Electronic supplementary information (ESI) for:

Luminescent Iridium(III)-Boronic Acid Complexes for Carbohydrate Sensing

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1. Synthesis

1a. To a mixture of benzoic acid (10 g, 0.082 mol) in ethanol (150 mL) sulfuric acid (8 drops) was added dropwise. The reaction mixture was then heated to reflux for 24 h. After cooling to room temperature (RT), all volatiles were evaporated under reduced pressure, and drying the residue in vacuo gave **1a** as colourless oil. (yield 11.37 g, 92%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.39 (t, $^3J_{HH}$=7.12 Hz, 3 H, $OCH_2C\mathit{H_3}$), 4.38 (q, $^3J_{HH}$=7.15 Hz, 2 H, $OC\mathit{H_2}CH_3$), 7.43 (t, $^3J_{ortho}$=$^4J_{metha}$ 7.57 Hz, 1 H, Ph*H*), 7.54 (dd, $^3J_{HH}$=7.18 Hz, 1 H, Ph*H*), 8.04-8.06 (d, 2 H, Ph*H*), ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 14.44 (OCH_2CH_3), 61.14 ($O\mathit{C}H_2CH_3$), 128.45 (Ph*C*), 129.67 (Ph *C*), 130.60 (Ph*C*), 132.97 (Ph*C*), 166.86 (*C*=O) ppm.

1b. To a mixture of 4-carboxyphenyl boronic acid pinacol ester (5 g, 0.02 mol) in ethanol (50 mL) sulfuric acid (5 drops) was added dropwise. The reaction mixture was then heated to reflux for 24 h. After cooling to room temperature (RT), all volatiles were evaporated under reduced pressure, and drying the residue in vacuo gave **1b** as colourless oil. (yield 5.17 g, 93%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.35 (s., 12 H, $C\mathit{H_3}$), 1.40 (t, $^3J_{HH}$=7.15 Hz, 3 H, $OCH_2C\mathit{H_3}$), 4.38 (q, $^3J_{HH}$=7.12 Hz, 2 H, $OC\mathit{H_2}CH_3$), 7.85-7.87 (m, 2 H, Ph*H*), 8.01-8.02 (m, 2 H, Ph*H*) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 14.5 ($OCH_2\mathit{C}H_3$), 25.1 (4-$\mathit{C}H_3$), 61.2 ($O\mathit{C}H_2CH_3$), 84.3 (2 C, *C*q), 128.7 (Ph*C*), 132.8 (Ph*C*), 134.8 (Ph*C*), 166.9 (*C*=O) ppm.

2a. A heterogenous mixture of **1a** (4.67 g, 0.03 mol) and hydrazine monohydrate (2.18 g, 0.04 mol) was heated to reflux for 24 h during which time a clear colourless solution was obtained. After cooling, the solvent was evaporated under reduced pressure which was solidified at ice-bath. Then the solid was recrystallized only from ethanol and washed with cold toluene which gave **2a** as colourless needles. (yield 3.59 g, 85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.14 (br. s, 2 H, $CONHN\mathit{H_2}$), 7.44 (t, $^3J_{ortho}$=$^4J_{meta}$= 7.76 Hz, 2 H, Ph*H*), 7.52 (dd, $^3J_{HH}$=7.44 Hz, 1 H, Ph*H*), 7.71 (br. s, 1 H, $CON\mathit{H}NH_2$), 7.74-7.76 (d, 2 H, Ph*H*), ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 126.9 (Ph*C*), 128.7 (Ph*C*), 131.9 (Ph*C*), 132.7 (Ph*C*), 168.7 (*C*=O) ppm.

2b. A heterogenous mixture of **1b** (5.17 g, 0.01 mol) and hydrazine monohydrate (1.12 g, 0.02 mol) was heated to reflux for 24 h during which time a clear colourless solution was obtained. After cooling, the solvent was evaporated under reduced pressure and the resulting colourless crystalline solid was dried in vacuo. The solid was recrystallised from a mixture of ethyl acetate and diethyl ether (1:1) which gave **2b** as colourless needles. (yield 2.10 g, 43%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.35 (s., 12 H, $C\mathit{H_3}$), 4.10 (br. s, 2 H, $CONHN\mathit{H_2}$), 7.38 (br. s, 1 H, $CON\mathit{H}NH_2$), 7.72-7.73 (m, 2 H, Ph*H*), 7.87-7.88 (m, 2 H, Ph*H*), ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 25.1 (4-$\mathit{C}H_3$), 84.4 (2 C, *C*q), 126.2 (Ph*C*), 135.0 (Ph*C*), 135.3 (Ph*C*), 168.8 (*C*=O) ppm.

