Electronic Supplementary Material (ESI) for Chemical Communications.

New Synthetic Pathways to the Preparation of Near-Blue Emitting Heteroleptic Ir(III)N_6 Complexes with Microsecond Emission Lifetimes.

Suraj Soman,[a,b] Jennifer C. Manton,[a] Jane L. Inglis,[a] Yvonne Halpin,[a] Brendan Twamley, [a] Edwin Otten,[c] Wesley R. Browne,[c] Luisa De Cola[d] Johannes G. Vos, [a] and Mary T. Pryce,[a]

Electronic Supplementary Information.

Materials and methods.

UV/Vis absorption and emission spectra were recorded in spectrophotometric grade acetonitrile. $HClO_4$ and NaOH were purchased from Sigma Aldrich and used as received.

UV/Vis spectra were recorded using an Agilent 8453 UV-Vis spectrophotometer using 1 cm quartz cuvettes. Emission spectra were recorded using a Perkin Elmer LS50B luminescence spectrophotometer with 1 cm quartz cuvette in acetonitrile (OD at 0.15 at the wavelength of excitation). Emission lifetimes (± 5%) were determined with excitation at 355 nm (Nd:YAG) as described elsewhere.[1] Emission decay lifetimes were wavelength independent. Emission quantum yields were determined with reference to $[Ru(bipy)_3](PF_6)$ in CH_3CN.[2] Quantum yield measurements were carried out in both acetonitrile and acetonitrile acidified with 1.6×10^{-3} M $HClO_4$. Fluorescence measurements were carried out by varying the OD between 0.01 and 0.1 at λ_{irr} 380 nm. A standard plot was generated of fluorescence intensity vs. absorbance.

Fluorescence quantum yields were calculated using the following equation:

$$Q = Q_R \cdot \left(\frac{m}{m_R}\right) \cdot \left(\frac{n^2}{{n_R}^2}\right)$$

Q_R: Emission quantum yield of $[Ru(bipy)_3]PF_6$ in acetonitrile (0.062) **m:** slope of the line obtained from the plot of the fluorescence intensity vs. absorbance, **n:** refractive index of solvent. The subscript R refers to the reference fluorophore of known quantum yield.

Synthetic Procedures.

Commercially obtained starting materials and solvents were used without further purification. Hphpytr was available from previous studies

Preparation of compounds of the type of $[Ir(L\text{-}L)_2Cl_2]PF_6$

$[Ir(dmbipy)_2Cl_2]PF_6$

Iridium trichloride hydrate (0.10 g, 0.28 mmol) was combined with two equivalents of 4,4'-dimethyl-2,2'-bipyridine (0.105 g, 0.57 mmol) dissolved in 1 cm^3 of glycerol The reaction was heated at vigorous reflux for 10 min at which point the colour of the solution changed from red to straw yellow. The solution was cooled to room temperature and 5 cm^3 of water was added. The mixture was filtered and washed with 5 cm^3 of diethyl ether. 10 ml of saturated NaCl(aq) was added to the filtrate yielding $[Ir(bipy\text{-}N,N)_2Cl_2]Cl$ which was filtered and air-dried. The complex was dissolved in water and saturated KPF_6(aq) added to yield a yellow precipitate that was recovered by filtration, washed with 20 cm^3 of deionised water and air-dried. The product was dissolved in a minimal amount of acetone and flash precipitated by addition of excess diethyl ether and hexane and recovered by vacuum filtration, washed with diethyl ether and hexane. This procedure was repeated 3-4 times in order to remove traces of glycerol. Yield: 0.21 g, 95 %. ^{1}H NMR (400 MHz, DMSO), δ (ppm): 2.557 (s, 3H), 2.762 (s, 3H), 7.316 (dd, 1H, H5⍰), 7.597 (d, 1H, H6⍰), 7.929 (dd, 1H, H5), 8.659 (s, 1H, H3⍰), 8.756 (s, 1H, H3), 9.423 (d, 1H, H6). Elemental analysis, $C_{24}H_{24}Cl_2F_6IrN_4P$; (calculated) : C :37.1, H :3.1, N :7.2; (found) : C :36.8, H :2.9, N :7.0.

