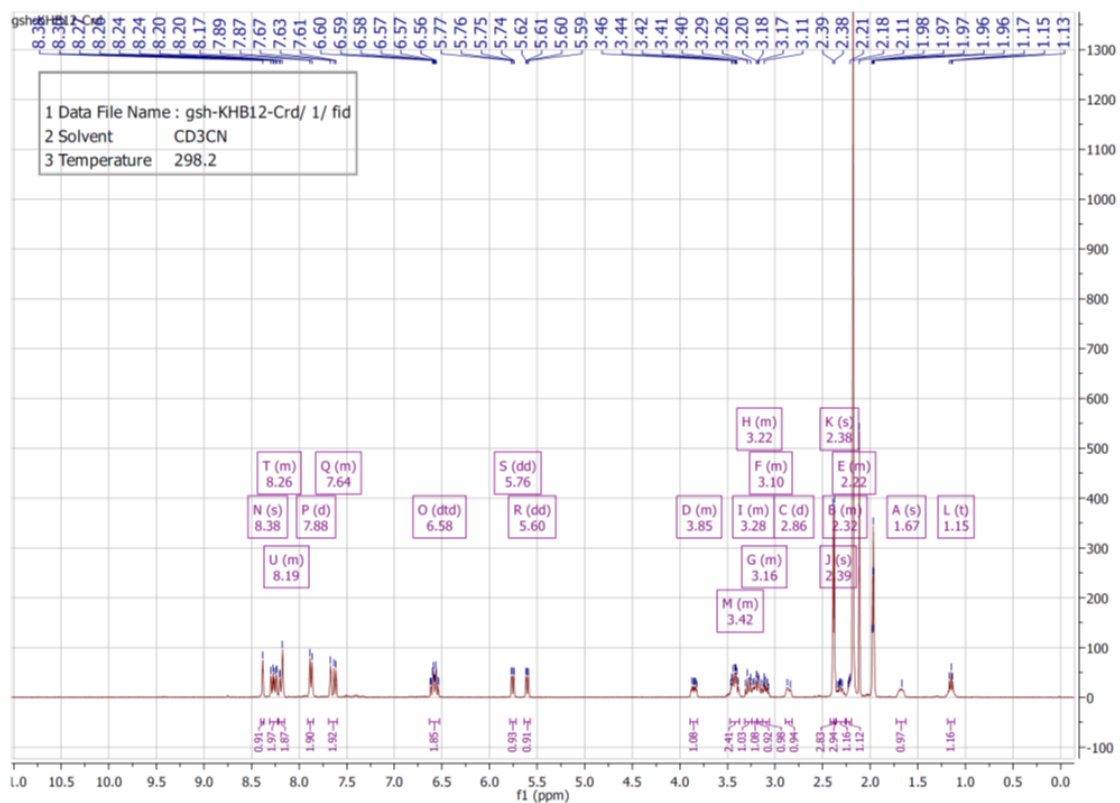


Figure S11.  $^1\text{H}$  NMR spectrum of  $[\text{Ir}(\text{dFMeppy})_2(\text{CF}_3\text{-gpy})]\text{PF}_6$ , **2a** in Acetonitrile- $d_3$  at 400 MHz.

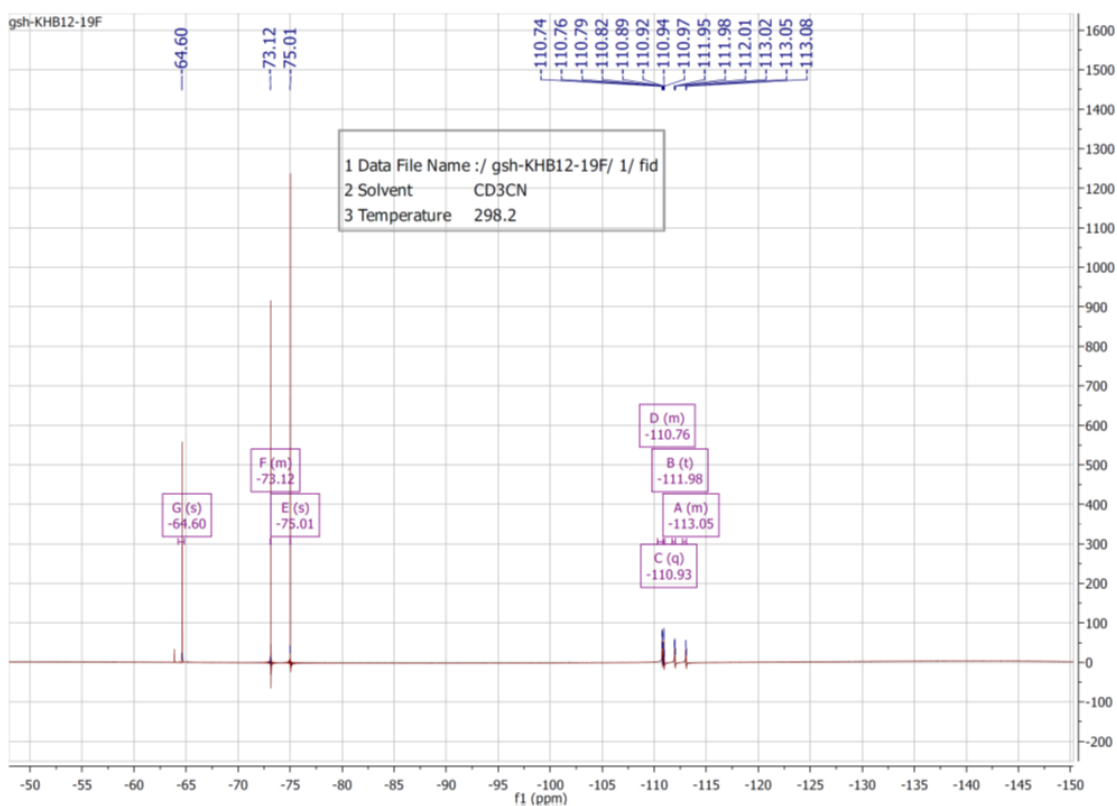


Figure S12.  $^{19}\text{F}$  NMR spectrum of  $[\text{Ir}(\text{dFMeppy})_2(\text{CF}_3\text{-gpy})]\text{PF}_6$ , **2a** in Acetonitrile- $d_3$  at 400 MHz.