3a. In a mixture of methylamine hydrochloride (7 g, 0.10 mol) and sulfur (9.967 g, 0.31 mol) in 2-methylpyridine (50 mL), sodium sulfide nonahydrate (0.50 g, 2 mol %) was added and the reaction mixture was then heated to reflux for 24 h. After cooling, all volatiles were evaporated under reduced pressure. The dark brown residue was taken up in 6 M hydrochloric acid (100 mL), and the mixture was filtered and solid NaOH (22.0 g, 0.55 mol) was added to the filtrate in several portions at 0 °C until the aqueous phase became neutral. The resulting heterogeneous mixture was then extracted with dichloromethane 50 mL (3×50 mL) and the combined organic layers were combined and dried with anhydrous sodium sulfate and all volatiles were evaporated under reduced pressure. A brown crystalline solid was obtained. The product was purified on silica with hexane and ethyl acetate 3:2 as the eluent. The filtrate was evaporated under reduced pressure and drying the residue in vacuo gave

3a as yellow needle crystalline. (yield 3.32 g, 21%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 3.40 (d, $^{3}J_{HH}$=5.17 Hz, 3 H, C*H*$_3$), 7.42 (t, $^{3}J_{HH}$=6.17 Hz, 1 H, Py*H*), 7.83 (t, $^{3}J_{HH}$=7.78 Hz, 1 H, Py*H*), 8.48 (d, $^{3}J_{HH}$=4.40 Hz, 1 H, Py*H*), 8.70 (d, $^{3}J_{HH}$=7.98 Hz, 1 H, Py*H*), 10.22 (br. s, 1 H, CSN*H*) ppm. ^{13}C NMR (500 MHz, CDCl$_3$): δ = 32.6 (*C*H$_3$), 124.6 (Py*C*), 126.0 (Py*C*), 137.3 (Py*C*), 146.9 (Py*C*), 151.1 (Py*C*), 191.8 (*C*SNH) ppm.

3b. A mixture of aniline (10.7 g, 0.11 mol), sulfur (11.05 g, 0.34 mol) and sodium sulfide nonahydrate (0.55 g, 2 mol %) in 2-methylpyridine (60 mL) was heated to reflux for 48 h. The mixture was then cooled to RT and all volatiles were evaporated under reduced pressure and the resulting dark brown liquid was dried in vacuo. Then the residue was recrystallized from ethanol and washed with hexane which gave **3b** as a dark brown oil liquid. (yield 17.37 g, 71%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.30 (t, $^{3}J_{HH}$=7.44 Hz, 1 H, Ph*H*), 7.45-7.49 (m, 3 H), 7.89 (t, $^{3}J_{HH}$=7.73 Hz, 1 H, Py*H*), 8.08-8.09 (m, 2 H, Ph*H*), 8.56 (d, $^{3}J_{HH}$=4.75 Hz, 1 H, Py*H*), 8.82 (d, $^{3}J_{HH}$=8.03 Hz, 1 H, Py*H*), 12.07 (br. s, 1 H, CSN*H*) ppm. ^{13}C NMR (500 MHz, CDCl$_3$): δ = 122.8 (Ph*C*), 124.9 (Py*C*), 126.2 (Py*C*), 126.7 (Ph*C*), 129.0 (Ph*C*), 137.6 (Py*C*), 138.8 (Ph*C*), 146.7 (Py*C*), 151.5 (Py*C*), 187.9 (*C*SNH) ppm.

2. High Resolution Mass Spectra

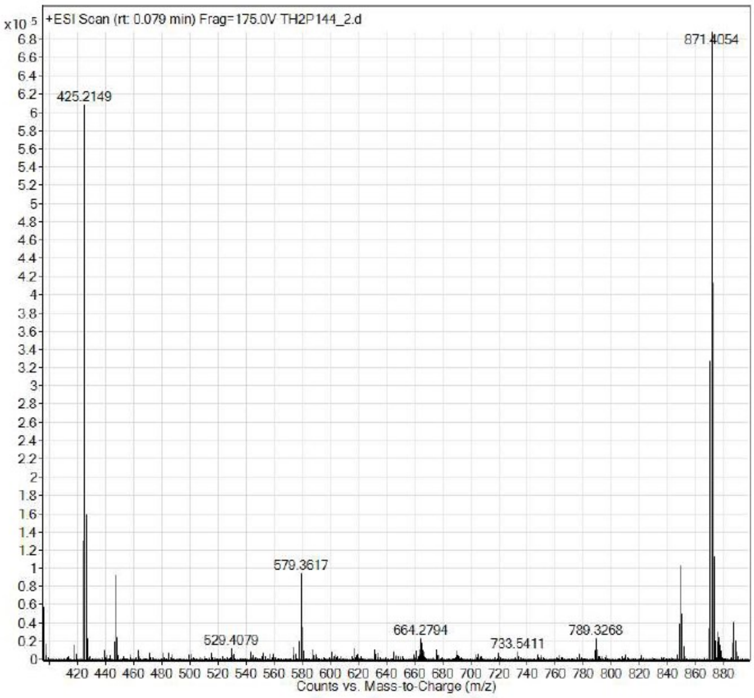

Figure **S1**. HRMS of ligand **5b**.