[Ir(dmbipy)$_2$(OSO$_2$CF$_3$)$_2$]CF$_3$SO$_3$

1,2 dichlorobenzene (10 cm^3) was added purged with N_2 for 30 min. [Ir(dmbipy)$_2$Cl$_2$]PF$_6$ (0.102 g, 0.13 mmol) was added and stirred under N_2 for 15 min after which 0.23 cm^3 of triflouromethanesulfonic acid was added and stirred at reflux for 2 h. The reaction mixture was cooled to room temperature. Diethyl ether was added resulting in the precipitation of the product, which was filtered and washed with diethyl ether. Yield: 0.108 g, 0.11 mmol, 82 %). ^{1}H NMR (400 MHz, DMSO-d$_6$), δ (ppm): 2.61 (s, 3H), 2.79 (s, 3H), 7.32 (d, 1H, H5⍰), 7.45 (d, 1H, H6⍰), 8.16 (d, 1H, H5), 8.68 (s, 1H, H3⍰), 8.79 (d, 1H, H6), 8.85 (s, 1H, H3). Elemental Analysis, $C_{27}H_{24}F_9IrN_4O_9S_3.H_2O$; (calculated) : C :31.6, H :2.6, N :5.5; (found) : C :31.2, H :2.3, N :5.2

[Ir(bipy)$_2$(OSO$_2$CF$_3$)$_2$]CF$_3$SO$_3$

1,2-dichlorobenzene (15 cm^3) was purged with N_2 for 30 min after which [Ir(bipy)$_2$Cl$_2$]PF$_6$ (0.156 g, 0.22 mmol) was added and stirred under N_2 for 15 min. 0.47 cm^3 of triflouromethanesulfonic acid was added and the solution was heated at refluxed for 3 h. The reaction mixture was cooled and diethyl ether was added resulting in the precipitation of the product, which was recovered by filtration and washed with diethyl ether. (Yield: 0.178 g, 85 %). ^{1}H NMR (400 MHz, DMSO-d$_6$), δ (ppm): 7.52 (t, 1H, H5⍰), 7.69 (d, 1H, H6⍰), 8.23 (t, 1H, H5), 8.34 (t, 1H, H4⍰), 8.67 (t, 1H, H4), 8.83 (d, 1H, H3⍰), 9.02 (m, 2H, H6, H3). Elemental Analysis for complex VII, $C_{23}H_{16}F_9IrN_4O_9S_3$: (calculated) : C :29.0, H :1.7, N :5.9; (found) :C :28.6, H :1.5, N :5.5

[Ir(dmbipy)$_2$(HPhpytr)](CF$_3$SO$_3$)$_3$

1,2 dichlorobenzene (15 ml) was purged with N_2 for 30 min after which Hphpytr (0.048 g, 0.218 mmol) was added and stirred in N_2 for 15 min to which [Ir(dmbipy)$_2$(OSO$_2$CF$_3$)$_2$].CF$_3$SO$_3$ (0.110 g, 0.109 mmol) was added and the reaction mixture was heated at reflux overnight. The reaction mixture was cooled and diethyl ether was added resulting in the precipitation of the product which was filtered, washed with diethyl ether and recrystalised from acetone: water (1:1) mixture to get the product in full purity. (Yield: 0.110 g, 80 %). ^{1}H NMR (400 MHz, DMSO-d$_6$), δ (ppm): 2.62 (dd, 6H), 2.66 (dd, 6H), 7.37 (m, 3H), 7.45 (d, 1H), 7.50 (d, 1H, H6⍰), 7.52 (dd, 1H, H5⍰), 7.57 (dd, 1H), 7.61 (m, 2H, H5, H6), 7.75 (m, 3H), 7.86 (m, 2H, H5⍰⍰, H6⍰⍰), 7.91 (d, 1H), 8.31 (m, 2H, H5⍰⍰⍰, H6⍰⍰⍰), 8.82 (s, 1H, H3⍰), 8.84 (s, 1H, H3), 8.88 (s, 1H, H3⍰⍰), 8.90 (s, 1H, H3⍰⍰⍰). Elemental Analysis, $C_{40}H_{35}F_9IrN_8O_9S_3$; (calculated) : C :39.8, H :2.8, N :9.1; (found) : C :39.1, H :2.8, N :9.0