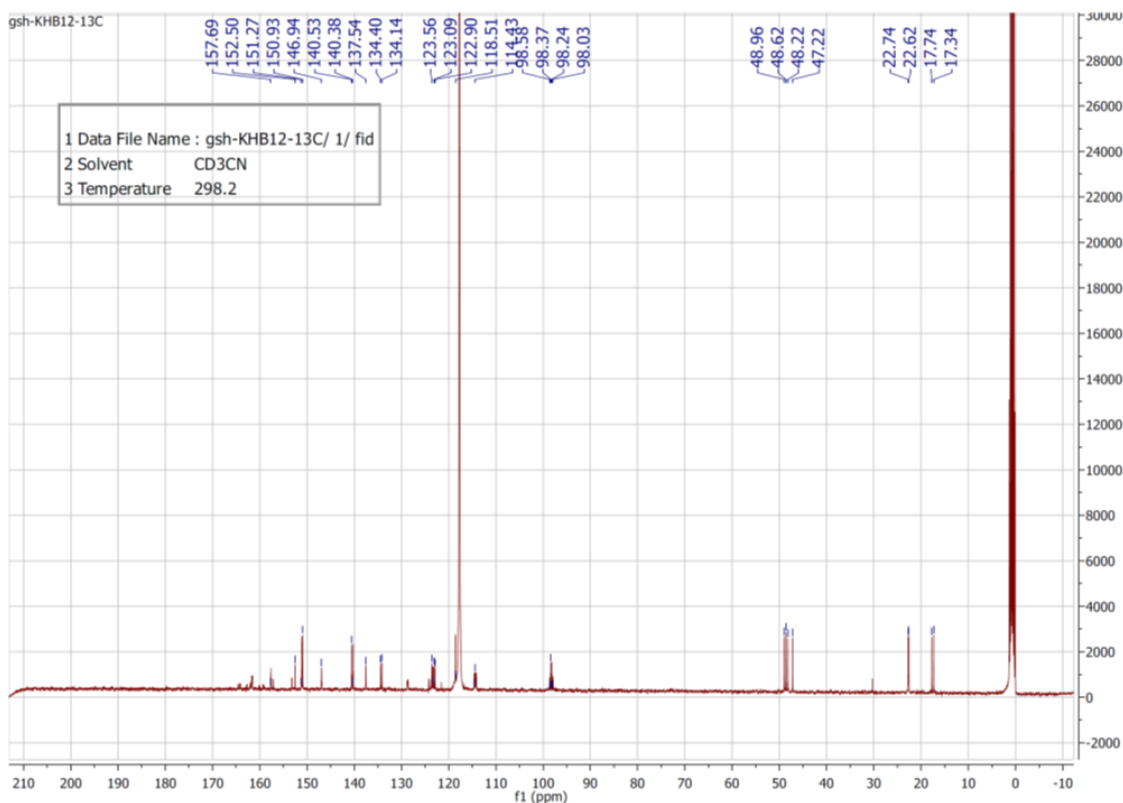


Figure S13.  $^{13}\text{C}$  NMR spectrum of  $[\text{Ir}(\text{dFMeppy})_2(\text{CF}_3\text{-gpy})]\text{PF}_6$ , **2a** in Acetonitrile- $d_3$  at 400 MHz.

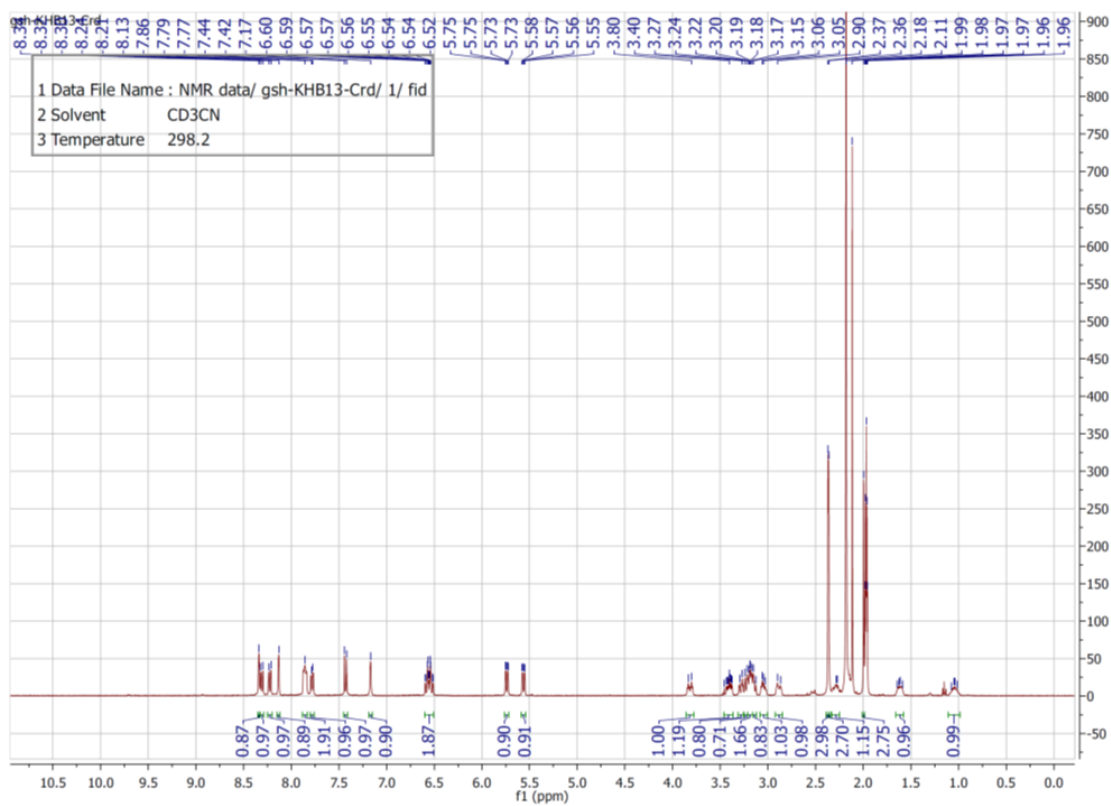


Figure S14.  $^1\text{H}$  NMR spectrum of  $[\text{Ir}(\text{dFMeppy})_2(\text{Me-gpy})]\text{PF}_6$ , **2b** in Acetonitrile- $d_3$  at 400 MHz.