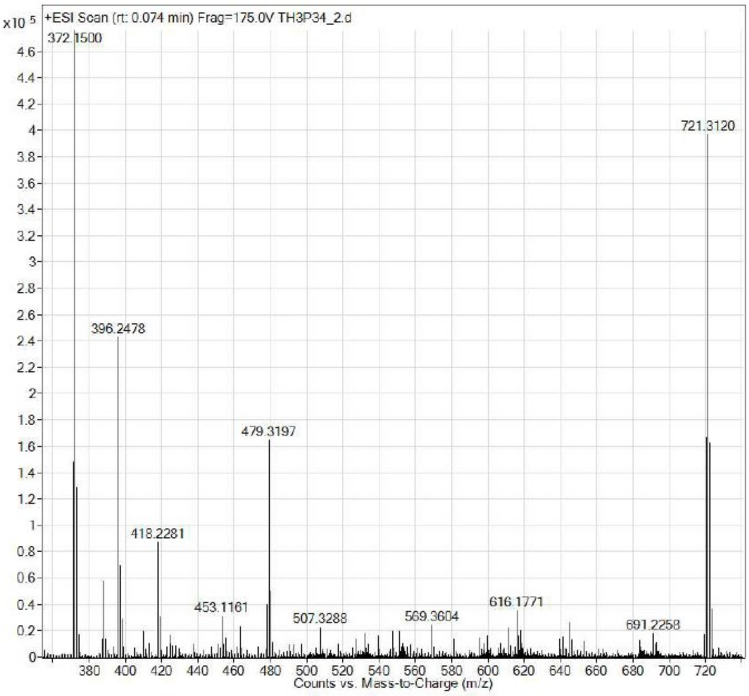

Figure **S2**. HRMS of ligand **5c**.

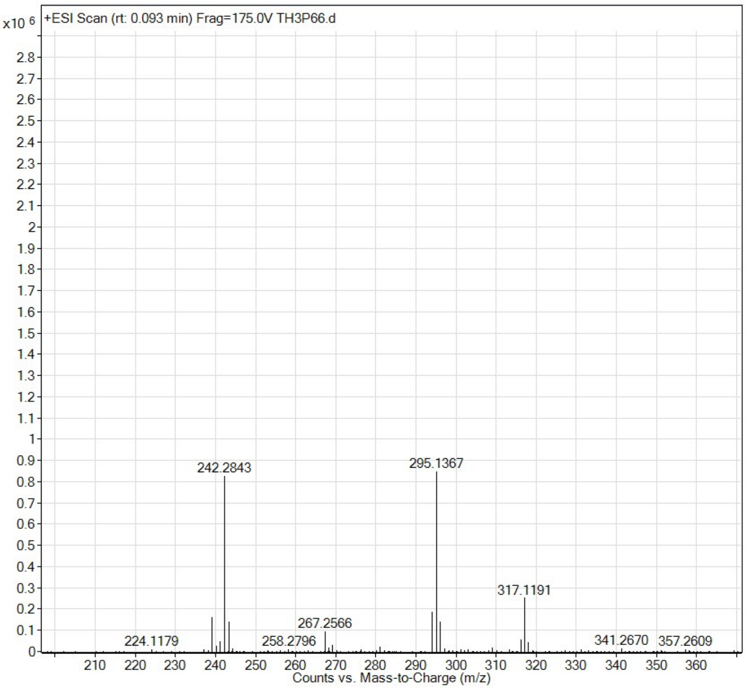

Figure **S3**. HRMS of ligand **7a**.