[Ir(bipy)$_3$](PF$_6$)$_3$

Bipy (0.163 g, 1.05 mmol) was added to 10 cm^3 of deoxygenated ethylene glycol and the solution stirred for 15 min. [Ir(bipy)$_2$(OSO$_2$CF$_3$)$_2$].CF$_3$SO$_3$ (0.05 g, 0.052 mmol) was added and the solution was heated at reflux for 5 h. The reaction mixture was cooled to room temperature, 5 ml of water was added and the mixture filtrated. Saturated aqueous KPF$_6$ was added resulting in the precipitation of the complex as pale yellow solid that was collected by vacuum filtration, washed with water and diethyl ether and air-dried. (Yield: 0.042 g, 72 %). ^{1}H NMR (400 MHz, DMSO), δ (ppm): 7.74 (t, 2H, H5, H5⍰), 7.85 (d, 2H, H6, H6⍰), 8.49 (t, 2H, H4, H4⍰), 9.01 (d, 2H, H3, H3⍰). Elemental Analysis, $C_{30}H_{24}F_{18}IrN_6P_3$; (calculated) : C :32.9: H :2.2: N :7.7; (found) : C :32.9: H :2.0: N :8.0

Figures

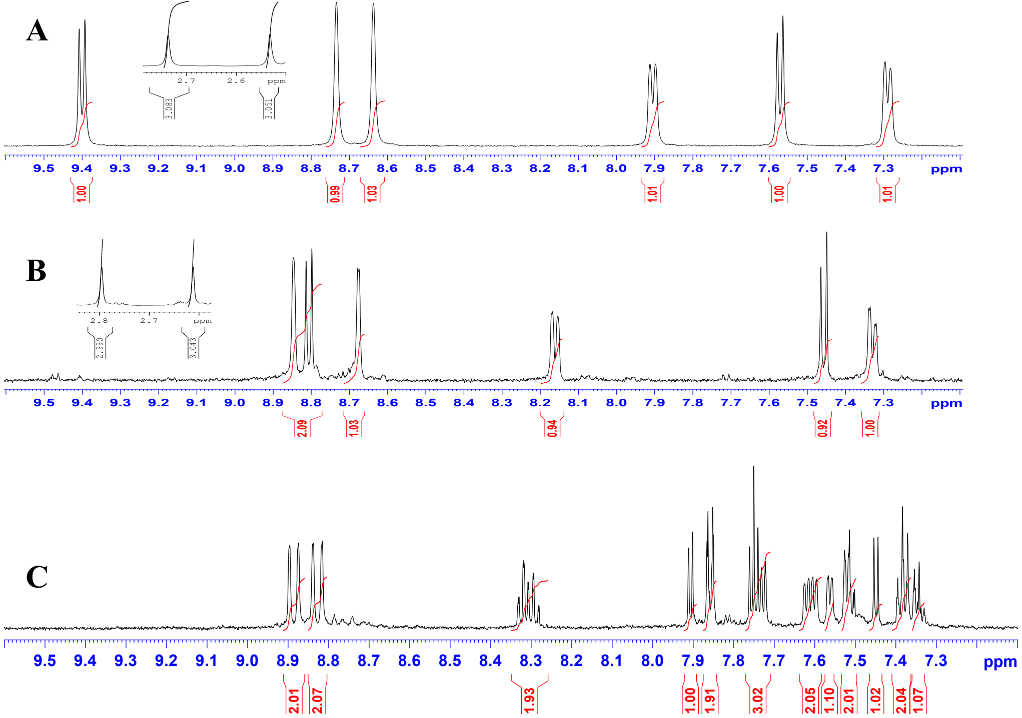

Figure S1 ^{1}H NMR spectra of **(A)** $[Ir(dmbipy)_2Cl_2]PF_6$, **(B)** $[Ir(dmbipy)_2(CF_3SO_3)_2]CF_3SO_3$, **(C)** $[Ir(dmbipy)_2(Hphpytr)](CF_3SO_3\ )_3$ in d^6 DMSO.