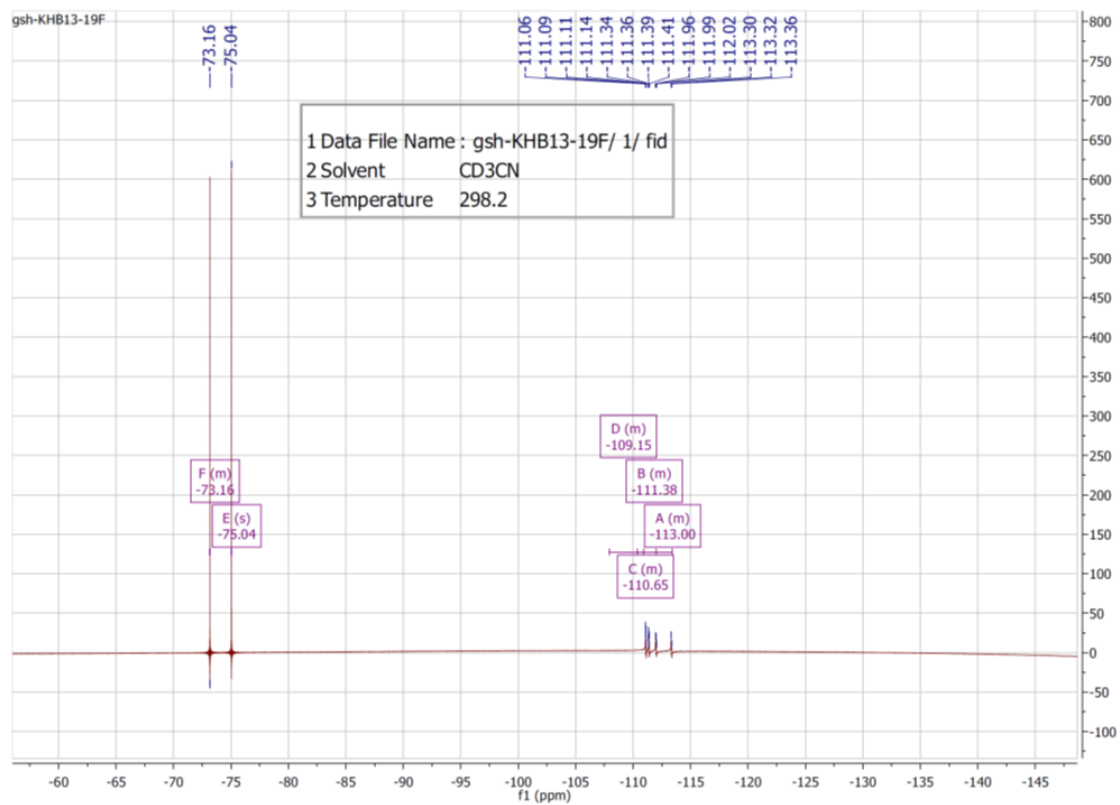


Figure S15.  $^{19}\text{F}$  NMR spectrum of  $[\text{Ir}(\text{dFMeppy})_2(\text{Me-gpy})]\text{PF}_6$ , **2b** in Acetonitrile- $d_3$  at 400 MHz.

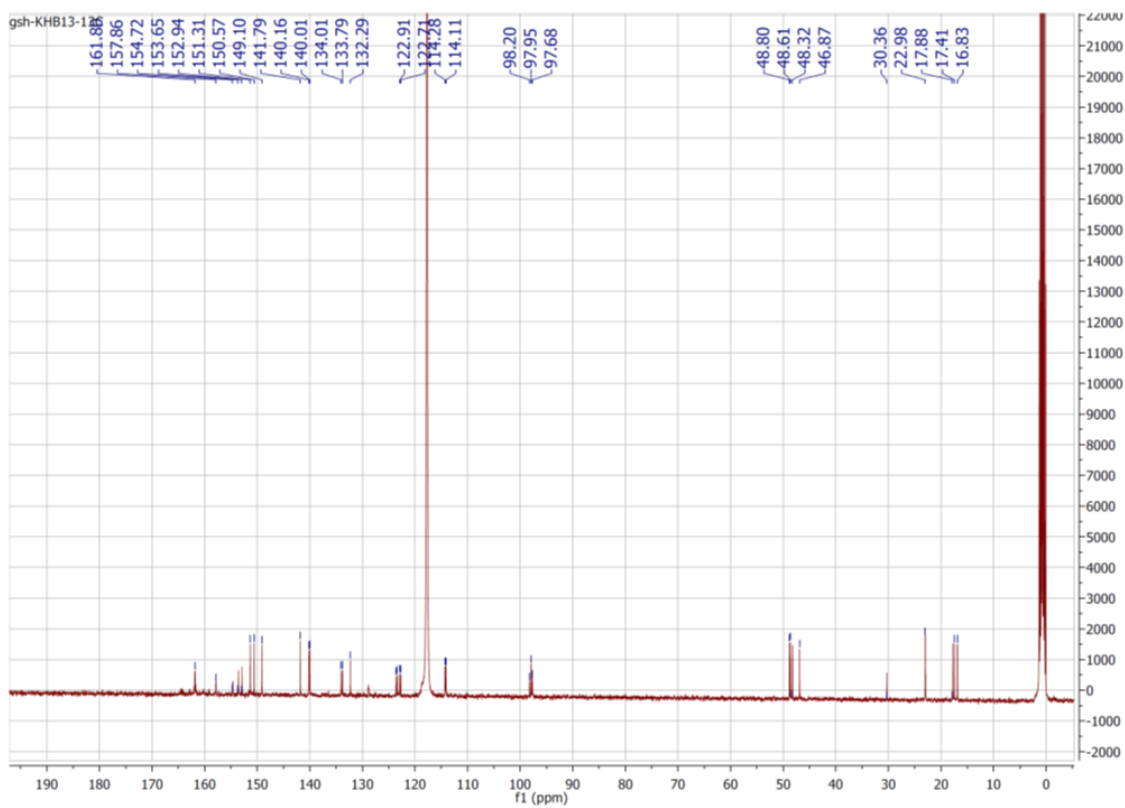


Figure S16.  $^{13}\text{C}$  NMR spectrum of  $[\text{Ir}(\text{dFMeppy})_2(\text{Me-gpy})]\text{PF}_6$ , **2b** in Acetonitrile- $d_3$  at 400 MHz at r.t.