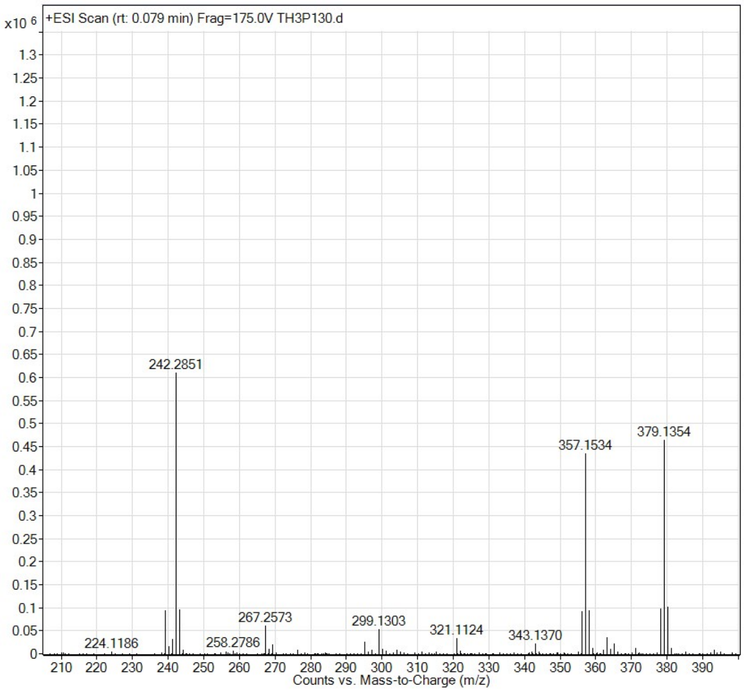

Figure **S4**. HRMS of ligand **7b**.

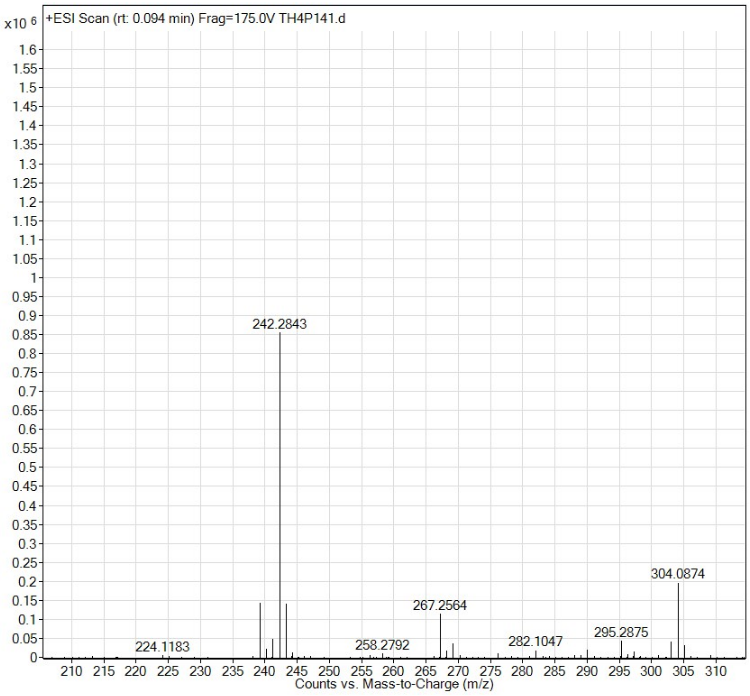

Figure **S5**. HRMS of ligand **7c**.

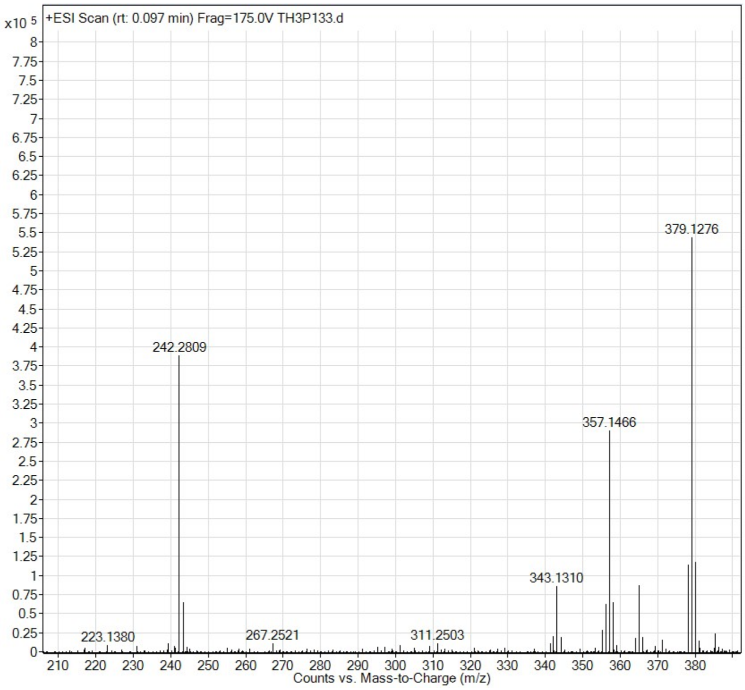

Figure **S6**. HRMS of ligand **7d**.