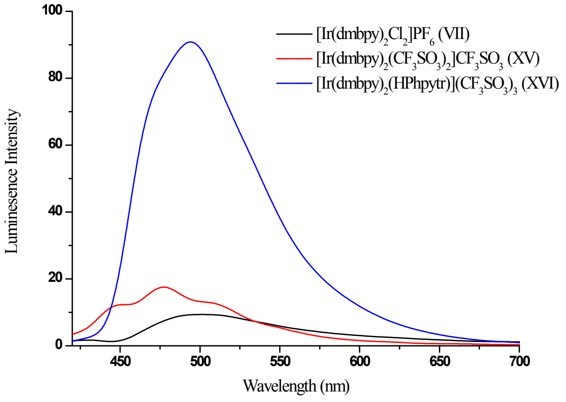

Figure S2 Emission spectra of $[Ir(dmbipy)_2Cl_2]PF_6$, (black) $[Ir(dmbipy)_2(OSO_2CF_3)_2]CF_3SO_3$ (red) and $[Ir(dmbipy)_2(HPhpytr)](CF_3SO_3)_3$ (blue) (1×10^{-4} M in CH_3CN).

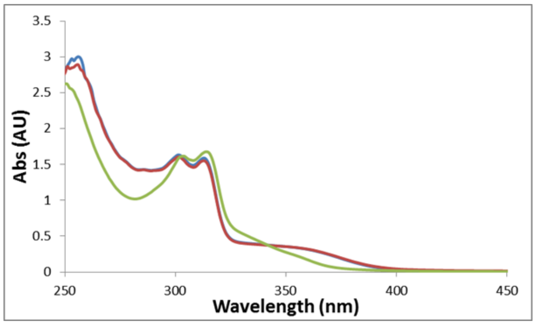

Figure S3- UV/Vis absorption spectra of $[Ir(dmbipy)_2(HPhPytr)]^{3+}$ in acetonitrile (blue line), with excess NaOH added (red line) and with $HClO_4$ (green line).

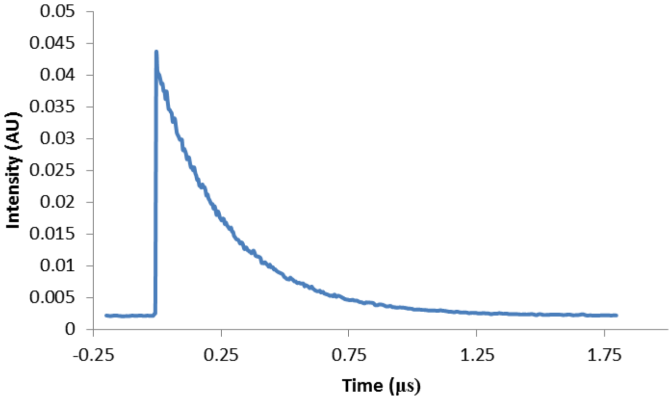

Figure. S4 Emission transient for $[Ir(dmbipy)_2(HPhPytr)]^{3+}$ in acidic conditions ($\tau = 8.43$ μs $\pm$ 5%) following excitation at 355 nm. Recorded at 470 nm.

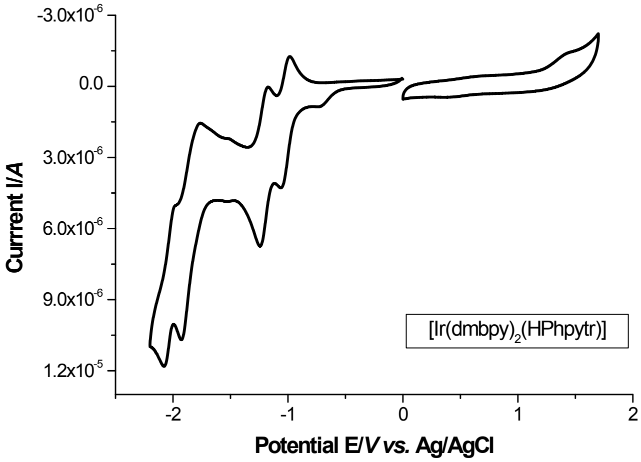

Figure S5A. Cyclic voltammetry of [Ir(dmbipy)$_2$(HPhpytr)](CF$_3$SO$_3$)$_3$ (vs. Ag/AgCl) on a GC working electrode at 20 mV/s in 0.1 M TBAPF$_6$ ACN.