## Photophysical Characterisation

### Aerated and Degassed Solution

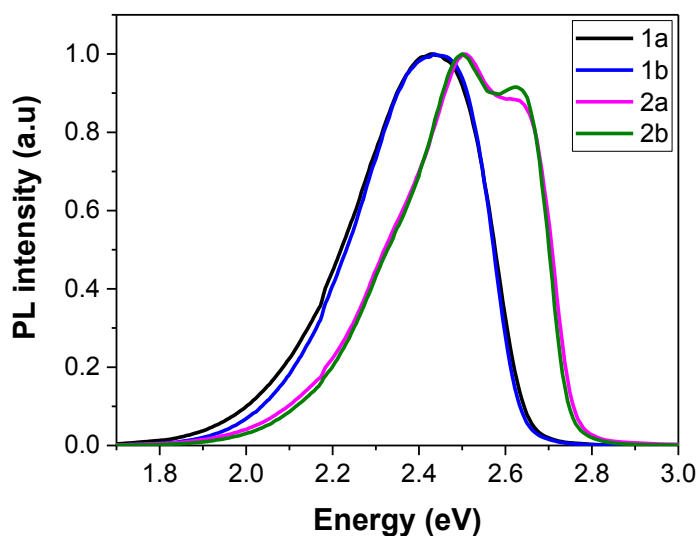
The photophysical properties of the complexes **1a–2b** in aerated and degassed MeCN solution were investigated using steady-state techniques by measuring UV-Vis absorption spectra, photoluminescence (PL) spectra, PL quantum yields ( $\Phi_{PL}$ ), and time-resolved PL spectra using Time Correlated Single Photon Counting (TCSPC).

A Cary 300-UV-Vis spectrophotometer was used to obtain the absorption spectra of samples in the wavelength range of 200 - 800 nm. The absorbance of the samples was adjusted to be close to 0.1 at 360 nm for all investigated complexes. The PL spectra were obtained at an excitation wavelength of 360 nm using an Edinburgh instruments FLS980 fluorimeter. Solution photoluminescence quantum yield ( $\Phi_{PL}$ ) was measured using the optically dilute method described by Demas and Crosby<sup>1</sup>  $\Phi_{PL}(x) = \Phi_{PL}(r) \left( \frac{A_r(\lambda_r)}{A_x(\lambda_x)} \right) \left( \frac{I(\lambda_r)}{I(\lambda_x)} \right) \left( \frac{n_x}{n_r} \right)^2 \left( \frac{D_x}{D_r} \right)$ , where  $A(\lambda)$  is absorbance at excitation wavelength of 360 nm,  $I(\lambda)$  is relative intensity of exciting light,  $n$  is the refractive index of the solvents and  $D$  is the integrated area under the corrected emission spectra (at an excitation wavelength of 360 nm). Here  $x$  and  $r$  refer to unknown and reference solutions, respectively. For  $\Phi_{PL}$  measurements, the solutions were prepared by mixing complexes in MeCN ( $n = 1.344$ ), whereas the reference solution was prepared by diluting quinine sulfate dihydrate in 0.5M H<sub>2</sub>SO<sub>4</sub> ( $n = 1.35$ ).  $\Phi_{PL}$  of 54.6% was used for reference solution.<sup>2</sup> For lifetime measurements, the sample was excited with a 375 nm PicoQuant picosecond laser and PL emission was detected at a detection wavelength of 512 nm for **1a, 1b** and 470 nm for **2a, 2b**.

PL decay traces in aerated solution are given in **Fig. 2(b)** (main manuscript). The PL decays were fitted with a single exponential decay and resulting lifetimes are given in Table 1 (main manuscript). The radiative ( $k_r$ ) and non-radiative decay ( $k_{nr}$ ) rate constants calculated using eq. **S1** and **S2** are also given in Table 1 (main manuscript)

$$k_r = \frac{\Phi_{PL}}{\tau} \quad (\text{S1})$$

$$k_{nr} = \frac{(1 - \Phi_{PL})}{\tau} \quad (\text{S2})$$



**Figure S18:** Emission spectra of MeCN degassed solutions, following excitation at 360 nm.

The PL spectra of degassed solutions are shown in **Fig. S18**. The PL spectra are qualitatively similar to aerated solution except with increased PL intensity in degassed solution. Huang Rhys factors were estimated by taking the ratio of the (0, 1) and (0, 0) peaks. PL decays of **1b** and **2b** in degassed solution follow mono-exponential decay whereas PL decays of **1a** and **2a** have biexponential decays (**Fig. 3**). The details about the fitting parameters are given in Table **S1**.

**Table S1:** The fitting parameters for time-resolved luminescence of complexes measured in degassed MeCN solution.

Materials	A <sub>1</sub>	$\tau_1(\mu\text{s})$	A <sub>2</sub>	$\tau_2(\mu\text{s})$
<b>1a</b>	0.87	0.09	0.13	1.60
<b>1b</b>	1.0	1.90	-	-
<b>2a</b>	0.93	0.11	0.07	0.98
<b>2b</b>	1.0	2.60	-	-

### Solid-state thin film

We measured the PL lifetime of 2 wt% of the complexes doped into 98 wt% PMMA as thin films at different temperatures and in different environments (air, vacuum). Table **S2** shows the fitted lifetime parameters.

**Table S2:** The fitting parameters for time-resolved luminescence of 2wt% of **2a** in PMMA (**Fig. 6(b)**) at various temperatures.

Environment	A <sub>1</sub>	$\tau_1(\mu\text{s})$	A <sub>2</sub>	$\tau_2(\mu\text{s})$
RT-air	0.09	0.82	0.91	2.80
RT-vacuum	0.10	0.92	0.90	3.00
150K-vacuum	1.0	3.20	-	-
77K-vacuum	1.0	3.70	-	-

In conjunction with transient PL measurements, we measured the  $\Phi_{\text{PL}}$  of complexes **2a** and **2b** in air and under N<sub>2</sub>. For films,  $\Phi_{\text{PL}}$  was measured using an integrating sphere and excitation wavelength of 380 nm and the results are compared with solution in Table **S3**. The  $\Phi_{\text{PL}}$  of **2a** increased by more than 30 times compared to degassed solution and increases even further when measured under N<sub>2</sub>. In the case of **2b**,  $\Phi_{\text{PL}}$  also increases on going from solution to film, but by a much smaller amount.