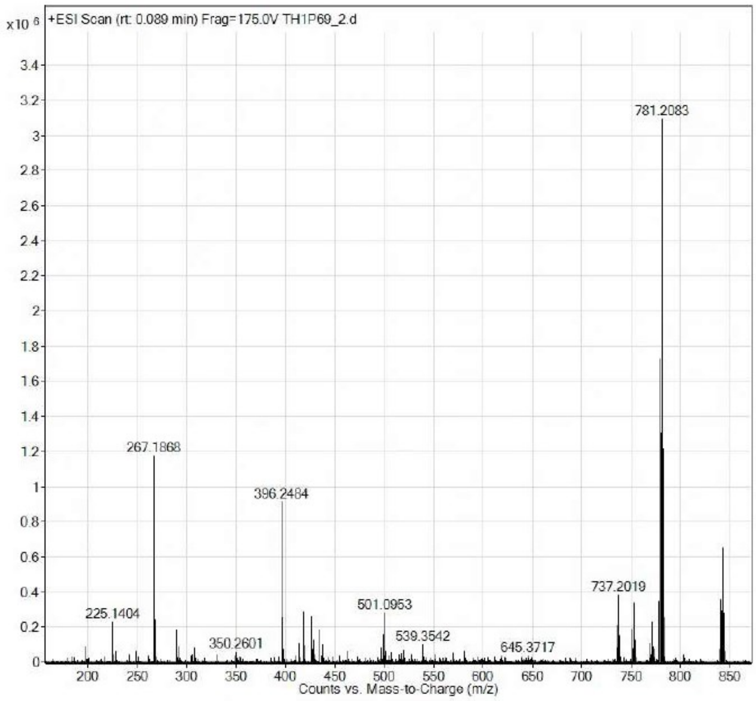

Figure **S7**. HRMS of Ir(III) complex **8a**.

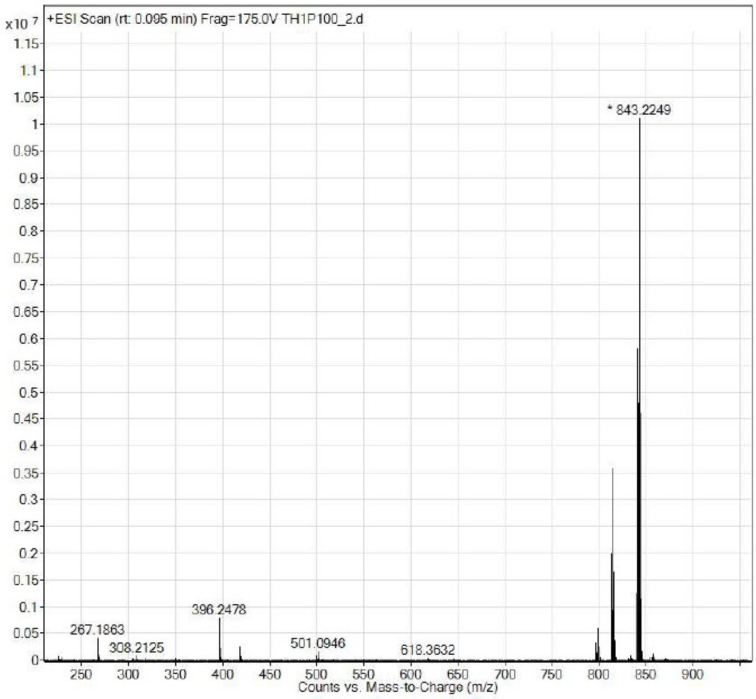

Figure **S8**. HRMS of Ir(III) complex **8b**.