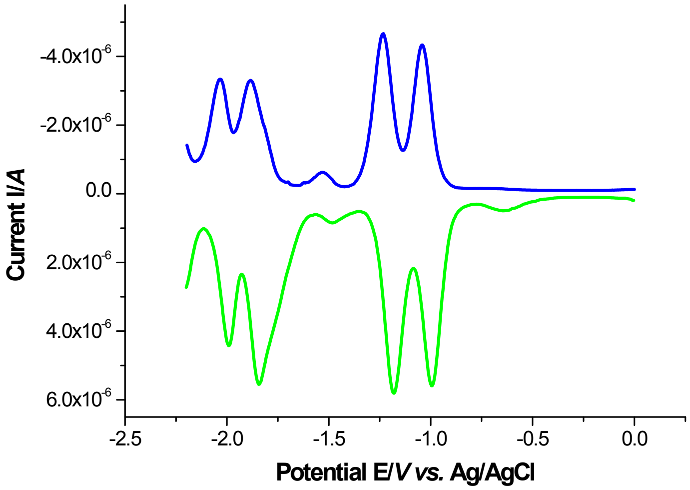

Figure S5B. Differential pulse voltammetry [Ir(dmbipy)$_2$(HPhpytr)](CF$_3$SO$_3$)$_3$ (vs. Ag/AgCl) at a GC working electrode in 0.1 M TBAPF$_6$/ACN. The green and blue lines correspond to the differential pulse of the reduction of the complex in the positive and negative directions respectively.

X-ray crystallography

A suitable crystal of [Ir(dmbipy)$_2$(phpytr)][CF$_3$SO$_3$]$_2$.toluene was mounted on top of a cryoloop and transferred into the cold nitrogen stream (100 K) of a Bruker-AXS D8 Venture diffractometer. Data collection and reduction was done using the Bruker software suite APEX2.[3] The final unit cell was obtained from the xyz centroids of 9800 reflections after integration. A multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS*).3 The structure was solved by direct methods using *SHELXS*.[4] From subsequent refinement of the structure (*SHELXL*)[5] it was clear that the cationic Ir-containing fragment was well-defined, but the one of the two CF_3SO_3 anions was disordered. Also, a toluene solvent molecule was disordered over an inversion centre and only partially occupied (40%). The observed disorder results in some of the atoms involved showing large displacement parameters, but the chemically relevant Ir fragment is not affected. All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were included riding on their carrier atoms. Crystal data and details on data collection and refinement are presented in Table S1.

Table 1. Crystal data and structure refinement for eoir.

Identification code	eoir	
Empirical formula	C41.80 H38.20 F6 Ir N8 O7 S2	
Formula weight	1134.92	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.0363(11) Å	□= 76.157(3)°.
	b = 13.4312(13) Å	□= 75.969(3)°.
	c = 15.4313(14) Å	□ = 71.057(3)°.
Volume	2253.8(4) Å^3	
Z	2	
Density (calculated)	1.672 Mg/m^3	
Absorption coefficient	3.138 mm^{-1}	
F(000)	1128	
Crystal size	0.16 x 0.09 x 0.05 mm^3	
Theta range for data collection	2.76 to 27.26°.	
Index ranges	$-15\le h\le 15$, $-17\le k\le 17$, $-19\le l\le 19$	
Reflections collected	63885	
Independent reflections	10001 [R(int) = 0.0510]	
Completeness to theta = 27.26°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8589 and 0.6337	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10001 / 12 / 580	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0470, wR2 = 0.1188	
R indices (all data)	R1 = 0.0556, wR2 = 0.1262	
Largest diff. peak and hole	5.529 and -1.635 e.Å^{-3}	

---

[1] A. Coleman, M. T. Pryce, *Inorg. Chem.,* 2008, **47**, 23.

[2] M. Osawa, M. Hoshino, Chem. Commun, 2008, **47**, 6384.

[3] Bruker, (2012). *APEX2* (v2012.4-3), *SAINT* (Version 8.18C) and *SADABS* (Version 2012/1). Bruker AXS Inc., Madison, Wisconsin, USA.

[4] G.M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.

[5] H.D Flack,, *Acta Cryst.*, 1983, **A39**, 876.