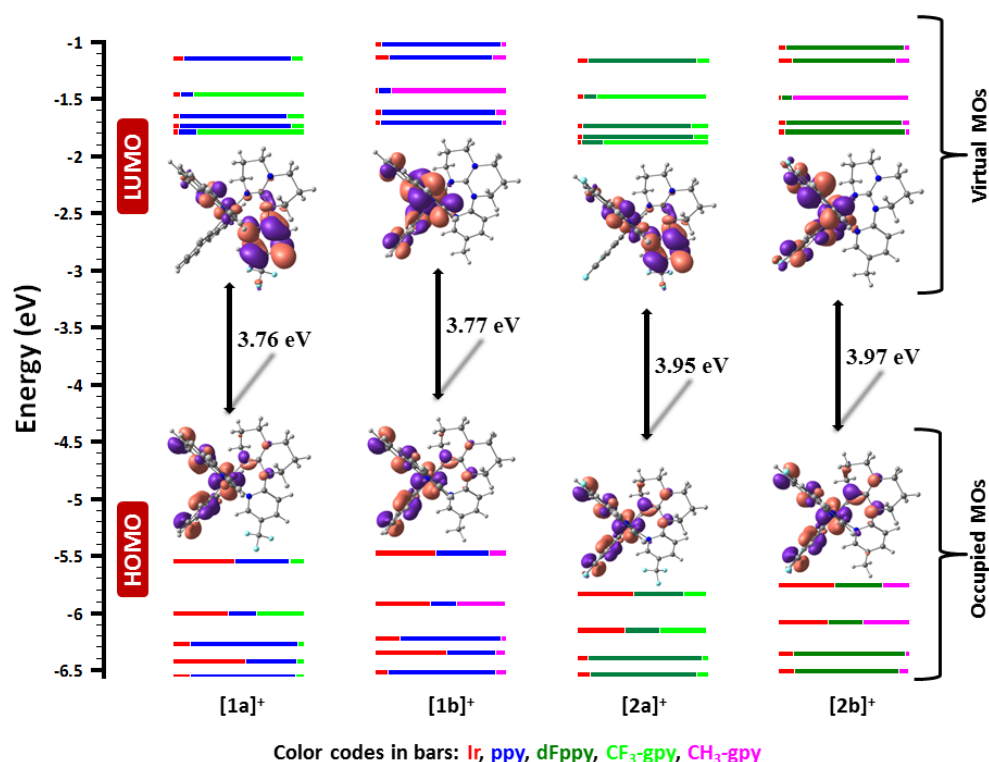
**Table S3:** Comparison of  $\Phi_{\text{PL}}$  values of solution (before degassing, after degassing) and solid-state films (in air and under N<sub>2</sub>) of **2a** and **2b**. For solution, an excitation wavelength of 360 nm was used and for solid-state, an excitation wavelength of 380 nm was used.

Materials	PLQY(%) Solution Before degassing	PLQY(%) Solution, after degassing	PLQY(%) Film RT-Air	PLQY(%) Film RT-N <sub>2</sub>
<b>2a</b>	1.0	1.7	65.9	72.4
<b>2b</b>	1.2	65.6	82.7	88.6

## DFT Calculations:

Computational details:

All calculations were performed with the Gaussian09, revision D.01<sup>3</sup> suite of programs employing the DFT method, the Becke three-parameter hybrid functional,<sup>4</sup> and Lee-Yang-Parr's gradient-corrected correlation functional (B3LYP).<sup>5</sup> Singlet and triplet ground state geometry optimizations for **[1a]<sup>+</sup>**, **[1b]<sup>+</sup>**, **[2a]<sup>+</sup>** and **[2b]<sup>+</sup>** were carried out at the (R)B3LYP and (U)B3LYP levels in the gas phase, using their respective crystallographic structures as starting points. All elements except Iridium were assigned the 6-31G(d,p) basis set.<sup>6</sup> The double- $\zeta$  quality SBKJC VDZ ECP basis set<sup>7</sup> with an effective core potential was employed for the Ir(III)-ion. Vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima and there are only positive eigenvalues, except frequency mode no. 1 for **1a** and **2a**, which were found to be rotational motion of the  $-\text{CF}_3$  group around the C-C bond of the pyridine ring of the guanidylpyridine (gpy) unit. The electronic distribution and localization of the singlet excited states were visualized using the electron density difference maps (ED-DMs).<sup>8</sup> *Gausssum 2.2* and *Chemission* were employed to visualize the absorption spectra (simulated with Gaussian distribution with a full-width at half maximum (fwhm) set to  $3000\text{ cm}^{-1}$ ) and to calculate the fractional contributions of various groups to each molecular orbital. All calculated structures and Kohn-Sham orbitals were visualized with ChemCraft.<sup>9</sup>



**Figure S20:** Calculated frontier MO energies of **[1a]<sup>+</sup>**, **[1b]<sup>+</sup>**, **[2a]<sup>+</sup>** and **[2b]<sup>+</sup>**, obtained from DFT [(B3LYP/SBKJC-VDZ for Ir(III)) and (6-31g\*\* for C,H,N,F) with CPCM(CH<sub>3</sub>CN) and 0.5 eV threshold of degeneracy (orbitals are isocontoured at 0.03). Kohn-Sham MOs of **[1a]<sup>+</sup>**, **[1b]<sup>+</sup>**, **[2a]<sup>+</sup>** and **[2b]<sup>+</sup>** are also shown.

**Table S4.** Vibrational modes and their associated energies contributing to deactivation in complex **2a** but less in complex **2b**.

Vibrational mode no.	Status	Energy associated (cm <sup>-1</sup> )	Nature of the mode
115	Present in <b>2a</b> but absent in <b>2b</b>	1029.62	Symmetric stretching of the C-C and C-N bonds in pyridine part of C <sup>^</sup> N ligand couples with wagging mode of C and N atoms of the pyridine ring of the gpy ligand
121	Strongly present in <b>2a</b> but very weakly present in <b>2b</b>	1054.21 (for <b>2a</b> ) 1090.90 (for <b>2b</b> )	Asymmetric stretching modes of the Ir-N <sub>dFppy</sub> bonds couple with the asymmetric stretching modes of the C-N and C-C bonds of the pyridine ring of the gpy ligand
148	Present in <b>2a</b> but very weakly present in <b>2b</b>	1293.30 (for <b>2a</b> ) 1315.06 (for <b>2b</b> )	Asymmetric stretching modes of the Ir-C <sub>dFppy</sub> bonds couple with the asymmetric stretching modes of the C-N and C-C bonds of the pyridine ring of the gpy ligand
149	Present in <b>2a</b> but absent in <b>2b</b>	1294.48	Asymmetric stretching modes of the Ir-C <sub>dFppy</sub> bonds couple with the asymmetric stretching modes of the C-N and C-C bonds of the pyridine ring of the gpy ligand
151	Present in <b>2a</b> but absent in <b>2b</b>	1311.82	Asymmetric wagging modes of the Ir-N <sub>dFppy</sub> bonds couple with the wagging mode of the C-N of the pyridine ring of the gpy ligand
153	Present in <b>2a</b> but very weakly present in <b>2b</b>	1317.10 (for <b>2a</b> ) 1340.73 (for <b>2b</b> )	Asymmetric wagging modes of the Ir-N <sub>dFppy</sub> bonds couple with the rocking mode of the C-N bonds of the pyridine ring of the gpy ligand
169	Present in <b>2a</b> but absent in <b>2b</b>	1450.11	Asymmetric stretching modes of C-C bonds in phenyl part of the C <sup>^</sup> N ligand couple with rocking mode of the C-H bond adjacent to pyridine N-atom of the gpy ligand.