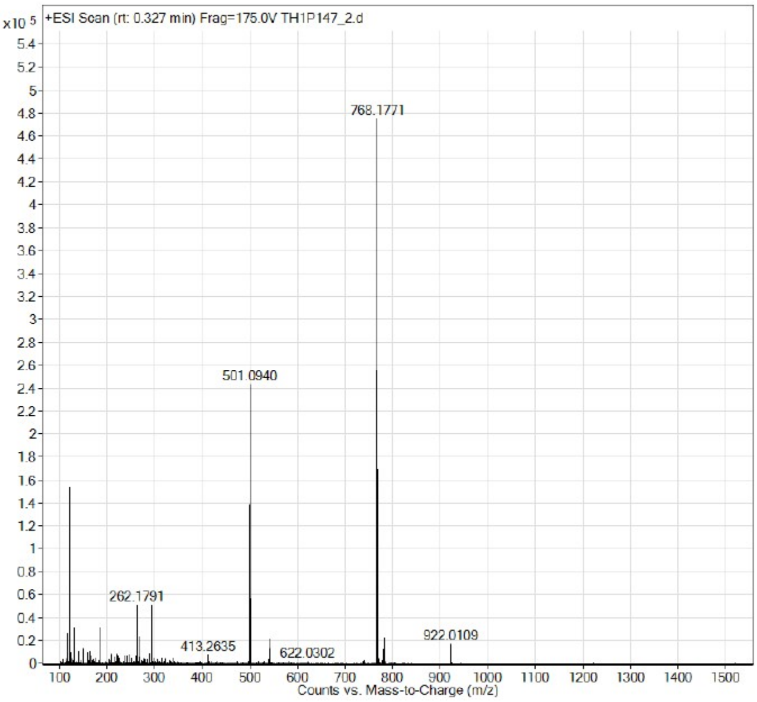

Figure **S9**. HRMS spectrum of Ir(III) complex **8c**.

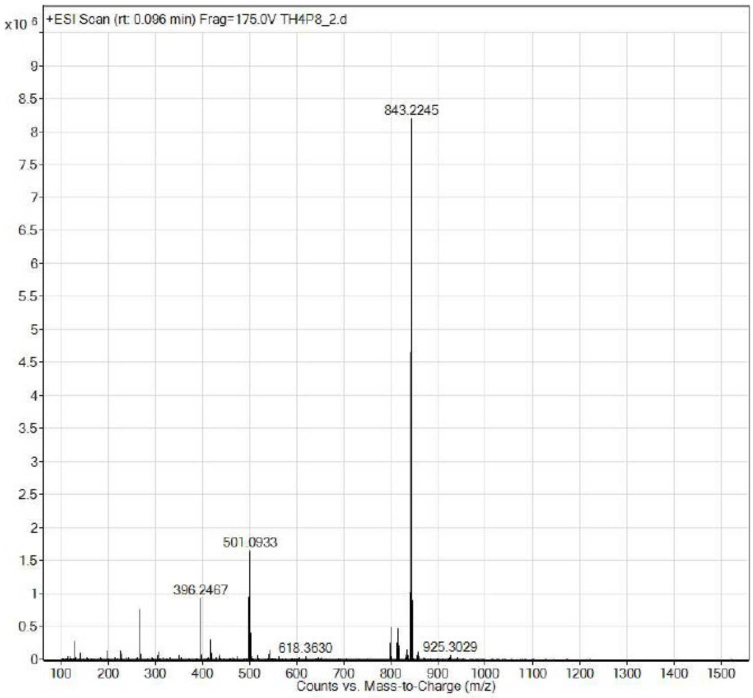

Figure **S10**. HRMS of Ir(III) complex **8d.**

3. Crystallography

Table **S1**. Summary of Crystallographic Data for **5c**, **8a** and **8c**.

Compound	**5c**	**8a**	**8c**
Empirical formula	$C_{19}H_{20}BN_3O_3$	$C_{38}H_{34}BClIrN_7O_3$	$C_{37}H_{32}BClIrN_5O_4$
Formula weight	349.19	875.18	849.13
Temperature/K	128(20)	116(20)	149.99(10)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1
a/Å	5.9916(3)	23.9525(4)	9.63340(10)
b/Å	18.1389(5)	17.7651(3)	14.15560(10)
c/Å	18.0161(8)	8.47345(16)	15.30640(10)
α/°	90	90	73.0990(10)
β/°	116.415(6)	98.7316(19)	77.2420(10)
γ/°	90	90	77.0460(10)
Volume/Å^3	1753.59(15)	3563.82(11)	1918.99(3)
Z	4	4	2
ρ_{calc}g/cm^3	1.323	1.631	1.47
μ/mm^{-1}	0.728	8.333	7.724
F(000)	736	1736	840
Crystal size/mm^3	0.05 × 0.04 × 0.02	0.08 × 0.07 × 0.06	0.06 × 0.06 × 0.05
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.332 to 130.062	7.468 to 148.984	6.624 to 136.776
Index ranges	$-6 \leq h \leq 7$, $-21 \leq k \leq 13$, $-21 \leq l \leq 21$	$-29 \leq h \leq 29$, $-18 \leq k \leq 22$, $-9 \leq l \leq 10$	$-10 \leq h \leq 11$, $-16 \leq k \leq 17$, $-18 \leq l \leq 18$
Reflections collected	5993	19088	37753
Independent reflections	2970 [R_{int} = 0.0357, R_{sigma} = 0.0351]	7279 [R_{int} = 0.0361, R_{sigma} = 0.0385]	7016 [R_{int} = 0.0194, R_{sigma} = 0.0110]
Data/restraints/parameters	2970/0/239	7279/0/467	7016/0/446
Goodness-of-fit on F^2	1.051	1.042	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0360, wR_2 = 0.0874	R_1 = 0.0359, wR_2 = 0.0898	R_1 = 0.0196, wR_2 = 0.0491
Final R indexes [all data]	R_1 = 0.0430, wR_2 = 0.0922	R_1 = 0.0418, wR_2 = 0.0937	R_1 = 0.0197, wR_2 = 0.0492
Largest diff. peak/hole / e Å^{-3}	0.23/-0.26	2.54/-1.29	0.91/-0.76