**Table S5.** Optimized Atomic coordinates obtained from DFT calculations of [1a]<sup>+</sup>

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	77	0	-0.299272	-0.503853	-0.031980
2	7	0	0.913081	-1.211374	-1.582674
3	7	0	-1.526542	-0.059153	1.598792
4	7	0	1.172939	1.161529	0.225251
5	6	0	3.147761	3.137383	0.194210
6	7	0	-0.540387	2.823468	0.083045
7	7	0	-2.500112	3.116895	-1.184572
8	7	0	-1.334831	1.065618	-1.265838
9	6	0	0.754321	-1.927677	0.965511
10	6	0	1.665614	-2.661658	0.156266
11	6	0	2.462984	-3.685094	0.700409
12	1	0	3.157746	-4.238774	0.075782
13	6	0	2.369384	-3.997542	2.050584
14	1	0	2.983249	-4.787238	2.471550
15	6	0	1.477979	-3.285347	2.860537
16	1	0	1.399294	-3.527708	3.917002
17	6	0	0.683603	-2.269890	2.324568
18	1	0	-0.004808	-1.747880	2.981926
19	6	0	1.728286	-2.260750	-1.248485
20	6	0	0.930157	-0.723103	-2.839741
21	1	0	0.279722	0.122174	-3.021608
22	6	0	1.726676	-1.257657	-3.840102
23	1	0	1.701150	-0.831911	-4.836581
24	6	0	2.546803	-2.345781	-3.526282
25	1	0	3.179881	-2.797207	-4.283655
26	6	0	2.548230	-2.839901	-2.230238
27	1	0	3.183677	-3.676607	-1.967159
28	6	0	-1.768675	-1.870010	-0.311825
29	6	0	-2.852851	-1.768379	0.602287
30	6	0	-3.979954	-2.601327	0.489519
31	1	0	-4.805961	-2.514777	1.189554
32	6	0	-4.045208	-3.553866	-0.520369
33	1	0	-4.913651	-4.199000	-0.606296
34	6	0	-2.978182	-3.679566	-1.416223
35	1	0	-3.018412	-4.431491	-2.199814
36	6	0	-1.858239	-2.851064	-1.311118
37	1	0	-1.046124	-2.978706	-2.020530
38	6	0	-2.688828	-0.778966	1.664623
39	6	0	-1.228198	0.818536	2.577693
40	1	0	-0.270546	1.314903	2.487538

41	6	0	-2.072821	1.064559	3.649177
42	1	0	-1.781239	1.773091	4.416116
43	6	0	-3.283807	0.367277	3.713881
44	1	0	-3.973273	0.532071	4.535927
45	6	0	-3.584606	-0.555602	2.723320
46	1	0	-4.505249	-1.124434	2.770868
47	6	0	0.826841	2.463124	0.104359
48	6	0	1.807424	3.469303	0.066864
49	1	0	1.520621	4.502190	-0.083968
50	6	0	3.493015	1.794231	0.343212
51	6	0	4.925424	1.365843	0.543636
52	6	0	2.478870	0.846560	0.335453
53	1	0	2.701165	-0.208929	0.435469
54	6	0	-0.944552	4.050635	0.795483
55	1	0	-0.119832	4.367345	1.432624
56	1	0	-1.785085	3.801303	1.454895
57	6	0	-1.354928	5.114057	-0.214459
58	1	0	-1.625148	6.052507	0.278184
59	1	0	-0.520119	5.325324	-0.891045
60	6	0	-2.556663	4.572869	-0.980864
61	1	0	-3.476440	4.786152	-0.420522
62	1	0	-2.659122	5.061550	-1.958254
63	6	0	-3.705963	2.597037	-1.858245
64	1	0	-3.769811	3.075152	-2.844636
65	1	0	-4.581682	2.925283	-1.284194
66	6	0	-3.675361	1.082056	-2.005235
67	1	0	-4.380674	0.776546	-2.783645
68	1	0	-3.973347	0.586768	-1.076193
69	6	0	-2.246952	0.672898	-2.350966
70	1	0	-2.168745	-0.404400	-2.489281
71	1	0	-1.942492	1.158507	-3.290736
72	6	0	-1.470573	2.290092	-0.825926
73	1	0	3.914337	3.903501	0.156200
74	9	0	5.776687	2.265072	0.013789
75	9	0	5.216947	1.248687	1.853581
76	9	0	5.161232	0.170996	-0.032945

---

**Table S6.** Optimized Atomic coordinates obtained from DFT calculations of [1b]<sup>+</sup>

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	77	0	0.379026	-0.180801	0.000920
2	7	0	1.684968	0.623467	-1.419849
3	7	0	-0.720280	-1.154964	1.483910
4	7	0	-0.197472	1.919051	0.514309
5	6	0	-0.736992	4.640390	0.739824
6	7	0	-2.524730	1.434885	0.220148
7	7	0	-3.814309	0.113446	-1.235787
8	7	0	-1.456714	-0.015041	-1.287898
9	6	0	2.117597	-0.227007	1.052760
10	6	0	3.259459	0.207161	0.323006
11	6	0	4.538084	0.221928	0.909524
12	1	0	5.404232	0.554390	0.344616
13	6	0	4.706009	-0.191160	2.225129
14	1	0	5.692199	-0.182301	2.678184
15	6	0	3.593380	-0.618892	2.958170
16	1	0	3.719716	-0.944996	3.987205
17	6	0	2.323216	-0.637863	2.379035
18	1	0	1.485715	-0.987084	2.974787
19	6	0	3.001689	0.659098	-1.043446
20	6	0	1.322115	1.076165	-2.636881
21	1	0	0.261374	1.044721	-2.848860
22	6	0	2.237792	1.556086	-3.560404
23	1	0	1.896869	1.903989	-4.528749
24	6	0	3.590741	1.571907	-3.208124
25	1	0	4.339562	1.930900	-3.907244
26	6	0	3.967091	1.129016	-1.948434
27	1	0	5.009790	1.142616	-1.655271
28	6	0	0.713391	-2.111650	-0.520330
29	6	0	0.013946	-3.066766	0.267144
30	6	0	0.097923	-4.442416	-0.011463
31	1	0	-0.442978	-5.165035	0.592950
32	6	0	0.883324	-4.894215	-1.065295
33	1	0	0.950725	-5.956039	-1.279374
34	6	0	1.592248	-3.969085	-1.838908
35	1	0	2.217980	-4.317465	-2.656376
36	6	0	1.508337	-2.601221	-1.568034
37	1	0	2.077428	-1.912259	-2.184852
38	6	0	-0.753421	-2.519599	1.383721
39	6	0	-1.327672	-0.546013	2.522029
40	1	0	-1.223386	0.530751	2.559865
41	6	0	-2.028294	-1.242014	3.495265
42	1	0	-2.490988	-0.705746	4.316005
43	6	0	-2.102106	-2.635097	3.392434
44	1	0	-2.640994	-3.216548	4.133955
45	6	0	-1.460405	-3.268614	2.338667
46	1	0	-1.486051	-4.348280	2.255010
47	6	0	-1.462957	2.364380	0.379016
48	6	0	-1.751758	3.735139	0.466577
49	1	0	-2.763310	4.088160	0.307000
50	6	0	0.575940	4.185239	0.915449



51	6	0	1.714650	5.117915	1.236083
52	6	0	0.780601	2.815853	0.770362
53	1	0	1.773039	2.393777	0.879672
54	6	0	-3.784624	1.695306	0.939422
55	1	0	-3.608904	2.490246	1.663068
56	1	0	-4.054273	0.794820	1.505977
57	6	0	-4.879589	2.041701	-0.061352
58	1	0	-5.822493	2.279184	0.439751
59	1	0	-4.583360	2.920592	-0.643585
60	6	0	-5.070557	0.827974	-0.963636
61	1	0	-5.753306	0.115348	-0.481761
62	1	0	-5.529277	1.109947	-1.920164
63	6	0	-4.020048	-1.093336	-2.058679
64	1	0	-4.439363	-0.774061	-3.022175
65	1	0	-4.780816	-1.713403	-1.567415
66	6	0	-2.728034	-1.868783	-2.274630
67	1	0	-2.839409	-2.531521	-3.137954
68	1	0	-2.489630	-2.492154	-1.407572
69	6	0	-1.603737	-0.858889	-2.483584
70	1	0	-0.655522	-1.361897	-2.667283
71	1	0	-1.830183	-0.232455	-3.360124
72	6	0	-2.568306	0.483430	-0.806102
73	1	0	-0.964039	5.700920	0.805628
74	1	0	1.803953	5.905753	0.480675
75	1	0	1.559670	5.610513	2.202032
76	1	0	2.666613	4.583962	1.281820

**Table S7.** Optimized Atomic coordinates obtained from DFT calculations of [2a]<sup>+</sup>

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	77	0	-0.264059	-0.177326	-0.088916
2	7	0	0.819579	-0.951519	-1.701762
3	7	0	-1.399419	0.328538	1.589484
4	7	0	1.401591	1.277765	0.189734
5	6	0	3.601406	2.999656	0.171194
6	7	0	-0.098087	3.138522	0.175821
7	7	0	-2.035698	3.727235	-1.019189
8	7	0	-1.143876	1.549775	-1.211228
9	6	0	0.637346	-1.755701	0.817518
10	6	0	1.423136	-2.562720	-0.060843
11	6	0	2.072270	-3.694440	0.464814
12	9	0	2.823521	-4.481819	-0.336582
13	6	0	1.988333	-4.058426	1.797497
14	1	0	2.500807	-4.935464	2.171668
15	6	0	1.218669	-3.248108	2.626209
16	9	0	1.119172	-3.576418	3.923619
17	6	0	0.548569	-2.118649	2.165397
18	1	0	-0.041718	-1.551914	2.875412
19	6	0	1.504713	-2.113581	-1.449359
20	6	0	0.861865	-0.397954	-2.930415
21	1	0	0.319305	0.531392	-3.042139
22	6	0	1.552894	-0.969946	-3.986549

23	1	0	1.552527	-0.488095	-4.957463
24	6	0	2.233293	-2.168633	-3.758764
25	1	0	2.780049	-2.654531	-4.560709
26	6	0	2.214145	-2.735773	-2.492134
27	1	0	2.743270	-3.655253	-2.293007
28	6	0	-1.882847	-1.355061	-0.388832
29	6	0	-2.928602	-1.169432	0.564562
30	6	0	-4.120306	-1.897768	0.406824
31	9	0	-5.138763	-1.733658	1.281384
32	6	0	-4.322776	-2.796642	-0.626530
33	1	0	-5.251599	-3.344917	-0.718826
34	6	0	-3.277050	-2.966220	-1.528271
35	9	0	-3.441190	-3.835226	-2.537538
36	6	0	-2.075819	-2.268912	-1.430468
37	1	0	-1.310284	-2.465268	-2.171797
38	6	0	-2.637511	-0.254805	1.665139
39	6	0	-0.970283	1.123493	2.589769
40	1	0	0.035526	1.508885	2.483440
41	6	0	-1.745721	1.420225	3.699603
42	1	0	-1.349134	2.055955	4.483027
43	6	0	-3.026522	0.866206	3.777090
44	1	0	-3.667760	1.073365	4.628048
45	6	0	-3.469725	0.028607	2.763527
46	1	0	-4.446542	-0.428041	2.814529
47	6	0	1.214114	2.614839	0.133900
48	6	0	2.309797	3.496174	0.102654
49	1	0	2.146416	4.561465	0.002267
50	6	0	3.784175	1.618197	0.257851
51	6	0	5.166232	1.028104	0.391216
52	6	0	2.663555	0.802405	0.244913
53	1	0	2.761757	-0.274351	0.293183
54	6	0	-0.324662	4.375823	0.948446
55	1	0	0.549871	4.559104	1.571213
56	1	0	-1.172159	4.205751	1.623828
57	6	0	-0.624290	5.523950	-0.005777
58	1	0	-0.761898	6.466511	0.531732
59	1	0	0.211834	5.659179	-0.699928
60	6	0	-1.904253	5.169475	-0.754037
61	1	0	-2.774891	5.468629	-0.155985
62	1	0	-1.971734	5.709003	-1.707128
63	6	0	-3.311659	3.393619	-1.682302
64	1	0	-3.331881	3.913664	-2.648924
65	1	0	-4.126108	3.808540	-1.075577
66	6	0	-3.479541	1.894230	-1.884116
67	1	0	-4.236199	1.711915	-2.652776
68	1	0	-3.817391	1.407093	-0.964193
69	6	0	-2.124191	1.319636	-2.284265
70	1	0	-2.187172	0.247636	-2.464846
71	1	0	-1.781204	1.798624	-3.213826
72	6	0	-1.112008	2.764309	-0.722421
73	1	0	4.453968	3.669675	0.135784
74	9	0	6.041623	1.681434	-0.397094
75	9	0	5.610507	1.127366	1.658652
76	9	0	5.180218	-0.274315	0.049924