5c: Solved in the monoclinic space group *P*2$_1$/*c*. The asymmetric unit contains one molecule of the title compound.

8a: Solved in the monoclinic space group *P*2$_1$/*c*. The asymmetric unit contains one molecule of the title cation, the chloride anion and one molecule each of water and acetonitrile as a solvent molecules of crystallisation.

8c: Solved in the triclinic space group *P*-1. The asymmetric unit contains one molecule of the title cation, the chloride anion and a molecule of methanol as a solvent molecule of crystallisation. In addition to the successfully modelled methanol molecule, residual electron density (76 electrons per unit cell or 38 electrons per asymmetric unit) indicated the presence of two additional highly disordered methanol solvent molecules per asymmetric unit. Attempts to model this disorder were unsuccessful and the Solvent Mask function of Olex2 was used. One level B Checkcif alerts result from the removal of the electron density associated with this disordered solvent (D-H Without

Acceptor O4 --H4A). This is associated with the successfully modelled methanol molecule lacking a hydrogen bond acceptor which should be associated with the disordered solvent.

4. Absorbance and Photoluminescence titration studies

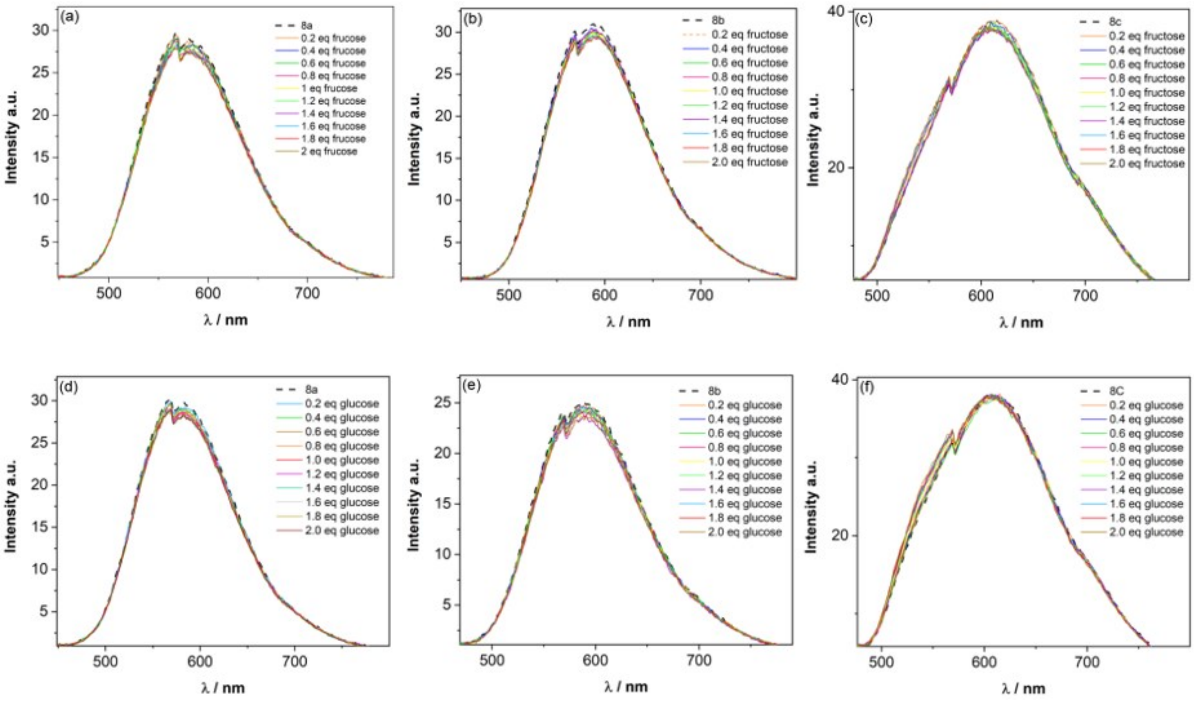

Figure **S11**. Luminescent titration of complexes **8a**, **8b** and **8c** with fructose (a - c) and glucose (d-f), pH = 9. [Complex] = 20 µM, [*tris* buffer] = 2.0 mM. The spike at 569 nm is an instrumental artefact due to the switch between diffraction gratings at that wavelength.