---

**Table S8.** Optimized Atomic coordinates obtained from DFT calculations of [2b]<sup>+</sup>

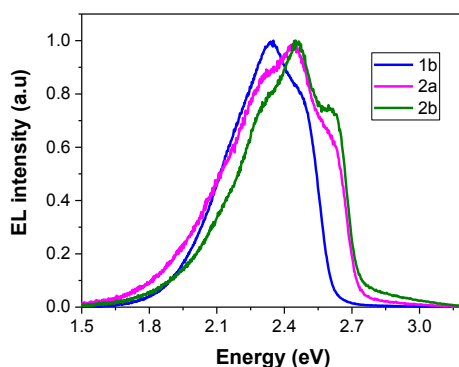
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	77	0	-0.142633	-0.039157	-0.058060
2	7	0	-1.245020	-0.921480	-1.598399
3	7	0	0.725250	0.981067	1.542126
4	7	0	0.672426	-2.067490	0.382242
5	6	0	1.557221	-4.702149	0.534669
6	7	0	2.926410	-1.266720	0.275670
7	7	0	4.115279	0.265789	-1.052353
8	7	0	1.764762	0.119142	-1.224658
9	6	0	-1.926250	-0.281285	0.881353
10	6	0	-2.956996	-0.814274	0.047487
11	6	0	-4.238481	-1.000257	0.595802
12	9	0	-5.238155	-1.503857	-0.163329
13	6	0	-4.546564	-0.695699	1.910317
14	1	0	-5.543660	-0.850203	2.302390
15	6	0	-3.519031	-0.183097	2.696227
16	9	0	-3.788051	0.120215	3.976273
17	6	0	-2.232153	0.027904	2.211306
18	1	0	-1.495208	0.443053	2.888408
19	6	0	-2.568838	-1.151856	-1.320918
20	6	0	-0.743541	-1.246387	-2.806566
21	1	0	0.314261	-1.060665	-2.936829
22	6	0	-1.520360	-1.785547	-3.819880
23	1	0	-1.070828	-2.024887	-4.776728
24	6	0	-2.877733	-1.999227	-3.569067
25	1	0	-3.524021	-2.409471	-4.338676
26	6	0	-3.399438	-1.688635	-2.320796
27	1	0	-4.443621	-1.855506	-2.104122
28	6	0	-0.707341	1.855249	-0.499942
29	6	0	-0.183106	2.844387	0.385738
30	6	0	-0.471581	4.195982	0.130534
31	9	0	0.022883	5.161906	0.937887
32	6	0	-1.251241	4.611939	-0.935464
33	1	0	-1.457813	5.661310	-1.102687
34	6	0	-1.759975	3.621259	-1.769246
35	9	0	-2.524534	3.994038	-2.807805
36	6	0	-1.503433	2.266879	-1.574529
37	1	0	-1.941064	1.558661	-2.268249
38	6	0	0.583633	2.344428	1.523778
39	6	0	1.337216	0.383586	2.583909
40	1	0	1.370858	-0.697667	2.549428
41	6	0	1.875063	1.092937	3.646460
42	1	0	2.347899	0.564124	4.466236
43	6	0	1.772630	2.486566	3.629505
44	1	0	2.180482	3.080582	4.441350
45	6	0	1.125867	3.110198	2.572054
46	1	0	1.016122	4.183956	2.550924
47	6	0	1.992839	-2.334877	0.321907
48	6	0	2.456772	-3.658617	0.376395
49	1	0	3.515073	-3.866561	0.278935
50	6	0	0.185347	-4.433925	0.627055
51	6	0	-0.836748	-5.524557	0.817269

52	6	0	-0.191047	-3.098214	0.524337
53	1	0	-1.236770	-2.818420	0.573545
54	6	0	4.170266	-1.400623	1.055892
55	1	0	4.056934	-2.238337	1.742742
56	1	0	4.295796	-0.496363	1.664452
57	6	0	5.349672	-1.571346	0.107226
58	1	0	6.287648	-1.710221	0.652573
59	1	0	5.197007	-2.457036	-0.518411
60	6	0	5.434582	-0.308792	-0.743524
61	1	0	6.004569	0.459819	-0.205135
62	1	0	5.965310	-0.496937	-1.685544
63	6	0	4.214690	1.528962	-1.808430
64	1	0	4.712540	1.310123	-2.762254
65	1	0	4.872098	2.207444	-1.250295
66	6	0	2.850441	2.157475	-2.055332
67	1	0	2.921691	2.874521	-2.878432
68	1	0	2.500057	2.699910	-1.171772
69	6	0	1.867655	1.034505	-2.371709
70	1	0	0.875607	1.428692	-2.586683
71	1	0	2.211259	0.485239	-3.261601
72	6	0	2.904868	-0.268589	-0.705748
73	1	0	1.920420	-5.725379	0.574448
74	1	0	-0.767594	-6.272111	0.020082
75	1	0	-0.681658	-6.047230	1.767142
76	1	0	-1.853137	-5.124015	0.817313

---

## Device Fabrication and Testing

The electrical and optical properties of EL devices using **1b**, **2a** and **2b** were investigated by fabricating OLEDs with the active layer deposited from solution. The device architecture is given in **Fig. 7** of the main text. The irradiance, current, and voltage of the device were measured under an ambient environment with a Keithley 2400 SourceMeter and 2000 Multimeter connected to a calibrated silicon photodiode. The electroluminescence spectrum was captured by an Andor DV420-BV CCD spectrometer. For a comparison between PL and EL, we plotted the EL spectra against energy.



**Figure S21:** Electroluminescence spectra of complexes **1b**, **2a** and **2b**.

## References

1. G. A. Crosby and J. N. Demas, *J. Phys. Chem.*, 1971, **75**, 991-1024.

2. W. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229-235.
3. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.
4. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
5. C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B: Condens. Matter*, 1988, **37**, 785–789.
6. A. D. McLean, G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639–5648.
7. J. S. Binkley, J. A. Pople, W. J. Hehre, *J. Am. Chem. Soc.*, 1980, **102**, 939.
8. W. R. Browne, N. M. O'Boyle, J. J. McGarvey, J. G. Vos, *Chem. Soc. Rev.*, 2005, **34**, 641–663.
9. D. A. Zhurko, G. A. Zhurko, ChemCraft 1.5; Plimus: San Diego, CA. Available at <http://www.chemcraftprog.com>.