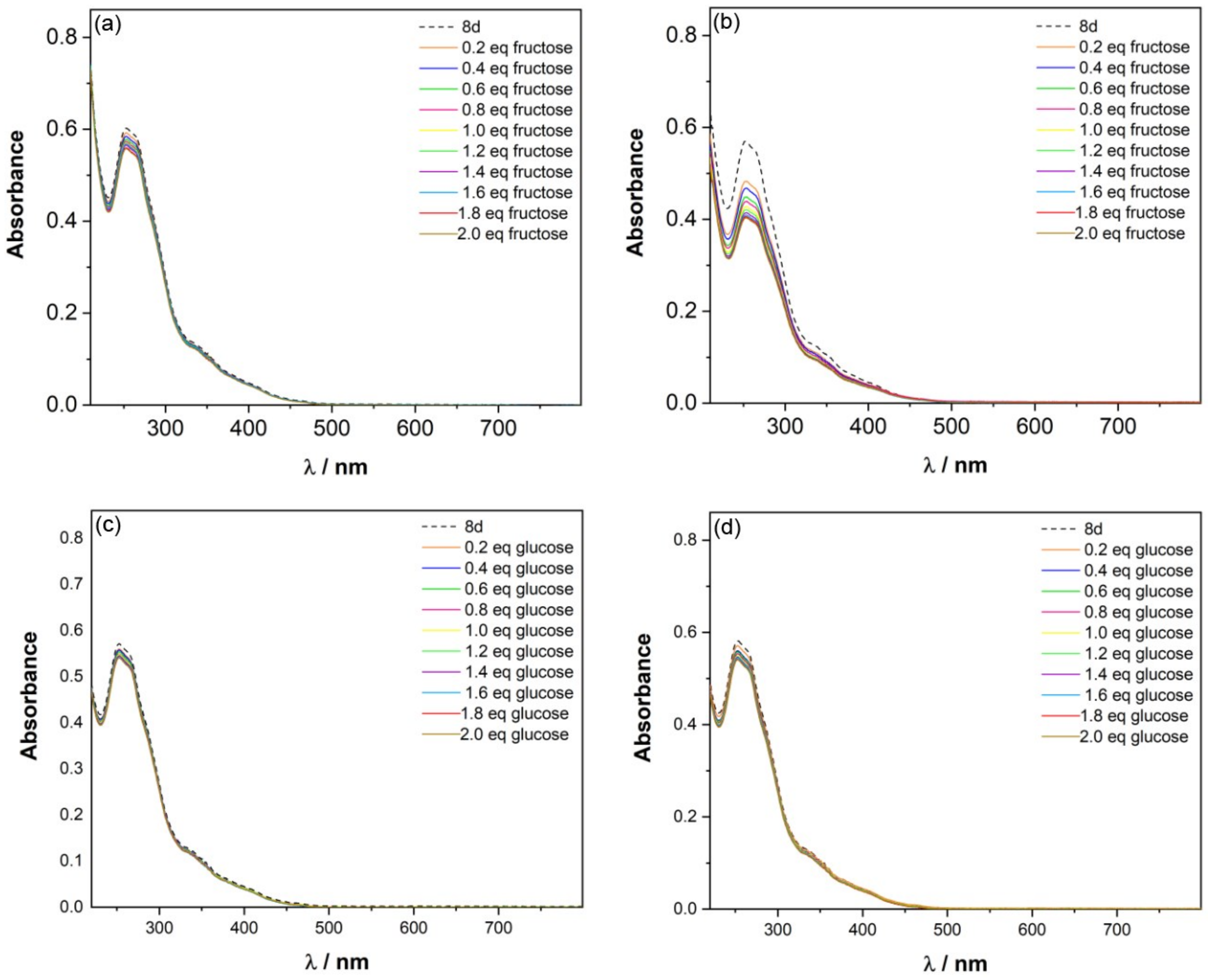

Figure **S12**. UV-visible titration of compound **8d** with the sugars (a) fructose pH = 7; (b) fructose pH = 9; (c) glucose, pH = 7 and (d) glucose pH = 9. [Complex] = 20 μM, [*tris* buffer] = 2.0 mM.